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Solutions of Potassium Formate and Acetate in Molten Acetamide

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Liquid–solid equilibrium temperatures and densities were determined for the binary systems CH_3CONH_2–HCOOK and CH_3CONH_2–CH_3COOK. The thermodynamic and experimental cryoscopic constants were compared. The density values were used to calculate the partial molar volume of the components.

Introduction

In a recent paper (*1*) we reported the volumetric and cryoscopic behavior of solutions of alkali thiocyanates in molten acetamide as preliminary research on the electrochemical properties of these solutions. These studies allowed us to characterize a solvent (KCNS–CH_3CONH_2, $x_{\text{KCNS}} = 0.26$), suitable for electrochemical and photoelectrochemical measurements.

In this note other solutes are taken into consideration in acetamide in order to obtain new solvents for analytical research.

Experimental Section

The experimental method concerning the cryoscopic measurements has been fully described in preceding papers (1, 2); the density measurements (*3*, *4*) were performed by means of the Archimedean method described in the literature (*5*). A Mettler H 20 T analytical balance mounted above the thermoregulated furnace was used. The level of the furnace was changed by means of a laboratory elevator. From the pan of the balance a gold chain, joined to a steel wire (0.05-mm diameter; 1-cm length), allowed the measurements to be performed. The melt was placed in a Pyrex container positioned in the central zone of the furnace, and the furnace was raised until the bob and half of the steel wire were submerged. This condition was observed by means of a set of mirrors. The temperature of the furnace was controlled by means of a chromel–alumel thermocouple connected to a Leeds and Northrup CAT system, and the temperature of the melt was read with a second thermocouple immersed in the fused substance. The thermocouple was checked against a Pt-resistance thermometer certified by NBS and connected to a Leeds and Northrup K-3 potentiometer. The system was calibrated by using H_2O, $LiNO_3$, and $NaNO_3$, for which the densities are known (*5*, *6*). The following equation was obtained for the volume of the bob up to 350 °C: $V(\text{cm}^3) = 1.172_0 + (8.71 \times 10^{-5})t$. In a previous note (*3*) the causes of errors are shown, and the precision is stated to be $\pm 2 \times 10^{-4}$ g/cm^3. In this note, 1 stands for acetamide, and 2 stands for the other component. The melting point for component 1 is 352.7 K, and that for component 2 is 442.2 K, in good agreement with previously reported data (*1*–*7*).

Results and Discussion

The temperatures of the liquid–solid equilibrium were studied over the range $0 \le x_2 \le 1$ for the binary system CH_3CONH_2–HCOOK and over the range $0 \le x_2 \le 0.55$ for the binary system CH_3CONH_2–CH_3COOK, for reasons of thermic stability.

The liquid–solid-phase boundary curve is of a simple eutectic type, and the trend T/x is shown in Figures 1 and 2; the experimental values are given in Tables I and II. The coordinates of the eutectic points are given in Table III.

Table I. Liquid–Solid Equilibrium Temperatures in the Binary System CH_3CONH_2-HCOOK

x_2	T, K	x_2	T, K
1.0000	442.2	0.3500	391.2
0.9762	435.8	0.3259	386.6
0.9608	434.5	0.2749	377.9
0.8701	430.1	0.2495	370.6
0.7990	424.8	0.2003	353.2
0.7502	423.4	0.1733	339.4
0.6650	416.9	0.1503	338.7
0.6000	415.5	0.0990	342.4
0.5499	410.8	0.0749	344.9
0.4999	410.0	0.0343	348.8
0.4505	403.0	0.0000	352.7
0.4020	397.4		

Table II. Liquid–Solid Equilibrium Temperatures in the Binary System CH_3CONH_2-CH_3COOK

x_2	T, K	x_2	T, K
0.5500	493.7	0.2250	329.8
0.5000	479.2	0.1995	331.2
0.4500	462.5	0.1493	336.8
0.4000	445.1	0.1003	342.1
0.3503	423.6	0.0525	346.4
0.3001	397.6	0.0274	349.2
0.2750	378.9	0.0000	352.7
0.2503	357.6		

Table III. Coordinates of the Invariant Points

	CH_3CONH_2-HCOOK	CH_3CONH_2-CH_3COOK
$x_{2,\text{eut}}$	0.1700	0.2250
T_{eut}, K	336.2	329.8

The thermodynamic cryoscopic constant of the acetamide and HCOOK may be calculated from data of fusion enthalpy, previously published (*1*, *7*) as 5.0 K m^{-1} for acetamide and 11.6 K m^{-1} for potassium formate. Experimentally, the values of $\Delta t/m$ extrapolated to $m = 0$ for acetamide are 7.6 K m^{-1} (solute HCOOK) and 7.8 K m^{-1} (solute CH_3COOK). The value $\Delta t/m$ for HCOOK shows an irregular trend (Figure 3) similar to that formed for HCOOTl (*8*), and only for $m > 0.5$ does the $\Delta t/m$ value tend to the thermodynamic value; for $m < 0.5$ $\Delta t/m$ tends to 40 K m^{-1}.

This behavior was not found with other solutes (*7*), but it may be consistent with the calorimetric measurement performed on a Tian-Calvet microcalorimeter (*9*). Following these measurements, the thermogram of fusion for HCOOK at a very low speed of heating splits into two peaks which are not completely separated. This behavior, probably due to a solid–solid transition near the solid–liquid transition, may qualitatively explain the cryoscopic behavior, but not quantitatively owing to the impossibility of separating with precision the two contributions (fusion and prefusion). The cryoscopic lowering $\Delta t/m$ reaches, at the lowest concentration, a value of ~40 K m^{-1}, which gives a value of ~0.8 kcal mol^{-1} for the fusion enthalpy. If one evaluates each peak of the fusion thermogram (*9*) approximately, the estimated fusion enthalpy is ~1.8 kcal mol^{-1}. Owing to the difficulty of separating the two peaks in the thermogram of fusion, a better agreement cannot be expected.

For $m > 0.5$, $\Delta t/m$ tends to $RT_0^2M_1/[1000(\Delta H_{\text{fus}} + \Delta H_{\text{prefus}})]$. In dilute solutions of HCOOK or CH_3COOK in ace-

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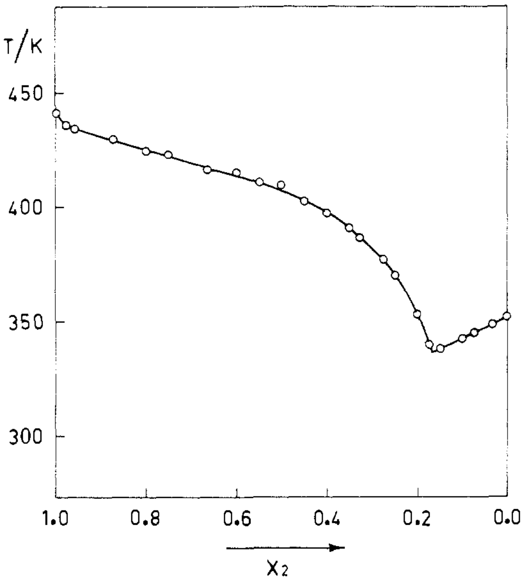

Figure 1. Liquid-solid equilibrium curve for the binary system CH_3CONH_2-HCOOK.

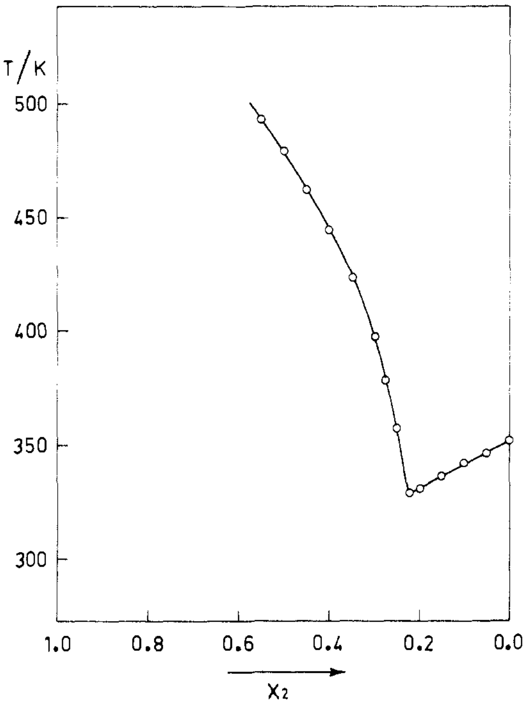

Figure 2. Liquid-Solid equilibrium curve for the binary system CH_3CONH_2-CH_3COOK.

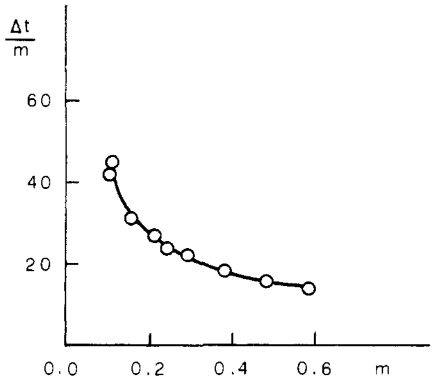

Figure 3. $\Delta t/m$ vs. m of acetamide in HCOOK solvent.

Table IV. Densities of the Solutions of HCOOK

T, K	d, g/mL	T, K	d, g/mL
$x_2 = 0.0499$			
361.4	1.0121	377.3	0.9960
363.4	1.0089	388.1	0.9848
369.1	1.0036		
$x_2 = 0.1000$			
342.4	1.0717	369.9	1.0459
355.7	1.0614	382.5	1.0340
356.8	1.0616	394.2	1.0223
$x_2 = 0.1495$			
351.0	1.0982	360.6	1.0874
353.1	1.0975	369.1	1.0795
359.8	1.0881	378.4	1.0711
$x_2 = 0.2001$			
343.6	1.1432	376.7	1.1109
353.3	1.1331	392.0	1.0963
359.9	1.1286		
$x_2 = 0.2492$			
378.6	1.1501	402.1	1.1265
386.8	1.1415	408.4	1.1215
397.9	1.1313		
$x_2 = 0.3000$			
396.1	1.1671	413.8	1.1508
405.2	1.1572		

Table V. Densities of the Solutions of CH_3COOK

T, K	d, g/mL	T, K	d, g/mL
$x_2 = 0.0499$			
353.9	1.0140	371.6	1.0003
356.6	1.0117	381.4	0.9901
363.8	1.0068		
$x_2 = 0.0998$			
347.0	1.0609	372.3	1.0332
357.1	1.0496	381.2	1.0239
362.7	1.0427		
$x_2 = 0.1496$			
344.5	1.0925	366.1	1.0679
350.4	1.0844	374.5	1.0594
358.8	1.0760		
$x_2 = 0.1993$			
336.8	1.1285	362.3	1.1058
347.6	1.1193	372.6	1.0962
355.1	1.1130		
$x_2 = 0.2491$			
360.5	1.1378	374.8	1.1255
367.8	1.1304	385.5	1.1145

tamide, the difference between the experimental and thermodynamic cryoscopic constant may be a consequence of partial dissociation of these salts in acetamide, if mixed crystals are not present, as seems probable in the solutions of CH_3CONH_2 in HCOOK.

The following probable dissociation constants of the potassium formate and acetate in molten acetamide, calculated as $[(1/K_{cr})(\Delta t/m)_{\text{extrapolated},m=0} - 1]$, may be proposed: 0.52 and 0.56 (for HCOOK and CH_3COOK, respectively).

In Tables IV and V are reported experimental values of density for the different investigated concentrations, measured at various temperatures in a temperature range above the crystallization curve. The mean volume, V_m, calculated from the density data is a linear function of the mole fraction in the investigated concentration range (i.e., $V_m = 43._9 + 17.4_6x_1$, at 107 °C) for the solutions of HCOOK, and the partial molar volume calculated by following the usual thermodynamic relation is a constant (at the precision of these measurements) in this concentration range.

The partial molar volume of HCOOK at 107 °C is 43.9 cm^3/mol, lower than the corresponding value of KCNS (*1*),

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probably due to a different interaction of the anions with acetamide.

The variation of V_m vs. the mole fraction for the solutions of CH_3COOK is on the order of the dispersion due to the experimental imprecision; for this reason the calculation of $\tilde{V}$ is not performed. The solutions of HCOOK in CH_3CONH_2 exhibit densities higher than the corresponding densities of the CH_3COOK mixtures.

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Densities of Aqueous Sodium Chloride Solutions from 75 to 200 °C at 20 bar

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A high-pressure dilatometer has been used to measure the densities of aqueous sodium chloride solutions from 0.05 to 4.4 *m*. The precision of a density determination is $\pm 2 \times 10^{-4}$ g cm^{-3} at 100 °C and decreases to $\pm 5 \times 10^{-4}$ g cm^{-3} at 200 °C. Within these limits, the density data are in agreement with the low-concentration measurements reported by Ellis at the same temperatures and pressure.

Introduction

The thermodynamic properties of aqueous sodium chloride solutions are of interest for research and engineering design in such areas as desalination, geothermal energy development, geothermal brine exploration, and hydrothermal ore deposition. Volumetric properties at high temperatures are of direct significance for their use in determining the pressure dependence of high-temperature activity coefficients, enthalpies, and heat capacities. Much of the data on thermal properties are reported at the saturation pressure, so precise volumetric data in this region, as well as at higher pressures, are required for calculations of pressure dependence. In preparation for a program to calculate the pressure dependence of thermal properties, we reviewed the literature data for sodium chloride solutions and found that the density data available at low pressures were inconsistent. The data of Khaibullin and Borisov (*1*), reported at saturation pressure, are of low precision. They differ by as much as 0.01 g cm^{-3} from the data of Fabuss, Korosi, and Hug (*2*). The more precise data of Ellis (*3*) are limited to concentrations below 1 *m*. We have used a high-pressure dilatometer to measure the densities of sodium chloride solutions to 4.4 *m* at 20.27 bar, from 75 to 200 °C.

Apparatus

The dilatometer is similar to that used by Ellis (*3*), in which changes in the volume of a solution are measured as a function of temperature. The apparatus is illustrated in Figure 1. A pressure vessel, constructed of corrosion-resistant Haynes Alloy No. 625, contains ~9 cm^3 of salt solution. The pressure vessel is connected to a mercury reservoir by 0.157-cm outside diameter, 0.018-cm inside diameter, stainless-steel capillary tubing. The mercury reservoir, which is made of a coil of 0.318-cm outside diameter stainless-steel tubing, is in turn connected to a glass capillary column. The entire system is pressurized with a high-pressure nitrogen gas cylinder.

To avoid possible hysteresis in the volume of the sample cell when the system is pressurized and depressurized, a double vessel is used as shown in Figure 2. The sample cell is welded to a thick top cap, so that it is permanently sealed except for the inlet and outlet ports. A thick outer vessel surrounds the sample cell and is sealed by using an annealed copper gasket. The inner and outer vessels are connected on the gas side of the apparatus, so that both can be slowly pressurized at the same time. Thus, there is never a pressure difference between the inner and outer vessels.

The high-pressure glass-to-metal seals, used to connect the glass capillary to the stainless-steel tubing system, are constructed of standard swagelock fittings (0.125-in. tubing to 0.25-in. MNPT) which have been drilled out to provide a loose fit for the glass tubing. The glass is simply glued into the fittings with epoxy (G. C. Electronics). Precision-bore glass tubing, 1.6-mm internal diameter, is carefully annealed before use. The combination of glass tubing and epoxy seal can contain 1-kbar pressure. For safety, the glass tubing is always surrounded by a Plexiglass pressure shield.

Temperature control is achieved by using two separate systems. The mercury reservoir and most of the capillary connecting tube are thermostated at 30 °C with a well-stirred water bath and circulation pump. The water-bath temperature of 30 °C is necessary because room temperature often exceeds 25 °C after prolonged operation of the high-temperature bath. At 30 °C, the water-bath temperature fluctuates by less than 0.01 K. The sample cell is surrounded by a large aluminum block and is placed in a high-temperature fluidized bath (Techne Model SB-7). Temperature control of the fluidized bath with an Electromax III controller (Leeds and Northrup) is good only to a few tenths of a degree, but the aluminum block serves as a heat sink to reduce temperature fluctuations. With the aluminum block, the temperature of the sample cell is stable

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