

Specific Heat Capacities of Aqueous Sodium Chloride Solutions at High Pressures

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The high-pressure specific heat capacities of aqueous sodium chloride solutions over the ranges of 0–1 *m*, 0–40 °C, and 0–1000 bar have been calculated from the high-pressure equation of state and the 1-atm C_p data to a precision of $\pm 0.1\%$ and an estimated accuracy of $\pm 0.5\%$. The results agree with the measured values of Liphard, Jost, and Schneider (LJS) to $\pm 3\%$ at a higher salt concentration range, and the agreement is better for more dilute solutions. The large discrepancy between the pure-water values is attributed to the uncertainties of extrapolating the literature data. Our data suggest that NaCl remains as a structure breaker at 2000 bar up to 2 *m* in NaCl concentration.

Introduction

The specific heat capacity of aqueous sodium chloride solutions has been extensively investigated at the pressure of 1 atm (1–4). However, the only high-pressure measurement of which we know is the work of Liphard, Jost, and Schneider (LJS) (5).

LJS measured the specific heat capacities (C_v) by the temperature-jump technique and calculated C_p from C_v and PVT properties. The accuracy of the data obtained was estimated to be $\pm 1\%$. They reported that all C_p and C_v values decrease with increasing pressure. At 0 bar (1 atm) and 1000 bar, C_p and C_v decrease steadily with increasing salt concentration, but at 2000 bar a maximum appears. They related the maximum to the structure effects, suggesting that, at 2000 bar, the effect of NaCl on water is "structure making" at low concentration and "structure breaking" at higher concentration.

We do not feel that the structure of water could change so drastically over such a small pressure range. Therefore, we decided to take a different approach, calculating the specific heat capacities from the high-pressure equation of state of NaCl (6, 7).

Specific Heat Capacity

The specific heat capacity at constant pressure, C_p , can be calculated from the following equation (8):

$$C_p^p = C_p^0 - T \int_0^p (\partial^2 V / \partial T^2) dp \quad (1)$$

where C_p^p and C_p^0 are the heat capacities at applied pressures *p* and 0, respectively; *T* is the absolute temperature; *V* is the specific volume. In order to derive C_p^p , we used the C_p^0 data of Desnoyer et al. (1) and Millero et al. (9) and the specific volume data of Chen and Millero (7) and Chen et al. (10). The values at several concentrations, temperatures, and pressures are listed in Table I.

Values for the specific heat capacity at constant volume, C_v , were also calculated by using the following equation (8):

$$C_v = C_p + T (\partial V / \partial T)^2 / (\partial V / \partial p) \quad (2)$$

The results of these calculations are listed in Table II. These C_p and C_v values are precise to within $\pm 0.1\%$ and are estimated to be accurate to within $\pm 0.5\%$ over the ranges of 0–1 *m*, 0–40 °C, and 0–1000 bar. The extrapolated values

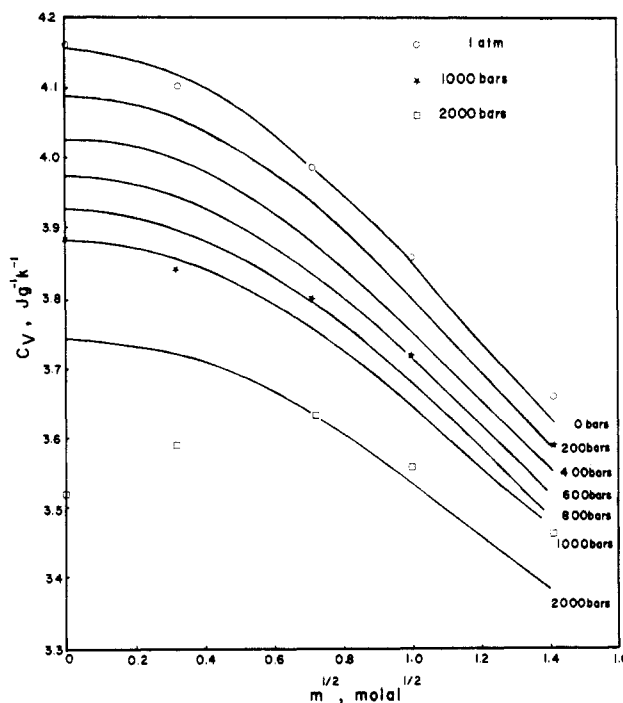


Figure 1. Specific heat capacity at constant volume (C_v) vs. $m^{1/2}$ at 20 °C and various pressures. Smoothed curves are from this study whereas symbols represent the data of LJS.

at higher concentrations and pressure are also given in Tables I and II.

Results and Discussion

In Figure 1, we have plotted the C_v values vs. $m^{1/2}$ for 20 °C at various pressures. Our results indicate that no maximum appears and the C_v values decrease steadily with increasing salt concentration for pressure up to 2000 bar. The values reported by LJS are also plotted in Figure 1. The two data sets agree very well at 1 atm. At 1000 bar our values are lower at higher concentrations. At 2000 bar the deviations are large at the lower salt concentration range with our values being higher. Our values are lower at higher salt concentrations.

LJS did not make any measurements for pure water. Rather they used the direct-measurement C_p data of Sirota and Beljakov (11) (20–105 °C, 50–500 bar); then they extrapolated the pure-water values to 2000 bar. Because our C_p results for pure water agree with those of Sirota and Beljakov (reported in ref 12) to within 0.1% over the ranges of 20–40 °C and 50–500 bar, it is rather unexpected that the agreement should be so poor at higher pressures for C_v . Our explanation for this is that the pure-water data of Sirota and Beljakov were extrapolated improperly.

LJS assumed that the relation between C_p and pressure ($\Delta C_p / \Delta p$) is linear over the range of 0–2000 bar, and they linearly extrapolated the pure-water data to 1000 and 2000 bar and then calculated C_v values (13). However, it is shown clearly in Table I that the values for $-\Delta C_p / \Delta p$ decrease with increasing pressure. As a result, the C_p and C_v values generated by the linear extrapolation are much too low. Conse-

Table I. Specific Heat Capacities of Aqueous Sodium Chloride Solutions ($10^{-3}C_p$, J kg $^{-1}$ K $^{-1}$) at Selected Concentrations, Temperatures, and Pressures

P, bar	0 m	0.1 m	0.5 m	1.0 m	2.0 m ^a	0 m	0.1 m	0.5 m	1.0 m	2.0 m ^a
0 °C						10 °C				
0	4.2188	4.1771	4.0341	3.8849	3.69	4.1930	4.1564	4.0284	3.8911	3.69
200	4.129	4.092	3.965	3.833	3.67	4.123	4.090	3.974	3.848	3.67
400	4.056	4.023	3.909	3.791	3.67	4.065	4.035	3.928	3.813	3.65
600	3.998	3.967	3.862	3.757	3.65	4.017	3.988	3.889	3.782	3.63
800	3.950	3.921	3.824	3.730	3.63	3.977	3.950	3.856	3.757	3.62
1000	3.911	3.883	3.793	3.706	3.63	3.943	3.917	3.828	3.735	3.61
2000 ^a	3.78	3.76	3.69	3.63	3.62	3.83	3.81	3.73	3.66	3.59
20 °C						25 °C				
0	4.1821	4.1492	4.0320	3.9037	3.71	4.1796	4.1480	4.0349	3.9098	3.72
200	4.124	4.094	3.985	3.865	3.68	4.126	4.096	3.990	3.872	3.69
400	4.075	4.046	3.944	3.831	3.65	4.079	4.052	3.952	3.839	3.66
600	4.033	4.006	3.909	3.802	3.63	4.039	4.013	3.918	3.810	3.63
800	3.997	3.971	3.879	3.776	3.61	4.004	3.980	3.888	3.783	3.61
1000	3.965	3.941	3.852	3.753	3.59	3.974	3.950	3.862	3.760	3.59
2000 ^a	3.86	3.84	3.76	3.67	3.52	3.87	3.85	3.77	3.68	3.52
30 °C						40 °C				
0	4.1783	4.1477	4.0376	3.9151	3.73	4.1780	4.1484	4.0413	3.9215	3.73
200	4.128	4.099	3.995	3.879	3.69	4.132	4.104	4.003	3.889	3.70
400	4.083	4.057	3.958	3.846	3.66	4.091	4.065	3.969	3.859	3.68
600	4.045	4.019	3.925	3.817	3.64	4.055	4.030	3.938	3.832	3.65
800	4.011	3.987	3.896	3.791	3.61	4.023	3.999	3.911	3.808	3.63
1000	3.982	3.958	3.870	3.767	3.59	3.994	3.972	3.886	3.786	3.61
2000 ^a	3.89	3.86	3.78	3.68	3.52	3.90	3.89	3.80	3.71	3.57

^a Extrapolated value.Table II. Specific Heat Capacities of Aqueous Sodium Chloride Solutions ($10^{-3}C_v$, J kg $^{-1}$ K $^{-1}$) at Selected Concentrations, Temperatures, and Pressures

P, bar	0 m	0.1 m	0.5 m	1.0 m	2.0 m ^a	0 m	0.1 m	0.5 m	1.0 m	2.0 m ^a
0 °C						10 °C				
0	4.2163	4.1760	4.0335	3.8767	3.64	4.1884	4.1500	4.0131	3.8621	3.63
200	4.129	4.092	3.960	3.817	3.61	4.112	4.077	3.950	3.810	3.59
400	4.054	4.018	3.896	3.766	3.58	4.045	4.012	3.893	3.763	3.56
600	3.988	3.955	3.841	3.721	3.56	3.987	3.955	3.844	3.722	3.54
800	3.931	3.899	3.792	3.681	3.55	3.934	3.904	3.799	3.685	3.52
1000	3.880	3.850	3.748	3.646	3.53	3.888	3.859	3.759	3.652	3.50
2000 ^a	3.71	3.69	3.60	3.53	3.46	3.73	3.71	3.63	3.54	3.43
20 °C						25 °C				
0	4.1547	4.1187	3.9893	3.8456	3.62	4.1359	4.1009	3.9751	3.8346	3.62
200	4.088	4.054	3.932	3.797	3.59	4.072	4.040	3.921	3.788	3.58
400	4.027	3.996	3.881	3.753	3.55	4.015	3.984	3.872	3.745	3.54
600	3.974	3.944	3.835	3.714	3.52	3.964	3.935	3.827	3.706	3.51
800	3.926	3.897	3.794	3.677	3.49	3.918	3.890	3.787	3.670	3.48
1000	3.883	3.855	3.756	3.644	3.47	3.876	3.849	3.750	3.636	3.45
2000 ^a	3.76	3.72	3.63	3.53	3.38	3.74	3.71	3.62	3.52	3.35
30 °C						40 °C				
0	4.1158	3.0818	3.9590	3.8213	3.60	4.9721	4.0396	3.9215	3.7880	3.57
200	4.056	4.024	3.907	3.776	3.57	4.018	3.987	3.876	3.748	3.54
400	4.001	3.971	3.861	3.735	3.53	3.968	3.940	3.833	3.711	3.50
600	3.952	3.923	3.818	3.697	3.50	3.923	3.896	3.794	3.676	3.47
800	3.908	3.880	3.778	3.661	3.46	3.882	3.856	3.758	3.643	3.44
1000	3.867	3.841	3.742	3.628	3.43	3.845	3.819	3.724	3.612	3.41
2000 ^a	3.73	3.71	3.62	3.52	3.33	3.72	3.70	3.61	3.51	3.31

^a Extrapolated value.

quently, maxima for C_p and C_v were obtained when the values for C_p and C_v were plotted vs. concentration. If we compare the data only for salt solutions, the agreement is generally within $\pm 3\%$ in the higher concentration range and better for more dilute solutions.

Conclusion

The high-pressure specific heat capacities (C_p and C_v) of aqueous sodium chloride solutions have been calculated from the high-pressure equation of state and the C_p data at 1 atm. The results are precise to $\pm 0.1\%$, and they are estimated to be accurate to $\pm 0.5\%$ over the ranges of 0–1 m, 0–40 °C, and 0–1000 bar. The values have been extrapolated to a

concentration of 2 m and a pressure of 2000 bar. Judging from our data, NaCl continues to act as a structure breaker at 2000 bar and a salt concentration of up to 2 m.

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Viscosity of Some Binary and Ternary Liquid Mixtures

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Kinematic viscosities and densities of eight binary and four ternary liquid mixtures of polar components are reported for various temperatures. Experimental viscosities were correlated with McAllister's equation of viscosity and with a modified form of the McAllister equation.

Introduction

The solution to many engineering problems requires quantitative information on the viscosity of liquid mixtures. Examples of such problems include heat transfer, mass transfer, and fluid flow in many technical situations.

In the present work, kinematic viscosities and densities of eight binary and four ternary systems of strongly polar components are presented. For comparison the viscosity data were correlated by means of the methods of McAllister (1) and that of Dizchi (2).

Experimental Section

Kinematic viscosities were measured with a Schott automated viscosity measuring system. This system consists of a basic control unit including a printer, a measuring stand, a constant-temperature-bath circulator, and a calibrated capillary viscometer depending on measuring range. For measurements at and below ambient temperature, this system was used in conjunction with a Model RTE-4 Neslab cooling system. Bath temperatures can be set and held constant to about ± 0.01 °C. Time measurements were made automatically with the help of a quartz timer with a resolution of 0.01 s and two light barriers across the viscometer. The light barriers detect the passing meniscus of the studied fluid and provide the start-stop signals for the time measurement.

Liquid mixtures were prepared with a Mettler precision digital balance Model PT 1200 with an accuracy of $\pm 10^{-2}$ g. The buoyancy effect was neglected, since errors in measured mass fractions introduced by this effect were much smaller than 0.1%.

Densities were determined with a Paar Model DMA 46 calculating density meter with built-in thermostat with an accuracy of $\pm 1 \times 10^{-4}$ g/cm³. This system simplifies the accurate determination of the density of the liquids by reducing the measuring procedure to the electronic measurement of a time period from which the density is automatically calculated with a built-in arithmetic processor. The instrument can measure densities between 15 and 40 °C. Extrapolation is used for lower or higher temperatures.

Table I. Physical Properties of Pure Components

component	M , g/mol	t_b , °C	Z
water	18.01	100.00	-1.10
methanol	32.04	64.70	+5.30
ethanol	46.07	78.30	+4.40
acetone	58.08	56.30	+10.90
1-propanol	60.10	97.20	+8.60
ethylene glycol	62.07	197.30	+1.60

Fluids used in this work were all purified, Spectar AR, with physical properties as listed in Table I. Evaporation rates were negligible in transferring the mixtures into capillary viscometers.

Results and Discussion

Viscosities and densities of the 12 following mixtures were measured at different temperatures, and the results of these measurements are listed in Table II; densities at 10 and 50 °C were found from extrapolation: acetone-water mixtures at 20, 25, 30, 37.8, and 50 °C; methanol-water mixtures at 10, 20, 30, 40, and 50 °C; ethanol-water mixtures at 10, 20, 30, 40, and 50 °C; methanol-ethanol mixtures at 10, 20, 30, 40, and 50 °C; methanol-ethanol-water mixtures at 10, 20, 30, 40, and 50 °C; 1-propanol-water mixtures at 30 °C; ethylene glycol-water mixtures at 30 °C; methanol-1-propanol mixtures at 30 °C; ethanol-1-propanol mixtures at 30 °C; methanol-1-propanol-water mixtures at 30 °C; ethanol-1-propanol-water mixtures at 30 °C; methanol-ethanol-1-propanol mixtures at 30 °C.

The binary and ternary data were correlated by means of the McAllister equation of viscosity (1), which for n -component mixtures reads

$$\ln \nu_m = \sum_{i=1}^n x_i^3 \ln \nu_i M_i - \ln M_{av} + \sum_{i=1}^n \sum_{j=1}^n x_i^2 x_j \ln \nu_{ij} M_{ij} + \sum_{i=1}^n \sum_{j=1}^n \sum_{k=1}^n x_i x_j x_k \ln \nu_{ijk} M_{ijk} \quad (1)$$

where

$$M_{av} = \sum_{i=1}^n x_i M_i$$

$$M_{ij} = (2M_i + M_j)/3$$

$$M_{ijk} = (M_i + M_j + M_k)/3$$

In eq 1, ν_m and x_i are the kinematic viscosity of the mixture and