CdI_2 were introduced as T_f into Equation 3. This is possible since the difference between the melting temperature of the pure salts and the eutectic temperature of their solutions with cadmium is relatively small. The values of k calculated by the interpolation of excess volumes at temperatures T_{corr} assuming $\alpha = 1.2$ are 15.3 ± 1.4 cm^3/mol and -4.6 ± 1.3 cm^3/mol for solutions of cadmium in its chloride and iodide. For the bromide the k value may be considered practically zero. In other words, the excess volume is distinctly positive for Cd–$CdCl_2$ solutions, equals zero for Cd–$CdBr_2$, and is negative for the Cd–CdI_2 systems.

A general theory concerning excess volumes in ionic liquid solutions does not yet exist. A comparison of excess volumes for solutions of several metals in their molten halides may contribute some progress in this field. This requires further experimental research.

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Ternary Systems of Sodium Thiocyanate, Formate, and Halides

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For various mixtures solid-liquid equilibria were studied by a visual method to draw the polythermal projections of ternary systems formed with sodium thiocyanate, formate, and halides. Four crystallization regions and two invariant points were identified within the accessible portion of each system. The areas of crystallization regions are considered in their relationship to the radius of the halogen ions.

This paper, a portion of our current research, reports on solid-liquid equilibria in the Na(CNS,HCOO,Cl), Na(CNS,HCOO,Br), and Na(CNS,HCOO,I) ternary systems.

EXPERIMENTAL

The crystallization temperatures of the melted mixtures were taken when the first crystals were formed. The measurements were carried out by a visual method described previously (*1*). The melts were frozen at a rate of nearly 0.25°C per minute, and only those values in agreement within ±0.25°C were accepted for the crystallization temperature. This temperature was determined by a Chromel-Alumel thermocouple, checked by comparison with an NBS-certified platinum resistance thermometer and connected with a Leeds and Northrup type of K-3 potentiometer.

An accuracy in temperature within ±0.05°C was possible by this method of calibration of the thermocouple. The furnace temperature for the melting of the salt mixtures contained in a pyrex cryostat was controlled by a second thermocouple connected with a Leeds and Northrup CAT control unit.

To avoid readjustment of the furnace temperature automatic control device, an auxiliary heater was used for a quick remelting of the salt mixture, partially frozen in the course of a previous run. When necessary to obtain more complete information, a Perkin-Elmer differential scanning calorimeter (DSC-1B) was used. The chemicals NaCNS, HCOONa, NaCl, NaBr, and NaI, whose purity was not less than 99%, were carefully dried before use. Sodium formate melted at 257.5°C and sodium thiocyanate at 307.5°C, both in agreement with recent literature data [257.5°C (*6*) and 258.0°C (*3*) for HCOONa and 307.5°C (*7, 8*) for NaCNS].

RESULTS AND DISCUSSION

For NaCNS + NaX and HCOONa + NaX (where X = Cl, Br, I) mixtures (*8, 5*), satisfactory and complete data were available. No references concerning the NaCNS + HCOONa system exist in the literature; thus, our study is the first of this system. The results are summarized in Table I. A

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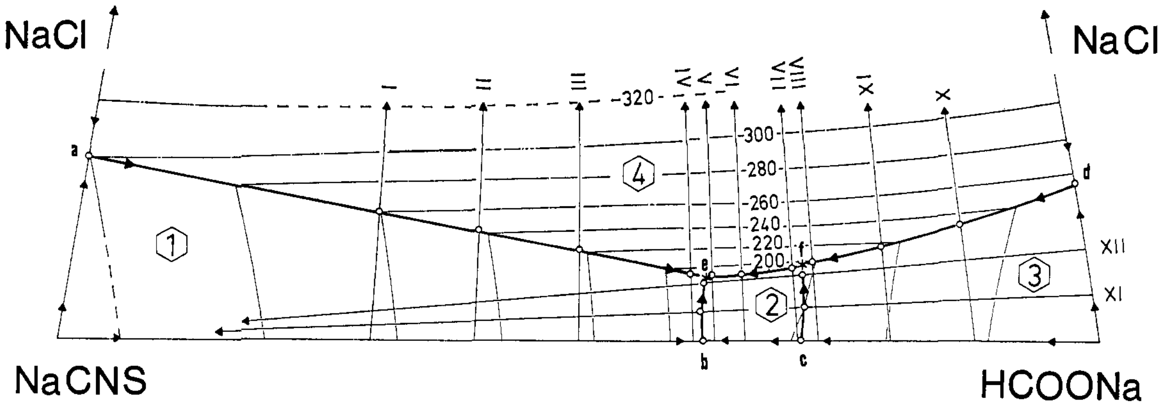

Figure 1. Polythermal projection of Na(CNS,HCOO,Cl) system

Table I. Liquidus Curve of Na(HCOO,CNS) Binary System[a]

X_{NaCNS}, mole fraction	Temp, °C	X_{NaCNS}, mole fraction	Temp, °C	X_{NaCNS}, mole fraction	Temp, °C	X_{NaCNS}, mole fraction	Temp, °C
0.000	257.5	0.389	193.0	0.302	199.5	0.500	223.5
0.045	251.0	0.391	193.0	0.321	197.0	0.530	231.0
0.101	241.0	0.410	199.0	0.342	195.0	0.544	234.5
0.146	232.5	0.424	203.5	0.348	194.0	0.577	241.0
0.201	221.0	0.427	203.5	0.351	193.0	0.655	257.0
0.239	212.0	0.457	213.0	0.373	190.5	0.729	268.5
0.282	202.5	0.478	217.0	0.381	189.5		

[a] Measurements at temp > 280°C could not be taken owing to thermal unstability of melts.

Table II. Sections in Na(CNS,HCOO,Cl), Na(CNS,HCOO,Br), and Na(CNS,HCOO,I) Systems

				Characteristic points			
Section	Composition of starting mixture, in mole		Added component, ac	x_{ac}, mole fraction	Temp, °C	x_{ac}, mole fraction	Temp, °C
			Na(CNS,HCOO,Cl)				
I	NaCNS + HCOONa	2.33:1	NaCl	0.042	260.0		
II	NaCNS + HCOONa	1.50:1		0.036	243.5		
III	NaCNS + HCOONa	1.00:1		0.029	222.5		
IV	NaCNS + HCOONa	0.64:1		0.022	192.0		
V	NaCNS + HCOONa	0.59:1		0.025	189.5		
VI	NaCNS + HCOONa	0.52:1		0.022	192.5		
VII	NaCNS + HCOONa	0.41:1		0.024	198.0		
VIII	NaCNS + HCOONa	0.37:1		0.026	200.5		
IX	NaCNS + HCOONa	0.25:1		0.031	216.0		
X	NaCNS + HCOONa	0.14:1		0.038	232.5		
XI	HCOONa + NaCl	64.96:1	NaCNS	0.277	200.0	0.380	187.5
XII	HCOONa + NaCl	32.33:1		0.274	199.0	0.370	186.5
			Na(CNS,HCOO,Br)				
I	NaCNS + HCOONa	2.33:1	NaBr	0.071	257.5		
II	NaCNS + HCOONa	1.00:1		0.051	218.0		
III	NaCNS + HCOONa	0.66:1		0.041	193.5		
IV	NaCNS + HCOONa	0.52:1		0.041	189.0		
V	NaCNS + HCOONa	0.43:1		0.046	193.5		
VI	NaCNS + HCOONa	0.35:1		0.048	199.5		
VII	NaCNS + HCOONa	0.32:1		0.052	203.5		
VIII	NaCNS + HCOONa	0.14:1		0.071	226.0		
IX	HCOONa + NaBr	49.00:1	NaCNS	0.270	200.5	0.380	187.0
X	HCOONa + NaBr	24.00:1		0.269	197.5	0.370	186.0
			Na(CNS,HCOO,I)				
I	NaCNS + HCOONa	2.33:1	NaI	0.129	251.0		
II	NaCNS + HCOONa	1.00:1		0.105	215.5		
III	NaCNS + HCOONa	0.61:1		0.088	185.5		
IV	NaCNS + HCOONa	0.52:1		0.088	180.5		
V	NaCNS + HCOONa	0.41:1		0.097	187.0		
VI	NaCNS + HCOONa	0.32:1		0.105	192.0		
VII	NaCNS + HCOONa	0.20:1		0.123	203.5		
VIII	HCOONa + NaI	19.00:1	NaCNS	0.256	199.0	0.362	184.5
IX	HCOONa + NaI	9.00:1		0.240	193.0	0.338	181.0
X	HCOONa + NaI	7.24:1		0.232	191.5	0.333	180.5

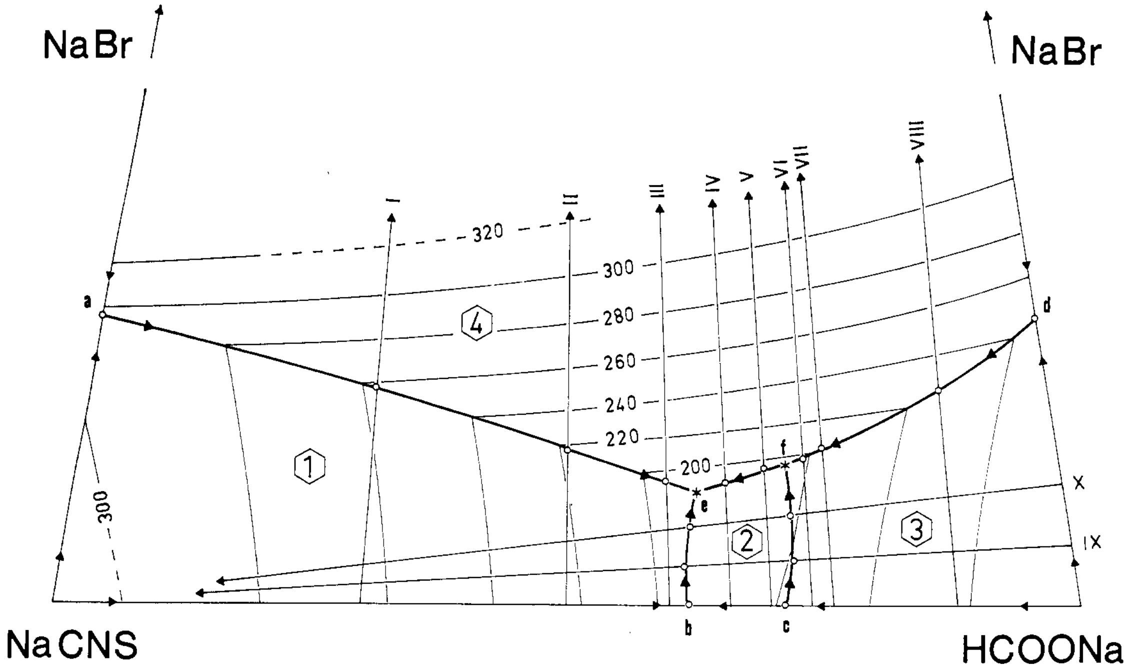

Figure 2. Polythermal projection of Na(CNS, HCOO, Br) system

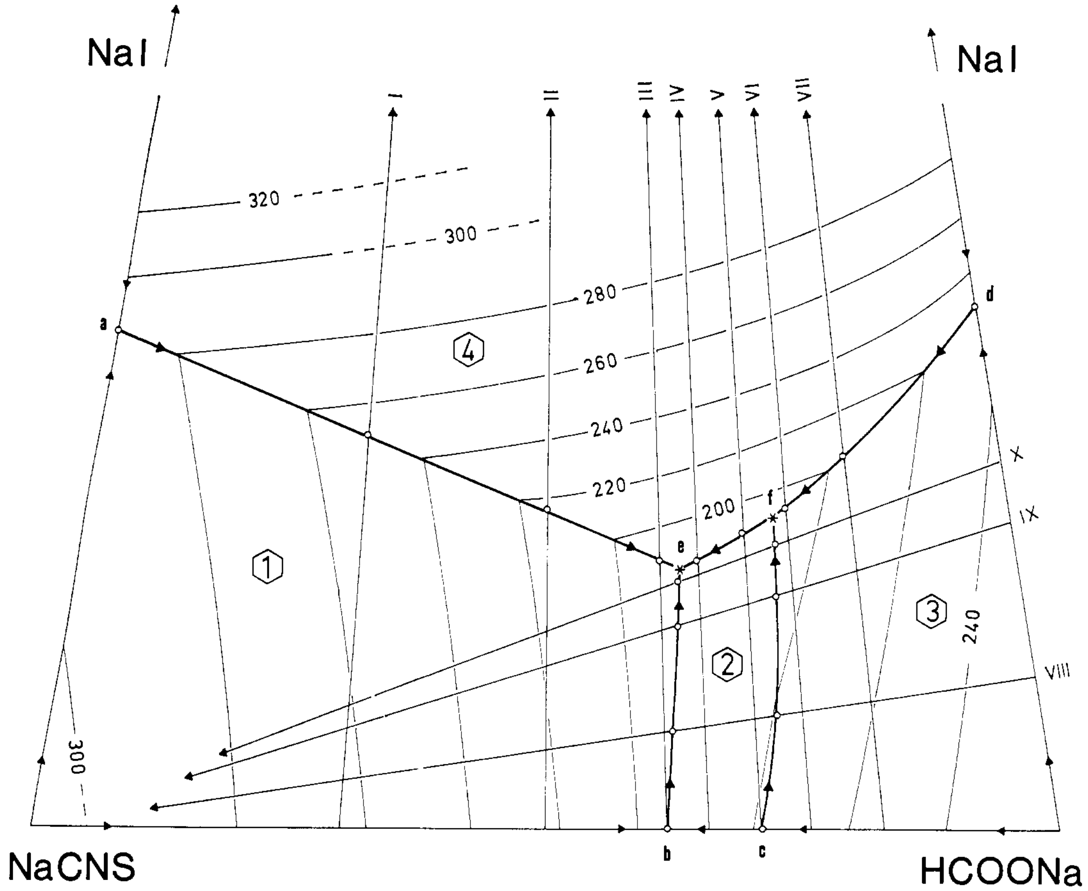

Figure 3. Polythermal projection of Na(CNS,HCOO,I) system

discontinuity at 200.8°C ($X_{\mathrm{NaCNS}} = 0.286$) and a eutectic at 189.5°C ($X_{\mathrm{NaCNS}} = 0.380$) were observed. The detected composition of the incongruently melting compound seemed to be 4HCOONa·NaCNS and was confirmed by differential scanning calorimeter measurements.

To give a picture of the simultaneous crystallization and isothermal curves, solid-liquid equilibria in the Na(CNS,HCOO,Cl) system were measured along 12 internal sections, in the Na(CNS,HCOO,Br) system along 10 sections, and in the Na(CNS,HCOO,I) system along 10 sections. The results are summarized in Table II.

In Figures 1, 2, and 3, respectively, is reported the polythermal projection of the Na(CNS,HCOO,Cl), Na(CNS,HCOO,Br), and Na(CNS,HCOO,I) systems. The sections

Table III. Coordinates of Invariant Points

System	Point	Composition X_{NaCNS}, mole fraction	Composition X_{HCOONa}, mole fraction	Temp, °C
Na(CNS,HCOO,Cl)	e	0.367	0.613	186.0
	f	0.273	0.702	198.5
Na(CNS,HCOO,Br)	e	0.356	0.607	185.0
	f	0.267	0.687	195.0
Na(CNS,HCOO,I)	e	0.328	0.586	180.0
	f	0.231	0.667	190.5

Table IV. Areas of Crystallization Region

System	Crystallization region	% Liquidus area
Na(CNS,HCOO,Cl)	1	4.95
	2	0.45
	3	2.00
Na(CNS,HCOO,Br)	1	8.10
	2	0.80
	3	3.65
Na(CNS,HCOO,I)	1	14.80
	2	1.80
	3	6.65

carried out and the characteristic points evident along each section are reproduced. The arrows show the direction of the falling temperature on the univariant curves a–e, b–e, c–f, d–f, f–e and on the binary sides of the system. The contour curves are isotherms. To make the details more evident, the two sides are magnified three times with respect to the base.

Four crystallization regions were apparent in each system. The first and third regions were sodium thiocyanate and formate, respectively, and the second, the compound 4HCOONa·NaCNS. The fourth region, the sodium halides, was investigated up to approximately 320°C since the salts which stabilize at lower temperatures showed unsatisfactory stability at higher temperatures.

The area observed was about $^1/_{10}$th of the triangle's total area for the Na(CNS,HCOO,Cl) system, $^1/_6$th for the Na(CNS, HCOO,Br) system, and $^1/_5$th for the Na(CNS,HCOO,I) system. Also evident in the observed area of the triangle were two ternary invariant points, the coordinates of which are determined by projecting the cocrystallization curves on 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 III.

The areas A(1), A(2), and A(3), expressed in percentages of the triangle's total area, are reported in Table IV. The dependence between the crystallization areas and the radius (*4*) of the halogen ions (Figure 4a) is different for each area and nearly linear only for A(1). By comparing the areas of the analogous systems K(CNS,HCOO,*X*) (where *X* = Cl, Br, I) (*2*) with the areas of the systems discussed here, we see that the area's sum, not related to the halides A′(1) and A′(3) for the systems with potassium salts, shows a linear dependence on the halogen radius. However, the area's sum, not related to the halides A(1), A(2), and A(3) for the systems with sodium salts, does not show a linear dependence on the halogen radius (Figure 4b).

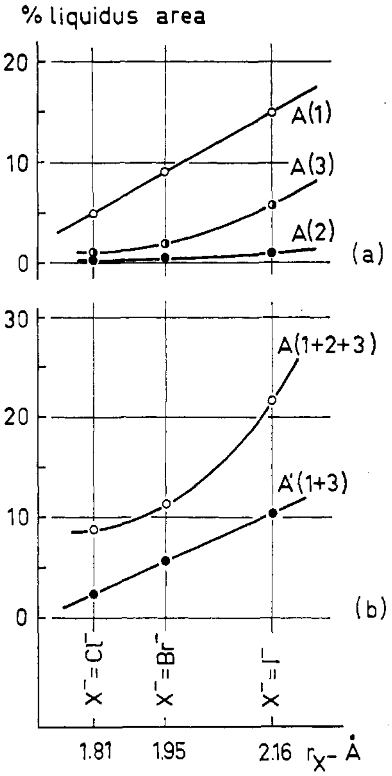

Figure 4. a. Dependence of areas of crystallization regions upon r_x. b. Comparison between area's sum A(1 + 2 + 3), this work, and area's sum A′(1 + 3) of previous work (2)

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