| COMPONENTS: | EVALUATOR: |
|---|---|
| (1) Potassium iso.pentanoate (potassium iso.valerate); $(i.C_5H_9O_2)K$; [589-46-8]<br>(2) Sodium iso.pentanoate (sodium iso.valerate); $(i.C_5H_9O_2)Na$; [539-66-2] | Schiraldi, A.,<br>Dipartimento di Chimica Fisica,<br>Universita' di Pavia (ITALY). |

CRITICAL EVALUATION:

This system was studied by Pochtakova (Ref. 1), and by Dmitrevskaya and Sokolov (Ref. 2): according to both papers, continuous series of solid solutions ought to be formed.

Both components, however, form liquid crystals (see Preface, Table 2). Consequently the fusion temperatures, $T_{fus}(1)$= 669 K (396 °C; Refs. 1, 2), and $T_{fus}(2)$= 533 K (260 °C; Ref. 1) or 535 K (262 °C; Ref. 2), are actually to be identified with the clearing temperatures, the corresponding values from Table 2 of the Preface being 679±2 K and 559±1 K, respectively. The latter figure is remarkably higher than those given by the Russian authors, although meeting rather satisfactorily those reported by Ubbelohde et al. (556 K; Ref. 3) and by Duruz et al. (553 K; Ref. 4).

No mention is made in Refs. 1, 2 of the actual fusion of component 1 which occurs at 531±3 K (Table 2): the latter figure is supported by the trend of the thermomagnetical curves plotted by Duruz and Ubbelohde (Ref. 5). As for the other phase transitions of the same component, Pochtakova quotes from Ref. 6 two $T_{trs}$ values, i.e., 327 and 618 K (54 and 345 °C, respectively), for which no comparison is possible with the findings by other investigators, inasmuch as: (i) no transformation is reported in Table 2 as occurring below $T_{fus}(1)$= 531±3 K; and (ii) no transformation is reported in Table 2 or in Ref. 5 as occurring within the field of existence of the mesomorphic liquid. It is a bit puzzling the fact that for potassium iso.pentanoate Dmitrevskaya and Sokolov (Ref. 2) quote from the same source (Ref. 6) transitions at 618, 493, and 473 K (ignoring that quoted by Pochtakova at 327 K).

In the case of component 2, the transition at 451 K (178 °C; quoted in Refs. 1, 2 from Ref. 5) should be indentified with the actual fusion temperature (the corresponding value from Table 2 of the Preface being 461.5±0.6 K).

Taking into account the above remarks, the upper part of Dmitrevskaya and Sokolov's diagram, Ref. 2, (to be compared with the upper part of Preface, Scheme C.1) supports the idea that continuous series of liquid crystal (instead of solid) solutions do form. Moreover, the left-hand side of the lower part of the same diagram might suggest that, at lower temperatures, solid solutions are also present.

REFERENCES:

(1) Pochtakova, E.I.
**Zh. Obshch. Khim.** 1963, 33, 342-347.

(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.; Duruz, J.J.
**Nature** 1970, 228, 50-52.

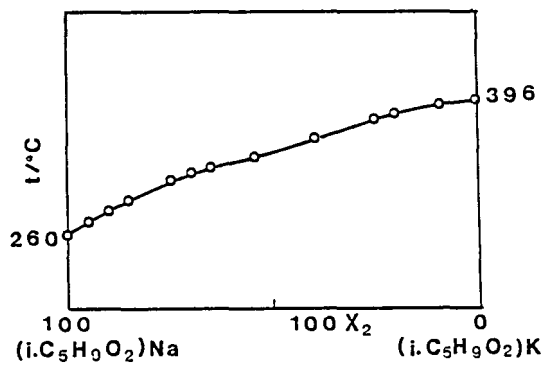
(4) Duruz, J.J.; Michels, H.J.; Ubbelohde, A.R.
**Proc. R. Soc. London** 1971, A 322, 281-299.

(5) Duruz, J.J.; Ubbelohde, A.R.
**Proc. R. Soc. London** 1975, A 342, 39-49.

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

| COMPONENTS: | ORIGINAL MEASUREMENTS: |
|---|---|
| (1) Potassium iso.pentanoate (potassium iso.valerate); $(i.C_5H_9O_2)K$; [589-46-8]<br>(2) Sodium iso.pentanoate (sodium iso.valerate); $(i.C_5H_9O_2)Na$; [539-66-2] | Pochtakova, E.I.<br>Zh. Obshch. Khim. 1963, 33, 342-347. |
| VARIABLES: | PREPARED BY: |
| Temperature. | Baldini, P. |

EXPERIMENTAL VALUES:




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

Characteristic point(s): Continuous series of solid solutions.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Visual polythermal analysis.

ESTIMATED ERROR:

Temperature: accuracy probably ±2 K (compiler).

REFERENCES:

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

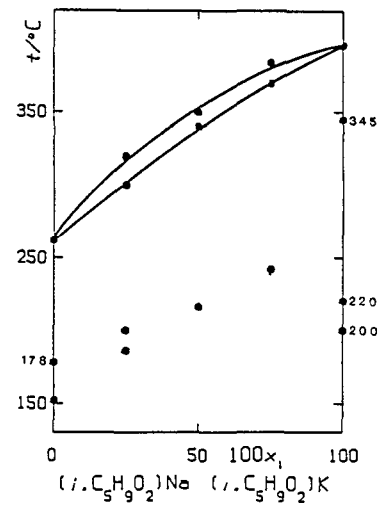
SOURCE AND PURITY OF MATERIALS:

Both components prepared from commercial iso.pentanoic acid (distilled twice before use) and the proper "chemically pure" hydrogen carbonate (Ref. 1, where, however, carbonates instead of hydrogen carbonates are employed; compiler). Component 1 undergoes phase transitions at $t_{trs}(1)/^{\circ}C$= 54, 345 (Ref. 2) and melts at $t_{fus}(1)/^{\circ}C$= 396. Component 2 undergoes phase transitions at $t_{trs}(2)/^{\circ}C$= 152, 178 (Ref. 2) and melts at $t_{fus}(2)/^{\circ}C$= 260.

| COMPONENTS: | ORIGINAL MEASUREMENTS: |
|---|---|
| (1) Potassium iso.pentanoate (potassium iso.valerate); $(i.C_5H_9O_2)K$; [589-46-8]<br>(2) Sodium iso.pentanoate (sodium iso.valerate); $(i.C_5H_9O_2)Na$; [539-66-2] | Dmitrevskaya, O.I.; Sokolov, N.M.<br>Zh. Obshch. Khim. 1967, 37, 2160-2166 (*);<br>Russ. J. Gen. Chem. (Engl. Transl.) 1967, 37, 2050-2054. |
| VARIABLES:<br><br>Temperature. | PREPARED BY:<br><br>Baldini, P. |

EXPERIMENTAL VALUES:

| t/°C | T/K[a] | $100x_1$ |
|---|---|---|
| 262 | 535 | 0 |
| 178[b] | 451 | 0 |
| 152[b] | 425 | 0 |
| 320 | 593 | 25 |
| 300[b] | 573 | 25 |
| 200[b] | 473 | 25 |
| 186[b] | 459 | 25 |
| 350 | 623 | 50 |
| 340[b] | 613 | 50 |
| 216[b] | 489 | 50 |
| 384 | 657 | 75 |
| 370[b] | 643 | 75 |
| 242[b] | 515 | 75 |
| 396 | 669 | 100 |
| 345[b] | 618 | 100 |
| 220[b] | 493 | 100 |
| 200[b] | 473 | 100 |




[a] T/K values calculated by the compiler.
[b] Transformation in phase.

Characteristic point(s): Continuous series of solid solutions.

AUXILIARY INFORMATION

| METHOD/APPARATUS/PROCEDURE: | SOURCE AND PURITY OF MATERIALS: |
|---|---|
| Thermographical investigation (heating curves recorded automatically).<br><br>NOTE:<br><br>The data tabulated (and plotted in the figure) refer to the thermographical investigation; other points of the liquidus, taken by visual polythermal analysis and consistent with the tabulated ones, are reported only in a graphical form (Fig. 2 of the original paper). For the latter, reference is made to a previous paper by Sokolov et al. (Ref. 1) where, however, the present binary is merely mentioned as a side of a reciprocal ternary. | Both components synthetized from iso.butanoic acid and the proper carbonate (Ref. 2).<br>Component 1 undergoes phase transitions at $t_{trs}(1)/°C$= 345, 220, 200 (Ref. 3).<br>Component 2 undergoes phase transitions at $t_{trs}(2)/°C$= 152, 178 (Ref. 3).<br><br>ESTIMATED ERROR:<br><br>Temperature: accuracy probably ±2 K (compiler). |

REFERENCES:

(1) Sokolov, N.M.; Tsindrik, N.M.; Dmitrevskaya, O.I.
Zh. Obshch. Khim. 1961, 31, 1051-1056.
(2) Sokolov, N.M.
Zh. Obshch. Khim. 1954, 24, 1581-1593.
(3) Sokolov, N.M.
Tezisy Dokl. X Nauch. Konf. S.M.I. 1956.