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Relative Permittivities, Densities, and Refractive Indices of the Binary Mixtures of Sulfolane with Ethylene Glycol, Diethylene Glycol, and Poly(ethylene glycol) at 303.15 K

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Relative permittivities ($\in$), densities (ρ), and refractive indices (n_D) were measured for binary mixtures of sulfolane with ethylene glycol, diethylene glycol, poly(ethylene glycol) with an average molecular weight of 200, and poly(ethylene glycol) with an average molecular weight of 600 at 303.15 K over the whole mole fraction range. From these experimental data, the excess molar volumes (V^E), and deviations in refractive indices (Δn_D), relative permittivities ($\Delta\in$), and molar polarization (ΔP_m) were calculated. These quantities were fitted to the Redlich−Kister polynomial equation to derive the binary adjustable parameters and standard errors.

Introduction

The present paper is a continuation of our studies[1−6] on the thermodynamic properties of binary and ternary mixtures containing sulfolane as a common solvent. Sulfolane is an important industrial solvent having several advantageous physicochemical properties and the ability to extract monocyclic aromatic hydrocarbons from petroleum products. Mixtures of sulfolane with other solvents are also of particular interest. Research on their thermophysical properties has been reported by several authors.[7−12] In the present work, we have measured the density (ρ), refractive index (n_D), and relative permittivity ($\in$) over the entire composition range at 303.15 K for binary mixtures of sulfolane with ethylene glycol (EG), diethylene glycol (DEG), poly(ethylene glycol) with an average molecular weight of 200 (PEG-200), and poly(ethylene glycol) with an average molecular weight of 600 (PEG-600). The experimental results for ρ, n_D, and $\in$ were used to calculate the excess functions V^E and deviations from mole fraction averages Δn, $\Delta\in$, and ΔP_m.

Experimental Section

Materials. Sulfolane (99 mol %), ethylene glycol (99 mol %), diethylene glycol (99 mol %), poly(ethylene glycol) with an average molecular weight of 200, and poly(ethylene glycol) with an average molecular weight of 600 were obtained from Aldrich. All chemicals were used without further purification but were kept over freshly activated molecular sieves of type 4A for several days before use. Experimental values of ρ, n_D, and $\in$ of the pure liquids, along with literature values at 303.15 K, are given in Table 1. The binary mixtures were prepared by mass using an electronic Mettler balance (model AE-200) with a precision of ±0.01 mg. The accuracy of the mole fraction was estimated to be ±(2 × 10^{-4}).

Table 1. Experimental and Literature Values for ρ, n_D, and $\in$ of Pure-Component Liquids at 303.15 K

liquid	ρ/(g cm^{-3})	n_D	$\in$
sulfolane	1.26140	1.4818	43.39
	1.2614[14]	1.4820[14]	43.30[14]
ethylene glycol	1.10662	1.4288	37.60
	1.106512[17]	1.4284[18]	39.95[16]
	1.10664[14]		
diethylene glycol	1.11224	1.4440	29.11
PEG-200	1.11630	1.4564	18.43
PEG-600	1.11893	1.4637	13.74

Measurements. Densities of pure liquids and their mixtures were measured with an Anton Paar digital densimeter (model DMA 60), equipped with a density measuring cell (model 602), with a sensitivity up to 1 × 10^{-6} g cm^{-3}, which was thermostated with a temperature stability better than ±0.01 K. The accuracy in density measurements was better than ±(3 × 10^{-5}) g cm^{-3}.

Refractive indices for the sodium D line were measured using a thermostatically controlled Abbe refractometer. The refractometer was calibrated using twice distilled and deionized water. A minimum of three independent readings were recorded for each composition. The refractive index values was ±(2 × 10^{-4}).

Relative permittivities were measured with a Dipolmeter DM-O1 instrument from Wissenshaftlich Technische Werkstaten GmbH. The thermostated measuring cells of types MFL$_2$ ($7 \le \in \le 20$) and MFL$_3$ ($20 \le \in \le 70$) were adequate to cover the relative permittivity range of sulfolane + glycol mixtures at 303.15 K. The temperature was maintained constant to within ±0.01 K by means of a Haake F$_3$−K digital thermostat. The cells were previously calibrated with the standard pure liquids ethanol, glycerol, acetone, and cyclohexanol. The reproducibility of permittivity data was within ±0.05.

Results and Discussion

The experimental values of densities (ρ), refractive indices (n_D), and relative permittivities ($\in$) are listed in

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Table 2. Densities (ρ), Refractive Indices (n_D), Dielectric Constants ($\in$), and Excess Molar Volumes (V^E) of Sulfolane (1) + Glycols (2) at 303.15 K

x_2	ρ/(g cm^{-3})	V^E/(cm^3 mol^{-1})	n_D	$\in$
sulfolane (1) + ethylene glycol (2)				
0.0000	1.26140	0.0000	1.4818	43.39
0.0439	1.25201	−0.0104	1.4777	42.24
0.10120	1.25194	−0.0178	1.4756	40.05
0.2144	1.24558	−0.2562	1.4709	38.60
0.2984	1.23562	−0.3529	1.4626	38.46
0.4092	1.22566	−0.5882	1.4579	38.84
0.5074	1.21633	−0.8218	1.4526	38.15
0.6064	1.20462	−0.9995	1.4452	38.36
0.7034	1.19058	−1.1009	1.4368	38.22
0.8046	1.17363	−1.1844	1.4320	38.31
0.9044	1.15417	−1.2442	1.4301	39.00
0.9533	1.13216	−0.6980	1.4295	38.42
1.0000	1.10662	0.0000	1.4288	37.60
sulfolane (1) + diethylene glycol (2)				
0.0483	1.25431	− 0.0104	1.4789	40.70
0.0942	1.24759	− 0.0205	1.4769	37.96
0.1933	1.23384	−0.1034	1.4834	35.64
0.2933	1.22148	− 0.3041	1.4713	35.01
0.3964	1.21398	−0.9264	1.4698	34.37
0.4874	1.20887	−1.5982	1.4680	34.05
0.5991	1.19733	−2.0218	1.4652	33.09
0.6916	1.18291	−1.9957	1.4614	31.96
0.7987	1.16115	−1.5568	1.4548	30.88
0.9058	1.13153	−0.4447	1.4492	29.46
0.9499	1.12004	−0.0288	1.4464	29.00
1.0000	1.11224	0.0000	1.4440	29.11
sulfolane (1) + poly(ethylene glycol)-200 (2)				
0.0514	1.25175	−0.3003	1.4778	35.77
0.0904	1.24400	−0.4504	1.4757	34.30
0.1992	1.22334	−0.7497	1.4719	31.71
0.3020	1.20882	−1.2496	1.4688	29.85
0.4024	1.19515	−1.6001	1.4660	28.26
0.5077	1.18501	−2.2505	1.4632	26.25
0.6031	1.17158	−2.2000	1.4612	24.67
0.7006	1.15934	−2.1469	1.4593	23.00
0.8059	1.14401	−1.5997	1.4578	21.37
0.9017	1.12933	−0.7494	1.4575	19.98
0.9545	1.12309	−0.5000	1.4568	19.16
1.0000	1.11630	0.0000	1.4564	18.43
sulfolane (1) + poly(ethylene glycol)-600 (2)				
0.0463	1.23433	−0.3276	1.4777	32.11
0.0992	1.21316	−0.7172	1.457	28.29
0.2008	1.18863	−1.6528	1.4726	24.87
0.3034	1.17063	−2.0378	1.4703	22.57
0.4069	1.15913	−2.5820	1.4683	20.02
0.5007	1.15021	−2.7045	1.4668	19.03
0.6078	1.14176	−2.6034	1.4655	17.69
0.7010	1.13529	−2.2546	1.4642	16.99
0.8063	1.12916	−1.7563	1.4641	15.37
0.9404	1.12267	−0.9786	1.4639	14.21
0.9560	1.12130	−0.5641	1.4638	13.97
1.0000	1.11893	0.000	1.4637	13.74

Table 2. Excess molar volumes (V^E) were calculated using the equation

$$V^E/(\mathrm{cm}^3\ \mathrm{mol}^{-1}) = \sum_i^k x_i M_i(\rho^{-1} - \rho_i^{-1}) \tag{1}$$

where ρ and ρ_i are the densities of the mixture and of the pure-component liquid i, respectively. M_i is the molecular weight of component i.

Deviations in refractive indices, relative permittivities, and molar polarization were calculated as

$$\Delta y = y_m - x_1 y_1 - x_2 y_2 \tag{2}$$

where Δy represents Δn, $\Delta\in$, and ΔP_m. y_1 and y_2 refer to the respective pure-component properties, viz., n_D, $\in$, and P.

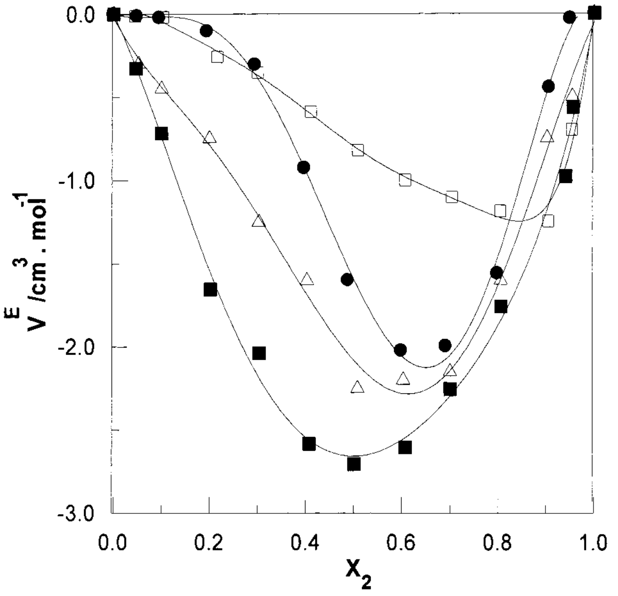

Figure 1. Excess molar volumes V^E for mixtures of sulfolane (1) + component (2) at 303.15 K as a function of mole fraction of component (2). x_2: ethylene glycol (□); diethylene glycol (●); PEG-200 (△); PEG-600 (■).

Table 3. Coefficients A_i and Standard Deviations σ in Equation 4 for Sulfolane (1) + Glycols (2) at 303.15 K

property	A_0	A_1	A_2	A_3	σ
sulfolane (1) + ethylene glycol (2)					
V^E/(cm^3 mol^{-1})	−2.9387	3.1016	−5.1600	7.3161	0.0951
Δn	0.0128	−0.0235	−0.0031	−0.0187	0.0003
$\Delta\in$	−0.16	−26.75	67.43	−40.57	0.11
ΔP_m/(cm^{-3} mol^{-1})	−3.54	1.55	−7.64	−0.40	0.09
sulfolane (1) + diethylene glycol (2)					
V^E/(cm^3 mol^{-1})	−6.4967	11.8289	5.0172	−12.6953	0.0620
Δn	0.0199	−0.0300	−0.0315	0.0155	0.0003
$\Delta\in$	−0.85	−28.24	75.51	−46.89	0.10
ΔP_m/(cm^{-3} mol^{-1})	−3.20	1.83	−3.87	−1.15	0.05
sulfolane (1) + poly(ethylene glycol)-200 (2)					
V^E/(cm^3 mol^{-1})	−8.3045	6.5013	1.8702	−5.8343	0.0973
Δn	−0.0220	0.0007	−0.0117	−0.0242	0.0002
$\Delta\in$	−1.58	−37.04	81.34	−43.26	0.10
ΔP_m/(cm^{-3} mol^{-1})	8.75	−3.49	−9.02	3.76	0.18
sulfolane (1) + poly(ethylene glycol)-600 (2)					
V^E/(cm^3 mol^{-1})	−10.6101	−0.0864	−0.3059	5.1533	0.1117
Δn	−0.0226	−0.0037	−0.0232	−0.0189	0.0003
$\Delta\in$	−4.15	−69.19	154.36	−82.01	0.09
ΔP_m/(cm^{-3} mol^{-1})	34.24	−18.78	−9.74	−1.18	0.48

The molar polarization P_m was calculated with the equation

$$P_m = (\epsilon - n_D^2)(2\epsilon - n_D^2)V_m/9\epsilon \tag{3}$$

where V_m is the molar volume of mixture

The excess functions V^E and deviations Δn, $\Delta\in$, and ΔP_m were fitted by a least-squares method to the Redlich–Kister equation[13]

$$V^E\ (\text{or}\ \Delta y) = x_1 x_2 \sum_{i=0}^k A_i (x_1 - x_2)^i \tag{4}$$

For each mixture, the optimum number of adjustable parameters was ascertained from an examination of the variation in the standard error σ

$$\sigma = \{\sum[V^E_{obs}\ (\text{or}\ \Delta y_{obs}) - V^E_{cal}\ (\text{or}\ \Delta y_{cal})]^2/n - p\}^{1/2} \tag{5}$$

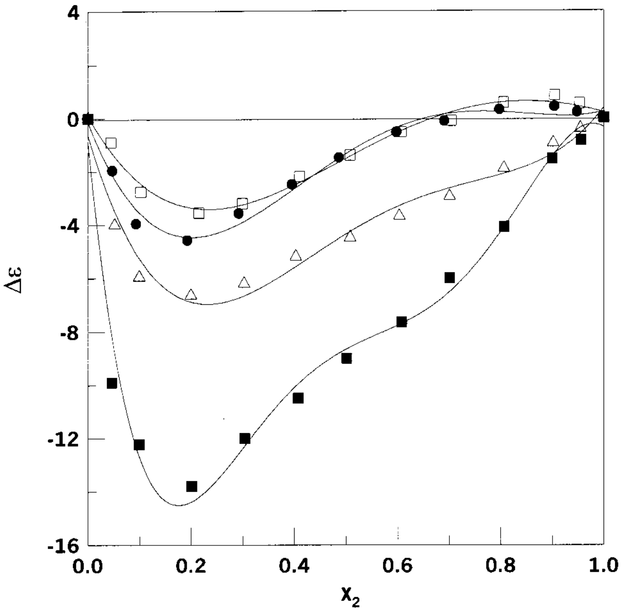

Figure 2. Dielectric constant deviations $\Delta\epsilon$ for mixtures of sulfolane (1) + component (2) at 303.15 K as a function of mole fraction of component (2). x_2: ethylene glycol (□); diethylene glycol (●); PEG-200 (△); PEG-600 (■).

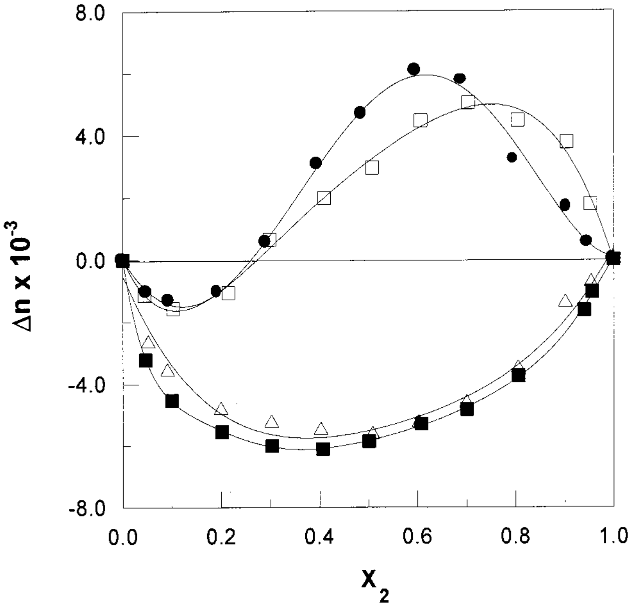

Figure 3. Refractive index deviations Δn for mixtures of sulfolane (1) + component (2) at 303.15 K as a function of mole fraction of component (2). x_2: ethylene glycol (□); diethylene glycol (●); PEG-200 (△); PEG-600 (■).

where n is the number of experimental points and p is the number of adjustable parameters A_i. The values of A_i and the standard errors σ are given in Table 3.

Excess molar volume versus mole fraction plots are shown in Figure 1. For all mixtures, the values of V^E are negative over the entire composition range, suggesting specific interactions between sulfolane and the glycol components of the mixture. The V^E results for the mixtures follow the sequence PEG-600 < PEG-200 < diethylene glycol < ethylene glycol, and the minima of the curves tend to shift toward the glycol-rich region of the mixtures. A large negative equimolar V^E value of -2.65 cm^3 mol^{-1} is shown by the PEG-600 + sulfolane mixture, which is 3 times higher than the -0.73 cm^3 mol^{-1} value observed for ethylene glycol + sulfolane. Generally, the values of V^E increase as the carbon chain length of the glycol increases. This is indicative of interstitial accommodation of sulfolane in the glycol structure and is corroborated by the $\Delta\epsilon$ data (Figure 2). The results of Δn vs x_2 at 303.15 K shown in Figure 3 exhibit almost the same trend as the V^E results.

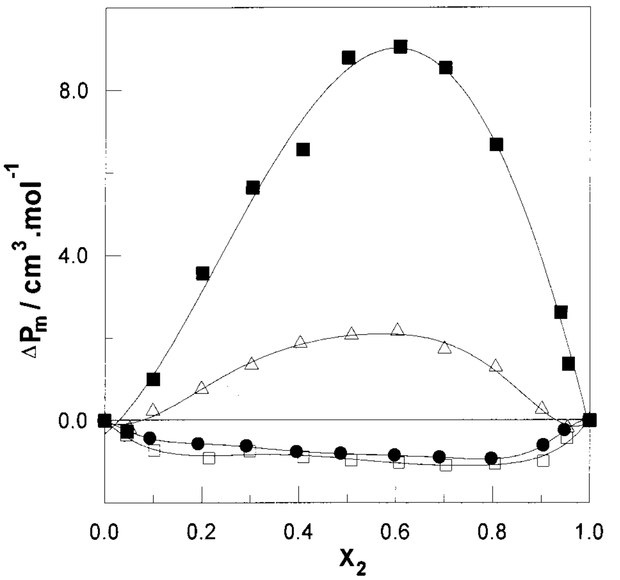

Figure 4. Molar polarization deviations ΔP_m for mixtures of sulfolane (1) + component (2) at 303.15 K as a function of mole fraction of component (2). x_2: ethylene glycol (□); diethylene glycol (●); PEG-200 (△); PEG-600 (■).

The deviations in the molar polarization, ΔP_m, for the binary mixtures of sulfolane + ethylene glycol and diethylene glycol are slightly negative and close to zero (Figure 4). The other two systems have positive ΔP_m values throughout the entire composition range. The curves show maxima at $x = 0.6$ mole fraction that increase as the carbon chain length in poly(ethylene glycol) increases.

The above data suggest that the specific interaction between sulfalone and glycols increases as the glycol carbon chain length increases and also as a result of molecular size differences.

Literature Cited

(1) Al-Azzawi, S. F.; Awwad, A. M. Excess Molar Volumes, Excess Logarithmic Viscosities, and Excess Activation Energies of Viscous Flow for 2-Ethoxyethanol + γ-Butyrolactone and + Sulfolane at 303.15 K. *J. Chem. Eng. Data* **1990**, *35*, 411−414.

(2) Al-Azzawi, S. F.; Awwad, A. M. Excess Molar Volumes and Viscosities of Binary Mixtures of an Aromatic Hydrocarbons and Sulfolane at 298.15 K. *Arab Gulf J. Sci. Res. Math. Phys.* **1988**, *A6*, 351−361.

(3) Al-Azzawi, S. F.; Awwad, A. M. Excess Molar Volumes and Viscosities of Binary Mixtures of γ-Butyrolactone and a Glycol at 303.15 K. *Fluid Phase Equilib.* **1990**, *60*, 289−293.

(4) Awwad, A. M.; Al-Dujaili, A. H.; Salman, T. A. Excess Molar Volumes and Viscosities of Binary and Ternary Mixture of Sulfolane + Benzene + 1-Alkanol at 303.15K. *Iraqi J. Chem.* **2001**, *27*, 121−125.

(5) Awwad, A. M.; Al-Dujaili, A. H.; Salman, H. E. Refractive Index, Relative Permittivity and Excess Properties of Substituted Benzenes + Sulfolane at 303.15 K. *Iraqi J. Chem.* **2001**, *27*, 115−120.

(6) Awwad, A. M.; Al-Dujaili, A. H.; Alian, N. R. Dielectric Constants of the Binary Mixtures of 2-Ethoxyethanol + γ-Butyrolactone and + Sulfolane at 303.15 K. Comparison with Theory. *Iraqi J. Chem.* **2000**, *26*, 94−100.

(7) Sacco, A.; Jannelli, L. Thermodynamic Behavior of Binary Mixtures Involving Sulfolane. I. Excess Volumes of Sulfolane with Benzene. *Thermodynamics* **1972**, *4*, 191−197.

(8) Sacco, A., Rakshit, A. K. Thermodynamic and Physical Properties of Binary Mixtures Involving Sulfolane. III. Excess Volumes of Sulfolane with Each of Nine Alcohols. *J. Chem. Thermodyn.* **1975**, 257−261.

(9) Karvo, M. Thermodynamic Properties of Binary and Ternary Mixtures Containing Sulfolane. V. Excess Enthalpies of Cyclohexane + Benzene, Cyclohexane + Toluene, Benzene + Sulfolane and Toluene + Sulfolane. *J. Chem. Thermodyn.* **1980**, *12*, 635−639.

(10) Karvo, M. Excess Enthalpies of Sulfolane + Benzene, + Toluene, + *p*-Xylene, and + Mesitylene as a Function of Temperature. *J. Chem. Thermodyn.* **1982**, *15*, 821−825.

(11) Jannelli, L.; Pansini, M.; Jalenti, R. Partial Molar Volumes of C_2-C_5 Normal and Branched Nitriles in Dilute Sulfolane Solutions at 30 °C. *J. Chem. Eng. Data* **1984**, *29*, 263−266.

(12) Chen, G.; Knapp, H. Densities and Excess Molar Volumes of Sulfolane + Ethylbenzene, Sulfolane + 1-Methylnaphthalene, Water + *N*,*N*-Dimethylformamide, Water + Methanol, Water + *N*-Formylmorpholine, and Water + *N*-Methylpyrrolidone. *J. Chem. Eng. Data* **1995**, *40*, 1001−1004.

(13) Redlich, O.; Kister, A. T. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345−348.

(14) Riddick, J. A.; Bunger, W. B. *Techniques of Chemistry*, 3rd ed.; Wiley: New York, 1970; Vol. II Organic Solvents.

(15) Aminabhavi, T. M.; Banerjee, K. Density, Viscosity, Refractive Index, and Speed of Sound in Binary Mixtures of Methyl Acetate + Ethylene Glycol or + Poly(ethylene glycol) in the temperature interval (298.15−308.15) K. *J. Chem. Eng. Data* **1998**, *43*, 852−855.

(16) Corradini, F.; Malugoli, M.; Marcheselli, L.; Marchetti, A.; Tassi, L.; Tosi, G. Dielectric Properties of Ethane-1,2-diol + 2-Methoxyethanol + Water Liquid Ternary Mixtures. *J. Chem. Eng. Data* **1993**, *38*, 565−568.

(17) Marchetti, A.; Tallazucche, M.; Tassi, L.; Tosi, G. Densities and Excess Volumes of 1,2-Ethanediol + 2-Methoxyethanol Solvent System at Various Temperatures. *J. Chem. Eng. Data* **1991**, *36*, 368−371.

(18) Marchetti, A.; Preti, C.; Tassi, L.; Tosi, G. The *N*,*N*-Dimethylformamide + Ethane-1,2-diol Solvent System. Dielectric Constant, Refractive Index, and Related Properties at Various Temperatures. *J. Chem. Eng. Data* **1991**, *36*, 365−368.

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