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Static Dielectric Constants and Kirkwood Correlation Factors of Dimethyl Sulfoxide/Carbon Tetrachloride Solutions

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Static dielectric constants of 19 solutions of dimethyl sulfoxide (Me_2SO) and carbon tetrachloride (CCl_4) were measured at 298 K. The data were used to calculate excess molar polarization, ΔP, and Kirkwood correlation factors, g, over a range of concentrations from 0.056 74 to 0.9549 mole fraction Me_2SO. Although deviations of the mixture dielectric constants from ideal values are small, a significant tendency toward antiparallel alignment of neighboring dipoles is found for dilute solutions of Me_2SO in CCl_4.

Introduction

The nonideality of Me_2SO/CCl_4 mixtures has been previously established by studies of the excess volumes (*1*, *2*), surface tensions (*3*), and other thermodynamic functions (*4*, *5*) of the binary solutions. In addition, data from infrared spectroscopy (*6–9*) have been taken as evidence for self-association of Me_2SO in the neat liquid and in CCl_4 solution. Dielectric data and calculated Kirkwood correlation factors for the neat liquid (*10*, *11*), however, have indicated that short-range orientational correlations are not very important in pure Me_2SO. The dielectric measurements reported in this paper were undertaken in order to address the question of orientational ordering of Me_2SO in solutions with CCl_4, and thus interpret the spectroscopic data more clearly.

Static dielectric constants of 19 solutions of Me_2SO and CCl_4 were determined at 298 ± 0.5 K by using oscillometry. Excess dielectric constants and excess molar polarizations were calculated in order to assess the deviation from ideality as a function of concentration. The dielectric data were employed in the Kirkwood–Fröhlich equation for mixtures in order to calculate the correlation factor g, a parameter which provides a measure of the average relative orientation of neighboring dipoles in the solution.

Experimental Section

Glass-distilled Me_2SO and spectrograde CCl_4 were used as purchased, except for being stored over molecular sieves and kept under a dry inert atmosphere. Water content was checked by infrared spectroscopy (*12*), since Me_2SO is quite hygroscopic. Solutions ranging from 0.056 74 to 0.9549 mole fraction Me_2SO in CCl_4 were prepared by weighing to the nearest ±0.1 mg on an analytical balance and stored under a dry inert atmosphere. The dielectric constants were measured at 298 ± 0.5 K by using a Sargent Model V oscillometer, a commercial instrument with a 5-megacycle resonant circuit. The cell constant was determined by measuring the capacitance of seven very pure standards: water, methanol, carbon tetrachloride, chloroform, dimethyl sulfoxide, acetone, and chlorobenzene. Except for the Millipore deionized water, all these solvents were spectrograde quality or better. The dielectric constants for the standards were taken from ref *13*, and the procedure for calculating the cell constant is described in ref *14*. The scale reading S depends on the dielectric constant ϵ according to

$$S = \frac{C_gC_0\epsilon}{C_g + C_0\epsilon} - \frac{C_gC_0}{C_g + C_0} \tag{1}$$

where C_g is the capacitance of the glass walls of the cell and C_0 is the capacitance of the empty cell. The best values of C_g and C_0 were determined from a least-squares fit to eq 1, by using handbook values of ϵ for each of the six standards and corresponding values of S obtained by averaging three oscillometer readings. The variance of each fitting parameter was estimated by twice the reciprocal of the curvature of the χ^2 error plot (*15*). Once the standard curve represented by eq 1 was obtained, the dielectric constant of each binary solution was calculated from the measured scale readings. Knowing the variances of C_g, C_0, and S, we calculated the variance σ_ϵ^2 of each dielectric constant by using ordinary propagation of errors. The uncertainties reported in Table I are standard deviations, σ_ϵ.

Theory

The Clausius–Mosotti formula relates the dielectric constant ϵ of a pure fluid to the molar polarization P according to

$$P = \frac{\epsilon - 1}{\epsilon + 2}\frac{M}{\rho} \tag{2}$$

where M is the molecular weight and ρ is the mass density. In an ideal binary solution, the molar polarizations are additive (*14*):

$$P_{\text{ideal}} = x_1\frac{\epsilon_1 - 1}{\epsilon_1 + 2}\frac{M_1}{\rho_1} + x_2\frac{\epsilon_2 - 1}{\epsilon_2 + 2}\frac{M_2}{\rho_2} \tag{3}$$

where x_1 and x_2 are the mole fractions and ϵ_1 and ϵ_2 the dielectric constants of the two components. Also for an ideal solution, the dielectric constant of the mixture is an additive function of the volume fractions, ϕ_1 and ϕ_2:

$$\epsilon_{\text{ideal}} = \phi_1\epsilon_1 + \phi_2\epsilon_2 \tag{4}$$

The experimentally determined molar polarization, P_{exptl}, is related to the measured dielectric constant, ϵ_{exptl}, as follows:

$$P_{\text{exptl}} = \frac{\epsilon_{\text{exptl}} - 1}{\epsilon_{\text{exptl}} + 2}\frac{x_1M_1 + x_2M_2}{\rho} \tag{5}$$

where ρ is the density of the solution. The excess molar polarization, ΔP, and the excess dielectric constant, $\Delta\epsilon$, can be taken as measures of the extent of deviation from ideality:

$$\Delta P = P_{\text{exptl}} - P_{\text{ideal}} \tag{6}$$

$$\Delta\epsilon = \epsilon_{\text{exptl}} - \epsilon_{\text{ideal}} \tag{7}$$

The dielectric constant can be used to calculate the Kirkwood correlation factor, g (*16*), defined by

$$g = 1 + z\cos\gamma \tag{8}$$

where z is the average number of nearest neighbors and γ is the angle between the dipole moments of neighboring molecules. Kirkwood g factors greater than 1 are indicative of a tendency toward parallel alignment of dipoles, values less than 1 are obtained when antiparallel alignment is favored, and a value of unity is expected when orientational ordering is absent.

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Table I. Dielectric Constants of Me_2SO/CCl_4 Solutions

x_1[a]	ϵ_{exptl}[b]	ϵ_{ideal}[c]	$\Delta\epsilon$[d]
0	2.23		
0.0567	3.46 ± 0.02	4.05	−0.59
0.112	4.90 ± 0.02	5.89	−0.99
0.122	5.24 ± 0.03	6.26	−1.02
0.186	7.24 ± 0.04	8.67	−1.43
0.231	9.08 ± 0.05	10.14	−1.06
0.298	11.51 ± 0.06	12.69	−1.18
0.361	14.09 ± 0.08	15.17	−1.08
0.418	16.59 ± 0.10	17.52	−0.93
0.479	19.29 ± 0.12	20.14	−0.85
0.517	21.20 ± 0.13	21.78	−0.58
0.629	26.49 ± 0.18	26.96	−0.47
0.675	28.49 ± 0.20	29.16	−0.67
0.705	30.14 ± 0.21	30.67	−0.53
0.754	32.52 ± 0.24	33.14	−0.62
0.801	34.76 ± 0.26	35.56	−0.80
0.844	37.38 ± 0.30	37.89	−0.51
0.903	40.75 ± 0.34	41.12	−0.37
0.917	41.60 ± 0.35	41.91	−0.31
0.955	43.55 ± 0.37	44.04	−0.49
1	46.68		

[a] Mole fraction of Me_2SO in CCl_4. [b] Observed dielectric constant. [c] Ideal solution dielectric constant. [d] Excess dielectric constant.

In this work, the Kirkwood *g* factors were calculated from the Kirkwood–Fröhlich equation for mixtures (*17*, *18*):

$$\phi_1\frac{\epsilon-\epsilon_{\infty,1}}{2\epsilon+\epsilon_{\infty,1}}+\phi_2\frac{\epsilon-\epsilon_{\infty,2}}{2\epsilon+\epsilon_{\infty,2}}=\frac{\epsilon(\epsilon_{\infty,1}+2)^2}{3(2\epsilon+\epsilon_{\infty,1})^2}\,\frac{4\pi N_1 g\mu_1^{\,2}}{3kT} \tag{9}$$

where ϵ is the experimentally observed dielectric constant of the mixture, $\epsilon_{\infty,i}$ is the high-frequency permittivity of component i (1 = Me_2SO, 2 = CCl_4), N_1 is the number of polar molecules per cm^3 of solution, and μ_1 is the gas-phase dipole moment. The usual approximation $\epsilon_\infty = 1.1n_D^{\,2}$ (*19*) was adopted in this work, where n_D is the refractive index at the frequency of the sodium D line.

Results

The measured dielectric constants of the pure liquids and 19 binary solutions are displayed in Table I, along with the ideal values of ϵ and the excess dielectric constants $\Delta\epsilon$. The ideal dielectric constants here are based on actual (rather than ideal) volume fractions, calculated by using the formulas for partial molar volumes given by Grigg et al.:

$$V_1 = V_1^* + V_e/x + x(1-x)[\partial(V_e/x)/\partial x] \tag{10}$$

$$V_2 = V_2^* + V_e/(1-x) - x(1-x)[\partial(V_e/(1-x))/\partial x] \tag{11}$$

where x is the mole fraction of component 1 and V_1^* and V_2^* are the molar volumes of the pure components. The values V_1^* = 71.30 (Me_2SO) and 97.09 (CCl_4) cm^3/mol were used. The excess volumes V_e and related derivatives were obtained by using the cubic equation provided in ref *1*:

$$V_x = x(1-x)\sum_{j=0}^{3}A_j(2x-1)^j$$

with

$$A_0 = -2.422 \qquad A_1 = 0.128 \qquad A_2 = 0.272$$
$$A_3 = 0.113$$

In Figure 1 the dielectric constant is shown as a function of mole fraction, and the results are seen to be in good agreement with those of Jain et al. (*20*), who measured the dielectric constants at 303.15 K. The ideal solution dielectric constant, however, is linear in volume fraction rather than mole fraction, so we have also displayed our data as a function of *ideal* volume fraction ϕ_1 in Figure 2, where the straight line represents the result expected for an ideal solution. In spite of the large excess thermodynamic functions observed for Me_2SO/CCl_4 solutions (*1–5*), we find that the excess dielectric constants for these mixtures are quite small.

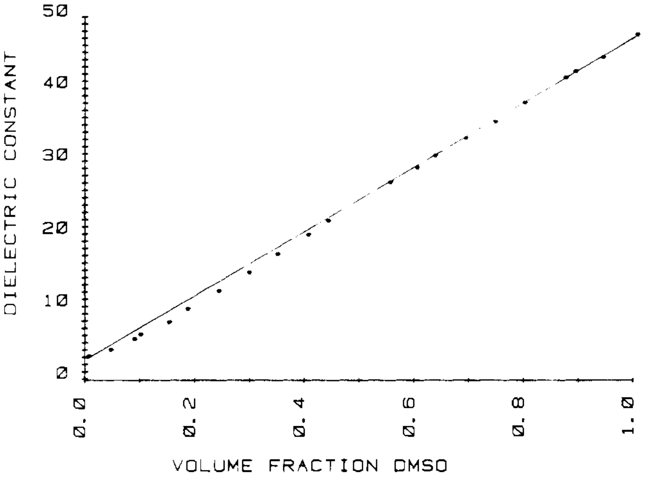

Figure 1. Dielectric constant vs. ideal volume fraction.

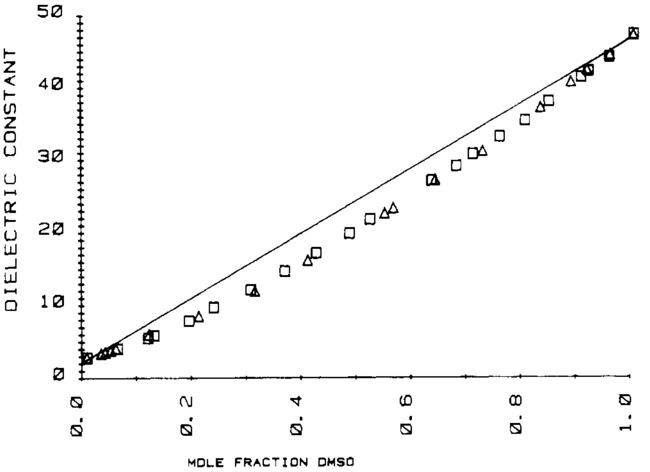

Figure 2. Dielectric constants of Me_2SO/CCl_4 solution vs. mole fraction: (□) this work, 298 K; (△) Jain et al. (*20*), 303 K.

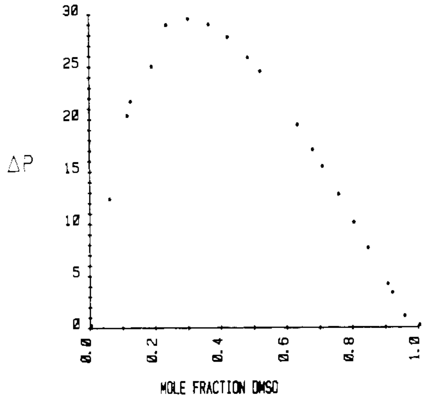

Figure 3. Excess molar polarization vs. mole fraction of Me_2SO.

The significance, however, of these small deviations is shown very clearly in Figure 3, where the excess molar polarization ΔP is displayed as a function of mole fraction Me_2SO. In the calculation of P_{ideal}, the densities of the pure liquids (ρ_1 = 1.0958 g/mL and ρ_2 = 1.58439 g/mL) were taken from ref *21*. The densities of the binary solutions, required to calculate P_{exptl}, were corrected by using the excess volume data and equations of ref *1*. (The excess volumes of Me_2SO/CCl_4 solutions are

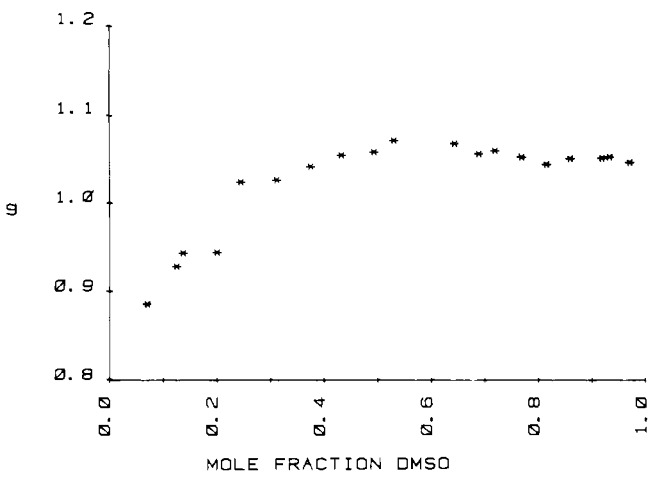

Figure 4. Kirkwood correlation factor vs. mole fraction of Me_2SO.

negative over the entire concentration range.) On the basis of excess molar polarization data, the maximum departure from ideal behavior occurs at about 0.33 mole fraction Me_2SO.

The Kirkwood correlation factors, shown in Figure 4, were evaluated according to eq 8. The gas-phase dipole moment, μ_1 = 3.96 D, was taken from ref *22*. The refractive indices used to approximate the high-frequency permittivity ($\epsilon_\infty \cong 1.1 n_D^2$) were n_1 = 1.45739 and n_2 = 1.4773 (*21*). As in pure Me_2SO, deviations from $g = 1$ are very small, indicating the absence of strong short-range orientational correlations. Nevertheless, in low-concentration solutions g is decidedly less than unity, a result consistent with the negative excess dielectric constants. The values of g for more concentrated solutions are only slightly greater than unity (1.04–1.06 for $x_1 > 0.5$).

Discussion

The limiting value of g as x_1 approaches 1 can be compared to the results of Amey (*10*) and Casteel and Sears (*11*) for pure Me_2SO. Amey calculated a g value slightly less than 1, which was independent of temperature in the range 290–350 K. However, he took μ_1 = 4.3 D, in contrast to μ_1 = 3.96 D used in this work. Our results are more in agreement with those of Casteel and Sears, who found g = 1.07 for neat Me_2SO at 298 K, than with those of Amey.

The dielectric data presented here indicate a slight tendency toward antiparallel alignment of neighboring dipoles in dilute solutions of Me_2SO in CCl_4. In view of the evidence from IR spectroscopy (*6*, *7*) that Me_2SO forms dimers in dilute solution in CCl_4, the dielectric data support the interpretation that antiparallel alignment, resulting in net cancellation of dipole moments, is favored in low dielectric constant media. At higher Me_2SO concentrations, on the other hand, g exceeds unity as the dielectric constant increases and aggregates with enhanced net dipole moments are stabilized. Recent evidence based on the observation of simultaneous vibrational transitions of Me_2SO in CCl_4 solution indicates the presence of Me_2SO n-mers over a wide range of concentrations, and theoretical analysis points to the importance of both parallel and antiparallel alignments (*7*). Thus, spectroscopic as well as thermodynamic (*1*–*5*) data support the conclusion that Me_2SO self-associates in nonpolar media, but the dielectric data reveal that the angular dependence of the intermolecular potential is insufficient to favor a particular relative orientation of neighboring dipoles.

Registry No. Me_2SO, 67-68-5; CCl_4, 56-23-5.

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Enthalpies for Toluene and Methylcyclohexane in the Fluid State

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A new electrical-matching, flow calorimeter has been used to measure enthalpies of toluene (333.15–513.15 K, 0.12–9.41 MPa) and of methylcyclohexane (353.15–513.15 K, 0.12–9.41 MPa) in both the liquid and vapor states. Perfect gas state enthalpies and heats of vaporization are shown to be in reasonable agreement with previous experiments and compilations.

Introduction

Liquid-phase heat capacities have been reported from 188.15 to 383.15 K for toluene by Burlew (*1*) and by Timmermans (*2*) plus from 383.15 to 523.15 K by San José et al. (*3*). Vapor-phase heat capacities were reported by Montgomery and DeVries (*4*) from 383.15 to 410.15 K. Yaws (*5*) has reviewed the thermophysical property data for toluene including vapor pressures, heats of vaporization, liquid-phase heat capacities, perfect gas state heat capacities, and saturated-liquid densities from roughly the triple point to critical point tempera-

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