Vapor−Liquid Equilibria of Binary Mixtures Containing Sulfolane

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Isothermal vapor−liquid equilibria at 338.15 K or 353.15 K for sulfolane + 1-heptyne, + tetrahydrofuran, + 1,4-dioxane, + tetrachloromethane, and + 1,1,1-trichloroethane have been determined using an ebulliometric method. The excess molar Gibbs energies determined from the vapor−liquid equilibria are positive for all mixtures, with the maximum varying from 480 J·mol^{-1} to 1550 J·mol^{-1}. The results reported are well correlated by the NRTL and UNIQUAC equations.

Introduction

Vapor−liquid equilibrium data are useful, not only for the design of separation processes but also in the study of theories of liquid mixtures. Because of the important industrial applications of sulfolane, several researchers have studied the vapor−liquid phase equilibria (VLE) for binary (Benoit and Charbonneau, 1969; De Fré and Verhoeye, 1976; Karvo, 1980) and ternary (Hauschild and Knapp, 1991) mixtures containing sulfolane and aromatic hydrocarbons (benzene, toluene, ethylbenzene), dichloromethane, or propan-2-ol. VLE for mixtures containing sulfolane have seldom been the subject of any theoretical interpretation.

In this paper we report experimental data for the binary mixtures of 1-heptyne, tetrahydrofuran, 1,4-dioxane, tetrachloromethane, or 1,1,1-trichloroethane + sulfolane at 338.15 K or 353.15 K. For these mixtures, no experimental data have been published in the literature. 1-Heptyne was chosen because it contained a triple carbon−carbon bond, tetrahydrofuran and 1,4-dioxane were chosen as cyclic ethers containing one and two ether groups, respectively, and tetrachloromethane and 1,1,1-trichloroethane were chosen as examples of compounds containing two different types of Cl atoms.

The experimental data have allowed us to obtain new interaction parameters for the above-mentioned groups with sulfolane (as an individual group) in the DISQUAC and modified UNIFAC models (Moollan *et al.*, 1995).

In addition parameters for the NRTL (Renon and Prausnitz, 1968) and UNIQUAC (Abrams and Prausnitz, 1975) equations have been obtained.

The NRTL and UNIQUAC equations for the molar excess Gibbs energy were chosen for the reduction of the VLE data as representatives of local composition equations and semiempirical enthalpic expressions, respectively.

Experimental Section

Materials. The chemicals 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 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% reagent) and was twice vacuum distilled 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 VLE was determined by an ebulliometric method, in which both the liquid and the vapor phase mole fractions were measured simultaneously with the pressure and temperature. The ebulliometer was designed by Rogalski and Malanowski (1980) and was used with some modifications of taking samples, made by Sporzyński and Gregorowicz (1990), to enable the sampling of the liquid and the condensate to be made without disturbing the working conditions. Pressure stability was obtained using a buffer vessel (50 dm³). Pressure measurements were made with a mercury manometer equipped with a cathetometer with a resolution of ±0.01 mm, which gives an accuracy of the vapor pressure measurements to better than ±0.03 kPa.

Vapor pressure measurements were corrected according to the standard method (Hala *et al.*, 1967). The temperature was measured using a calibrated platinum resistance thermometer (Autotherm2 by Gallenkamp), with an accuracy of ±0.01 K. All the measurements were conducted in a purified argon atmosphere.

The composition of the liquid and vapor was determined by a precision refractometer (Carl Zeiss, Jena), with an accuracy of ±0.000 01 at 303.15 K ± 0.01 K. A calibration curve was made for each mixture, and the mole fractions were determined from

$$n_{\mathrm{D}}(303.15 \text{ K}) = Kx_2{}^2 + Lx_2 + M \qquad (1)$$

where x_2 is the mole fraction of sulfolane and n_{D} is the refractive index of the mixture. The coefficients of this equation for each of the mixtures are given in Table 2. The accuracy of the composition determination was better than ±0.0005 in mole fraction. Within this limit, the measured sulfolane concentration in the vapor phase was close to zero for all the mixtures investigated. The binary VLE measurements were made at 338.15 K for tetrahydrofuran, tetrachloromethane, and 1,1,1-trichloroethane and at 353.15

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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_{fus}

component	$V_{mi}{}^a$/(cm³·mol⁻¹)	n_D		T_{fus}/K	
		exptl	lit.ᵃ	exptl	lit.ᵇ
1-heptyne	138.10	1.40821	1.4080ᶜ		
tetrahydrofuran	81.09	1.40512	1.40496		
1,4-dioxane	85.66	1.02786	1.02797		
tetrachloromethane	97.15	1.58435	1.58439		
1,1,1-trichloroethane	100.37	1.43612	1.4359		
sulfolane	95.26	1.48114	1.4810ᵈ,ᵉ	301.60	301.60

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

Table 2. Coefficients of Eq 1 for Mixtures Involving Sulfolane and a Second Component

second component	K	L	M
1-heptyne	−0.001 99	0.080 27	1.403 90
tetrahydrofuran	−0.038 88	0.118 50	1.402 86
1,4-dioxane	−0.014 07	0.079 12	1.417 77
tetrachloromethane	−0.033 32	0.061 96	1.454 18
1,1,1-trichloroethane	−0.031 82	0.074 15	1.431 04

Table 3. Coefficients Used in the Determination of the Pure Vapor Pressure of the Component

component	A	B	C	10⁶D	E
1-heptyneᵃ	−1.4196	22.509	7.3533		
tetrahydrofuranᵃ	5.8946	1155	231		
1,4-dioxaneᵇ	52.2272	−5677.77	−4.364	1.9626	2.0
tetrachloromethaneᵇ	78.4339	−6128.10	−8.576	6.8461	2.0
1,1,1-trichloroethaneᵃ	0.1504	34.2963	−55.8452		
sulfolaneᶜ	5759	267683	61965.89		

ᵃ Coefficients of the equation $\log(P_i^0/\text{kPa}) = A - B/(C + (t/°\text{C}))$ (Riddick *et al*., 1986). ᵇ Coefficients of the equation $\ln(P_i^0/\text{Pa}) = A + B/(T/\text{K}) + C\ln(T/\text{K}) + [D(T/\text{K})]E$ (Gess *et al*., 1991). ᶜ Coefficients of the equation $\log(P_i^0/\text{kPa}) = A - B/(T/\text{K}) - C\log(T/\text{K})$ (Riddick *et al*., 1986).

K for 1-heptyne, tetrahydrofuran, and 1,4-dioxane over the whole concentration range.

Because the vapor pressures of sulfolane in the temperature range investigated are so low (close to the accuracy limit of the experimental method), no vapor pressure measurements on pure sulfolane were made and the vapor pressure was obtained from fitted parameters given in Table 3.

Results and Discussion

The isothermal VLE data obtained for the mixtures studied are presented in Table 4. The activity coefficients γ_i were calculated using the following equation:

$$\phi_i P y_i = \gamma_i P_i^0 x_i \phi_{x_i}^0 \exp[V_{mi}(P - P_i^0)/RT] \quad (2)$$

where ϕ_i and ϕ_i^0, the fugacity coefficients of component i in the mixture and pure vapor, respectively, were evaluated by using the second virial coefficients obtained by the Hayden−O'Connell (1975) method. The vapor pressures of the pure components, P_i^0, were obtained using fitted parameters from Riddick *et al*. (1986) and from Gess *et al*. (1991). These are reproduced in Table 3. The pure vapor pressures of the solvents P_i^0 measured in this work agree with the literature values (Riddick *et al*., 1986) within 3 kPa. The liquid molar volumes, V_{mi} were calculated from the densities at 298.15 K (Riddick *et al*., 1986) and are included in Table 1. The critical properties and other parameters required for estimating the second virial coefficients, obtained from Ashcroft *et al*. (1979), Gess *et al*. (1991), and Prausnitz *et al*. (1980) are listed in Table 5.

The VLE data are reported in Table 4 along with the activity coefficients of both components and the excess molar Gibbs energies (G^E) calculated from

$$G^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \quad (3)$$

The activity coefficients and the excess molar Gibbs energies were correlated with the nonrandom two-liquid NRTL model of Renon and Prausnitz (1968) and UNIQUAC model of Abrams and Prausnitz (1975). The parameters in each equation were obtained by using the method of Marquardt (1963), and the technique of optimization was similar to that of Prausnitz et al. (1980). UNIQUAC pure component parameters for the surface area (q) and volume (r) of the molecules were taken from Gess *et al*. (1991) and Walas (1985) and are listed in Table 6. Only the results obtained with the UNIQUAC equation are shown in Table 4. Table 7 lists the parameters and the root mean square deviations of pressure $\sigma(P)$ and the excess molar Gibbs energy, $\sigma(G^E)$, obtained from the NRTL and UNIQUAC equations.

Calculations done using the van Laar, Margules, or Wilson (Wilson, 1994) equations were found to be inferior to those using the NRTL and UNIQUAC equations. The nonrandomness parameter α (in the NRTL equation), listed in Table 7, was obtained as a third adjustable parameter and is in the range of 0.3−1.4, being especially high for the 1,4-dioxane + sulfolane mixture.

The experimental data were shown to be thermodynamically consistent by using the integral or area test described by Gmehling and Onken (1977). The calculated results using the UNIQUAC equation for the activity coefficients and the excess molar Gibbs energies are shown by solid lines in Figures 1 and 2. All systems studied exhibit zeotropic behavior. Each of the five mixtures studied in this work showed significant positive deviations from ideality. The largest deviation was found for the mixture 1-heptyne + sulfolane ($G_{max}^E \approx 1550$ J·mol⁻¹).

The maximum values of G^E for tetrahydrofuran + sulfolane at 353.15 K and 1,4-dioxane + sulfolane at 353.15 K are $G_{max}^E \approx 1400$ J·mol⁻¹ and $G_{max}^E \approx 500$ J·mol⁻¹, respectively, and reflect a stronger AB interaction in the case of the 1,4-dioxane + sulfolane mixture.

A comparison of the excess molar Gibbs energies for the tetrachloromethane + sulfolane mixture ($G_{max}^E \approx 1360$ J·mol⁻¹) and the 1,1,1-trichloroethane + sulfolane mixture ($G_{max}^E \approx 1050$ J·mol⁻¹) with the excess molar Gibbs energy obtained by Benoit and Charbonneau (1969) for the related mixture of dichloromethane + sulfolane, ($G_{min}^E \approx -130$ J·mol⁻¹ at 303.15 K) suggests complex-forming interaction between the dichloromethane and sulfolane molecules. This indicates a different type of interaction between tetrachloromethane and sulfolane on the one hand and between 1,1,1-trichloroethane and sulfolane on the other. The asymmetric molecule 1,1,1-trichloroethane shows weaker interactions with sulfolane than does dichloromethane.

Table 4. Vapor−Liquid Equilibrium Data for the Solvent (1) + Sulfolane (2) Mixtures at the Temperature T: Experimental Vapor Pressure, P, Liquid Phase, x_1, and Vapor Phase, y_1, Mole Fractions, Activity Coefficient, γ_i, and G^E As Calculated by UNIQUAC

P/kPa	x_1	y_1	γ_1	γ_2	G^E/(J·mol^{-1})	P/kPa	x_1	y_1	γ_1	γ_2	G^E/(J·mol^{-1})
					1-Heptyne (1) + Sulfolane (2) at T = 353.15 K						
0.058	0.0000	0.0000			0.0	45.488	0.3710	0.9990	2.423	1.254	1382.1
32.509	0.1480	0.9985	4.144	1.033	699.6	46.741	0.4720	0.9991	1.948	1.474	1524.2
35.901	0.1770	0.9986	3.852	1.048	814.8	47.446	0.5570	0.9992	1.645	1.766	1552.6
39.700	0.2170	0.9987	3.487	1.075	961.3	49.217	0.7400	0.9993	1.218	3.114	1293.6
41.349	0.2400	0.9988	3.296	1.093	1038.8	50.070	0.8670	0.9994	1.059	5.580	815.9
44.143	0.3180	0.9999	2.766	1.176	1263.9	54.047	1.0000	1.0000			0.0
					Tetrahydrofuran (1) + Sulfolane (2) at T = 338.15 K						
0.022	0.0000	0.0000			0.0	76.460	0.6560	0.9998	1.318	1.313	739.6
53.220	0.3520	0.9998	1.868	1.021	625.2	79.720	0.7130	0.9998	1.245	1.442	696.6
56.840	0.3960	0.9998	1.787	1.037	665.5	82.240	0.7650	0.9998	1.177	1.602	634.5
62.000	0.4520	0.9998	1.663	1.071	717.2	86.930	0.8300	0.9999	1.108	1.888	522.2
66.440	0.5100	0.9998	1.558	1.116	748.2	90.970	0.8920	0.9999	1.055	2.304	374.0
70.610	0.5680	0.9998	1.455	1.176	760.7	98.035	1.0000	1.0000			0.0
72.860	0.6100	0.9998	1.387	1.234	757.0						
					Tetrahydrofuran (1) + Sulfolane (2) at T = 353.15 K						
0.058	0.0000	0.0000			0.0	78.453	0.3100	0.9995	3.199	1.015	1058.9
49.959	0.1700	0.9990	3.822	0.989	623.9	82.374	0.3250	0.9995	3.135	1.021	1100.2
54.233	0.1970	0.9992	3.699	0.991	714.1	90.694	0.3850	0.9995	2.881	1.052	1253.4
65.480	0.2350	0.9993	3.528	0.996	836.2	99.827	0.4500	0.9996	2.616	1.104	1394.8
71.526	0.2670	0.9994	3.387	1.002	934.4	151.55	1.0000	1.0000			0.0
76.907	0.2950	0.9994	3.264	1.010	1016.5						
					1,4-Dioxane (1) + Sulfolane (2) at T = 353.15 K						
0.058	0.0000	0.0000			0.0	38.619	0.6720	0.9993	1.190	1.161	473.3
26.100	0.3960	0.9988	1.391	1.009	385.8	40.868	0.7250	0.9995	1.150	1.735	456.4
29.212	0.4590	0.9989	1.349	1.023	425.1	42.974	0.7900	0.9996	1.104	1.371	412.9
31.596	0.5080	0.9990	1.312	1.041	449.0	45.271	0.8500	0.9997	1.064	1.570	344.8
31.632	0.5110	0.9990	1.310	1.043	450.3	47.562	0.9160	0.9998	1.027	1.941	229.8
34.260	0.5670	0.9991	1.269	1.071	468.8	49.715	0.9690	0.9999	1.006	2.468	97.8
36.292	0.6120	0.9992	1.235	1.103	476.1	50.957	1.0000	1.0000			0.0
					Tetrachloromethane (1) + Sulfolane (2) at T = 338.15 K						
0.022	0.0000	0.0000			0.0	66.248	0.6100	0.9998	1.631	1.614	1362.0
55.839	0.3050	0.9997	2.581	1.075	952.3	66.627	0.6680	0.9998	1.487	1.897	1341.0
59.646	0.3790	0.9998	2.323	1.134	1115.1	66.880	0.7370	0.9998	1.334	2.445	1256.7
63.361	0.4430	0.9998	2.113	1.209	1227.3	66.968	0.7860	0.9998	1.238	3.084	1150.2
64.743	0.4910	0.9998	1.965	1.287	1291.5	67.244	0.8470	0.9998	1.168	4.527	951.9
65.563	0.5480	0.9998	1.799	1.414	1342.4	69.956	1.0000	1.0000			0.0
					1,1,1,-Trichloroethane (1) + Sulfolane (2) at T = 338.15 K						
0.022	0.0000	0.0000			0.0	64.047	0.6120	0.9998	1.444	1.474	1053.2
46.670	0.2780	0.9996	2.174	1.047	698.0	65.702	0.6720	0.9998	1.339	1.682	1029.0
51.208	0.3300	0.9997	2.046	1.073	795.5	67.089	0.7300	0.9998	1.247	1.950	969.6
55.664	0.4060	0.9997	1.868	1.129	914.1	68.377	0.7800	0.9998	1.176	2.362	885.4
59.375	0.4740	0.9997	1.719	1.203	992.5	69.545	0.8070	0.9999	1.141	2.642	825.5
61.692	0.5400	0.9998	1.582	1.306	1039.7	78.005	1.0000	1.0000			0.0

Table 5. Critical Properties and Parameters Characterizing Vapor Phase Nonideality, Where T_c Is the Critical Temperature, P_c the Critical Pressure, V_c the Critical Volume, ω the Acentric Factor, RD the Mean Radius of Gyration, and DM the Dipole Moment^{a-c}

component	T_c/K	P_c/kPa	V_c/(cm^3·mol^{-1})	ω	RD/Å	DM/D
1-heptyne	537.30	3210	387.0	0.3580	0.358	0.00
tetrahydrofuran	540.15	5187	224.0	1.9280	2.600	1.63
1,4-dioxane	588.00	5140	238.0	0.2804	3.110	0.00
tetrachloromethane	556.30	4557	276.0	0.1926	3.759	0.00
1,1,1-trichloroethane	533.15	5066	220.0	0.1905	3.759	1.10
sulfolane	776.00	4990	286.9	0.8608	2.910	4.10

[a] Ashcroft *et al.* (1979). [b] Gess *et al.* (1991). [c] Prausnitz *et al.* (1980).

The G^E results obtained in this work are in the same range as the literature data (Ashcroft *et al.*, 1979) for the 2-propanol + sulfolane system ($G^E_{max} \approx 1590$ J·mol^{-1} at 303.15 K). For benzene + sulfolane (Karvo, 1980) and toluene + sulfolane the results according to Ashcroft *et al.* (1979) are $G^E_{max} \approx 670$ J·mol^{-1} at 303.15 K and $G^E_{max} \approx 980$ J·mol^{-1} at 303.15 K, respectively.

The experimental values of the excess molar enthalpies H^E for two of the systems studied here have been reported

Table 6. UNIQUAC Pure Component Parameters for Volume (r) and Surface Area (q) of Each Compound^{a,b}

component	r	q
1-heptyne	4.891	4.096
tetrahydrofuran	2.919	2.722
1,4-dioxane	3.185	2.640
tetrachloromethane	3.390	2.910
1,1,1-trichloroethane	3.541	3.032
sulfolane	4.036	3.206

[a] Gess *et al.* (1991). [b] Walas (1985).

in the literature by Pansini and Jannelli (1986). H^E_{max} for tetrachloromethane + sulfolane at 303.15 K was found to be 220 J·mol^{-1}. The H^E_{max} versus mole fraction plot for the 1,4-dioxane + sulfolane mixture (also at 303.15 K) was found to be sinusoidal with an H^E_{min} of −40 J·mol^{-1} in the sulfolane rich region and an H^E_{max} of 45 J·mol^{-1} in the 1,4-dioxane rich region. The excess enthalpy of mixing for the 1-heptyne + sulfolane system has also been measured at 303.15 K by our group, and shows endothermic deviations from ideality with $H^E_{max} \approx 340$ J·mol^{-1} (Letcher *et al.*, 1995). These enthalpic results reflect the same interaction as we have interpreted from the Gibbs energy results above.

Table 7. Parameters for the NRTL and UNIQUAC Equations Determined from Binary Vapor−Liquid Equilibria for the Systems Solvent (1) + Sulfolane (2), as Well as the Calculated Standard Deviation for the Total Pressure and the Calculated Gibbs Energy

	parameters				
	NRTL			UNIQUAC	
component	$(g_{12} - g_{22})/(\text{J·mol}^{-1})$	$(g_{21} - g_{11})/(\text{J·mol}^{-1})$	α	$(u_{12} - u_{22})/(\text{J·mol}^{-1})$	$(u_{21} - u_{11})/(\text{J·mol}^{-1})$
1-heptyne	5861.27	4055.48	0.47	2532.93	−387.22
tetrahydrofuran (338.15 K)	3536.88	2703.35	0.94	1993.08	−774.27
tetrahydrofuran (358.15 K)	12964.17	418.34	0.31	5813.39	−1295.09
1,4-dioxane	3230.87	1326.03	1.38	2820.19	−1381.27
tetrachloromethane	7306.35	2941.97	0.46	3308.94	−651.30
1,1,1-trichloroethane	5202.51	2820.52	0.61	2758.08	−772.98

	deviations			
	NRTL		UNIQUAC	
	$\sigma(P)^a/\text{Pa}$	$\sigma(G^E)^b/(\text{J·mol}^{-1})$	$\sigma(P)^a/\text{Pa}$	$\sigma(G^E)^b/\text{J·mol}^{-1}$
1-heptyne	2.4	67.96	1.1	50.77
tetrahydrofuran (338.15 K)	1.2	54.82	0.4	24.15
tetrahydrofuran (353.15 K)	0.7	45.86	0.6	2.65
1,4-dioxane	0.5	31.51	0.9	21.15
tetrachloromethane	1.2	93.23	2.6	62.09
1,1,1-trichloroethane	1.4	67.80	3.4	52.23

^{a} $\sigma(P) = [\sum_{i=1}(P_i^{\text{exptl}} - P_i^{\text{calcd}})^2/(n-2)]^{1/2}$. ^{b} $\sigma(G^E) = [\sum_{i=1}(G_i^{\text{E,exptl}} - G_i^{\text{E,calcd}})^2/(n-2)]^{1/2}$.
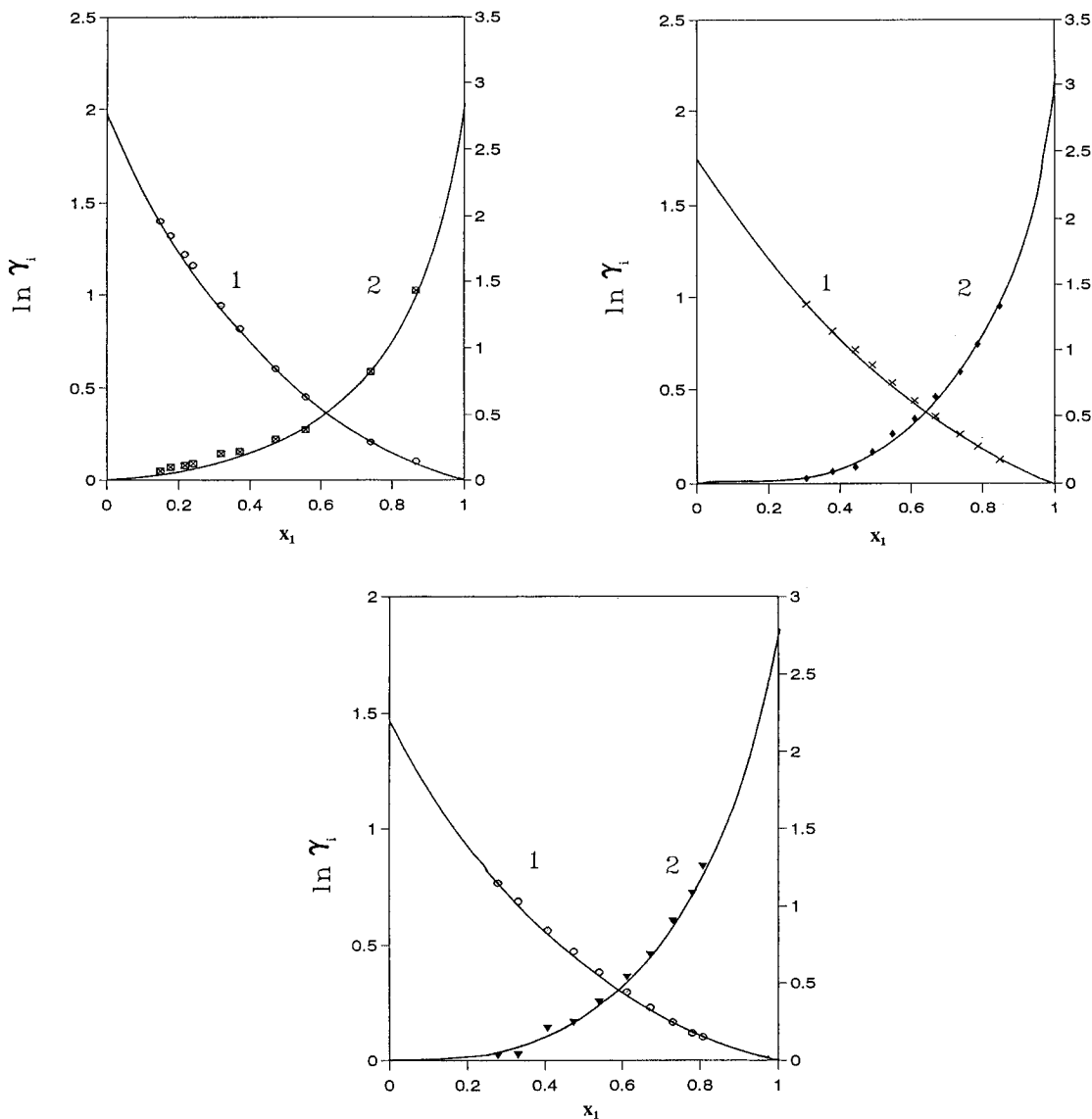
Figure 1. Activity coefficient−liquid composition diagram for (a, top, left) 1-heptyne (1) + sulfolane (2) at 353.15 K, (b, top right) tetrachloromethane (1) + sulfolane (2) at 338.15 K, and (c, bottom) 1,1,1-trichloroethane (1) + sulfolane (2) at 338.15 K. Solid lines calculated by the UNIQUAC equation.
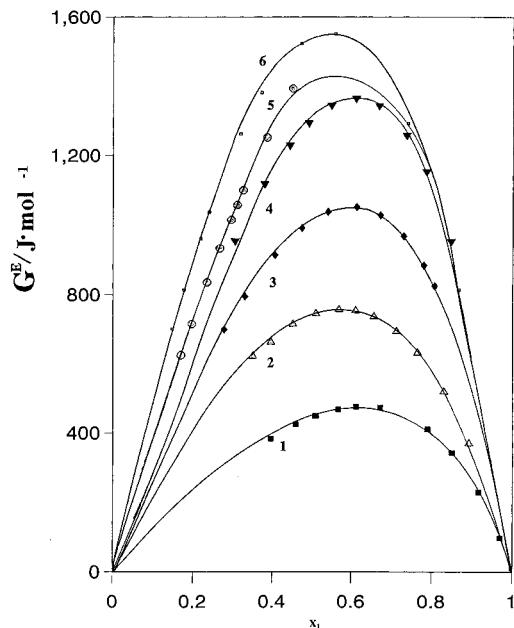
Figure 2. Excess molar Gibbs energies, G^E, for the systems (1) 1,4-dioxane (1) + sulfolane (2) at 358.15 K, (2) tetrahydrofuran (1) + sulfolane (2) at 338.15 K, (3) 1,1,1-trichloroethane (1) + sulfolane (2) at 338.15 K, (4) tetrachloromethane (1) + sulfolane (2) at 338.15 K, (5) tetrahydrofuran (1) + sulfolane (2) at 353.15 K, and (6) 1-heptyne (1) + sulfolane (2) at 358.35 K, calculated by the UNIQUAC equation.

For the mixtures studied in this work, strong nonideal behavior is evident from the magnitude of the activity coefficients, given in Table 4. The values of γ_i range from 1 to 4 for $x_1 > 0.15$. The 1,4-dioxane + sulfolane mixture (with small values for both G^E_{max} and H^E_{max}) is the least nonideal mixture, with γ_i never exceeding 1.5 for $x_1 > 0.15$.

The activity coefficient at infinite dilution, γ_1^∞, for each of the solvents in sulfolane was calculated using UNIQUAC parameters obtained from VLE correlations. The values of γ_1^∞ for the mixtures 1-heptyne + sulfolane at 353.15 K, tetrahydrofuran + sulfolane at 338.15 K, and tetrahydrofuran + sulfolane at 353.15 K are 6.2, 2.3, and 3.8, respectively. Two of the authors recently reported γ_1^∞, obtained by the GLC technique, for these two systems. The results for the mixtures 1-heptyne + sulfolane at 313.15 K and 303.15 K (Letcher and Whitehead, 1995), and tetrahydrofuran + sulfolane (Letcher and Moollan, 1995) at 303.15 K are 7.80, 8.05, and 2.24, respectively. A further system, 1,4-dioxane + sulfolane, at 298.15 K has also been measured by the GLC technique (Gmehling et al., 1994), and the resulting γ_1^∞ obtained is 3.32 whereas the value obtained in this work is 1.5 at 353.15 K.

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