Table II

temp, °C	density of mercury,[a] g cm^{-3}	no. of determinations over 2 yr	surface tension, mN m^{-1}	SD, mN m^{-1}	uncertainty apart from SD, mN m^{-1}
15	13.558	47	487.6 ± 1.1	0.1	± 1.0
20	13.546	49	486.4 ± 1.1	0.1	± 1.0
25	13.534	70	485.3 ± 1.1	0.1	± 1.0
50	13.473	50	480.0 ± 1.1	0.1	± 1.0

[a] References *4* and *8*.

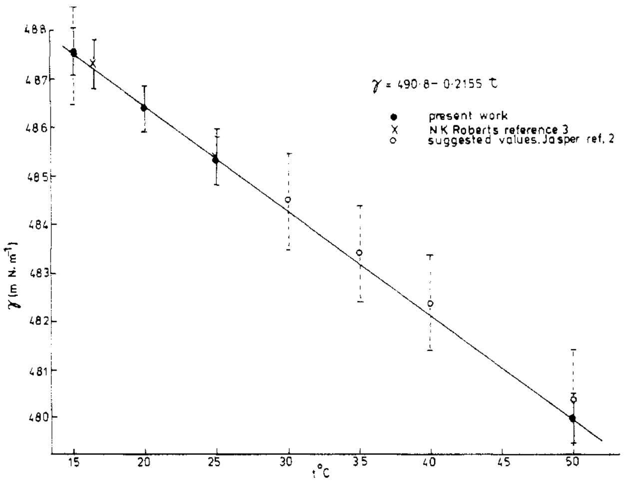

Figure 2. Temperature dependence of surface tension of mercury.

$\times \exp(-R/a + 0.58578)$ cm^{-1}.

The measured height, h, of the sessile drop from the equator to the vertex was subject to two corrections: (a) The wedge angle of the window through which the drop was measured was 15 s; i.e., 0.0001 cm^4 had to be subtracted from h. The wedge angle of the window used here is very much smaller than other wedge angles reported for the sessile drop method. For example, Kemball's two windows had wedge angles of 0.40° and 0.04° leading to corrections of 0.0082 and 0.0010 cm, respectively. In the apparatus used in this study the uncertainty in the wedge angle correction was 2×10^{-6} cm, i.e., beyond the limit of measurement of the traveling microscope. (b) The glass slab over which the traveling microscope was moved to detect the equator and the vertex of the mercury pool was not exactly level. There was a rise of 0.035 mm in 1 m toward the measuring vessel. Since the microscope moved over approximately the radius of the pool, i.e., ~2.5 cm, between readings, 0.8×10^{-4} cm had to be added to the observed height h.

The values for the surface tension obtained over a period of 2 yr are listed in Table II. The results in Table II fit a linear equation of the form

$$\gamma = 490.75 - 0.2155t$$

The correlation coefficient is 0.9998. This equation is in excellent agreement with that suggested by Jasper (*2*) from a bewildering array of experimental data for the surface tension of mercury (*1*), viz.

$$\gamma = 490.6 - 0.2049t$$

The results are shown in Figure 2 with the results obtained previously by one of the authors (*3*) and selected values suggested by Jasper (*2*).

The temperature coefficient obtained in this work, −0.2155 mN m^{-1} K^{-1}, is in slightly better agreement with the average of all previous experimental values (*1*), −0.224 mN m^{-1} K^{-1}, than with the value selected by Jasper (*2*), −0.2049 mN m^{-1} K^{-1}. It is difficult to draw any worthwhile conclusions from this comparison. A much more extended temperature range would be required to decide on the exact value of the temperature coefficient of the surface tension of mercury.

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Received for review August 5, 1980. Accepted February 12, 1981.

Molar Excess Volumes of Mixing of Tetrahydrofuran with Some Aliphatic Compounds Having Different Functional Groups

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Excess volumes of mixing for binary mixtures of tetrahydrofuran with a variety of aliphatic organic compounds containing different functional groups, namely, chloroform, carbon tetrachloride, 1,2-dichloroethane, acetonitrile, nitromethane, acetone, methyl formate, and ethyl acetate, have been determined from the experimental density measurements at 298.15 K over the entire composition range. The data do not indicate any obvious relationship between V^E and the electron donor–acceptor abilities of the solution constituents.

Introduction

The unlike interactions between different functional groups in the molecules of a binary mixture dictate the behavior of the system not only in the liquid phase but also in the gaseous and solid state (*1*, *2*). The strength of these interactions relative to the average of the strengths of the interactions in the two pure unmixed components can, to a fair extent, be predicted from the magnitude of the molar excess thermodynamic function (*3*–*5*).

A perusal of the literature revealed that the thermodynamic studies on the binary mixture containing tetrahydrofuran, a most commonly used organic solvent, are scanty. Recent communications from our laboratory reported excess volumes for the binary mixtures of tetrahydrofuran with aliphatic alcohols and amides (*6*, *7*). As an extension to these studies, excess volumes of mixing for the binary mixtures of tetrahydrofuran with some aliphatic organic compounds, namely, chloroform, carbon tetrachloride, 1,2-dichloroethane, acetonitrile, nitromethane, acetone, methyl formate, and ethyl acetate, have been deter-

0021-9568/81/1726-0268$01.25/0

Table I. Excess Volumes of Mixing, V^E, for the Binary Mixtures of Tetrahydrofuran with Some Aliphatic Organic Compounds at 298.15 K

X_1	$V^E/(cm^3\ mol^{-1})$	X_1	$V^E/(cm^3\ mol^{-1})$
Tetrahydrofuran (1) + Chloroform (2)			
0.0878	−0.072	0.6614	−0.341
0.1805	−0.158	0.7447	−0.298
0.3085	−0.261	0.8566	−0.228
0.4090	−0.325	0.9036	−0.182
0.6387	−0.351		
Tetrahydrofuran (1) + Carbon Tetrachloride (2)			
0.0778	−0.247	0.6038	−0.652
0.1819	−0.485	0.7447	−0.538
0.2619	−0.586	0.8395	−0.390
0.3551	−0.657	0.9421	−0.162
0.5069	−0.686		
Tetrahydrofuran (1) + 1,2-Dichloroethane (2)			
0.0873	0.041	0.5662	0.016
0.1564	0.078	0.6462	−0.011
0.3222	0.084	0.7042	−0.042
0.3979	0.070	0.8054	−0.091
0.4637	0.054	0.9093	−0.074
Tetrahydrofuran (1) + Acetonitrile (2)			
0.1134	−0.116	0.6318	−0.235
0.2235	−0.206	0.7409	−0.185
0.2962	−0.257	0.8017	−0.142
0.3839	−0.283	0.9225	−0.057
0.5378	−0.266		
Tetrahydrofuran (1) + Nitromethane (2)			
0.0672	0.034	0.5598	0.051
0.1363	0.065	0.6859	0.019
0.2403	0.104	0.7977	−0.015
0.3131	0.103	0.8468	−0.018
0.3888	0.078	0.9074	−0.015
0.4607	0.071		
Tetrahydrofuran (1) + Acetone (2)			
0.0858	−0.008	0.4693	−0.033
0.1373	−0.009	0.5593	−0.041
0.2206	−0.019	0.6488	−0.043
0.2838	−0.026	0.7887	−0.029
0.3937	−0.032	0.8918	−0.017
Tetrahydrofuran (1) + Methyl Formate (2)			
0.0684	0.086	0.6892	0.221
0.1427	0.170	0.7778	0.157
0.3172	0.272	0.8483	0.096
0.5326	0.277	0.9082	0.065
0.6018	0.261		
Tetrahydrofuran (1) + Ethyl Acetate (2)			
0.0718	0.031	0.5857	0.099
0.1866	0.070	0.6840	0.079
0.2468	0.087	0.7488	0.072
0.3384	0.104	0.8442	0.056
0.4574	0.107	0.9311	0.028
0.5376	0.102		

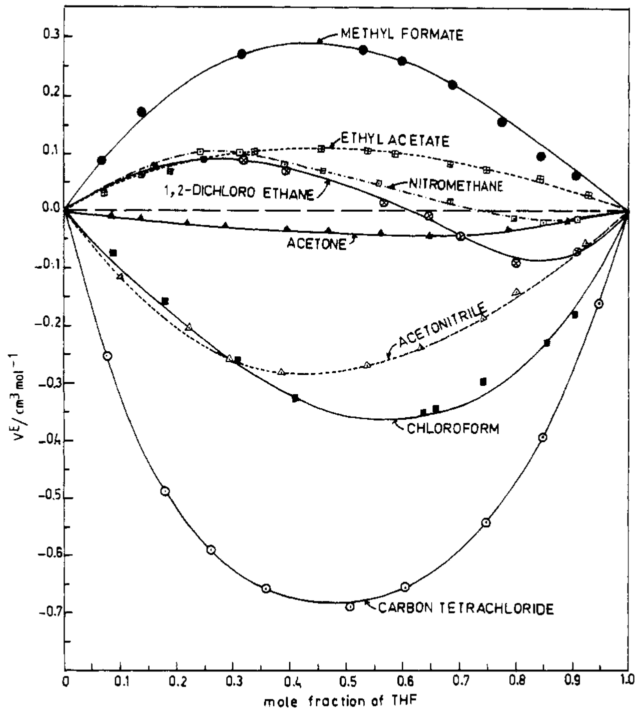

Figure 1. Molar excess volumes at 298.15 K for the binary mixtures.

Table II. Parameters of Excess-Volume Equation and the Standard Deviation, $\sigma(V^E)$, for Binary Mixtures of Tetrahydrofuran with Some Aliphatic Organic Compounds at 298.15 K

system	A	B	C	D	$\sigma(V^E)/(cm^3\ mol^{-1})$
tetrahydrofuran + chloroform	−1.4052	−0.3291	0.0158	−0.6009	0.005
tetrahydrofuran + carbon tetrachloride	−2.7684	0.2211	−0.6144	−0.0178	0.006
tetrahydrofuran + 1,2-dichloroethane	0.1827	−0.7504	−0.4774	−0.3105	0.006
tetrahydrofuran + acetonitrile	−1.1173	0.3520	0.1893	−0.2695	0.004
tetrahydrofuran + nitromethane	0.2625	−0.5411	−0.0770	0.0727	0.006
tetrahydrofuran + acetone	−0.1543	−0.0879	0.0281	−0.0629	0.004
tetrahydrofuran + methyl formate	1.1533	−0.3102	−0.1476	−0.1683	0.005
tetrahydrofuran + ethyl acetate	0.4190	−0.1413	0.0348	0.0209	0.006

mined at 298.15 K over the entire composition range and are reported in this paper.

Experimental Section

Aldrich IR–GC analyzed grade nitromethane and Fisher ACS certified grade tetrahydrofuran, chloroform, carbon tetrachloride, 1,2-dichloroethane, acetonitrile, acetone, and ethyl acetate were purified according to standard established procedures (*8*). Spectro-grade methyl formate supplied by Eastman Kodak Co. was fractionally distilled in a spinning band still with a reflux ratio of ~1:20. The reagents were stored in brown bottles and fractionally distilled immediately before use. The densities and refractive indexes of the solvents agreed closely with the accepted literature values (*8*, *9*).

The excess volumes of mixing, V^E, at 298.15 ± 0.001 K were calculated from the experimental density data which were obtained by using a vibrating flow densimeter (Sodev Inc.). The details of the experimental technique for the preparation of solutions and the measurement of density have been described earlier (*7*). The maximum uncertainty in the V^E data reported by us is expected to be around ±0.005 $cm^3\ mol^{-1}$.

Results and Discussion

The excess volumes of mixing for the binary mixture are recorded in Table I and plotted as a function of composition in Figure 1. The data were fitted to a smoothing equation

$$V^E = X_1(1 - X_1)[A + B(2X_1 - 1) + C(2X_1 - 1)^2 + D(2X_1 - 1)^3] \qquad (1)$$

where X_1 is the mole fraction of tetrahydrofuran. The values of the constants A, B, C, and D evaluated by the method of least squares, and the standard deviation for the excess volumes, $\sigma(V^E)$, are given in Table II.

It is observed that the V^E values for the binary mixtures of tetrahydrofuran with chloroform, carbon tetrachloride, acetonitrile, and acetone are negative over the entire composition range. For mixtures containing 1,2-dichloroethane, chloroform, and carbon tetrachloride, V^E at equimolar concentration decreases linearly with the number of chlorine atoms in the molecule. These observations support the view of Bolinga et al. (*10*) that the specific interactions of the type $-\mathrm{Cl}\cdots\mathrm{O}<$, $-\mathrm{C}{\equiv}\mathrm{N}\cdots\mathrm{O}<$, and $>\mathrm{C}{=}\mathrm{O}\cdots\mathrm{O}<$ may be responsible for negative excess volumes. Mixtures of tetrahydrofuran with methyl formate, ethyl acetate, and nitromethane have been found to exhibit positive V^E. The data do not indicate any obvious relationship between V^E and the electron donor-acceptor abilities of the solution constituents. Simultaneous thermodynamic and structural investigations on these solutions might yield some qualitative insight to distinguish the contributions to thermodynamic behavior of liquid solutions due to specific and nonspecific interactions. Further investigations on these mixtures are under way.

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Received for review July 11, 1980. Accepted February 25, 1981.

Equations of State for NaCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ Aqueous Solutions at High Pressures

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Equations of state for NaCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ aqueous solutions have been determined from the sound speeds over the ranges of I = 0–1 m, 0–40 °C, and 0–1000 bar with a precision estimated to be better than 30×10^{-6} cm^3 g^{-1} in specific volume. The results agree reasonably well with the data of various direct measurements.

Introduction

Few measurements have been made on the high-pressure *PVT* properties of NaCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$, aqueous solutions. Probably the most extensive and precise data given to date are the direct specific volume measurements of Emmet (*1*) and Chen, Emmet, and Millero (*2*). The direct specific volumes were measured on a high-precision magnetic float densimeter (*1*, *3*, *4*). In this study, we will take a different approach and determine the *PVT* properties from the sound-speed data (*5*) and the 1-atm density equations obtained in a recent article (*6*). The results will be compared with the data of various direct measurements.

Equation of State from Sound Speeds

The method used to determine an equation of state from sound speed has been described in detail elsewhere (*7*, *8*). The equation of state is in the form

$$K^P = v^0P/(v^0 - v^P) = K^0 + AP + BP^2 \qquad (1)$$

where K^P and K^0 are the secant bulk moduli at applied pressures P and 0 (1 atm), respectively, v^P and v^0 are respectively the specific volumes of the solutions at applied pressures P and 0, and A and B are temperature- and concentration-dependent parameters. Specific volumes are used in preference to densities because we have found that significantly simpler equations can be used to represent volume data at high pressures.

The specific volumes of the aqueous solutions at 1 atm are represented by eq 2 (*6*), where $v^0 = 1/d_0$ is the specific

$$1/v^0 = d_0 + am + bm^{3/2} + cm^2 + dm^{5/2} \qquad (2)$$

volume of pure water at 1 atm, m is the concentration in molality, and a, b, c, and d are temperature-dependent parameters. The constants for eq 2 are given in a previous paper (*6*).

The 1-atm sound speeds in the NaCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ aqueous solutions (*5*) are combined with the 1-atm specific volumes and heat capacities (*7*, *9*–*11*) to determine K^0 following the procedures described elsewhere (*7*, *8*). Values of K^0 are fit into the following equation

$$K^0 - K_0^{\,0} = em + fm^{3/2} + gm^2 \qquad (3)$$

where e, f, and g are temperature-dependent parameters given in Table I, and $K_0^{\,0}$ is the secant bulk modulus of pure water at 1 atm (*12*, *13*).

$$K_0^{\,0} = 19652.17 + 148.183t - 2.29995t^2 + 0.012810t^3 - 4.91564 \times 10^{-5}t^4 + 1.03553 \times 10^{-7}t^5 \qquad (4)$$

It should be noted that eq 3 reduces to $K^0 = K_0^{\,0}$ when the concentration of the salt, m, reduces to zero. This makes the equation for the salts consistent with the pure-water equation

0021-9568/81/1726-0270$01.25/0