Molten Mixtures of K, Na Formates with Alkali Halides. Note I *

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The eutectic compositions and temperatures were determined in a series of mixtures type *HCOOK+MeX* and *HCOONa+MeX* (where Me=Li, Na, K, Rb, Cs, and X=Cl, Br, I). Moreover, a detailed map of the accessible portion of the liquidus area in the system K^+, $Na^+/HCOO^-$, Cl^-, showing the isotherms up to 300 °C, was drawn.

We recently referred on a series of binary and reciprocal ternary systems containing alkali thiocyanates [1]: according to our investigation program on the properties of low melting salts, alkali formates were then to be taken into account.

Concerning the latter, we measured first the heat and entropy of fusion of HCOOK and HCOONa both cryometrically and calorimetrically [2], and found (as the mean values between the data by the two methods)

$$\Delta H_\mathrm{f} = 2{,}825 \text{ and } 4{,}075 \text{ cal/mole,}$$

and $$\Delta S_\mathrm{f} = 6.39 \text{ and } 7.68 \text{ cal/deg}\cdot\text{mole,}$$

respectively: these figures were used to calculate the ideal curves drawn in Fig. 1 and 2.

In the present paper the liquidus curves of the mixtures formed with the same formates and 14 alkali halides, and the reciprocal system K^+, $Na^+/HCOO^-$, Cl^- are discussed.

Experimental

As usual, we employed a visual method, the details of which were reported in a previous paper [3]. The following chemicals (dried by heating under vacuum): C. Erba RP LiCl; K & K LiBr; C. Erba RP sodium and potassium formates, chlorides, bromides and iodides; high purity Merck Rb(Cl, Br, I), and 99.9% Schuchardt Cs(Cl, Br, I) were used.

Results

1. As far as we know, no previous systematic investigation was carried out on the liquidus curves of mixtures type *alkali formates + alkali halides*. The results of our measurements on

$$HCOO(K,Na) + Li(Cl,Br)$$

and

$$HCOO(K,Na) + (Na,K,Rb,Cs)(Cl,Br,I)$$

are collected in Table 1 (where the eutectic compositions and temperatures are reported), and in Fig. 1 and 2.

MeX	Mixtures with HCOOK		Mixtures with HCOONa	
	$x_{\mathrm{MeX,E}}$	t_E (°C)	$x_{\mathrm{MeX,E}}$	t_E (°C)
LiCl	0.033	158.$_4$	0.045	244.$_0$
LiBr	0.044$_5$	154.$_7$	0,076	233.$_5$
NaCl	0.034	159.$_4$	0.051$_5$	249.$_8$
NaBr	0.048	155.$_7$	0.095	243.$_5$
NaI	(0,073)	(148.$_9$)	0.172$_5$	227.$_7$
KCl	0.037	163.$_5$	0.058	242.$_1$
KBr	0.053	161.$_3$	0.106	232.$_4$
KI	0.087	156.$_3$	0.087$_5$	237.$_2$
RbCl	0.038	161.$_3$	0.062$_5$	241.$_6$
RbBr	0.055	158.$_8$	0.103$_5$	234.$_6$
RbI	0.090	152.$_4$	0.060$_5$	244.$_2$
CsCl	0.039	158.$_3$	0.063	241.$_8$
CsBr	0.063$_5$	152.$_5$	0.082$_5$	239.$_6$
CsI	0.069$_5$	152.$_2$	0.031	250.$_0$

Table 1. Eutectics in molten mixtures of K, Na formates with alkali halides.

Between formate melting points and eutectic temperatures the ideal curves (whenever lying far enough from the experimental ones to avoid confusion in the graphs) were also drawn [4].

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[1] The paper by G. PIANTONI, M. BRAGHETTI, and P. FRANZOSINI, Z. Naturforsch. **23 a**, 2069 [1968] is our most recent publication on this subject.

[2] D. LEONESI, G. PIANTONI, G. BERCHIESI, and P. FRANZOSINI, Ric. Sci. **38**, 702 [1968]. — M. BRAGHETTI, G. BERCHIESI, and P. FRANZOSINI, Ric. Sci., in press.

[3] M. BRAGHETTI, D. LEONESI, and P. FRANZOSINI, Ric. Sci. **38**, 116 [1968].

[4] According to C. SINISTRI and P. FRANZOSINI, Ric. Sci. **33** (II-A), 419 [1963].

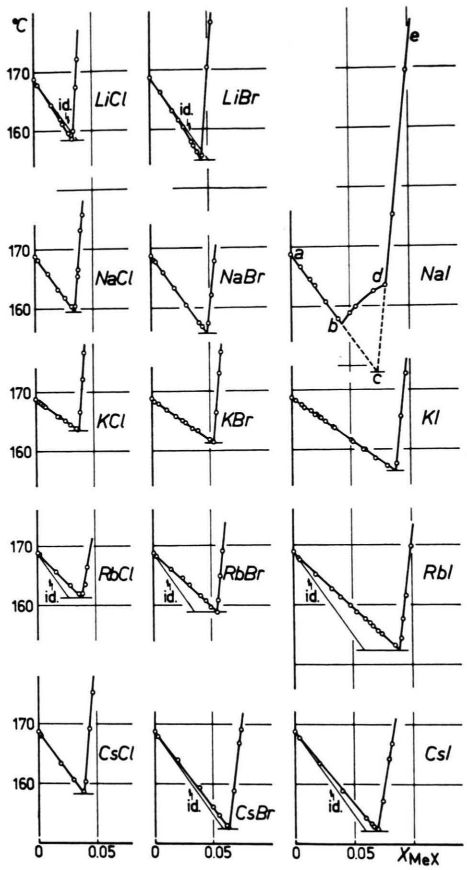

Fig. 1. Liquidus curves of systems type *HCOOK+MeX*. Within the investigated composition range, two liquidus branches were exhibited by each mixture, except *HCOOK+NaI:* here three branches were observed, that is the richest in HCOOK (a—b branch), the richest in NaI (d—e branch), and an intermediate b—d branch, the significance of which becomes apparent as soon as the map of K^+, Na^+/$HCOO^-$, I^- liquidus area is looked at (see Note II of the present series; *HCOOK +NaI* represents a diagonal in the composition quadrilateral of the reciprocal system K^+, Na^+/$HCOO^-$, I^-). In Table 1 we reported the coordinates (taken by extrapolation) of point c; those of points b and d were 157 °C and $x_{NaI}=0.043$, and $163._5$ °C and $x_{NaI}=0.080$, respectively.

With regard to the branches rich in formate, it may be noted that: a) in both series *HCOOK + MeX* and *HCOONa + MeX* the experimental data deviate negatively (with respect to ideality) when Me = Li, and positively when Me = Cs; b) X being the same, in each series the deviations proper to the systems containing Na, K, Rb halides are generally intermediate between those of the homologous systems containing Li and Cs salts.

The most evident exception to the latter regularity is given by the mixtures *HCOOK + Rb(Cl, Br, I)*,

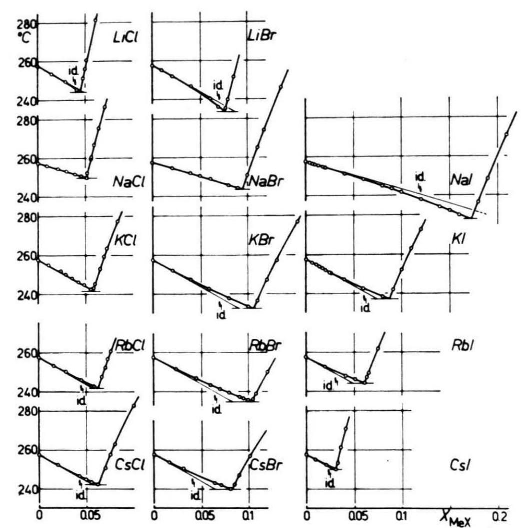

Fig. 2. Liquidus curves of systems type *HCOONa+MeX*.

for which the anomalously large positive deviations from ideality are probably to be ascribed to the formation of remarkable amounts of mixed crystals (anyhow, nearly parallel events were already observed in the *KCNS + MeX* mixtures [1]). On the contrary, the formation of mixed crystals in the remaining systems ought to be insignificant (as our previous cryometric measurements proved, e. g., for

$$HCOOK + (Li, K, Cs)Cl$$

and

$$HCOONa + (Li, Na, Cs)Cl\ ^{2)},$$

or at least contained within narrow limits.

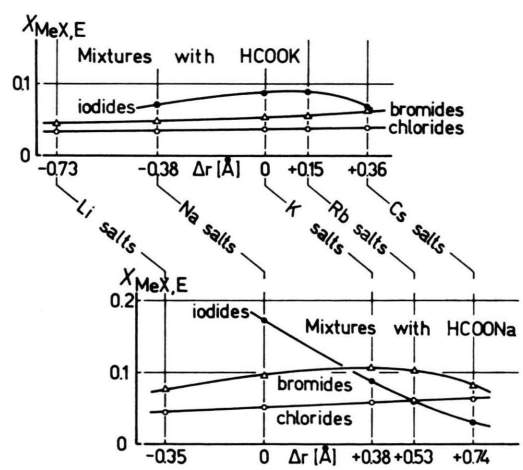

Fig. 3. Eutectic compositions as a function of the differences Δr.

The qualitative dependence of the eutectic compositions, $x_{\mathrm{MeX,E}}$, upon the difference $\Delta r = r_{\mathrm{Me}^+} - r_{\mathrm{K}^+}$ or $r_{\mathrm{Me}^+} - r_{\mathrm{Na}^+}$, respectively for the mixtures containing K or Na formate, is shown in Fig. 3 (cationic radii, in Å, by JANZ [5]).

2. The topology of the liquidus area in the reciprocal ternary system K^+, $Na^+/HCOO^-$, Cl^- was so far unknown.

Solid-liquid equilibria were first taken along the sides and diagonals of the composition quadrilateral: however, 300 °C could never be exceeded, since the stability of the melts became unsatisfactory at higher temperatures. The results are summarized in Table 2.

Nineteen offdiagonal cuts, for which the compositions of the starting mixtures, the added components and the characteristic points are reported in Table 3, were then studied.

t (°C)	molar fractions of the second component salt in the mixtures: HCOOK + KCl (W side)	HCOONa + NaCl (E side)	HCOONa+HCOOK (S side) *	HCOOK + NaCl (NE-SW diag.)	HCOONa + KCl (NW-SE diag.)
$159._4$	—	—	—	0.034, E	—
$163._5$	0.037, E	—	0.957, E_1	—	—
$165._0$	—	—	0.505, E_2	—	—
$168._7$	0.—	—	1.—	0.—	—
$180._0$	—	—	0.750, m. p. 3HCOOK.HCOONa	—	—
180	0.043	—	0.444	0.042	—
200	0.051_5	—	0.342	0.050_5	—
220	0.061_5	—	0.237	0.060	—
240	0.072_5	—	0.116	0.071	—
$242._1$	—	—	—	—	0.058, E
$249._8$	—	0.051_5, E	—	—	—
$257._5$	—	0.—	0.—	—	0.—
260	0.084_5	0.056_5	—	0.082_5	0.070
280	0.097	0.067_5	—	0.095	0.086_5
300	0.111	0.079_5	—	0.109_5	0.104_5

Table 2. Sides and diagonals in the composition quadrilateral of the system K^+, $Na^+/HCOO^-$, Cl^-.

* Concerning HCOO(K, Na), O. I. DMITREVSKAYA, Zh. Obshch. Khim. **28**, 299 [1958], previously found E_1 at 167 °C and $x_{\mathrm{HCOOK}}=0.96$, and E_2 at 168 °C and $x_{\mathrm{HCOOK}}=0.495$. She found also: 167°, 258° and 182 °C as the melting points of HCOOK, HCOONa and 3 HCOOK·HCOONa, respectively.

Cut	Composition of the starting mixture (in mole)		Added component (ac)	Characteristic points x_{ac}	t (°C)	x_{ac}	t (°C)
VI	HCOOK + KCl	49.00 : 1	HCOONa	0.048	$160._5$	0.491	164
XII		29.30 : 1		0.046_5	$159._5$	0.487	$163._5$
XIII		21.22 : 1		—	—	0.485_5	$163._5$
IX	HCOOK + HCOONa	11.50 : 1	KCl	0.036_5	166	—	—
X		3.00 : 1		0.035_5	176	—	—
XI		1.27 : 1		0.030_5	168	—	—
XIV		1.06 : 1		0.030	164	—	—
VIII		0.25 : 1		0.070	$212._5$	—	—
I	HCOOK + HCOONa	3.00 : 1	NaCl	0.035	175	—	—
XIX		1.17 : 1		0.028_5	$163._5$	—	—
II		1.00 : 1		0.031_5	$169._5$	—	—
V		0.47 : 1		0.059	206	—	—
III		0.33 : 1		0.082_5	216	—	—
XVIII		0.31_5 : 1		0.081	$217._5$	—	—
IV		0.19 : 1		0.069_5	229	—	—
XV	HCOONa + NaCl	7.70 : 1	HCOOK	0.233	225	—	—
XVI		6.69 : 1		0.240_5	236	—	—
XVII		5.25 : 1		0.252	254	—	—
VII		4.00 : 1		0.273	$276._5$	—	—

Table 3. Cuts in the system K^+, $Na^+/HCOO^-$, Cl^-.

[5] G. J. JANZ, Molten Salts Handbook, Academic Press, New York 1967, p. 1.

The collected data (covering approximatively 12% of the liquidus area) were employed to draw the map in Fig. 4, where the projections of the cuts, the isotherms at 180, 200, ..., 300 °C and the curves of simultaneous crystallization are put into evidence.

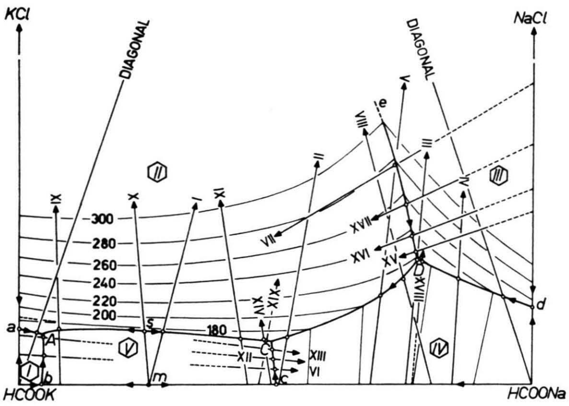

Fig. 4. Map of the liquidus area in the system K^+, $Na^+/HCOO^-$, Cl^- (the East and West sides are magnified three times with respect to the South one).

Five crystallization regions were apparent, of which the first, second and fifth ones touched in point *A* (a ternary eutectic at $158._5$ °C, whose composition was $x_{HCOOK} = 0.92_1$, $x_{HCOONa} = 0.04_5$ and $x_{KCl} = 0.03_4$); the second, fourth and fifth in point *C* (another ternary eutectic at 163 °C, and $x_{HCOOK} = 0.48_6$, $x_{HCOONa} = 0.48_5$ and $x_{KCl} = 0.02_9$); the second, third and fourth in point *D* (a transition point at 216 °C, and $x_{HCOOK} = 0.14_8$, $x_{HCOONa} = 0.77_0$ and $x_{KCl} = 0.08_2$).

The coordinates of the mentioned invariant points were deduced from the projections of the curves of simultaneous crystallization onto the East and South sides of the map, as drawn in the left and right section of Fig. 5, respectively.

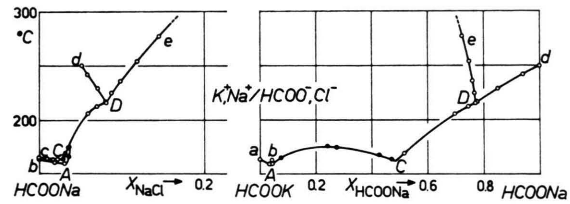

Fig. 5. Projections of the co-crystallization curves onto the East and South sides of the map.

It may be noted that the eutectic at 176 °C observed along the tenth cut [which is starting from the congruently melting compound

$$3\,HCOOK \cdot HCOONa$$

(point *m* in Fig. 4) and moving towards the KCl corner] represents a "saddle" in the eutectic valley connecting the ternary eutectics *A* and *C*: as a consequence the projection of this very cut onto the map should act as a triangulation line in the system.

Moreover, the fact that in the exchange reaction:

$$HCOOK + NaCl = HCOONa + KCl$$

the heat effect at 298.16 °K [deduced from the heats of formation ΔH_f^0(298.16 °K) [6] of the salts taken into account] was negative (−2.973 kcal/mole) suggested to select the NW−SE diagonal as the principal one (and, obviously, as the second triangulation line).

The first, fourth and fifth crystallization regions, whose boundaries could be fully drawn, occupy 0.17, 2.98 and 1.57% of the liquidus area, respectively.

[6] Nat. Bur. Stand. Circular **500**, U.S. Dept. Commerce, Washington 1952.