The Ternary System K(CNS, HCOO, NO_3)

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As a part of our current researches, we report in the present paper on solid-liquid equilibria in the K(CNS, HCOO, NO_3) ternary system.

Experimental

A visual method was adopted, the details of which were given in a previous paper [1]. Moreover, in the present investigation we used, whenever necessary to get more complete information, a Perkin Elmer differential scanning calorimeter (DSC-1B).

Merck recrystallized KCNS, and C. Erba HCOOK and KNO_3, carefully dried before used were employed.

Potassium formate melted at 168.7 °C, and potassium thiocyanate at 176.0 °C, both in agreement with recent literature data [2, 3].

Results and Discussion

Previous authors formerly referred on the side systems. As for KCNS + KNO_3 and HCOOK + KCNS mixtures [3, 4] satisfactory and complete data were available, while, concerning HCOOK + KNO_3, we already observed [2] (within the molar fraction range $0 \leqq X_{KNO_3} \leqq 0{,}2$) considerable differences from the figures by DMITREVSKAYA [5]. Then, we thought it necessary to study the mentioned system thoroughly again (see Table 1).

X_{KNO_3}	t °C	X_{KNO_3}	t °C
0.000	168.7	0.365	115.9
0.053	161.6	0.376	114.3
0.102	154.3	0.388	118.6
0.155	146.0	0.400	124.5
0.179	142.3	0.426	138.0
0.204	138.0	0.479	163.4
0.225	133.9	0.500	173.4
0.238	131.2	0.554	196.2
0.252	128.5	0.600	212.5
0.275	125.9	0.630	221.6
0.303	123.3	0.660	232.9
0.315	122.2	0.697	245.5
0.325	120.9	0.746	261.0
0.350	118.1	0.800	278.1

Table 1. Liquidus curve of the binary system * K(HCOO, NO_3).

* Measurements at $t > 280$ °C could not be taken owing to the thermal unstability of the melts.

According to DMITREVSKAYA, the congruently melting compound 2 HCOOK·KNO_3, and eutectics at 150 °C ($X_{HCOOK} = 0.675$) and at 146 °C ($X_{KNO_3} = 0.440$) ought to be found. We observed, on the contrary, only a discontinuity at 126.5 °C ($X_{KNO_3} = 0.262$) and eutectic at 114 °C ($X_{KNO_3} = 0.379$). The composition of the incongruently melting compound detected by us seemed to be 4 HCOOK·KNO_3, and was confirmed by differential calorimetric measurements.

In order to give a picture of the simultaneous crystallization and isothermal curves in the K(CNS, HCOO, NO_3) system, solid-liquid equilibria were measured along 14 internal cuts. The results are summarized in

Cut	Composition of the starting mixture (in mole)		Added Component (ac)	Characteristic points			
				x_{ac}	t (°C)	x_{ac}	t (°C)
I	KCNS+KNO_3	4.00 : 1	HCOOK	0.515	$66._5$		
II	KCNS+HCOOK	4.55 : 1	KNO_3	0.300	$111._5$		
III	KCNS+HCOOK	1.78 : 1	KNO_3	0.252	90		
IV	KCNS+HCOOK	1.00 : 1	KNO_3	0.209	$71._5$		
V	KCNS+HCOOK	0.79 : 1	KNO_3	0.040	$71._5$	0.182	$58._5$
VI	KCNS+HCOOK	0.69 : 1	KNO_3	0.179	$57._5$		
VII	KCNS+HCOOK	0.61 : 1	KNO_3	0.199	63		
VIII	KCNS+HCOOK	0.56 : 1	KNO_3	0.207	67		
IX	KCNS+HCOOK	0.51 : 1	KNO_3	0.206	71	0.216	70
X	KCNS+HCOOK	0.49 : 1	KNO_3	0.202	76	0.226	76
XI	KCNS+HCOOK	0.35 : 1	KNO_3	0.200	90	0.257	84
XII	KCNS+HCOOK	0.14 : 1	KNO_3	0.240	109	0.325	$102._5$
XIII	HCOOK+KNO_3	15.67 : 1	KCNS	0.426	74		
XIV	HCOOK+KNO_3	3.00 : 1	KCNS	0.350	57		

Table 2. Cuts in the system K(CNS, HCOO, NO_3).

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

[2] D. LEONESI, G. PIANTONI, G. BERCHIESI, and P. FRANZOSINI, Ric. Sci. **38**, 702 [1968].

[3] G. PIANTONI, M. BRAGHETTI, and P. FRANZOSINI, Ric. Sci. **38**, 942 [1968].

[4] M. BRAGHETTI, G. BERCHIESI, and P. FRANZOSINI, Ric. Sci. **39**, 576 [1969].

[5] O. I. DMITREVSKAYA, Zhur. Obshchei Khim. **28**, 299 [1958].

Table 2, while the projections of the characteristic points, observed along each cut, are shown in Fig. 1. The collected data were employed to draw the map in Fig. 2.

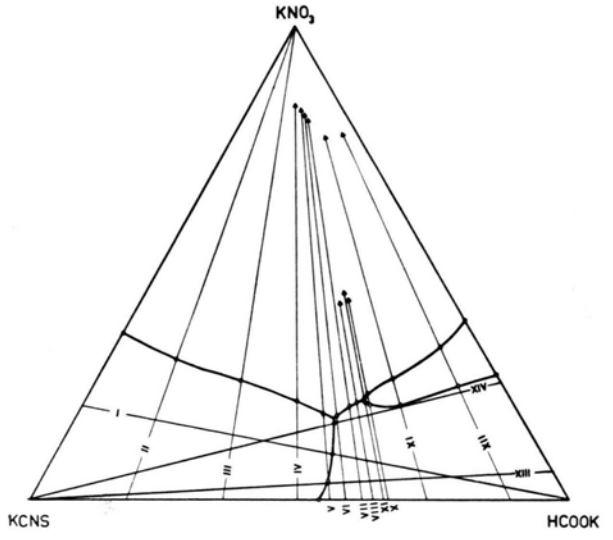

Fig. 1. Cuts in the K(CNS, HCOO, NO_3) ternary system.

Four crystallization regions (whose areas, expressed in % of the total area of the triangle, are reported in Table 3) were apparent, the first, second and fourth belonging to potassium thiocyanate, nitrate and formate respectively, and the third to the compound 4 HCOOK $\cdot KNO_3$.

Region	1	2	3	4
%	26.27	53.39	3.55	16.79

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

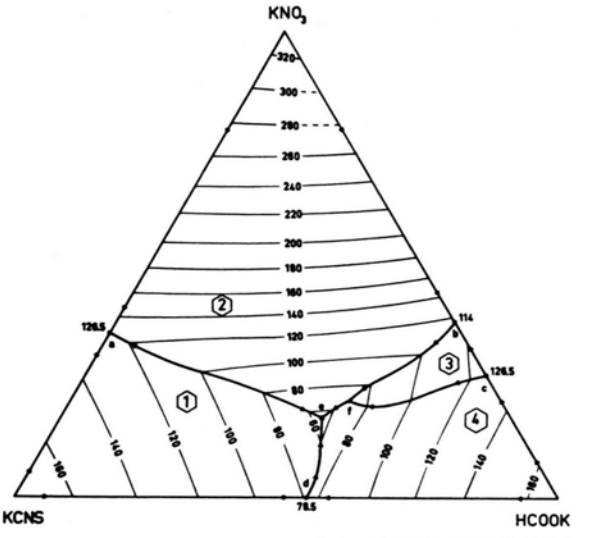

Fig. 2. Map of the liquids area of the K(CNS, HCOO, NO_3) ternary system.

Two ternary invariant points were also put into evidence, the co-ordinates of which were determined by projecting the co-crystallization curves onto two sides: their melting temperatures were then confirmed by measuring the melting points of samples of the detected compositions. The data concerning the ternary eutectic e and the transition point f are reported in Table 4.

Point	Composition		Temp. °C
	X_{KCNS}	X_{HCOOK}	
e	0.349	0.483	$55._5$
f	0.276	0.516	$69._0$

Table 4. Coordinates of the invariant points.