- (1) Sodium bromide; NaBr; [7647-15-6]
- (2) Sodium methanoate (sodium formate); NaCHO₂; [141-53-7]

ORIGINAL MEASUREMENTS:

Leonesi, D.; Braghetti, M.; Cingolani, A.; Franzosini, P. Z. Naturforsch. 1970, 25a, 52-55.

VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

t/ºC	T/K ^a	100 x 1
257.5	530.7	0
254.5	527.7	2.02
251.8	525.0	3.91
250.4	523.6	4.99
248.8	522.0	6.01
245.7	518.9	8.00
244.2	517.4	8.98
250.9	524.1	10.00
265.1	538.3	11.04
274.0	547.2	11.76
296.1	569.3	13.55

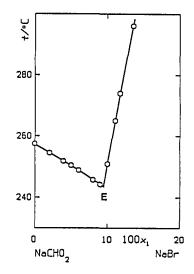
 $^{\mathbf{a}}$ T/K values calculated by the compiler.

Note 1 - In the original paper the results were shown in a graphical form. The above listed numerical values represent a personal communication by one of the authors (F., P.) to the compiler.

Note 2 - The system could not be investigated above 300 $^{\circ}$ C due to the thermal instability of the methanoate.

Characteristic point(s):

Eutectic, E, at 243.5 °C and $100x_1 = 9.5$ (authors).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A Pyrex device, suitable for work under an inert atmosphere, and allowing one to observe the system visually, was employed (for details, see Ref. 1). The initial crystallization temperatures were measured with a Chromel-Alumel thermocouple checked by comparison with a certified Pt resistance thermometer, and connected with a L&N Type K-3 potentiometer.

SOURCE AND PURITY OF MATERIALS:

C. Erba RP meterials, dried by heating under vacuum.

ESTIMATED ERROR:

Temperature: accuracy probably +0.1 K (compiler).

REFERENCES:

(1) Braghetti, M.; Leonesi, D.; Franzosini, P. Ric. Sci. 1968, 38, 116-118.

- (1) Sodium bromide; NaBr; [7647-15-6]
- (2) Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3]

ORIGINAL MEASUREMENTS:

Il yasov. I.I.; Bergman, A.G. Zh. Obshch. Khim. 1961, 31, 368-370.

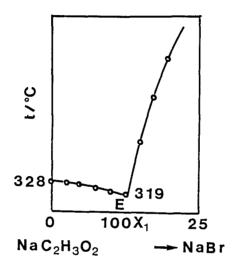
VARIABLES:

Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:



The results are given only in graphical form (see figure). The system was investigated at 0 \leq 100x $_1$ \leq 25.

Characteristic point(s): Eutectic, E, at 319 $^{\circ}$ C and 100 x_1 = 12.5 (authors).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis; temperatures measured with a Nichrome-Constantane thermocouple and a millivoltmeter (Ref. 1).

SOURCE AND PURITY OF MATERIALS:

Not stated.

Component 1: $t_{fus}(1)/{}^{o}C = 755$. Component 2: $t_{fus}(1)/{}^{o}C = 328$.

ESTIMATED ERROR:

Temperature: accuracy probably ±2 K (compiler).

REFERENCES:

(1) Il'yasov, I.I.; Bergman, A.G. Zh. Obshch. Khim. 1960, 30, 355-358.

- (1) Sodium bromide; NaBr; [7647-15-6]
- (2) Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3]

ORIGINAL MEASUREMENTS:

Piantoni, G.; Leonesi, D.; Braghetti, M.; Franzosini, P. Ric. Sci., 1968, 38, 127-132.

VARIABLES:

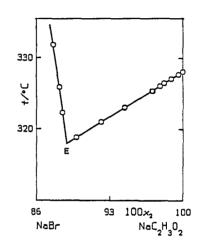
Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

t/°C	T/K ^a	100 x 2
328.1	601.3	100
327.7	600.9	99.6
327.1	600.3	98.9
326.5	599.7	98.2
326.1	599.3	97.8
325.4	598.6	97.1
325.4	598.6	97.1
325.4	598.6	97.0
323.0	596.2	94.4
323.1	596.3	94.4
321.0	594.2	92.2
318.8	592.0	89.8
322.3	595.5	88.5
325.9	599.1	88.2
331.8	605.0	87.6



Note 1 - In the original paper the results were shown in graphical form. The above listed numerical values represent a private communication by one of the authors (F., P.) to the compiler.

Note 2 - The system was investigated at $0 \le 100x_1 \le 12.5$.

Characteristic point(s): Eutectic, E, at 317.9 °C and 100x2= 88.9 (authors).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A Pyrex device, suitable for work under an inert atmosphere, and allowing one to observe the system visually, was employed (for details, see Ref. 1). The initial crystallization temperatures were measured with a Chromel-Alumel thermocouple checked by comparison with a certified Pt resistance thermometer, and connected with a L&N Type K-3 potentiometer.

SOURCE AND PURITY OF MATERIALS:

C. Erba RP materials, dried by heating under vacuum.

NOTE:

The authors discuss their own results in comparison with both the expected ideal behaviour of the molten mixtures and the previous data from Ref. 2. Extension of this comparison to the cryometric constant at null molality for different solutes in molten sodium ethanoate allowed them to argue that sodium bromide and sodium ethanoate show a remarkable tendency to give mixed crystals.

ESTIMATED ERROR:

Temperature: accuracy probably +0.1 K.

- (1) Braghetti, M.; Leonesi, D.; Franzosini, P. Ric. Sci. 1968. 38. 116-118.
- Ric. Sci. 1968, 38, 116-118.
 (2) Il'yasov. T.I.; Bergman, A.G.
 Zh. Obshch. Khim. 1961, 31, 368-370.

a T/K values calculated by the compiler.

- (1) Sodium methanoate (sodium formate); NaCHO₂; [141-53-7]
- (2) Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1581-1593.

VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

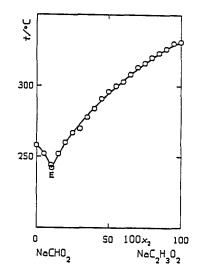
EXPERIMENTAL VALUES:

t/°C	T/Kª	100 x 2	t/°C	T/K ^a	100 x 2
258	531	0	296	569	50
252	525	5	300	573	55
244	517	10	303	576	60
242	515	10.5	308	581	65
252	525	15	313	586	70
260	533	20	316	589	75
267	540	25	320	593	80
270	543	30	323	596	85
278	551	35	326	599	90
284	557	40	330	603	95
291	564	45	331	604	100

a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E, at 242 °C and $100x_2 = 10.5$ (author).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

Melts contained in a glass tube and stirred.

Temperatures measured with a NichromeConstantane thermocouple and a 17 mV full
scale millivoltmeter. The temperature
readings refer to the disappearance of isotropicity in the melt on cooling.

SOURCE AND PURITY OF MATERIALS:

Component 1: prepared by reacting aqueous ("chemically pure") Na_2CO_3 with a slight excess of methanoic acid of analytical purity. The solvent and excess acid were removed by heating to $160\,^{\circ}\text{C}$. Component 2: "chemically pure" material.

ESTIMATED ERROR:

Temperature: accuracy probably ± 2 K (compiler).

- (1) Sodium methanoate (sodium formate); NaCHO₂; [141-53-7]
- (2) Sodium propanoate (sodium propionate); NaC₃H₅O₂ [137-40-6]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.; Minchenko, S.P. Zh. Obshch. Khim. 1971, 41, 1656-1659.

VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

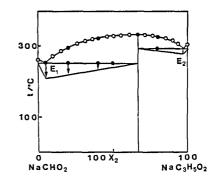
The results are reported only in graphical form (see figure; empty circles: visual polythermal analysis; filled circles: thermographical analysis).

Characteristic point(s):

Eutectic, E_1 , at 255 °C and $100x_2 = 6$ (authors). Eutectic, E_2 , at 293 °C and $100x_2 = 98$ (authors).

Intermediate compound(s):

Na₃CHO₂(C₃H₅O₂)₂, congruently melting.



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis supplemented with thermographical analysis.

NOTE:

The fusion temperature reported for component 1 (531 K) coincides with that listed in Preface, Table 1 (530.7+0.5 K), whereas the T_{trs} values from Ref. 2 and Table 1 are significantly discrepant. 2, Concerning the component fusion temperature (571 K) looks as somewhat too high; moreover, doubts are to be cast about the reliability of the highest transition temperature (560 K) quoted by the authors from Ref. 2, inasmuch as both DSC (Table 1) and adiabatic calorimetry (Table 3 of the Preface) proved the occurrence of solid state transformations only at 467-470 and 491-494 K, respectively.

SOURCE AND PURITY OF MATERIALS:

Both components prepared from the proper acid and the carbonate (Ref. 1). Component 1 melts at $t_{fus}(1)/^{\circ}C=258$ and undergoes a phase transition at $t_{trs}(1)/^{o}C=242$ (Ref. 2). Component 2 melts at $t_{fus}(2)/^{o}C=298$ of the original (according to Fig.s 3, 4, paper; compiler) or 300 (Fig. 1), and undergoes phase transitions t_{trs}(2)/°C= 195, 217, 287 (Ref. 2).

ESTIMATED ERROR:

Temperature: accuracy probably ± 2 K (compiler).

- (1) Sokolov, N.M.
 Zh. Obshch. Khim. 1954, 24, 1581-1593.
- (2) Sokolov, N.M.
 Tezisy Dokl. X Nauch. Konf. S.M.I. 1956,

- (1) Sodium methanoate (sodium formate); NaCHO₂; [141-53-7]
- (2) Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7]

EVALUATOR:

Franzosini, P., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

This system was studied only by Sokolov (Ref. 1), who suggested the existence of: (i) a eutectic, E_1 , at 525 K (252 °C) and $100x_2=2.5$; (ii) a eutectic, E_2 , at 581 K (308 °C) and $100x_2=89$; and (iii) an intermediate compound, $Na_2CHO_2C_4H_7O_2$, congruently melting at 614 K (341 °C).

Component 2, however, forms liquid crystals. Therefore, the fusion temperature, $T_{fus}(2) = 603$ K (330 °C; Ref. 1), should be identified with the clearing temperature, the corresponding value from Table 1 of the Preface being $T_{clr}(2) = 600.4 \pm 0.2$ K. No mention is made by the author of the other phase transitions occurring in component 2, including that corresponding to the actual fusion, viz., $T_{fus}(2) = 524.5 \pm 0.5$ K (Table 1).

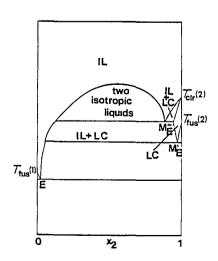
Conversely, the fusion temperature of component 1, $T_{fus}(1) = 531$ K (258 °C; Ref. 1), satisfactorily corresponds to the value of Table 1, viz., $T_{fus}(1) = 530.7 \pm 0.5$ K.

In conclusion, Sokolov's assertion of the existence of the congruently melting intermediate compound is a reasonable interpretation of the trend of the available data. In this case, however, the phase diagram could be interpreted with reference to Scheme D.1 of the Preface: in particular, the eutectic $\rm E_2$ could be actually identified with an $\rm M^*_E$ point, Sokolov's diagram likely being similar to that shown in Preface, Scheme D.1.

The unusual size of the dome and the absence of any information about the solidus does not allow one to exclude that Sokolov's points might be at least in part relevant to liquid-liquid instead of solid-liquid equilibria. One might therefore take into account the occurrence of liquid layering as shown in the figure: in particular, the eutectic \mathbf{E}_2 could be actually identified with an invariant at which equilibrium occurs among two isotropic liquid and one crystalline liquid phases.

REFERENCES:

(1) Sokolov, N.M.
Zh. Obshch. Khim. 1954, 24, 1581-1593.



- (1) Sodium methanoate (sodium formate); NaCHO₂; [141-53-7]
- (2) Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1581-1593.

VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

t/ºC	T/K ^a	100 x 2	t/°C	T/K ^a	100 x 2
258	531	0	340	613	55
252	525	2.5	340	613	60
287	560	5	339	612	65
301	574	10	338	611	70
312	585	15	336	609	75
318	591	20	331	604	80
324	597	25	324	597	85
327	600	30	308	581	89
333	606	35	311	584	90
337	610	40	322	595	95
339	612	45	330	603	100
341	614	50			

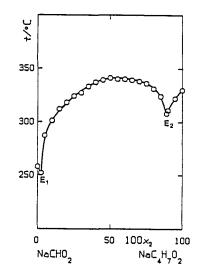
a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E_1 , at 252 °C and $100x_2=2.5$ (author). Eutectic, E_2 , at 308 °C (erroneously reported as 318 °C in the text, compiler) and $100x_2=89$ (author).

Intermediate compound(s):

 $Na_2CHO_2C_4H_7O_2$, congruently melting at 341 $^{\circ}C$.



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

Melts contained in a glass tube and stirred.

Temperatures measured with a Nichrome-Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of isotropicity in the melt on cooling.

SOURCE AND PURITY OF MATERIALS:

Materials prepared by reacting aqueous ("chemically pure") Na_2CO_3 with a slight excess of the proper acid of analytical purity. The solvent and excess acid were removed by heating to $160~^{\circ}\mathrm{C}$.

ESTIMATED ERROR:

Temperature: accuracy probably ± 2 K (compiler).

- (1) Sodium methanoate (sodium formate); NaCHO₂; [141-53-7]
- (2) Sodium iso.butanoate (sodium iso.butyrate); Nai.C₄H₇O₂; [996-30-5]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1581-1593.

VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

t/°C	T/K ^a	100x ₂	t/ ^o C	T/Kª	100 x ₂
258	531	0	329	602	55
252	525	1.3	327	600	60
290	563	5	325	598	65
305	578	10	320	593	70
314	587	15	314	587	75
319	592	20	306	579	80
321	594	25	296	569	85
324	597	30	282	555	90
326	599	35	258	531	95
327	600	40	250	523	96.5
329	602	45	260	533	100
330	603	50			
1					

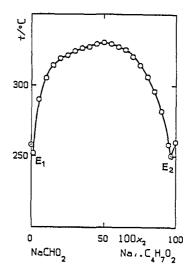
a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E₁, at 252 °C and $100x_{2}$ 1.3 (author). Eutectic, E₂, at 250 °C and $100x_{2}$ 96.5 (author).

Intermediate compound(s):

Na₂CHO₂i.C₄H₇O₂, congruently melting at 330 °C.



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

Melts contained in a glass tube and stirred.

Temperatures measured with a Nichrome-Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of isotropicity in the melt on cooling.

NOTE:

As an interpretation alternative to that by Sokolov, the large liquidus dome might be due to the occurrence of a miscibility gap in the liquid state.

SOURCE AND PURITY OF MATERIALS:

Materials prepared by reacting aqueous ("chemically pure") Na_2CO_3 with a slight excess of the proper acid of analytical purity. The solvent and excess acid were removed by heating to $160~^{\circ}\text{C}$.

ESTIMATED ERROR:

Temperature: accuracy probably ± 2 K (compiler).

(1) Sodium methanoate (sodium formate);

NaCHO₂; [141-53-7]
(2) Sodium iso.pentanoate (sodium iso.valerate);
Nai.C₅H₉O₂; [539-66-2]

EVALUATOR:

Franzosini, P., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

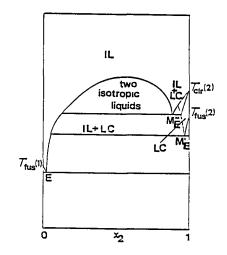
CRITICAL EVALUATION:

This system was studied only by Sokolov (Ref. 1), who claimed the existence of:

(i) a eutectic, E_1 , at 525 K (252 °C) and $100x_2$ = 0.75; (ii) a eutectic, E_2 , at 518 K (245 °C) and $100x_2$ = 94.5; and (iii) an intermediate compound, $Na_5(CHO_2)_3(i.C_5H_9O_2)_2$ congruently melting at 593 K (320 °C).

Component 2, however, forms liquid crystals. Therefore, the fusion temperature reported in Ref. 1, $T_{fus}(2) = 535$ K (262 °C) is actually to be identified with the clearing temperature, the corresponding value from Table 2 of the Preface being $T_{clr}(2) = 559 \pm 1$ K. The remarkable discrepancy between these values might be attributed to the presence of some impurity in Sokolov's sample, inasmuch as the value from Table 2 meets rather satisfactorily those reported by Ubbelohde et al. (556 K; Ref. 2), and by Duruz et al. (553 K; Ref. 3). According to Table 2, component 2 melts at 461.5+0.6 K.

Conversely, the fusion temperature reported in Ref. 1 for component 1, $T_{fus}(1)$ = 531 K (238 °C) is in satisfactory agreement with the value from Table 1, viz., $T_{fus}(1)$ = 530.7 \pm 0.5 K.



In conclusion, Sokolov's assertion of the existence of the congruently melting intermediate compound is a reasonable interpretation of the trend of the available data. In this case, however, the phase diagram should be modified as follows: the eutectic $\rm E_2$ should be identified with an M' $\rm E$ point, Sokolov's diagram being likely similar to that shown in Scheme D.1.

The unusual size of the dome and the absence of any information about the solidus does not allow one to exclude that Sokolov's points might be at least in part relevant to liquid-liquid instead of solid-liquid equilibria. One might therefore take into account the occurrence of liquid layering as shown in the figure: in particular, the eutectic \mathtt{E}_2 could be actually identified with an invariant at which equilibrium occurs among two isotropic liquid and one crystalline liquid phases.

- (1) Sokolov, N.M.
 Zh. Obshch. Khim. 1954, 24, 1581-1593.
- (2) Ubbelohde, A.R.; Michels, H.J.; Duruz, J.J. Nature 1970, 228, 50-52.
- (3) Duruz, J.J.; Michels, H.J.; Ubbelohde, A.R. Proc. R. Soc. London <u>1971</u>, A322, 281-299.

- (1) Sodium methanoate (sodium formate); NaCHO₂; [141-53-7]
- (2) Sodium iso-pentanoate (sodium iso-valerate); Nai-C₅H₉O₂; [539-66-2]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1581-1593.

VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

t/°C	T/K ^a	100x ₂	t/°C	T/K ^a	100 x 2
258	531	0	317	590	50
252	525	0.75	315	588	55
287	560	5	312	585	60
300	573	10	309	582	65
308	581	15	306	579	70
311	584	20	301	574	75
314	587	25	297	570	80
316	589	30	284	557	85
318	591	35	265	538	90
320	593	40	245	518	94.5
319	592	45	262	535	100

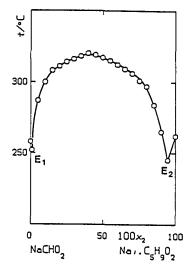
a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E₁, at 252 $^{\rm o}$ C and 100x₂= 0.75 (author). Eutectic, E₂, at 245 $^{\rm o}$ C and 100x₂= 94.5 (author).

Intermediate compound(s):

 $Na_5(CHO_2)_3(1.C_5H_9O_2)_2$, congruently melting at 320 °C.



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

Melts contained in a glass tube and stirred.

Temperatures measured with a Nichrome-Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of isotropicity in the melt on cooling.

SOURCE AND PURITY OF MATERIALS:

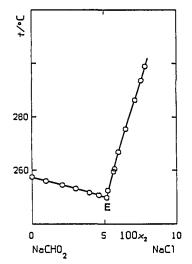
Materials prepared by reacting aqueous ("chemically pure") Na_2CO_3 with a slight excess of the proper acid of analytical purity. The solvent and excess acid were removed by heating to $160~^{\circ}C$.

ESTIMATED ERROR:

Temperature: accuracy probably ±2 K (compiler).

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Sodium methanoate (sodium formate); NaCHO₂; [141-53-7] Sodium chloride; NaCl; [7647-14-5] 	Leonesi, D.; Braghetti, M.; Cingolani, A.; Franzosini, P. Z. Naturforsch. 1970, 25a, 52-55.
VARIABLES:	PREPARED BY:
Temperature.	Baldini, P.

EXPERI	MENTAL	VALUES:	
t/°C	T/K ^a	100x ₂	
257.5	530.7	0	
256.0	529.2	0.95	
254.5	527.7	2.10	
253.2	526.4	3.00	
251.6	524.8	3.94	
250.7	523.9	4.60	
249.8	523.0	5.14	
252.5	525.7	5.22	
259.5	532.7	5.63	
260.5	533.7	5.70	
266.8	540.0	5.98	
275.4	548.6	6.48	
286.3	559.5	7.13	
293.6	566.8	7.55	
298.9	572.1	7.83	



a T/K values calculated by the compiler.

Note 1 - In the original paper the results were shown in graphical form. The above listed numerical values represent a personal communication by one of the authors (f., P.) to the compiler.

Note 2 - The system could not be investigated above 300 $^{\rm O}{\rm C}$ due to the thermal instability of the methanoate.

Characteristic point(s): Eutectic, E, at 249.8 $^{\rm O}{\rm C}$ and $100{\rm x_2}$ = 5.15 (authors).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A Pyrex device, suitable for work under an inert atmosphere, and allowing one to observe the system visually, was employed (for details, see Ref. 1). The initial crystallization temperatures were measured with a Chromel-Alumel thermocouple checked by comparison with a certified Pt resistance thermometer, and connected with a L&N Type K-3 potentiometer.

NOTE:

Previous investigations by the same group (Ref. 2) stated that the cryometric constant of sodium methanoate was $K=9.4\pm0.2$ K molality⁻¹, and that

$$\lim_{m \to 0} (\Delta T/m) = 9.6 \text{ K molality}^{-1}$$

(where ΔT : experimental freezing point depression; m: molality of the solute) when NaCl was the solute. Consequently, the solubility of component 2 in component 1 in the solid state ought to be insignificant.

SOURCE AND PURITY OF MATERIALS:

C. Erba RP materials, dried by heating under vacuum.

ESTIMATED ERROR:

Temperature: accuracy probably ±0.1 K (compiler).

- (1) Braghetti, M.; Leonesi, D.; Franzosini, P. Ric. Sci. 1968, 38, 116-118
- Ric. Sci. 1968, 38, 116-118.

 (2) Leonesi, D.; Piantoni, G.; Berchiesi, G.; Franzosini, P.
 Ric. Sci. 1968, 38, 702-705.

- (1) Sodium methanoate (sodium formate); NaCHO₂; [141-53-7]
- (2) Sodium thiocyanate; NaCNS; [540-72-7]

EVALUATOR:

Ferloni, P., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

The system sodium methanoate - sodium thiocyanate was investigated by Sokolov, 1954 (Ref. 1), Sokolov and Pochtakova, 1958 (Ref. 2), Cingolani et al., 1971 (Ref. 3), and Storonkin et al., 1974 (Ref. 4).

The liquidus curve drawn on the basis of visual polythermal observations led Sokolov (Ref. 1) to express the opinion that the system was a eutectic one.

Sokolov and Pochtakova (Ref. 2) re-examined the system (as a side of the composition square of the reciprocal ternary K, Na/CHO₂, CNS) using the same method and came to parallel conclusions. It is however to be noted that: (i) differences up to 8 K exist between the fusion temperatures listed in either paper for mixtures of equal composition; and (ii) the coordinates of the eutectic are somewhat different, i.e., 460 K and $100\text{x}_2\text{=} 36$ according to Ref. 1, and 462 K and $100\text{x}_2\text{=} 38$ according to Ref. 2.

Cingolani et al. (Ref. 3), not aware of Ref.s 1, 2, found two invariants, viz. a eutectic at 462.7 K and $100\mathbf{x}_2$ = 38.0 (in excellent agreement with Ref. 2) and the other one corresponding to the incongruent melting of the intermediate compound Na₅(CHO₂)₄CNS. They supplemented their visual observations (carried out at a cooling rate of about 0.25 K min⁻¹) with DSC analysis, and, in particular, asserted that the composition of the intermediate compound "was confirmed by DSC measurements". They could also observe in the composition triangle of each of the ternaries Na/Br, CHO₂, CNS, Na/CHO₂, C1, CNS, and Na/CHO₂, CNS, I a crystallization region belonging to the binary intermediate compound and covering respectively 0.45, 0.80, and 1.80 % of the liquidus area.

Storonkin et al. (Ref. 4) employed DTA to investigate the ternary Na/CHO $_2$, CNS, NO $_3$, and once more found, for the binary system of interest here, just one eutectic at 443 K and $100\mathbf{x}_2$ = 36; they also claimed the distribution coefficient of NaCHO $_2$ in NaCNS to be zero in the thiocyanate crystallization field. They were apparently not aware of Ref. 3.

Because of the better accuracy of the experimental approach, the evaluator is inclined to recommend (among those available so far) the data by Berchiesi et al. (Ref. 3). The fact that Storonkin et al. (Ref. 4), by employing a DTA technique, where not able to detect the intermediate compound still remains surprising. This fact, however, might be explained if the large supercooling effect found by the latter authors in the region of the ternary eutectic could not be prevented in the region of the binary eutectic. Efficient stirring and slow cooling rate have likely allowed Cingolani et al. (Ref. 3) to avoid this drawback. The presence of some impurity in Storonkin et al. (Ref. 4) methanoate is even possible, inasmuch as their $T_{\rm fus}(1)/K$ value (528) is some 3 K lower than those reported in Ref.s 1 (531), 2 (531), and 3 (530.65), and in Table 3 [530.46+0.04 (adiabatic calorimetry); 530.7+0.5 (DSC)].

- (1) Sokolov, N.M.
 Zh. Obshch. Khim. 1954, 24, 1150-1156.
- (2) Sokolov, N.M.; Pochtakova, E.I. Zh. Obshch. Khim. 1958, 28, 1391-1397 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1958, 28, 1449-1454.
- (3) Cingolani, A.; Berchiesi, G; Piantoni, G. J. Chem. Eng. Data 1971, 16, 464-467.
- (4) Storonkin, A.V.; Vasil kova, I.V.; Potemin, S.S. Vestn. Leningr. Univ., Fiz., Khim. 1974, (10), 84-88.

(1) Sodium methanoate (sodium formate);

NaCHO₂; [141-53-7]
(2) Sodium thiocyanate;
NaCNS; [540-72-7]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1150-1156.

VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

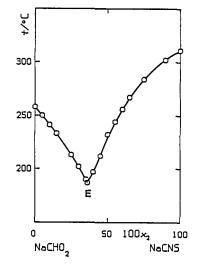
EXPERIMENTAL VALUES:

t/°C	T/K ^a	100 x ₂	t/ ^o C	T/K ^a	100 x 2
258 250 241 233 213 202	531 523 514 506 486 475	0 5 10 15 25 30	212 232 244 256 267 284	485 505 517 529 540 557	45 50 55 60 65 75
190 187 197	463 460 470	35 36 40	302 311	575 584	90 100

a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E, at 187 $^{\circ}$ C and $100x_{2}$ = 36 (author).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.
Salt(s) melted in a test tube. Temperature measured with a Nichrome-Constantane thermocouple and a millivoltmeter with mirror reading to 17 mV.

SOURCE AND PURITY OF MATERIALS:

Component 1 synthetized from methanoic acid and NaHCO3. Component 2 of analytical purity recrystallized once from water and once from ethanol.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

- (1) Sodium methanoate (sodium formate);
- NaCHO₂; [141-53-7]
 (2) Sodium thiocyanate;
 NaCNS; [540-72-7]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.; Pochtakova, E.I. Zh. Obshch. Khim. 1958, 28, 1391-1397 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1958, 28, 1449-1454.

VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

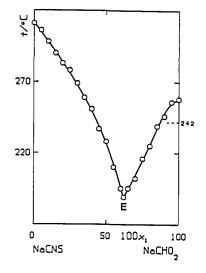
EXPERIMENTAL VALUES:

t/ºC	T/K ^a	100 x 1	t/°C	T/K ^a	100 x 1
311	584	0	210	483	55
306	579	5	195	468	60
298	571	10	189	462	62
290	563	15	195	468	65
283	556	20	202	475	70
278	551	25	216	489	75
269	542	30	225	498	80
259	532	35	239	512	85
251	524	40	246	519	90
237	510	45	256	529	95
228	501	50	258	531	100

a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E, at 189 °C and $100x_1 = 62$ (authors).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

SOURCE AND PURITY OF MATERIALS:

Component 1: commercial material recrystallized from water; it undergoes a phase transition at t_{trs}(1)/°C= 242 (Ref. 1).

Component 2: commercial material recrystallized from alcohol.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

REFERENCES:

(1) Sokolov, N.M.
Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

- (1) Sodium methanoate (sodium formate); NaCHO₂; [141-53-7]
- (2) Sodium thiocyanate; NaCNS; [540-72-7]

ORIGINAL MEASUREMENTS:

Cingolani, A.; Berchiesi, G; Piantoni, G. J. Chem. Eng. Data 1971, 16, 464-467.

VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

t/ºC	T/K ^a	100 _{x2}	t/°C	T/K ^a	100 x 2
257.5	530.7	0	199.5	472.7	30.2
251.0	524.2	4.5	197.0	470.2	32.1
241.0	514.2	10.1	195.0	468.2	34.2
232.5	505.7	14.6	194.0	467.2	34.8
221.0	494.2	20.1	193.0	466.2	35.1
212.0	485.2	23.9	190.5	463.7	37.3
202.5	475.7	27.2	189.5	462.7	38.1
193.0	466.2	38.9	223.5	496.7	50.0
193.0	466.2	39.1	231.0	504.2	53.0
199.0	472.2	41.0	234.5	507.7	54.4
203.5	476.7	42.4	241.0	514.2	57.7
203.5	476.7	42.7	257.0	530.2	65.5
213.0	486.2	45.7	268.5	541.7	72.9
217.0	490.2	47.8			
a T/V			L		

T/K values calculated by the compiler.

Note 1 - Measurements at $t/^{\circ}C > 280$ not taken due to instability of the melts (authors). Note 2 - Despite the high accuracy of their temperature measurements, the authors chose

to tabulate temperatures rounded at 0.5 K (compiler).

250 200 40 100x2 NaCHO, NaCNS

Characteristic point(s):

Eutectic, E, at 189.5 °C and $100x_2$ = 38.0 (authors). Peritectic, P, at 200.8 °C and $100x_2$ = 28.6 (authors).

Intermediate compound(s):

Na₅(CHO₂)₄CNS, incongruently melting (authors).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual method (for details, see Ref. 1). The melts contained in a Pyrex cryostat were cooled at a rate of about 0.25 K/min; the temperatures of initial crystallization were measured with a Chromel-Alumel thermocouple checked by comparison with a certified Pt resistance thermometer, and connected with a L&N potentiometer type K-3. Supplementary DSC measurements were also performed.

SOURCE AND PURITY OF MATERIALS:

Materials of stated purity > 99 % were employed after careful drying.

ESTIMATED ERROR:

Temperature: accuracy + 0.05 K (authors).

REFERENCES:

(1) Braghetti, M.; Leonesi, D.; Franzosini, P. Ric. Sci. 1968, 38, 116-118.

- (1) Sodium methanoate (sodium formate);
- NaCHO₂; [141-53-7]
 (2) Sodium thiocyanate;
 NaCNS; [540-72-7]

ORIGINAL MEASUREMENTS:

Storonkin, A.V.; Vasil kova, I.V.; Potemin, S.S.

Vestn. Leningr. Univ., Fiz., Khim. 1974, (10), 84-88.

VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

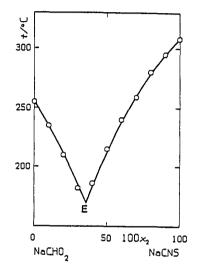
t/°C	T/K ^a	100 x 2
255	528	0
235 210	508 483	10 20
182	455	30
186 215	459 488	40 50
240	513	60
259	532	70
280 295	553 568	80 90
308	581	100

a T/K values calculated by the compiler.

Note - The data tabulated were drawn by the compiler from Fig. 1 of the original paper.

Characteristic point(s):

Eutectic, E, at 170 °C and $100x_2 = 36$ (authors).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

DTA.

Thermograph with photorecorder. Salt(s) sealed under vacuum in Pyrex ampoules.

No other information given.

SOURCE AND PURITY OF MATERIALS:

 ${
m NaCHO}_2$ of analytical purity and "chemically pure" NaCNS, heated 10-15 h at temperatures 50-60 $^{
m OC}$ below their fusion temperatures, were employed.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

- (1) Sodium methanoate (sodium formate);
 NaCHO: [141-53-7]
- NaCHO₂; [141-53-7] (2) Sodium iodide; NaI; [7681-82-5]

ORIGINAL MEASUREMENTS:

Leonesi, D.; Braghetti, M.; Cingolani, A.; Franzosini, P. Z. Naturforsch. 1970, 25a, 52-55.

VARIABLES:

Temperature.

PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

t/°C	T/K ^a	100 x 2	t/°C	T/K ^a	100 x 2
257.5	530.7	0	243.5	516.7	9.00
256.8	530.0	0.42	241.6	514.8	9.98
256.3	529.5	0.73	237.7	510.9	12.01
255.9	529.1	0.98	234.0	507.2	13.99
255.4	528.6	1.34	232.2	505.4	15.00
254.7	527.9	1.79	230.0	503.2	15.99
254.3	527.5	2.03	236.5	509.7	17.99
251.2	524.4	4.02	248.4	521.6	18.98
248.3	521.5	6.00	270.9	544.1	20.99
244.9	518.1	7.99	306.3	579.5	24.61

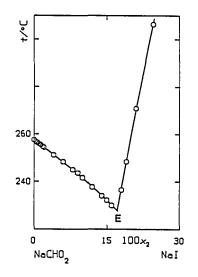
 $^{^{\}mathbf{a}}$ T/K values calculated by the compiler.

Note 1 - In the original paper the results were shown in a graphical form. The above listed numerical values represent a personal communication by one of the authors (F., P.) to the compiler.

Note 2 - The system could not be investigated above about 300 °C due to the thermal instability of the methanoate.

Characteristic point(s):

Eutectic, E, at 227.7 °C and $100x_2$ = 17.25 (authors).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A Pyrex device, suitable for work under an inert atmosphere, and allowing one to observe the system visually, was employed (for details, see Ref. 1). The initial crystallization temperatures were measured with a Chromel-Alumel thermocouple checked by comparison with a certified Pt resistance thermometer, and connected with a L&N Type K-3 potentiometer.

SOURCE AND PURITY OF MATERIALS:

C. Erba RP meterials, dried by heating under vacuum.

ESTIMATED ERROR:

Temperature: accuracy probably ± 0.1 K (compiler).

REFERENCES:

(1) Braghetti, M.; Leonesi, D.; Franzosini, P. Ric. Sci. 1968, 38, 116-118.

- (1) Sodium methanoate (sodium formate); NaCHO₂; [141-53-7]
- (2) Sodium nitrite; NaNO₂; [7632-00-0]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1957, 27, 840-844 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1957, 27, 917-920.

VARIABLES:

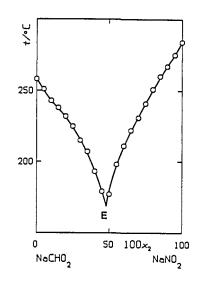
Temperature.

PREPARED BY:

Baldini, P.

EXPERIMENTAL VALUES:

t/°C	T/K ^a	$100x_{2}$
		-
258	531	0
251	524	5
243	516	10
238	511	15
232	505	20
225	498	25
215	488	30
207	480	35
193	466	40
179	452	45
177	450	50
198	471	55
211	484	60
222	495	65
231	504	70
241	514	75
251	524	80
260	533	85
267	540	90
275	548	95
284	557	100



Characteristic point(s): Eutectic, E, at 169 $^{\circ}$ C and $100x_{2}$ = 48 (author).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis; salt mixtures melted in a glass tube (surrounded by a wider tube) and stirred with a glass thread. The temperatures of initial crystallization were measured with Nichrome-Constantane thermocouple checked at the fusion points of water, benzoic acid, mannitol, AgNO3, Cd, KNO3, and $\rm K_2Cr_2O_7$.

SOURCE AND PURITY OF MATERIALS:

"Chemically pure" materials recrystallized from water.

ESTIMATED ERROR:

Temperature: accuracy probably ± 2 K (compiler).

REFERENCES:

NOTE:

The fusion temperature of component 1 (531 K) is in excellent agreement with the value (530.7+0.5 K) listed in Table 1 of the Preface, where a solid state transition (at 502+5 K), not mentioned by the author, is also reported.

a T/K values calculated by the compiler.

(1) Sodium methanoate (sodium formate); NaCHO₂; [141-53-7]

(2) Sodium nitrate; NaNO₃; [7631-99-4] **EVALUATOR:**

Ferloni, P., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

The system sodium methanoate - sodium nitrate was investigated by Sokolov, 1954 (Ref. 1), Tsindrik, 1958 (Ref. 2), Berchiesi et al., 1972 (Ref. 3), and Storonkin et al., 1974 (Ref. 4).

The liquidus curve drawn on the basis of visual polythermal observations led Sokolov (Ref. 1) to express the opinion that the formation of any intermediate compound was to be excluded, and consequently the system was a eutectic one.

Tsindrik (Ref. 2), who belonged to the same Smolensk Medical Institute (S.M.I.) as Sokolov, re-examined the system (as a side of the composition square of the reciprocal ternary Li, Na/CHO₂, NO₃) using the same method and came to parallel conclusions. Significant discrepancies, however, exist in the trend of the liquidus curves given by either author; and for the coordinates of the eutectic, Tsindrik (Ref. 2) quoted figures (from a paper discussed in 1956 by Sokolov - Ref. 5) which coincide neither with those reported by Sokolov himself in his 1954 paper (Ref. 1) nor with those the evaluator could obtain by plotting Tsindrik's experimental points (Ref. 2).

Berchiesi et al. (Ref. 3), being aware of Sokolov's paper (Ref. 1), found two invariant points: a eutectic and one corresponding to the incongruent melting of the intermediate compound $Na_4(CHO_2)_3NO_3$. They supplemented their visual observations with DSC analysis of four mixtures. In the recorded traces they recognized: for $x_1=0.7926$, "peaks corresponding to the peritectic transition (477 K) and to complete fusion"; for $x_1=0.7312$, "peaks corresponding to the eutectic fusion (464 K), to the peritectic transition (477 K) and to complete fusion"; for $x_1=0.6560$, "peaks corresponding to the eutectic fusion and to the peritectic transition"; for $x_1=0.5190$, one "peak corresponding to the eutectic fusion". They could also observe in the composition triangle of the ternary Na/CHO_2 , CNS, NO_3 a crystallization region belonging to the binary intermediate compound and covering 5.30 % of the liquidus area.

Storonkin et al. (Ref. 4) employed DTA to investigate the same ternary, and once more found, for the binary system of interest here, just one eutectic although at coordinates different from those reported by Sokolov (Ref. 1) and by Tsindrik (Ref. 2); they also claimed the distribution coefficient of NaCHO₂ in NaNO₃ to be zero in the nitrate crystallization field. Storonkin et al. (Ref. 4) were apparently aware only of a 1971 paper by Sokolov and Khaitina (Ref. 6), where in turn only Sokolov's 1954 findings (Ref. 1) were quoted.

Finally, it is to be mentioned that the cryometric data of Leonesi et al., 1968 (Ref. 7), proved that the nitrate has no tendency (or at least a negligibly small tendency) to dissolve in the methanoate in the solid state.

In order to evaluate the consistency of the above sets of measurements, the following considerations may be useful.

In any binary system where solid solutions are absent, the branch of the liquidus curve rich in component 1 may often be represented satisfactorily by means of the approximate equation (Ref. 8)

$$T(1) = \{H(1)/R + (A/R)(x_2)^2\} / \{S(1)/R + \ln (x_2)\}$$

where A is an empirical constant which of course is zero for ideal systems, and

$$H(1) = \Delta_{fus}(1)H_{m};$$
 $S(1) = \Delta_{fus}(1)S_{m}.$

When T(1) is between $[T_{fus}(1)]$ and $T_{trs}(1)$,

$$H(1) = \Delta_{fus}(1)H_m + \Delta_{trs}(1)H_m;$$
 $S(1) = \Delta_{fus}(1)S_m + \Delta_{trs}(1)S_m.$

Taking now the DSC numerical values listed in Table 3 of the Preface, which concern component 1, i.e. sodium methanoate, one obtains for the ideal behaviour the curve denoted as "ideal" in the Figure of the next page.

- (1) Sodium methanoate (sodium formate); NaCHO₂; [141-53-7]
- (2) Sodium nitrate; NaNO₃; [7631-99-4]

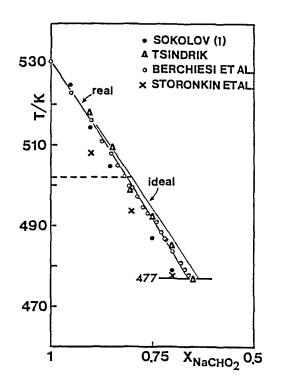
EVALUATOR:

Ferloni, P., Dipartimento di Chimica Fisica, Universita' di Pavia (ITALY).

CRITICAL EVALUATION (continued):

For the system K/CHO₂, NO₃ Leonesi et al. (Ref. 7) were able to fit their experimental points fairly well for the branch rich in methanoate, when A/R was assigned the value -175 K. In the present binary, formed with the common cation Na and the same pair of different anions, it seemed not unreasonable to expect analogous behavior. Introducing into Eq. (1) the above $\Delta(1)H_m$ and $\Delta(1)S_m$ values, and again A/R= -175 K, the "real" curve of the Figure is obtained. It can be seen that Berchiesi et al.'s (Ref. 3) points are the closest to whereas progressively this curves, increasing discrepancies are observed for the data of Tsindrik (Ref. 2), Sokolov (Ref. 1), and Storonkin et al. (Ref. 4) (each temperature being corrected in order to make allowance for the differences in the fusion temperatures of the methanoate given by the different authors).

evaluator is inclined to recommend (among those available so far) the data by Berchiesi et al. (Ref. 3). The fact that Storonkin et al. (Ref. 4), by employing a DTA technique, where not able to detect the intermediate compound seems rather surprising. This fact, however, might be related to the large supercooling effect found by the latter authors in the region of the ternary eutectic and difficult to prevent also in the region of the binary eutectic. Efficient stirring and slow cooling rate have likely allowed Berchiesi et al. (Ref. 3) to avoid this drawback. The presence of some impurity in Storonkin et al.'s (Ref. 4) methanoate is even possible, inasmuch as their $\mathbf{T}_{\mathrm{fus}}(1)/\mathrm{K}$ value (528) is some 3 K lower than those reported in Ref.s 1 (531), 2 (531), and 3 (530.65), and in Table 3 [530.46+0.04 (adiabatic calorimetry); 530.7+0.5 (DSC)].



- (1) Sokolov, N.M.; Zh. Obshch. Khim. 1954, 24, 1150-1156.
- (2) Tsindrik, N.M.; Zh. Obshch. Khim. 1958, 28, 830-834.
 (3) Berchiesi, M.A.; Cingolani, A.; Berchiesi, G.; J. Chem. Eng. Data, 1972, 17, 61-64.
 (4) Storonkin, A.V.; Vasil kova, I.V.; Potemin, S.S.; Vestn. Leningr. Univ., Fiz., Khim.
 - 1974, (10), 84-88.
- (5) Sokolov, N.M.; Tezisy Nauch. Konf. S.M.I. 1956a. (6) Sokolov, N.M.; Khaitina, M.V.; Zh. Obshch. Khim. 1971, 41, 1417.
- (7) Leonesi, D.; Piantoni, G.; Berchiesi, G.; Franzosini, P.; Ric. Sci. 1968, 38, 702. (8) Sinistri, C.; Franzosini, P.; Ric. Sci. 1963, 33(II-A), 419-430. (9) Braghetti, M.; Berchiesi, G.; Franzosini, P.; Ric. Sci. 1969, 39, 576.

- a This quotation as given by Tsindrik (Ref. 2) is probaly to be completed as follows: Tezisy Dokl. X Nauch. Konf. S.M.I. 1956. The evaluator did not succeed in obtaining a reprint from the author, but it is highly probable that numerical data are not given in the Tezisy, since such documents usually report only summaries of the discussions held at the pertinent conferences.

COMPONENTS: (1) Sodium methanoate (sodium formate); NaCHO₂; [141-53-7] (2) Sodium nitrate;

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1150-1156.

VARIABLES:

PREPARED BY:

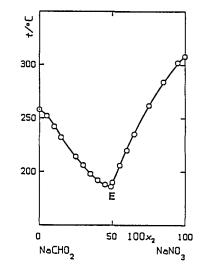
Temperature.

D'Andrea, G.

EXPERIMENTAL VALUES:

NaNO3; [7631-99-4]

t/°C	T/K ^a	100 x 2
258	531	0
252	525	5
242	515	10
232	505	15
214	487	25
206	479	30
198	471	35
192	465	40
188	461	45
186 ^b	459	49
190	463	50
206	479	55
220	493	60
235	508	65
262	535	75
284	557	85
302	575	95
308	581	100



Characteristic point(s):

Eutectic, E, at 186 °C and $100x_2$ = 49 (author).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis. Salt(s) melted in a test tube. Temperature measured with a Nichrome-Constantane thermocouple and a millivoltmeter with mirror reading to $17\,\mathrm{mV}$.

SOURCE AND PURITY OF MATERIALS:

Component 1 synthetized from methanoic acid and ${\rm NaHCO}_3$. Commercial component 2 further purified by the author according to Laiti.

ESTIMATED ERROR:

Temperature: accuracy probably ± 2 K (compiler).

a T/K values calculated by the compiler. b Eutectic temperature (author).

- (1) Sodium methanoate (sodium formate); NaCHO₂; [141-53-7]
- (2) Sodium nitrate; NaNO₃; [7631-99-4]

ORIGINAL MEASUREMENTS:

Tsindrik, N.M.

Zh. Obshch. Khim. 1958, 28, 830-834.

VARIABLES:

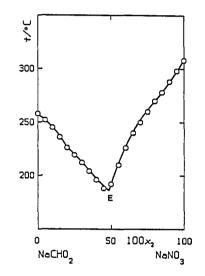
Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

t/°C	T/K ^a	100x ₂
258	531	0
252	525	5
245	518	10
236	509	15
226	499	20
219	492	25
212	485	30
204	477	35
196	469	40
188	461	45
192	465	50
210	483	55
226	499	60
240	513	65
250	523	70
260	533	75
270	543	80
278	551	85
288	561	90
298	571	95
308	581	100



Characteristic point(s):

Eutectic, E, at 187 °C and $100x_2$ = 48 (author, Ref. 1)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis; temperatures measured with a Nichrome-Constantane thermocouple. Salt(s) melted in a test tube, hand-stirred.

SOURCE AND PURITY OF MATERIALS:

Materials of analytical purity twice recrystallized. Component 1 undergoes a solid state transition at $t_{\rm trs}(1)/^{\rm C}$ C= 242 (Ref. 1). Component 2 undergoes a solid state transition at $t_{\rm trs}(2)/^{\rm C}$ C= 275 (current literature).

ESTIMATED ERROR:

Temperature: accuracy probably ± 2 K (compiler).

REFERENCES:

(1) Sokolov, N.M.
Tezisy Nauchn. Konf. S.M.I. 1956.

a T/K values calculated by the compiler.

- (1) Sodium methanoate (sodium formate); NaCHO₂; [141-53-7]
- (2) Sodium nitrate; NaNO₃; [7631-99-4]

ORIGINAL MEASUREMENTS:

Berchiesi, M.A.; Cingolani, A.; Berchiesi, G. J. Chem. Eng. Data, 1972, 17, 61-64.

VARIABLES:

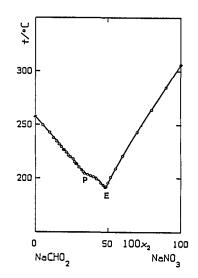
Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

t/°C	T/K ^a	100 x 2	t/°C	T/Kª	100 x 2
257.50	530.65	0	205.85	479.00	33.07
249.50	522.65	5.17	204.50	477.65	33.99
242.73	515.88	9.88	203.50	476.65	35.98
237.58	510.73	12.69	202.13	475.28	38.09
234.43	507.58	15.04	201.25	474.40	39.99
231.65	504.80	16.59	199.25	472.40	42.01
229.03	502.18	18.12	195.38	468.53	44.96
226.58	499.73	19.41	193.50	466.65	46.61
226.13	499.28	20.08	192.10	465.25	48.57
223.98	497.13	21.53	195.75	468.90	49.93
221.35	494.50	22.78	200.87	474.02	51.67
219.85	493.00	24.00	208.93	482.08	55.09
217.73	490.88	26.08	220.70	493.85	60.01
215.08	488.23	27.19	243.03	516.18	70.02
213.55	486.70	28.04	263.95	537.10	79.90
213.05	486.20	28.61	284.98	558.13	90.04
210.30	483.45	30.07	306.00	579.15	100.00
207.54	480.69	32.03			



a T/K values calculated by the compiler.

Characteristic points: Peritectic, P, at 204 $^{\rm o}$ C and $100x_2$ = 34.4 (authors). Eutectic, E, at 191 $^{\rm o}$ C and $100x_2$ = 48.1 (authors).

Intermediate compound: Na₄(CHO₂)₃NO₃, incongruently melting (authors).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual method, supplemented by DSC analysis. Salt(s) melted in a Pyrex device (1) put into a furnace whose temperature was controlled by means of a Chromel-Alumel thermocouple connected with a L&N CAT control unit. Temperature of the melted measured with a second thermocouple checked by comparison with a certified Pt resistance thermometer, and a L&N K-5 potentiometer. Stirring by a Chemap Mod.E-1 Vibro-mixer.

SOURCE AND PURITY OF MATERIALS:

C.Erba (Milano, Italy) NaCHO₂ and NaNO₃ of stated purity not less than 99% were used after thorough dehydration.

ESTIMATED ERROR:

Temperature: accuracy +0.03 K (authors).

REFERENCES:

(1) Braghetti, M.; Leonesi, D.; Franzosini, P. Ric. Sci. 1968, 38, 116-118.

COMPONENTS: (1) Sodium methanoate (sodium formate); NaCHO ₂ ; [141-53-7] (2) Sodium nitrate; NaNO ₃ ; [7631-99-4]	ORIGINAL MEASUREMENTS: Storonkin, A.V.; Vasil kova, I.V.; Potemin, S.S. Vestn. Leningr. Univ., Fiz., Khim. 1974, (10), 84-88.
VARIABLES:	
Temperature.	PREPARED BY: D'Andrea, G.

EXPERI	VALUES:	
t/°C	T/K ^a	100x2

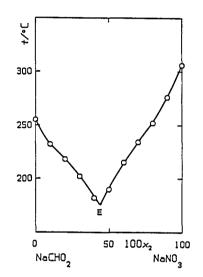
-, -	-, -,	-00-2
255	528	0
232	505	10
218	491	20
202	475	30
182	455	40
190	463	50
215	488	60
234	507	70
252	525	80
276	549	90
306	579	100

a T/K values calculated by the compiler.

Note - The data tabulated were drawn by the compiler from Fig. 1 of the original paper.

Characteristic point(s):

Eutectic, E, at 176 °C and $100x_2$ = 44 (authors).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

DTA: Thermograph with photorecorder. Salt(s) sealed under vacuum in Pyrex ampoules. No other information given.

SOURCE AND PURITY OF MATERIALS:

 ${
m NaCHO}_2$ of analytical purity and "chemically pure" ${
m NaNO}_3$, heated 10-15 h at temperatures 50-60 ${
m ^{O}C}$ below their fusion temperatures, were employed.

ESTIMATED ERROR:

Temperature: accuracy probably ±2 K (compiler).

- (1) Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3]
- (2) Sodium propanoate (sodium propionate); NaC₃H₅O₂; [137-40-6]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.; Pochtakova, E.I. Zh. Obshch. Khim. 1958, 28, 1397-1404.

VARIABLES:

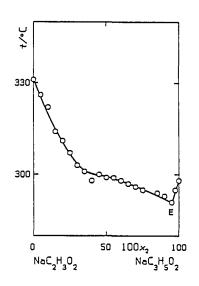
Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

T/K ^a	100 x 2
604	0
599	5
595	10
587	15
584	20
580	25
576	30
574	35
571	40
573	45
572	50
572	55
571	60
570	65
569	70
568	75
567	85
566	90
564	95
568	97.5
571	100
	604 599 595 587 584 580 576 574 571 573 572 572 571 570 569 568 564 564



Characteristic point(s): Eutectic, E, at 291 $^{\circ}$ C and $100x_{2}$ = 95 (authors).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

NOTE:

The fusion and solid state transition temperatures reported for component 1 (604 and 527 K, respectively) agree reasonably with the $T_{fus}(1)$ and $T_{trs}(1)$ values (601.3+0.5 and 527+15 K, respectively) listed in Table $\overline{1}$ of the Preface. 2, Concerning component the fusion temperature (571 K) looks, on the contrary, as somewhat too high; moreover, doubts are to be cast about the reliability of the lowest (350 K) and highest (560 K) transition temperatures quoted by the author from Ref. 2, inasmuch as both DSC (Table 1) and adiabatic calorimetry (Table 3) proved the occurrence of solid state transformations only at 491-494 and 467-470 K, respectively.

SOURCE AND PURITY OF MATERIALS:

Component 1: "chemically pure" material; it undergoes a phase transition at $t_{\rm trs}(1)/^{\rm C}$ = 254 (Ref.1). Component 2: prepared from commercial propanoic acid (distilled before use) and "chemically pure" sodium carbonate; the solid recovered was recrystallized from n-butano1; it undergoes phase transitions at $t_{\rm trs}(2)/^{\rm C}$ = 77, 195, 217, 287 (Ref. 2).

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

- (1) Bergman, A.G.; Evdokimova, K.A. Izv. Sektora Fiz.-Khim. Anal. 1956, 27, 296-314.
- (2) Sokolov, N.M.; Tezisy Dokl. X Nauch-Konf. S.M.I. 1956.

a T/K values calculated by the compiler.

- (1) Sodium ethanoate (sodium acetate); $NaC_2H_3O_2$; [127-09-3]
- (2) Sodium butanoate (sodium butyrate); NaC4H7O2; [156-54-7]

EVALUATOR:

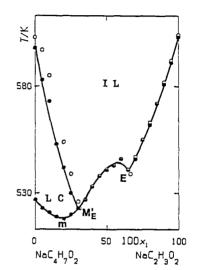
Ferloni, P., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

The visual polythermal method was employed by Sokolov (Ref. 1) to study the lower boundary of the isotropic liquid field: the results were subsequently reviewed by Sokolov and Pochtakova (Ref. 2). According these authors, the [congruently melting at 546 K (273 °C)] intermediate compound Na₅(C₂H₃O₂)₃(C₄H₇O₂)₂ is formed, and two invariants exist, 1.e., a eutectic E₁ [at 539 K (266 °C), and $100x_2$ = 33.5], and a eutectic E₂ [at 523 K (250 °C), and $100x_2$ = 691. to these authors, the [congruently melting $100x_2 = 69$].

Component 2, however, forms liquid crystals. Accordingly, the fusion temperature, $T_{fus}(2) = 603 \text{ K } (330 \text{ }^{\circ}\text{C}),$ reported in Refs. 1, 2 should be identified with the clearing temperature, $T_{\rm clr}(2)$, of component 2, the corresponding value from Table 1 of the Preface being 600.4+0.2 K.

For the same component, Table 1 of the Preface [besides the $T_{clr}(2)$ value] provides the values 450.4±0.5, 489.8±0.2,



498.3+0.3, and 508.4+0.5 K respectively, for $\overline{T^{1}v}_{trs}(2)$ to $\overline{T^{1}t}_{trs}(2)$, and $T_{fus}(2)/K=524.5+0.5$. These phase relations, first stated on the basis of DSC records, were subsequently confirmed by Schiraldi and Chiodelli's conductometric results (Ref. 3). Phase relations are quoted in Ref. 2 from Ref. 4 as occurring at 390, 505, 525, and 589 K, respectively. A comparison of the two sets of data allows one to compare the two intermediate transition temperatures from Ref. 4 with $T^{1}_{trs}(2)$ and $T_{fus}(2)$ from Table 1 of the Preface. Reasonable doubts can be cast, on the contrary, about the actual existence of Ref. 4 highest and lowest transformations (the former - if present - ought to represent the transformation from one liquid crystalline phase into another).

More recently, Prisyazhnyi et al. (Ref. 5) - to whom Refs. 1, 2 seem to be unknown - carried out a derivatographical re-investigation of the system, which allowed them to draw the lower boundaries of both the isotropic liquid, and the liquid crystal field. Their clearing $[T_{clr}(2) = 598 \text{ K } (325 ^{\circ}\text{C})]$ and fusion $[T_{fus}(1) = 603 \text{ K } (330 ^{\circ}\text{C});$ $T_{fus}(2) = 527 \text{ K } (254 ^{\circ}\text{C})]$ temperatures substantially agree with those from Table 1 of the Preface; moreover, it is to be stressed that they do not mention any transition intermediate between T_{clr}(2) and T_{fus}(2).

Prisyazhnyi et al.'s, and Sokolov's results (filled and empty circles,

respectively) are compared in the figure (IL: isotropic liquid; LC: liquid crystals), an inspection of which allows one to state that: (i) the invariant at about $100x_2=70$ is actually an M_E point, and (ii) a further characteristic point exists (at about $100x_2$ = 80) which escaped Sokolov's attention, and is probably a minimum, m, in a series of solid solutions. Prisyazhnyi et al. s results suggest at $0 \le 100x_1 \le 60$ a behavior similar to that shown in Scheme A.3 of the Preface.

The two two-phase regions pertinent to the liquid crystal - isotropic liquid equilibria, and to solid solutions formation, respectively, might be so narrow as to have prevented Prisyazhnyi et al. to observe two distinct sets of points in each of these regions, whereas one cannot explain the lack of information by the same authors about eutectic fusion at $60 \le 100x_1 \le 100$.

- (1) Sokolov, N.M.; Zh. Obshch. Khim. 1954, 24, 1581-1593. (2) Sokolov, N.M.; Pochtakova, E.I.; Zh. Obshch. Khim. 1960, 30, 1401-1405 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1960, 30, 1429-1433.
- (3) Schiraldi, Λ.; Chiodelli, G.; J. Phys. E: Sci. Instr. 1977, 10, 596-599.
- (4) Sokolov, N.M.; Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
 (5) Prisyazhnyi, V.D.; Mirnyi, V.N.; Mirnaya, T.A.; Zh. Neorg. Khim. 1983, 28, 253-255; Russ. J. Inorg. Chem. (Engl. Transl.) 1983, 28, 140-141 (*).

- (1) Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3]
- (2) Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1581-1593.

VARIABLES:

Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

t/°C	T/Kª	100 x 2	t/ ^o C	T/Kª	100 x 2
331	604	0	268	541	50
319	592	5	265	538	55
309	582	10	260	533	60
299	572	15	254	527	65
290	563	20	250	523	69
282	555	25	253	526	70
274	547	30	266	539	75
266	539	33.5	281	554	80
268	541	35	312	585	90
273	546	40	324	597	95
270	543	45	330	603	100

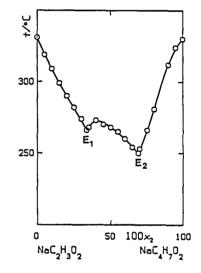
a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E₁, at 266 $^{\rm o}{\rm C}$ and $100{\rm x}_2$ = 33.5 (author). Eutectic, E₂, at 250 $^{\rm o}{\rm C}$ and $100{\rm x}_2$ = 69 (author).

Intermediate compound:

 $\rm Na_5(C_2H_3O_2)_3(C_4H_7O_2)_2$ congruently melting at 273 $^{\rm o}{\rm C}_{\rm \bullet}$



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis. Melts contained in a glass tube and stirred. Temperatures measured with a Nichrome-Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of isotropicity in the melt on cooling.

SOURCE AND PURITY OF MATERIALS:

Component 1: "chemically pure" material. Component 2: prepared by reacting aqueous ("chemically pure") Na_2CO_3 with a slight excess of n-butanoic acid of analytical purity. The solvent and excess acid were removed by heating to $160\,^{\circ}C$.

ESTIMATED ERROR:

Temperature: accuracy probably ± 2 K (compiler).

COMPONENTS: ORIGINAL MEASUREMENTS: (1) Sodium ethanoate (sodium acetate); $NaC_2H_3O_2$; [127-09-3] Sokolov, N.M.; Pochtakova, E.I. Zh. Obshch. Khim. 1960, 30, 1401-1405 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1960, (2) Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7] 30, 1429-1433. PREPARED BY: VARIABLES: Temperature. D'Andrea, G. **EXPERIMENTAL VALUES:** Characteristic point(s): Eutectic, E₁, at 266 $^{\rm o}$ C and $100x_2=33.5$ (authors). Eutectic, E₂, at 250 $^{\rm o}$ C and $100x_2=69$ (authors). Intermediate compound(s): $Na_5(C_2H_3O_2)_3(C_4H_7O_2)_2$, congruently melting at 273 °C. AUXILIARY INFORMATION METHOD/APPARATUS/PROCEDURE: SOURCE AND PURITY OF MATERIALS: Visual polythermal analysis. Component 1: "chemically pure" material recrystallized; it undergoes a phase transition at $t_{trs}(1)/^{\circ}C=254$ (Ref. 1), and melts at $t_{fus}(1)/^{\circ}C=331$. Component 2: prepared by reacting NaHCO₃ with n-butanoic acid, and recrystallized from n-butanol (Ref. 2, where, however, carbonate insted of hydrogen carbonate was employed; compiler); it undergoes phase transitions at $t_{\rm trs}(2)/^{\rm C}$ C= 117, 232, 252, 316 (Ref. 3), and melts at $t_{\rm fus}(2)/^{\rm C}$ C= 330. ESTIMATED ERROR: REFERENCES: Temperature: accuracy probably +2 K (compiler). (1) Bergman, A.G.; Evdokimova, K.A. Izv. Sektora Fiz.-Khim. Anal. 1956, 27 296-314. (2) Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1581-1593. (3) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

- (1) Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3]
- (2) Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7]

ORIGINAL MEASUREMENTS:

Prisyazhnyi, V.D.; Mirnyi, V.N.; Mirnaya, T.A. Zh. Neorg. Khim. 1983, 28, 253-255; Russ. J. Inorg. Chem. (Engl. Transl.) 1983, 28, 140-141 (*).

VARIABLES:

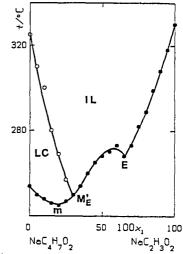
Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

The results are reported only in graphical form (see figure; data read with a digitizer by the compiler from Fig. 1 of the original paper; empty circles: liquid crystal - isotropic liquid equilibria; filled circles: solid - liquid crystal or solid - isotropic liquid equilibria).



Characteristic point(s):

Eutectic, E, at about 268 °C and $100\mathbf{x}_1$ about 65 (compiler). Minimum, m, at about 245 °C and $100\mathbf{x}_1$ about 20 (compiler). Invariant point, M'E, at about 250 °C and $100\mathbf{x}_1$ about 30 (compiler).

Intermediate compound(s):

 $Na_5(C_2H_3O_2)_3(C_4H_7O_2)_2$, congruently melting at about 273 °C (compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

heating and cooling traces were recorded in an atmosphere of purified argon with an OD-102 derivatograph (MOM, Hungary) working at a rate of 6-8 K min⁻¹, and using Al₂0₃ as the reference material. Temperatures were measured with a Pt/Pt-Rh A hot-stage thermocouple. Amplival polarizing microscope was employed detect the transformation points from the liquid crystalline into the isotropic liquid phase.

SOURCE AND PURITY OF MATERIALS:

Not stated. Component 1: $t_{fus}(1)/^{o}C$ about 329 (compiler). Component 2: $t_{fus}(2)/^{o}C$ about 254; $t_{clr}(2)/^{o}C$ about 325 (compiler).

ESTIMATED ERROR:

Temperature: accuracy not evaluable (compiler).

- (1) Sodium ethanoate (sodium acetate);
- NaC₂H₃O₂; [127-09-3] (2) Sodium **iso**-butanoate (sodium **iso**-butyrate); Nai-C₄H₇O₂; [996-30-5]

ORIGINAL MEASUREMENTS:

Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1581-1593.

VARIABLES:

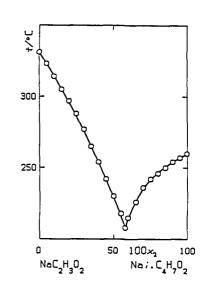
Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

		-
t/ºC	T/K ^a	100 x 2
331	604	0
323	596	5
314	587	10
305	578	15
297	570	20
288	561	25
277	550	30
265	538	35
254	527	40
242	515	45
230	503	50
218	491	55
208	481	58
215	488	60
226	499	65
236	509	70
242	515	75
246	519	80
250	523	85
254	527	90
257	530	95
260	533	100
i		



Characteristic point: Eutectic, E, at 208 $^{\circ}$ C and $100x_{2}$ = 58 (author).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis. Melts contained in a glass tube and stirred. Temperatures measured with a Nichrome-Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of isotropicity in the melt on cooling.

SOURCE AND PURITY OF MATERIALS:

Component 1: "chemically pure" material. Component 2: prepared by reacting aqueous ("chemically pure") Na_2CO_3 with a slight excess of iso butanoic acid of analytical purity. The solvent and excess acid were removed by heating to $160~^{\circ}C$.

ESTIMATED ERROR:

Temperature: accuracy probably ± 2 K (compiler).

a T/K values calculated by the compiler.

- (1) Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3]
- (2) Sodium pentanoate (sodium valerate); NaC₅H₉O₂; [6106-41-8]

EVALUATOR:

Ferloni, P., Dipartimento di Chimica Fisica, Universita' di Pavia (ITALY).

CRITICAL EVALUATION:

This system was studied only by Pochtakova (Ref. 1), who claimed the existence of: (i) a eutectic, E_1 , at 537 K (264 $^{\rm O}$ C) and $100x_2=31.5$; (ii) a eutectic, E_2 , at 526 K (253 $^{\rm O}$ C) and $100x_2=54$; and (iii) an intermediate compound, ${\rm Na_3(C_2H_3O_2)_2C_5H_9O_2}$, congruently melting at 541 K (268 $^{\rm O}$ C).

Component 2, however, forms liquid crystals. Therefore, the fusion temperature reported in Ref. 1, $T_{fus}(2)=630$ K (357 °C), has to be identified with the clearing temperature, the corresponding value from Table 1 of the Preface being $T_{clr}(2)=631\pm4$ K. This Table provides also $T_{fus}(2)=498\pm2$ K, a figure which can be identified (even if not fully satisfactorily) with that (489 K) corresponding to the highest phase transformation temperature quoted by Pochtakova from Ref. 2. For the same component, Table 1 of the Preface reports no solid state transition, whereas Pochtakova quotes (from Ref. 2) $T_{trs}(2)/K=482$ and 453. It is, however, to be stressed that the single transition observed (at 479±1 K) with DTA in sodium n-pentanoate by Duruz et al. (Ref. 3) was no more mentioned in a subsequent DSC investigation by the same group (Ref. 5).

Concerning component 1, the fusion temperature, $T_{fus}(1)$ = 604 K (331 o C; Ref. 1), is reasonably identified with the corresponding value from Table 1 of the Preface, viz., 601.3+0.5 K.

Allowance being made for the remarkable discrepancy, one might also connect the phase transition quoted from Ref. 2 and occurring at 511 K (238 °C) with that at 527+15 K reported in Table 1 of the Preface.

No reasonable correspondence, however, can be hazarded between the other $T_{\rm trs}$ values quoted from Ref. 2 [viz., 403 K (130 °C), 391 K (118 °C), and 331 K (58 °C)] and the superambient $T_{\rm trs}$'s given in Table 1.

On the basis of the available data, the phase diagram of this system could be supposed to be similar to that shown in Scheme D.1 of the Preface, Pochtakova's eutectic $\rm E_2$ being intended as an $\rm M^*_E$ point.

- (1) Pochtakova, E.I. Zh. Obshch. Khim. 1966, 36, 3-8.
- (2) Sokolov, N.M.
 Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
- (3) Duruz, J.J.; Michels, H.J.; Ubbelohde, A.R. Proc. R. Soc. London 1971, A322, 281-299.
- (4) Michels, H.J.; Ubbelohde, A.R. JCS Perkin II 1972, 1879-1881.

- (1) Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3]
- (2) Sodium pentanoate (sodium valerate); NaC₅H_QO₂; [6106-41-8]

ORIGINAL MEASUREMENTS:

Pochtakova, E.I.

Zh. Obshch. Khim. 1966, 36, 3-8.

VARIABLES:

PREPARED BY:

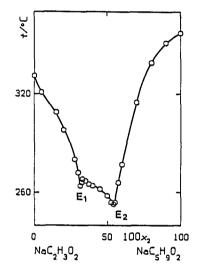
Temperature.

D'Andrea, G.

EXPERIMENTAL VALUES:

t/ºC	T/K ^a	100 x 2	t/°C	T/K ^a	100 x 2
331	604	0	262	535	45
321	594	5	258	531	50
309	582	15	254	527	52.5
298	571	20	253	526	54
280	553	27.5	254	527	55
272	545	30	266	539	57.5
264	537	31.5	277	550	60
266	539	32.5	315	588	70
268	541	33	339	612	80
267	540	35	351	624	90
265	538	37.5	357	630	100
264	537	40			

a T/K values calculated by the compiler.



Characteristic points:

Eutectic, E_1 at 264 °C and $100x_2$ = 31.5 (author). Eutectic, E_2 at 253 °C and $100x_2$ = 54 (author).

Intermediate compound:

Na₃(C₂H₃O₂)₂C₅H₉O₂, congruently melting at 268 °C (author).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

SOURCE AND PURITY OF MATERIALS:

Visual polythermal analysis.

Component 1: "chemically pure" material. Component 2: prepared from n-pentanoic acid and the hydrogen carbonate (Ref. 1, where, however, carbonate instead of hydrogen carbonate was employed; compiler). Component 1 undergoes phase transitions at ttrs(1)/°C= 58, 118, 130, 238 (Ref. 2). Component 2 undergoes phase transitions at ttrs(2)/°C= 180, 209, 216 (Ref. 2).

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

- (1) Sokolov, N.M.
 Zh. Obshch. Khim. 1954, 24, 1581-1593.
- (2) Sokolov, N.M.
 Tezisy Dokl. X Nauch. Konf. S.M.I. 1956

(1) Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3]

(2) Sodium iso pentanoate (sodium iso valerate); Nai C₅H₉O₂; [539-66-2]

EVALUATOR:

Ferloni, P., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

This system was studied by Sokolov (Ref. 1), and by Pochtakova (Ref. 2) who reviewed Sokolov's results. Both of them suggested the phase diagram to be of the eutectic type, with the invariant point at either 429 K (156 °C) and $100x_2$ = 73 (Ref. 1), or 433 K (160 °C) and $100x_2$ = 80.0 (Ref. 2).

Component 2, however, forms liquid crystals. Therefore, the fusion temperature, $T_{\rm fus}(2) = 535$ K (262 °C; Ref. 1) or 533 K (260 °C; Ref. 2), should be identified with the clearing temperature, the corresponding value from Table 2 of the Preface being $T_{\rm clr}(2) = 559 \pm 1$ K. The remarkable discrepancy between the latter value and the former ones might be attributed to some impurity in the samples of the Russian authors, inasmuch as the value from Table 2 meets rather satisfactorily those reported by Ubbelohde et al. (556 K; Ref. 3) and by Duruz et al. (553 K; Ref. 4).

For the same component, Pochtakova quotes from Ref. 5 two phase transition temperatures, viz., 451 K (178 $^{\rm O}$ C), and 425 K (152 $^{\rm O}$ C). The higher one can be reasonably identified with the actual fusion temperature, and compared with the value ${\rm T_{fus}(2)}$ = 461.5±0.6 K reported in Table 2 of the Preface, whereas the lower one has no correspondence in the same Table.

Both authors report $T_{fus}(1)=604$ K (331 $^{\rm O}$ C; Ref.s 1, 2), which may be satisfactorily identified with the value from Table 1 of the Preface, viz., 601.3 ± 0.5 K. Allowance being made for the discrepancy, one might also connect the phase transition quoted (by Pochtakova) from Ref. 5 as occurring at 511 K (238 $^{\rm O}$ C), with that at 527 \pm 15 K reported in Table 1. No reasonable correspondence, however, can be hazarded between the other $T_{\rm trs}$ values quoted by Pochtakova from Ref. 5 [viz., 403 K (130 $^{\rm O}$ C), 391 K (118 $^{\rm O}$ C), and 331 K (58 $^{\rm O}$ C)] and the superambient $T_{\rm trs}$'s given in Table 1.

Taking into account the available experimental data, one may suggest that the phase diagram of this system should not be far from those shown either in Scheme A.1, or in Scheme A.3 of the Preface, the eutectic being actually intended as an M_E point.

- (1) Sokolov, N.M.
 Zh. Obshch. Khim. 1954, 24, 1581-1593.
- (2) Pochtakova, E.I. Zh. Obshch. Khim. 1963, 33, 342-347.
- (3) Ubbelohde, A.R.; Michels, H.J.; Duruz, J.J. Nature 1970, 228, 50-52.
- (4) Duruz, J. J.; Michels, H. J.; Ubbelohde, A. R. Proc. R. Soc. London 1971, A 322, 281-299.
- (5) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

- (1) Sodium ethanoate (sodium acetate); NaCaHaOa: 1127-09-31
- NaC₂H₃O₂; [127-09-3]
 (2) Sodium iso-pentanoate (sodium iso-valerate);
 Nai-C₅H₉O₂; [539-66-2]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1581-1593.

VARIABLES:

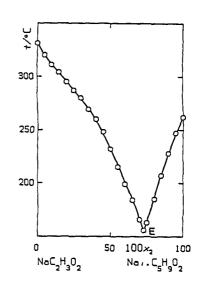
Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

t/°C	T/Kª	100×2
331	604	0
320	593	5
311	584	10
304	577	15
295	568	20
287	560	25
280	553	30
269	542	35
260	533	40
248	521	45
232	505	50
215	488	55
199	472	60
184	457	65
166	439	70
156	429	73
163	436	75
185	458	80
207	480	85
228	501	90
247	520	95
262	535	100



Characteristic point: Eutectic, E, at 156 °C and $100x_2=73$ (author).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis. Melts contained in a glass tube and stirred. Temperatures measured with a Nichrome-Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of isotropicity in the melt on cooling.

SOURCE AND PURITY OF MATERIALS:

Component 1: "chemically pure" material. Component 2: prepared by reacting aqueous ("chemically pure") Na₂CO₃ with a slight excess of iso-pentanoic acid of analytical purity. The solvent and excess acid were removed by heating to 160 °C.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

a T/K values calculated by the compiler.

- (1) Sodium ethanoate (sodium acetate);
- NaC₂H₃O₂; [127-09-3] (2) Sodium **iso**-pentanoate (sodium iso.valerate); Nai.C5H9O2; [539-66-2]

ORIGINAL MEASUREMENTS:

Pochtakova, E.I.

Zh. Obshch. Khim. 1963, 33, 342-347.

VARIABLES:

Temperature.

PREPARED BY:

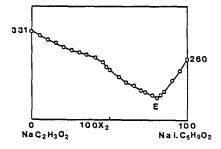
Baldini, P.

EXPERIMENTAL VALUES:

results are reported only in graphical form (see figure).

Characteristic point(s):

Eutectic, E, at 160 °C and $100x_2 = 80.0$.



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

SOURCE AND PURITY OF MATERIALS:

Component 1: "chemically pure" material. Component 2: prepared from commercial iso.pentanoic acid (distilled twice before use) and the "chemically pure" hydrogen carbonate (Ref. 1).
Component 1 undergoes phase transitions at

t_{trs}(1)/ $^{\circ}$ C= 58, 118, 130, 238 (Ref. 2) and melts at t_{fus}(1)/ $^{\circ}$ C= 331. Component 2 undergoes phase transitions at t_{trs}(2)/ $^{\circ}$ C= 152, 178 (Ref. 2) and melts at t_{fus}(2)/ $^{\circ}$ C= 260.

ESTIMATED ERROR:

Temperature: precision probably +2 K (compiler).

- (1) Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1581-1593.
- (2) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

- (1) Sodium ethanoate (sodium acetate);
- NaC₂H₃O₂; [127-O9-3] (2) Sodium hexanoate (sodium caproate); NaC₆H₁₁O₂; [10051-44-2]

EVALUATOR:

Ferloni, P.,

Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

This system was studied by Sokolov (Ref. 1), and by Pochtakova (Ref. 2). The former author claims the existence of two eutectics $[E_1$, at 541 K (268 °C) and $100x_2$ = 34.5; E_2 , at 533 K (260 °C) and $100x_2$ = 49.5], and of the intermediate compound at 533 K (260 °C) and $100x_2 = 49.5$], and of the intermediate compound $Na_8(C_2H_3O_2)_5(C_6H_{11}O_2)_3$, which congruently melts at 543 K (270 °C). The latter author claims in turn the existence of a eutectic [at 546 K (273 °C) and $100x_2 = 48.5$], the incongruently melting compound $Na_5(C_2H_3O_2)_4C_6H_{11}O_2$, and a "perekhodnaya tochka" [at 550 K (277 °C) and 100x2= 34.0].

Component 2, however, forms liquid crystals. Therefore, the fusion temperature, $T_{\rm fus}(2)$ = 638 K (365 $^{\rm O}$ C; Ref.s 1, 2), should be identified with the clearing temperature, the corresponding value from Table 1 of the Preface being $T_{\rm clr}(2)$ = 639.0±0.5 K. The transition temperature $T_{\rm trs}(2)$ = 499 K (226 $^{\rm O}$ C) quoted by Pochtakova from Ref. 3 has in turn to be intended as the fusion temperature, the corresponding value from Table 1 being 499.6+0.6 K.

The following point also deserves attention. Two more transitions are quoted in Ref. 2 from Ref. 3 as occurring in component 2 at 615 K (342 $^{\rm o}$ C) and 476 K (203 $^{\rm o}$ C), respectively. The latter agrees with that reported at 473+2 K in Table 1, whereas no evidence was obtained by subsequent investigators (Ref. 4) for a transition comparable with the former one: should it exist, it might mean that two different mesomorphic phases are present in sodium hexanoate.

As for component 1, Sokolov and Pochtakova report $T_{fus}(1) = 603 \text{ K} (330 \text{ }^{\circ}\text{C})$ and 604 K(331 °C), respectively, i.e., values which favorably meet that from Table 1 $(601.3\pm0.5~{\rm K})$. For the same component, Pochtakova quotes from Ref. 3 a few other phase transition temperatures, viz., 511 K (238 °C), 403 K (130 °C), 391 K (118 °C), and 331 K (58 $^{\circ}$ C), of which only the first one finds some correspondence with one of the $T_{\rm trs}$ values from Table 1, i.e., T'trs= 527+15 K.

In conclusion, either author's suggestions for the phase diagram require modifications. Indeed, the invariant occurring at 533 K and $100x_2$ = 49.5 (Ref. 1), or at 546 K and $100x_2 = 48.5$ (Ref. 2), should likely be identified with an M_E point, the actual coordinates of which, however, should be verified with better accuracy. Moreover, the composition of the intermediate compound and the nature of the second invariant are not sufficiently supported by the available data, and need as well a further investigation, e.g., by DSC or DTA.

- (1) Sokolov, N.M.
 - Zh. Obshch. Khim. 1954, 24, 1581-1593.
- (2) Pochtakova, E.I. Zh. Obshch. Khim. 1959, 29, 3183-3189 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1959, **29,** 3149-3154.
- (3) Sokolov, N.M.
 - Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
- (4) Sanesi, M.; Cingolani, A.; Tonelli, P.L.; Franzosini, P. Properties of Organic Thermal Properties, in Thermodynamic and Transport Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors), Pergamon Press, Oxford, 1980, 29-115.

- (1) Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3]
- (2) Sodium hexanoate (sodium caproate); NaC₆H₁₁O₂; [10051-44-2]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1581-1593.

VARIABLES:

Temperature.

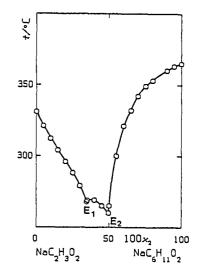
PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

t/ºc	T/K ^a	100 x ₂	t/ ^o C	T/K ^a	100 x 2
331	604	0	260	533	49.5
321	594	5	265	538	50
312	585	10	300	573	55
304	577	15	321	594	60
296	569	20	332	605	65
288	561	25	342	615	70
279	552	30	349	622	75
268	541	34.5	353	626	80
269	542	35	360	633	90
269	542	40	363	636	95
265	538	45	365	638	100

 $^{\mathbf{a}}$ T/K values calculated by the compiler.



Characteristic point(s):

Eutectic, E₁, at 268 $^{\rm o}$ C and 100x₂= 34.5 (author). Eutectic, E₂, at 260 $^{\rm o}$ C and 100x₂= 49.5 (author).

Intermediate compound(s):

 $Na_8(C_2H_3O_2)_5(C_6H_{11}O_2)_3$ (author), congruently melting at 270 °C (compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.
Melts contained in a glass tube and stirred.
Temperatures measured with a NichromeConstantane thermocouple and a 17 mV full
scale millivoltmeter. The temperature
readings refer to the disappearance of isotropicity in the melt on cooling.

SOURCE AND PURITY OF MATERIALS:

Component 1: "chemically pure" material. Component 2: prepared by reacting aqueous ("chemically pure") Na_2CO_3 with a slight excess of n-hexanoic acid of analytical purity. The solvent and excess acid were removed by heating to $160~^{\circ}C$.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

- (1) Sodium ethanoate (sodium acetate);
- NaC₂H₃O₂; [127-09-3] (2) Sodium hexanoate (sodium caproate); NaC₆H₁₁O₂; [10051-44-2]

ORIGINAL MEASUREMENTS:

Pochtakova, E.I.

Zh. Obshch. Khim. 1959, 29, 3183-3189 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1959, 29, 3149-3154.

VARIABLES:

Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

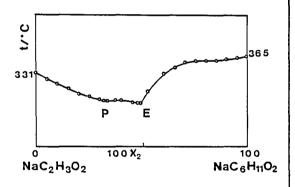
The results are reported only in graphical form (see figure).

Characteristic point(s):

Eutectic, E at 273 °C and $100x_2=48.5$ (author). Characteristic point, P (perekhodnaya tochka in the original text; see the Introduction), at 277 °C and $100x_2=34.0$.

Intermediate compound:

 $Na_5(C_2H_3O_2)_4C_6H_{11}O_2$ incongruently melting. (the composition is approximate).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

SOURCE AND PURITY OF MATERIALS:

"Chemically pure" $NaC_2H_3O_2$ and $NaC_6H_{11}O_2$ prepared by reacting Na_2CO_3 with n-hexanoic acid (Ref. 1). Component 1 undergoes phase transitions at $t_{trs}(1)/^{OC} = 58$, 118, 130, 238 (Ref. 2). Component 2 undergoes phase transitions at

 $t_{trs}(1)/{}^{0}C=58$, 118, 130, 238 (Ref. 2). Component 2 undergoes phase transitions at $t_{trs}(2)/{}^{0}C=203$, 226, 342 (Ref. 2).

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

- (1) Sokolov, N.M.
 - Zh. Obshch. Khim. 1954, 24, 1581-1593.
- (2) Sokolov, N.M.
 Tezisy Dokl. X Nauch. Konf. S.M.I. 1956

- (1) Sodium ethanoate (sodium acetate);
- NaC₂H₃O₂; [127-09-3] (2) Sodium benzoate; NaC₇H₅O₂; [532-32-1]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1581-1593.

VARIABLES:

PREPARED BY:

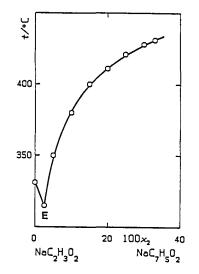
Temperature.

D'Andrea, G.

EXPERIMENTAL VALUES:

t/°C	T/K ^a	100 x 2
331	604	0
315	588	2.6
350	623	5
380	653	10
400	673	15
411	684	20
421	694	25
428	701	30
431	704	33
465	738	100

a T/K values calculated by the compiler.



Characteristic point(s):

Eutectic, E, at 315 °C and $100x_2=2.6$ (author).

Note — The system was investigated at 0 \leq 100 $\mathbf{x}_2 \leq$ 33 due to thermal instability of the benzoate.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.
Melts contained in a glass tube and stirred.
Temperatures measured with a NichromeConstantane thermocouple and a 17 mV full
scale millivoltmeter. The temperature
readings refer to the disappearance of isotropicity in the melt on cooling.

SOURCE AND PURITY OF MATERIALS:

"Chemically pure" materials.

ESTIMATED ERROR:

Temperature: accuracy probably ± 2 K (compiler).

- (1) Sodium ethanoate (sodium acetate);
- NaC₂H₃O₂; [127-09-3] (2) Sodium chloride; NaCl; [7647-14-5]

ORIGINAL MEASUREMENTS:

Il'yasov, I.I.; Bergman, A.G. Zh. Obshch. Khim. 1960, 30, 355-358.

VARIABLES:

Temperature.

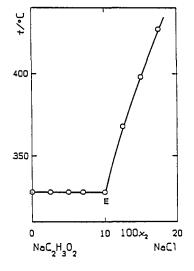
PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

t/°C	T/Kª	100 x 2
328	601	0
328	601	2.5
328	601	5.0
328	601	7.0
328	601	10.0
368	641	12.5
398	671	15.0
427	700	17.5

a T/K values calculated by the compiler.



Characteristic point(s):

Eutectic, E, at 328 $^{\circ}$ C and $100x_2 = 10$ (authors).

Note - The system was investigated at $0 \le 100x_2 \le 17.5$ due to thermal instability of component 1.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis; temperatures measured with a Nichrome-Constantane thermocouple and a millivoltmeter.

SOURCE AND PURITY OF MATERIALS:

Not stated.

NOTE:

See the NOTE relevant to the investigation by Piantoni et al. (Ref. 1) on the same system (next Table).

ESTIMATED ERROR:

Temperature: accuracy probably ± 2 K (compiler).

REFERENCES:

(1) Piantoni, G.; Leonesi, D.; Braghetti, M.; Franzosini, P. Ric. Sci., 1968, 38, 127-132.

- (1) Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3]
- (2) Sodium chloride; NaCl; [7647-14-5]

ORIGINAL MEASUREMENTS:

Piantoni, G.; Leonesi, D.; Braghetti, M.; Franzosini, P. Ric. Sci., 1968, 38, 127-132.

VARIABLES:

Temperature.

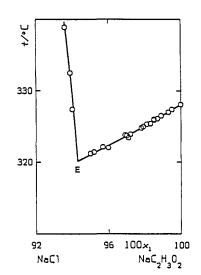
PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

t/°C	T/K ^a	100 x 1	t/°C	T/K ^a	100 x 1
328.1	601.3	100	323.9	597.1	97.2
327.4	600.6	99.5	323.4	596.6	97.1
327.0	600.2	99.3	323.7	596.9	97.0
326.5	599.7	98.9	323.8	597.0	96.9
326.1	599.3	98.7	322.0	595.2	96.0
326.0	599.2	98.5	322.1	595.3	95.7
325.9	599.1	98.5	321.4	594.6	95.2
325.4	598.6	98.3	321.2	594.4	95.0
325.3	598.5	98.1	327.4	600.6	94.0
325.0	598.2	97.9	332.5	605.7	93.9
324.8	598.0	97.8	338.9	612.1	93.6

a T/K values calculated by the compiler.



The system was investigated at $0 \le 100x_2 \le 6.5$.

Characteristic point(s):

Eutectic, E, at 320.1 °C and $100x_1 = 94.3$ (authors).

Note - In the original paper the results were shown in graphical form. The above listed numerical values represent a private communication by one of the authors (F., P.) to the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A Pyrex device, suitable for work under an inert atmosphere, and allowing one to observe the system visually, was employed (for details, see Ref. 1). The initial crystallization temperatures were measured with a Chromel-Alumel thermocouple checked by comparison with a certified Pt resistance thermometer, and connected with a L&N Type K-3 potentiometer.

SOURCE AND PURITY OF MATERIALS:

C. Erba RP materials, dried by heating under vacuum.

NOTE:

The authors discuss their own results in comparison with both the expected ideal behaviour of the molten mixtures and the previous data from Ref. 1. They observed that the liquidus branch richer in sodium chloride is not far from ideality.

ESTIMATED ERROR:

Temperature: accuracy probably +0.1 K.

REFERENCES:

(1) Il'yasov. I.I.; Bergman, A.G. Zh. Obshch. Khim. 1960, 30, 355-358.

- (1) Sodium ethanoate (sodium acetate);
- NaC₂H₃O₂; [127-09-3] (2) Sodium thiocyanate; NaCNS; [540-72-7]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1150-1156.

VARIABLES:

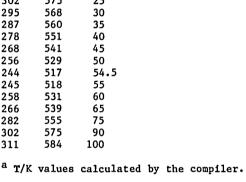
Temperature.

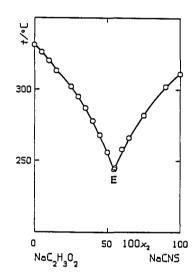
PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

t/°C	T/Kª	100 x 2
331	604	0
326	599	5
320	593	10
313	586	15
302	575	25
295	568	30
287	560	35
278	551	40
268	541	45
256	529	50
244	517	54.5
245	518	55
258	531	60
266	539	65
282	555	75
302	575	90
311	584	100





Characteristic point(s):

Eutectic, E, at 244 $^{\circ}$ C and $100x_2 = 54.5$ (author).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis. Salt(s) melted in a test tube. Temperature measured with a Nichrome-Constantane thermocouple and a millivoltmeter (17 mV full scale) with mirror reading.

SOURCE AND PURITY OF MATERIALS:

Component 1 synthetized from ethanoic acid and ${\rm NaHCO_3}$. Component 2 of analytical purity recrystallized once from water and once from ethanol.

NOTE:

See the NOTE attached to the investigation by Storonkin et al. (Ref.1) on the same system.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

REFERENCES:

(1) Storonkin, A.V.; Vasil kova, I.V.; Potemin, S.S.; Vestn. Leningr. Univ., Fiz., Khim. 1974, (16), 73-76.

- (1) Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3]
- (2) Sodium thiocyanate; NaCNS; [540-72-7]

ORIGINAL MEASUREMENTS:

Golubeva, M.S.; Aleshkina, N.N.; Bergman, A.G.
Zh. Neorg. Khim. 1959, 4, 2606-2610; Russ.

Zh. Neorg. Khim. 1959, 4, 2606-2610; Russ. J. Inorg. Chem., Engl. Transl., 1959, 4, 1201-1203 (*).

VARIABLES:

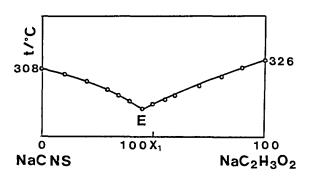
Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

The results are reported only in graphical form (see figure).



Characteristic point(s):

Eutectic, E, at 236 $^{\circ}$ C and $100x_1 = 44.5$ (authors).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual observation of fusion of the salt mixtures contained in a glass tube surrounded by a wider tube to secure a more uniform heating. Temperatures measured with a Chromel-Alumel thermocouple.

SOURCE AND PURITY OF MATERIALS:

Materials of analytical purity twice recrystallized.

NOTE:

See the NOTE attached to the investigation by Storonkin et al. (Ref.1) on the same system (see following Table).

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

REFERENCES:

(1) Storonkin, A.V.; Vasil'kova, I.V.; Potemin, S.S.; Vestn. Leningr. Univ., Fiz., Khim. 1974, (16), 73-76.

- (1) Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3]
- (2) Sodium thiocyanate; NaCNS; [540-72-7]

ORIGINAL MEASUREMENTS:

Storonkin, A.V.; Vasil'kova, I.V.; Potemin, S.S.

Vestn. Leningr. Univ., Fiz., Khim. 1974, (16), 73-76.

VARIABLES:

Temperature.

PREPARED BY:

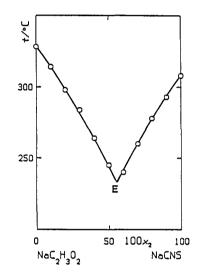
D'Andrea, G.

EXPERIMENTAL VALUES:

t/ ^o C	T/K ^a	100 x ₂
328	601	0
314	587	10
298	571	20
284	557	30
264	537	40
245	518	50
240	513	60
260	533	70
278	551	80
293	566	90
308	581	100

a T/K values calculated by the compiler.

Note - The tabulated data were drawn by the compiler from Fig. 1 of the original paper.



Characteristic point(s):

Eutectic, E, at 234 °C and $100x_2=55$ (authors).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

DTA. Thermograph with photorecorder.
Salt(s) sealed under vacuum in Pyrex ampoules.

No other information given.

SOURCE AND PURITY OF MATERIALS:

 ${
m NaC_2H_3O_2}$ of analytical purity and "chemically pure" NaCNS, heated 10-15 h at temperatures 50-60 $^{
m OC}$ below their fusion temperatures, were employed.

NOTE:

This binary was also submitted to visual polythermal analysis by Sokolov (Ref. 1), and Golubeva et al. (Ref. 2). The eutectic composition detected by Storonkin et al. $(100x_2=55)$ fairly agrees with those reported both in Ref. 1 (54.5) and Ref. 2 (55.5). Sokolov's eutectic temperature (517 K), on the contrary, is significantly higher than those given both by Storonkin et al. (507 K) and Golubeva et al. (509 K; Ref. 2).

ESTIMATED ERROR:

Temperature: accuracy probably ±2 K (compiler).

- (1) Sokolov, N.M.
- Zh. Obshch. Khim. 1954, 24, 1150-1156.
 2) Golubeya. M.S. Alechkins N.N.
- (2) Golubeva, M.S.; Aleshkina, N.N.; Bergman, A.G.; Zh. Neorg. Khim. 1959, 4, 2606-2610; Russ. J. Inorg. Chem. (Engl. Transl.) 1959, 4, 1201-1203 (*).

(1) Sodium ethanoate (sodium acetate);

NaC₂H₃O₂; [127-09-3] (2) Sodium iodide; NaI; [7681-82-5]

ORIGINAL MEASUREMENTS:

Diogenov, G.G.; Erlykov, A.M. Nauch. Dokl. Vysshei Shkoly, Khim. i Khim. Tekhnol. 1958, No. 3, 413-416.

VARIABLES:

Temperature.

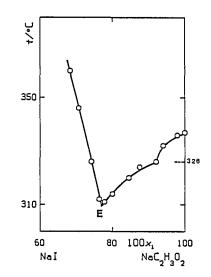
PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

t/°C	T/Kª	100 x 1
337	610	100
336	609	97.9
332	605	94.0
326	599	92.1
324	597	87.5
320	593	84.5
314	587	80.0
311	584	77.8
312	585	76.3
326	599	74.2
346	619	70.7
360	633	68.3

a T/K values calculated by the compiler.



Note - The system was investigated at $100 \ge 100x_1 \ge 68.3$.

Characteristic point(s):

Eutectic, E, at 310 °C and $100x_2 = 23$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

SOURCE AND PURITY OF MATERIALS:

Not stated.

Component 1 undergoes a phase transition at $t_{\rm trs}(1)/^{\rm o}{\rm C}$ = 326. Component 2 melts at $t_{\rm fus}(1)/^{\rm o}{\rm C}$ = 670.

NOTE:

See the NOTE relevant to the investigation by Piantoni et al. (Ref. 1) on the same system.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

REFERENCES:

(1) Piantoni, G.; Leonesi, D.; Braghetti, M.; Franzosini, P. Ric. Sci., 1968, 38, 127-132.

- (1) Sodium ethanoate (sodium acetate);
 NaC₂H₃O₂; [127-09-3]
 (2) Sodium iodide;
- (2) Sodřum řodide; NaI; [7681-82-5]

ORIGINAL MEASUREMENTS:

Piantoni, G.; Leonesi, D.; Braghetti, M.; Franzosini, P.

Ric. Sci., 1968, 38, 127-132.

VARIABLES:

Temperature.

PREPARED BY:

D'Andrea, G.

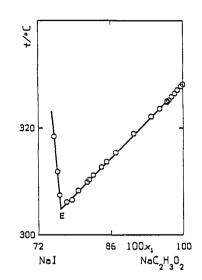
EXPERIMENTAL VALUES:

t/°C	T/K ^a	100 x 1	t/°C	T/K ^a	100 x 1
328.1	601.3	100	315.3	588.5	87.0
327.7	600.9	99.6	313.6	586.8	85.2
327.0	600.2	98.9	312.6	585.8	84.2
326.4	599.6	98.4	311.1	584.3	82.6
325.8	599.0	97.8	310.2	583.4	81.8
325.2	598.4	97.3	309.8	583.0	81.4
324.9	598.1	97.0	308.2	581.4	79.7
325.0	598.2	96.9	306.5	579.7	78.5
324.8	598.0	96.9	306.1	579.3	77.5
323.6	596.8	95.5	307.4	580.6	76.1
322.1	595.3	93.8	311.8	585.0	75.7
318.9	592.1	90.4	318.4	591.6	75.0

a T/K values calculated by the compiler.

Note 1 - In the original paper the results were shown in graphical form. The above listed numerical values represent a private communication by one of the authors (F., P.) to the compiler.

Note 2 - The system was investigated at 0 \leq 100x2 \leq 25.



Characteristic point(s): Eutectic, E, at 304.8 $^{\rm o}$ C and 100 \mathbf{x}_1 = 76.3 (authors).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A Pyrex device, suitable for work under an inert atmosphere, and allowing one to observe the system visually, was employed (for details, see Ref. 1). The initial crystallization temperatures were measured with a Chromel-Alumel thermocouple checked by comparison with a certified Pt resistance thermometer, and connected with a L&N Type K-3 potentiometer.

NOTE:

The authors discuss their own results in comparison with both the expected ideal behaviour of the molten mixtures and the previous data from Ref.s 1 and 2. They observed that the liquidus branch richer in sodium iodide is not far from ideality.

SOURCE AND PURITY OF MATERIALS:

C. Erba RP materials, dried by heating under vacuum.

ESTIMATED ERROR:

Temperature: accuracy probably +0.1 K.

- (1) Il'yasov. I.I.; Bergman, A.G. Zh. Obshch. Khim. 1961, 31, 368-370.
- (2) Diogenov, G.G.; Erlykov, A.M. Nauch. Dokl. Vysshei Shkoly, Khim. 1958, No. 3, 413-416.

- (1) Sodium ethanoate (sodium acetate);
- NaC₂H₃O₂; [127-09-3] (2) Sodium nitrite; NaNO₂; [7632-00-0]

ORIGINAL MEASUREMENTS:

Bergman, A.G.; Evdokimova, K.A.

Izv. Sektora Fiz.-Khim. Anal., Inst.

Obshchei i Neorg. Khim. Akad. Nauk SSSR

1956, 27, 296-314.

VARIABLES:

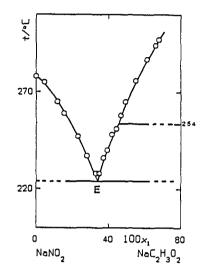
Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

t/°C	T/Kª	100 x 1
278	551	0
275	548	4.6
265	538	11.8
259	532	15.5
247	520	23.0
237	510	28.1
228	501	33.0
228	501	34.9
236	509	37.2
240	513	39.3
248	521	41.8
251	524	44.2
258	531	46.9
265	538	49.4
276	549	55.0
287	560	61.3
294	567	66.0
297	570	68.0



a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E, at 224 °C and $100x_1 = 34$ (authors).

Note - The system was investigated at $0 \le 100x_1 \le 68$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis: the temperatures of initial crystallization were measured with a Nichrome-Constantane thermocouple and a 17 mV full-scale millivoltmeter.

SOURCE AND PURITY OF MATERIALS:

Component 1: "chemically pure" ${\rm NaC_2H_3O_2.3H_2O}$ dried to constant mass; it undergoes a phase transition at ${\rm t_{trs}(1)/^{O}C^{=}}$ 254 and fusion at ${\rm t_{fus}(1)/^{O}C^{=}}$ 326. Component 2: source not stated.

ESTIMATED ERROR:

Temperature: accuracy probably ±2 K (compiler).

REFERENCES:

- (1) Sokolov, N.M.
 Zh. Obshch. Khim. 1957,27, 840-844(*);
 Russ. J. Gen. Chem. (Engl. Transl.)
 1957, 27, 917-920.
- (2) Sokolov, N.M.; Tsindrik, N.M.; Khaitina, M.V.

 Zh. Neorg. Khim. 1970, 15, 852-855; Russ. J. Inorg. Chem. (Engl. Transl.) 1970, 15, 433-435 (*).

NOTE:

Concerning component 1, the fusion (599 K) and solid state transition (527 K) temperatures can be identified respectively with the $T_{fus}(1)$ (601.3+0.5 K) and $T_{trs}^{\circ}(1)$ (527+15 K) values listed in Preface, Table 1. The coordinates of the eutectic (497 K and $100x_2$ = 66) are in reasonable agreement with those reported by both Sokolov (500-501 K) and $100x_2$ = 65; Ref. 1), and Sokolov et al. (499 K) and $100x_2$ = 65; Ref. 2).

- (1) Sodium ethanoate (sodium acetate);
- NaC₂H₃O₂; [127-09-3] (2) Sodium nitrite; NaNO₂; [7632-00-0]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1957, 27, 840-844 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1957, 27, 917-920.

VARIABLES:

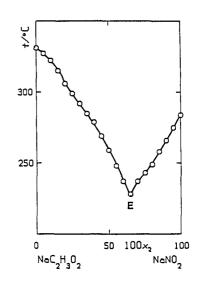
Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

t/°C	T/K ^a	100 x 2
331	604	0
327	600	5
322	595	10
315	588	15
306	579	20
299	572	25
292	565	30
285	558	35
279	552	40
269	542	45
259	532	50
248	521	55
237	510	60
228	501	65
237	510	70
243	516	75
249	522	80
258	531	85
266	539	90
275	548	95
284	557	100



Characteristic point(s): Eutectic, E, at 227 $^{\circ}$ C (from table 2 of the original paper) or 228 $^{\circ}$ C (according to the above tabulated data; compiler) and $100x_2=65$ (author).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis; salt mixtures melted in a glass tube (surrounded by a wider tube) and stirred with a glass thread. The temperatures of initial crystallization were measured with a Nichrome-Constantane thermocouple checked at the fusion points of water, benzoic acid, mannitol, AgNO $_3$, Cd, KNO $_3$, and K $_2$ Cr $_2$ O $_7$.

NOTE:

The fusion temperature (604 K) of component 1 can be identified with the $T_{\rm fus}(1)$ value (601.3±0.5 K) listed in Preface, Table 1. The coordinates of the eutectic (500-501 K and $100x_2$ = 65) are in reasonable agreement with those reported by both Bergman and Evdokimova (497 K and $100x_2$ = 66; Ref. 1), and by Sokolov et al. (499 K and $100x_2$ = 65; Ref. 2).

SOURCE AND PURITY OF MATERIALS:

"Chemically pure" materials recrystallized from water.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

- (1) Bergman, A.G. Evdokimova, K.A. Izv. Sektora Fiz.-Khim. Anal., Inst. Obshchei i Neorg. Khim. Akad. Nauk SSSR 1956,27,296-314.
- (2) Sokolov, N.M.; Tsindrik, N.M.; Khaitina, M.V.; Zh. Neorg. Khim. 1970, 15, 852-855; Russ. J. Inorg. Chem. (Engl. Transl.) 1970, 15, 433-435 (*).

a T/K values calculated by the compiler.

- (1) Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3]
- (2) Sodium nitrite; NaNO₂; [7632-00-0]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.; Tsindrik, N.M.; Khaitina, M.V. Zh. Neorg. Khim. 1970, 15, 852-855; Russ. J. Inorg. Chem. (Engl. Transl.) 1970, 15, 433-435 (*).

VARIABLES:

Temperature.

PREPARED BY:

D'Andrea, G.

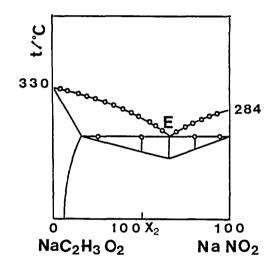
EXPERIMENTAL VALUES:

The results are given only in graphical form (see figure).

Characteristic point(s):

Eutectic, E, at 226 $^{\circ}$ C and $100x_{2}$ 65 (authors).

Note - Restricted solid solutions are formed as far as $100x_2 = 15$.



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis supplemented with differential thermal analysis.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

NOTE:

Concerning component 1: (1) the fusion temperature (603 K) can be identified with the $T_{\rm fus}(1)$ value (601.3+0.5 K) listed in Preface Table 1; and (ii) among the solid state transition temperatures (331, 391, 403, and 511 K) quoted by the authors from Ref. 1, only the third and fourth ones find some correspondence in the $T_{\rm trs}$ values listed in Table 1. The coordinates of the eutectic (499 K and $100x_2$ = 65) are in reasonable agreement with those previously reported by both Bergman and Evdokimova (497 K and $100x_2$ = 66; Ref. 3), and Sokolov (500-501 K and $100x_2$ = 65; Ref. 4).

SOURCE AND PURITY OF MATERIALS:

Not stated.

Component 1 undergoes phase transitions at $t_{\rm trs}(1)/^{\rm C}$ C= 58, 118, 180, 288 (Ref. 1; the figures 180, 288 are most probably misprints, inasmuch as the same authors quoting the same source report 130, 238 in several other papers; compiler). Component 2 undergoes a phase transition at $t_{\rm trs}(2)/^{\rm C}$ C= 170 (Ref. 2).

- (1) Sokolov, N.M.; Tezisy Dokl. X Nauch-Konf. S.M.I. 1956.
- (2) Bergman, A.G.; Berul, S.I.; Izv. Sektora Fiz.-Khim.Anal.1958,21,178-183.
- (3) Bergman, A.G. Evdokimova, K.A.; Izv-Sektora Fiz.-Khim. Anal., Inst-Obshchei i Neorg. Khim. Akad. Nauk SSSR 1956, 27, 296-314.
- (4) Sokolov, N.M.; Zh. Obshch. Khim. 1957, 27, 840-844 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1957, 27, 917-920.

- (1) Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3]
- (2) Sodium nitrate; NaNO3; [7631-99-4]

EVALUATOR:

Ferloni, P., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

The system $Na/C_2H_3O_2$, NO_3 was studied by Sokolov (Ref. 1), Bergman and Evdokimova (as a side of the reciprocal ternary K, $Na/C_2H_3O_2$, NO_3 ; Ref. 2), Diogenov (as a side of the reciprocal ternary Li, $Na/C_2H_3O_2$, NO_3 ; Ref. 2), Gimel'shtein and Diogenov (as a side of the reciprocal ternary Cs, $Na/C_2H_3O_2$, NO_3 ; Ref. 4), Storonkin et al. (as a side of the ternary $Na/C_2H_3O_2$, CNS, NO_3 ; Ref. 5), and Diogenov and Chumakova (as a side of the reciprocal ternary K, $Na/C_2H_3O_2$, NO_3 ; Ref. 6). The visual polythermal analysis, and DTA were employed in Ref.s 1-4 and 6, and in Ref. 5, respectively; moreover, in Ref. 4, X-ray diffraction patterns were taken on some compositions.

The fusion temperature of component 1 should be 604, 599, 610, 600, 601, and 599 K according to Ref.s 1,2,3,4,5, and 6, respectively, the corresponding value listed in Preface, Table 1 being 601.3 ± 0.5 K. For the same component, a solid state transition is reported by Ref.s 2, 3, and 4. The transition temperatures given by Ref.s 2 and 4 (527 and 543 K, respectively) can be identified with the $T_{trs}(1)$ value (527±15 K) listed in Table 1 of the Preface, whereas no reliability is to be attached to Diogenov's figures (596 K; Ref.3) which has no correspondence in Table 1, and, moreover, was not confirmed in subsequent investigations by the same group (Ref. 4).

Diogenov (Ref. 3) claimed the existence of two intermediate compounds, i.e.: (i) Na₃ (C₂H₃O₂)₂NO₃, incongruently melting, with a peritectic at 539 K and $100x_2$ = 38.5; and (ii) Na₅C̄₂H₃O₂(NO₃)₄, congruently melting, with a distectic at 545 K. In the evaluator's opinion, however, the discontinuities Diogenov (Ref. 3) found on either branch of his liquidus are relevant rather to the occurrence of solid state transitions in either component, than to the formation of any intermediate compound. In fact, in their reinvestigations of the binary Na/C₂H₃O₂, NO₃ neither Gimel'shtein and Diogenov (who supplemented their visual observations with some X-ray diffraction patterns; Ref. 4), nor Diogenov and Chumakova (Ref. 6) could confirm Diogenov's former point.

Therefore, the system can be safely classified as of the eutectic type, with the invariant at 494+4 K and $100x_2$ at about 58.

- (1) Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1150-1156.
- (2) Bergman, A.G.; Evdokimova, K.A. Izv. Sektora Fiz.-Khim. Anal., Inst. Obshchei i Neorg. Khim. Akad. Nauk SSSR 1956, 27, 296-314.
- (3) Diogenov, G.G.
 Zh. Neorg. Khim. 1956, 1, 799-805 (*); Russ. J. Inorg. Chem. (Engl. Transl.) 1956, 1
 (4), 199-205.
- (4) Gimel'shtein, V.G.; Diogenov, G.G. Tr. Irkutsk. Politekh. Inst., Ser. Khim., 1966, 27, 69-75.
- (5) Storonkin, A.V.; Vasil'kova, I.V.; Potemin, S.S. Vestn. Leningr. Univ., Fiz., Khim. 1974, (16), 73-76.
- (6) Diogenov, G.G.; Chumakova, V.P. Fiz.-Khim. Issled. Rasplavov Solei, Irkutsk, 1975, 7-12.

- (1) Sodium ethanoate (sodium acetate); $NaC_2H_3O_2$; [127-09-3]
- (2) Sodium nitrate; NaNO₃; [7631-99-4]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1150-1156.

VARIABLES:

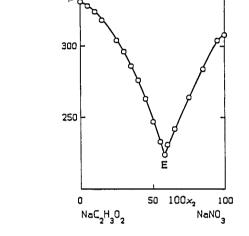
Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

t/°C	T/K ^a	100 x 2
331	604	0
328	601	5
324	597	10
318	591	15
304	577	25
296	569	30
286	559	35
276	549	40
263	536	45
247	520	50
233	506	55
224	497	58
231	504	60
242	515	65
264	537	75
284	557	85
304	577	95
308	581	100



^a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E, at 224 $^{\circ}$ C and $100x_2 = 58$ (author).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.
Salt(s) melted in a test tube. Temperature measured with a Nichrome-Constantane thermocouple and a millivoltmeter with mirror reading to 17 mV.

SOURCE AND PURITY OF MATERIALS:

Component 1 synthetized from ethanoic acid and NaHCO3. Commercial component 2 further purified by the author according to Laiti.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

COMPONENTS: (1) Sodium ethanoate (sodium acetate); NaC₂H₃O₂; [127-09-3] (2) Sodium nitrate; NaNO₃; [7631-99-4] VARIABLES: Temperature. ORIGINAL MEASUREMENTS: Bergman, A.G.; Evdokimova, K.A. Izv. Sektora Fiz.-Khim. Anal., Inst. Obshchei i Neorg. Khim. Akad. Nauk SSSR 1956, 27, 296-314. PREPARED BY: D'Andrea, G.

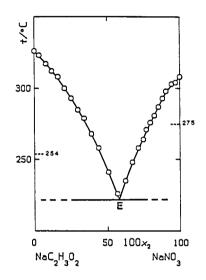
EXPERIMENTAL VALUES:

t/ºC	T/K ^a	100 x 2	t/°C	T/K ^a	100 x ₂
326	599	0	235	508	62.3
323	596	3.3	248	521	67.1
317	590	8.0	258	531	71.2
312	585	11.9	264	537	74.7
308	581	16.2	271	544	76.8
300	573	20.7	276	549	79.6
293	566	25.2	281	554	82.4
285	558	29.8	287	560	85.2
279	552	34.2	293	566	88.0
268	541	39.1	298	571	90.4
258	531	44.0	303	576	94.3
241	514	50.7	304	577	97.0
226	499	56.8	308	581	100

a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E, at 222 °C and $100x_2$ 58 (authors).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis: the temperatures of initial crystallization were measured with a Nichrome-Constantane thermocouple and a 17 mV full-scale millivoltmeter.

SOURCE AND PURITY OF MATERIALS:

Component 1: "chemically pure" $NaC_2H_3O_2.3H_2O$ dried to constant mass; it undergoes a phase transition at $t_{trs}(1)/^{O}C=254.$ Component 2: source not stated; it undergoes a phase transition at $t_{trs}(2)/^{O}C=275$ (Ref. 1).

ESTIMATED ERROR:

Temperature: accuracy probably ±2 K (compiler).

REFERENCES:

(1) Bergman, A.G.; Berul, S.I. Izv. Sektora Fiz.-Khim. Anal. 1952, 21, 178-183.

- (1) Sodium ethanoate (sodium acetate);
- NaC₂H₃O₂; [127-09-3] (2) Sodium nitrate; NaNO₃; [7631-99-4]

ORIGINAL MEASUREMENTS:

Diogenov, G.G.

Zh. Neorg. Khim. 1956, 1, 799-805 (*); Russ. J. Inorg. Chem. (Engl. Transl.) 1956, 1 (4), 199-205.

VARIABLES:

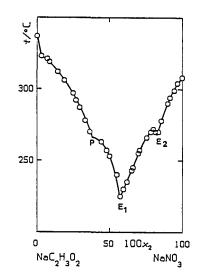
Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

t/ºC	T/K ^a	100 x 2	t/ ^o C	T/Kª	100 x 2
337	610	0	235	508	62
323	596	3	243	516	65.2
321	594	7	245	518	66
319	592	8.5	255	528	69.7
312	585	14.5	257	530	70.5
306	579	19	266	539	75.5
297	570	25	270	543	78.4
292	565	27	272	545	80
287	560	29.5	270	543	81.5
278	551	33.3	270	543	83.5
270	543	36.5	278	551	85.5
263	536	44.5	290	563	90
257	530	48	294	567	91.5
253	526	50	299	572	94.5
240	513	55	304	577	96.7
225	498	57.3	308	581	100
230	503	59.5			



Characteristic point(s):

Peritectic, P, at 266 $^{\rm o}$ C (author) and $100{\rm m_2}$ = 38.5 (compiler). Eutectic, E₁, at 225 $^{\rm o}$ C and $100{\rm m_2}$ = 57.5 (author). Eutectic, E₂, at about 268 $^{\rm o}$ C and $100{\rm m_2}$ about 82.5 (compiler).

Intermediate compound(s):

 $\rm Na_3(C_2H_3O_2)_2NO_3$, incongruently melting (author). $\rm Na_5C_2H_3O_2(NO_3)_4$, congruently melting at 272 $^{\rm O}{\rm C}$ (author).

Note - On the branch rich in component 1 an inflexion at 323 $^{\mathrm{o}}\mathrm{C}$ corresponds to a phase transition of NaC2H3O2.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

SOURCE AND PURITY OF MATERIALS:

Visual polythermal analysis.

Not stated.

ESTIMATED ERROR:

<u>+</u>2 K Temperature: accuracy probably (compiler).

a T/K values calculated by the compiler.

- (1) Sodium ethanoate (sodium acetate);
- NaC₂H₃O₂; [127-09-3] (2) Sodium nitrate; NaNO₃; [7631-99-4]

ORIGINAL MEASUREMENTS:

Gimel'shtein, V.G.; Diogenov, G.G. Tr. Irkutsk. Politekh. Inst., Ser. Khim., 1966, 27, 69-75.

VARIABLES:

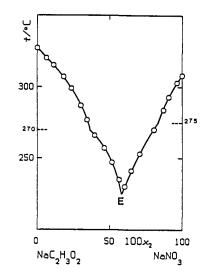
Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

t/°C	T/Kª	100 x 2
327	600	0
320	593	6.5
315	588	11.5
307	580	18.3
299	572	23.5
287	560	30.0
277	550	34.3
266	539	39.5
257	530	46.2
247	520	51.5
235	508	56.4
230	503	60.2
241	514	64.7
253	526	70.6
270	543	80.5
284	557	87.0
293	566	90.7
303	576	96.4
308	581	100



Characteristic point(s):

Eutectic, E, at 225 °C and $100x_2$ = 58 (authors).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis supplemented with X-ray investigations. Temperatures measured with a Chromel-Alumel thermocouple and a 17 mV millivoltmeter.

SOURCE AND PURITY OF MATERIALS:

Not stated.

Component 1 undergoes a phase transition at

Component 1 undergoes a phase transition at $t_{\rm trs}(1)/^{\rm C}$ = 270. Component 2 undergoes a phase transition at $t_{\rm trs}(2)/^{\rm C}$ = 275.

ESTIMATED ERROR:

+2 K Temperature: accuracy probably (compiler).

a T/K values calculated by the compiler.

	T I			
COMPONENTS:	ORIGINAL MEASUREMENTS:			
(1) Sodium ethanoate (sodium acetate); NaC ₂ H ₃ O ₂ ; [127-09-3] (2) Sodium nitrate; NaNO ₃ ; [7631-99-4]	Storonkin, A.V.; Vasil'kova, I.V.; Potemin, S.S.; Vestn. Leningr. Univ., Fiz., Khim. 1974, (16), 73-76.			
VARIABLES:	PREPARED BY:			
Temperature.	D'Andrea, G.			
EXPERIMENTAL VALUES:				
t/°C T/K ^a 100x ₂ t/°C T/K ^a 100x ₂), }			
328 601 0 224 497 60 314 587 10 242 515 70 300 573 20 261 534 80 284 557 30 281 554 90 259 532 40 306 579 100 235 508 50 a T/K values calculated by the compiler.	250			
Note - The tabulated data were drawn by the compiler from Fig. 1 of the original paper.	E			
Characteristic point(s): 0 50 100x ₂ 100				
Eutectic, E, at 218 °C and 100x ₂ = 56 (authors	B). NaC ₂ H ₃ O ₂ NaNO ₃			
AUXILIARY I	NFORMATION			
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:			
DTA. Thermograph with photorecorder. Salt(s) sealed under vacuum in Pyrex ampoules. No other information given.	NaC ₂ H ₃ O ₂ of analytical purity and "chemically pure" NaNO ₃ , heated 10-15 h at temperatures 50-60 ^{OC} below their fusion temperatures, were employed.			
ESTIMATED ERROR:	REFERENCES:			
Temperature: accuracy probably +2 K (compiler).				
COMPONENTS:	ORIGINAL MEASUREMENTS:			
(1) Sodium ethanoate (sodium acetate); NaC ₂ H ₃ O ₂ ; [127-09-3] (2) Sodium nitrate; NaNO ₃ ; [7631-99-4]	Diogenov, G.G.; Chumakova, V.P. FizKhim. Issled. Rasplavov Solei, Irkutsk, 1975, 7-12.			
VARIABLES:	PREPARED BY:			
Temperature.	D'Andrea, G.			
EXPERIMENTAL VALUES:				
Eutectic, E, at 222 °C (Fig. 1 of the original paper); composition not stated (100x ₁ about 43 in compiler's graphical estimation).				
AUXILIARY I	NFORMATION			
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:			
Visual polythermal analysis.	Not stated. Component 1: $t_{fus}(1)/{}^{OC}=326$; component 2: $t_{fus}(2)/{}^{OC}=308$ (Fig. 1 of the original paper).			
ESTIMATED ERROR:				
Temperature: accuracy probably +2 K (compiler).	REFERENCES:			

- (1) Sodium propanoate (sodium propionate);
- NaC₃H₅O₂; [137-40-6] (2) Sodium thiocyanate; NaCNS; [540-72-7]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1150-1156.

VARIABLES:

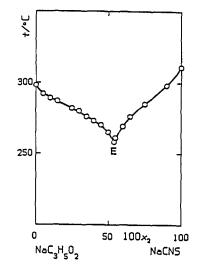
Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

t/°C	T/K ^a	100 x 2
298	571	0
292	565	5
289	562	10
287	560	15
282	555	25
280	553	30
276	549	35
273	546	40
270	543	45
265	538	50
258	531	54
261	534	55
269	542	60
276	549	65
285	558	75
298	571	90
311	584	100



Characteristic point(s):

Eutectic, E, at 258 $^{\circ}$ C and $100x_2$ = 54 (author).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.
Salt(s) melted in a test tube. Temperature measured with a Nichrome-Constantane thermocouple and a millivoltmeter with mirror reading to 17 mV.

SOURCE AND PURITY OF MATERIALS:

Component 1 synthetized from propanoic acid and NaHCO3. Component 2 of analytical purity recrystallized once from water and once from ethanol.

NOTE:

See the NOTE relevant to the investigation by Storonkin et al. (Ref. 1) on the same system.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

REFERENCES:

(1) Storonkin, A.V.; Vasil'kova, I.V.; Potemin, S.S. Vestn. Leningr. Univ., Fiz., Khim. 1974, (10), 84-88.

a T/K values calculated by the compiler.

- (1) Sodium propanoate (sodium propionate); NaC₃H₅O₂; [137-40-6]
- (2) Sodium thiocyanate; NaCNS; [540-72-7]

ORIGINAL MEASUREMENTS:

Storonkin, A.V.; Vasil'kova, I.V.; Potemin, S.S.;

Vestn. Leningr. Univ., Fiz., Khim. 1974, (10), 84-88.

VARIABLES:

Temperature.

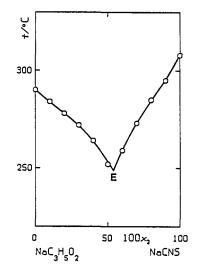
PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

t/°C	T/K ^a	100 x 2
290	563	0
284	557	10
278	551	20
272	545	30
264	537	40
252	525	50
259	532	60
273	546	70
285	558	80
295	568	90
308	581	100

a T/K values calculated by the compiler.



Note - The tabulated data were drawn by the compiler from Fig. 3 of the original paper.

Characteristic point(s):

Eutectic, E, at 249 $^{\circ}$ C and $100x_{2}$ = 54 (authors).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

DTA.

Thermograph with photorecorder.

Salt(s) sealed under vacuum in Pyrex ampoules.

No other information given.

NOTE:

Concerning component 1, the fusion temperature (563 K) fairly agrees with the values listed in Preface, Tables 1 and 3 [562.4+0.5 K (DSC) and 561.88+0.03 K (adiabatic calorimetry) respectively], whereas the figure by Sokolov (571; Ref. 1) seems somewhat too high. An approximately equal difference exists also between Storonkin et al.'s and Sokolov's eutectic temperatures (522 and 531 K, respectively). The temperature values measured by Storonkin et al. are likely more reliable.

SOURCE AND PURITY OF MATERIALS:

 ${
m NaC_3H_5O_2}$ prepared from propanoic acid and NaOH, and "chemically pure" NaCNS, heated 10-15 h at temperatures 50-60 °C below their fusion temperatures, were employed.

ESTIMATED ERROR:

Temperature: accuracy probably ± 2 K (compiler).

REFERENCES:

(1) Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1150-1156.

- (1) Sodium propanoate (sodium propionate); NaC₃H₅O₂; [137-40-6]
- (2) Sodium nitrite; NaNO₂; [7632-00-0]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1957, 27, 840-844 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1957, 27, 917-920.

VARIABLES:

Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

t/ºC	T /K ^a	100 x 2	t/°C	T/K ^a	100 x 2
298	571	0	296	569	55
306	579	5	286	559	60
311	584	10	284	557	65
312	585	15	276	549	70
314	587	20	269	542	75
315	588	25	256	529	80
313	586	30	262	535	85
311	584	35	267	540	90
308	581	40	272	545	95
306	579	45	284	557	100
303	576	50			

a T/K values calculated by the compiler.

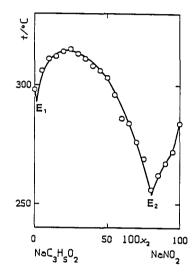
Characteristic point(s):

Eutectic, E_1 , at 293 °C and $100x_2=1.4$ (author). Eutectic, E_2 , at 254 °C and $100x_2=80.5$ (author).

Note - The coordinates of the first eutectic are given in table 2 of the original paper; they cannot, however, be drawn from the tabulated data.

Intermediate compound(s):

 $Na_4(C_3H_5O_2)_3NO_2$ congruently melting at 315 °C.



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis; salt mixtures melted in a glass tube (surrounded by a wider tube) and stirred with a glass thread. The temperatures of initial crystallization were measured with a Nichrome-Constantane thermocouple checked at the fusion points of water, benzoic acid, mannitol, AgNO $_3$, Cd, KNO $_3$, and $K_2Cr_2O_7$.

SOURCE AND PURITY OF MATERIALS:

Component 1: prepared from "chemically pure" sodium hydrogen carbonate (carbonate in the reference quoted; compiler) and commercial propanoic acid distilled before use (Ref. 1); the recovered salt was recrystallized from n-butanol. Component 2: "chemically pure" material recrystallized from water.

NOTE:

The fusion temperature of component 1 (571 K) is somewhat too high: both DSC and adiabatic calorimetry provide a value close to 562 K (see Preface, Table 3).

ESTIMATED ERROR:

Temperature: accuracy probably ± 2 K (compiler).

REFERENCES:

(1) Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1581-1593.

- (1) Sodium propanoate (sodium propionate);
- NaC₃H₅O₂; [137-40-6] (2) Sodium nitrate; NaNO₃; [7631-99-4]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1150-1156.

VARIABLES:

Temperature.

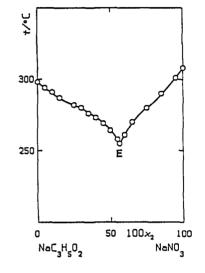
PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

	
298 571 0 264 5	37 50
294 567 5 258 5	31 55
291 564 10 255 5	28 56.5
287 560 15 261 5	34 60
282 555 25 270 5	43 65
280 553 30 280 5	53 75
276 549 35 290 5	63 85
273 546 40 301 5	74 95
269 542 45 308 5	81 100

 $^{^{\}mathbf{a}}$ T/K values calculated by the compiler.



Characteristic point(s):

Eutectic, E, at 255 °C and $100x_2 = 56.5$ (author).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.
Salt(s) melted in a test tube. Temperature measured with a Nichrome-Constantane thermocouple and a millivoltmeter with mirror reading to 17 mV.

SOURCE AND PURITY OF MATERIALS:

Component 1 synthetized from propanoic acid and NaHCO₃. Commercial component 2 further purified by the author according to Laiti.

NOTE:

The fusion temperature of component 1 (571 K) is somewhat too high: both DSC and adiabatic calorimetry provide a value close to 562 K (see Preface, Table 3).

ESTIMATED ERROR:

Temperature: accuracy probably ± 2 K (compiler).

REFERENCES:

(1) Sokolov, N.M.
Zh. Obshch. Khim. 1954, 24, 1581-1593.

- (1) Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7]
- (2) Sodium iso.butanoate (sodium iso.butyrate);
 Nai.C₄H₇O₂; [996-30-5]

EVALUATOR:

Ferloni, P., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

The system was studied only by Sokolov (Ref. 1), who claimed the existence of a continuous series of solid solutions, with a minimum at 494 K and $100x_2=72.5$.

Component 1, however, forms liquid crystals in a stability field ranging between $T_{\rm clr}(1)/K=600.4+0.2$ and $T_{\rm fus}(1)/K=524.5+0.5$ (according to Preface, Table 1). Consequently: (i) Sokolov's fusion temperature of component 1 (603 K) should be identified with the clearing temperature; (ii) at low values of $100x_2$, Sokolov's points should refer to the formation of liquid crystals (pseudo-liquidus), and not of solid solutions (true liquidus). Besides the minimum, m, an M point should exist (although its coordinates are hard to detect on the basis of the available data, and the phase diagram should be not too different from that shown in Scheme B.3 of the Preface.

REFERENCES

(1) Sokolov, N.M.; Zh. Obshch. Khim. 1954, 24, 1581-1593.

COMPONENTS:

- (1) Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7]
 (2) Sodium iso.butanoate (sodium
- (2) Sodium iso.butanoate (sodium iso.butyrate); Nai.C₄H₇O₂; [996-30-5]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1581-1593.

VARIABLES:

Temperature.

PREPARED BY:

D'Andrea, G.

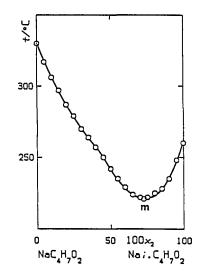
EXPERIMENTAL VALUES:

t/°C	T/K ^a	100 x 2	t/°C	T/K ^a	100 x 2
330	603	0	235	508	55
317	590	5	229	502	60
306	579	10	224	497	65
297	570	15	222	495	70
287	560	20	221	494	72.5
279	552	25	222	495	75
270	543	30	225	498	80
264	537	35	228	501	85
257	530	40	235	508	90
250	523	45	248	521	95
242	515	50	260	533	100

a T/K values calculated by the compiler.

Characteristic point(s):

Continuous series of solid solutions with a minimum, m, at 221 $^{\rm O}{\rm C}$ and $100{\rm x_2}$ = 72.5 (author).



METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

Melts contained in a glass tube and stirred.

Temperatures measured with a Nichrome-Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of isotropicity in the melt on cooling.

SOURCE AND PURITY OF MATERIALS:

Materials prepared by reacting aqueous ("chemically pure") Na_2CO_3 with a slight excess of the proper acid of analytical purity. The solvent and excess acid were removed by heating to 160 °C.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

- (1) Sodium butanoate (sodium butyrate);
- NaC₄H₇O₂; [156-54-7]
 (2) Sodium **iso**-pentanoate (sodium **iso**-valerate);
 Na1•C₅H₉O₂; [539-66-2]

EVALUATOR:

Ferloni, P., Dipartimento di Chimica Fisica, Universita´ di Pavia (ITALY).

CRITICAL EVALUATION:

This system was studied only by Sokolov (Ref. 1), who suggests a eutectic phase diagram, the invariant point being at 530 K (257 $^{\circ}$ C) and $100x_2$ =90.5. Both components, however, form liquid crystals.

Therefore, the fusion temperatures, $T_{\rm fus}(1)$ =603 K (330 °C) and $T_{\rm fus}(2)$ =535 K (262 °C), should be identified with the clearing temperatures, the corresponding values from Tables 1, 2 of the Preface being $T_{\rm clr}(1)$ =600.4+0.2 K, and $T_{\rm clr}(2)$ =559+1 K, respectively. The discrepancy between the values concerning component 2 might be attributed to some impurity of Sokolov's samples, inasmuch as the value from Preface (Table 2) meets rather satisfactorily those reported by Ubbelohde et al. (556 K; Ref. 2) and by Duruz et al. (553 K; Ref. 3). No mention is made by the author of other phase transitions occurring in either component, including those corresponding to the actual fusion, which should be $T_{\rm fus}(1)$ =524+0.5 K (Preface, Table 1) and $T_{\rm fus}(2)$ = 461.5+0.5 K (Table 2).

Accordingly, the phase diagram of the system should be modified. The available data do not allow one to rule out neither of the following possibilities: (i) the eutectic point should be identified with a minimum point in a continuous series of liquid crystal solutions; (ii) the eutectic point should be identified with an M"_E point, at which the isotropic liquid should be in equilibrium with two liquid crystal solutions of different composition (Preface, Scheme C.3, Fig. 3.3).

- (1) Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1581-1593.
- (2) Ubbelohde, A.R.; Michels, H.J.; Duruz, J.J. Nature 1970, 228, 50-52.
- (3) Duruz, J.J.; Michels, H.J.; Ubbelohde, A.R. Proc. R. Soc. London 1971, A322, 281-299.

- (1) Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7]
 (2) Sodium iso.pentanoate (sodium
- iso.valerate); $Na1.C_5H_9O_2$; [539-66-2]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1581-1593.

VARIABLES:

Temperature.

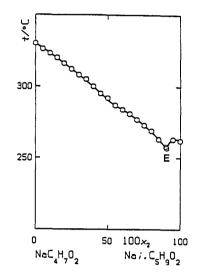
PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

t/°C	T/K ^a	100 x 2			
330	603	0	287	560	55
326	599	5	284	557	60
323	596	10	281	554	65
320	593	15	277	550	70
316	589	20	273	546	75
312	585	25	269	542	80
308	581	30	263	536	85
305	578	35	258	531	90
300	573	40	257	530	90.5
295	568	45	263	536	95
292	565	50	262	535	100

 $^{\mathbf{a}}$ T/K values calculated by the compiler.



Characteristic point(s): Eutectic, E, at 257 °C and 100x2 = 90.5 (author).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual Melts polythermal analysis. contained in a glass tube and stirred. Temperatures measured with a Nichrome-Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of isotropicity in the melt on cooling.

SOURCE AND PURITY OF MATERIALS:

Materials prepared by reacting aqueous ("chemically pure") Na_2CO_3 with a slight excess of the proper acid of analytical purity. The solvent and excess acid were removed by heating to $160~^{\circ}C$.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

- (1) Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7]
- (2) Sodium hexanoate (sodium caproate); NaC₆H₁₁O₂; [10051-44-2]

EVALUATOR:

Ferloni, P., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

This system was studied only by Sokolov (Ref. 1), who claimed the existence of two eutectics [E₁, at 590 K (317 $^{\circ}$ C) and $100\mathbf{x}_{2}^{=}$ 22.5; E₂, at 590 K (317 $^{\circ}$ C) and $100\mathbf{x}_{2}^{=}$ 27.5], and of the intermediate compound $\mathrm{Na_{4}(C_{4}H_{7}O_{2})_{3}C_{6}H_{11}O_{2}}$, congruently melting at 594 K (321 $^{\circ}$ C).

Both components, however, form liquid crystals. Therefore, Sokolov's fusion temperatures, $T_{\rm fus}(1)$ = 603 K (330 °C) and $T_{\rm fus}(2)$ = 638 K (365 °C), should be identified with clearing temperatures, the corresponding values from Preface, Table 1 being $T_{\rm clr}(1)$ = 600.4±0.2 K and $T_{\rm clr}(2)$ = 639.0±0.5 K, respectively.

No mention is made by the author of other phase transitions of either component, including those corresponding to their actual fusions, which ought to occur at $T_{fus}(1) = 524.5 \pm 0.5$ K and $T_{fus}(2) = 499.6 \pm 0.6$ K, respectively (see Table 1).

Concerning the phase diagram, the available data suggest the following interpretations as possible. If the maximum at 594 K (321 $^{\rm O}$ C) and $100{\rm m_2}$ = 25 does exist, Sokolov's eutectics could be identified with either M' $_{\rm E}$ points at the opposite sides of the distectic pertinent to a congruently melting intermediate compound (Preface, Scheme D.2), or m points in a situation similar to that shown in Scheme C.3. Conversely, if the occurrence of the maximum is considered as insufficiently proved, one might think of the existence of either an M' $_{\rm E}$ point (with limited series of liquid crystal solutions on both sides; Scheme C.2), or a (single) minimum in a continuous series of liquid crystal solutions.

REFERENCES:

(1) Sokolov, N.M.
Zh. Obshch. Khim. 1954, 24, 1581-1593.

- (1) Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7]
- (2) Sodium hexanoate (sodium caproate); NaC₆H₁₁O₂; [10051-44-2]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1581-1593.

VARIABLES:

Temperature.

PREPARED BY:

D'Andrea, G.

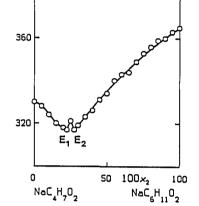
EXPERIMENTAL VALUES:

t/ºC	T/Kª	100 x 2	t/ ^o C	T/K ^a	100 x 2
330	603	0	334	607	50
328	601	5	340	613	55
324	597	10	343	616	60
320	593	15	344	617	65
318	591	20	349	622	70
317	590	22.5	353	626	75
321	594	25	356	629	80
317	590	27.5	359	632	85
319	592	30	360	633	90
323	596	35	363	636	95
326	599	40	365	638	100
331	604	45			
1					

^aT/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E₁, at 317 $^{\rm o}$ C and $100x_2$ = 22.5 (author). Eutectic, E₂, at 317 $^{\rm o}$ C and $100x_2$ = 27.5 (author).



Intermediate compound(s):

 $Na_4(C_4H_7O_2)_3C_6H_{11}O_2$ [erroneously indicated as $Na_5(C_4H_7O_2)_4C_6H_{11}O_2$ in the text, compiler], congruently melting at 321 $^{\circ}C_*$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

Melts contained in a glass tube and stirred.

Temperatures measured with a Nichrome-Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of isotropicity in the melt on cooling.

SOURCE AND PURITY OF MATERIALS:

Materials prepared by reacting aqueous ("chemically pure") ${\rm Na_2CO_3}$ with a slight excess of the proper acid of analytical purity. The solvent and excess acid were removed by heating to 160 °C.

ESTIMATED ERROR:

Temperature: precision probably +2 K (compiler).

- (1) Sodium butanoate (sodium butyrate);
- NaC₄H₇O₂; [156-54-7] (2) Sodium benzoate; NaC₇H₅O₂; [532-32-1]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1581-1593.

VARIABLES:

Temperature.

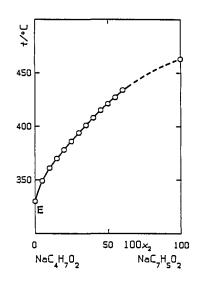
PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

t/ºC	T/K ^a	100 x 2
330	603	0
330	603	0.13
349	622	5
361	634	10
370	643	15
378	651	20
386	659	25
394	667	30
401	674	35
408	681	40
415	688	45
421	694	50
427	700	55
434	707	60
463	736	100

 $^{\mathbf{a}}$ T/K values calculated by the compiler.



Characteristic point(s):

Eutectic, E, at 330 °C and $100x_2 = 0.13$ (author).

Note - The system was investigated at $0 \le 100 x_2 \le 60$ due to thermal instability of the butanoate.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

Melts contained in a glass tube and stirred.

Temperatures measured with a Nichrome-Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of isotropicity in the melt on cooling.

SOURCE AND PURITY OF MATERIALS:

Component 1: prepared by reacting aqueous ("chemically pure") Na₂CO₃ with a slight excess of n-butanoic acid of analytical purity. The solvent and excess acid were removed by heating to 160 °C. Component 2: "chemically pure" material.

NOTE:

Component 1 forms liquid crystals. Therefore Sokolov's fusion temperature, $T_{fus}(1)=603$ K, should be identified with the clearing temperature, the corresponding value in Table 1 of the Preface being 600.4 ± 0.2 K. It is hard to infer the topology of the system from the available data: indeed, the phase diagram might be similar to that shown in Preface, Scheme A.1, but other possibilities remain open.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

- (1) Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7]
- (2) Sodium octadecanoate (sodium stearate); NaC₁₈H₃₅O₂; [822-16-2]

EVALUATOR:

Spinolo, G., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

This system was studied only by Sokolov (Ref. 1) who employed the visual polythermal analysis to draw the lower boundary of the isotropic liquid field. From the shape of this boundary, he concluded that the intermediate compound $Na_5(C_4H_7O_2)_3(C_18H_35O_2)_2$ [congruently melting at 663 K (390 °C)] was formed, and that the limits of the stability field of this compound were a eutectic at 521 K (248 °C) and $100x_2=15$, and a "perekhodnaya tochka" at 582 K (309 °C) and $100x_2=96.5$.

Actually, both components form liquid crystals, the liquid crystalline phases being one for component 1 (see Preface, Table 1), and two for component 2 (see Table 4 of the Preface). Sokolov's fusion temperatures, $T_{fus}(1) = 603 \text{ K } (330 \, ^{\circ}\text{C})$, and $T_{fus}(2) = 581 \text{ K } (308 \, ^{\circ}\text{C})$, consequently should be identified with the clearing temperatures, the corresponding values from Tables 1 and 4 being 600.4+0.2 and 552.7 K, respectively.

Since the complete topology of the binary can hardly be interpreted from the available data, it is more realistic to list here the few points which, in the evaluator's opinion, seem to be sufficiently reliable.

- (1) At intermediate compositions it seems reasonable to assume that a continuous series of liquid crystal solutions is formed, with an azeotrope at 663 K and $100x_2=40$.
- (ii) Accordingly, the left hand section (0 \leq 100 \mathbf{x}_2 \leq 40) of the phase diagram might be interpreted with reference to Preface, Scheme C.2: in this case, Sokolov's eutectic should be identified with an M"_E point.

Conversely, no definite interpretation of the phase diagram at high $100\mathrm{m}_2$ values seems possible. Indeed, it is not clear how Sokolov could argue the occurrence of an invariant (the "perekhodnaya tochka" at $100\mathrm{m}_2$ = 96.5) from the trend of his experimental data which does not support unambiguously any significant slope change of the curve in this region. Moreover, Sokolov's "fusion" temperature of component 2 (581 K) looks as fully unreliable, being 18 K higher than the second highest $T_{\rm clr}$ value determined during the last 30 years (Ref. 2), and 28 K higher than the clearing temperature listed in Table 4 of the Preface.

- (1) Sokolov, N.M.
 Zh. Obshch. Khim. 1954, 24, 1581-1593.
- (2) Sanesi, M.; Cingolani, A.; Tonelli, P.L.; Franzosini, P. Thermal Properties, in Thermodynamic and Transport Properties of Organic Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors), Pergamon Press, Oxford, 1980, 29-115.

- (1) Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7]
- (2) Sodium octadecanoate (sodium stearate); NaC₁₈H₃₅O₂; [822-16-2]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1581-1593.

VARIABLES:

Temperature.

PREPARED BY:

D'Andrea, G.

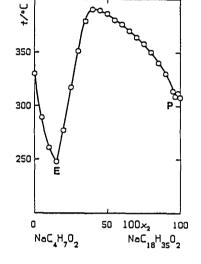
EXPERIMENTAL VALUES:

t/°C	T/Kª	100 x 2	t/°C	T/K ^a	100 x 2
330	603	0	376	649	60
289	562	5	370	643	65
261	534	10	364	637	70
248	521	15	358	631	75
277	550	20	350	623	80
317	590	25	340	613	85
351	624	30	330	603	90
379	652	35	314	587	95
390	663	40	309	582	96.5
389	662	45	312	585	98.5
386	659	50	308	581	100
380	653	55			

a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E, at 248 °C and $100x_2 = 15$ (author). Characteristic point, P ("perekhodnaya tochka" in the original text; see the Introduction), at 309 °C and 100x2= 96.5 (author).



Intermediate compound(s):

 $Na_5(C_4H_7O_2)_3(C_{18}H_{35}O_2)_2$, congruently melting at 390 °C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

Melts contained in a glass tube and stirred.

Temperatures measured with a Nichrome-Constantane thermocouple and a 17 mV $\,$ full scale millivoltmeter. The temperature readings refer to the disappearance of isotropicity in the melt on cooling.

SOURCE AND PURITY OF MATERIALS:

Component 1: prepared by reacting aqueous ("chemically pure") Na_2CO_3 with a slight excess of n-butanoic acid of analytical purity. The solvent and excess acid were removed by heating to $160\,^{\circ}\text{C}$.

Component 2: "chemically pure" material.

ESTIMATED ERROR:

Temperature: +2 K precision probably (compiler).

- (1) Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7]
- (2) Sodium thiocyanate; NaCNS; [540-72-7]

EVALUATOR:

Spinolo, G., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

This system was studied only by Sokolov (Ref. 1), who restricted his visual polythermal investigation to the lower boundary of the isotropic liquid field. He asserted the existence of the intermediate compound $Na_4(C_4H_7O_2)_3CNS$, which melts incongruently at 541 K (268 °C), and of a eutectic at 535 K (262 °C) and $100x_2$ 48.5.

Component 1, however, forms liquid crystals, which are stable between $T_{\mathrm{fus}}(1)$ = 524.5+0.5 K and $T_{\mathrm{clr}}(1)$ = 600.4+0.2 (see Preface, Table 1). Sokolov's fusion temperature (603 K) consequently should be identified with the clearing temperature, whereas the T_{trs} value (525 K), reported by the same author in a subsequent paper (Ref. 2), is in close agreement with the fusion temperature given in Table 1.

In the evaluator's opinion, Sokolov's findings are not sufficient to prove unambiguously the existence of the intermediate compound. Consequently, more than one interpretation can be given for the topology of this binary.

Indeed, if the compound does exist:

- (i) the phase diagram could be similar to that shown in Preface, Scheme D.3, (ii) Sokolov's "Perekhodnaya tochka" should to be identified with an M_p point; and (iii) the occurrence of a (so far undetected) $M_{\rm E}$ point is required.
- If, on the contrary, one assumes that the intermediate coumpound does not exist, Sokolov's invariant at $541~\rm K$ and $100x_2=31.5$ might be connected with the fusion of component 1 in the way shown in Scheme B.2 of the Preface.

- (1) Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1150-1156.
- (2) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

- (1) Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7]
- (2) Sodium thiocyanate; NaCNS; [540-72-7]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1150-1156.

VARIABLES:

Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

t/°C	T/K ^a	100 x 2	t/°C	T/K ^a	100 x 2
330	603	0	263	536	45
328	601	5	262	535	48.5
324	597	10	269	542	50
316	589	15	280	553	55
291	564	25	287	560	60
275	548	30	290	563	65
268	541	31.5	298	571	75
266	539	35	304	577	90
264	537	40	311	584	100

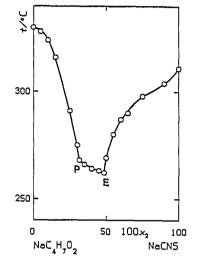
a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E, at 262 °C and $100x_2$ = 48.5 (author). Invariant point, P ("perekhodnaya tochka" in the original text, see the Introduction), at 268 °C and $100x_2$ = 31.5 (author).

Intermediate compound(s):

 $Na_4(C_4H_7O_2)_3CNS$, incongruently melting (author).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.
Salt(s) melted in a test tube. Temperature measured with a Nichrome-Constantane thermocouple and a millivoltmeter with mirror reading to 17 mV.

SOURCE AND PURITY OF MATERIALS:

Component 1 synthetized from n-butanoic acid and NaHCO3.

Component 2 of analytical purity recrystallized once from water and once from ethanol.

ESTIMATED ERROR:

Temperature: precision probably +2 K (compiler).

- (1) Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7]
- (2) Sodium nitrite; NaNO₂; [7632-00-0]

EVALUATOR:

Spinolo, G., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

This system was studied only by Sokolov (Ref. 1) who restricted his polythermal investigation to the lower boundary of the isotropic liquid field. He claimed that an intermediate compound, i.e., $Na_4(C_4H_7O_2)_3NO_2$, exists which forms eutectics with either pure component at 590 K (317 °C) and $100x_2 = 17.5$, and at 347 K (274 °C) and $100x_2 = 96$, respectively.

No data on the solidus are available, and consequently the existence of the intermediate compound is not fully proved. Nevertheless, the evaluator is inclined to accept - at least in part - Sokolov's interpretation of the topology of the system.

It must, however, be specified that, due to the fact that component 1 forms liquid crystals stable between 524.5±0.5 K and 600.4±0.2 K (see Preface, Table 1), (i) the first eutectic at 590 K ought to be identified with an M_E^* point; and (ii) a further (so far undetected) invariant, presumably an M_E point, should exist.

In conclusion, the phase diagram ought to be similar to that shown in Scheme D.1 of the Preface.

REFERENCES:

(1) Sokolov, N.M. Zh. Obshch. Khim. 1957, 27, 840-844 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1957, 27, 917-920.

- (1) Sodium butanoate (sodium butyrate);
- NaC₄H₇O₂; [156-54-7] (2) Sodium nitrite; NaNO₂; [7632-00-0]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.
Zh. Obshch. Khim. 1957, 27, 840-844 (*); Russ. J. Gen. Chem., Engl. Transl., 1957, 27, 917-920.

VARIABLES:

Temperature.

PREPARED BY:

D'Andrea, G.

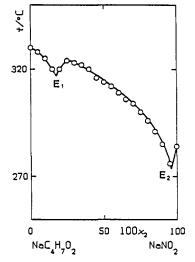
EXPERIMENTAL VALUES:

t/ºC	T/K ^a	100 x 2	t/°C	T/K ^a	100 x 2
330	603	0	312	585	55
328	601	5	309	582	60
325	598	10	306	579	65
320	593	15	304	577	70
320	593	20	300	573	75
324	597	25	296	569	80
323	596	30	291	564	85
322	595	35	285	558	90
320	593	40	276	549	95
316	589	45	284	557	100
314	587	50			

a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E_1 , at 317 °C and $100x_2=17.5$ (author). Eutectic, E_2 , at 274 °C and $100x_2=96$ (author).



Note - The coordinates of the second eutectic are given in Table 2 of the original paper; they cannot, however, be drawn from the tabulated data; compiler).

Intermediate compound(s):

 $Na_4(C_4H_7O_2)_3NO_2$ congruently melting at 324 °C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis; salt mixtures melted in a glass tube (surrounded by a wider tube) and stirred with a glass thread. The temperatures of initial crystallization were measured with a Nichrome-Constantane thermocouple checked at the fusion points of water, benzoic acid, mannitol, AgNO3, Cd, KNO3, and K2Cr207.

SOURCE AND PURITY OF MATERIALS:

Component 1: prepared from "chemically pure" sodium hydrogen carbonate (carbonate in the reference quoted; compiler) and commercial n-butanoic acid distilled before use (Ref. 1); the salt recovered was recrystallized from n-butanol.
Component 2: "chemically pure" material recrystallized from water.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

REFERENCES:

(1) Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1581-1593.

- (1) Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7]
- (2) Sodium nitrate; NaNO₃; [7631-99-4]

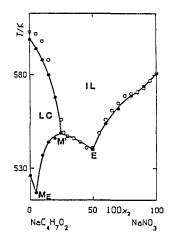
EVALUATOR:

Ferloni, P., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

The visual polythermal method was employed by Dmitrevskaya (Ref. 1) [see also Sokolov, (Ref. 2)] to study the lower boundary of the isotropic liquid field: according to this author, an incongruently melting intermediate compound of probable composition Na₄(C₄H₇O₂)₃NO₃ is formed, and two invariants exist, i.e., a eutectic, E [at 540 K (267 $^{\rm O}$ C), and $100\mathbf{x}_2$ = 50], and a "perekhodnaya tochka", P [at 549 K (276 $^{\rm O}$ C), and $100\mathbf{x}_2$ = 27].

Component 1, however, forms liquid crystals. Accordingly, the fusion temperature, $T_{fug}(1) = 603 \text{ K } (330 \, ^{\circ}\text{C})$, reported in Ref. 1 should be identified with the clearing temperature, $T_{clr}(1)$, of component 1, the corresponding value from Preface, Table 1 being $600.4 \pm 0.2 \text{ K}$.



For the same component, Table 1 of the Preface [besides the $T_{clr}(1)$ value] provides four solid state transitions (at 450.4+0.5, 489.8+0.2, 498.3+0.3, and 508.4+0.5) and $T_{fus}(1)/K=524.5+0.5$. These phase relations, first stated on the basis of DSC records, were subsequently confirmed by Schiraldi and Chiodelli's conductometric results (Ref. 3). Phase transformations are quoted in Ref. 1 from Ref. 4 as occurring at 390, 505, 525, and 589 K, respectively. A comparison of the two sets of data allows one to identify the two intermediate transition temperatures from Ref. 4 with the first $T_{trs}(2)$ and $T_{fus}(2)$ from Table 1. Reasonable doubts can be raised, on the contrary, about the actual existence of Ref. 4 highest transition (which - if present - should represent the transformation from a liquid crystalline phase into another one) and of the lowest transformations.

More recently, Prisyazhnyi et al. (Ref. 5) - to whom Refs. 1, 2 seem to be unknown carried out a derivatographical re-investigation of the system, which allowed them to draw the lower boundaries of both the isotropic liquid, and the liquid crystal field. Concerning component 1, their clearing [$T_{\rm clr}(1)=599~{\rm K}~(326~{\rm ^{O}C})$] and fusion [$T_{\rm fus}(1)=526~{\rm K}~(253~{\rm ^{O}C})$] temperatures substantially agree with those from Table 1 of the Preface; it is moreover to be stressed that they do not mention any transition intermediate between $T_{\rm clr}(1)$ and $T_{\rm fus}(1)$.

Prisyazhnyi et al.'s, and Dmitrevskaya's results (filled and empty circles, respectively) are compared in the figure (IL: isotropic liquid; LC: liquid crystals), an inspection of which allows one to make the following remarks. An invariant exists, which escaped Dmitrevskaya's attention, and is reasonably to be classified as an $M_{\rm E}$ point. Moreover, the invariant at about $100 {\rm m_2}$ = 25 is actually an M' point: its abscissa being known only approximately, it can hardly be decided if it is of the M'E or of the M'p type: in the former case, the complete phase diagram should be similar to Scheme D.1 of the Preface; in the latter one, to Scheme D.3.

The two-phase region pertinent to the liquid crystal - isotropic liquid equilibria might be so narrow as to have prevented Prisyazhnyi et al. to observe two distinct sets of points in this region, whereas the lack of information by the same authors about eutectic fusion in the different samples studied by derivatographical analysis remains rather surprising.

- (1) Dmitrevskaya, O.I.; Zh. Obshch. Khim. 1958, 28, 2007-2013 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1958, 28, 2046-2051.
- (2) Sokolov, N.M.; Zh. Obshch. Khim. 1954, 24, 1150-1156.
- (3) Schiraldi, A.; Chiodelli, G.; J. Phys. E: Sci. Instr. 1977, 10, 596-599.
- (4) Sokolov, N.M.; Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
- (5) Prisyazhnyi, V.D.; Mirnyi, V.N.; Mirnaya, T.A.; Zh. Neorg. Khim. 1983, 28, 253-255.

- (1) Sodium butanoate (sodium butyrate); $NaC_4H_7O_2$; [156-54-7]
- (2) Sodium nitrate; NaNO3; [7631-99-4]

ORIGINAL MEASUREMENTS:

Dmitrevskaya, 0.I. Zh. Obshch. Khim. 1958, 28, 2007-2013 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1958, 28, 2046-2051.

VARIABLES:

Temperature.

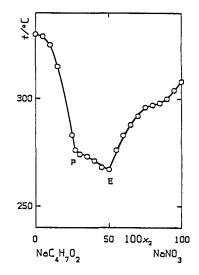
PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

330 ^b 603 0 276 ^b 549 55 329 ^b 602 5 283 ^b 556 60 325 ^b 598 10 288 ^b 561 65 315 ^b 588 15 292 ^b 565 70 283 ^b 556 25 296 ^b 569 75 276 ^b 549 27 297 570 80 274 ^b 547 30 298 ^b 571 85 273 ^b 546 35 300 573 90 271 ^b 544 40 304 ^c 577 95 268 ^b 541 45 308 ^b 581 100	t/ ^o C	T/K ^a	100 x 2	t/°C	T/Kª	100 x ₂
267 ^b 540 50	329 ^b 325 ^b 315 ^b 283 ^b 276 ^b 274 ^b 273 ^b	598 588 556 549 547 546 544 541	5 10 15 25 27 30 35 40	283 ^b 288 ^b 292 ^b 296 ^b 297 298 ^b 300	556 561 565 569 570 571 573	60 65 70 75 80 85 90

a T/K values calculated by the compiler. Value already reported in a previous paper by Sokolov (Ref. 1); the compiler preferred to employ the values tabulated by Dmitrevskaya which are more complete. c 302 in Sokolov's paper (Ref. 1).



Characteristic point(s): Eutectic, E, at 267 $^{\rm O}{\rm C}$ and $100x_2=50$ (author).

Characteristic point, P ("perekhodnaya tochka" in the original text; see the Introduction), at 276 $^{\circ}$ C and $100x_{2}^{=}$ 27 (author).

Intermediate compound(s):

Probably Na₄(C₄H₇O₂)₃NO₃, incongruently melting (author).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis. Temperatures measured with a Nichrome-Constantane thermocouple.

SOURCE AND PURITY OF MATERIALS:

Component 1 synthetized from "chemically pure" sodium hydrogen carbonate and nbutanoic acid that first had been distilled

"Chemically pure" component 2

recrystallized and dried to constant mass. Component 1 undergoes phase transitions at $t_{trs}(1)/^{o}C = 117$, 232, 252, 316 (Ref. 2). Component 2 undergoes a phase transition at t_{trs}(2)/°C= 270 (current literature).

ESTIMATED ERROR:

<u>+</u>2 K Temperature: accuracy probably (compiler).

REFERENCES:

- (1) Sokolov, N.M.
 - Zh. Obshch. Khim. 1954, 24, 1150-1156.
- (2) Sokolov, N.M.

Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

- (1) Sodium butanoate (sodium butyrate); NaC₄H₇O₂; [156-54-7]
- (2) Sodium nitrate; NaNO₃; [7631-99-4]

ORIGINAL MEASUREMENTS:

Prisyazhnyi, V.D.; Mirnyi, V.N.; Mirnaya, T.A.

Zh. Neorg. Khim. 1983, 28, 253-255; Russ.

J. Inorg. Chem. (Engl. Transl.) 1983, 28, 140-141 (*).

VARIABLES:

Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

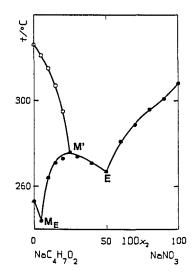
The results are reported only in graphical form (see figure; data read with a digitizer by the compiler on Fig. 1 of the original paper; empty circles: liquid crystal - isotropic liquid equilibria; filled circles: solid - liquid crystal or solid - isotropic liquid equilibria).

Characteristic point(s):

Invariant point, $M_{\rm E}$, at about 244 °C and 100 ${\bf x}_2$ about 5 (compiler). Eutectic, E, at about 267 °C and 100 ${\bf x}_2$ about 50 (compiler). Invariant point, M´, at about 276 °C and 100 ${\bf x}_2$ about 25 (compiler).

Intermediate compound(s):

 $Na_4(C_4H_7O_2)_3NO_3$, melting at about 276 $^{\rm o}C$ (compiler).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The heating and cooling traces were recorded in an atmosphere of purified argon with an OD-102 derivatograph (MOM, Hungary) working at a rate of 6-8 K min⁻¹, and using Al₂O₃ as the reference material. Temperatures were measured with a Pt/Pt-Rh thermocouple. A hot-stage Amplival polarizing microscope was employed to detect the transformation points from the liquid crystalline into the isotropic liquid phase.

SOURCE AND PURITY OF MATERIALS:

Not stated. Component 1: $t_{fus}(1)/^{o}C$ about 253; $t_{clr}(1)/^{o}C$ about 326 (compiler). Component 2: $t_{fus}(2)/^{o}C$ about 308 (compiler).

ESTIMATED ERROR:

Temperature: accuracy is not evaluable (compiler).

COMPONENTS:	EVALUATOR:
(1) Sodium iso.butanoate (sodium iso.butyrate); Nai.C ₄ H ₇ O ₂ ; [996-30-5] (2) Sodium iso.pentanoate (sodium iso.valerate); Nai.C ₅ H ₉ O ₂ ; [539-66-2]	Ferloni, P., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

This system was studied only by Sokolov (Ref. 1), who claimed the existence of a continuous series of solid solutions, with a minimum at 461-462 K and $100x_2=50$.

The fusion temperature of component 1 (533 K) is not far from that reported in Preface, Table 2 (526.9+0.7 K).

Component 2, however, forms liquid crystals in a stability field ranging between $T_{\rm clr}(2)/K=559\pm1$ and $T_{\rm fus}(2)/K=461.5\pm0.6$ (according to Table 2).

Consequently, Sokolov's fusion temperature of component 2 should reasonably be identified as the clearing temperature of this component. Its value, 1.e., 535 K, is remarkably lower than that listed in Table 2, i.e., 559+1 K: the latter figure, however, meets rather satisfactorily those reported by Ubbelohde et al. (556 K; Ref. 2), and by Duruz et al. (553 K; Ref. 3), so that the discrepancy might be attributed to insufficient purity of Sokolov's sample (indeed, due to the — usually small — value of the enthalpy change associated with clearing, a small amount of impurities is often sufficient to cause a dramatic drop of the clearing temperature).

Many of Sokolov's points should represent isotropic liquid - liquid crystal, rather than isotropic liquid - solid equilibria.

Details of the phase diagram, however, are hard to be inferred from the available data.

- (1) Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1581-1593.
- (2) Ubbelohde, A.R.; Michels, H.J.; Duruz, J.J. Nature 1970, 228, 50-52.
- (3) Duruz, J.J.; Michels, H.J.; Ubbelohde, A.R. Proc. R. Soc. London 1971, A322, 281-299.

- (1) Sodium iso.butanoate (sodium iso.butyrate); Nai.C₄H₇O₂; [996-30-5]
 (2) Sodium iso.pentanoate
- (2) Sodium iso.pentanoate (sodium iso.valerate); Nai.C₅H₉O₂; [539-66-2]

ORIGINAL MEASUREMENTS:

Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1581-1593.

VARIABLES:

Temperature.

PREPARED BY:

D'Andrea, G.

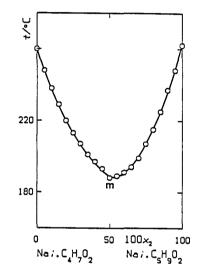
EXPERIMENTAL VALUES:

t/ºC	T/Kª	100 x 2	t/°C	T/K ^a	100 x 2
260	533	0	189	462	55
248	521	5	191	464	60
238	511	10	194	467	65
229	502	15	199	472	70
220	493	20	207	480	75
213	486	25	215	488	80
207	480	30	225	498	85
201	474	35	237	510	90
197	470	40	248	521	95
193	466	45	262	535	100
188	461	50			_

a T/K values calculated by the compiler.

Characteristic point(s):

Minimum, m, at 189 $^{\rm O}$ C (188 $^{\rm O}$ C, according to the table, compiler) and $100{\rm m}_2$ = 50 (author).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

Melts contained in a glass tube and stir red.

Temperatures measured with a Nichrome-Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of isotropicity in the melt on cooling.

SOURCE AND PURITY OF MATERIALS:

Materials prepared by reacting aqueous ("chemically pure") Na_2CO_3 with a slight excess of the proper acid of analytical purity. The solvent and excess acid were removed by heating to 160 $^{\circ}C$.

ESTIMATED ERROR:

Temperature: accuracy is probably ± 2 K (compiler).

- (1) Sodium iso.butanoate (sodium iso.butyrate); Nai.C₄H₇O₂; [996-30-5]
- (2) Sodium hexanoate (sodium caproate); NaC₆H₁₁O₂; [10051-44-2]

EVALUATOR:

Spinolo, G., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

This system was studied only by Sokolov (Ref. 1) who restricted his visual polythermal investigations to the lower boundary of the isotropic liquid field; and claimed the existence of a single eutectic at 433 K (160 $^{\circ}$ C) and $100x_{2}$ = 23.5:

Component 2, however, forms liquid crystals which are stable between 639.0 ± 0.5 K and 499.6 ± 0.6 K (see Preface, Table 1). Consequently, the fusion temperature 638 K ($365^{\circ}\overline{\text{C}}$; Ref. 1) should be identified with the clearing temperature, and Sokolov's outline of the phase diagram is incomplete. In particular, at least two invariants should exist, although the available data do not allow one to state with certainty their nature.

The following hypotheses can be tentatively suggested.

- (i) Sokolov's invariant should be considered as an M_E point; a second one (an M_E point so far undetected) should exist at a lower temperature and at a higher x_2 value.
- (ii) Sokolov's invariant is actually a eutectic, E, and a second invariant (an M_p point so far undetected) should exist at higher temperature and at a higher x_2 value.

If hypothesis (1) is the correct one, the phase diagram ought to be similar to that shown in Scheme A.2 of the Preface.

However, taking into account that $T_{\rm fus}(2)$ (499.6+0.6 K; Table 1 of the Preface) is significantly higher than the fusion temperature of Sokolov's invariant, and that the enthalpy change pertinent to fusion is usually much larger than that pertinent to clearing, the evaluator is inclined to prefer hypothesis (ii). Reference should be therefore made to Preface, Scheme B.1 or B.2.

REFERENCES:

(1) Sokolov, N.M.
Zh. Obshch. Khim. 1954, 24, 1581-1593.

- (1) Sodium iso.butanoate (sodium iso.butyrate);
 Nai.C.H.O.: 1996-30-51
- Nai-C₄H₇O₂; [996-30-5] (2) Sodium hexanoate (sodium caproate); NaC₆H₁₁O₂; [10051-44-2]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1581-1593.

VARIABLES:

Temperature.

PREPARED BY:

D'Andrea, G.

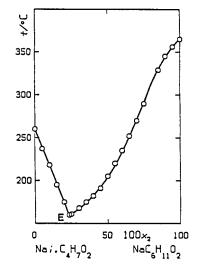
EXPERIMENTAL VALUES:

t/°C	T /K ^a	100 x 2	t/°C	T/Kª	100 x 2
260	533	0	205	478	50
237	510	5	220	493	55
218	491	10	235	508	60
195	468	15	252	525	65
175	448	20	270	543	70
160	433	23.5	290	563	75
161	434	25	329	602	85
168	441	30	345	618	90
175	448	35	356	629	95
182	455	40	365	638	100
191	464	45			

a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E, at 160 $^{\circ}$ C and 100 \mathbf{x}_2 = 23.5 (author).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

Melts contained in a glass tube and stir-red.

Temperatures measured with a Nichrome-Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of isotropicity in the melt on cooling.

SOURCE AND PURITY OF MATERIALS:

Materials prepared by reacting aqueous ("chemically pure") ${\rm Na_2CO_3}$ with a slight excess of the proper acid of analytical purity. The solvent and excess acid were removed by heating to 160 $^{\rm O}{\rm C}$.

ESTIMATED ERROR:

Temperature: accuracy is probably ± 2 K (compiler).

(1) Sodium iso.butanoate (sodium
 iso.butyrate);

Nai.C₄H₇O₂; [996-30-5] (2) Sodium benzoate;

(2) Sodium benzoate; NaC₇H₅O₂; [532-32-1]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1581-1593.

VARIABLES:

Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

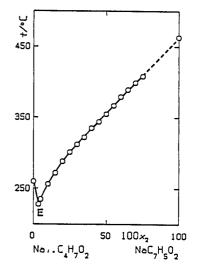
t/ºC	T/K ^a	100 x 2	t/°C	T/K ^a	100 x 2
260	533	0	335	608	40
228	501	3.5	344	617	45
235	508	5	355	628	50
256	529	10	367	640	55
272	545	15	379	652	60
288	561	20	389	662	65
301	574	25	399	672	70
312	585	30	408	681	75
322	595	35	463	736	100

^a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E, at 228 $^{\circ}$ C and $100x_{2}=3.5$ (author).

Note - The system was investigated at $0 \le 100x_2 \le 80$ due to thermal instability of the iso-butanoate.



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

Melts contained in a glass tube and stirred.

Temperatures measured with a Nichrome-Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of isotropicity in the melt on cooling.

SOURCE AND PURITY OF MATERIALS:

Component 1: prepared by reacting aqueous ("chemically pure") Na_2CO_3 with a slight excess of iso butanoic acid of analytical purity. The solvent and excess acid were removed by heating to $160\,^{\circ}\text{C}$.

Component 2: "chemically pure" material.

ESTIMATED ERROR:

Temperature: accuracy is probably ± 2 K (compiler).

- (1) Sodium iso.butanoate (sodium iso.butyrate); NaiC₄H₇O₂; [996-30-5]
- (2) Sodium octadecanoate (sodium stearate); NaC₁₈H₃₅O₂; [822-16-2]

EVALUATOR:

Ferloni, P., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

This system was studied only by Sokolov (Ref. 1) who employed the visual polythermal analysis to draw the lower boundary of the isotropic liquid field. From the shape of this boundary, he concluded that the intermediate compound $Na_5(i\cdot C_4H_7O_2)_2(C_{18}H_35O_2)_3$ [congruently melting at 596 K (323 °C)] was formed, and that the limits of the stability field of this compound were a eutectic at 435 K (162 °C) and $100x_2=25.5$, and a "perekhodnaya tochka" at 584 K (311 °C) and $100x_2=94.5$.

Component 2, however, forms liquid crystals. Thence, the fusion temperature by Sokolov, viz., $T_{fus}(2)$ = 581 K (308 °C), should be identified with the clearing temperature and compared with the $T_{c1r}(2)$ value reported in Preface, Table 4 (552.7 K). Conversely, Sokolov's $T_{fus}(1)$ [533 K (260 °C)] seems sufficiently reliable, being not far from the value (526.9±0.7 K) reported in Table 2 of the Preface.

In the evaluator's opinion, the phase diagram at $0 \le 100 \text{m}_2 \le 60$ is to be reconsidered, e.g., with reference to Preface, Scheme A.2: Sokolov's eutectic could be an M'_E point, whereas the maximum at 100m_2 = 60 could represent an azeotrope.

On the contrary, no definite interpretation of the phase diagram at high $100\mathbf{x}_2$ values seems possible. Indeed, it is not clear how Sokolov could argue the occurrence of an invariant (the "perekhodnaya tochka" at $100\mathbf{x}_2$ = 94.5) from the trend of his experimental data which does not unambiguously support any significant slope change of the curve in this region. Moreover, Sokolov's "fusion" temperature of component 2 (581 K) looks as fully unreliable, being 18 K higher than the second highest \mathbf{T}_{clr} value determined during the last 30 years (Ref. 2), and 28 K higher than the clearing temperature listed in Table 4 of the Preface.

- (1) Sokolov, N.M.
 Zh. Obshch. Khim. 1954, 24, 1581-1593.
- (2) Sanesi, M.; Cingolani, A.; Tonelli, P.L.; Franzosini, P. Thermal Properties, in Thermodynamic and Transport Properties of Organic Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors), Pergamon Press, Oxford, 1980, 29-115.

(1) Sodium iso.butanoate (sodium iso.butyrate);

 $Nai \cdot C_4 H_7 O_2$; [996-30-5]

(2) Sodium octadecanoate (sodium stearate); NaC₁₈H₃₅O₂; [822-16-2]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1581-1593.

VARIABLES:

Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

t/°C	T/K ^a	100 x 2	t/°C	T/K ^a	100 x 2
260	533	0	319	592	50
240	513	5	321	594	55
215	488	10	323	596	60
196	469	15	322	595	65
177	450	20	321	594	70
163	436	25	320	593	75
162	435	25.5	317	590	85
217	490	30	314	587	90
260	533	35	311	584	94.5
291	564	40	312	585	97.5
309	582	45	308	581	100

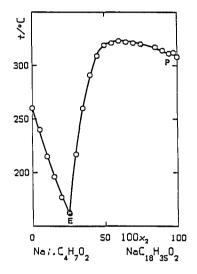
a T/K values calculated by the compiler.

Characteristic point(s): Eutectic, E, at 162 $^{\rm O}{\rm C}$ and $100{\rm x_2}$ = 25.5 (author).

Characteristic point, P ("perekhodnaya tochka" in the original text; see the Introduction), at 311 °C (author) and $100x_2 = 94.5$ (erroneously reported as 312 °C and $100x_2 = 97.5$ in the text, compiler).

Intermediate compound(s): $Na_5(1.C_4H_7O_2)_2(C_{18}H_{35}O_2)_3$, melting at 323 °C.

congruently



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

and Melts contained in a glass tube stirred.

Temperatures measured with a Nichrome-Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of isotropicity in the melt on cooling.

SOURCE AND PURITY OF MATERIALS:

Component 1: prepared by reacting aqueous ("chemically pure") Na₂CO₃ with a slight excess of iso butanoic acid of analytical purity. The solvent and excess acid were removed by heating to 160 °C. Component 2: "chemically pure" material.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

(1) Sodium iso.butanoate (sodium
iso.butyrate);

Nai-C₄H₇O₂; [996-30-5] (2) Sodium thiocyanate; NaCNS; [540-72-7]

ORIGINAL MEASUREMENTS:

Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1150-1156.

VARIABLES:

Temperature.

PREPARED BY:

D'Andrea, G.

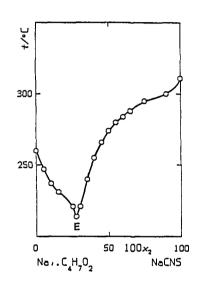
EXPERIMENTAL VALUES:

t/ºC	T/K ^a	100 x 2
260	533	0
247	520	5
237	510	10
231	504	15
221	494	25
214	487	27.4
221	494	30
240	513	35
255	528	40
266	539	45
274	547	50
280	553	55
284	557	60
288	561	65
295	568	75
300	573	90
311	584	100

a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E, at 214 $^{\rm O}{\rm C}$ (compiler; erroneously reported as 240 $^{\rm O}{\rm C}$ in table 3 of the original paper) and $100{\rm x_2}$ = 27.4 (author).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.
Salt(s) melted in a test tube. Temperature measured with a Nichrome-Constantane thermocouple and a millivoltmeter with mirror full scale 17 mV.

SOURCE AND PURITY OF MATERIALS:

Component 1 synthetized from iso.butanoic acid and NaHCO3.

Component 2 of analytical purity recrystallized once from water and once from ethanol.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

- (1) Sodium iso.butanoate (sodium iso.butyrate); Nai.C₄H₇O₂; [996-30-5]
- (2) Sodium nitrite; NaNO₂; [7632-00-0]

ORIGINAL MEASUREMENTS:

Sokolov, N.M. Zh. Obshch. Khim. 1957, 27, 840-844 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1957, 27, 917-920.

VARIABLES:

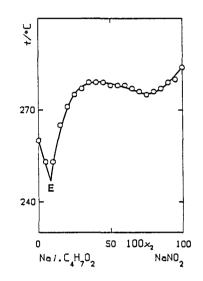
Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

EXPERIMENTAL	
T/K ^a	100 x 2
533	0
526	5
526	10
538	15
544	20
548	25
550	30
552	35
552	40
552	45
551	50
551	55
551	60
550	65
549	70
548	75
549	80
550	85
552	90
553	95
557	100
	T/K ^a 533 526 526 538 544 548 550 552 552 551 551 550 549 548 549 550 552 553



Characteristic point(s):

Eutectic, E, at 247 °C and $100x_2=8$ (author).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis; salt mixtures melted in a glass tube (surrounded by a wider tube) and stirred with a glass thread. The temperatures of initial crystallization were measured with a Nichrome-Constantane thermocouple checked at the fusion points of water, benzoic acid, mannitol, AgNO3, Cd, KNO3, and $\rm K_2Cr_2O_7$.

SOURCE AND PURITY OF MATERIALS:

Component 1: prepared from "chemically pure" sodium hydrogen carbonate (carbonate in the reference quoted; compiler) and commercial iso.butanoic acid distilled before use (Ref. 1); the salt recovered was recrystallized from n-butanol.

Component 2: "chemically pure" material recrystallized from water.

NOTE:

The author does not comment on the minimum at 548 K and $100x_2=75$. A possible explanation might be that liquid layering occurs: in this case, the points at $25 \le 100x_2 \le 75$ should represent liquid-liquid instead of solid-liquid equilibria, the monotectic temperature being 548 K. It is worth mentioning that stratification was reported by the same author in the same paper for the binary Na/i.C₅H₉O₂, NO₂.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

REFERENCES:

(1) Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1581-1593.

a T/K values calculated by the compiler.

- (1) Sodium iso.butanoate (sodium
 iso.butyrate);
- Nai.C₄H₇O₂; [996-30-5] (2) Sodium nitrate; NaNO₃; [7631-99-4]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1150-1156.

VARIABLES:

Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

t/ ^o C	T/K ^a	100 x 2
260	533	0
248	521	5
242	515	10
238	511	15
219	492	25
233	506	30
244	517	35
258	531	40
267	540	45
274	547	50
276	549	55
280	553	60
284	557	65
288	561	75
292	565	85
300	573	95
308	581	100

250 E 0 Na..C₄H₂O₂ NeNO₃

Characteristic point(s):

Eutectic, E, at 219 $^{\circ}$ C and $100x_{2}$ = 25 (author).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

Salt(s) melted in a test tube. Temperature measured with a Nichrome-Constantane thermocouple and a millivoltmeter with mirror reading to 17 mV.

SOURCE AND PURITY OF MATERIALS:

Component 1 synthetized from iso.butanoic acid and NaHCO3. Commercial component 2 further purified by the author according to Laiti.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

a T/K values calculated by the compiler.

COMPONENTS: (1) Sodium iso.butanoate (sodium iso.butyrate); Nai.C₄H₇O₂; [996-30-5] (2) Sodium nitrate; NaNO₃; [7631-99-4] VARIABLES: Temperature. ORIGINAL MEASUREMENTS: Dmitrevskaya, 0.I.; Sokolov, N.M. Zh. Obshch. Khim. 1960, 30, 20-25 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1960, 30, 19-24. PREPARED BY: Temperature. D'Andrea, G.

EXPERIMENTAL VALUES:

Characteristic point(s):

The paper reports - inter alia - on a refinement of the title binary, previously studied by one of the authors (Ref. 1). According to the present investigation, the coordinates of the eutectic are:

Eutectic, E, at 220 °C and $100x_2 = 25$ (authors).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

NOTE:

Concerning component 1, no mention is made in Table 2 of solid state phase transformations, although three transitions are quoted by the authors (from Ref. 3), at 493, 364, and 340 K (220, 91, and 67 °C), respectively. Duruz et al. (Ref. 4) report in turn $T_{trs}^{c}(1)=493$ K (in agreement with the highest transition temperature from Ref. 3), and $T_{trs}^{c}(1)=468$ K (a figure which has no correspondence in Ref. 3). Finally, Ferloni et al. (Ref. 5) are inclined to think that Sokolov's transformation at 340 K (Ref. 3) actually represents a transition of a hydrated form of the salt.

SOURCE AND PURITY OF MATERIALS:

Component 1 synthetized from iso.butanoic acid and Na₂CO₃ (Ref. 2). "Chemically pure" component 2 recrystallized.

Component 1 undergoes phase transitions at $t_{trs}(1)/^{\circ}C=$ 67, 91, 220 (Ref. 3).

Component 2 undergoes a phase transition at $t_{\rm trs}(2)/^{\rm C}$ = 270 (current literature).

ESTIMATED ERROR:

Temperature: accuracy probably ±2 K (compiler).

- (1) Sokolov, N.M.
- Zh. Obshch. Khim. 1954, 24, 1150-1156.
- (2) Sokolov, N.M.

 Zh. Obshch. Khim. 1954, 24, 1581-1593.
- (3) Sokolov, N.M.
 - Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
- (4) Duruz, J.J.; Michels, H.J.; Ubbelohde, A.R.
 Proc. Roy. Soc. London 1971, A 322,
- 281-299. (5) Ferloni, P.; Sanesi, M.; Tonelli, P.L.;
- Franzosini, P. Z. Naturforsch. 1978, A 33, 240-242.

- (1) Sodium pentanoate (sodium valerate); NaC₅H₉O₂; [6106-41-8]
 (2) Sodium thiocyanate;
- (2) Sodium thiocyanate; NaCNS; [540-72-7]

EVALUATOR:

Spinolo, G., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

This system was studied by Sokolov (Ref. 1) and by Sokolov and Khaitina (Ref. 2): in both papers the visual polythermal investigation was restricted to the lower boundary of the isotropic liquid field. The authors claimed the existence of a 1:1 intermediate compound which melts congruently at 564 K (291 $^{\rm O}$ C; Ref. 1), and forms eutectics with either pure component, at eutectics at 562 K (289 $^{\rm O}$ C) and $100{\rm m_2}$ = 46, and at 560 K (287 $^{\rm O}$ C) and $100{\rm m_2}$ = 56.5 or 55, respectively.

Component 1, however, forms liquid crystals, which are stable between 498±2 K and 631±4 K (Preface, Table 1). The latter value fairly agrees with the fusion temperature (630 K) given in Ref. 1 and 2; the former can be identified (even if not fully satisfactorily) with that (489 K) corresponding to the highest phase transformation temperature quoted by Ref. 2 from Ref. 3. Once more for component 1, Table 1 reports no solid state transition, whereas Sokolov and Khaitina quote (from Ref. 3) $T_{\rm trs}(2)/K=482$ and 453. It is, however, to be stressed that the single transition observed (at 479±1 K) with DTA in sodium n-pentanoate by Duruz et al. (Ref. 4) was not more mentioned in a subsequent DSC investigation by the same group (Ref. 5).

In the evaluator's opinion, therefore,

- i) the invariant at 562 K ($289 \text{ }^{\circ}\text{C}$) and $100\text{m}_{2}\text{=}$ 46 should be identified with an M'_E point, ii) a (so far undetected) M_E invariant should exist within the composition range between M'_E and pure component 1, and iii) the phase diagram ought to be similar to that shown in Scheme D.1 of the Preface,
- iil) the phase diagram ought to be similar to that shown in Scheme D.1 of the Preface, but for the fact that the liquid crystal-isotropic liquid diphasic field exhibits a maximum.

- (1) Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1150-1156.
- (2) Sokolov, N.M.; Khaitina, M.V. Zh. Obshch. Khim. 1972, 42, 2121-2123.
- (3) Sokolov, N.M.
 Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
- (4) Duruz, J.J.; Michels, H.J.; Ubbelohde, A.R. Proc. Roy. Soc. London 1971, A322, 281-299.
- (5) Michels, H.J.; Ubbelohde, A.R. JCS Perkin II 1972, 1879-1881.

- (1) Sodium pentanoate (sodium valerate); NaC₅H₉O₂; [6106-41-8]
- (2) Sodium thiocyanate; NaCNS; [540-72-7]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1150-1156.

VARIABLES:

Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

t/ºC	T/K ^a	100 x 2	t/ ^o C	T/K ^a	100 x 2
357	630	0	289	562	46
370	643	5	291	564	50
378	651	10	288	561	55
375	648	15	287	560	56.5
356	629	25	290	563	60
344	617	30	293	566	65
331	604	35	297	570	75
316	589	40	302	575	90
296	569	45	311	584	100

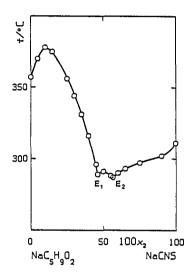
a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E_1 , at 289 °C and $100x_2$ = 46 (author). Eutectic, E_2 , at 287 °C and $100x_2$ = 56.5 (author).

Intermediate compound(s):

 ${\rm Na_2C_5H_9O_2CNS}$, congruently melting at 291 $^{\rm OC}$ (author).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.
Salt(s) melted in a test tube. Temperature measured with a Nichrome-Constantane

measured with a Nichrome-Constantane thermocouple and a millivoltmeter with mirror reading to 17 mV.

SOURCE AND PURITY OF MATERIALS:

Component 1 synthetized from n-pentanoic acid and NaHCO3. Component 2 of analytical purity recrystallized once from water and once from ethanol.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

305 COMPONENTS: ORIGINAL MEASUREMENTS: Sokolov, N.M.; Khaitina, M.V. Sodium pentanoate (sodium valerate); $NaC_5H_9O_2$; [6106-41-8] Zh. Obshch. Khim. 1972, 42, 2121-2123. (2) Sodium Thiocyanate; NaCNS; [540-72-7] VARIABLES: PREPARED BY: Temperature. D'Andrea, G. **EXPERIMENTAL VALUES:** Characteristic point(s): Eutectic, E_1 , at 289 $^{\rm o}{\rm C}$ and $100{\rm m}_2$ about 46 (estimated by the compiler from Fig. 1 of the original paper). Eutectic, E_2 , at 287 °C and $100x_2$ about 55 (estimated by the compiler from Fig. 1 of the original paper). Intermediate compound(s): Na₂C₅H₉O₂CNS, congruently melting. AUXILIARY INFORMATION METHOD/APPARATUS/PROCEDURE: SOURCE AND PURITY OF MATERIALS: Visual polythermal analysis. Not stated. Component 1 undergoes phase transitions at $t_{\rm trs}(1)^{\rm O}$ C= 180, 209, 216 (Ref. 1) and melts at $t_{\rm fus}(1)^{\rm O}$ C= 356. Component 2 melts at $t_{\rm fus}(2)^{\rm O}$ C= 311. ESTIMATED ERROR:

Temperature: +2 K accuracy probably (compiler).

REFERENCES:

(1) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

- (1) Sodium pentanoate (sodium valerate);
- NaC₅H₉O₂; [6106-41-8] (2) Sodium nitrite; NaNO₂; [7632-00-0]

EVALUATOR:

Ferloni, P., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

This binary was studied only by Sokolov (Ref. 1) who, on the basis of his visual polythermal observations, claimed the phase diagram to be of the eutectic type, the invariant occurring at 555 K (282 °C) and $100\mathbf{x}_1$ = 0.04. This investigation was restricted to the range $0 \le 100\mathbf{x}_1 \le 55$, because of decomposition of mixtures richer in component 1.

Component 1, however, forms liquid crystals. Thence, Sokolov's $T_{fus}(1)$ [i.e., 610 K (357°C)] should be identified with a clearing temperature, and compared with the value $T_{clr}(1) = 631\pm4$ K reported in Preface, Table 1.

The topology of the phase diagram has therefore to be reconsidered with reference to Preface, Schemes A, among which, however, the available data, unfortunately, do not allow one to make a definite choice.

Anyway, Sokolov's invariant should be an M'R point and not a conventional eutectic.

REFERENCES:

(1) Sokolov, N.M. Zh. Obshch. Khim. 1957, 27, 840-844 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1957, 27, 917-920.

- (1) Sodium pentanoate (sodium valerate); NaC₅H₉O₂; [6106-41-8]
- (2) Sodíum nitrite; NaNO₂; [7632-00-0]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1957, 27, 840-844 (*);
Russ. J. Gen. Chem. (Engl. Transl.) 1957,

27, 917-920.

VARIABLES:

Temperature.

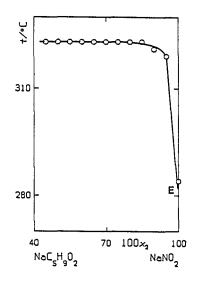
PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

a T/K values calculated by the compiler.

Note - The system was investigated at $0 \le 100x_1 \le 55$ since further increase in component $\overline{1}$ content causes decomposition of the mixtures.



Characteristic point(s):

Eutectic, E, at 282 °C and $100 \text{m}_1 = 0.04$ (both figures, listed in table 2 of the original paper, cannot be drawn from the tabulated data; moreover, in the same table the eutectic composition is erroneously reported as $100 \text{m}_2 = 0.04$; compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis; salt mixtures melted in a glass tube (surrounded by a wider tube) and stirred with a glass thread. The temperatures of initial crystallization were measured with a Nichrome-Constantane thermocouple checked at the fusion points of water, benzoic acid, mannitol, ${\rm AgNO_3}, {\rm Cd}, {\rm KNO_3}, {\rm and} {\rm K_2Cr_2O_7}.$

SOURCE AND PURITY OF MATERIALS:

Component 1: prepared from "chemically pure" sodium hydrogen carbonate (carbonate in the reference quoted; compiler) and commercial pentanoic acid distilled before use (Ref. 1); the salt recovered was recrystallized from n-butanol; $\mathbf{t_{fus}}(1)/^{\circ}\mathbf{C}=357$.

Component 2: "chemically pure" material recrystallized from water.

ESTIMATED ERROR:

Temperature: accuracy probably ± 2 K (compiler).

REFERENCES:

(1) Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1581-1593.

- (1) Sodium pentanoate (sodium valerate); NaC₅H₉O₂; [6106-41-8]
- (2) Sodium nitrate; NaNO₃; [7631-99-4]

EVALUATOR:

Spinolo, G., Dipartimento di Chimica Fisica, Universita' di Pavia (ITALY).

CRITICAL EVALUATION:

This system was studied by Sokolov (Ref. 1), and by Sokolov and Khaitina (Ref. 2). In both cases, the visual polythermal analysis was employed to detect the lower boundary of the isotropic liquid field. Accordingly, the authors claimed that a 1:1 intermediate compound forms, which melts congruently at 568 K (295 $^{\circ}$ C), and gives eutectics with either component. Concerning the precise location of these invariants, some values given in the text of the original papers should be corrected with a closer inspection of the pertinent figures. The correct values seem therefore to be T= 564 K (291 $^{\circ}$ C) and $100x_2$ = 40.5 (Ref. 2), and T= 554 K (281 $^{\circ}$ C) and $100x_2$ = 58.5, respectively.

Component 1, however, forms liquid crystals, which are stable between 498 ± 2 K and 631 ± 4 K (Preface, Table 1). The latter value fairly agrees with the fusion temperature $(63\overline{0}$ K) given in Ref. 1 and 2; the former can be identified (even if not fully satisfactorily) with that (489 K) corresponding to the highest phase transformation temperature quoted by Ref. 3. Once more for component 1, Table 1 reports no solid state transition, whereas Sokolov quotes (Ref. 3) $T_{\rm trs}(1)/{\rm K}$ 482 and 453. It is, however, to be stressed that the single transition observed (at 479 ± 1 K) with DTA in sodium nepentanoate by Duruz et al. (Ref. 4) was no more mentioned in a subsequent DSC investigation by the same group (Ref. 5).

Taking into account the above remaks, the eutectic at $564 \text{ K } (291^{\circ}\text{C})$ and $100\text{m}_{2}\text{=}40.4$ ought to be an M^{*}_E point, and the occurrence of a further invariant (so far undetected and probably an M^{*}_E point) is to be expected. The phase diagram could be similar to that shown in Scheme D.1 of the Preface, but for the fact that the liquid crystal-isotropic liquid field is splitted into two parts by a maximum.

- (1) Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1150-1156
- (2) Sokolov, N.M.; Khaitina, M.V. Zh. Obshch. Khim. 1972, 42, 2121-2123
- (3) Sokolov, N.M.
 Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.
- (4) Duruz, J.J.; Michels, H.J.; Ubbelohde, A.R. Proc. Roy. Soc. London 1971, A322, 281-299.
- (5) Michels, H.J.; Ubbelohde, A.R. JCS Perkin II 1972, 1879-1881.

- (1) Sodium pentanoate (sodium valerate); NaC₅H₉O₂; [6106-41-8]
- (2) Sodium nitrate; NaNO₃; [7631-99-4]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1150-1156.

VARIABLES:

PREPARED BY:

Temperature.

D'Andrea, G.

EXPERIMENTAL VALUES:

t/°C	T/K ^a	100 x 2	t/°C	T/Kª	100 x 2
357 366 372 369 350 336 320 296 291 ^b	630 639 645 642 623 609 593 569	0 5 10 15 25 30 35 40 40.5	295 288 281 ^c 285 293 298 300 305 308	568 561 554 558 566 571 573 578 581	50 55 58.5 60 65 75 85 95
294	567	45			

a T/K values calculated by the compiler.
b 295 in the original table, corrected by
the compiler on the basis of Fig. 2 of the
original paper.

original paper.

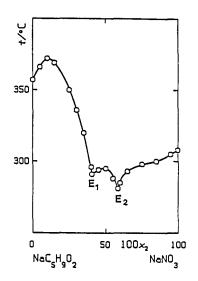
C 291 in the original table, corrected by the compiler on the basis of Fig. 2 of the original paper.

Characteristic point(s):

Eutectic, E₁, at 291 $^{\rm o}$ C and 100x₂= 40.5 (author). Eutectic, E₂, at 281 $^{\rm o}$ C and 100x₂= 58.5 (author).

Intermediate compound(s):

Na₂C₅H₉O₂NO₃, congruently melting at 295 °C (compiler).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

Salt(s) melted in a test tube. Temperature measured with a Nichrome-Constantane thermocouple and a millivoltmeter with mirror reading to 17 mV.

SOURCE AND PURITY OF MATERIALS:

Component 1 synthetized from n-pentanoic acid and NaHCO3. Commercial component 2 further purified by the author according to Laiti.

ESTIMATED ERROR:

Temperature: accuracy probably ± 2 K (compiler).

COMPONENTS: ORIGINAL MEASUREMENTS: (1) Sodium pentanoate (sodium valerate); Sokolov, N.M.; Khaitina, M.V. NaC₅H₉O₂; [6106-41-8] (2) Sodium nitrate; Zh. Obshch. Khim. 1972, 42, 2121-2123. NaNO₃; [7631-99-4] **VARIABLES:** PREPARED BY: D'Andrea, G. Temperature. **EXPERIMENTAL VALUES:** Characteristic point(s): Eutectic, E1, at 291 °C and 100x2 about 40.5 (estimated by the compiler from Fig. 1 of the original paper). Eutectic, E₂, at 281 $^{\rm oC}$ and $100{\bf x}_2$ about 58.5 (estimated by the compiler from Fig. 1 of the original paper). Intermediate compound(s): Na₂C₅H₉O₂NO₃, congruently melting. AUXILIARY INFORMATION METHOD/APPARATUS/PROCEDURE: SOURCE AND PURITY OF MATERIALS: Not stated. Visual polythermal analysis. Not stated. Component 1 undergoes phase transitions at $t_{\rm trs}(1)/^{\rm O}{\rm c}$ = 180, 209, 216 (Ref. 1) and melts at $t_{\rm fus}(1)/^{\rm O}{\rm c}$ = 356. Component 2 undergoes a phase transition at $t_{\rm trs}(2)/^{\rm O}{\rm c}$ = 275 (current literature value), and melts at $t_{\rm fus}(2)/^{\rm O}{\rm c}$ = 308. ESTIMATED ERROR: Temperature: accuracy probably <u>+</u>2 K (compiler). REFERENCES:

(1) Sokolov, N.M.

Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

- (1) Sodium iso.pentanoate (sodium iso.valerate);
 Nai.C₅H₉O₂; [539-66-2]
- (2) Sodium hexanoate (sodium caproate); NaC₆H₁₁O₂; [10051-44-2]

EVALUATOR:

Ferloni, P., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

This system was studied only by Sokolov (Ref. 1), who claimed that a continuous series of solid solutions is formed, with a minimum, m, at 512 K (239 $^{\circ}$ C), and 100 x_2 = 20.

Both components, however, form liquid crystals (see Preface, Tables 2, 1). Therefore, Sokolov's fusion temperatures, $T_{\rm fus}(1)/K^-$ 535 (262 °C) and $T_{\rm fus}(2)/K^-$ 638 (365 °C), should be identified with clearing temperatures, the corresponding data from Tables 2 and 1 being 559+1 K and 639.0+0.5 K, respectively.

Concerning component 1, the remarkable discrepancy might be attributed to insufficient purity of Sokolov's sample, inasmuch as the value from Table 2 (559+1) meets rather satisfactorily those reported by Ubbelohde et al. (556 K; Ref. 2), and by Duruz et al. (553 K; Ref. 3). Indeed, due to the - usually small - value of the enthalpy change associated with clearing, very small amounts of impurities are often sufficient to cause a dramatic drop of the clearing temperature.

A continuous series of liquid crystal (instead of solid) solutions should form, and the complete phase diagram should be similar to that shown in Scheme C.1 of the Preface, with a common minimum of the curves limiting the isotropic liquid - liquid crystal diphasic field.

- (1) Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1581-1593.
- (2) Ubbelohde, A.R.; Michels, H.J.; Duruz, J.J. Nature 1970, 228, 50-52.
- (3) Duruz, J.J.; Michels, H.J.; Ubbelohde, A.R. Proc. R. Soc. London 1971, A322, 281-299.

- (1) Sodium iso.pentanoate (sodium iso.valerate);
- Nai.C₅H₉O₂; [539-66-2] (2) Sodium hexanoate (sodium caproate); NaC₆H₁₁O₂; [10051-44-2]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1581-1593.

VARIABLES:

Temperature.

PREPARED BY:

D'Andrea, G.

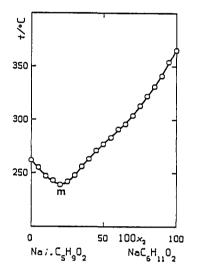
EXPERIMENTAL VALUES:

t/°C	T/K ^a	100 x 2	t/ ^o C	T/K ^a	100 x 2
262	535	0	283	556	55
255	528	5	291	564	60
247	520	10	296	569	65
243	516	15	304	577	70
239	512	20	313	586	75
242	515	25	322	595	80
248	521	30	331	604	85
256	529	35	341	614	90
263	536	40	354	627	95
271	544	45	365	638	100
277	550	50			

a T/K values calculated by the compiler.

Characteristic point(s):

Continuous series of solid solutions with a minimum, m, at 239 $^{\circ}$ C and $100x_2=20$ (author).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

Melts contained in a glass tube and stirred.

Temperatures measured with a Nichrome-Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of isotropicity in the melt on cooling.

SOURCE AND PURITY OF MATERIALS:

Materials prepared by reacting aqueous ("chemically pure") Na_2CO_3 with a slight excess of either iso.pentanoic or n-hexanoic acid of analytical purity. The solvent and excess acid were removed by heating to $160~^{\circ}C$.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

(1) Sodium iso.pentanoate (sodium
iso.valerate);

Nai.C₅H₉O₂; [539-66-2] (2) Sodium benzoate; NaC₇H₅O₂; [532-32-1]

EVALUATOR:

Spinolo, G., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

This binary was studied only by Sokolov (Ref. 1), who restricted his polythermal analysis to the lower boundary of the isotropic liquid field, and claimed the existence of a eutectic at 534 K (261 $^{\circ}$ C) and 100 x_2 = 3.

Component 1, however, forms liquid crystals [at $T_{fus}(1)$ = 461.5±0.6 K; Preface, Table 2] before being transformed in a clear melt. Therefore, Sokolov's fusion temperature, (535 K) should be identified with the clearing temperature, the corresponding value from Table 2 being 559±1 K. The latter figure is remarkably higher than that given by Ref. 1, and it agrees rather satisfactorily with those reported by Ubbelohde et al. (556 K, Ref. 2) and by Duruz et al. (553 K, Ref. 3).

Thus, in the evaluator's opinion, the phase diagram could be more correctly interpreted with reference to Scheme A.1 of the Preface, and Sokolov's eutectic should be identified with an $M_{\rm F}$ point.

- (1) Sokolov, N.M.
 Zh. Obshch. Khim. 1954, 24, 1581-1593.
- (2) Ubbelohde, A.R., Michels, H.J., and Duruz, J.J. Nature 1970, 228, 50-52.
- (3) Duruz, J.J., Michels, H.J., and Ubbelohde, A.R. Proc. R. Soc. London 1971, A322, 281-299.

- (1) Sodium iso.pentanoate (sodium iso.valerate); $Nai \cdot C_5 H_9 O_2$; [539-66-2]
- (2) Sodium benzoate; $NaC_7H_5O_2$; [532-32-1]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1581-1593.

VARIABLES:

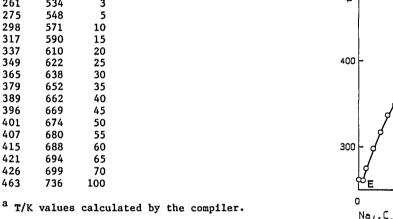
Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

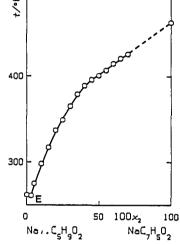
t/°C	T/K ^a	100 x 2
262	535	0
261	534	3
275	548	5
298	571	10
317	590	15
337	610	20
349	622	25
365	638	30
379	652	35
389	662	40
396	669	45
401	674	50
407	680	55
415	688	60
421	694	65
426	699	70
463	736	100



Characteristic point(s):

Eutectic, E, at 261 °C and $100x_2 = 3$ (author).

- The system was investigated at $0 < 100x_2 < 70$ due to thermal instability of the iso pentanoate.



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

Melts contained in a glass tube and stirred.

Temperatures measured with a Nichrome-Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of isotropicity in the melt on cooling.

SOURCE AND PURITY OF MATERIALS:

Component 1: prepared by reacting aqueous ("chemically pure") Na₂CO₃ with a slight excess of iso.pentanoic acid of analytical purity. The solvent and excess acid were removed by heating to 160 $^{\rm o}{\rm C}$. Component 2: "chemically pure" material.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

- (1) Sodium iso.pentanoate (sodium iso.valerate); Nai.C₅H₉O₂; [539-66-2]
- Nai.C₅H₉O₂; [539-66-2] (2) Sodium octadecanoate (sodium stearate); NaC₁₈H₃₅O₂; [822-16-2]

EVALUATOR:

Ferloni, P., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

This system was studied only by Sokolov (Ref. 1) who employed the visual polythermal analysis to draw the lower boundary of the isotropic liquid field. From the shape of this boundary, he concluded that the intermediate compound ${\rm Na_3(i.C_5H_9O_2)(C_{18}H_{35}O_2)_2}$ [congruently melting at 596 K (323 °C)] was formed, and that the limits of the stability field of this compound were a eutectic at 413 K (140 °C) and $100\mathbf{x_2}$ = 17.3, and a "perekhodnaya tochka" at 582 K (309 °C) and $100\mathbf{x_2}$ = 93.5.

Actually, both components form liquid crystals, the liquid crystalline phases being one for component 1 (see Preface, Table 2), and two for component 2 (see Preface, Table 4). Therefore, Sokolov's fusion temperatures, $T_{\rm fus}(1)=535~{\rm K}$ (262 $^{\rm O}$ C), and $T_{\rm fus}(2)=581~{\rm K}$ (308 $^{\rm O}$ C), should be identified with clearing temperatures, the corresponding values from Tables 2 and 4 being 559±1 and 552.7 K, respectively.

At intermediate compositions it seems reasonable to assume that a continuous series of liquid crystal solutions is formed, with an azeotrope at 596 K and 100m_2 = 70. Accordingly, the left hand section ($0 \le 100 \text{m}_2 \le 70$) of the phase diagram might be interpreted with reference to Scheme C. $\overline{2}$ of the Preface: in this case, Sokolov's eutectic should be intended as an M"E point, allowance being made for the fact that Sokolov's "fusion" temperature of component 1 is 24 K lower than the relevant T_{clr} value listed in Table 2, i.e., 559 ± 1 K. It is, however, to be stressed that the latter figure agrees rather satisfactorily with those reported by Ubbelohde et al. (556 K; Ref. 3) and by Duruz et al. (553 K; Ref. 4).

Conversely, no definite interpretation of the phase diagram at high $100\mathbf{x}_2$ values seems possible. Indeed, it is not clear how Sokolov could argue the occurrence of an invariant (the "perekhodnaya tochka" at $100\mathbf{x}_2$ = 93.5) from the trend of his experimental data which does not unambiguously support any significant slope change of the curve in this region. Moreover, Sokolov's "fusion" temperature of component 2 (581 K) looks as fully unreliable, being 18 K higher than the second highest \mathbf{T}_{clr} value determined during the last 30 years (Ref. 2), and 28 K higher than the clearing temperature listed in Table 4.

- (1) Sokolov, N.M. Zh. Obshch. Khim. 1954, 24, 1581-1593.
- (2) Sanesi, M.; Cingolani, A.; Tonelli, P.L.; Franzosini, P. Thermal Properties, in Thermodynamic and Transport Properties of Organic Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors), Pergamon Press, Oxford, 1980, 29-115.
- (3) Ubbelohde, A.R.; Michels, H.J.; Duruz, J.J. Nature 1970,228, 50-52.
- (4) Duruz, J.J.; Michels, H.J.; Ubbelohde, A.R. Proc. R. Soc. London 1971, A 322, 281-299.

- (1) Sodium iso.pentanoate (sodium iso.valerate);
 - Nai.C₅H₉O₂; [539-66-2]
- (2) Sodium ocradecanoate (sodium stearate); NaC₁₈H₃₅O₂; [822-16-2]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1581-1593.

VARIABLES:

Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

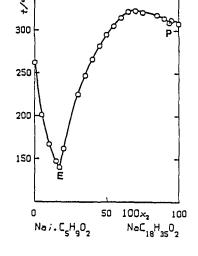
t/°C	T/Kª	100x ₂	t/°C	T/Kª	100 x 2
262	535	0	305	578	55
201	474	5	315	588	60
167	440	10	322	595	65
147	420	15	323	596	70
140	413	17.3	321	594	75
162	435	20	318	591	85
225	498	30	314	587	90
247	520	35	309	582	93.5
266	539	40	312	585	95
282	555	45	308	581	100
295	568	50			

a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E, at 140 $^{\rm o}{\rm C}$ and $100{\rm m_2}$ = 17.3 (author).

Characteristic point, P ("perekhodnaya tochka" in the original text; see the Introduction), at 309 °C (author) and $100x_2$ = 93.5 (erroneously reported as 92 in the text, compiler).



Intermediate compound(s):

 $\text{Na}_3\text{i.C}_5\text{H}_9\text{O}_2(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$, congruently melting at 323 °C (compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

Melts contained in a glass tube and stirred.

Temperatures measured with a Nichrome-Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of isotropicity in the melt on cooling.

SOURCE AND PURITY OF MATERIALS:

Component 1: prepared by reacting aqueous ("chemically pure") Na₂CO₃ with a slight excess of **iso**-pentanoic acid of analytical purity. The solvent and excess acid were removed by heating to 160 °C.

Component 2: "chemically pure" material.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

(1) Sodium iso.pentanoate (sodium iso.valerate); Nai.C₅H₉O₂; [539-66-2] (2) Sodium thiocyanate;

NaCNS; [540-72-7]

EVALUATOR:

Spinolo, G., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

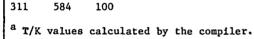
This binary was studied only by Sokolov (Ref. 1), who restricted his polythermal investigation to the lower boundary of the isotropic liquid field, and claimed the existence of a cutectic at 523 K (250 $^{\circ}$ C) and $100x_{2}$ = 32.

Component 1, however, forms liquid crystals [at $T_{fus}(1)$ = 461.5±0.6 K; Preface, Table 2] before turning into a clear melt. Sokolov's fusion temperature (535 K) consequently should be identified with the clearing temperature, the corresponding value from Table 2 being 559+1 K. The latter figure is remarkably higher that that given by Ref. 1, altough meeting rather satisfactorily those reported by Ubbelohde et al. (556 K, Ref. 2) and by Duruz et al. (553 K, Ref. 3).

Therefore, in the evaluator's opinion, the phase diagram could be more correctly interpreted with reference to Scheme A.2. of the Preface. Accordingly, Sokolov's eutectic should be identified with an M'R point.

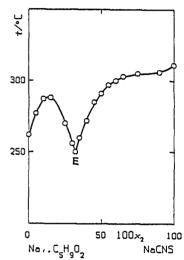
- (1) Sokolov, N.M.
 - Zh. Obshch. Khim. 1954, 24, 1150-1156.
- (2) Ubbelohde, A.R., Michels, H.J., and Duruz, J.J. Nature 1970, 228, 50-52.
- (3) Duruz, J.J., Michels, H.J., and Ubbelohde, A.R. Proc. R. Soc. London 1971, A322, 281-299.

Systems with Common Cation COMPONENTS: ORIGINAL MEASUREMENTS: (1) Sodium iso.pentanoate (sodium Sokolov, N.M. iso.valerate); Zh. Obshch. Khim. 1954, 24, 1150-1156. Nai-C₅H₉O₂; [539-66-2] (2) Sodium thiocyanate; NaCNS; [540-72-7] VARIABLES: PREPARED BY: Temperature. D'Andrea, G. **EXPERIMENTAL VALUES:** t/°C T/Ka 100x2



Characteristic point(s):

Eutectic, E, at 250 $^{\circ}$ C and $100x_{2}$ = 32 (author).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.
Salt(s) melted in a test tube. Temperature measured with a Nichrome-Constantane thermocouple and a millivoltmeter with mirror reading to 17 mV.

SOURCE AND PURITY OF MATERIALS:

Component 1 synthetized from iso.pentanoic acid and NaHCO3.

Component 2 of analytical purity recrystallized once from water and once from ethanol.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

(1) Sodium iso.pentanoate (sodium iso.valerate);
Nai.C₅H₉O₂; [539-66-2]

(2) Sodium nitrite; NaNO₂; [7632-00-0]

EVALUATOR:

Spinolo, G., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

This binary was studied only by Sokolov (Ref. 1), who restricted his polythermal investigation to the lower boundary of the isotropic liquid field, and claimed the existence of a eutectic at 542 K (269 $^{\circ}$ C) and $100x_2$ = 21.

Component 1, however, forms liquid crystals [at $\mathbf{T}_{\text{fus}}(1)$ = 461.5+0.6 K; Preface, Table 2] before turning into a clear melt. Sokolov's fusion temperature (535 K) consequently should be identified with the clearing temperature, the corresponding value from Table 2 being 559+1 K. The latter figure is remarkably higher that that given by Ref. 1, although meeting rather satisfactorily those reported by Ubbelohde et al. (556 K, Ref. 2) and by Duruz et al. (553 K, Ref. 3).

Allowance being made for the fact that a liquid-liquid miscibility gap impinges on the liquidus branch richer in the higher melting component (NaNO₂), the phase diagram could be more correctly interpreted with reference to Scheme A.2 of the Preface, and Sokolov's eutectic ought to be identified with an M'_E point.

- (1) Sokolov, N.M.
 Zh. Obshch. Khim. 1957, 27, 840-844 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1957, 27, 917-920.
- (2) Ubbelohde, A.R., Michels, H.J., and Duruz, J.J. Nature 1970, 228, 50-52.
- (3) Duruz, J.J., Michels, H.J., and Ubbelohde, A.R. Proc. R. Soc. London 1971, A322, 281-299.

(1) Sodium iso.pentanoate (sodium
iso.valerate);

Nai.C₅H₉O₂; [539-66-2] (2) Sodium nitrite;

2) Sodium nitrite; NaNO₂; [7632-00-0]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1957, 27, 840-844 (*);
Russ. J. Gen. Chem. (Engl. Transl.) 1957,
27, 917-920.

VARIABLES:

Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

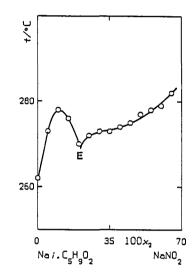
t/ ^o C	T/K ^a	100x ₂
262	535	0
273	546	5
278	551	10
276	549	15
270	543	20
272	545	25
273	546	30
273	546	35
274	547	40
275	548	45
277	550	50
278	551	55
279	552	60
282	555	65

a T/K values calculated by the compiler.

Note - Liquid layering occurs at $66 \le 100x_2 \le 98.4$ (author).

Characteristic point(s):

Eutectic, E, at 269 $^{\circ}$ C and $100x_{2}$ = 21 (author).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis; salt mixtures melted in a glass tube (surrounded by a wider tube) and stirred with a glass stirrer. The temperatures of initial crystallization were measured with a Nichrome-Constantane thermocouple checked at the fusion points of water, benzoic acid, mannitol, AgNO $_3$, Cd, KNO $_3$, and K $_2$ Cr $_2$ O $_7$.

SOURCE AND PURITY OF MATERIALS:

Component 1: prepared from "chemically pure" sodium hydrogen carbonate (carbonate in the reference quoted by the author; compiler), and commercial iso.pentanoic acid distilled before use (Ref. 1); the recovered salt was recrystallized from n-butanol.

Component 2: "chemically pure" material recrystallized from water; $t_{\rm fus}(2)/{}^{\rm C}$ = 284.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

REFERENCES:

(1) Sokolov, N.M.
Zh. Obshch. Khim. 1954, 24, 1581-1593.

- (1) Sodium iso-pentanoate (sodium iso-valerate) Nai-C₅H₉O₂; [539-66-2]
- (2) Sodium nitrate; NaNO₃; [7631-99-4]

EVALUATOR:

Ferloni, P., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

This binary was studied by visual polythermal and thermographical analysis by Sokolov (Ref. 1), and Dmitrevkaya and Sokolov (Ref. 2), respectively, with substantially analogous results. The phase diagram was claimed by these authors to be of the eutectic type with the invariant at either 527 K (254 $^{\circ}$ C) and $100x_1=31$ (Ref. 1), or 526 K (253 $^{\circ}$ C) and $100x_1=31.5$ (Ref. 2).

Component 1, however, forms liquid crystals. Consequently, the fusion temperature, $T_{fus}(1)=535 \text{ K } (262^{\circ}\text{C}; \text{ Ref.s 1, 2})$ should be identified with the clearing temperature, the corresponding value from Table 2 of the Preface being $559\pm1 \text{ K}$. The latter figure is remarkably higher than that by the above mentioned investigators, and agrees rather satisfactorily with those reported by Ubbelohde et al. (556 K; Ref. 3) and by Duruz et al. (553 K; Ref. 4).

For the same component: (1) the transition at 451 K (178 $^{\rm O}$ C) quoted in Ref. 2 from Ref. 5 should be identified with the actual fusion temperature, the corresponding value from Table 2 being 461.5+0.6 K, whereas (11) the transition at 425 K (152 $^{\rm O}$ C) also quoted in Ref. 2 from Ref. 5 has no correspondence in Table 2.

Thus the whole phase diagram should be re-interpreted, e.g., with reference to Scheme A.2 of the Preface. In particular, the invariant at 526 K and $100x_1$ = 31.5 should be an M_E^r point and not a conventional eutectic.

- (1) Sokolov, N.M.
 Zh. Obshch. Khim. 1954, 24, 1150-1156.
- (2) Dmitrevskaya, O.I.; Sokolov, N.M. Zh. Obshch. Khim. 1967, 37, 2160-2166 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1967, 37, 2050-2054.
- (3) Ubbelohde, A.R., Michels, H.J., and Duruz, J.J. Nature 1970, 228, 50-52.
- (4) Duruz, J.J., Michels, H.J., and Ubbelohde, A.R. Proc. R. Soc. London 1971, A322, 281-299.
- (5) Sokolov, N.M. Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

(1) Sodium iso.pentanoate (sodium
iso.valerate);

iso.valerate); Nai.C₅H₉O₂; [539-66-2]

(2) Sodium nitrate; NaNO₃; [7631-99-4]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1150-1156.

VARIABLES:

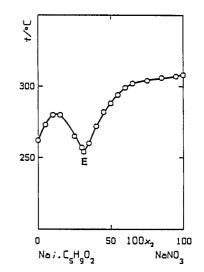
Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

t/°C	T/K ^a	100 x 2
262	535	0
273	546	5
280	553	10
280	553	15
265	538	25
257	530	30
254	527	31.2
260	533	35
272	545	40
282	555	45
288	561	50
294	567	55
299	572	60
302	575	65
304	577	75
306	579	85
307	580	95
308	581	100



Characteristic point(s):

Eutectic, E, at 254 $^{\rm o}$ C and $100{\rm m}_2$ = 31 (author).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.
Salt(s) melted in a test tube. Temperature measured with a Nichrome-Constantane thermocouple and a millivoltmeter with mirror reading to 17 mV.

SOURCE AND PURITY OF MATERIALS:

Component 1 synthetized from iso.pentanoic acid and NaHCO3.

Commercial component 2 further purified by the author according to Laiti.

ESTIMATED ERROR:

Temperature: accuracy probably ± 2 K (compiler).

^a T/K values calculated by the compiler.

- (1) Sodium iso.pentanoate (sodium iso.valerate); Nai.C₅H₉O₂; [539-66-2] (2) Sodium nitrate;
- NaNO₃; [7631-99-4]

ORIGINAL MEASUREMENTS:

Dmitrevskaya, O.I.; Sokolov, N.M. Zh. Obshch. Khim. 1967, 37, 2160-2166 (*); Russ. J. Gen. Chem. (Engl. Transl.) 1967, 37, 2050-2054.

VARIABLES:

Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

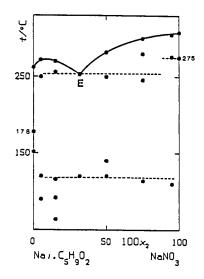
t/ ^o C	T/K ^a	100 x 2	t/ ^o C	T/K ^a	100 x 2
262	535	0	120 ^b	393	31.5
178 ^b	451	0	282	555	50
152 ^b	425	0	250 ^C	523	50
272	545	5	140 ^b	413	50
250 ^c	523	5	120 ^b	393	50
120 ^b	393	5	300	573	75
90b	363	5	246°	519	75
270	543	15	280 ^b	553	75
256 ^C	529	15	114 ^b	387	75
64 ^b	337	15	305	578	95
116 ^b	389	15	276 ^b	549	95
92 ^b	365	15	110 ^b	383	95
253	526	31.5	308	581	100
253 ^c	526	31.5	275 ^b	548	100

a T/K values calculated by the compiler.

Characteristic point(s):

Note - The present thermographical data supplement the previous visual polythermal investigation by Sokolov (Ref. 1).

Eutectic, E, at 253 $^{\circ}$ C and $100x_2=31.5$.



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Thermographical analysis (heating curves recorded automatically).

SOURCE AND PURITY OF MATERIALS:

Component 1: synthetized from iso.pentanoic acid and the carbonate (Ref. 2). Component 2: "chemically pure" material recrystallized.

Component 1 undergoes phase transitions at $t_{\rm trs}(1)/{}^{\rm OC}=$ 152, 178 (Ref. 3). Component 2 undergoes a phase transition at t_{trs}(2)/°C= 275 (current literature).

ESTIMATED ERROR:

+2 K Temperature: accuracy probably (compiler).

- (1) Sokolov, N.M.
 - Zh. Obshch. Khim. 1954, 24, 1150-1156.
- (2) Sokolov, N.M.
 - Zh. Obshch. Khim. 1954, 24, 1581-1593.
- (3) Sokolov, N.M.
 - Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.

b Transformation in the solid state.

^c Eutectic temperature.

- (1) Sodium hexanoate (sodium caproate); $NaC_6H_{11}O_2$; [10051-44-2]
- (2) Sodium benzoate; NaC₇H₅O₂; [532-32-1]

EVALUATOR:

Spinolo, G., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

This binary was studied only by Sokolov (Ref. 1), who restricted his polythermal investigation to the lower boundary of the isotropic liquid field, and claimed the existence of a "perekhodnaya tochka" (P) at $644 \text{ K } (371 \text{ }^{\text{O}}\text{C})$ and $100x_2 = 13$.

Component 1, however, forms liquid crystals [above T_{fus}(1)= 499.6+0.6 K; Table 1 of the Preface] before turning into a clear melt. Sokolov's fusion temperature (638 K) should be consequently identified with the clearing temperature, the corresponding value from Table 1 being 639.0+0.5 K.

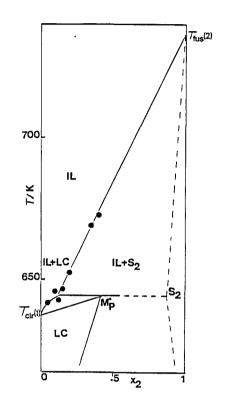
Sokolov's P point at $100 \text{m}_2 = 13$ corresponds to a slightly marked minimum of the data listed in Ref. 1: the experimental temperature values at $5 \le 100 \text{m}_2 \le 15$ actually range between 642 and 647 K, $\frac{1}{1}$.e. approximately within the accuracy limits estimated by the compiler.

If the temperature differences between the maximum at 646 K (and $100x_2=10$) and the P point at 644 K is thought to be meaningful, the phase diagram could be interpreted with reference to Scheme A.2 of the Preface: accordingly, Sokolov's invariant should be identified with an M'_E point).

If, on the contrary, the above mentioned temperature difference is thought to be meaningless, reference can be made to the front figure, where Sokolov's data are reported. In this case a peritectic equilibrium should exist (at about 644 K) among a liquid crystal, an isotropic liquid and a solid crystal. Accordingly, Sokolov's P point should be identified with an M'P point, and a further invariant should exist, e.g. an $\rm M_E$ at T $\leq \rm T_{fus}(1)$.

REFERENCES:

(1) Sokolov, N.M.
Zh. Obshch. Khim. 1954, 24, 1581-1593.



- (1) Sodium hexanoate (sodium caproate);
- NaC₆H₁₁O₂; [10051-44-2] (2) Sodium benzoate;
- (2) Sodium benzoate; NaC₇H₅O₂; [532-32-1]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1581-1593.

VARIABLES:

Temperature.

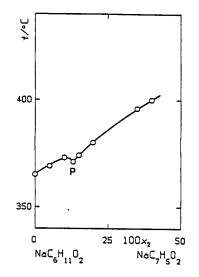
PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

t/°C	T/Kª	100 x 2	
365	638	0	
369	642	5	
373	646	10	
371	644	13	
374	647	15	
380	653	20	
396	669	35	
400	673	40	
463	736	100	

a T/K values calculated by the compiler.



Characteristic point(s):

Characteristic point, P ("perekhodnaya tochka" in the original text; see the Introduction), at 371 $^{\rm O}$ C and 100 x_2 = 13 (author).

Note - The system was investigated between $0 \le 100 x_2 \le 40$ due to thermal instability of the hexanoate.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis. Melts contained in a glass tube and stirred. Temperatures measured with a Nichrome-Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of isotropicity in the melt on cooling.

SOURCE AND PURITY OF MATERIALS:

Component 1: prepared by reacting aqueous ("chemically pure") Na_2CO_3 with a slight excess of hexanoic acid of analytical purity. The solvent and excess acid were removed by heating to $160\,^{\circ}\text{C}$. Component 2: "chemically pure" material.

ESTIMATED ERROR:

Temperature: accuracy probably ± 2 K (compiler).

- (1) Sodium hexanoate (sodium caproate);
- Na C₆H₁₁O₂; [10051-44-2] (2) Sodium octadecanoate (sodium stearate); Na $C_{18}H_{35}O_2$; [822-16-2]

EVALUATOR:

Ferloni, P., Dipartimento di Chimica Fisica, Universita' di Pavia (ITALY).

CRITICAL EVALUATION:

This system was studied only by Sokolov (Ref. 1) who employed the visual polythermal analysis to draw the lower boundary of the isotropic liquid field. From the shape of this boundary, he concluded that the intermediate compound $Na_5(C_6H_{11}O_2)_2(C_{18}H_{35}O_2)_3$ [congruently melting at 602 K (329 °C)] was formed, and that the limits of the stability field of this compound were a eutectic at 512 K (239 °C) and $100x_2$ = 17.5, and a "perekhodnaya tochka" at 587 K (314 °C) and $100x_2$ = 94.5.

Actually, both components form liquid crystals, the liquid crystalline phases being one for component 1 (see Table 1 of the Preface), and two for component 2 (see Table 4 of the Preface). Sokolov's fusion temperatures, $T_{\rm fus}(1)$ = 638 K (365 °C), and $T_{\rm fus}(2)$ = 581 K (308 °C), are consequently to be identified with the clearing temperatures, the corresponding values from Tables 1 and 4 being 639.0+0.5 and 552.7 K, respectively.

Since the complete topology of the binary can hardly be interpreted from the data available, it is more realistic to list here the few points which, in the evaluator's opinion, seem to be sufficiently reliable.

- (i) At intermediate compositions it seems reasonable to assume that a continuous series of liquid crystal solutions is formed, with an azeotrope at 602 K and $100x_2=60$.
- (ii) Accordingly, the left hand section (0 \leq 100 \mathbf{x}_2 \leq 60) of the phase diagram might be interpreted with reference to Scheme C.2 of the Preface: in this case, Sokolov's eutectic should be intended as an M"E point.

Conversely, no definite interpretation of the phase diagram at high $100x_2$ values seems possible. Indeed, it is not clear how Sokolov could argue the occurrence of an invariant (the "perekhodnaya tochka" at $100x_2 = 94.5$) from the trend of his experimental data which does not unambiguously support any significant slope change of the curve in this region. Moreover, Sokolov's "fusion" temperature of component 2 (581 K) looks as fully unreliable, being 18 K higher than the second highest T_{clr} value determined during the last 30 years (Ref. 2), and 28 K higher than the clearing temperature listed in Table 4.

- (1) Sokolov, N.M.
- Zh. Obshch. Khim. 1954, 24, 1581-1593.

 (2) Sanesi, M.; Cingolani, A.; Tonelli, P.L.; Franzosini, P.

 Thermal Properties, in Thermodynamic and Transport Properties of Organic Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors) Pergamon Press, Oxford, 1980, 29-115.

- (1) Sodium hexanoate (sodium caproate); NaC₆H₁₁O₂; [10051-44-2]
- (2) Sodium octadecanoate (sodium stearate); NaC₁₈H₃₅O₂; [822-16-2]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1581-1593.

VARIABLES:

Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

t/ºC	T/K ^a	100 x 2	t/ ^o C	T/K ^a	100 x 2
365	638	0	326	599	55
320	593	5	329	602	60
272	545	10	328	601	65
242	515	15	327	600	70
239	512	17.5	326	599	75
248	521	20	324	597	80
264	537	25	321	594	85
280	553	30	319	592	90
293	566	35	314	587	94.5
305	578	40	316	589	95
313	586	45	308	581	100
320	593	50			

a T/K values calculated by the compiler.

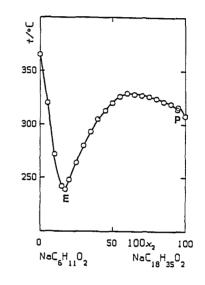
Characteristic point(s):

Characteristic point, P ("perekhodnaya tochka" in the original text; see the Introduction), at 314 $^{\circ}$ C and $100x_2$ = 94.5 (author).

Eutectic, E, at 239 °C and $100x_2 = 17.5$ (author).

Intermediate compound(s):

 $^{\rm Na}{}_5(^{\rm C}_6{}^{\rm H}_{11}{}^{\rm O}_2)_2(^{\rm C}_{18}{}^{\rm H}_{35}{}^{\rm O}_2)_3$ (author), congruently melting at 329 $^{\rm O}{\rm C}$ (compiler).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis. Melts contained in a glass tube and stirred. Temperatures measured with a Nichrome-Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of isotropicity in the melt on cooling.

SOURCE AND PURITY OF MATERIALS:

Component 1: prepared by reacting aqueous ("chemically pure") Na₂CO₃ with a slight excess of n-hexanoic acid of analytical purity. The solvent and excess acid were removed by heating to 160 °C. Component 2: "chemically pure" material.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

(1) Sodium hexanoate (sodium caproate);

NaC₆H₁₁O₂; [10051-44-2] (2) Sodium thiocyanate; NaCNS; [540-72-7]

EVALUATOR:

Spinolo, G., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

This binary was studied only by Sokolov (Ref. 1), who restricted his polythermal investigation to the lower boundary of the isotropic liquid field, and claimed the existence of a cutectic at 568 K (295 $^{\circ}$ C) and $100x_2$ = 63.

Component 1, however, forms liquid crystals [at $T_{fus}(1)$ = 499.6±0.6 K; Preface, Table 1] before turning into a clear melt. Sokolov's fusion temperature (638 K) is consequently to be identified with the clearing temperature, the corresponding value from Table 1 being 639.0±0.5 K.

Therefore, in the evaluator's opinion, the phase diagram could be more correctly interpreted with reference to Scheme A.2 of the Preface, and Sokolov's eutectic ought to be intended as an M_E point.

REFERENCES:

(1) Sokolov, N.M.; Zh. Obshch. Khim. 1954, 24, 1150-1156.

COMPONENTS:

- (1) Sodium hexanoate (sodium caproate);
- NaC₆H₁₁O₂; [10051-44-2] (2) Sodium thiocyanate; NaCNS; [540-72-7]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1150-1156.

VARIABLES:

Temperature.

PREPARED BY:

D'Andrea, G.

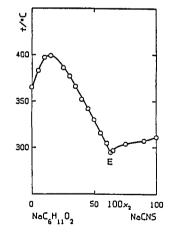
EXPERIMENTAL VALUES:

t/°C	T/K ^a	100x ₂	t/°C	T/K ^a	100 x 2
365	638	0	330	603	50
383	656	5	316	589	55
397	670	10	305	578	60
399	672	15	295	568	63
386	659	25	297	570	65
377	650	30	304	577	75
366	639	35	307	580	90
352	625	40	311	584	100
342	615	45			

a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E, at 295 °C and $100x_2$ = 63 (author).



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis. Salt(s) melted in a test tube. Temperature measured with a Nichrome-Constantane thermocouple and a millivoltmeter with mirror reading to 17 mV.

SOURCE AND PURITY OF MATERIALS:

Component 1 synthetized from n-hexanoic acid and NaHCO3. Component 2 of analytical purity recrystallized once from water and once from ethanol.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

(1) Sodium hexanoate (sodium caproate); NaC₆H₁₁O₂; [10051-44-2]

(2) Sodium nitrate; NaNO₃; [7631-99-4] **EVALUATOR:**

Ferloni, P., Dipartimento di Chimica Fisica, Universita di Pavia (ITALY).

CRITICAL EVALUATION:

This binary was studied only by Sokolov (Ref. 1), who restricted his polythermal investigation to the lower boundary of the isotropic liquid field, and claimed the existence of a eutectic at 560 K (287 $^{\circ}$ C) and $100x_2$ = 56.5, and the occurrence of liquid layering at 576 K (302 $^{\circ}$ C) and $100x_2$ > 60.

Component 1, however, forms liquid crystals [at $T_{fus}(1)$ = 499.6+0.6 K; Preface, Table 1] before turning into a clear melt. Sokolov's fusion temperature (638 K) is consequently to be identified with the clearing temperature, the corresponding value from Table 1 being 639.0+0.5 K. Therefore, in the evaluator's opinion, the phase diagram could be more correctly interpreted with reference to Scheme A.2 of the Preface, allowance being made for the fact that a liquid-liquid miscibility gap impinges on the liquidus branch richer in the higher melting component (NaNO3). Consequently, Sokolov's eutectic should be an M_{E} point.

REFERENCES:

(1) Sokolov, N.M.; Zh. Obshch. Khim. 1954, 24, 1150-1156.

COMPONENTS:

(1) Sodium hexanoate (sodium caproate); $NaC_6H_{11}O_2$; [10051-44-2]

(2) Sodium nitrate; NaNO₃; [7631-99-4]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1150-1156.

VARIABLES:

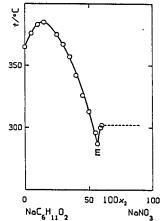
Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

t/°C	T/K ^a	100 x 2	
365	638	0	
376	649	5	
383	656	10	
385	658	15	
375	648	25	
367	640	30	
357	630	35	
342	615	40	
326	599	45	
313	586	50	
296	569	55	
287	560	56.5	
300	573	59	
302	575	60	



^a T/K values calculated by the compiler. Characteristic point(s): Eutectic, E, at 287 $^{\circ}$ C and $100x_{2}$ = 56.5 (author).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis. Salt(s) melted in a test tube. Temperature measured with a Nichrome-Constantane thermocouple and a millivoltmeter with mirror reading to 17 mV.

NOTE:

At $100x_2 > 60$, liquid layering occurs.

SOURCE AND PURITY OF MATERIALS:

Component 1 synthetized from n-hexanoic acid and NaHCO3. Commercial component 2 further purified by the author according to Laiti.

ESTIMATED ERROR:

Temperature: accuracy probably ± 2 K (compiler).

- (1) Sodium benzoate; NaC₇H₅O₂; [532-32-1]
- (2) Sodium octadecanoate (sodium stearate); NaC₁₈H₃₅O₂; [822-16-2]

EVALUATOR:

Ferloni, P.

Dipartimento di Chimica Fisica. Universita di Pavia (ITALY).

CRITICAL EVALUATION:

This binary was studied only by Sokolov (Ref. 1) who reported a phase diagram of the eutectic type with the invariant at 574 K (301 $^{\circ}$ C) and 100 $x_1 = 1.3$.

Component 2, however, forms liquid crystals. Thence, the fusion temperature by Sokolov, viz., $T_{fus}(2)$ = 581 K (308 °C), should be intended as a clearing temperature and compared with the $T_{clr}(2)$ value reported in Table 4 (552.7 K). It is to be stressed that Sokolov's "fusion" temperature looks as fully unreliable, being 18 K higher than the second highest T_{clr} value determined during the last 30 years (Ref. 2), and 28 K higher than the clearing temperature listed in Table 4.

The whole phase diagram is therefore to be reconsidered.

- (1) Sokolov, N.M.
 Zh. Obshch. Khim. 1954, 24, 1581-1593.
- (2) Sanesi, M.; Cingolani, A.; Tonelli, P.L.; Franzosini, P. Thermal Properties, in Thermodynamic and Transport Properties of Organic Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors), Pergamon Press, Oxford, 1980, 29-115.

- (1) Sodium benzoate;
 - NaC₇H₅O₂; [532-32-1]
- (2) Sodium octadecanoate (sodium stearate); NaC₁₈H₃₅O₂; [822-16-2]

ORIGINAL MEASUREMENTS:

Sokolov, N.M.

Zh. Obshch. Khim. 1954, 24, 1581-1593.

VARIABLES:

Temperature.

PREPARED BY:

D'Andrea, G.

EXPERIMENTAL VALUES:

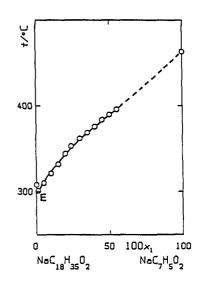
t/°C	T/Kª	100 x 1
308	581	0
301	574	1.3
310	583	5
321	594	10
332	605	15
344	617	20
353	626	24
362	635	30
369	642	35
376	649	40
384	657	45
390	663	50
396	669	55
463	736	100

a T/K values calculated by the compiler.

Characteristic point(s):

Eutectic, E, at 301 $^{\circ}$ C and $100x_1 = 1.3$ (author).

Note – The system was investigated at $0 \le 100x_1 \le 55$ due to thermal instability of the octadecanoate.



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis. Melts contained in a glass tube and stirred.

Temperatures measured with a Nichrome-Constantane thermocouple and a 17 mV full scale millivoltmeter. The temperature readings refer to the disappearance of isotropicity in the melt on cooling.

NOTE:

Component 2 forms liquid crystals. Thence, the fusion temperature by Sokolov, viz., $T_{fus}(2)$ = 581 K (308 °C), should be intended as a clearing temperature and compared with the $T_{clr}(2)$ value (552.7 K) reported on Preface, Table 4. It is to be stressed that Sokolov's "fusion" temperature looks as fully unreliable, being 18 K higher than the second highest T_{clr} value determined during the last 30 years (Ref. 1), and 28 K higher than the clearing temperature listed in Table 4. The whole phase diagram 1s therefore to be reconsidered.

SOURCE AND PURITY OF MATERIALS:

"Chemically pure" materials.

ESTIMATED ERROR:

Temperature: accuracy probably +2 K (compiler).

REFERENCES:

(1) Sanesi, M.; Cingolani, A.; Tonelli, P.L.; Franzosini, P. Thermal Properties, in Thermodynamic and Transport Properties of Organic Salts, IUPAC Chemical Data Series No. 28 (Franzosini, P.; Sanesi, M.; Editors), Pergamon Press, Oxford, 1980, 29-115.