J. Chem. Eng. Data **2007,** *52,* 2212−2219

Solid−Liquid Equilibria of Dibenzothiophene and Dibenzothiophene Sulfone in Organic Solvents

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This work reports the solid−liquid equilibria of several binary systems formed by solvent (1) + dibenzothiophene (2) and solvent (1) + dibenzothiophene sulfone (2). At least six experimental points were obtained to trace the solid−liquid equilibrium curve, using the visual technique to determine the change of phase. The experimental data were obtained at atmospheric pressure and from a (280 to 353) K temperature range. The experimental uncertainties were ± 0.0005 in mole fraction and ± 0.5 K in temperature, respectively. A classical equilibrium solid−liquid equation was used to derive the activity coefficient from the solubility experimental data. The following solution models were employed to correlate the activity coefficient: UNIQUAC, Wilson, Tsuboka−Katayama−Wilson, van Laar, and Margules. A good agreement can be obtained between derived and correlated activity coefficients for selected systems. Additionaly, the following thermophysical properties were obtained experimentally for the pure dibenzothiophene sulfone: enthalpy of fusion, melting temperature, and heat capacity for both solid and liquid phases. These values have not been previously reported in the open literature, and the corresponding entropy of fusion was derived from the experimental information. The systems studied in this work are of industrial importance in the production of ultralow sulfur fuels.

Introduction

Dibenzothiophene and dibenzothiophene sulfone are two polynuclear aromatic compounds that are used as model compounds in the oxidation−extraction process.[1,2] Recently, the oxidation−extraction process has been considered as an alternative or complementary process for the conventional hydrodesulfurization process used to remove organosulfur compounds from intermediate distillates obtained from oil.[3,4]

The oxidation−extraction process is constituted by two stages. First, a selective oxidation process is carried out to transform the alkyldibenzothiophene compounds to sulfones. Thereafter, the sulfones are removed by extraction using high polar solvents.[5,6]

A few activity coefficient data for the solvent (1) + dibenzothiophene (2) binary system have been reported by Coon et al. and Domaska et al.[7−9] In the case of the solvent (1) + dibenzothiophene sulfone (2) binary system, there are not reported data in the open literature.

The activity coefficient data are usually obtained from vapor−liquid equilibrium (VLE) measurements. However, in some binary systems with polynuclear aromatic compounds, it is difficult to obtain the VLE because of their high boiling points. Consequently, the only source to obtain the needed data is by means of the solid−liquid equilibrium (SLE).[10]

This work reports the activity coefficients obtained through SLE experiments for ten binary systems: cyclohexane (1) + dibenzothiophene (2), *n*-tetradecane (1) +, *n*-hexadecane (1) +, *γ*-butyrolactone (1) +, acetonitrile (1), acetonitrile (1) + dibenzothiophene sulfone (2), 1-propanol (1) +, 2-ethoxyethanol (1) +, and *N*,*N*-dimethylformamide (1) +. Furthermore, five solution models were used to correlate the activity coefficient data.

The enthalpy of fusion, melting temperature, and heat capacity for both solid and liquid phases were determined experimentally for the pure dibenzothiophene sulfone, and these values have not been previously reported in the open literature. The entropy of fusion was derived from the experimental information.

Additionally, several group contribution models were used to calculate the enthalpy and entropy of fusion for dibenzothiophene sulfone, and the results were compared with the experimental data obtained in this work.

Experimental Section

Materials. Commercially available reactives were directly used for the solid−liquid equilibrium experiments without further purification. Cyclohexane (99.9 %), *n*-tetradecane (99.0 %), *n*-hexadecane (99.0 %), *γ*-butyrolactone (99.0 %), dibenzothiophene (98.0 %), 1-propanol (99.5 %), 2-ethoxyethanol (99.0 %), and *N*,*N*-dimethylformamide (99.9 %) from Aldrich and acetonitrile (99.9 %) from the Fermont company were used in the experimental program.

Procedure. The solid−liquid equilibrium temperature was determined using the visual technique to observe the phase change in a closed cell. This technique has been previously described by Ramírez-Verduzco et al.[11] To study the solubility of dibenzothiophene or dibenzothiophene sulfone in the selected

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10.1021/je700234e CCC: $37.00

solvents, first the mixtures of solute and solvent in binary systems were prepared by weighting them (therefore a global composition in mole fraction was obtained). The samples were slowly heated, and the temperature at which the last trace of a known quantity of the solid solute disappears was measured. The temperature obtained represents the saturation point for this composition. Hence, the whole saturation curve can be obtained by running samples at several compositions, as was reported by Coon et al.[7] The cyclohexane (1) + dibenzothiophene (2) binary system was used as a reference to estimate the uncertainties of the activity coefficients reported in this work.

The enthalpy of fusion and melting temperature of the dibenzothiophene sulfone were determined using a DSC-7 Perkin-Elmer differential scanning calorimeter. Aluminum capsules (0219-0062 Perkin-Elmer model) were employed as sample pans for the volatile substances. The calorimeter was calibrated previously, for both energy and temperature, using indium metal of high purity ($\Delta_{\text{fus}}H = 28\,450\ \text{J}\cdot\text{kg}^{-1}$, $T_{\text{fus}} = 429.7\ \text{K}$). The dibenzothiophene sulfone samples were weighted in a Sartorius balance (4503 model) with a sensitivity of $\pm 1\cdot 10^{-6}$ g.

Prior to the heat capacity measurement, the dibenzothiophene sulfone was purified by sublimation at 433.1 K and a residual pressure of 0.03 kPa. In a first experiment, the optimal temperature range on the purified substance, as well as the heating rate and the necessary amount of material in the fusion experiments, was established. In the experiments, the mass of the sample was 0.006600 g, and it was heated from (298 to 523) K at the scanning rate of $0.17\ \text{K}\cdot\text{s}^{-1}$. All the experiments were carried out, keeping the sample under nitrogen at a constant flow rate of $3.33\cdot 10^{-7}\ \text{m}^3\cdot\text{s}^{-1}$.

There was not a crystalline transition state in the temperature range (298 to 503) K, because no thermal signal was observed. To ensure the reproducibility and accuracy, further measurements were restricted to the temperature range (493 to 513) K with a rate of scanning of $0.017\ \text{K}\cdot\text{s}^{-1}$.

The enthalpy of fusion and melting temperature were determined from the fusion signal analysis. The melting temperature corresponds to the average temperature of the thermal signal's first slope. The purity of the samples was determined from the analysis curve using the van't Hoff method.[12]

The heat capacities of the dibenzothiophene sulfone for both solid and liquid phases were also determined in the DSC-7 Perkin−Elmer differential scanning calorimeter, with the previous calibration methodology described in this paper. The solid heat capacity data were obtained from (298 to 498) K, whereas liquid heat capacity data were measured from (513 to 573) K. The uncertainty of the heat capacity data was determined previously with a reference compound (Zafiro batch #720 of the National Institute of Standards and Technology, Washington D.C., USA). The heat capacities of the reference sample were (88.4, 95.4, 106.5, and 112.3) $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ at (350, 400, 500, and 600) K, respectively. These values are in good agreement with the recommended values[13] of (88.8, 96.1, 106.1, and 112.6) $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ at the respective temperatures, which means a maximal inaccuracy of 0.7 % for these measurements.

Correlation

The activity coefficient was obtained by the classic SLE equation reported by Coon et al.[7]

$$\gamma_2 = \exp\left[-\frac{\Delta_{\text{fus}}S_2}{R}\left(\frac{T_{\text{fus}}}{T} - 1\right) + \frac{\Delta C_{p,2}}{R}\left(\frac{T_{\text{fus}}}{T} - 1\right) - \frac{\Delta C_{p,2}}{R}\ln\left(\frac{T_{\text{fus}}}{T}\right) - \ln x_2\right] \quad (1)$$

where $\Delta_{\text{fus}}S_2$ is the molar entropy of fusion of the solute; $\Delta C_{p,2}$ is the difference between solid and liquid heat capacities of the solute; x_2 is the mole fraction of the solute; T_{fus} is the melting temperature of the solute; T is the absolute temperature; γ_2 is the liquid-phase activity coefficient of the solute; and R is the universal gas constant, respectively. In this work, subscripts 1 and 2 represent the solvent and solute compounds, respectively.

Thermodynamic properties of dibenzothiophene reported by Coon et al.[7] are collected in Table 1. These properties are necessary in eq 1 to calculate the corresponding activity coefficient.

The $\Delta C_{p,2}$ and T_{fus} values (eq 1) for the dibenzothiophene sulfone were obtained in this work, since this information is not available in the open literature. Furthermore, the entropy and enthalpy of fusion of the dibenzothiophene sulfone were estimated using the Marrero−Gani methods by the commercial software Integrated Computer Aided System (ICAS). The results are shown in Table 2.

The activity coefficient γ_2 (derived from eq 1) was correlated using the following solution models: UNIQUAC, Wilson, Tsuboka−Katayama−Wilson (TKW), van Laar, and Margules. A detailed description of each model is shown in Table 3.[12]

As can be observed in Table 3, there is not a direct functionality between the activity coefficient and temperature in the van Laar and Margules models.

The temperature and the molar volumes (V_{m}) of pure compounds evaluated at their melting point are required by the Wilson and TKW models to estimate γ_2.

Additionally, the V_{m} value and temperature, the UNIQUAC model also requires the values of the r_i and q_i interaction parameters ($r_i = \Sigma\nu_k^{(i)}R_K$ and $q_i = \Sigma\nu_k^{(i)}Q_K$).

Table 4 shows the r_i and q_i interaction parameters for several solvents and hydrocarbon compounds. Otherwise, the R_k and Q_k individual parameters of each group can be obtained from the open literature.[12,14]

In this work, the V_{m} (evaluated at the melting point of the solute) was obtained through the Rackett and Yamada−Gunn methods, given by eqs 2 and 3, respectively.[15]

$$V_{\text{m}} = V_{\text{c}}Z_{\text{c}}^{(1-T/T_{\text{c}})2/7} \quad (2)$$

$$V_{\text{m}} = V_{\text{c}}(0.29056 - 0.08775\omega)^{(1-T/T_{\text{c}})2/7} \quad (3)$$

where V_{c} is the critical volume; T_{c} is the critical temperature; P_{c} is the critical pressure; ω is the acentric factor; and Z_{c} is the critical compressibility factor ($Z_{\text{c}} = P_{\text{c}}V_{\text{c}}/RT_{\text{c}}$).

Table 5 shows the critical parameters reported in the open literature[16−25] for the several solvents considered. These properties were used to estimate the V_{m} values by the Rackett and Yamada−Gunn methods.

The critical properties and acentric factor for both dibenzothiophene sulfone and 2-ethoxyethanol were estimated using the group contribution methods through the ASPEN software because there are no available T_{c}, P_{c}, and V_{c} data in the open literature. The values obtained by this methodology are reported in Table 6.

Finally, the Gaussian 98W (version 5.1) software was used to calculate the dipole moment of the dibenzothiophene and dibenzothiophene sulfone. The PM3 (parametric model 3)

Table 1. Thermodynamic Properties for the Dibenzothiophene Reported by Coon et al. (1988)

compound	ΔC_p J•mol^{-1}•K^{-1}	T_{fus} K	$\Delta_{\mathrm{fus}}H$ kJ•mol^{-1}	$\Delta_{\mathrm{fus}}S$ J•mol^{-1}•K^{-1}
dibenzothiophene	31.4	372.0	21.0	56.42

Table 2. Comparison of Enthalpy and Entropy of Fusion for the Dibenzothiophene Sulfone Compound

compound	$\Delta_{\mathrm{fus}}H$ kJ•mol^{-1}	$\Delta_{\mathrm{fus}}H$ kJ•mol−1	$\Delta_{\mathrm{fus}}S$ J•mol^{-1}•K^{-1}	$\Delta_{\mathrm{fus}}S$ J•mol^{-1}•K^{-1}
dibenzothiophene sulfone	27.17[a]	28.09[b]	53.36[a]	66.73[b]

[a] This work. [b] Marrero−Gani method.

semiempirical Hamiltonian method was employed to solve the Schrödinger equation to calculate the optimum geometry and electronic properties of the dibenzothiophene and dibenzothiophene sulfone.

Results and Discussion

Solid−Liquid Equilibrium. Figure 1 compares the experimental solubility results for the cyclohexane (1) + dibenzothiophene (2) with those reported by Coon et al.[7] This figure shows the difference in temperature as a function of the DBT mole fraction.

As can be observed, the results obtained in this work are in good agreement with the corresponding values reported by Coon et al.[7] The highest deviation in temperature was 1.2 K. The estimated experimental uncertainties were ± 0.0005 in mole fraction and ± 0.5 K for temperature. These uncertainties have a negligible effect on the derived activity coefficients.

Table 7 shows the experimental solid−liquid equilibrium for the binary systems cyclohexane (1) + dibenzothiophene (2), *n*-tetradecane (1) + dibenzothiophene (2), *n*-hexadecane (1) + dibenzothiophene (2), γ-butyrolactone (1) + dibenzothiophene (2), and acetonitrile (1) + dibenzothiophene (2) obtained in this work.

A eutectic point was determined for the *n*-tetradecane (1) + dibenzothiophene (2) and *n*-hexadecane (1) + dibenzothiophene (2) binary systems at ($x_{\mathrm{DBT}} = 0.0230$ and $T = 278.2$ K) and ($x_{\mathrm{DBT}} = 0.0439$ and $T = 290.6$ K), respectively. The eutectic point is the single condition at which a liquid is in equilibrium with two solid phases, and the temperature is presented as a minimum on the liquid curves of the T vs x_i diagram.

Table 7 shows that for the dibenzothiophene mole fraction range (0.0 to 0.1) there exists a large increase of solubility temperature for the acetonitrile (1) + dibenzothiophene (2) system, and for a dibenzothiophene mole fraction higher than 0.1, the solubility temperature is increased more slowly. In contrast, a permanent increase of temperature with respect to the mole fraction was observed in the γ-butyrolactone (1) + dibenzothiophene (2) binary system.

The solubility of dibenzothiophene sulfone in the solvents decreases in the following order: *N*,*N*-dimethylformamide > γ-butyrolactone > acetonitrile ≈ 2-ethoxyethanol > 1-propanol. This information can be useful to select a solvent for the extraction step in the oxidation−extraction process. This tendency is in good agreement with the extraction capacity of these solvents reported in a previous publication.[11]

The enthalpy of fusion and melting temperature of dibenzothiophene sulfone were also obtained experimentally in this work. Table 8 shows the enthalpy and melting temperature of dibenzothiophene sulfone including the mass and purity used during the experimental runs, and the uncertainty associated with the average results represents the standard deviation.

The entropy of fusion of dibenzothiophene sulfone (evaluated at its melting point) can be calculated from the results reported previously in Table 8, according to the following equation.

$$\Delta_{\mathrm{fus}}S = \frac{\Delta_{\mathrm{fus}}H}{T_{\mathrm{fus}}} = \frac{27.17\ \mathrm{kJ{\bullet}mol^{-1}}}{509.2\ \mathrm{K}} = (53.36 \pm 0.35)\ \mathrm{J{\bullet}mol^{-1}{\bullet}K^{-1}} \quad (4)$$

Figure 2 shows the measured profile with temperature of the heat capacity for both solid and liquid phases of the dibenzothiophene sulfone.

The experimental measurements to obtain the solid heat capacity were performed in the temperature range (298 to 500) K. The experimental data were fitted by a second-order polynomial equation. The regression coefficient and standard deviation were (0.9995 and 0.9) J•mol^{-1}•K^{-1}, respectively.

$$C_{p,\,\mathrm{solid}}/(\mathrm{J{\bullet}mol^{-1}{\bullet}K^{-1}}) = 1.69{\bullet}10^{2} + 3.28{\bullet}10^{-2}\ T/\mathrm{K} + 5.73{\bullet}10^{-4}\ T^{2}/\mathrm{K}^{2} \quad (5)$$

With regard to the heat capacity in the liquid phase, the experiments were performed in the temperature range (513 to 613) K. However, a thermal signal on the range (555 to 613) K (that can be associated with the slight sample decomposition) forces the generation of the quadratic regression only in the temperature range (513 to 555) K. The equation for the liquid heat capacity is given by the following expression

$$C_{p,\mathrm{liquid}}/(\mathrm{J{\bullet}mol^{-1}{\bullet}K^{-1}}) = 4.99{\bullet}10^{2} - 1.26\ T/\mathrm{K} + 1.09{\bullet}10^{-3}T^{2}/\mathrm{K}^{2} \quad (6)$$

For this expression, the regression coefficient and standard deviation were (0.9953 and 0.1) J•mol^{-1}•K^{-1}, respectively.

A sensitivity analysis of eqs 5 and 6 was performed to determine the significant decimal digit coefficients.

An important difference between solid and liquid heat capacities of 195.9 J•mol^{-1}•K^{-1} for the dibenzothiophene sulfone could be observed at 509.2 K (Figure 2).

Table 2 shows a comparison between experimental and calculated values for the enthalpy and entropy of fusion of the dibenzothiophene sulfone. The Marrero−Gani method was used to estimate the values for both $\Delta_{\mathrm{fus}}H$ and $\Delta_{\mathrm{fus}}S$. This calculation was performed by means of the ICAS software.

Owing to the relative error between experimental and calculated data for the enthalpy and entropy of fusion of the dibenzothiophene sulfone [(3.4 and 25) %], the Marrero−Gani method was only acceptable to predict the $\Delta_{\mathrm{fus}}H$ value.

The activity coefficients for the dibenzothiophene and dibenzothiophene sulfone were calculated using eq 1. The thermophysical properties needed to calculate this parameter were previously reported in Tables 1, 2, and 8.

Table 9 shows the activity coefficient for the solvent (1) + dibenzothiophene (2) and solvent (1) + dibenzothiophene sulfone (2) binary systems.

The character of nonideality is more remarkable in the solvent (1) + dibenzothiophene sulfone (2) systems in comparison with the solvent (1) + dibenzothiophene (2) systems. This behavior could be explained through the large dibenzothiophene sulfone dipole moment.

Table 3. Equations of Activity Coefficients of Binary Mixtures

parameters	$\ln \gamma_2$
Margules	
Γ_{12}, Γ_{21}	$[\Gamma_{21} + 2(\Gamma_{12} - \Gamma_{21})x_2]x_1^2$
van Laar	
Ω_{12}, Ω_{21}	$\Omega_{21}\left(\frac{\Omega_{12}x_1}{\Omega_{12}x_1 + \Omega_{21}x_2}\right)^2$
Wilson	
$\lambda_{12}, \lambda_{21}$, $\Psi_{12} = \frac{V_{m2}}{V_{m1}}\exp\left(-\frac{\lambda_{12}}{RT}\right), \Psi_{21} = \frac{V_{m1}}{V_{m2}}\exp\left(-\frac{\lambda_{21}}{RT}\right)$ V_{mi}, molar volume of pure liquid component i	$-\ln(x_2 + \Psi_{21}x_1)$ $-x_1\left(\frac{\Psi_{12}}{x_1 + \Psi_{12}x_2} - \frac{\Psi_{21}}{\Psi_{21}x_1 + x_2}\right)$
Tsuboka−Katayama−Wilson	
$\lambda_{12}, \lambda_{21}$, $\beta = \frac{\Psi_{12}}{x_1 + \Psi_{12}x_2} - \frac{\Psi_{21}}{\Psi_{21}x_1 + x_2}, \beta_v = \frac{V_{m2}/V_{m1}}{x_1 + V_{m2}x_2/V_{m1}} - \frac{V_{m1}/V_{m2}}{V_{m1}x_1/V_{m2} + x_2}$ Ψ_{12} and Ψ_{21} as for the Wilson equation V_{mi}, molar volume of pure liquid component i	$\ln\frac{V_{m1}x_1/V_{m2} + x_2}{\Psi_{21}x_1 + x_2} - (\beta - \beta_v)x_1$
UNIQUAC	
Π_{12}, Π_{21} $\ln \gamma_2^{C} = \ln\frac{\varphi_2}{x_2} + \frac{z}{2}q_2 \ln\frac{\vartheta_2}{\varphi_2} + \varphi_1\left(l_2 - \frac{r_2}{r_1}l_1\right)$ $\ln \gamma_2^{R} = -q_2 \ln(\vartheta_1\tau_{12} + \vartheta_2) + \vartheta_1 q_2\left(\frac{\tau_{12}}{\vartheta_1\tau_{12} + \vartheta_2} - \frac{\tau_{21}}{\vartheta_1 + \vartheta_2\tau_{21}}\right)$ $l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1), \tau_{ij} = \exp\left(-\frac{\Pi_{ij}}{RT}\right)$ q_i = area parameter of component i; r_i = volume parameter of component i; z = coordination number; γ_2^{C} = combinatorial part of activity coefficient of component 2;γ_2^{R} = residual part of activity coefficient of component 2 $\vartheta_i = \frac{q_i x_i}{\sum_j q_j x_j}$ area fraction of component i $\varphi_i = \frac{r_i x_i}{\sum_j r_j x_j}$ volume fraction of component i	$\ln \gamma_2^{C} + \ln \gamma_2^{R}$

Table 4. r_i and q_i Parameters for the Compounds Used in the UNIQUAC Model

compound	r_i	q_i
cyclohexane	4.0464	3.240
n-tetradecane	9.8950	8.176
n-hexadecane	11.2438	9.256
γ-butyrolactone	3.0384	2.500
acetonitrile	1.8701	1.724
dibenzothiophene	6.4429	4.220
1-propanol	3.2499	3.128
2-ethoxyethanol	4.1682	3.901
N,*N*-dimethylformamide	2.000	2.093
dibenzothiophene sulfone	7.6677	5.560

Table 5. Thermodynamic Critical Parameters of Several Solvents and Hydrocarbon Compounds

compound	P_c/kPa	T_c/K	$10^3 \cdot V_c/m^3 \cdot mol^{-1}$	ω
cyclohexane	4080[a]	553.8[a]	0.3080[a]	0.213[k]
n-tetradecane	1600[b]	693.0[b]	0.8940[b]	0.644[k]
n-hexadecane	1400[b]	723.0[b]	1.0340[b]	0.718[k]
γ-butyrolactone	5131[c]	731.0[c]	0.2435[i]	0.316[c]
acetonitrile	4890[d]	545.5[d]	0.1730[j]	0.321[k]
dibenzothiophene	3857[e]	897.0[e]	0.5118[e]	0.397[e]
1-propanol	5170[f]	536.8[f]	0.2180[f]	0.629[k]
N,*N*-dimethylformamide	5499[g]	649.6[h]	0.2490[j]	0.389[g]

[a] Daubert (1996). [b] Ambrose and Tsonopoulos (1995). [c] Wilson et al. (1996). [d] Duran-Valencia et al. (2002). [e] Gude and Teja (1995). [f] Castillo-López and Trejo (1987). [g] Chirico et al. (1991). [h] Teja and Anselme (1990). [i] Estimated from Lebedev and Yevstropov (1983). [j] Riddick and Bunger (1970). [k] Poling et al. (2001).

The dipole moment of dibenzothiophene and dibenzothiophene sulfone molecules has been calculated by the PM3 semiempirical Hamiltonian method. Table 10 shows the results obtained in this work.

From these data, a difference of around four times between dibenzothiophene and dibenzothiophene sulfone can be observed in the dipole moment values, then a higher deviation from the ideality ($\gamma_2 >> 1$) for the systems formed with dibenzothiophene sulfone could be expected.

Correlation of the Experimental Data. As was indicated before, solution models were used to correlate the solid−liquid equilibrium data, and the corresponding thermophysical properties for these models were obtained as described in the following section.

The critical properties of 2-ethoxyethanol and dibenzothiophene sulfone are required to calculate the molar volume by the Racket and Yamada−Gunn methods. These parameters are shown in Table 6. All critical values were calculated by the

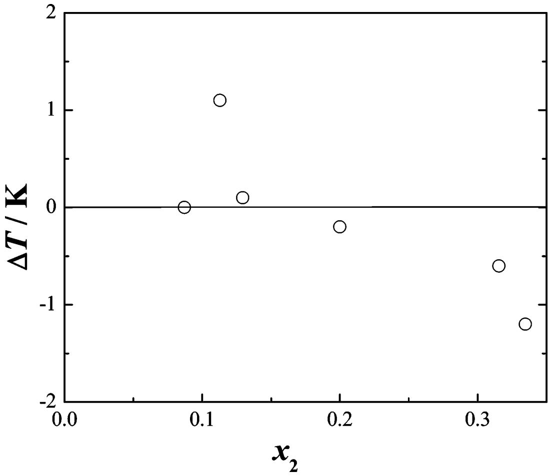


Figure 1. Deviation plot for the solid−liquid equilibrium of the cyclohexane (1) + dibenzothiophene (2) binary system.

Table 6. Estimated Critical Temperature, Critical Pressure, and Critical Volume of the 2-Ethoxyethanol and Dibenzothiophene Sulfone Compounds

compound	T_c/K	P_c/kPa	$10^3 \cdot V_c$/m$^3 \cdot$mol^{-1}
2-ethoxyethanol	602.5	4178	0.2919
dibenzothiophene sulfone	936.0	4879	0.5423

Marrero−Gani group contribution method using the ICAS software.

Additionally to the Marrero−Gani method, the Joback, Lydersen, Ambrose, and Fedors methods were used to estimate the critical properties of 2-ethoxyethanol. Only small deviations were observed with respect to the results obtained by means of the Marrero−Gani method (< 5.5 %).

It was not possible to obtain the critical properties and acentric factor of the dibenzothiophene sulfone compound because the group parameters for the $ACSO_2AC$ group are not available in the database of the ASPEN software. However, it was possible to obtain the critical properties through the Marrero−Gani method.

The acentric factor of the 2-ethoxyethanol compound was calculated by the Pitzer and Lee−Kesler methods using the ASPEN software, and the obtained values were 0.758 and 0.775, respectively. The value of 0.758 was used to derive the molar volume by means of the Yamada−Gunn method (Table 11).

The molar volumes of the compounds studied in this work (evaluated at the melting point of the solutes dibenzothiophene and dibenzothiophene sulfone) which were calculated by eqs 2 and 3 are shown in Table 11.

On the other hand, the values obtained for the volume parameter (r_i) and area parameter (q_i) for the dibenzothiophene compound in the UNIQUAC model were 6.4429 and 4.22, respectively (Table 4). These values are different from the values reported by Coon et al.[7] ($r_{DBT} = 6.5190$ and $q_{DBT} = 4.97$). The differences can be appearing from the continued updating of the R_k and Q_k parameters. Table 12 shows the R_k and Q_k parameters used in this work to calculate the UNIQUAC volume and UNIQUAC area parameters for dibenzothiophene.[12,14] Estimation details for the r_i and q_i interaction parameters are performed by eqs 7 and 8.

$$r_{DBT} = 8(0.5313) + 2(0.3652) + 1(1.4621) = 6.4429 \quad (7)$$

$$q_{DBT} = 8(0.4) + 2(0.12) + 1(0.78) = 4.22 \quad (8)$$

The R_k and Q_k UNIQUAC parameters are not available in the open literature for the $ACSO_2AC$ group for dibenzothiophene sulfone. In this work, an approximation of the r_i and q_i UNIFAC parameters was done for the dibenzothiophene sulfone molecule. We considered $R_k = 2.6870$ and $Q_k = 2.120$ of the subgroup $CH_2SO_2CH_2$ reported by Witting et al.,[26] instead of the R_k and Q_k parameters for the real subgroup $ACSO_2AC$ in the dibenzothiophene sulfone. Table 12 shows the R_k and Q_k parameters for the dibenzothiophene sulfone compound, and eqs 9 and 10 show the estimation of r_i and q_i parameters for dibenzothiophene sulfone.

$$r_{DBTO_2} = 8(0.5313) + 2(0.3652) + 1(2.6869) = 7.6677 \quad (9)$$

$$q_{DBTO_2} = 8(0.4) + 2(0.12) + 1(2.12) = 5.56 \quad (10)$$

Table 7. Solid−Liquid Equilibrium for the Solvent (1) + Dibenzothiophene (2) and Solvent (1) + Dibenzothiophene Sulfone (2) Binary Systems

x_2	T/K	x_2	T/K	x_2	T/K	x_2	T/K
Cyclohexane (1) + Dibenzothiophene (2)							
0.0496	309.3	0.1291	328.8	0.4924	349.6		
0.0871	321.1	0.1989	335.6	0.5930	353.5		
n-Tetradecane (1) + Dibenzothiophene (2)							
0.0230	278.2	0.0400	291.0	0.0959	316.1	0.2982	346.7
0.0300	283.9	0.0525	298.3	0.2035	337.2	0.4007	352.6
						0.4965	356.2
n-Hexadecane (1) + Dibenzothiophene (2)							
0.0061	291.1	0.0451	290.7	0.0726	304.4	0.2565	341.5
0.0184	290.9	0.0463	291.0	0.1008	315.0	0.3737	350.9
0.0305	290.8	0.0475	292.2	0.1201	319.9	0.5021	356.9
0.0427	290.6	0.0487	293.0	0.1783	331.5	0.5094	357.0
0.0439	290.6	0.0504	293.7	0.2000	334.7	0.6047	360.1
						0.6954	362.7
γ-Butyrolactone (1) + Dibenzothiophene (2)							
0.0599	281.3	0.1348	307.9	0.2376	325.2	0.4635	344.6
0.0762	289.7	0.1668	314.6	0.2743	329.4	0.5833	351.5
0.1047	300.1	0.2011	320.2	0.3630	337.6	0.6503	354.8
						0.8076	362.4
Acetonitrile (1) + Dibenzothiophene (2)							
0.0199	303.7	0.1021	332.0	0.3092	341.8	0.4604	347.1
0.0522	323.1	0.1986	338.1	0.3956	344.8		
1-Propanol (1) + Dibenzothiophene Sulfone (2)							
0.0039	344.0	0.0056	353.0	0.0076	361.2	0.0087	364.9
0.0048	349.0	0.0064	356.6	0.0083	363.6	0.0093	366.7
						0.0094	367.0
2-Ethoxyethanol (1) + Dibenzothiophene Sulfone (2)							
0.0106	323.4	0.0170	343.8	0.0223	355.5	0.0286	368.3
0.0127	332.1	0.0200	350.3	0.0232	357.4		
0.0159	340.5	0.0215	353.8	0.0254	361.9		
Acetonitrile (1) + Dibenzothiophene Sulfone (2)							
0.0123	330.2	0.0173	342.6	0.0226	352.5	0.0284	361.4
0.0152	338.3	0.0206	348.8	0.0256	357.3	0.0317	366.1
						0.0335	368.5
γ-Butyrolactone (1) + Dibenzothiophene Sulfone (2)							
0.0379	320.3	0.0760	351.6	0.0921	358.2	0.1166	363.7
0.0515	334.8	0.0780	352.7	0.1013	360.8		
0.0653	346.9	0.0853	355.9	0.1134	363.2		
N,*N*-Dimethylformamide (1) + Dibenzothiophene Sulfone (2)							
0.0556	319.5	0.0875	346.2	0.1234	361.5	0.1502	369.4
0.0663	329.7	0.1013	352.0	0.1302	363.8		
0..0774	338.8	0.1123	357.3	0.1401	366.7		

Table 8. Experimental Thermophysical Properties for Dibenzothiophene Sulfone

m/mg	purity/mol fraction	T_{fus}/K	$\Delta_{fus}H$/kJ$\cdot$mol^{-1}
5.190	0.9940	509.8	27.39
5.264	0.9949	509.3	27.20
4.413	0.9945	509.1	27.43
5.497	0.9948	509.3	27.46
5.089	0.9943	509.3	27.51
5.350	0.9941	508.8	26.71
5.056	0.9938	508.6	26.49
average	0.9943	509.2	27.17

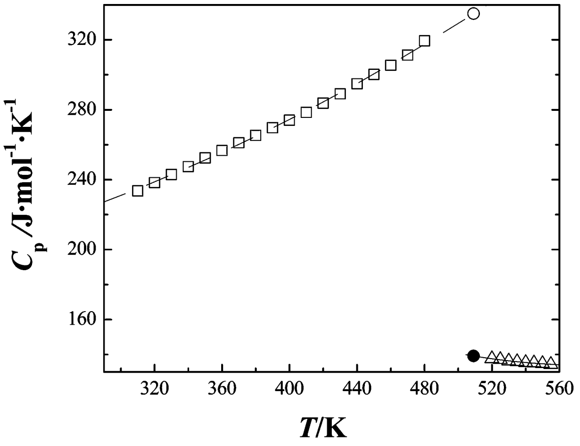


Figure 2. Heat capacity versus temperature for the solid and liquid phases. □, solid phase; Δ, liquid phase; ○, extrapolated at 509.2 K for the solid phase; ●, extrapolated at 509.2 K for the liquid phase; quadratic regression for solid (- - -) and liquid (—) phases, respectively.

Table 9. Activity Coefficients for the Solvent (1) + Dibenzothiophene (2) and Solvent (1) + Dibenzothiophene Sulfone (2) Binary Systems

x_2	γ_2	x_2	γ_2	x_2	γ_2	x_2	γ_2
Cyclohexane (1) + Dibenzothiophene (2)							
0.0496	5.455	0.1291	3.272	0.4924	1.325		
0.0871	4.087	0.1989	2.459	0.5930	1.188		
n-Tetradecane (1) + Dibenzothiophene (2)							
0.0230	5.261	0.0400	4.280	0.0959	3.311	0.2982	2.063
0.0300	4.721	0.0525	3.934	0.2035	2.486	0.4007	1.728
						0.4965	1.496
n-Hexadecane (1) + Dibenzothiophene (2)							
0.0463	3.697	0.0726	3.311	0.2000	2.399	0.5094	1.481
0.0475	3.719	0.1008	3.071	0.2565	2.157	0.6047	1.324
0.0487	3.703	0.1201	2.885	0.3737	1.791	0.6954	1.210
0.0504	3.644	0.1783	2.513	0.5021	1.500		
γ-Butyrolactone (1) + Dibenzothiophene (2)							
0.0599	2.202	0.1348	1.941	0.2376	1.643	0.4635	1.272
0.0762	2.171	0.1668	1.839	0.2743	1.561	0.5833	1.161
0.1047	2.064	0.2011	1.735	0.3630	1.405	0.6503	1.111
						0.8076	1.036
Acetonitrile (1) + Dibenzothiophene (2)							
0.0199	11.871	0.1021	4.435	0.3092	1.801	0.4604	1.347
0.0522	7.134	0.1986	2.596	0.3956	1.496		
1-Propanol (1) + Dibenzothiophene Sulfone (2)							
0.0039	93.026	0.0056	62.281	0.0076	45.277	0.0093	36.764
0.0048	74.521	0.0064	56.293	0.0083	39.358	0.0094	36.366
2-Ethoxyethanol (1) + Dibenzothiophene Sulfone (2)							
0.0106	40.336	0.0170	21.435	0.0223	15.628	0.0286	11.945
0.0127	31.073	0.0200	17.714	0.0232	14.948		
0.0159	23.489	0.0215	16.291	0.0254	13.532		
Acetonitrile (1) + Dibenzothiophene Sulfone (2)							
0.0123	32.613	0.0173	21.217	0.0226	15.565	0.0284	12.112
0.0152	24.915	0.0206	17.350	0.0256	13.550	0.0317	10.790
						0.0335	10.197
γ-Butyrolactone (1) + Dibenzothiophene Sulfone (2)							
0.0379	11.718	0.0760	4.643	0.0921	3.758	0.1166	2.941
0.0515	7.521	0.0780	4.508	0.1013	3.399		
0.0653	5.510	0.0853	4.081	0.1134	3.025		
N,*N*-Dimethylformamide (1) + Dibenzothiophene Sulfone (2)							
0.0556	8.066	0.0875	4.125	0.1234	2.787	0.1502	2.274
0.0663	6.090	0.1013	3.479	0.1302	2.633		
0.0774	4.865	0.1123	3.089	0.1401	2.440		

UNIQUAC, Wilson, TKW, van Laar, and Margules solution models were utilized to calculate the activity coefficient. The Levenberg−Marquardt optimization algorithm was employed to estimate the corresponding interaction parameters.[27]

Table 10. Dipole Moment for Dibenzothiophene and Dibenzothiophene Sulfone Calculated by the PM3 Method

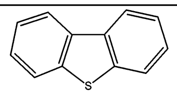
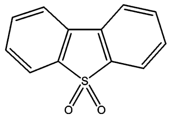
Compound	Chemical structure	Dipole Moment/D
Dibenzothiophene		1.36
Dibenzothiophene sulfone		5.45

Table 11. Molar Volume for the Compounds Studied in This Work

compound	*T*/K	$10^3 \cdot V_m$/m^3·mol^{-1}	
cyclohexane	372.0	0.1198[a]	0.1194[b]
n-tetradecane	372.0	0.2922[a]	0.2787[b]
acetonitrile	372.0	0.0516[a]	0.0659[b]
n-hexadecane	372.0	0.3248[a]	0.3101[b]
γ-butyrolactone	372.0	0.0670[a]	0.0818[b]
dibenzothiophene	372.0	0.1636[a]	0.1588[b]
γ-butyrolactone	509.2	0.0790[a]	0.0941[b]
N,*N*-dimethylformamide	509.2	0.1027[a]	0.1034[b]
1-propanol	509.2	0.1209[a]	0.1173[b]
acetonitrile	509.2	0.0798[a]	0.0934[b]
2-ethoxyethanol	509.2	0.1472[a]	0.1339[b]
dibenzothiophene sulfone	509.2	0.2290[a]	−

[a] Rackett method. [b] Yamada−Gunn method.

Table 12. R_k, Q_k, and ν_k UNIQUAC Parameters for the Dibenzothiophene and Dibenzothiophene Sulfone Molecules

main group	subgroup	R_k	Q_k	ν_k
ACH	ACH	0.5313	0.40	8
ACH	AC	0.3652	0.12	2
ACS	AC2S	1.4621	0.78	1
sulfone	$CH_2SO_2CH_2$	2.6869	2.12	1

Adequate interaction parameters were obtained for the solvent (1) + dibenzothiophene (2) binary systems using the five solution models. For instance, the binary interaction parameters obtained by the Wilson model for the cyclohexane (1) + dibenzothiophene (2) system were in good agreement with the corresponding values reported by Coon et al. ($\lambda_{12} = 2221$ and $\lambda_{21} = 3387$),[2] considering the confidence interval (CI) obtained in this work. When the five models were compared to each other, a better estimation of the interaction parameters by the Wilson model was observed. The average absolute deviation between the estimated and calculated activity coefficients was 1.3, 2.3, 3.5, and 5.8 times smaller than the corresponding value obtained by the TKW, UNIQUAC, van Laar, and Margules models, respectively.

In the case of the solvent (1) + dibenzothiophene sulfone (2) binary system, the Wilson and TKW interaction parameters calculated were not appropriate because a large CI value was obtained. In contrast, a good estimation with the UNIQUAC, Margules, and van Laar models was obtained. However, it is recommended to use only the UNIQUAC model to predict the activity coefficient for these binary systems because the activity coefficient has a direct functionality with temperature and composition (the Margules and van Laar models only have a direct functionality with composition), and under this point of view the UNIQUAC model is more robust.

Table 13 only reports the estimated interaction parameters for the models that produce the best statistical and meaningful data. The calculated $t_{0.95}$ values for the UNIQUAC and Wilson models were in the interval of the accepted $t_{0.95}$ value based on the statistical *t*-test reported values. These results indicate that

Table 13. Wilson and UNIQUAC Interaction Parameters for the Solvent (1) + Dibenzothiophene (2) and Solvent (1) + Dibenzothiophene Sulfone (2) Binary Systems

model	binary system	correlated data points	interaction parameters	95 % confidence interval	$t_{0.95}$	AARE[a]
Wilson	cyclohexane (1)	6	$\lambda_{12} = 1969$	± 97	56	0.4
	+ dibenzothiophene (2)		$\lambda_{21} = 3709$	± 114	89	
Wilson	*n*-tetradecane (1)	9	$\lambda_{12} = 1662$	± 1384	3	2.7
	+ dibenzothiophene (2)		$\lambda_{21} = 3619$	± 473	18	
Wilson	*n*-hexadecane (1)	15	$\lambda_{12} = 2898$	± 280	22	0.5
	+ dibenzothiophene (2)		$\lambda_{21} = 3074$	± 57	116	
Wilson	γ-butyrolactone (1)	13	$\lambda_{12} = 3978$	± 129	68	0.5
	+ dibenzothiophene (2)		$\lambda_{21} = -1293$	± 81	−35	
Wilson	acetonitrile (1)	7	$\lambda_{12} = 4248$	± 119	92	1.5
	+ dibenzothiophene (2)		$\lambda_{21} = 3234$	± 121	69	
UNIQUAC	1-propanol (1)	9	$\Pi_{12} = 10733$	± 273	93	2.0
	+ dibenzothiophene sulfone (2)		$\Pi_{21} = -3726$	± 43	−204	
UNIQUAC	2-ethoxyethanol (1)	10	$\Pi_{12} = 14411$	± 5847	6	3.2
	+ dibenzothiophene sulfone (2)		$\Pi_{21} = -3628$	± 89	−94	
UNIQUAC	Acetonitrile(1)	9	$\Pi_{12} = 3646$	± 448	19	2.6
	+ dibenzothiophene sulfone (2)		$\Pi_{21} = -935$	± 260	−8	
UNIQUAC	γ-butyrolactone (1)	10	$\Pi_{12} = 4047$	± 376	25	2.6
	+ dibenzothiophene sulfone (2)		$\Pi_{21} = -1419$	± 143	−23	
UNIQUAC	*N*,*N*-dimethylformamide (1)	10	$\Pi_{12} = 4437$	± 831	12	2.4
	+ dibenzothiophene sulfone (2)		$\Pi_{21} = -1667$	± 215	−18	

[a] AARE = absolute average relative error. Relative error is defined by: $\% \Delta = (\{\gamma_{\text{calcd}} - \gamma_{\text{exptl}}\}/\gamma_{\text{exptl}})(100)$.

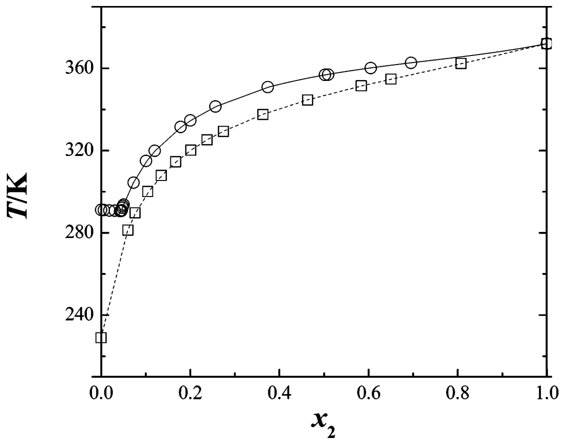


Figure 3. Solid−liquid diagram for: ○, *n*-hexadecane (1) + dibenzothiophene (2); □, γ-butyrolactone (1) + dibenzothiophene (2). The lines are predicted by the Wilson (−) and UNIQUAC (- -) models.

each of these binary interaction parameters represent well the estimated activity coefficients.

Finally, Figure 3 shows a comparison between experimental and calculated composition−temperature values using the Wilson model for the *n*-hexadecane (1) + dibenzothiophene (2) system and the UNIQUAC model for the γ-butyrolactone (1) + dibenzothiophene (2) system as representative examples studied in this work. A good agreement between experimental and estimated values can be observed, according to the absolute average relative error reported in Table 13.

Conclusions

The solid−liquid equilibrium of ten binary systems containing dibenzothiophene and dibenzothiophene sulfone solutes was determined by the visual method in a closed cell. The experimental error was ± 0.0005 in mole fraction and ± 0.5 K in temperature. These results have been used to derive the activity coefficient of the solute in the liquid solution. It was determined that a eutectic point exists for each one of the *n*-tetradecane (1) + dibenzothiophene (2) and *n*-hexadecane (1) + dibenzothiophene (2) binary systems.

Additionally, original experimental data for enthalpy of fusion, as well as for melting temperature and heat capacities, of the dibenzothiophene sulfone were obtained. The precision of enthalpy of fusion was ± 0.41 $\text{kJ}\cdot\text{mol}^{-1}$. The accuracy of the heat capacities was verified through a Zafiro reference sample.

During the correlation of the experimental data, a whole series of thermodynamic properties (T_c, V_c, P_c, $\Delta_{\text{fus}}H$, and $\Delta_{\text{fus}}S$) which were not available in the open literature for the dibenzothiophene sulfone and 2-ethoxyethanol compounds were calculated. These properties were correlated by several group contribution models using the ICAS and ASPEN softwares.

Finally, the solid−liquid equilibria data reported present industrial interest to generate fundamental information to develop and design a process based on the oxidation−extraction scheme for the desulfurization of middle distillates.

Acknowledgment

The authors are grateful to the Instituto Mexicano del Petróleo (IMP) and the Centro de Investigación y de Estudios Avanzados (CINVESTAV) for support and the use of facilities to perform the experimental work.

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Received for review May 1, 2007. Accepted August 31, 2007.

JE700234E