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# Cryoscopic and Volumetric Behavior of Acetamide–(Na,K)CNS Binary Systems

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**The liquid–solid equilibriums and the density of the acetamide–NaCNS and acetamide–KCNS binary systems were studied. The thermodynamic cryoscopic constant, obtained from the calorimetric measurements of $\Delta H_{\text{fus}}$, was compared with the cryoscopic experimental lowering. Density values were used to calculate the partial molar volumes of the thiocyanates.**

## Introduction

As a part of a larger-scale research on electrolytic solutions in molten acetamide, we report in this note the results of cryoscopic and densimetric measurements of binary systems between acetamide and potassium and sodium thiocyanates, with the aim of taking these mixtures into consideration as solvents for analytical research.

## Experimental Methods

The experimental methods have been fully described in preceding publications (*1*–*3*).

***Cryoscopy.*** The Pyrex apparatus is described in detail in a previous note (*3*). Briefly it consists of an external jacket, an auxiliary heating device, a test vessel, a head, a mixing device, and a furnace. The jacket is fastened to the furnace and is supplied with a couple of thin Pt tubes and with a flange. On the inside edge of this flange lies the flange of the test vessel, whose lower end, surrounded with the auxiliary heating device, can be observed through the windows of the furnace. The head is supplied with a flange and three tubings (the first, through which dry $N_2$ is blown; the second, where the solute pills are placed and then pushed in the test vessel by means of a magnet; the third, through which a mixer is run). The mixer consists of a Pyrex road connected to a vibromixer, whose frequency of vibration may be regulated; the chromel–alumel thermocouple is placed inside this road, and it is checked by comparison with a NBS-certified Pt-resistance thermometer and connected with a Leeds & Northrup K3 potentiometer. The furnace is controlled by means of a second thermocouple, together with a Leeds & Northrup CAT control unit. The auxiliary heater is used for a quick remelting of the mixture partially frozen in a previous run. For the measurements carried out at less than room temperature, the furnace was substituted by a container with double glass walls (Dewar type) (*4*), containing oil of vaseline, thermoregulated by the circulation between the double walls of a thermostatic liquid of a KIR Lauda thermostat.

The following technique is employed. The molten mixture is cooled at ~0.25 K/min, and the temperature is continuously read. A small crystalline seed is casted in the mixture, near the freezing point, and the mixture is observed through the windows. Sometimes the frequency of vibration of the mixer must be increased; the temperature corresponding to the appearance of the first crystals is taken. At this temperature, if the melt is a pure substance, a stop of the cooling is observed (practically also if the melt is a dilute solution). All measurements are repeated 2 or 3 times, and the agreement is within 0.03 °C when the melting temperature is obtained as a stop of the cooling (dilute solutions), or within 0.1 °C when the visual method is adopted.

Table I. Liquid–Solid Equilibrium Temperatures in the Binary Systems

| $x_2$ | $T$, K | $x_2$ | $T$, K |
|---|---|---|---|
| | $CH_3CONH_2$–NaCNS | | |
| 0.5005 | 505.5 | 0.1999 | 304.8 |
| 0.4516 | 481.9 | 0.1800 | 310.2 |
| 0.4002 | 451.4 | 0.1502 | 322.2 |
| 0.3850 | 435.9 | 0.0995 | 335.8 |
| 0.3506 | 395.4 | 0.0490 | 344.9 |
| 0.3400 | 377.7 | 0.0291 | 348.3 |
| 0.3203 | 325.2 | 0.0231 | 349.1 |
| 0.2998 | 322.9 | 0.0171 | 349.3 |
| 0.2750 | 316.5 | 0.0114 | 350.2 |
| 0.2499 | 302.1 | 0.0056 | 350.9 |
| 0.2249 | 289.5 | 0.0000 | 352.0 |
| | $CH_3CONH_2$–KCNS | | |
| 1.0000 | 447.8 | 0.4502 | 394.8 |
| 0.9902 | 446.6 | 0.3998 | 382.0 |
| 0.9803 | 445.8 | 0.3497 | 368.0 |
| 0.9700 | 444.6 | 0.3023 | 341.3 |
| 0.9694 | 444.4 | 0.2699 | 314.8 |
| 0.9573 | 442.9 | 0.2031 | 312.6 |
| 0.9516 | 443.2 | 0.1624 | 323.5 |
| 0.9226 | 439.4 | 0.1505 | 325.7 |
| 0.8957 | 437.6 | 0.0986 | 336.7 |
| 0.8500 | 434.4 | 0.0502 | 345.0 |
| 0.8093 | 431.7 | 0.0378 | 346.8 |
| 0.7498 | 427.2 | 0.0230 | 349.2 |
| 0.7015 | 424.4 | 0.0177 | 349.7 |
| 0.6532 | 419.9 | 0.0090 | 350.8 |
| 0.6008 | 415.2 | 0.0088 | 351.0 |
| 0.5495 | 408.9 | 0.0062 | 351.2 |
| 0.5036 | 403.8 | 0.0000 | 352.0 |

***Density.*** The buoyancy method described in the literature (*5*) and previously reported (*1*) was used. A double steel cone was connected by a 0.05-mm steel wire and a gold chain to a Mettler H 20 T balance. The double cone was calibrated according to liquids of known density by using the values given by Janz as described before (*1*).

***Calorimetry.*** The fusion enthalpy was measured by means of a Perkin-Elmer DSC-1B differential calorimeter. The calibrations have been previously reported (*4*). The products used were Merck extrapure acetamide, Merck GR KCNS, and Baker analyzed reagent NaCNS, used without further purification. NaCNS and KCNS were hot dried under dynamic vacuum. The acetamide was dried for several days under dynamic vacuum at room temperature. In this note, 1 stands for acetamide, and 2 stands for the other component.

## Results and Discussion

The temperatures of the liquid–solid equilibrium were studied over the range $0 \le x_1 \le 1$ for the system with KCNS, and the range $0.5 < x_1 \le 1$ for the system with NaCNS, for reasons of thermal stability. The experimental values of the temperatures of the solid–liquid equilibriums are given in Table I, while in Figure 1 are given the relative trends.

The acetamide–NaCNS binary system exhibits an inflection point (A) in the crystallization branch of the NaCNS, attributable

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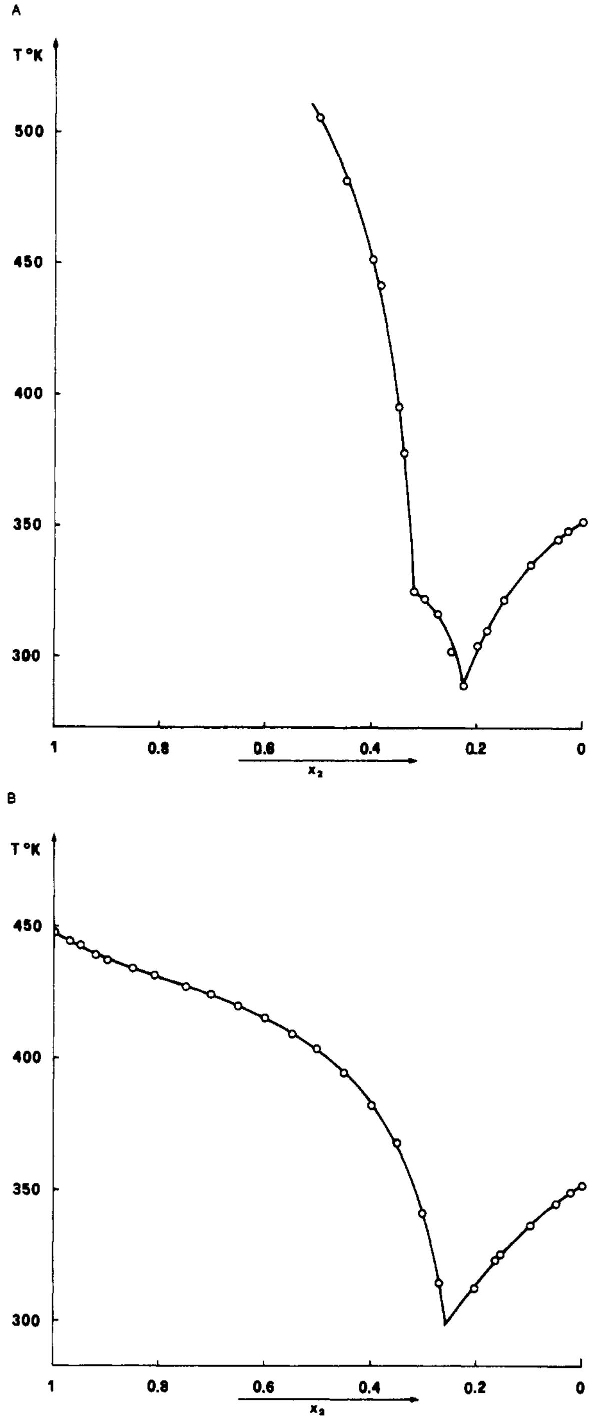

**Figure 1.** Liquid–solid equilibrium curves in the binary systems: (A) $CH_3CONH_2$–NaCNS; (B) $CH_3CONH_2$–KCNS.

Table II. Coordinates of the Invariant Points

| | $CH_3CONH_2$-NaCNS | $CH_3CONH_2$-KCNS |
|---|---|---|
| $x_{2,\mathrm{eut}}$ | 0.225 | 0.260 |
| $T_{\mathrm{eut}}$ (K) | 288.0 | 298.5 |
| $x_{2,\mathrm{per}}$ | 0.320 | |
| $T_{\mathrm{per}}$ (K) | 325.0 | |

perhaps to the formation of an intermediate compound, given that the existence of a solid–solid transition at that temperature did not show up (*6*). The mixtures in the concentration range between point A and the eutectic must be shaken vigorously owing to a tendency of these mixtures to overcool. In Table II the coordinates of the eutectic and peritectic points of the solutions studied are given. The fusion thermograms of the acetamide are of λ type whose diffusion is from 10 to 12 K. In Table III the thermodynamic parameters of fusion are given. From the thermodynamic data given in Table III it is possible to deduce the value of the thermodynamic cryoscopic constant of acetamide, 5.0 K $m^{-1}$. The experimental values of $\Delta T/m$, extrapolated to $m = 0$, is 8.2 K $m^{-1}$ when the solute is KCNS and 7.0 when the solute is NaCNS, that is, lower than double that of the thermodynamic cryoscopic constant. The value of the thermodynamic cryoscopic constant of KCNS may be calculated from thermodynamic data previously reported (*5*), and it results in $K_{Cr} = 12.7$ K $m^{-1}$, higher than the experimental one (≃10.5 K $m^{-1}$). This cryoscopic behavior of the two crystallization branches, in the respective zones $x_2 \rightarrow 1$ and $x_1 \rightarrow 1$, cannot be attributed with certainty to one of the two possible causes: (1) a slight tendency to separate mixed crystals; (2) an association equilibrium $MCNS \rightleftharpoons M^+ + CNS^-$ and $nCH_3CONH_2 \rightleftharpoons (CH_3CONH_2)_n$. Different techniques are required in order to explain the behavior of these solutions, as pointed out by Petit (*7*).

Table III. Calorimetric Data of Fusion of $CH_3CONH_2$

| $\Delta H_{\mathrm{fus}}$, kcal/mol | $\Delta S_{\mathrm{fus}}$, cal/(K mol) | $T_{\mathrm{fus}}$, K |
|---|---|---|
| $2.9_3 \pm 0.02$ | $8.3_2 \pm 0.06$ | 352.0 |

Table IV. Density of Solutions of KCNS and NaCNS

KCNS

| $x_2 = 0.0$ | | $x_2 = 0.0192$ | | $x_2 = 0.0214$ | | $x_2 = 0.0498$ | |
|---|---|---|---|---|---|---|---|
| T, K | d, g/mL | T, K | d, g/mL | T, K | d, g/mL | T, K | d, g/mL |
| 366.3 | 0.9793 | 368.6 | 0.9892 | 367.5 | 0.9897 | 371.6 | 1.0208 |
| 378.3 | 0.9689 | 380.8 | 0.9766 | 381.4 | 0.9705 | 385.4 | 1.0078 |
| 383.5 | 0.9624 | 393.7 | 0.9640 | 399.2 | 0.9539 | 402.1 | 0.9897 |
| 401.2 | 0.9454 | 406.8 | 0.9528 | 424.3 | 0.9296 | 414.6 | 0.9813 |
| 415.6 | 0.9337 | 414.6 | 0.9383 | 448.5 | 0.9053 | 428.6 | 0.9684 |
| 433.0 | 0.9146 | 437.7 | 0.9138 | 471.0 | 0.8776 | 443.0 | 0.9560 |
| 451.2 | 0.8933 | 471.2 | 0.8741 | | | 443.2 | 0.9547 |
| 463.5 | 0.8783 | | | | | 443.4 | 0.9545 |
| | | | | | | 462.1 | 0.9334 |

| $x_2 = 0.1000$ | | $x_2 = 0.2014$ | | $x_2 = 0.4008$ | | $x_2 = 0.6017$ | |
|---|---|---|---|---|---|---|---|
| T, K | d, g/mL | T, K | d, g/mL | T, K | d, g/mL | T, K | d, g/mL |
| 370.2 | 1.0446 | 364.5 | 1.1267 | 383.3 | 1.2542 | 422.2 | 1.3563 |
| 384.2 | 1.0206 | 376.2 | 1.1153 | 393.1 | 1.2445 | 426.8 | 1.3541 |
| 407.6 | 1.0074 | 375.7 | 1.1149 | 409.7 | 1.2302 | 435.2 | 1.3499 |
| 428.5 | 0.9873 | 389.7 | 1.1038 | 425.4 | 1.2213 | 443.6 | 1.3457 |
| 429.5 | 0.9865 | 405.3 | 1.0914 | 441.0 | 1.2098 | 456.3 | 1.3393 |
| 458.8 | 0.9588 | 428.1 | 1.0730 | 461.6 | 1.1945 | 464.5 | 1.3342 |
| | | 444.8 | 1.0574 | 462.1 | 1.1938 | | |
| | | 445.0 | 1.0573 | 461.9 | 1.1940 | | |

NaCNS

| $x_2 = 0.0400$ | | $x_2 = 0.0992$ | | $x_2 = 0.2136$ | | $x_2 = 0.3003$ | |
|---|---|---|---|---|---|---|---|
| T, K | d, g/mL | T, K | d, g/mL | T, K | d, g/mL | T, K | d, g/mL |
| 368.6 | 0.9893 | 365.9 | 1.0337 | 338.2 | 1.1318 | 352.5 | 1.1830 |
| 384.6 | 0.9758 | 384.0 | 1.0164 | 357.3 | 1.1145 | 350.9 | 1.1843 |
| 404.5 | 0.9608 | 403.1 | 0.9984 | 375.3 | 1.0937 | 362.3 | 1.1747 |
| 423.7 | 0.9431 | 423.2 | 0.9836 | 398.6 | 1.0754 | 382.6 | 1.1556 |
| 445.8 | 0.9176 | 437.7 | 0.9694 | 429.9 | 1.0501 | 403.3 | 1.1368 |
| 463.7 | 0.8946 | 461.6 | 0.9411 | | | 427.2 | 1.1163 |
| | | | | | | 446.3 | 1.0990 |

In Table IV are given the experimental values of density in relation to the temperature of the various mixtures studied. Because of a certain volatility of the acetamide, less precision in comparison with previous data was obtained (±4 × $10^{-4}$ g/cm$^3$) (*1*, *2*). The density data permit the calculation of the mean volume of the mixtures from which, using the thermodynamic relation

$$\bar{V}_1 = V_m - x_2(\partial V_m/\partial x_2) \qquad (1)$$

one can calculate the partial molar volume of the components, and the following values are arrived at for salts in infinite dilution: $51._5$ (180 °C) and $57._8$ (100 °C) $cm^3/mol$ for KCNS; $44._1$ (180 °C) and $45._7$ (100 °C) $cm^3/mol$ for NaCNS.

The molar volumes of pure acetamide at 180 and 100 °C are $66._4$ and $60._6$ $cm^3/mol$, respectively, notably higher than the intrinsic volume, according to Bondi (*8*) of 35.9 $cm^3/mol$. This fact evidences a notable component of disorder volume and dead space in the packing of the molecules of acetamide. It is to be noted that the molar volumes of MCNS lessen with the increase of temperature; this fact depends upon an increase in the electrostriction component of the molar volume and can be imputed to an increase in the dissociation of salt as a function of the temperature, as well as to the natural trend of the electrostriction volume with the increasing temperature (*9*). The continuation of the research will serve to establish the entity and the influence of the dissociation of the electrolytes in acetamide as regards the properties of the solutions.

## Glossary

| | |
|---|---|
| $x_i$ | mole fraction of the *i*th component |
| $K_{cr}$ | cryoscopic constant |
| $\bar{V}_i$ | partial molar volume of the *i*th component |
| $V_m$ | mean volume |
| $T$ | absolute temperature |
| $\Delta H_{fus}$ | fusion enthalpy |
| $\Delta S_{fus}$ | fusion entropy |
| $d$ | density |
| eut | eutectic |
| per | peritectic |

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# Liquid–Liquid and Solid–Liquid Equilibria in the Reciprocal Ternary System Ag,Li/Br,I

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**The liquid–liquid and solid–liquid equilibria in the mixture Ag,Li/Br,I were studied as a function of composition and temperature. The system presents a miscibility gap, with the upper critical solution point at $x_{AgI} = 0.5 = x_{LiBr}$ and $T = 706$ °C. The projection of the gap occupies 45.6% of the composition square. Moreover, an "a priori" prediction of the gap was calculated by means of the CIS theory.**

The characterization of liquid immiscibility in molten salts has been one of the objects of our investigations for many years (*1–3*). Demixing phenomena are particularly stimulating, being rather infrequent in fused salts and very interesting from both the theoretical and applicative viewpoints. To continue a systematic analysis of the salt mixtures which could possibly give rise to liquid–liquid equilibria, we took into account the reciprocal ternary systems (i.e., mixtures containing two cations and two anions) formed by lithium or sodium halides and silver halides. Preliminary experimental tests along with theoretical considerations suggested this family as a suitable one to study.

This paper reports detailed results for liquid–liquid (LL) and solid–liquid (SL) equilibria in the mixture Ag,Li/Br,I; to our knowledge no such data on this system have yet been reported.

## Experimental Section

The experimental technique, based on direct visual observation of the sample possibly integrated by DTA, was the same as in ref *4*. The materials used were LiBr (Merck SP), LiI (Merck P), and AgI (Fluka puriss.), while AgBr was obtained from $AgNO_3$ (Fluka puriss.) and KBr (Fluka puriss.). Particular care was devoted to the drying of lithium salts following the procedures suggested in the literature (*5*).

## Results

Figure 1 reports the SL equilibria of the four binaries which are the sides of the composition square. Dashed lines, which are mainly based on DTA measurements, should be taken as being only indicative; even working at very low heating rates, we found that the resolution of the two peaks in the thermogram was sometimes imprecise.

AgBr + LiBr: this system presents a peritectic point at 430 °C and $x_{AgBr} = 0.77$ ($x$ = mole fraction).

LiBr + LiI: this system shows complete solubility in the solid phase with a minimum at 417 °C and $x_{LiBr} = 0.40$.

AgI + LiI: this system shows complete solubility in the solid phase with a minimum at 437 °C and $x_{AgI} = 0.20$.

AgBr + AgI: this system presents a eutectic at 364 °C and $x_{AgBr} = 0.77_5$. The extension of the various solid phases in this mixture is beyond the aim of the present research and is still under question (see, e.g., ref *6* and *7*).

The LL and SL equilibria temperatures along the two diagonal and the four off-diagonal cuts are reported in Table I. The off-diagonal cuts a and b were obtained by adding increasing amounts of LiI to mixtures of silver iodide and bromide with the fixed composition $x_{AgBr} = 0.20$ and 0.50, respectively. On the other hand, the off-diagonal cuts c and d were obtained by starting from a mixture of silver and lithium bromide with the fixed composition $x_{AgBr} = 0.50$ and 0.20, respectively, to which increasing amounts of LiI were added.

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