very short time. It is also clear that this technique can also be used without any problems for the measurement of systems containing more than two components.

Acknowledgment

We thank Professor U. Onken for his great interest in this work and G. Schlensog for his technical assistance.

Glossary

A, B, C	Antoine constants
A_i	peak area of component i
A_{ij}	parameters used in the Margules, van Laar, Wilson, NRTL, and Uniquac equations
a_{mn}	interaction parameter in the Unifac equation
f_i	substance-specific correction factor for component i
g_i	mass fraction of component i
q_i	relative van der Waals surface area of component i
r_i	relative van der Waals volume of component i
v_i	liquid molar volume of component i

Greek Letters

α_{12}	nonrandomness parameter in the NRTL equation

Registry No. Benzene, 71-43-2; toluene, 108-88-3; *n*-butyraldehyde, 123-72-8; isobutyraldehyde, 78-84-2; valeraldehyde, 110-62-3; *n*-heptane, 142-82-5; *n*-octane, 111-65-9; *n*-decane, 124-18-5; *tert*-butyl alcohol, 75-65-0; 1-octene, 111-66-0.

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Viscosities of Solutions of Lithium Chloride in Water–Dimethyl Sulfoxide Mixtures at 25, 35, and 45 °C

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The viscosities and densities of a wide range of lithium chloride concentrations in water–dimethyl sulfoxide mixtures have been determined at 25, 35, and 45 °C. Jones–Dole *B* coefficients were calculated from the less concentrated solutions for 0.1, 0.3, 0.5, 0.7, and 0.9 mole fraction dimethyl sulfoxide solutions. Plots of Jones–Dole *B* coefficients vs. mole fraction show a positive deviation from linearity.

Introduction

Since early work by Jacob and co-workers (*1*) concerning the therapeutic promise of dimethyl sulfoxide, this compound has been the center of considerable controversy (*2*, *3*). However, it has been unequivocally shown that Me_2SO does enhance penetration through plant and animal membranes (*4*), and is particularly useful in enhancing percutaneous absorption (*5*, *6*). This property of Me_2SO is of special importance for enhancing the transdermal delivery rate of drugs (*7*).

With these applications in mind, an investigation of the transport properties of Me_2SO–water mixtures was considered of interest. This study reports on the viscosity measurements of a range of Me_2SO–water solutions with LiCl as an added electrolyte at 25, 35, and 45 °C. Viscosities of dilute electrolyte solutions can be analyzed in terms of the Jones–Dole equation (*8*).

Table I. Viscosity of Water-Me_2SO Mixtures at 25 °C

X_{Me_2SO}	η	X_{Me_2SO}	η
0.100	1.822	0.700	2.528
0.300	3.622	0.899	2.081
0.500	3.252		

$$\eta_{rel} = \eta/\eta_0 = 1 + AC^{1/2} + BC \qquad (1)$$

where η_{rel} is the relative viscosity, η is the measured viscosity, η_0 is the viscosity of the pure solvent, C is the molarity of the electrolyte, and A and B are the Jones–Dole coefficients.

The Jones–Dole A coefficient has been related to ion–ion interactions, and its value calculated theoretically (*9*). The B coefficient is related to ion–solvent interactions and has been used to make inferences concerning size, structure, and orientation of the solvated ion (*10*–*13*). Although many studies have considerable single solvent systems (*11*–*17*), fewer have used mixed solvent systems (*18*, *19*).

Experimental Section

Anhydrous LiCl (Fisher, Reagent) was dried at 125 °C for 2 h, cooled, and stored in a desiccator prior to sample preparation. Spectroscopic grade dimethyl sulfoxide was kept under nitrogen gas and used as received.

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Table II. Viscosities and Densities of Solutions of LiCl in Water-Me_2SO at 298, 308, and 318 K

C, M	$C^{1/2}$	η_{298}, cP	η_{308}, cP	η_{318}, cP	d_{298}, g/mL	d_{308}, g/mL	d_{318}, g/mL
(1) $0.100X_{Me_2SO}$							
0.0		1.822	1.406	1.130			
0.1169	0.3419	1.867	1.436	1.156	1.045	1.039	1.033
0.1953	0.4419	1.926	1.486	1.192	1.047	1.041	1.036
0.3949	0.6284	2.007	1.556	1.241	1.052	1.046	1.040
0.5046	0.7104	2.036	1.586	1.264	1.055	1.050	1.044
0.8893	0.9430	2.251	1.736	1.385	1.063	1.058	1.051
1.3083	1.1438	2.443	1.890	1.509	1.074	1.068	1.061
2.3394	1.5295	3.192	2.437	1.932	1.096	1.091	1.086
3.4743	1.8639	4.275	3.223	2.542	1.120	1.115	1.108
(2) $0.300X_{Me_2SO}$							
0.0		3.662	2.704	2.093			
0.1172	0.3423	3.834	2.844	2.187	1.090	1.082	1.074
0.2356	0.4854	4.038	3.022	2.305	1.094	1.086	1.078
0.3665	0.6054	4.337	3.207	2.471	1.098	1.090	1.082
0.5526	0.7434	4.728	3.459	2.639	1.103	1.095	1.088
0.7411	0.8609	5.505	4.019	3.036	1.112	1.105	1.096
1.8588	1.3634	10.71	7.342	5.366	1.141	1.133	1.125
2.8410	1.6855	20.57	13.50	9.498	1.164	1.157	1.150
3.7943	1.9479	42.53	26.27	17.13	1.185	1.178	1.168
(3) $0.500X_{Me_2SO}$							
0.0		3.252	2.496	1.972			
0.07944	0.2819	3.464	2.648	2.109	1.101	1.092	1.083
0.1062	0.3259	3.544	2.706	2.147	1.102	1.093	1.084
0.1583	0.3979	3.659	2.791	2.205	1.104	1.095	1.086
0.2073	0.4553	3.798	2.893	2.270	1.105	1.096	1.087
0.3532	0.5943	4.234	3.169	2.490	1.109	1.100	1.091
0.4723	0.6872	4.514	3.427	2.655	1.113	1.104	1.095
1.2131	1.1014	7.844	5.793	4.316	1.134	1.125	1.117
1.8492	1.3599	13.10	9.106	6.609	1.150	1.142	1.134
2.6921	1.6408	24.86	16.13	11.07	1.167	1.159	1.151
3.1866	1.7851	36.90	22.97	15.32	1.177	1.169	1.161
3.6291	1.9050	69.02	40.27	25.45	1.191	1.183	1.175
(4) $0.700X_{Me_2SO}$							
0.0		2.528	2.019	1.662			
0.06141	0.2478	2.677	2.139	1.760	1.101	1.091	1.082
0.1432	0.3784	2.805	2.230	1.832	1.104	1.094	1.085
0.2180	0.4669	3.033	2.397	1.957	1.106	1.096	1.087
0.3271	0.5719	3.281	2.576	2.097	1.109	1.099	1.090
0.5865	0.7658	4.139	3.198	2.552	1.119	1.109	1.099
1.1356	1.0656	6.815	5.069	3.915	1.135	1.127	1.118
1.7733	1.3317	13.34	9.330	6.823	1.153	1.145	1.132
2.5557	1.5987	28.69	18.39	12.78	1.172	1.164	1.155
(5) $0.899X_{Me_2SO}$							
0.0		2.081	1.713	1.439			
0.02127	0.1458	2.137	1.753	1.477	1.097	1.088	1.078
0.02732	0.1653	2.168	1.791	1.514	1.098	1.088	1.078
0.04288	0.2071	2.172	1.782	1.497	1.098	1.088	1.079
0.07365	0.2714	2.223	1.836	1.527	1.099	1.089	1.079
0.1226	0.3501	2.318	1.896	1.582	1.101	1.091	1.081
0.1521	0.3900	2.377	1.942	1.615	1.102	1.093	1.083
0.2581	0.5080	2.619	2.133	1.771	1.106	1.096	1.087
0.3740	0.6116	2.798	2.256	1.857	1.109	1.100	1.090
1.0728	1.0358	5.535	4.724	3.311	1.133	1.123	1.114
1.4361	1.1984	8.046	5.927	4.537	1.144	1.135	1.126
2.0937	1.4470	17.49	11.87	8.536	1.162	1.154	1.145

Table III. Jones-Dole B Coefficients for LiCl in Water-Me_2SO at 298, 308, and 318 K

	X_{Me_2SO}				
T, K	0.1	0.3	0.5	0.7	0.9
298	0.25	0.59	0.75	0.93	1.10
308	0.24	0.54	0.72	0.79	0.92
318	0.24	0.51	0.68	0.71	0.88

Viscosities were measured in Ostwald viscometers with flow times being read to ±0.1 s. The viscometers were calibrated with distilled, deionized water and absolute ethanol. Temperatures were maintained to 25.00 ± 0.01 °C, 35.00 ± 0.02 °C, and 45.00 ± 0.05 °C.

Densities were measured in 10-mL Weld pycnometers using 0.99707 g/mL as the calibrating density of water.

Results

The viscosities of the water-Me_2SO mixtures show a dramatic increase until approximately $0.3X_{Me_2SO}$, and then decrease in magnitude until reaching the value for pure Me_2SO (Figure 1). These results agree well with literature values (*20-23*). Figure 2 shows the Jones-Dole plots for the data at 25 °C. As seen, these plots are linear for LiCl concentrations below 0.36 M ($C^{1/2} = 0.6$). The Jones-Dole B coefficient is given by the slope of this linear region. Values of the B coefficients are plotted against X_{Me_2SO} for 25, 35, and 45 °C in Figure 3. For ideal behavior, the B coefficient should vary linearly with the change in mole fraction of Me_2SO. For LiCl in the water-Me_2SO system, a positive deviation exists that becomes less predominant as temperature increases.

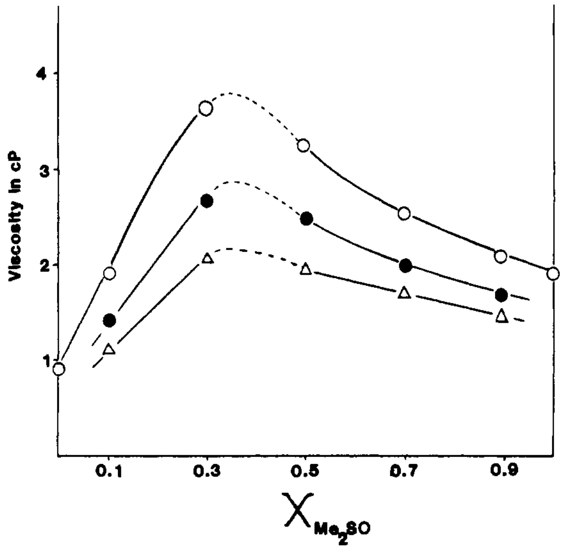

Figure 1. Viscosities of water-Me_2SO mixtures at 25 °C (○), 35 °C (●), and 45 °C (△).

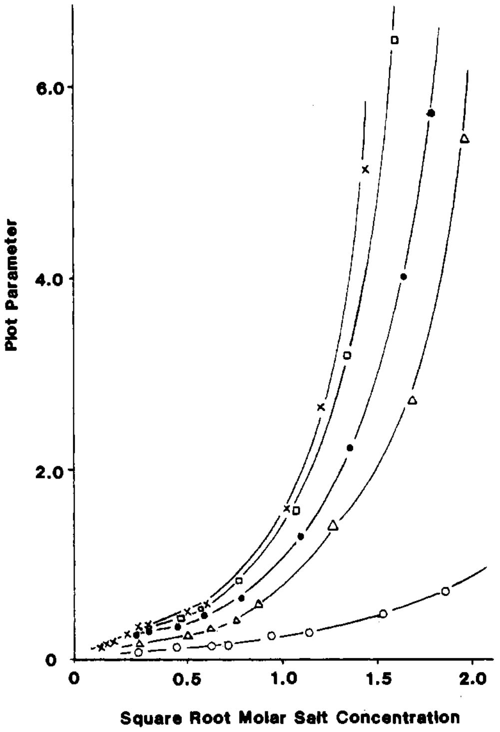

Figure 2. Jones–Dole plots for the data at 25 °C. The plot parameter is $(\eta/\eta_0 - 1)/C^{1/2}$: ○, 0.1 mole fraction Me_2SO; △, 0.3 mole fraction Me_2SO; ●, 0.5 mole fraction Me_2SO; □, 0.7 mole fraction Me_2SO; ×, 0.9 mole fraction Me_2SO.

Tables I and II give the viscosities and densities measured in this investigation.

Discussion

The maximum in viscosity for the water–Me_2SO solvent system can be attributed to the strong interaction of dimethyl sulfoxide with water. It has been estimated that the hydrogen bond between Me_2SO and water is $1^1/_3$ times as strong as the hydrogen bond between water and water (*24*). It is also noteworthy that this maximum occurs at a water/Me_2SO mole ratio of 2/1. There is abundant evidence for maxima in the deviation of several H_2O–Me_2SO properties from average values. Such maxima in "excess" properties have been found in viscosity (*21–23*), density (*22*, *23*), ΔH_{mix} (*22*, *25*), surface tension (*23*), dielectric constant (*23*), and ESR splitting constant (*26*). Often the maximum deviation occurs near mole fraction of Me_2SO = 0.33 (*27*). Our H_2O–Me_2SO viscosities (no salt added) are given in Table I. They compare well with previously reported results. A table listing additional literature values is available as supplementary material.

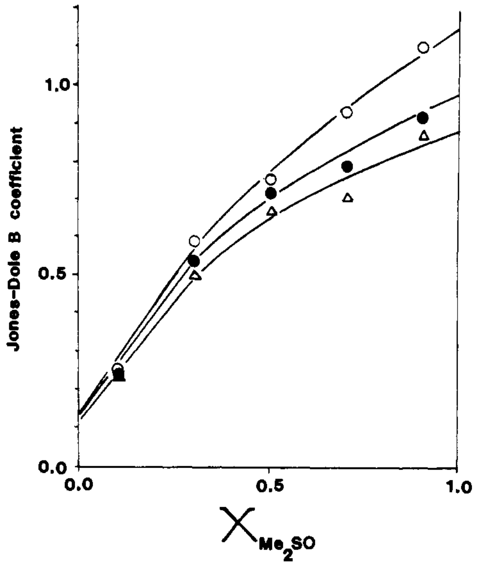

Figure 3. Jones–Dole *B* coefficients for LiCl in the binary solvent system water–Me_2SO: ○, 25 °C; ●, 35 °C; △, 45 °C.

As seen in Table II, measurements were made at concentrations which exceed the traditional maximum for the Jones–Dole treatment (*C* = 0.1). The *B* coefficients were obtained from the linear regions of the plots shown in Figure 2. Other systems have exhibited linear Jones–Dole plots at concentrations above 0.1 M (*28*, *29*). Figure 3 also demonstrates the possibility of extrapolating binary systems data to obtain *B* values for pure solvents. Such an extrapolation could be useful in cases where measurements in the pure solvent are difficult (*17*), or when an electrolyte has limited solubility.

The values of the Jones–Dole *B* coefficients (Table III) reflect changes in solution structure brought about by addition of the LiCl. All *B* values are positive, indicating that LiCl is a structure maker in all compositions of H_2O–Me_2SO.

Positive deviations from linearity are found in the *B* vs. *X* plots of Figure 3. Minima in such plots have been interpreted as suggesting that the mixed solvent H_2O–MeOH has even more structure than pure H_2O (*19*). That interpretation would imply that the maximum found here is due to less solvent structure in the mixed solvent. Yet the viscosity of the mixed solvent is greater than that of either component. Such a result is possible if the very strong interaction between H_2O and Me_2SO results in a breaking up of the network structure found in H_2O. Data on additional salts in H_2O–Me_2SO are needed. The effect of molar volume on viscosity may also play an important role. The molar volume of Me_2SO is much larger than that of H_2O or MeOH. NMR studies have indicated that the Li^+ ion shows a preference for H_2O over Me_2SO. Work with activity coefficients indicated no preference by Li^+ for either solvent (*30*).

Glossary

A	Jones–Dole *A* coefficient
B	Jones–Dole *B* coefficient
C	concentration in moles/liter
d	density in grams/milliliter
T	temperature in kelvin
X	mole fraction
η	absolute viscosity of solution in centipoise
η_0	absolute viscosity of pure solvents in centipoise

Registry No. Me_2SO, 67-68-5; LiCl, 7447-41-8; H_2O, 7732-18-5.

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Supplementary Material Available: Table entitled "Viscosity of Water–Me_2SO Mixtures at 25 °C"; it reports viscosities of 38 different mole fractions and is compiled from four separate works (1 page). Ordering information is given on any current masthead page.

Densities and Apparent Molar Volumes of Aqueous Magnesium Sulfate and Sodium Sulfate to 473 K and 100 bar

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Densities of aqueous solutions of $MgSO_4$ and Na_2SO_4 have been measured up to 473 K, 100 bar, and 1 m ionic strength. The derived apparent molar volumes along with the available literature data on these substances have been analyzed by using the ion-interaction (Pitzer) approach. $\bar{V}_2^0$ for $MgSO_4$ is obtained indirectly from values for $MgCl_2$, Na_2SO_4, and NaCl. The term in $\beta^{(2)}$ represents adequately the ion-association effect in $MgSO_4$ up to 473 K. The present results yield the pressure effect on various thermodynamic properties.

Introduction

Recently we (*1*) completed a study which yielded a comprehensive equation for the thermodynamic properties of aqueous magnesium sulfate at low pressure based on our own heat capacity measurements and heats of dilution and osmotic coefficients from the literature. In the present study we present the measurements of densities of aqueous magnesium sulfate and sodium sulfate to 473 K, 100 bar, and 1 m ionic strength. In addition to the intrinsic interest of the volumetric properties, they also yield the pressure dependence of the thermodynamic properties already determined for low pressure.

Sodium sulfate behaves as a normal strong electrolyte and the present results are readily fitted to the same form of ion-interaction (Pitzer) equations used earlier by Rogers and Pitzer (*2*) for the heat capacity of aqueous Na_2SO_4. Magnesium sulfate, however, shows significant electrostatic ion-pairing. Our study of the heat capacity (*1*) showed that it was possible to use the ion-interaction equations up to 473 K provided that a special binary interaction term was included. Also, one cannot unambiguously extrapolate the $MgSO_4$ data to zero molality to obtain $\bar{V}_2^0$; rather this quantity for $Mg^{2+} + SO_4^{2-}$ is obtained indirectly from the values of $\bar{V}_2^0$ for $MgCl_2$, Na_2SO_4, and NaCl. Values for NaCl are taken from the recent comprehensive studies (*3*, *4*) from this laboratory. For Na_2SO_4, we have generated equations based on Pitzer's equations using our measurements and literature values (*5*–*15*). For $MgCl_2$, we have fitted the recent measurements of Saluja (*15*) along with the other available literature data to the same equations. The details of the $MgCl_2$ calculations will be presented separately (*16*) along with the similar results for $CaCl_2$ and $SrCl_2$, and their heat capacities.

With the infinitely dilute values fixed, our measurements along with literature data (*5*, *7*–*10*, *12*, *13*) on aqueous $MgSO_4$ were satisfactorily fitted by the ion-interaction equations. This type of equation has been very successful for mixed electrolytes. Thus it is valuable to have the required parameters for Na_2SO_4 and $MgSO_4$ since these ions are prominent in sea water and in other natural or industrial waters.

Experimental Method

A dilatometer has been used to measure the changes in the volume of a solution as a function of temperature. The volume at room temperature is known from the literature. The constructional details and operation of the dilatometer are described elsewhere (*17*).

The pressure vessel, which contains about 5.75 cm^3 of solution, was modified in design and rebuilt to stand higher pressures. The pressure vessel is connected through a stainless-steel capillary to a mercury reservoir made of a coil of stainless-steel tubing which in turn is connected to a glass capillary column. The entire system can be pressurized with nitrogen gas.

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