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 $\bar{V}$ 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 ±2 × 10^{-4} g cm^{-3} at 100 °C and decreases to ±5 × 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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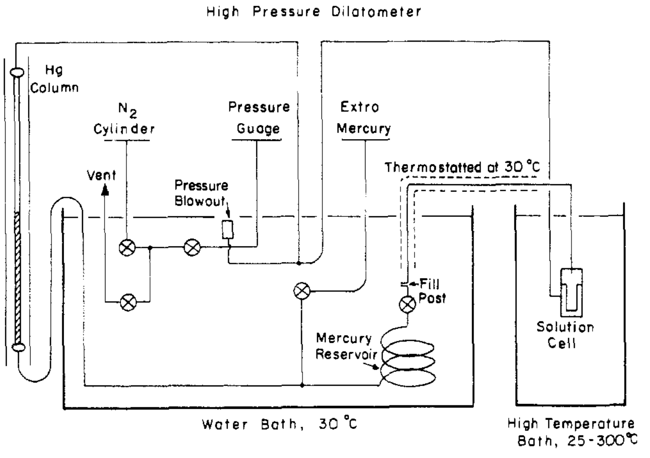

Figure 1. Schematic diagram of high-pressure dilatometer.

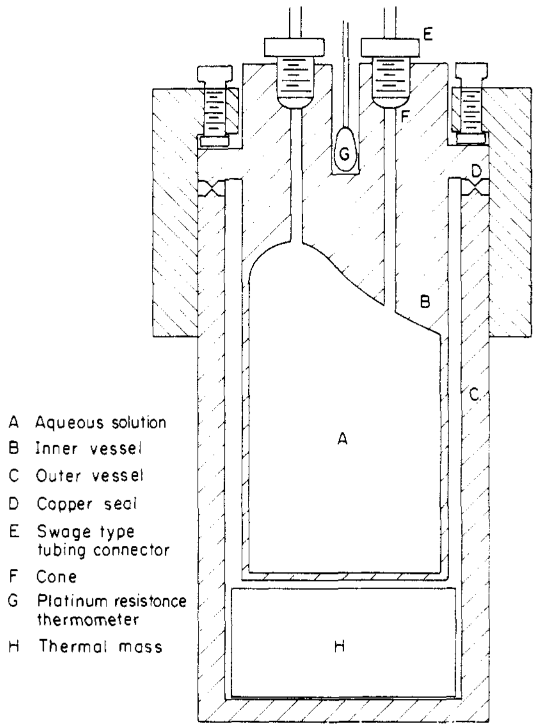

Figure 2. Schematic diagram of high-pressure solution cell.

to ±0.01 K over a period of 30 min.

Experimental Method

The solution density was determined by measuring the change in the volume of the solution as the temperature was raised. To begin a measurement, solution of known molality was prepared with freshly degassed water which had been distilled and passed through a Millipore Q filter system (final resistivity was greater than 18 mΩ). Baker reagent-grade NaCl was used without further purification. The salt was dried overnight at 200 °C and cooled under vacuum before being weighed.

The procedure used to fill the sample cell without introducing any air bubbles was somewhat complicated. The cell was filled and emptied by syringe a minimum of 5 times to eliminate contamination by any old solution still in the cell. As the final slug of solution was placed in the sample cell, a fine needle was used to stir the solution in the inlet hole and dislodge any air bubbles trapped in the narrow opening. A syringe containing 10 mL of the solution was then attached to the inlet fitting, and the solution was forced through the sample cell, the connecting tube, and then out an opening at the mercury/solution interface. A Swagelock cap used to close this opening was tightened while pressure was applied by the syringe. The syringe was removed and the inlet fitting was topped off with a few drops of solution. As the inlet cap was tightened, solution was forced out through the cracks, displacing any remaining air. Finally, the apparatus was pressurized. Any air bubbles in the system could be detected immediately by a large displacement in the level of the mercury column.

The sample cell was then placed in the fluidized bath and the solution was allowed to come to equilibrium at room temperature. The pressure of the system and the level of the mercury column were monitored overnight to check for leakage. The temperature of the sample was increased in 25 K increments, and the height of the mercury column was measured to ±0.01 mm at each step by using a Wilde cathatometer. The temperature of the sample cell was determined to ±0.005 K with a 25-Ω, calibrated platinum resistance thermometer and G-2 Mueller bridge. A bourdon-tube pressure gauge (Ashcroft Digiguge Model 7781), calibrated with a Ruska Deadweight Tester, was used to determine the pressure of the system to ±0.1 bar. The temperature of the water bath and the room temperature were measured with mercury-in-glass thermometers.

Derivation of Equations

The change in the height of the mercury column can be related to the density of the solution as follows. Let T be the experimental temperature, T_R the reference temperature, and T_B the water-bath temperature in degrees Celsius. The density of the solution at the experimental temperature, ρ_T, is equal to the mass of solution in the cell divided by the volume of the cell

$$\rho_T = g_T/V_T \qquad (1)$$

The mass of solution in the sample cell at temperature T is equal to the mass in the cell at the reference temperature, T_R, less the amount that has expanded from the cell. The mass of solution expanded is equal to

$$\Delta h\, A\, \rho_{T_B} \qquad (2)$$

where Δh is the total change in the height of the mercury column between temperatures T_R and T, A is the cross-sectional area of the mercury column, and ρ_{T_B} is the density of the solution at the temperature of the water bath. Thus, the density of the solution is given by

$$\rho_T = (1/V_T)[\rho_{T_R}V_{T_R} - \Delta h\, A\, \rho_{T_B}] \qquad (3)$$

Assume that the temperature dependence of the volume of the sample cell is

$$V_T = V_0 e^{\alpha T} \qquad (4)$$

where V_0 is the volume of the cell at 0 °C and α is the unknown expansivity of the cell. Substituting eq 4 into eq 3 one obtains

$$\rho_T = \rho_{T_R}e^{-\alpha(T-T_R)} - (A/V_0)\,\Delta h\,\rho_{T_B}e^{-\alpha T}$$

Expansion of the exponential yields

$$\rho_T = \rho_{T_R}[1 - \alpha(T - T_R)] - \Delta h\,(A/V_0)\rho_{T_B}[1 - \alpha T]$$

or

$$\rho_T = \rho_{T_R} - \frac{A}{V_0}\,\Delta h\,\rho_{T_B} + \alpha\rho_{T_R}(T_R - T) + \alpha\frac{A}{V_0}T\,\Delta h\,\rho_{T_B} \qquad (5)$$

This is the final equation relating the density of the solution to the observed change in the height of the mercury column.

Small corrections to the observed column height were made to account for variations in water-bath temperature, room temperature, hydrostatic head, and system pressure. These

Table I. Density (g/cm³) of Aqueous NaCl at 20.27 bar

molality	$T = 30$ °C[a]	$T = 75$ °C	$T = 100$ °C	$T = 125$ °C	$T = 150$ °C	$T = 175$ °C	$T = 200$ °C
0.0000	0.996 51	0.975 72	0.959 30	0.939 99	0.917 94	0.893 08	0.865 10
0.0530	0.998 67	0.977 82	0.961 41	0.942 16	0.920 21	0.895 49	0.867 67
0.2719	1.007 43	0.986 33	0.969 95	0.950 85	0.929 20	0.904 94	0.877 74
0.5571	1.018 54	0.996 95	0.980 68	0.961 84	0.940 55	0.916 76	0.890 24
0.9775	1.034 44	1.012 30	0.996 15	0.977 64	0.956 89	0.933 88	0.908 47
1.0360	1.036 62	1.014 39	0.998 21	0.979 70	0.958 94	0.935 92	0.910 42
3.0610	1.106 22	1.082 02	1.066 04	1.048 39	1.029 12	1.008 20	0.985 56
3.2428	1.112 00	1.087 64	1.071 56	1.053 82	1.034 46	1.013 48	0.990 81
4.3933	1.147 04	1.121 90	1.105 94	1.088 59	1.069 86	1.049 76	1.028 31

[a] Determined from literature data (*4*, *7-16*).

corrections are discussed in detail in ref *4*. A correction for the variable mass of solution in the connecting tube was found to be negligible to 200 °C.

Calibration

Equation 5 contains two unknowns, the expansivity of the sample cell, α, and the ratio of the cross-sectional area of the column to the volume of the cell at 0 °C, A/V_0. To evaluate these two constants, we performed six calibration runs, using pure water in the solution cell, in the same manner as the density determinations. Observed values of Δh, from 25 to 200 °C at 25 °C intervals, were combined with known densities of water (*5*) in a nonlinear least-squares regression to determine the values $\alpha = (3.81 \pm 0.04) \times 10^{-5}$ K^{-1} and $A/V_0 = (2.333 \pm 0.001) \times 10^{-3}$ cm^{-1}. The value for the expansivity of the sample cell is in good agreement with the expansivity of a similar Hastelloy alloy, 3.6×10^{-5} K^{-1} (*6*). The overall standard deviation of fit for all calibration data was 4×10^{-5} g cm^{-3} in the density values for pure water.

Results and Discussion

The results of density measurements for sodium chloride solutions, from 0.05 to 4.4 *m*, are given in Table I. Observed values of Δh were used directly in eq 5, in combination with the known calibration constants, to obtain densities which were then corrected to rounded temperatures and 20.27 bar. The largest temperature correction was over a 2.5 K interval and introduced a maximum error of 2×10^{-5} g cm^{-3}.

Densities of sodium chloride solutions at the reference temperature and at the water-bath temperature also are required in eq 5. These were obtained from an analysis of literature data (*7*–*16*) as a function of temperature, pressure, and concentration. The details of this analysis are given in ref 4 and 17. While the reference temperature varied for each experimental run (generally between 20 and 25 °C), the water-bath temperature remained constant at 30 °C. Densities at this temperature also are included in Table I. Complete listings of the raw data for both sodium chloride solutions and calibration runs are included in ref *4*.

The precision of the density data can be estimated by examining the data as a function of molality at constant temperature. The estimated uncertainty increases from $\pm 2 \times 10^{-4}$ g cm^{-3} at 100 °C to $\pm 5 \times 10^{-4}$ g cm^{-3} at 200 °C. This uncertainty is larger than that quoted by Ellis (*3*); however, a comparison of the two data sets indicates that the uncertainties are roughly the same. This is illustrated in Figure 3, where values of the apparent molal volume are plotted against $m^{1/2}$. The values of ϕV have been calculated from the density data as

$$\phi V = \left(\frac{1000 + mM_2}{m}\right)\left(\frac{1}{\rho}\right) - \left(\frac{1000}{m}\right)\left(\frac{1}{\rho_0}\right)$$

where M_2 is the molecular weight of sodium chloride and ρ_0 is the density of pure water. Figure 3 indicates that the present measurements are in good agreement with the low-concentration data of Ellis and that they greatly extend the concentration range covered by volumetric data.

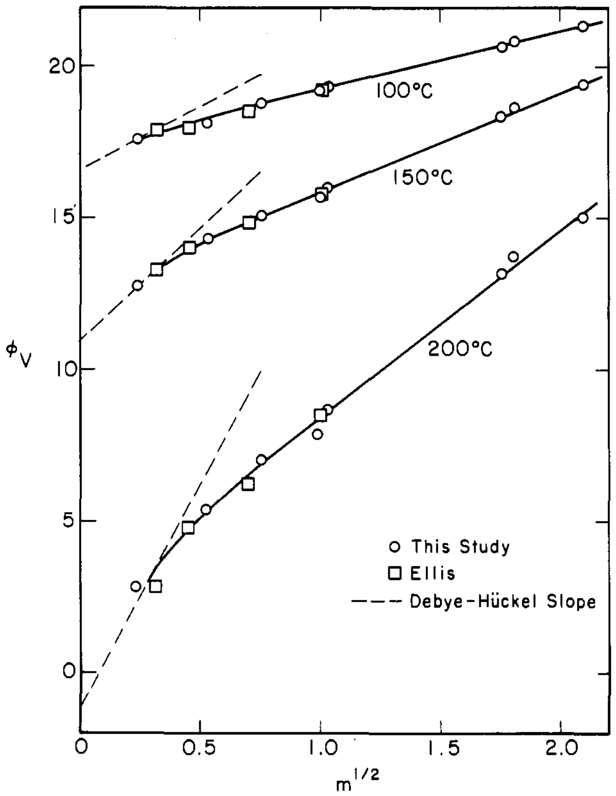

Figure 3. Comparison of values of the apparent molal volume, ϕV, calculated from the density data of this study and of Ellis (*3*). Values of the Debye–Hückel slope are taken from Bradley and Pitzer (*18*).

A comprehensive equation of state for aqueous sodium chloride has been developed on the basis of these measurements and many literature data extending to 300 °C and 1 kbar. This will be published separately (*17*), together with a general discussion of the volumetric properties of aqueous sodium chloride.

Glossary

A	cross-sectional area of mercury column (cm^2)
T	temperature (°C)
V	volume of sample cell (cm^3)
α	expansivity of sample cell (K^{-1})
ρ	density of solution (g/cm^3)
ρ_0	density of pure water (g/cm^3)

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Excess Volume and Excess Polarizability during Mixing of Binary Solvents

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Refractive-index and density data are presented for 10 binary solvent mixtures comprising benzene, chlorobenzene, bromobenzene, toluene, acetophenone, dimethyl sulfoxide, carbon tetrachloride, and water. All of these data were collected at 20 °C over the entire composition ranges of the mixtures. Previously developed relations for the excess volume and excess polarizability of mixing were employed to analyze the binary data.

Introduction

In an earlier study (*1-3*), we measured the hydrodynamic properties of binary solvent mixtures. In this study, as part of a general program to pursue our investigation of the properties of binary mixtures, we have undertaken an extensive investigation of the measurement of refractive index at three different wavelengths (589, 546, and 436 nm) and density at 20 °C as a function of composition of the mixtures. The 10 binary mixtures studied were benzene (1)-acetophenone (2), bromobenzene (1)-acetophenone (2), acetophenone (1)-chlorobenzene (2), acetophenone (1)-toluene (2), dimethyl sulfoxide (1)-bromobenzene (2), water (1)-dimethyl sulfoxide (2), benzene (1)-chlorobenzene (2), carbon tetrachloride (1)-chlorobenzene (2), bromobenzene (1)-benzene (2), and bromobenzene (1)-chlorobenzene (2). These binary data were further analyzed by using the relations developed earlier (*1*, *4*, *5*).

Experimental Part

The solvents used in this study were of reagent grade. All of the solvents were purified by fractionating through a 6-ft column. Further purity of these solvents was tested by using gas chromatography. The various physicochemical properties of the solvents used together with mol % impurity are presented in Table I. Double-distilled water was used throughout the entire work. Particular care was taken in handling hygroscopic liquids as the slightest traces of water were found to affect the data of pure solvents quite markedly.

The solvent mixtures were prepared by weighing appropriate volumes of pure solvents; the volume fractions were calculated from the weights and from densities of pure components. Refractive indexes of pure solvents and solvent mixtures were measured with a Bausch and Lomb precision refractometer equipped with mercury and sodium light sources. The precision of the instrument as quoted by the manufacturer is ±0.000 03 unit. The initial calibration of the instrument was made at 20 °C by using the standard glass test piece provided by the manufacturer. Calibration checks were made routinely with distilled water, and occasional rechecks were made with the glass test piece. Samples were applied to the prism of the refractometer as quickly as possible to minimize possible evaporation and changes in composition. all measurements were made at 20 °C by using the sodium (589 nm) line and the mercury green (546 nm) and blue (436 nm) lines. All densities were measured with a precision density meter, Model DMA 02C, manufactured by Anton Paar K.G., Austria, by a procedure described earlier (*6*). The data for density and refractive index for pure solvents agreed very well (Table I) with the literature values (*11*).

Results and Discussion

The experimental data for both density and refractive index are presented in Tables II-XI. In the calculation of the excess properties from these data, we have used the following relations for the changes in volume and refractivity during mixing (*1*, *4*, *5*):

$$\Delta V_{\text{mix}} = \left(\sum_{i=1}^{2} N_i V_i\right) A_{12} \phi_1 \phi_2 \qquad (1)$$

$$\Delta R_{\text{mix}} = \left(\sum_{i=1}^{2} N_i V_i\right) B_{12} \phi_1 \phi_2 \qquad (2)$$

Here, N_i, V_i, and ϕ_i represent the number of moles, the molar volume, and the volume fraction ($\phi_i \equiv N_i V_i / \sum_j N_j V_j$) of the *i*th

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