

PREFACE

1. Phase relationships of alkali alkanoates.

1.1. Solid state transitions of alkali alkanoates.

Most alkali alkanoates (either linear or branched) exhibit polymorphism in the solid state, and the number of phases tends to increase with increasing chain length. However, controversy often exists about the number, nature, and stability range of the polymorphs present in a given salt. Since different hydrates appear as well, "in the literature one may find almost the whole Greek alphabet, primed and unprimed, each notation supposed to define a separate phase. It has been maintained that each such phase is associated with a unique crystal structure, while others have claimed that the different X-ray diffraction patterns do not necessarily represent true crystal structures, but instead are merely associated with different types of disorder of the chains. There is also the additional problem of the descendant phases, i.e., structures that occur at some elevated temperature and remain unaltered at room temperature in a pseudoequilibrium for a long time" (Ref. 1). The present volume discusses solubilities of those linear alkali alkanoates marked with a cross in the scheme below, and, as well, the iso-butanoates and iso-pentanoates of Na and K. No information is available so far on the solubilities of other alkali alkanoates.

Number of carbon atoms, n _C ,										
Cation	1	2	3	4	5	6	7	8	9	18

Li	x	x	x	x						
Na	x	x	x	x	x	x				x
K	x	x	x	x	x	x	x	x	x	
Rb		x								
Cs		x								

In order to obtain a homogeneous picture of the thermal behavior (in terms of phase transformation temperatures and enthalpy changes) of alkali alkanoates, more than 100 linear and branched homologues belonging to the different alkali families have been submitted to DSC analysis during the last few years in the editor's laboratory. The results obtained on heating are thought to offer an acceptable degree of trustworthiness and internal consistency. Therefore, as useful background material for discussion of the solubility curves, the pertinent superambient solid state transition temperature, T_{trs}, are collected in Tables 1 and 2. These temperatures represent first order, or predominantly first order, phase transitions. For completeness, the temperatures of fusion, T_{fus}, and of clearing, T_{clr}, (when they exist) are also listed in Tables 1 and 2. However, the data on sodium octadecanoate (produced in a different laboratory) are listed separately in Table 4.

The following remarks can be made about the precision and accuracy of the data reported in Tables 1, 2.

Precision is not infrequently better than ±1 K, although becoming poorer in some cases: in particular, very poor reproducibility was obtained for solid state transitions of sodium methanoate and ethanoate.

Accuracy is thought to be often of the same order of magnitude as precision. However, one must consider that DSC is a dynamic method of investigation, and that some solid state transitions of methanoates and ethanoates are characterized (even on heating at a moderate scanning rate) by a remarkable sluggishness. Consequently, in Tables 1, 2 the T_{trs} data for the shortest homologues can be somewhat too high. This disadvantage tends

to decrease in the next higher homologues, and does not involve fusion and clearing. As an example, high accuracy equilibrium adiabatic calorimetric data, taken very recently by Franzosini et al. (Refs. 8, 9) on sodium methanoate and propanoate, are compared in Table 3 with the previous DSC values. The comparison also includes the enthalpy changes involved.

For sodium octadecanoate, reference will be made to the recent DSC data by Forster et al. (Ref. 10), collected in Table 4.

Table 1 - T_{clr} , T_{fus} , and superambient T_{trs} values determined by DSC for 21 linear alkali alkananoates.

n_C	Cation	T_{clr}/K	T_{fus}/K	T'_{trs}/K	T''_{trs}/K	T'''_{trs}/K	T^{IV}_{trs}/K	Ref.
1	Li	-	546+1	496+2	-	-	-	2
	Na	-	530.7+0.5	502+5	-	-	-	3
	K	-	441.9+0.5	418+1	-	-	-	3
2	Li	-	557+2	-	-	-	-	2
	Na	-	601.3+0.5	527+15	465+3	414+10	-	2
	K	-	578.7+0.5	422.2+0.5	-	-	-	2
	Rb	-	514+1	498+1	-	-	-	2
	Cs	-	463+1	-	-	-	-	2
3	Li	-	606.8+0.5*	533+2	-	-	-	2
	Na	-	562.4+0.5	494+1	470.2+0.5	-	-	2
	K	-	638.3+0.5	352.5+0.5	-	-	-	2
4	Li	-	591.7+0.5	-	-	-	-	2
	Na	600.4+0.2	524.5+0.5	508.4+0.5	498.3+0.3	489.8+0.2	450.4+0.5	4
	K	677.3+0.5	626.1+0.7	562.2+0.6	540.8+1.1	467.2+0.5	461.4+1.0	4
5	Na	631+4	498+2	-	-	-	-	5
	K	716+2	586.6+0.7	399.5+0.9	-	-	-	5
6	Na	639.0+0.5	499.6+0.6	473+2	386+2	-	-	5
	K	725.8+0.8	531.7+0.5	-	-	-	-	5
7	K	722+3	571.3+0.9	345.4+0.6	332.0+0.8	-	-	5
8	K	712+2	560.6+0.8	326.6+0.1	-	-	-	6
9	K	707.4+0.8	549.1+0.8	390.5+0.4	367.5+0.5	-	-	6

clr: clearing; fus: fusion; trs: transition

* A metastable fusion point was also detected at $T_{fus(m)}/K = 584+1$

Table 2 - T_{clr} , T_{fus} , and superambient T_{trs} values determined by DSC for 4 alkali iso-alkananoates.

n_C	Cation	T_{clr}/K	T_{fus}/K	T'_{trs}/K	Ref.
4	Na	-	526.9+0.7	-	7
	K	625.6+0.8	553.9+0.5	424+3	7
5	Na	559+1	461.5+0.6	-	7
	K	679+2	531+3	-	7

clr: clearing; fus: fusion; trs: transition

Table 3 - Comparison between adiabatic calorimetric and DSC data.

n_C	Cation	Quantity	Value	Method	Ref
1	Na	T_{fus}/K	530.46+0.04	ad.cal.	8
			530.7+0.5	DSC	3
		T_{trs}/K	491.5+1	ad.cal.	8
			502+5	DSC	3
		$(\Delta_{fus}H_m/R)/K$	2130 (*)	ad.cal.	8
			(2.06+0.05) 10^3	DSC	3
		$(\Delta_{trs}H_m/R)/K$	150 (*)	ad.cal.	8
			(1.41+0.05) 10^2	DSC	3
3	Na	T_{fus}/K	561.88+0.03	ad.cal.	9
			562.4+0.5	DSC	2
		T'_{trs}/K	491+1	ad.cal.	9
			494+1	DSC	2
		T''_{trs}/K	467+1	ad.cal.	9
			470.2+0.5	DSC	2
		$(\Delta_{fus}H_m/R)/K$	1597.3+0.6	ad.cal.	9
			(1.61+0.05) 10^3	DSC	2
		$(\Delta_{trs}H_m/R)/K(**)$	(0.91+0.02) 10^3	ad.cal.	9
			(0.89+0.05) 10^3	DSC	2

fus: fusion; trs: transition

(*) Single determination.

(**) Cumulative enthalpy change relevant to both solid state transitions.

Table 4 - T_{clr} , T_{fus} , and superambient T_{trs} values determined by DSC for sodium octadecanoate.

T_{clr}/K	T'_{trs}/K	T_{fus}/K	T''_{trs}/K	T'''_{trs}/K	T^{IV}_{trs}/K	T^V_{trs}/K	T^{VI}_{trs}/K
552.7	547.7	527.2	469/476	448	408	390	368
L	NI	NII	SN	SpW	W	SW	CI CII

clr: clearing; fus: fusion; trs: transition

L: isotropic liquid; N: neat; SN: subneat; SpW: superwaxy; W: waxy; SW: subwaxy; C: crystal.

1.2. Mesomorphism in alkali alkanooates.

Mesomorphic phases (liquid crystalline, or plastic crystalline, or both) can also form in alkali alkanooates, the stability range of the mesomorphic state being intermediate between those of the "true" crystalline and of the "true" liquid phases. In particular, liquid crystals (likely of the smectic type) form in linear alkanooates, starting with butanoate when the cation is either sodium or potassium, from pentanoate when the cation is rubidium, and from hexanoate when the cation is caesium. No liquid crystals form when the cation is lithium. In long chain homologues (which, however, are of little relevance to the present purposes) plastic crystals form for all alkali cations. (See, e.g., the data reported in Table 4 for sodium octadecanoate.)

Unfortunately, the nomenclature employed by different authors is far from homogeneous. In particular, most Russian investigators call "fusion" the transformation of either a crystalline solid or a liquid crystal into an isotropic liquid which is often misleading in the interpretation of phase diagrams. More reasonably, in non - Russian literature a distinction is usually made between clearing temperature, T_{clr} (i.e., the temperature at which a liquid crystal transforms into an isotropic liquid), and fusion temperature, T_{fus} (i.e., the temperature at which a "true" crystal transforms into either an isotropic liquid or a liquid crystal)(*). Further details on these points are given in Section 2.2.

(*) It might be further considered whether in the sequence (met in several long chain alkali alkanooates): crystal \rightarrow plastic crystal(s) \rightarrow liquid crystal(s) \rightarrow isotropic liquid the term "fusion" should be applied to the first or to the second transformation, but such a discussion would be of little relevance here. In Table 4 the term fusion was applied to the transformation from the (plastic crystalline) subneat to the (liquid crystalline) neat I phase.

The literature contains reports on the phase diagrams of 58 binaries (9 with common anion, and 49 with common cation), involving alkali alkanoates which exhibit mesomorphism: they are listed in Table 5 where the component(s) which can exist in the mesomorphic liquid state are underlined.

Unfortunately, information is mostly restricted to the lower boundary of the isotropic liquid field. More details are available only in a limited number of cases among which special interest is to be attached to the following: a) $(C_4H_7O_2)K + (C_4H_7O_2)Na$, b) $(C_4H_7O_2)Li + (C_4H_7O_2)Na$, c) $KC_2H_3O_2 + KC_4H_7O_2$, d) $NaC_2H_3O_2 + NaC_4H_7O_2$, and e) $NaC_4H_7O_2 + NaNO_3$, inasmuch as a comparison is here possible between the results obtained by Prisyazhnyi et al. (Refs. 11, 12), who studied the lower boundaries of both the isotropic liquid and the liquid crystal fields, and those obtained by previous authors, who studied only the lower boundary of the isotropic liquid.

Table 5 - Binaries involving at least one alkali alkanoate able to exist in the liquid crystalline state.

Systems with common anion:

1) $\sim(C_4H_7O_2)_2K_2$	$(C_4H_7O_2)_2Mg$	2) $\sim(C_4H_7O_2)K$	$\sim(C_4H_7O_2)Na$
3) $\sim(i.C_4H_7O_2)K$	$(i.C_4H_7O_2)Na$	4) $(C_4H_7O_2)Li$	$\sim(C_4H_7O_2)Na$
5) $(C_4H_7O_2)_2Mg$	$\sim(C_4H_7O_2)_2Na_2$	6) $\sim(C_5H_9O_2)K$	$\sim(C_5H_9O_2)Na$
7) $\sim(i.C_5H_9O_2)K$	$\sim(i.C_5H_9O_2)Na$	8) $(C_5H_9O_2)_2Mg$	$\sim(C_5H_9O_2)_2Na_2$
9) $\sim(C_6H_{11}O_2)K$	$\sim(C_6H_{11}O_2)Na$		

Systems with common cation:

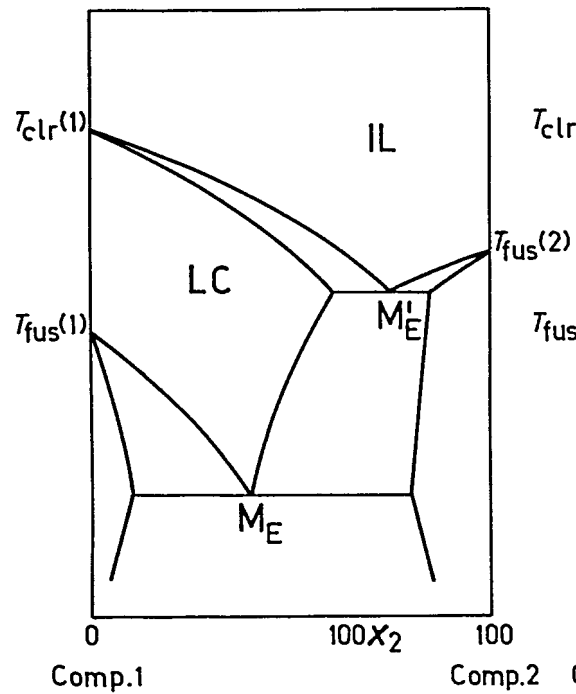
10) $KC_2H_3O_2$	$\sim KC_4H_7O_2$	11) $KC_2H_3O_2$	$\sim Ki.C_4H_7O_2$
12) $KC_2H_3O_2$	$\sim KC_5H_9O_2$	13) $KC_2H_3O_2$	$\sim Ki.C_5H_9O_2$
14) $KC_2H_3O_2$	$\sim KC_6H_{11}O_2$	15) $\sim KC_4H_7O_2$	KCNS
16) $\sim KC_4H_7O_2$	KNO ₂	17) $\sim KC_4H_7O_2$	KNO ₃
18) $\sim Ki.C_4H_7O_2$	KNO ₂	19) $\sim Ki.C_4H_7O_2$	KNO ₃
20) $\sim KC_5H_9O_2$	KNO ₂	21) $\sim KC_5H_9O_2$	KNO ₃
22) $\sim Ki.C_5H_9O_2$	KNO ₂	23) $\sim Ki.C_5H_9O_2$	KNO ₃
24) $\sim KC_6H_{11}O_2$	KNO ₂	25) $\sim KC_7H_{13}O_2$	KNO ₂
26) $\sim KC_8H_{15}O_2$	KNO ₂	27) $\sim KC_9H_{17}O_2$	KNO ₂
28) $NaCHO_2$	$\sim NaC_4H_7O_2$	29) $NaCHO_2$	$\sim Na i.C_5H_9O_2$
30) $NaC_2H_3O_2$	$\sim NaC_4H_7O_2$	31) $NaC_2H_3O_2$	$\sim NaC_5H_9O_2$
32) $NaC_2H_3O_2$	$\sim Na i.C_5H_9O_2$	33) $NaC_2H_3O_2$	$\sim NaC_6H_{11}O_2$
34) $\sim NaC_4H_7O_2$	$Na i.C_4H_7O_2$	35) $\sim NaC_4H_7O_2$	$\sim Na i.C_5H_9O_2$
36) $\sim NaC_4H_7O_2$	$\sim NaC_6H_{11}O_2$	37) $\sim NaC_4H_7O_2$	$NaC_7H_5O_2$
38) $\sim NaC_4H_7O_2$	$\sim NaC_{18}H_{35}O_2$	39) $\sim NaC_4H_7O_2$	NaCNS
40) $\sim NaC_4H_7O_2$	NaNO ₂	41) $\sim NaC_4H_7O_2$	NaNO ₃
42) $Na i.C_4H_7O_2$	$\sim Na i.C_5H_9O_2$	43) $Na i.C_4H_7O_2$	$\sim NaC_6H_{11}O_2$
44) $Na i.C_4H_7O_2$	$\sim NaC_{18}H_{35}O_2$	45) $\sim NaC_5H_9O_2$	NaCNS
46) $\sim NaC_5H_9O_2$	NaNO ₂	47) $\sim NaC_5H_9O_2$	NaNO ₃
48) $\sim Na i.C_5H_9O_2$	$\sim NaC_6H_{11}O_2$	49) $\sim Na i.C_5H_9O_2$	$NaC_7H_5O_2$
50) $\sim Na i.C_5H_9O_2$	$\sim NaC_{18}H_{35}O_2$	51) $\sim Na i.C_5H_9O_2$	NaCNS
52) $\sim Na i.C_5H_9O_2$	NaNO ₂	53) $\sim Na i.C_5H_9O_2$	NaNO ₃
54) $\sim NaC_6H_{11}O_2$	$NaC_7H_5O_2$	55) $\sim NaC_6H_{11}O_2$	$\sim NaC_{18}H_{35}O_2$
56) $\sim NaC_6H_{11}O_2$	NaCNS	57) $\sim NaC_6H_{11}O_2$	NaNO ₃
58) $NaC_7H_5O_2$	$\sim NaC_{18}H_{35}O_2$		

\sim Compounds which form liquid crystals.

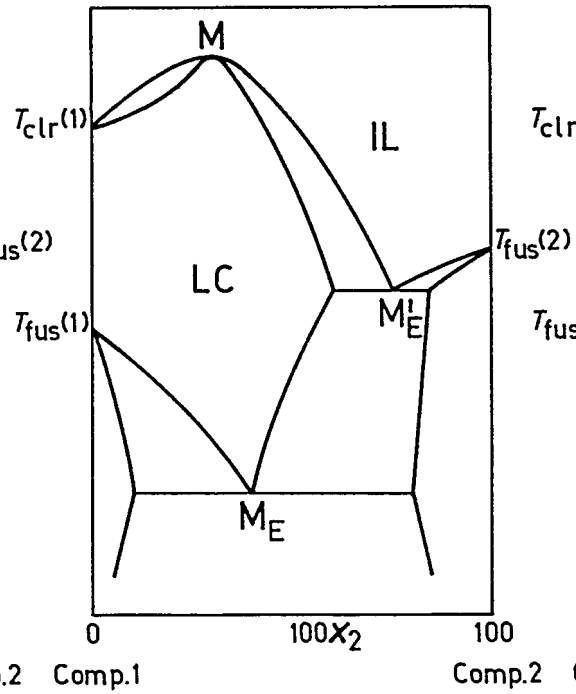
In order to improve homogeneity and succinctness in discussing the systems in Table 5, it seemed convenient to present here a selection of model phase diagrams [see Schemes A, ..., D (*)] to which reference will be made in the subsequent critical evaluations.

(*) Schemes A, ..., D were drawn in the - usually accepted - assumption that any (actually known) transformation mesomorphic phase \Leftrightarrow isotropic liquid is first order.

SCHEME A.1



SCHEME A.2



SCHEME A.3

