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

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By employing a visual method, solid-liquid equilibria were studied in a wide series of molten mixtures in order to draw the maps of the reciprocal systems formed with K, Na formates and bromides or iodides. Within the accessible portion of each system, five crystallization regions, three ternary eutectics and two saddle points were identified. The interdependence between the areas of some crystallization regions and the sizes of the halogen ions was put into evidence.

In the present paper we report on the topology of the liquidus areas in the reciprocal ternary systems $K^+, Na^+/HCOO^-, (Br^-, I^-)$.

Free energy data being unavailable, it was only possible to try to identify the stable pairs merely on the basis of the heats of formation of the component salts, which were tabulated [1] as follows:

for HCOOK ΔH_f^0(298.16 °K) = −158.0 kcal/mole

HCOONa	−155.03
KBr	− 93.73
NaBr	− 86.030
KI	− 78.31
NaI	− 68.84

Concerning the exchange reactions

$$HCOOK + NaBr = HCOONa + KBr$$

and

$$HCOOK + NaI = HCOONa + KI$$

heat effects (at 298.16 °K) of −4.73 and −6.50 kcal/mole respectively were easily deduced. As a consequence, the diagonals connecting the HCOONa with the KX corners ought to be the principal ones (and also act as triangulation lines), and the straight lines connecting the 3:1 congruently melting compound in the binary system HCOO(K, Na) [2] with the same KX corners ought to be triangulation lines too.

Should these conclusions be correct, and the three [3] invariant points expected within each composition quadrilateral be ternary eutectics, "saddles" were to be found along each of the mentioned lines. Now, though only about the seventh part of each liquidus area was accessible (since measurements at temperatures higher than 300 °C were prevented by the thermal unstability of the melts), the collected data seem to fit the picture outlined in a sactisfactory way.

Experimental

A visual method [4] was adopted to take the solid-liquid equilibrium temperatures of the mixtures, which were prepared with C. Erba RP chemicals carefully dried before use by heating under vacuum. The melting points of the formates were 168.$_7$ °C for HCOOK and 257.$_5$ °C for HCOONa.

Results

In each composition quadrilateral, 21 offdiagonal cuts were studied: the characteristics of those referring to the bromide containing and to the iodide containing system are summarized in Table 1 and 2, respectively.

Taking also into account a few previous data [2] concerning the sides and diagonals of the quadrilaterals, it was possible to draw maps (see Fig. 1 and Fig. 2, in which, to put details into a better evidence, y was taken equal to $3x$), where the projections of the cuts and the isotherms at 160, 180, ..., 300 °C are shown, as well as the crystallization regions and the curves of simultaneous crystallization.

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

[2] Note I of the present series: D. LEONESI, M. BRAGHETTI, A. CINGOLANI, and P. FRANZOSINI, Z. Naturforsch. **25 a**, 52 [1970].

[3] Obviously, this figure is correct only if no intermediate compounds (but 3 HCOOK·HCOONa) are formed.

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

Cut	Composition of the starting mixture (in mole)		Added component (ac)	Characteristic points			
				x_{ac}	t (°C)	x_{ac}	t (°C)
XVII	HCOOK + KBr	39.49 : 1	HCOONa	0.044_5	159	—	—
IV		24.00 : 1		0.046	158	0.482	163.5
VIII	HCOOK + HCOONa	48.95 : 1	KBr	0.051	160	—	—
XX		24.06 : 1		0.049	157	—	—
VII		13.30 : 1		0.049	163.5	—	—
XXI		3.96 : 1		0.045_5	174.5	—	—
III		3.00 : 1		0.043_5	175.5	—	—
XVIII		1.37 : 1		0.033	169	—	—
XVI		1.03_5 : 1		0.028_5	163	—	—
XIV		1.00 : 1		0.028_5	166	—	—
II	HCOOK + HCOONa	3.00 : 1	NaBr	0.041	175	—	—
XV		0.67 : 1		0.035_5	191	—	—
VI		0.43 : 1		0.046	210	—	—
V		0.25 : 1		0.064_5	225	—	—
I		0.06_4 : 1		0.113	235.5	—	—
IX		0.02_0 : 1		0.103	240.5	—	—
X	HCOONa + NaBr	6.69 : 1	HCOOK	0.079	232	0.091	230.5
XIII		6.19 : 1		0.089	233.5	—	—
XI		5.67 : 1		0.095	243	—	—
XII		4.94 : 1		0.105_5	255	—	—
XIX		3.69_5 : 1		0.127	283.5	—	—

Table 1. Cuts in the system K^+, $Na^+/HCOO^-$, Br^-.

Cut	Composition of the starting mixture (in mole)		Added component (ac)	Characteristic points			
				x_{ac}	t (°C)	x_{ac}	t (°C)
XI	HCOOK + KI	13.27 : 1	HCOONa	0.042	154	0.466	163
XVIII	HCOOK + HCOONa	49.00 : 1	KI	0.084	154.5	—	—
XIX		23.96 : 1		0.078_5	153	—	—
XIV		20.69 : 1		0.080	154	—	—
XII		13.34 : 1		0.080	161	—	—
I		3.00 : 1		0.065	173.5	—	—
X		1.00 : 1		0.038	166	—	—
II	HCOOK + HCOONa	3.00 : 1	NaI	0.059	172.5	—	—
XX		1.50 : 1		0.042_5	166.5	—	—
IX		0.43 : 1		0.045	212	—	—
IV		0.25 : 1		0.054	227.5	—	—
III		0.06_4 : 1		0.132	233.5	—	—
XVI		0.03_7 : 1		0.182	226	—	—
XV		0.02_0 : 1		0.178	226.5	—	—
V	HCOONa + NaI	19.00 : 1	HCOOK	0.521	164	—	—
XXI		13.29 : 1		0.530	163.5	—	—
VII		4.26 : 1		0.033	226.5	—	—
VI		4.00 : 1		0.036	235.5	0.706	173
VIII		3.76 : 1		0.040	243.5	—	—
XIII		3.17 : 1		0.049_5	269	—	—
XVII	HCOONa + NaI	6.14 : 1	KI	0.036_5	227.5	—	—

Table 2. Cuts in the system K^+, $Na^+/HCOO^-$, I^-.

By projecting the latter onto the East and South sides (see Fig. 3), we were enabled to identify the coordinates of the invariant points as follows:

in the system K^+, $Na^+/HCOO^-$, Br^-

point A at 156 °C ($x_{HCOOK} = 0.90_4$; $x_{KBr} = 0.04_8$; $x_{HCOONa} = 0.04_8$)
point C at 163 °C ($x_{HCOOK} = 0.49_7$; $x_{KBr} = 0.02_9$; $x_{HCOONa} = 0.47_4$)
point D at 230 °C ($x_{NaBr} = 0.03_4$; $x_{KBr} = 0.08_8$; $x_{HCOONa} = 0.87_8$)

in the system K^+, $Na^+/HCOO^-$, I^-

point A at 153 °C
point C at 163 °C
point D at 226 °C

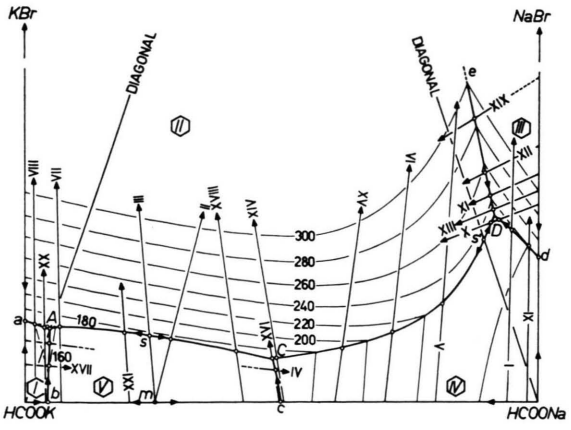

Fig. 1. Map of the system K^+, $Na^+/HCOO^-$, Br^-.

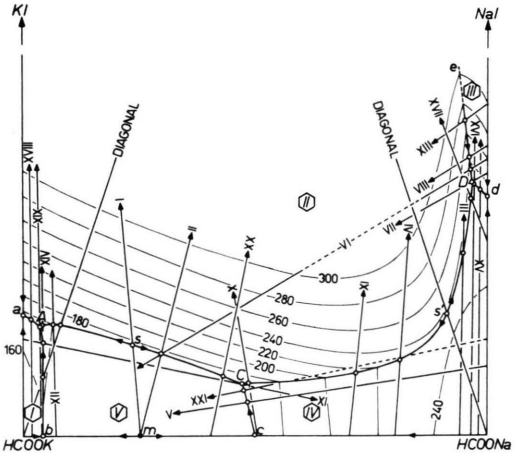

Fig. 2. Map of the system K^+, $Na^+/HCOO^-$, I^-.

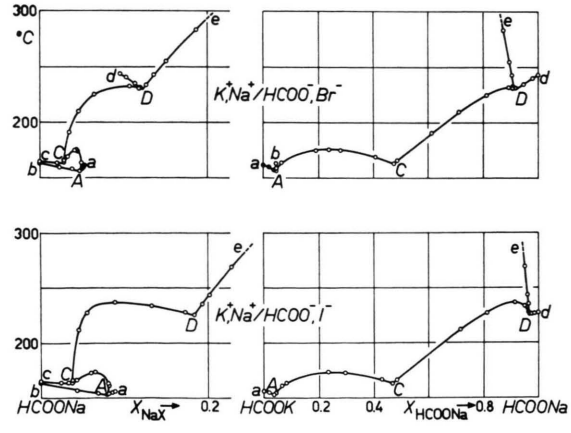

Fig. 3. Projections of the co-crystallization curves on the East and South sides of the map.

$(x_{HCOOK} = 0.88_4;\ x_{KI} = 0.07_9;\ x_{HCOONa} = 0.03_7)$
$(x_{HCOOK} = 0.49_6;\ x_{KI} = 0.03_7;\ x_{HCOONa} = 0.46_7)$
$(x_{NaI} = 0.14_8;\ x_{KI} = 0.03_5;\ x_{HCOONa} = 0.81_7)$

All of the invariant points were ternary eutectics. In each system, both the eutectic valley connecting *A* and *C*, and that connecting *C* and *D* exhibited a (relative) maximum (saddle points *s* and *s'* respectively; see Fig. 1 and 2), in agreement with what discussed in the introductory section.

The co-crystallization curves were (in each system) the boundaries of five crystallization regions, two of which could be only partially, and three were thoroughly investigated.

Let us now compare the areas of the latter with one another and with those of the corresponding regions in the homologous system containing (K, Na) Cl [2] (see Table 3). As Cl^- is successively replaced by

System	Crystallization region	% liquidus area
K^+, $Na^+/HCOO^-$, Cl^-	(I)	0.17
	(IV)	2.98
	(V)	1.57
K^+, $Na^+/HCOO^-$, Br^-	(I)	0.24
	(IV)	3.31
	(V)	1.88
K^+, $Na^+/HCOO^-$, I^-	(I)	0.35
	(IV)	3.39
	(V)	2.70

Table 3. Areas of a number of crystallization regions (in % of the total liquidus area).

Br^- and I^-, the area α (I) of the first region increases exhibiting a first power dependence upon the X^- radius (see Fig. 4). The fact is also noteworthy that, though $\alpha(IV) = f(r_{X^-})$ and $\alpha(V) = f(r_{X^-})$ are not straight lines, the sum $[\alpha(IV) + \alpha(V)]$ is still linearly depending upon r_{X^-}.

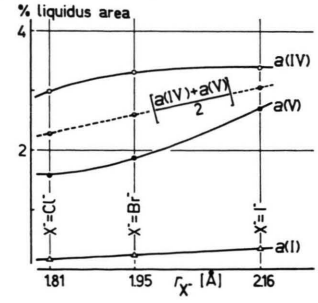

Fig. 4. Dependence of the areas of the crystallization regions upon r_{X^-} (halogen ion radii by JANZ [5]).

The only observed intermediate compound was the already known [2] congruently melting binary 3 HCOOK·HCOONa (point m in Fig. 1 and 2), to whom the fifth crystallization region belongs.

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