Liquid−Liquid Equilibria of the Ternary Mixtures with Sulfolane at 303.15 K

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Liquid−liquid equilibrium data are presented for mixtures of tetrahydrothiophene 1,1-dioxide (sulfolane) + 1-heptyne (or +benzene or +*p*-xylene) + heptane and for mixtures of sulfolane + benzene + decane (or +dodecane) at 303.15 K. The addition of benzene to sulfolane is found to increase the solubility of hydrocarbons (heptane > decane > dodecane). The influence of benzene on the solubility of the hydrocarbons is greater than that of *p*-xylene or of 1-heptyne. The relative mutual solubility of benzene is higher in heptane + sulfolane mixtures then in decane + sulfolane or dodecane + sulfolane mixtures. Three three-parameter equations have been fitted to the results. These equations are compared and discussed in terms of statistical consistency. The NRTL and UNIQUAC models were used to correlate the experimental results and to calculate the phase compositions of the ternary systems. The UNIQUAC equation fitted the experimental data better than the NRTL equation: the average mean square deviations phase composition error was 0.011 for UNIQUAC as compared to 0.027 for NRTL.

Introduction

A great number of industrial separation processes are concerned with liquid mixtures containing aromatics (benzene, toluene, *p*-xylene, alkylbenzenes) and saturated hydrocarbons (hexane, heptane, octane, decane, dodecane). In liquid−liquid extraction processes, solvents such as sulfur dioxide, *N*-methylpyrrolidone, *N*-formylmorpholine, dimethyl sulfoxide, and tetrahydrothiophene 1,1-dioxide (sulfolane) have, according to Bailes (1977), been used extensively. Sulfolane is a particularly important solvent and has been the subject of many studies.

Liquid−liquid equilibria (LLE) data on a number of ternary mixtures containing sulfolane have been published in the literature: sulfolane + benzene + heptane at 298.15 K and 383.15 K by Rawat and Prasad (1980); sulfolane + xylene (mixtures of isomers with ethylbenzene) + heptane at 290.15 K, 298.15 K, and 323.15 K by Cassell *et al.* (1989a); sulfolane + benzene + octane and sulfolane + *p*-xylene + octane at 298.15 K, 308.15 K, and 318.15 K by Lee and Kim (1995); sulfolane + toluene + heptane by Tripathi *et al.* (1975) and Ashcroft *et al.* (1982); sulfolane + toluene + hexane (or +cyclohexane) by Cassell *et al.* (1989b); sulfolane + ethylbenzene + heptane by Hauschild and Knapp (1991); and sulfolane + alkylbenzene + hydrocarbon by Masohan *et al.* (1990).

The main purpose of this study is to generate new LLE data on sulfolane (1) + 1-heptyne (or +benzene or +*p*-xylene) (2) + heptane (3) and sulfolane (1) + benzene (2) + decane (or +dodecane) (3) at 303.15 K and to correlate the data by using the NRTL model of Renon and Prausnitz (1968) and the UNIQUAC model of Abrams and Prausnitz (1975).

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

component	V_{mi}/cm^3·mol^{-1} [a]	n_D exp	n_D lit.[a]
1-heptyne	138.10	1.408 21	1.408 0[b]
p-xylene	123.94	1.493 21	1.493 25
heptane	147.40	1.385 10	1.385 11
decane	195.84	1.409 69	1.409 67
dodecane	228.60	1.419 50	1.419 52
benzene	89.40	1.497 85	1.497 92
sulfolane	95.26	1.481 14	1.481 0[c]

[a] Riddick *et al.* (1986). [b] At 293.15 K. [c] At 303.15 K.

In this paper the effect of 1-heptyne is compared to the effect of benzene or *p*-xylene on the phase separation properties of sulfolane + an *n*-hydrocarbon mixture. Furthermore, the effect of the hydrocarbon chain length on the phase properties of the ternary mixtures sulfolane + benzene + an *n*-hydrocarbon is investigated.

Experimental Section

Chemicals. The solvents were obtained from Aldrich Chemical Co. (with a quoted purity of 99.9 mass %). The compounds were dried using activated type 5 Å molecular sieves and analyzed using the Karl-Fisher technique, showing that the water content was less than 0.01 mass %. Sulfolane was purchased from Fluka Chemie AG with a minimum purity of 99.5 mass %.

The physical properties of the reagents used in this work are listed in Table 1 together with literature values.

Procedure. The binodal curves were carried out by the titration method. The experimental details have been described by Letcher and Siswana (1992). The tie lines were analyzed by two methods which proved to be consistent. The previously described, by Letcher and Siswana (1992), refractive index method of Briggs and Comings

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0021-9568/96/1741-0634$12.00/0

Table 2. Compositions of Points on the Binodal Curve at 303.15 K, Equilibrium Mole Fractions x_1 and x_2

x_1	x_2	x_1	x_2
Sulfolane (1) + 1-Heptyne (2) + Heptane (3)			
0.985	0.000	0.075	0.720
0.951	0.031	0.027	0.683
0.871	0.108	0.013	0.555
0.714	0.251	0.011	0.388
0.608	0.350	0.009	0.230
0.510	0.441	0.008	0.101
0.345	0.584	0.007	0.067
0.220	0.674	0.006	0.000
0.150	0.711		
Sulfolane (1) + Benzene (2) + Heptane (3)			
0.985	0.000	0.154	0.625
0.921	0.060	0.101	0.617
0.884	0.098	0.064	0.586
0.817	0.163	0.028	0.515
0.764	0.214	0.014	0.400
0.641	0.332	0.011	0.302
0.494	0.456	0.010	0.200
0.420	0.511	0.008	0.101
0.342	0.558	0.007	0.061
0.245	0.605	0.006	0.000
0.193	0.619		
Sulfolane (1) + *p*-Xylene (2) + Heptane (3)			
0.985	0.000	0.280	0.639
0.964	0.019	0.216	0.675
0.937	0.045	0.139	0.706
0.861	0.119	0.048	0.645
0.774	0.204	0.019	0.503
0.634	0.334	0.012	0.380
0.545	0.420	0.010	0.250
0.439	0.511	0.008	0.105
0.355	0.580	0.006	0.000
Sulfolane (1) + Benzene (2) + Decane (3)			
0.992	0.000	0.053	0.660
0.934	0.057	0.031	0.598
0.830	0.159	0.020	0.506
0.716	0.270	0.015	0.410
0.564	0.414	0.010	0.295
0.462	0.503	0.008	0.210
0.359	0.589	0.006	0.100
0.208	0.669	0.004	0.000
0.116	0.692		
Sulfolane (1) + Benzene (2) + Dodecane (3)			
0.995	0.000	0.125	0.722
0.933	0.060	0.035	0.655
0.829	0.163	0.015	0.504
0.724	0.266	0.010	0.404
0.572	0.416	0.008	0.300
0.467	0.515	0.005	0.134
0.365	0.598	0.002	0.000
0.225	0.690		

Table 3. Compositions of the Conjugate Solutions, x_1', x_2' and x_1'', x_2'', at 303.15 K

n-hydrocarbon rich		sulfolane rich	
x_1'	x_2'	x_1''	x_2''
Sulfolane (1) + 1-Heptyne (2) + Heptane (3)			
0.007	0.060	0.941	0.040
0.008	0.140	0.911	0.070
0.010	0.298	0.829	0.147
0.012	0.450	0.756	0.213
0.018	0.621	0.681	0.281
0.059	0.711	0.582	0.370
0.112	0.720	0.514	0.436
0.253	0.652	0.465	0.481
Sulfolane (1) + Benzene (2) + Heptane (3)			
0.008	0.118	0.928	0.054
0.011	0.295	0.850	0.130
0.021	0.485	0.803	0.177
0.071	0.599	0.752	0.228
0.155	0.624	0.707	0.272
0.341	0.562	0.571	0.397
Sulfolane (1) + *p*-Xylene (2) + Heptane (3)			
0.008	0.105	0.942	0.039
0.011	0.322	0.868	0.111
0.017	0.477	0.817	0.161
0.025	0.548	0.780	0.197
0.040	0.620	0.724	0.247
0.088	0.701	0.655	0.314
0.142	0.703	0.598	0.370
0.258	0.651	0.548	0.419
Sulfolane (1) + Benzene (2) + Decane (3)			
0.006	0.119	0.930	0.061
0.010	0.308	0.819	0.170
0.019	0.469	0.760	0.228
0.045	0.643	0.730	0.256
0.110	0.690	0.704	0.280
0.248	0.652	0.650	0.330
Sulfolane (1) + Benzene (2) + Dodecane (3)			
0.004	0.111	0.924	0.071
0.008	0.290	0.810	0.180
0.011	0.458	0.769	0.221
0.023	0.612	0.701	0.290
0.060	0.699	0.655	0.336
0.118	0.721	0.590	0.398
0.279	0.658	0.536	0.452

(1943) was used and supported by a similar technique which involved density measurements as opposed to refractive index measurements. The densities were determined using a high-precision Anton Paar DMA (601) vibrating-tube density meter. The temperature was measured with an accuracy of 0.05 K, refractive index of 0.000 01 and density of 0.0001. The accuracy of the composition determination was 0.0001.

Results

The compositions of mixtures on the binodal curve at 303.15 K are given in Table 2, and tie line compositions are given in Table 3. These compositions are plotted in Figure 1.

Three equations have been fitted to the data following the work of Hlavatý (1972). The coefficients A_i relate to a modified Hlavatý equation:

$$x_2 = A_1 x_A \ln x_A + A_2 x_B \ln x_B + A_3 x_A x_B \qquad (1)$$

the coefficients B_i relate to a β function equation

$$x_2 = B_1(1 - x_A)^{B_2} x_A^{B_3} \qquad (2)$$

and the coefficients C_i relate to a log γ equation

$$x_2 = C_1(-\ln x_A)^{C_2} x_A^{C_3} \qquad (3)$$

where

$$x_A = (x_1 + 0.5x_2 - x_1^0)/(x_{11}^0 - x_1^0) \qquad (4)$$

$$x_B = (x_{11}^0 - x_1 - 0.5x_2)/(x_{11}^0 - x_1^0) \qquad (5)$$

and x_1 refers to the mole fraction composition of the sulfolane, x_2 refers to the mole fraction of 1-heptyne, benzene, or *p*-xylene, and x_{11}^0 and x_1^0 are the values of x_1 on the binodal curve which cuts the $x_2 = 0$ axis and have been used to summarize the binodal curve data. These equations have been discussed by Letcher *et al.* (1992). The coefficients A_i, B_i, and C_i are given in Table 4.

Equations 1−5 have been fitted to the binodal curves with the standard deviations σ. This is defined as

$$\sigma = [\sum[x_2(\text{calc}) - x_2(\text{exp})]^2/(n - 3)]^{1/2} \qquad (6)$$

where n is the number of data points and 3 is the number

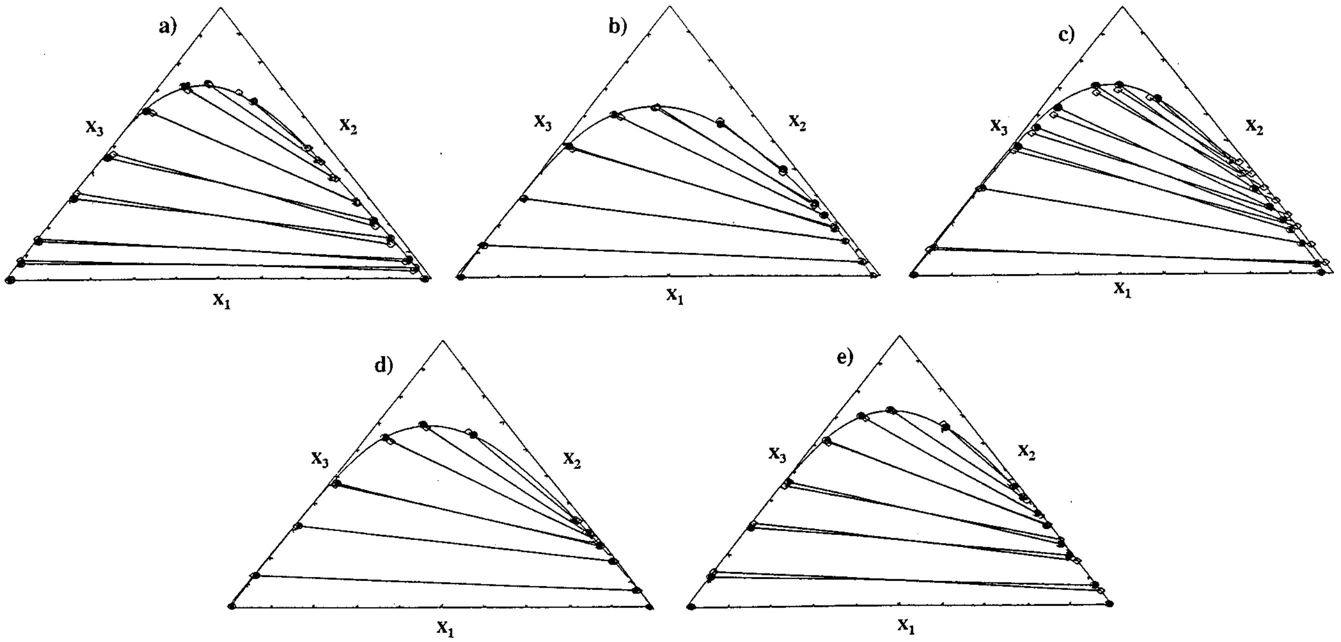

Figure 1. UNIQUAC correlations for the liquid–liquid equilibrium data for the systems (a) sulfolane (1) + 1-heptyne (2) + heptane (3), (b) sulfolane (1) + benzene (2) + heptane (3), (c) sulfolane (1) + *p*-xylene (2) + heptane (3), (d) sulfolane (1) + benzene (2) + decane (3), and (e) sulfolane (1) + benzene (2) + dodecane (3): (●) experimental points, (◇) predicted points; (solid line) calculated by log γ equation.

Table 4. Coefficients A_i, B_i, and C_i in Eqs 1–3 at 303.15 K[a]

Hlavatý	β	log γ
Sulfolane (1) + 1-Heptyne (2) + Heptane (3)		
$A_1 = 0.95(0.17)$	$B_1 = 3.62(0.20)$	$C_1 = 3.21(0.15)$
$A_2 = 1.24(0.18)$	$B_2 = 1.22(0.02)$	$C_2 = 1.18(0.02)$
$A_3 = 5.82(0.48)$	$B_3 = 1.23(0.03)$	$C_3 = 1.65(0.03)$
$\sigma = 0.060$	$\sigma = 0.060$	$\sigma = 0.059$
Sulfolane (1) + Benzene (2) + Heptane (3)		
$A_1 = 0.49(0.06)$	$B_1 = 3.22(0.17)$	$C_1 = 2.83(0.12)$
$A_2 = 0.55(0.01)$	$B_2 = 1.18(0.01)$	$C_2 = 1.13(0.01)$
$A_3 = 3.94(0.15)$	$B_3 = 1.20(0.01)$	$C_3 = 1.59(0.01)$
$\sigma = 0.021$	$\sigma = 0.024$	$\sigma = 0.027$
Sulfolane (1) + *p*-Xylene (2) + Heptane (3)		
$A_1 = 0.86(0.13)$	$B_1 = 3.39(0.18)$	$C_1 = 3.12(0.14)$
$A_2 = 0.92(0.12)$	$B_2 = 1.18(0.01)$	$C_2 = 1.16(0.01)$
$A_3 = 5.18(0.34)$	$B_3 = 1.21(0.02)$	$C_3 = 1.64(0.02)$
$\sigma = 0.020$	$\sigma = 0.036$	$\sigma = 0.033$
Sulfolane (1) + Benzene (2) + Decane (3)		
$A_1 = 0.83(0.10)$	$B_1 = 3.48(0.19)$	$C_1 = 3.11(0.14)$
$A_2 = 0.84(0.11)$	$B_2 = 1.18(0.02)$	$C_2 = 1.14(0.02)$
$A_3 = 5.02(0.29)$	$B_3 = 1.21(0.02)$	$C_3 = 1.63(0.03)$
$\sigma = 0.057$	$\sigma = 0.045$	$\sigma = 0.046$
Sulfolane (1) + Benzene (2) + Dodecane (3)		
$A_1 = 0.95(0.12)$	$B_1 = 3.71(0.22)$	$C_1 = 3.36(0.17)$
$A_2 = 0.91(0.11)$	$B_2 = 1.21(0.02)$	$C_2 = 1.17(0.02)$
$A_3 = 5.38(0.32)$	$B_3 = 1.23(0.03)$	$C_3 = 1.67(0.03)$
$\sigma = 0.054$	$\sigma = 0.033$	$\sigma = 0.042$

[a] The corresponding standard errors are given in parentheses.

of estimated coefficients (Sen and Srivastava, 1990). The standard errors defined by Sen and Srivastava (1990) as the square root of the variance of the estimated coefficients are larger for the modified Hlavatý equation (4% to 18%) than the standard errors for the β function and the log γ equations (0.5% to 5%).

Discussion

Our solubility results for the ternary systems sulfolane (1) + *p*-xylene (2) + heptane (3) at 303.15 K are fairly close to previously published values by Lee and Kim (1995) of sulfolane (1) + *p*-xylene (2) + octane (3) at 298.15 K and 308.15 K and indicate that the increase in carbon number of the alkane from 7 to 8 had only a small effect.

The slopes of the binodal curves for sulfolane + 1-heptyne (or +benzene or +*p*-xylene) + heptane are similar, with the 1-heptyne mixture showing a slight skewing toward the heptane axis. Figure 1 shows that area of the two-phase region increases in the order benzene < *p*-xylene < 1-heptyne.

The relative solubility of 1-heptyne, benzene, or *p*-xylene in an *n*-hydrocarbon or in sulfolane is evident from the tie lines. The slopes of the tie lines presented here (Figure 1) show that 1-heptyne, benzene, or *p*-xylene is more soluble in an *n*-hydrocarbon than in sulfolane with the order of solubility being benzene > *p*-xylene > 1-heptyne. The slopes of the tie lines show also that benzene is more soluble in the heptane then in decane or in dodecane. This solubility effect is also reflected in the size of the two-phase region, increasing slightly in the order dodecane > decane > heptane (see Figure 1).

The effectiveness of extraction of compound 2 by the sulfolane is given by its selectivity (ω), which is a measure of the ability of sulfolane to separate compound 2 from heptane:

$$\omega = \frac{\text{distribution coefficient of aromatics}}{\text{distribution coefficient of } n\text{-hydrocarbons}} = \frac{\dfrac{\%\text{ compound (2) of TMS rich phase}}{\%\text{ compound (2) of heptane rich phase}}}{\dfrac{\%\text{ heptane of TMS rich phase}}{\%\text{ heptane of heptane rich phase}}}$$

where TMS defines sulfolane.

The values of selectivity for the middle of the area of measured tie lines are 15.3, 14.2, and 11.0 for benzene, 1-heptyne, and *p*-xylene, respectively.

Data Correlation

Thermodynamic models such as the nonrandom two liquid equation (NRTL) (Renon and Prausnitz, 1968) and the universal quasichemical equation (UNIQUAC) (Abrams and Prausnitz, 1975) are used to correlate the experimental data for five ternary systems discussed here. The equations and algorithms used in the calculation of the compositions of liquid phases follow the method used by Walas (1985). The objective function $F(P)$, was used to minimize the difference between the experimental and calculated concentrations:

$$F(P) = \sum_{i=1}^{n}[x'^{\mathrm{exp}}_{1i} - x'^{calc}_{1i}(\mathrm{PT})]^2 + [x'^{\mathrm{exp}}_{2i} - x'^{\mathrm{calc}}_{2i}(\mathrm{PT})]^2 + [x''^{\mathrm{exp}}_{1i} - x''^{\mathrm{calc}}_{1i}(\mathrm{PT})]^2 + [x''^{\mathrm{exp}}_{2i} - x''^{\mathrm{calc}}_{2i}(\mathrm{PT})]^2 \quad (7)$$

where P is the set of parameters vector, n is the number of experimental points, x'^{exp}_{1i}, x'^{exp}_{2i} and $x'^{\mathrm{calc}}_{1i}(\mathrm{PT})$, $x'^{\mathrm{calc}}_{2i}(\mathrm{PT})$ are the experimental and calculated mole fractions of one phase and x''^{exp}_{1i}, x''^{exp}_{2i} and $x''^{\mathrm{calc}}_{1i}(\mathrm{PT})$, $x''^{\mathrm{calc}}_{2i}(\mathrm{PT})$ are the experimental and calculated mole fractions of the second phase.

The pure component structural parameters R (volume parameter) and Q (surface parameter) in the UNIQUAC equation were obtained in accordance with the method suggested by Vera *et al.* (1977) and the relationship given by Hofman and Nagata (1986):

$$R_i = 0.029281 V_{\mathrm{m}i} \quad (8)$$

$$Q_i = \frac{(Z-2)R_i}{Z} + \frac{2(1-l_i)}{Z} \quad (9)$$

where $V_{\mathrm{m}i}$ is the molar volume of pure component i at 298.15 K (see Table 1), Z is the coordination number, assumed equal to 10, and l_i is the bulk factor which was equated to zero for chainlike molecules and equated to unity for ring molecules (Hofman and Nagata, 1986).

For the NRTL model, the third nonrandomness parameter, α_{ij}, was set at a value of 0.2 (Cassell *et al.*, 1989b). The values of the starting parameters for binary systems with sulfolane were taken from solid−liquid equilibrium data (Domańska *et al.*, 1996a) or vapor−liquid equilibrium data (Domańska *et al.*, 1996b). The parameters calculated in this way are shown in Table 5. A comparison of the experimental and predicted tie lines, by the UNIQUAC model are shown for each system in Figure 1.

The model correlation parameters are included in Table 5, together with the rms values, which can be taken as a measure of the precision of the correlations:

$$\mathrm{rms} = (\sum_i \sum_l \sum_m [x^{\mathrm{exp}}_{ilm} - x^{calc}_{ilm}]^2/6k)^{1/2} \quad (10)$$

where x is the mole fraction and the subscripts i, l, and m designate the component, phase, and tie line, respectively. As can be seen from the tables and figure, the correlation obtained with the UNIQUAC model is significantly better than that obtained with the NRTL model.

Conclusions

Liquid−liquid equilibrium data for the five ternary systems sulfolane (1) + 1-heptyne (or +benzene or +*p*-xylene) (2) + heptane (3) and sulfolane (1) + benzene (2) + decane (or +dodecane) (3) were determined at 303.15 K.

The separation of 1-heptyne, benzene, or *p*-xylene from heptane, decane, or dodecane by extraction with sulfolane is feasible, as can be concluded from the distribution and selectivity data. Both benzene and *p*-xylene are better solvents for the sulfolane + an *n*-hydrocarbon mixtures than is 1-heptyne at 303.15 K.

Three equations have been fitted to the binodal curve data. The calculation based on the NRTL and UNIQUAC models showed that, in general, the best results are given by the UNIQUAC model.

Table 5. Values of the Parameters for the NRTL and UNIQUAC Equations, Determined from Ternary Liquid−Liquid Equilibria at 303.15 K, as Well as the Calculated Root Mean Square Deviation, rms[b]

	parameters (J·mol^{-1})			
	NRTL[a]		UNIQUAC	
component $i-j$	$g_{ij} - g_{jj}$	$g_{ji} - g_{ii}$	Δu_{ij}	Δu_{ji}
Sulfolane (1) + 1-Heptyne (2) + Heptane (3)				
	(0.009)		(0.014)	
1−2 2−1	438.81	5830.99	−902.18	3867.98
1−3 3−1	6913.53	33013.67	150.70	9807.68
2−3 3−2	7523.75	−2552.26	105.68	215.51
Sulfolane (1) + Benzene (2) + Heptane (3)				
	(0.041)		(0.007)	
1−2 2−1	446.94	6129.74	1926.46	688.69
1−3 3−1	6956.26	32964.91	717.84	12884.36
2−3 3−2	7515.24	−2556.16	-277.39	1926.77
Sulfolane (1) + *p*-Xylene (2) + Heptane (3)				
	(0.008)		(0.016)	
1−2 2−1	1615.83	4245.02	1304.18	1331.46
1−3 3−1	6553.37	27196.19	6411.68	12361.86
2−3 3−2	8307.38	−3608.21	241.76	2049.67
Sulfolane (1) + Benzene (2) + Decane (3)				
	(0.027)		(0.007)	
1−2 2−1	2393.20	3895.39	1843.71	869.02
1−3 3−1	4030.85	25386.42	751.53	15065.28
2−3 3−2	10746.10	−4108.97	-407.63	2523.96
Sulfolane (1) + Benzene (2) + Dodecane (3)				
	(0.048)		(0.012)	
1−2 2−1	2422.96	3918.69	1888.01	886.97
1−3 3−1	4070.45	25573.12	1076.19	14820.95
2−3 3−2	10556.55	−3863.09	-406.69	2531.27

[a] Calculated with $\alpha_{ij} = 0.2$. [b] The rms deviations are given in parentheses.

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Received for review December 8, 1995. Accepted February 29, 1996.⊗ The authors wish to thank the FRD (South Africa) for the financial support of this project.

JE950308J

⊗ Abstract published in *Advance ACS Abstracts*, April 15, 1996.