describes the variation of the molal activity coefficient of HSCN in a mixture of electrolytes as a function of the molality (m_c) of the second electrolyte. $\gamma_\pm(\chi, m)$ is the molal activity coefficient of HSCN in a solution containing a second electrolyte at a certain molality, and $\gamma_\pm(\chi, o)$ is the molal activity coefficient of pure HSCN at the same total molality. Harned's coefficient, α_B, is a function of the total molality of the solution but is independent of the variation of m_c and can be used as an indication of the salting-out capacity of a foreign electrolyte in a system. Figures 2 and 3 show the validity of Equation 3 for the systems HSCN-$HClO_4$ and HSCN-NaSCN at a total molality of 0.8*m* and 1.0*m*. At NaSCN concentrations exceeding 0.5*m*, deviations from linearity exist but can be attributed to a limit in the accuracy of the experimental results at these concentrations. Extractions of HSCN in the presence of $NaClO_4$ were too low to derive an equation of type 3 to any accuracy.

The α_B value found for the systems HSCN-$HClO_4$ ($\alpha_B = -0.508$ at $m = 1.0$, and $\alpha_B = -0.627$ at $m = 0.8$) and HSCN-NaSCN ($\alpha_B = -0.486$ at $m = 1.0$, and $\alpha_B = -0.532$ at $m = 0.8$) illustrates that $HClO_4$ exerts a greater salting-out effect upon HSCN than NaSCN. The greater the hydration number of the salting-out agent, the less "free water" exists in the vicinity of HSCN, resulting in an increase in the effective concentration of HSCN. Since the hydration of H^+ is greater than Na^+, $HClO_4$ would increase the extraction of HSCN more than NaSCN.

Harned's coefficients determined for the systems HNO_3-$HClO_4$ (*3*) ($\alpha_B = -0.048$ at $m = 1.0$) and HCl-NaCl (*5*) ($\alpha_B = +0.0315$ at $m = 1.0$) show that $HClO_4$ and NaCl have less effective salting-out capacities in these systems than the salting-out effect of $HClO_4$ and NaSCN upon HSCN. If HSCN is less strongly hydrated than $HClO_4$ and NaSCN, the addition of either $HClO_4$ or NaSCN will cause a large increase in the effective concentration of the HSCN and, consequently, an increase in the activity coefficients.

LITERATURE CITED

(1) Apraksiw, I. A., Korovin, S. S., Musorin, V. A., Reznik, A. M., Rozen, A. M., *Russ. J. Phys. Chem.*, **40** (6), 692 (1966).

(2) Bartlett, H. E., Jurriaanse, A., De Haas, K., *Can. J. Chem.*, **47** (16), 2981 (1969).

(3) Fritz, J. S., Frazee, R. T., *Anal. Chem.*, **37**, 1358 (1965).

(4) Harned, H. S., *J. Amer. Chem. Soc.*, **57**, 1865 (1935).

(5) International Critical Tables of Numerical Data, Physics, Chemistry, and Technology, Vol III (1928).

(6) Jurriaanse, A., Kemp, D. M., *Talanta*, **15**, 1287 (1968).

(7) Korovin, S. S., Lebedeva, E. N., Dedich, K., Reznik, A. M., Rozen, A. M., *Russ. J. Inorg. Chem.*, 278 (1965).

(8) Overholser, L. G., Barton, C. J., Grimes, W. R., USAEC Report Y477 (Sept. 9, 1949).

(9) Rozen, A. M., Reznik, A. M., Korovin, S. S., Metonidze, Z. A., *Russ. J. Inorg. Chem.*, **8** (4), 516 (1963).

RECEIVED for review November 16, 1970. Accepted June 7, 1971

Radiometric Determination of Solubility and Excess Volume in Molten Systems of Cadmium–Cadmium Bromide and Cadmium–Cadmium Iodide

JACEK MOŚCIŃSKI

Institute of Nuclear Techniques, School of Mining and Metallurgy, Cracow, Poland

LESZEK SUSKI[1] and JERZY GALKA

Institute of Physical Chemistry, Polish Academy of Sciences, al. Mickiewicza 30, Cracow, Poland

Solubility limits and excess volumes in Cd–$CdBr_2$ and Cd–CdI_2 liquid solutions were determined by a γ-ray absorption method described previously. This method was modified and developed. For both systems the phase diagram reported by Topol and Landis was confirmed. The proportionality of the excess volumes of these systems, as well as Cd–$CdCl_2$ solution, to the product of the molar fractions of both components was sought. The excess volumes were positive in Cd–$CdCl_2$, nearly zero in Cd–$CdBr_2$, and negative in Cd–CdI_2 liquid systems.

Previously, we presented a radiometric method for the determination of the solubility limits and excess volumes in liquid binary solutions at high temperatures (*11–13*). This method, consisting of measurements of the absorption of γ-rays by these solutions, was successfully applied to the Cd-$CdCl_2$ molten system at 903–1073°K. The limiting solubility of the metal, as dependent on temperature, agreed with the results of classical measurements reported in the literature. The excess volume determination proved possible with an accuracy slightly lower than that obtained in molten salt systems by other methods (*2, 5, 9, 15*).

If we consider the results obtained for the Cd-$CdCl_2$ system, the radiometric method seems particularly appropriate for the determination of excess volume in liquid solutions of metals in their own molten salts. In the literature concerning those systems, few data exist on the excess volume, which has been determined in bismuth–bismuth halide solutions only (*6–8*).

Knowledge of excess volumes is important for structural investigations of liquid solutions. In this study excess volumes in Cd-$CdBr_2$ and Cd-CdI_2 liquid systems were determined.

---

[1] To whom correspondence should be addressed.

These results, together with similar data for the Cd-$CdCl_2$ solutions, should show the influence of the halide ion on the volume effect on mixing of cadmium with its molten salts.

The solubility limits of cadmium in its bromide and iodide were also measured. Another purpose of our investigation was to develop the radiometric measurement technique for research in this field.

EXPERIMENTAL

The physical principle of the method, the experimental setup and procedure, and the manner of calculating the values to be derived were described in our previous papers (*11-13*). In the present work the experimental conditions were generally identical. Following is a discussion of the few differences.

Materials. The cadmium bromide and iodide were analytical reagent grade. Before introduction to the absorption cell, the bromide was fused under hydrogen bromide atmosphere, and the iodide was filtered in the molten state through a sintered silica filter under vacuum.

Radiometric Measurements Conditions. The isotope, Am-241, with an activity of 30 mC was used as a γ-ray source. This nucleide emits α-particles as well as a variety of γ-quanta, in which the radiation of 0.060 MeV energy has the highest branching ratio, 36% (*10*). The radiation of other energies is emitted with much lower efficiency; thus, the mass absorption coefficients of the Am-241 radiation for a given absorbing substance may be assumed constant and practically independent of its thickness in a limited range of this thickness. In other words, the Am-241 γ-ray source may be considered monoenergetic for purposes of radiometric measurements. The other advantage of this source is its half-life of 458 years.

With use of the Am-241 source, the thickness of the absorption cell (the absorbing solution layer thickness) had to be reduced to 0.317 ± 0.003 and 0.188 ± 0.002 cm for systems with bromide and iodide, respectively.

The mass absorption coefficients for the pure salts were not determined experimentally, as in the case of $CdCl_2$, but were calculated indirectly from the measured mass absorption coefficient of cadmium, assuming the following relationship (*13*):

$$\frac{\bar{\mu}_{Cd}}{\bar{\mu}_{CdX_2}} = \frac{\bar{\mu}^*_{Cd}}{\bar{\mu}^*_{CdX_2}} \qquad (1)$$

where $\bar{\mu}_{Cd}$ and $\bar{\mu}_{CdX_2}$ are the mass absorption coefficients of Am-241 γ-rays for cadmium and its halides for the given experimental geometry and $\bar{\mu}^*_{Cd}$, $\bar{\mu}^*_{CdX_2}$ are "theoretical" coefficients for 0.060 MeV radiation for metal and salts, respectively. The theoretical mass absorption coefficients for cadmium metal, cadmium bromide, and cadmium iodide were taken from the literature (*14*). These coefficients, measured in cadmium metal and calculated for cadmium bromide and iodide for the 0.060 MeV radiation energy, are 5.176 ± 0.032, 3.683 ± 0.025, and 6.196 ± 0.040 cm^2/g, respectively.

The use of the Am-241 source with its relatively low energy necessitates reduction of the distance between the scintillation counter and the radiation source to obtain the highest possible radiation counting rate. For this purpose a special furnace was constructed with an external diameter of 18 cm, which is half of the diameter of the furnace used in the previous investigations (*11*). A schematic diagram of the essential parts of the apparatus is presented in Figure 1.

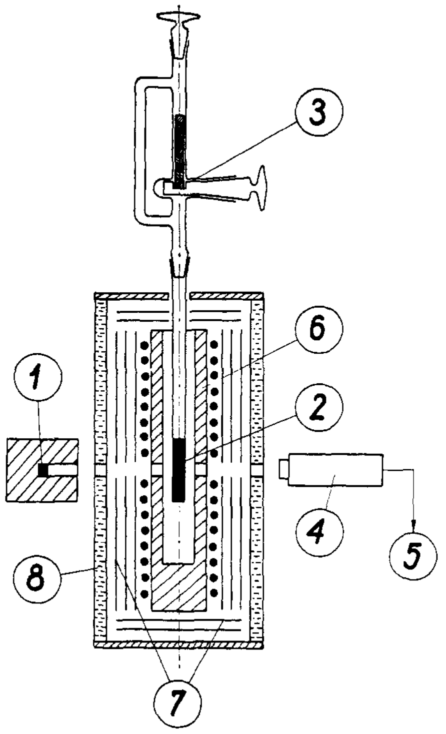

Figure 1. Schematic diagram of apparatus

1, Am-241 source; 2, absorption cell; 3, cadmium dosing device; 4, scintillation counter; 5, counting unit; 6, nickel block with Kanthal heating wire; 7, heat radiation shieldings; 8, water cooling

RESULTS FOR Cd–$CdBr_2$ SYSTEM

The solubility of cadmium in molten cadmium bromide was determined earlier by other authors; however, the results of Topol and Landis are the most complete and precise (*16*). The density of Cd-$CdBr_2$ liquid solutions with a mole fraction of metal equal to 0.0607 and 0.1339 was measured by Vesnin in the temperature range 833-973°K (*17*). The present radiometric measurements were carried out at 903° and 973°K. Owing to the experimental parameters used, the change of the γ-ray intensity traversing the solution as a function of molar fraction of metal dissolved was much higher than that obtained in the Cd-$CdCl_2$ system. The dependence of the logarithm of the relative radiation intensity on the metal molar fraction in the solution is shown in Figure 2. The experimental points represent the mean value of four radiation counting rates for a given concentration of cadmium in the course of two or three independent experiments. The vertical arrows represent the solubility limits of the metal in the salt as determined by the method previously described (*11*). These solubility limits are 0.167 ± 0.005 and 0.202 ± 0.004 molar fraction of metal at 903° and 973°K, respectively, in agreement with results calculated from the phase diagram reported by Topol and Landis, 0.17 and 0.19, respectively (*16*).

The relationships between the logarithm of the relative radiation intensity and the molar fraction of the metal reported in Figure 2 are linear with high correlation coefficients. Assuming the linear dependences pass through the origin of the coordinate systems, these correlation coefficients are 0.997 for both experimental temperatures.

For the evaluation of the excess volumes in the Cd-$CdBr_2$ solutions at both temperatures, the values of $CdBr_2$ molar volumes of 67.82 ± 0.08 and 69.01 ± 0.17 cm^3/mol are used and are the mean values taken from the data available in the literature (*2*, *17*). The molar volumes of cadmium at both temperatures are mean values taken from the data of several authors, and were tabulated in our previous work (*12*). These molar volumes are 14.66 ± 0.02 and 14.81 ± 0.02 cm^3/mol, respectively.

The excess volumes of the Cd-$CdBr_2$ solution as a function of the molar fraction of cadmium are represented in Figure 3, as well as the excess volumes calculated from the density data of

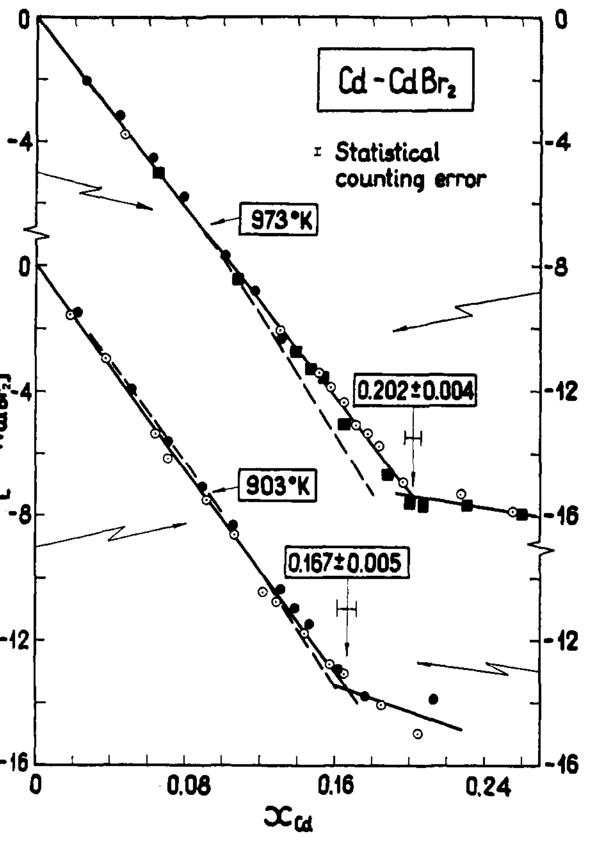

Figure 2. Logarithm of relative counting rate of radiation traversing Cd–$CdBr_2$ solution vs. molar fraction of cadmium

N_c and N_{CdBr_2} denote counting rate of radiation traversing Cd–$CdBr_2$ solution and pure $CdBr_2$, respectively. Dashed lines correspond to values of function lg (N_c/N_{CdBr_2}) = f(x_{Cd}) computed for additive volumes

Vesnin (*17*) for two concentrations investigated by him. The analysis of experimental errors, identical to that carried out in our previous works (*12*, *13*), shows the excess volume of Cd–$CdBr_2$ at 903°K to be practically zero within standard deviation limits in contrast to the Cd–$CdCl_2$ system which shows distinctly positive excess volumes. At 973°K the Cd–$CdBr_2$ system shows the small positive value of this function at molar fraction of the metal higher than 0.1.

RESULTS FOR Cd–CdI_2 SYSTEM

Of all the cadmium–cadmium halide systems, the Cd–CdI_2 system has been least investigated. The literature data concerning the solubility of cadmium in this salt are in disagreement. Corbett et al. (*4*) give a solubility value of 0.015 molar fraction of metal at 873°K, whereas Topol and Landis (*16*) report 0.1 molar fraction of dissolved metal at this temperature. According to Bredig (*3*), the last result seems doubtful since the increase of solubility with temperature is exceptionally high. The latter dependence requires confirmation. No molar volume data for the Cd–CdI_2 liquid system have been reported in the literature.

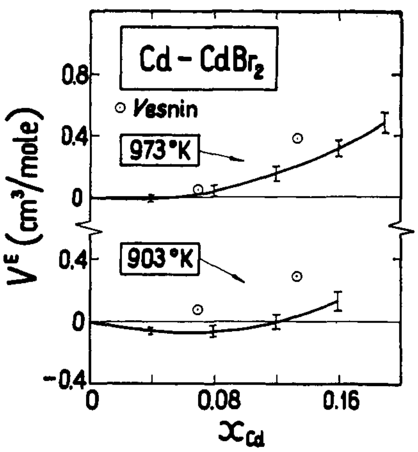

Figure 3. Excess molar volumes, V^E, of Cd–$CdBr_2$ solutions vs. molar fraction of Cd

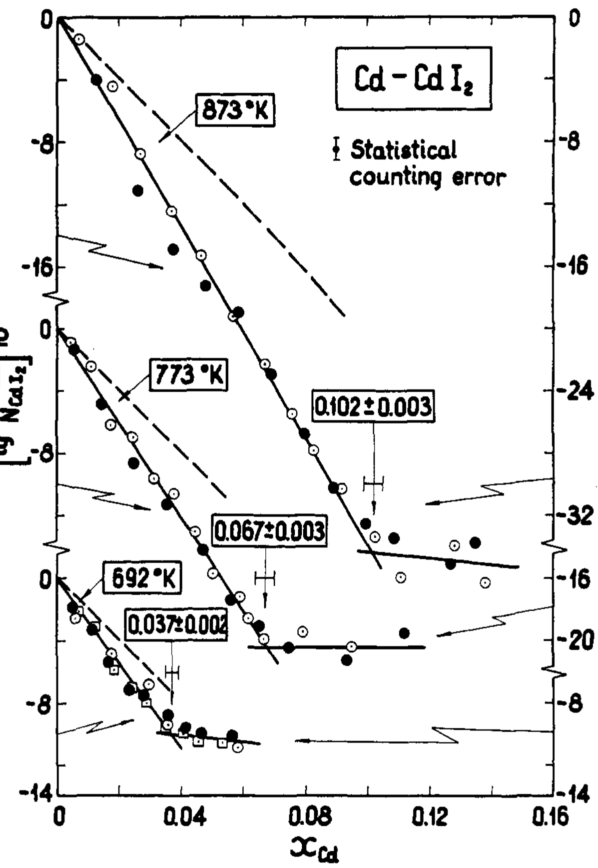

Figure 4. Logarithm of relative counting rate of radiation traversing Cd–CdI_2 solution vs. molar fraction of cadmium

N_c and N_{CdI_2} denote counting rate of radiation traversing Cd–CdI_2 solution and pure CdI_2, respectively. Dashed lines correspond to values of function lg (N_c/N_{CdI_2}) = f(x_{Cd}) computed for additive volumes

Our radiometric measurements were carried out at 692°, 773°, and 873°K. Figure 4 represents the logarithm of the relative radiation counting rate as dependent on the metal molar fraction at these three temperatures. As in the Cd–$CdBr_2$ system, the experimental points in this figure are mean values for the four radiation counting rates in a given molar fraction of cadmium, measured in the course of two or three experiments. Also, the reported relations are linear ones, and the correlation coefficients of straight lines traversing the coordinate origin are 0.914, 0.987, and 0.992 at 692°, 773°, and 873°K, respectively. The solubility limits determined by us and shown in Figure 4 by vertical arrows are 0.037 ± 0.002, 0.067 ± 0.003, and 0.102 ± 0.003 in molar fraction, respectively, for the three temperatures. In Figure 5 these results are compared with the corresponding data obtained by Topol and Landis (*16*). Our results confirm the increase of the solubility with temperature and the phase diagram of the Cd–CdI_2 system given by these authors.

For the calculations of the excess molar volumes of Cd–CdI_2 liquid solutions at the three temperatures, the molar volume

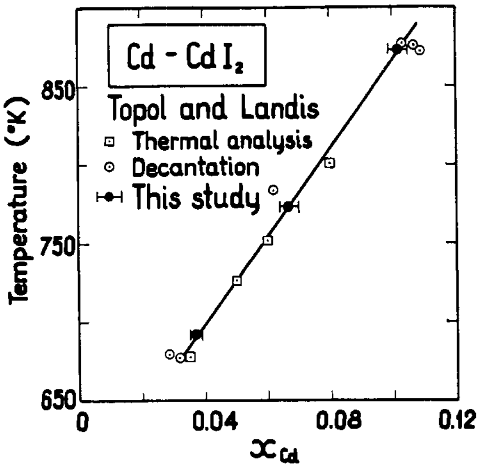

Figure 5. Comparison of solubility results for Cd in CdI_2 with Topol and Landis (16) data

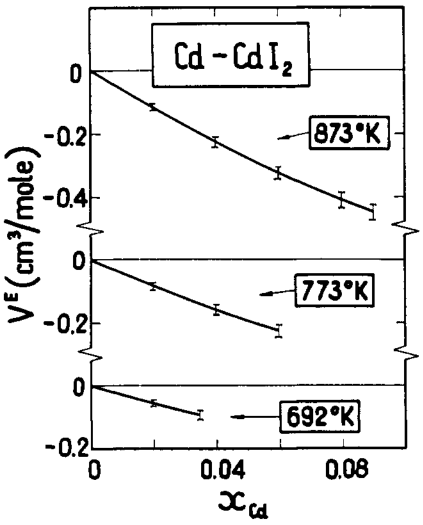

Figure 6. Excess molar volumes, V^E, of Cd-CdI_2 solutions vs. molar fraction of Cd

values for CdI_2 are taken from the literature (1). These molar volumes are 84.0 ± 0.1, 85.8 ± 0.1, and 88.1 ± 0.1 cm³/mol at 692°, 773°, and 873°K, respectively. The molar volumes of cadmium at these temperatures, calculated from the same data as the Cd–$CdBr_2$ system, are 14.22 ± 0.02, 14.36 ± 0.02, and 14.59 ± 0.02 cm³/mol.

The excess volumes in the Cd–CdI_2 solutions for the three temperatures vs. the molar fraction of cadmium are given in Figure 6. If we take into account the standard deviations of measurements, at all three temperatures the excess volumes of this system are distinctly negative, the absolute values increasing with increasing temperature.

DISCUSSION

The results obtained in our previous studies and in the present work confirm once more the influence of anions on the solubility of cadmium in its molten halides. At temperatures higher than 973°K, the solubility of cadmium increased in the sequence $I^- < Cl^- < Br^-$. At 903°K the solubilities of cadmium in its chloride and bromide are equal but higher than those in iodide. The behavior of the Cd–CdI_2 system is exceptional in comparison to other metal–metal halide systems in which the solubility of metals is generally highest in iodides.

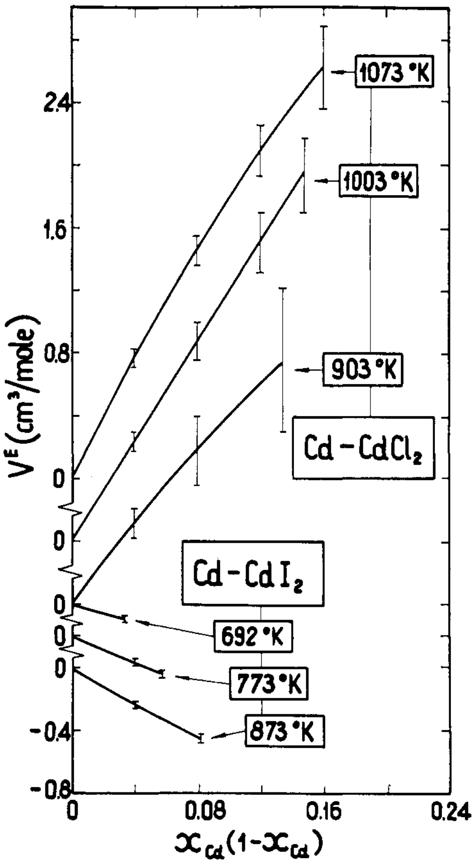

Figure 7. Excess molar volumes, V^E, in Cd-$CdCl_2$ and Cd-CdI_2 solutions vs. components molar fraction product

Our results also confirmed the extremely high temperature coefficient of the solubility of cadmium in CdI_2. This is another abnormal property of this system.

The determination of the excess volumes of cadmium–cadmium halide liquid systems was carried out with an accuracy sufficiently high to make possible the comparison of this property for all three systems investigated. The thermodynamic excess functions for binary solutions, $F^E(x_1, x_2)$, can often be presented with sufficient approximation by the relationship

$$F^E(x_1, x_2) = kx_1x_2 \qquad (2)$$

where x_1 and x_2 are molar fractions of both components of the solutions and k is a constant. Many binary solutions of ionic liquids also fulfill this relationship. In Figure 7 the excess volumes for Cd-$CdCl_2$ and Cd-CdI_2 systems are shown as a function of the $x_{Cd}x_{CdX_2}$ product. The results presented in Figure 7 show that the investigated systems obey Equation 2 with sufficient approximation. The lowest values of the excess molar volumes for the Cd–$CdBr_2$ solution are not given since this system does not fulfill Equation 2.

A quantitative confrontation of the influence of the anion on the excess molar volume values for the three systems under investigation may be carried out by comparison of the three k values from Equation 2 for these systems. This should be made at a chosen temperature considered as a corresponding state temperature for these liquids. For one component ionic liquids such as temperature, T_{corr}, is often defined as:

$$T_{corr} = \alpha T_f \qquad (3)$$

where α is an arbitrary chosen constant, and T_f is the melting point of the salt. This definition seems useful also for the evaluation of the corresponding state temperature of the systems investigated, if the melting points of $CdCl_2$, $CdBr_2$, and

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.

LITERATURE CITED

(1) Bloom, H., Knaggs, I. W., Molloy, J. J., Welch, O., *Trans. Faraday Soc.*, **49**, 1458 (1953).
(2) Boardman, N. K., Dorman, F. H., Heymann, E., *J. Phys. Colloid Chem.*, **53**, 375 (1949).
(3) Bredig, M. A., in "Molten Salt Chemistry," M. Blander, Ed., Interscience, New York, N. Y., 1964, p 415.
(4) Corbett, J. D., von Winbush, S., Albers, F. C., *J. Amer. Chem. Soc.*, **79**, 3020 (1957).
(5) Katz, J. L., Powers, B. F., Kleppa, O. J., *J. Chem. Phys.*, **35**, 765 (1961).
(6) Keneshea, F. J., Cubicciotti, D., *J. Phys. Chem.*, **62**, 843 (1958).
(7) Keneshea, F. J., Cubicciotti, D., *ibid.*, **63**, 1112 (1959).
(8) Keneshea, F. J., Cubicciotti, D., *ibid.*, p 1472.
(9) Lantratov, M. F., Shevlyakova, T. N., "Fis. Khim. Rasplavlen. Solei i Shlakov," Tr. 2-go Vses. Soveshch., Moscow, USSR, 1965, p 13.
(10) Lederer, C. M., Hollander, J. M., Perlman, I., "Table of Isotopes," 6th ed., Wiley, New York, N. Y., 1968, p 146.
(11) Mościński, J., Suski, L., *J. Phys. Chem.*, **70**, 1727 (1966).
(12) Mościński, J., Suski, L., *ibid.*, **72**, 441 (1968).
(13) Mościński, J., Suski, L., "Symposium on the Thermodynamics of Nuclear Materials with Emphasis on Solution Systems," p 167, International Atomic Energy Agency, Ed., Vienna, Austria, 1968.
(14) Plechaty, E. F., Terrall, J. R., Report UCRL-50400 in "An Integrated System for Production of Neutronics and Photonics Calculational Constants," Vol. VI, Lawrence Radiation Lab., Univ. of California Ed., Calif., October 22, 1968.
(15) Powers, B. F., Katz, J. L., Kleppa, O. J., *J. Phys. Chem.*, **66**, 103 (1962).
(16) Topol, L. E., Landis, A. L., *J. Amer. Chem. Soc.*, **82**, 6291 (1960); North American Aviation Rept. NAA-SR-5310, Atomics International Ed., Canoga Park, Calif., July 1960.
(17) Vesnin, Y. I., *Isv. Sibirskhogo Otdel. AN SSSR, Ser. Khim. Nauk.*, **7**, (3) 57 (1967).

RECEIVED for review November 19, 1970. Accepted May 10, 1971

Ternary Systems of Sodium Thiocyanate, Formate, and Halides

AUGUSTO CINGOLANI,[1] GIANFRANCESCO BERCHIESI, and GIAMMARIO PIANTONI
Istituto Chimico della Università, Camerino 62032, Italy

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

---

[1] To whom correspondence should be addressed.