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Solubility of Sulfolane in Selected Organic Solvents

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The solubilities of sulfolane (tetrahydrothiophene 1,1-dioxide, tetramethylene sulfone (TMS)) have been determined experimentally in six solvents, 1-heptyne, tetrahydrofuran, 1,4-dioxane, 1,1,1-trichloroethane, benzene and cyclohexane, by a dynamic method in the temperature range (250 to 301) K. The results have been correlated by the Wilson, NRTL, and UNIQUAC equations. The existence of solid−solid first-order phase transition in sulfolane has been taken into consideration in the solubility curve calculations. The average root mean square deviations of the solubility temperatures for all the measured data vary from (1.5 to 1.6) K and depend on the particular equation used.

Introduction

As part of a study (Letcher and Moollan, 1995; Domańska *et al.*, 1995) into the physicochemical properties of binary mixtures involving sulfolane (tetrahydrothiophene 1,1-dioxide), the solubilities of sulfolane in six solvents, 1-heptyne, tetrahydrofuran, 1,4-dioxane, 1,1,1-trichloroethane, benzene, and cyclohexane, have been measured. Sulfolane has been extensively used in the petroleum industry for the recovery, by liquid extraction, of aromatic compounds and other organic liquids. Its mixtures have been the subject of many experimental investigations over the past 20 years.

The cryoscopic behavior of pure sulfolane and its solutions in some organic compounds has been investigated by Della Monica *et al.* (1968). Their results show that sulfolane solidifies as plastic crystals (phase I, mesomorphic phase), which undergoes a solid phase transition at 288.60 K, forming a new solid phase (phase II, crystalline nonrotational). The solid−liquid equlibrium (SLE) phase diagrams for benzene + sulfolane (Jannelli and Sacco, 1972), 1,4-dioxane + sulfolane (Jannelli *et al.*, 1975), carbon tetrachloride + sulfolane (Sacco *et al.*, 1976), 2-methyl-2-propanol + sulfolane (Inglese and Jannelli, 1978), and nitrobenzene + sulfolane (Jannelli *et al.*, 1982) have also been reported in the literature. Two different types of phase diagrams for the systems of 1,4-dioxane, carbon tetrachloride, or nitrobenzene + sulfolane were obtained; one is of a simple eutectic type, while the other exhibits two eutectics and a flat maximum corresponding to a solid molecular compound. The SLE phase diagram, published by Sacco *et al.* (1976), of carbon tetrachloride + sulfolane exhibits a miscibility gap at a mole fraction of sulfolane of $0.08 \leq x_2 \leq 0.58$ and a compound which melts incongruently into the immiscible liquids. The occurrence of an AB_2 solid compound in the mixture 1,4-dioxane + sulfolane and an AB solid compound in the mixture of carbon tetrachloride + sulfolane was ascribed to weak electrostatic attractions in a system involving a favorable crystal packing geometry rather than to bonding or other strong specific interactions. This was evident from viscosity and dielectric constant measurements of the binary liquid mixtures developed by Jannelli *et al.* (1975) and Sacco *et al.* (1976). The system benzene + sulfolane exhibits a simple eutectic with no strong interactions. The deviations from ideality were ascribed by Jannelli and Sacco (1972) to structural effects.

Sulfolane is a dipolar aprotic substance with a low donor number of 14.81 and a large dipole moment in the liquid phase, $\mu = 4.8$ D (Jannelli *et al.*, 1982). The steric hinderance resulting from the large globular hydrocarbon moeity is responsible for the weakly structured substance below its melting point (plastic phase I), and also the large enthalpy change of the solid−solid transition, which considerably exceeds the enthalpy of fusion (Della Monica *et al.*, 1968).

In the papers cited above, little attention has been paid to the analysis of the SLE data using modern theories of mixing. Jannelli *et al.* (1982) published data only for the nitrobenzene + sulfolane mixture and described the liquidus curve together with numerical values of the differences between the heat capacity of the solute (compound 2) in the solid (plastic phase I) and the heat capacity of the liquid phase $\Delta_{\mathrm{fus}}C_{p2}(\mathrm{l,pI})$, at a melting temperature equal to zero. This assumes that there is no loss of rotational freedom of sulfolane molecules on solidification. During the phase transition between plastic phase I and crystalline phase II, which was assumed as an orientational fusion, the $\Delta_{\mathrm{trs}}C_{p2}(\mathrm{pI,pII})$ was calculated to be 45.51 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$.

In this work, the results of the correlation of the solubility of sulfolane in various solvents with respect to the solid−solid phase transition in sulfolane are given in terms of the Wilson (Wilson, 1964), NRTL (Renon and Prausnitz, 1968), and UNIQUAC (Abrams and Prausnitz, 1975) equations, utilizing parameters taken from solid−liquid equilibrium for the simple eutectic mixtures only. The correlations have been done using the data reported here as well as the data published earlier.

Experimental Section

Materials. The solvents were obtained from Aldrich Chemical Co. (with a quoted purity of 99.9 mass %) and were purified by fractional distillation through a 30 plate distillation column. The compounds were dried using

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Table 1. Physical Properties of the Pure Components at 298.15 K, Molar Volumes V_{mi}, Refractive Indexes n_D, and Melting Point T_{fus2}

component	V_{mi}/ $(cm^3 \cdot mol^{-1})^a$	n_D		T_{fus2}/K	
		exptl	lit.[a]	exptl	lit.[b]
1-heptyne	138.10	1.40821	1.4080[c]		
tetrahydrofuran	81.09	1.40512	1.40496		
1,4-dioxane	85.66	1.02786	1.02797		
1,1,1-trichloro-ethane	100.37	1.43612	1.4359		
benzene	89.40	1.49785	1.49792		
cyclohexane	108.70	1.42352	1.42354		
sulfolane	95.26	1.48114	1.4810[d,e]	301.60	301.60

[a] Riddick *et al*., (1986). [b] Inglese and Jannelli (1978). [c] At 293.15 K. [d] Shell (1964). [e] At 303.15 K.

Table 2. Solubility Measurements for Solvent (1) + Sulfolane (2), Liquid Phase Mole Fraction, x_2, Experimental Equilibrium Temperature, T_2^{I} and T_2^{II}, for the Plastic Crystals I and Crystalline Phase II, and Activity Coefficient, γ_2

x_2	T_2^{II}/K	γ_2	x_2	T_2^{II}/K	γ_2	T_2^{I}/K
1-Heptyne (1) + Sulfolane (2)						
0.1654	266.09	4.65	0.6696	276.85	1.29	
0.2175	268.82	3.63	0.7005	277.10	1.24	
0.2409	269.32	3.31	0.7035	276.74	1.23	
0.2685	270.45	3.01	0.7395	277.75	1.18	
0.2891	270.90	2.81	0.7697	278.15	1.14	
0.3138	271.43	2.60	0.7889	278.00	1.11	
0.3386	271.82	2.42	0.8217	278.86	1.07	
0.3722	272.44	2.22	0.8361	280.16	1.07	
0.4046	273.00	2.05	0.8499	279.45	1.05	
0.4310	273.35	1.93	0.8800	280.74	1.02	
0.4839	273.80	1.73	0.9062	282.05	1.08	
0.5191	274.15	1.62	0.9294	283.38	1.00	
0.5395	274.50	1.56	0.9259	283.62	1.00	
0.5533	274.57	1.53	0.9467	285.19	1.00	
0.5597	274.90	1.51	0.9718	286.82	1.00	
0.5846	275.30	1.46	0.9872	288.03	1.00	
0.6102	276.00	1.40	0.9959		1.00	293.35
0.6236	275.60	1.37	1.0000		1.00	301.60
0.6421	276.55	1.35				
Tetrahydrofuran (1) + Sulfolane (2)						
0.1952	235.46	2.66	0.8509	272.07	0.97	
0.2421	238.94	2.26	0.8968	275.93	0.96	
0.3010	241.50	1.88	0.9278	279.43	0.96	
0.3510	243.94	1.67	0.9437	281.26	0.96	
0.4364	248.35	1.42	0.9599	282.76	0.96	
0.4801	251.14	1.34	0.9644	284.10	0.96	
0.5391	254.25	1.24	0.9728	285.05	0.97	
0.5766	256.05	1.18	0.9773	285.96	0.97	
0.6211	258.79	1.14	0.9787	286.47	0.97	
0.6706	261.00	1.08	0.9811	286.95	0.98	
0.7269	264.75	1.04	0.9830	287.08	0.98	
0.7775	266.85	1.00	0.9910		0.99	292.54
0.8164	269.10	0.97	1.0000		1.00	301.60
1,1,1-Trichloroethane (1) + Sulfolane (2)						
0.6630	276.74	1.25	0.9081	281.75	1.02	
0.7100	270.15	1.19	0.9294	283.05	1.01	
0.7610	273.38	1.14	0.9462	284.35	1.00	
0.7869	274.12	1.11	0.9594	285.05	0.99	
0.8081	275.45	1.09	0.9753	287.94	0.99	
0.8201	276.29	1.08	0.9764		1.00	289.55
0.8386	277.45	1.07	0.9837		1.00	292.25
0.8534	278.29	1.06	0.9861		1.00	295.25
0.8689	279.25	1.05	1.0000		1.00	301.60
0.8951	280.74	1.03				
Benzene (1) + Sulfolane (2)						
0.4910	257.55	1.41	0.9401	286.72	1.02	
0.5001	257.59	1.39	0.9722	288.32	1.00	
0.5923	264.42	1.27	0.9869		1.00	294.67
0.7003	270.33	1.15	0.9899		1.00	295.80
0.8384	280.12	1.07	1.0000		1.00	301.60
0.8853	283.21	1.04				
Cyclohexane (1) + Sulfolane (2)						
0.9398					(LLE)	301.60
0.9412	292.35	1.04	0.9570		1.03	294.00
0.9500	292.71	1.03	0.9662		1.02	294.46
0.9523	293.11	1.03	0.9706		1.01	294.67
			0.9772		1.01	295.01
			0.9856		1.00	296.39
			1.0000		1.00	301.60

activated type 5 Å molecular sieves, and the water content was found to be less than 0.01 mass %, as determined by GLC analysis. Sulfolane was also supplied by Aldrich Chemical Co. (98 mass % reagent) and was vacuum distilled twice at a pressure below 2.7 kPa to yield a colorless and odorless product. To minimize the contact of this deliquescent reagent with moist air, the product was kept in sealed bottles in a desiccator. The physical properties of the reagents used in this work are listed in Table 1 together with literature values.

Procedure. The solubilities were determined using a dynamic method described by Domańska (1986). The mixtures of solute and solvent were prepared by mass. The mixture was well stirred using a magnetic stirrer and heated very slowly with a heating rate which did not exceed 2 K·h^{-1} near the equilibrium temperature. The temperature at which the last crystals disappeared (disappearence of solution cloudiness) was taken as the temperature of the solution−crystal equilibrium. Measurements were performed in a small range of solute (compound 2) mole fractions from $x_2 = 0.16$ (1-heptyne, tetrahydrofuran), 0.6 (1,1,1-trichloroethane), 0.5 (1,4-dioxane), or 0.9 (cyclohexane) to $x_2 = 1$ over the temperature range from (250 to 310) K. The temperature was measured using a calibrated platinum resistance thermometer (Autotherm2 by Gallenkamp), with an accuracy of 0.01 K. The reproducibility of the measurements was better than 0.1 K, which corresponded to a estimated error in composition of $\Delta x_2 = 0.001$. The experimental results of the solubility and activity coefficients (γ_2) of sulfolane as a solute at equilibrium temperatures are given in Tables 2 and 3.

Results and Discussion

Sulfolane is most soluble in tetrahydrofuran and least soluble in 1-heptyne. The order of solubility of sulfolane is tetrahydrofuran > 1,4-dioxane > 1,1,1-trichloroethane > benzene > carbon tetrachloride > 2-methyl-2-propanol > 1-heptyne. These results indicate that no hydrogen bonds or other strong interactions exist between sulfolane and 1-heptyne or 2-methyl-2-propanol. This is supported by work done by Della Monica *et al.* (1968), which revealed that no hydrogen bonds exist between benzoic acid and sulfolane.

In all the solvents used in this work, with the exception of tetrahydrofuran over a small concentration range, the solubility of sulfolane is lower than the ideal value. The effect of the interactions between sulfolane and the solvents observed by Domańska *et al.* (1995) in vapor−liquid equilibrium measurements was similar to that observed in this work. The solubility of sulfolane in 1-heptyne is much lower than ideal, and the experimental activity coefficients of the solute (γ_2) for $x_2 > 0.16$ are in the range 4.6−1.0. The solubility of sulfolane in 1,4-dioxane for $x_2 > 0.84$ is close to ideal with experimental activity coefficients $\gamma_2 \approx 1.0$. This corresponds to the liquidus curve related to the sulfolane crystal phases I and II. Evidence for the formation of a solid molecular compound which largely decomposes on melting was observed by Jannelli *et al.* (1975) and in our results, presented in Table 3. This indicates the possibility of strong interactions between sulfolane and 1,4-dioxane in the concentration range $x_2 < 0.84$. The maximum compound formation was observed at $x_2 = 0.7$

Table 3. Solubility Measurements for 1,4-Dioxane (1) + Sulfolane (2), Liquid Phase Mole Fraction, x_2, Experimental Equilibrium Temperature, T_2^{I} and T_2^{II}, for the Plastic Crystals I and Crystalline Phase II, and Activity Coefficient, γ_2

x_2	T_1/K	T_2^{II}/K	x_2	T_2^{II}/K	T_2^{I}/K	γ_2
0.0000	284.95[a]		0.6286	277.62[c]		
0.1100	282.88[a]		0.6610	278.38[c]		
0.1284	282.18[a]		0.6628	278.21[c]		
0.1530	280.81[a]		0.7029	278.73[c]		
0.1949	279.49[a]		0.7426	278.70c		
0.2300	278.28[a]		0.7487	278.66c		
0.2581	277.19[a]		0.7730	267.67[b]		
0.2961	275.80[a]		0.7737	278.30[c]		
0.3316	274.35[a]		0.7964	277.86[c]		
0.4020	271.46[a,b]	274.24[c]	0.8137	277.28[c]		
0.4152	270.65[a,b]	274.44[c]	0.8137	271.29[b]		
0.4252	270.57[a,b]	274.62[c]	0.8148	271.32[b]		
0.4860	268.25[a,b]	275.70[c]	0.8180	277.29[c]		
0.5200		276.11[c]	0.8361	273.24		1.03
0.5806		276.81[c]	0.9384	274.20		1.03
0.6039		277.44[c]	0.8471	275.33		1.02
0.6089		277.51[c]	0.8732	277.13		1.02
			0.8738	277.65		1.02
			0.9066	280.30		1.02
			0.9372	283.35		1.02
			0.9553	285.15		1.02
			0.9620	286.30		1.02
			0.9665	286.80		1.02
			0.9759	287.65		1.02
			0.9821	293.20		1.02
			0.9860		293.25	1.02
			0.9880		293.35	1.02
			0.9915		297.40	1.02
			0.9950		297.50	1.00
			1.0000		301.60	1.00

[a] T_1/K = solute (1) liquidus equilibrium temperature. [b] Solute (1) or (2) liquidus metastable form. [c] Solute (2) compound equilibrium curve.

(T = 278.7 K) and also at the two eutectic points, $x_2 = 0.36$ (T = 272.1 K) and $x_2 = 0.68$ (T = 258.2 K). The latter eutectic refers to the metastable crystalline phase II. Although the shape of the phase diagram reported by Jannelli *et al.* (1975) is similar to that reported here, the results are not identical. The difference could be a result of the different experimental techniques used, DSC as opposed to our dynamic method, as well as the fact that both cooling and heating curves were used in the DSC method. Typical examples of the shapes of the liquidus curves are shown in Figures 1 and 2 for the 1,1,1-trichloroethane + sulfolane and 1-heptyne + sulfolane mixtures.

The solubility of a solid nonelectrolyte, 2, in a liquid solvent can be expressed as

$$-[\ln x_2] = \frac{\Delta_{\mathrm{fus}}H_2}{R}\left[\frac{1}{T} - \frac{1}{T_{\mathrm{fus2}}}\right] - \frac{\Delta_{\mathrm{fus}}C_{p2}(\mathrm{l,pI})}{R}\left[\ln\left(\frac{T}{T_{\mathrm{fus2}}}\right) + \frac{T_{\mathrm{fus2}}}{T} - 1\right] + \ln \gamma_2 \quad (1)$$

where x_2, γ_2, $\Delta_{\mathrm{fus}}H_2$, $\Delta_{\mathrm{fus}}C_{p2}$, T_{fus2}, and T are the mole fraction of compound 2 (sulfolane), activity coefficient of compound 2, enthalpy of fusion, solute heat capacity during the melting process (l,pI), melting temperature of the solute, and equilibrium temperature, respectively. If the solid–solid transition occurs before fusion, an additional term must be added to the right hand side of eq 1 (Wiemer and Prausnitz, 1965; Choi and McLaughlin, 1983):

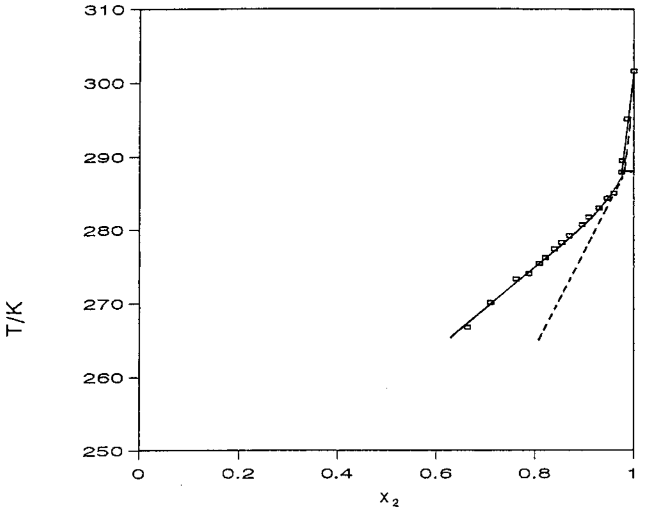

Figure 1. Solubility of sulfolane (2) in 1,1,1-trichloroethane (1): Solid line, calculated by the Wilson equation; dotted line, ideal solubility.

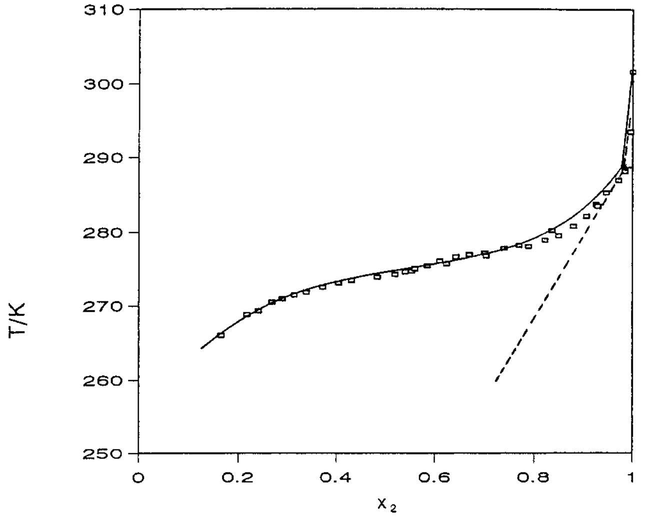

Figure 2. Solubility of sulfolane (2) in 1-heptyne (1): solid line, calculated by the UNIQUAC equation; dotted line, ideal solubility.

$$-[\ln x_2] = \frac{\Delta f_{\mathrm{us}}H_2}{R}\left[\frac{1}{T} - \frac{1}{T_{\mathrm{fus2}}}\right] - \frac{\Delta_{\mathrm{fus2}}C_{p2}(\mathrm{1,pI})}{R}\left[\ln\left(\frac{T}{T_{\mathrm{fus2}}}\right) + \frac{T_{\mathrm{fus2}}}{T} - 1\right] + \frac{\Delta_{\mathrm{trs}}H_2}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{trs2}}}\right) - \frac{\Delta_{\mathrm{trs2}}C_{p2}(\mathrm{pI,pII})}{R}\left[\ln\left(\frac{T}{T_{\mathrm{trs2}}}\right) + \frac{T_{\mathrm{trs2}}}{T} - 1\right] + \ln \gamma_2 \quad (2)$$

where $\Delta_{\mathrm{trs}}H_2$, T_{trs2}, and $\Delta_{\mathrm{trs}}C_{p2}(\mathrm{pI,pII})$ are the enthalpy and temperature of the solid–solid transition of the solute and the solute heat capacity during the transition process, respectively. Equation 1 was used for temperatures above the transition temperature and eq 2 at lower temperatures. Equations 1 and 2 assume the absence of miscibility in the solid phase. The enthalpy of fusion and phase transition of sulfolane were $\Delta_{\mathrm{fus}}H_2 = 1427.70$ J·mol^{-1} (Riddick *et al.*, 1986) and $\Delta_{\mathrm{trs}}H_2 = 5353.90$ J·mol^{-1} (obtained from the cooling curve of pure sulfolane by comparison with the fusion area from Della Monica *et al.* (1968)), whereas the differences between the heat capacities of the solute in the

Table 4. Parameters for the Wilson, NRTL, and UNIQUAC Equations, Determined from Binary Solid–Liquid Equilibria for the Systems Solvent (1) + Sulfolane (2), as Well as the Calculated Root Mean Square Deviation, σ_T

	parameters		
component 1	Wilson $(g_{12} - g_{11})/(\mathrm{J \cdot mol^{-1}})$ $(g_{12} - g_{22})/(\mathrm{J \cdot mol^{-1}})$	NRTL[a] $(g_{12} - g_{22})/(\mathrm{J \cdot mol^{-1}})$ $(g_{21} - g_{11})/(\mathrm{J \cdot mol^{-1}})$	UNIQUAC $\Delta u_{12}/(\mathrm{J \cdot mol^{-1}})$ $\Delta u_{21}/(\mathrm{J \cdot mol^{-1}})$
1-heptyne	2704.97	4162.25	2152.81
	6092.50	3552.97	44.95
tetrahydrofuran	816.45	3884.61	2209.08
	13096.26	653.30	317.33
1,4-dioxane	−1185.56	5307.28	237.01
	3425.35	−853.25	−181.92
1,4-dioxane[b]	4076.43	−1326.12	−1325.18
	−1268.74	4042.91	2871.88
tetrachloromethane[c]	6986.77	−3289.31	−2350.03
	−2381.72	7606.35	4896.38
1,1,1-trichloroethane	3227.25	10653.42	−371.82
	1361.98	3688.83	1935.61
benzene	3394.58	−64.86	−663.68
	−56.31	3243.00	2133.11
benzene[d]	3575.91	−207.47	−753.40
	−169.02	3449.04	2284.83
2-methyl-2-propanol[e]	6895.15	−2654.21	−1919.41
	−1621.34	7499.24	4571.38

	deviations σ_T[f]/K		
	Wilson	NRTL	UNIQUAC
1-heptyne	1.70	1.65	1.99
tertrahydrofuran	3.50	3.49	3.44
1,4-dioxane	1.03	1.02	1.03
1,4-dioxane[b]	0.61	0.66	0.64
tetrachloromethane[c]	1.77	2.04	1.95
1,1,1-trichloroethane	0.91	0.89	0.89
benzene	0.76	0.84	0.82
benzene[d]	1.07	1.14	1.12
2-methyl-2-propanol[e]	2.75	3.04	2.97

[a] Calculated with the third nonrandomness parameter $\alpha = 0.45$. [b] Jannelli *et al.* (1975). [c] Sacco *et al.* (1976). [d] Jannelli and Sacco (1972). [e] Inglese and Jannelli (1978). [f] $\sigma_T = \sum_{i=1}^{n}(T_i^{\mathrm{cal}} - T_i)^2/(n-2)]^{1/2}$.

solid and liquid phases and two solid phases are $\Delta_{\mathrm{fus}}C_{p2}(\mathrm{l,pI}) = 0$ and $\Delta_{\mathrm{trs}}C_{p2}\ (\mathrm{pI,pII}) = 45.51\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, respectively (Jannelli *et al.*, 1982).

In this study, three methods that describe the excess Gibbs free energy of mixing (G^{E}) were used to represent the solute activity coefficient (γ_2): the Wilson equation (Wilson, 1964), the nonrandom two-liquid theory (NRTL) (Renon and Prausnitz, 1968), and the UNIQUAC equation (Abrams and Prausnitz, 1975). Calculations were performed on the data obtained from this work and also for mixtures of sulfolane in benzene, 1,4-dioxane, 1,1,1-trichloroethane, and 2-methyl-2-propanol from literature data in the sulfolane rich region, for liquidus curves giving simple eutectic points. The parameters were fitted by the optimization technique. The objective function used was

$$F(A_1,A_2) = \sum_{i=1}^{n} w_i^{-2}[\ln x_{2i}\gamma_{2i}(T_i,x_{2i},A_1,A_2) - \ln a_{2i}(T_i)]^2 \quad (3)$$

where $\ln a_{2i}$ denotes an "experimental" value of the logarithm of the solute activity, taken as the right side of eq 1 or 2, w_i is the weight of an experimental point, A_1 and A_2 are the two adjustable parameters of the correlation equations, i denotes the ith experimental point, and n is the number of experimental data. The weights were calculated by means of the error propagation formula

$$w_i^2 = \left(\frac{\partial \ln x_2\gamma_2 - \partial \ln a_i}{\partial T}\right)^2_{T=T_i}(\Delta T_i)^2 + \left(\frac{\partial \ln x_2\gamma_2}{\partial x_2}\right)^2_{x_1=x_{2i}}(\Delta x_{2i}) \quad (4)$$

where ΔT and Δx_2 are the estimated errors of T and x_2, respectively.

The objective function is consistent with the maximum likelihood principle, provided that the first-order approximation is valid according to Neau and Peneloux (1981). The experimental errors of temperature and solute mole fraction were fixed for all cases at $\Delta T = 0.1$ K and $\Delta x_2 = 0.001$. The root mean square deviation of temperature given below was used as a measure of the goodness of the fit of the solubility curves:

$$\sigma_T = \left[\sum_{i=1}^{n}\frac{(T_i^{\mathrm{cal}} - T_i)^2}{(n-2)}\right]^{1/2} \quad (5)$$

where T_i^{cal} and T_i are, respectively, the calculated and experimental temperatures of the ith point and n is the number of experimental points. The calculated values of the parameters and corresponding root mean square deviations are presented in Table 4.

The pure component structural parameters r (volume parameter) and q (surface parameter) in UNIQUAC were obtained in accordance with the methods suggested by Vera *et al.* (1977) and relationships 6 and 7 published by Hofman and Nagata (1986):

$$r_i = 0.029281V_{\mathrm{m}i} \quad (6)$$

and

$$q_i = (z-2)r_i/z + 2(1-l_i)/z \quad (7)$$

where $V_{\mathrm{m}i}$ is the molar volume of pure component i at

298.15 K, z is the coordination number, further assumed equal to 10, and l_i is the bulk factor; it was accepted that $l_i = 0$ for the chainlike molecules and $l_i = 1$ for the ring molecules.

The solubility of sulfolane in cyclohexane was only measured in the sulfolane rich region ($x_2 > 0.94$) as a result of the nonmiscibility gap in the lower sulfolane concentrations. The NRTL parameters obtained were $g_{12} - g_{22} = -4151.16$ J·mol^{-1} and $g_{21} - g_{11} = 11461.16$ J·mol^{-1} with a root mean square deviation of 0.26 K.

For the nine solubility curves (shown in Table 4), the results obtained from the Wilson equation are slightly better than those derived from the NRTL and UNIQUAC equations. The average deviations are 1.56, 1.64, and 1.65 K for the Wilson, NRTL, and UNIQUAC equations, respectively.

The experimental data of SLE obtained in this work and the VLE data published elsewhere by Domańska *et al.* (1995) have been used to obtain new interaction parameters for the specific solvent groups with sulfolane using the DISQUAC and modified UNIFAC models (Moollan *et al.*, 1995).

Literature Cited

Abrams, D. S.; Prausnitz, J. M. Statistical thermodynamics of liquid mixtures; a new expression for the excess Gibbs energy of partly or completely miscible systems. *AIChE J.***1975**, *21*, 116−128.

Choi, P. B.; McLaughlin, E. Effect of phase transition on the solubility of solid. *AIChE J.* **1983**, *29*, 150−153.

Della Monica, M.; Janelli, L.; Lamanna, U. Physicochemical properties of sulfolane. *J. Phys. Chem.* **1968**, *72*, 1068−1071.

Domańska, U. Vapour-liquid-solid equilibrium of eicosanoic acid in one- and two-component solvents. *Fluid Phase Equilib.* **1986**, *26*, 201−220.

Domańska, U.; Sporzyński, A.; Moollan, W. C.; Letcher T. M. Vapor-Liquid equilibria of binary mixtures containing sulfolane. *J. Chem. Eng. Data* **1996**, in press.

Hofman, T.; Nagata, J. Determination of association constants for alcohols based on ethers as homomorphs. *Fluid Phase Equilib.* **1986**, *25*, 113−128.

Inglese, A.; Jannelli, L. Diagramme de phase liquide-solide pour le systeme binaire sulfolane + 2-methyl-2-propanol. *Thermochim. Acta* **1978**, *23*, 263−268.

Jannelli, L.; Sacco, A. Thermodynamic and physical behaviour of binary mixtures involving sulfolane II. Viscosity, dielectric constants and solid + liquid phase diagrams of mixtures of benzene + sulfolane. *J. Chem. Thermodyn.* **1972**, *4*, 715−722.

Jannelli, L.; Inglese, A.; Sacco, A.; Ciani, P. Thermodynamic and physical behaviour of binary mixtures involving sulfolane. Viscosity, dielectric constants and solid + liquid phase diagrams of mixtures of dioxane + sulfolane. *Z. Naturforsch.* **1975**, *30a*, 87−91.

Jannelli, L.; Lopez, A.; Jalent, R.; Silvestri, L. Solid-liquid phase diagrams for the system nitrobenzene (1) + sulfolane(2). An improved method for the calculation of activity coefficients of sulfolane as solvent, for solutions in equilibrium with crystal I or crystal II. *J. Chem. Eng. Data* **1982**, *27*, 28−32.

Letcher, T. M.; Moollan, W. C. The determination of activity coefficients of hydrocarbons at infinite dilution using a g.l.c. technique with the polar solvent tetrahydrothiophene - 1,1-dioxide, c-$(CH_2)_4SO_2$, (sulfolane) at the temperature 303.15 K. *J. Chem. Thermodyn.* **1995**, *27*, 867−872.

Moollan, W.; Domańska, U.; Letcher, T. M. DISQUAC and Modified UNIFAC applications to thermodynamic properties of binary mixtures containing sulfolane. *Fluid Phase Equilib.* **1995**, submitted for publication.

Neau, E.; Peneloux, A. Estimation of model parameters. Comparison of methods based on the maximum likelihood principle. *Fluid Phase Equilib.* **1981**, *6*, 1−19.

Renon, H.; Prausnitz, J. M. Local composition in thermodynamics excess function for liquid mixtures. *AIChE J.* **1968**, *14*, 135−144.

Riddick, J. A.; Bunger, W.; Sakano, T. K. *Organic Solvents Physical Properties and Methods of Purification*, 4th ed.; John Wiley & Sons: New York, 1986.

Sacco, A.; Inglese, A.; Ciani, P.; Dell'Atti, A.; Rakshit, A. K. Thermodynamics and physical properties of carbon tetrachloride + sulfolane mixtures. *Thermochim. Acta* **1976**, *15*, 71−78.

Shell Chemical Co. *Sulfolane*; Shell Technical Bulletin; March 1964.

Vera, J. H.; Sayegh, G. S.; Ratcliff, G. M. A quasi-lattice local composition model for the excess Gibbs free energy of liquid mixtures. *Fluid Phase Equilib.* **1977**, *1*, 113−135.

Weimer, R. F.; Prausnitz, J. M. Complex formation between carbon tetrachloride and aromatic hydrocarbons. *J. Chem. Phys.* **1965**, *42*, 3643−3644.

Wilson, G. M. Vapor-liquid equilibrium. XI. A new expression for the excess free energy of mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127−130.

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