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THERMODYNAMICS OF LIQUID MIXTURES OF SOME ORGANIC COMPOUNDS WITH SULPHUR DIOXIDE

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ABSTRACT

An association model capable of correlating the vapor–liquid and liquid–liquid equilibrium data of binary liquid mixtures containing sulphur dioxide and organic compounds is presented. The model requires an association constant for sulphur dioxide (component A), solvation constants between unlike molecules, a self-association constant for component B and a nonpolar interaction term among chemical complexes. The model is tested on binary mixtures of benzene, acetone, diethylaniline and ethylene glycol with sulphur dioxide and is extended to calculate phase equilibria for the partially miscible sulphur dioxide–benzene–normal paraffin systems successfully.

INTRODUCTION

Lorimer et al. [1] interpreted the excess Gibbs functions for binary liquid mixtures of arenes, olefins and certain organic compounds with sulphur dioxide by using association models which involve a chain association constant for sulphur dioxide (component A) plus binary solvation constants for AB and possibly A_2B chemical complexes and either a constant describing intermolecular interactions among complexes or a self-association constant for component B. However, the method of Lorimer et al. [1] was unable to reproduce mutual solubility data for binary sulphur dioxide-saturated hydrocarbon mixtures correctly and, hence, was not suitable for calculation of ternary liquid–liquid equilibria for sulphur dioxide–aromatic hydrocarbon–saturated hydrocarbon mixtures.

In this work, we present an association model which can calculate phase equilibria for binary and ternary liquid mixtures containing sulphur dioxide.

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THEORY

The effect of complex formation on thermodynamic properties for mixtures of certain organic compounds with sulphur dioxide could be explained by assuming associated mixtures for all the systems studied. Lorimer et al. [1] assumed chain association of sulphur dioxide plus AB solvation in analyzing the data for the arene–SO_2 mixtures and suggested that the concept of self-association in liquids diethylaniline and ethylene glycol is reasonable, because the Trouton constants for these compounds are relatively high.

Binary mixtures

The association model used in this work includes self-association for each component and two binary solvation steps

$$A_1 + A_i = A_{i+1} \qquad K_A = x_{A_{i+1}}/x_{A_i}x_{A_1} \tag{1}$$

$$B_1 + B_i = B_{i+1} \qquad K_B = x_{B_{i+1}}/x_{B_i}x_{B_1} \tag{2}$$

$$A_1 + B_1 = AB \qquad K_1 = x_{AB}/x_{A_1}x_{B_1} \tag{3}$$

$$2A_1 + B_1 = A_2B \qquad K_2 = x_{A_2B}/x_{A_1}^2x_{B_1} \tag{4}$$

The sum of the mole fractions of all the chemical species is unity [2].

$$\sum_{i=1}^{\infty} x_{A_i} + x_{AB} + x_{A_2B} + \sum_{i=1}^{\infty} x_{B_i}$$
$$= x_{A_1}/(1 - K_A x_{A_1}) + K_1 x_{A_1} x_{B_1} + K_2 x_{A_1}^2 x_{B_1} + x_{B_1}/(1 - K_B x_{B_1}) = 1 \tag{5}$$

The stoichiometric mole fractions of components A and B are given with the monomer mole fractions.

$$x_A = \left[K_1 x_{A_1} x_{B_1} + 2K_2 x_{A_1}^2 x_{B_1} + x_{A_1}/(1 - K_A x_{A_1})^2\right]/S \tag{6}$$

$$x_B = \left[K_1 x_{A_1} x_{B_1} + K_2 x_{A_1}^2 x_{B_1} + x_{B_1}/(1 - K_B x_{B_1})^2\right]/S \tag{7}$$

where the stoichiometric sum, S, is given by

$$S = 2K_1 x_{A_1} x_{B_1} + 3K_2 x_{A_1}^2 x_{B_1} + x_{A_1}/(1 - K_A x_{A_1})^2 + x_{B_1}/(1 - K_B x_{B_1})^2 \tag{8}$$

The activity coefficients of both components can be expressed as described elsewhere [2,3].

$$\ln \gamma_A = \ln(x_{A_1}/x_{A_1}^* x_A) + x_B^2\left[\tau_{BA} G_{BA}^2/(x_A + x_B G_{BA})^2 + \tau_{AB} G_{AB}/(x_B + x_A G_{AB})^2\right] \tag{9}$$

$$\ln \gamma_B = \ln(x_{B_1}/x_{B_1}^* x_B) + x_A^2\left[\tau_{AB} G_{AB}^2/(x_B + x_A G_{AB})^2 + \tau_{BA} G_{BA}/(x_A + x_B G_{BA})^2\right] \tag{10}$$

where

$$\tau_{BA} = a_{BA}/T \qquad \tau_{AB} = a_{AB}/T \tag{11}$$

$$G_{BA} = \exp(-\alpha_{BA}\tau_{BA}) \qquad G_{AB} = \exp(-\alpha_{AB}\tau_{AB}) \tag{12}$$

and the nonrandomness parameter, $\alpha_{BA}(=\alpha_{AB})$, is usually taken as 0.3. $x^*_{A_1}$ and $x^*_{B_1}$ are the mole fractions of monomers in the pure liquids A and B, respectively. The NRTL terms [3] allow for non-specific molecular interactions among all the chemical species. x_{A_1} and x_{B_1} could be solved simultaneously by iteration using eqn. (5) and either eqn. (6) or (7) if the equilibrium constants are known.

At the pure liquid A, $x_{A_1} = x^*_{A_1}$ and $x_B = x_{B_1} = 0$, then eqn. (5) reduces to

$$\sum_{i=1}^{\infty} x^*_{A_i} = x^*_{A_1}/(1 - K_A x^*_{A_1}) = 1 \tag{13}$$

A similar relation holds for $x^*_{B_1}$.

Ternary mixtures

The activity coefficient of any component I in a ternary mixture containing sulphur dioxide (A), benzene (B) and a saturated hydrocarbon (C) is given by

$$\ln \gamma_I = \ln\left(\frac{x_{I_1}}{x^*_{I_1} x_I}\right) + \frac{\sum_J \tau_{JI} G_{JI} x_J}{\sum_K G_{KI} x_K} + \sum_J \frac{\sum_J x_J G_{IJ}}{\sum_K G_{KJ} x_K}\left(\tau_{IJ} - \frac{\sum_R x_R \tau_{RJ} G_{RJ}}{\sum_K G_{KJ} x_K}\right) \tag{14}$$

where for the components B and C, $x^*_{B_1} = x^*_{C_1} = 1$

$$\tau_{JI} = a_{JI}/T \tag{15}$$

and

$$G_{JI} = \exp(-\alpha_{JI}\tau_{JI}) \tag{16}$$

The nominal mole fractions of the components are related to the monomer mole fractions.

$$x_A = \left[K_1 x_{A_1} x_{B_1} + x_{B_1}/(1 - K_A x_{A_1})^2\right]/S \tag{17}$$

$$x_B = \left[K_1 x_{A_1} x_{B_1} + x_{B_1}\right]/S \tag{18}$$

$$x_C = x_{C_1}/S \tag{19}$$

where the stoichiometric sum, S, is expressed by

$$S = 2K_1 x_{A_1} x_{B_1} + x_{A_1}/(1 - K_A x_{A_1})^2 + x_{B_1} + x_{C_1} \tag{20}$$

The monomer mole fractions satisfy the relation

$$K_1 x_{A_1} x_{B_1} + x_{A_1}/(1 - K_A x_{A_1}) + x_{B_1} + x_{C_1} = 1 \tag{21}$$

Equation (17) with either eqns. (18) or (19) and (21) provide three simultaneous equations in x_{A_1}, x_{B_1} and x_{C_1}, which may be solved by iteration.

CALCULATED RESULTS

Binary mixtures of benzene, acetone, diethylaniline and ethylene glycol with sulphur dioxide

The van't Hoff equation fixes the temperature dependence of the equilibrium constant.

$$\frac{\partial \ln K}{\partial(1/T)} = -\frac{h}{R} \tag{22}$$

The values of K_A and h_A for chain association of SO_2 were taken from Lorimer et al. [1]: $K_A = 2.2$ at -23.2°C and $h_A = -6.6$ kJ mol^{-1}. The value of K_B for diethylaniline is 0.027 at 0°C [1]. Table 1 shows the values of equilibrium constants and enthalpies of complex formation. For SO_2–benzene mixtures the value of K_1 is equal to that of Andrews and Keefer [4] and the enthalpy of complex formation was estimated by taking the difference between the SO_2 enthalpy of solution at infinite dilution for saturated hydrocarbons and that for benzene [5]. The values of solvation constants for the other mixtures are not the same as those given by Lorimer et al. [1]. Table 2 gives binary calculated results. The monomer mole fractions were calculated using pertinent mass balance equations and subroutine NOLBR built in a FACOM M-170F computer. The binary energy parameters were obtained by minimizing the sum-of-squares of deviation in the excess Gibbs energy with the simplex method [10]. The experimental excess Gibbs energies were derived from Redlich–Kister polynomials [1,7]. Since vapor–liquid equilibrium data for benzene–*n*-heptane mixtures at -17.8 and -28.9°C have not been reported in the literature, the binary parameters for benzene–*n*-heptane were estimated from the NRTL equation whose three

TABLE 1

Solvation constants and enthalpies of complex formation

System	Temp. (°C)	K	$-h$ (kJ mol^{-1})
Sulphur dioxide–acetone	−23.2	8.5	13.2
Sulphur dioxide–benzene	25	0.47	9.2
Sulphur dioxide–diethylaniline, 1 : 1 complex	0	12	
2 : 1 complex	0	28	
Sulphur dioxide–ethylene glycol	0	4.8	

TABLE 2

Calculated results obtained in binary phase equilibrium data reduction

System (A–B)	Temp. (°C)	No. of data points	Parameters a_{BA} (K)	a_{AB} (K)	α_{AB}	Abs. arith. mean dev. in excess Gibbs energy (J mol^{-1})	Ref.
Acetone–sulphur dioxide	−23.2	9	−474.30	152.80	0.3	17.1	1
	−35.8	9	−494.14	197.04	0.3	20.2	1
	−45.6	9	−419.34	20.45	0.3	17.5	1
Benzene–sulphur dioxide	−17.8	19	47.03	−62.76	0.3	16.4	6
Diethylaniline–sulphur dioxide	0.0	15	−342.68	300.31	0.3	16.6	7
Ethylene glycol–sulphur dioxide	0.0	11	−177.54	759.99	0.3	12.1	7
Benzene–*n*-heptane	−17.8		112.94	−42.23	0.18		8
	−28.9		106.55	−34.34	0.18		8
Benzene–*n*-pentane [a]	−17.8	18	236.44	74.39	0.3		6
n-Heptane–sulphur dioxide	−17.8	MS [b]	840.19	0.73	0.3		9
	−28.9	MS	801.50	38.71	0.3		9
n-Pentane–sulphur dioxide	−17.8	MS	554.33	13.82	0.3		6

[a] The abs. arith. mean dev. in vapor mole fraction is 0.0024 and that in pressure is 0.63 Torr.

[b] MS = mutual solubilities.

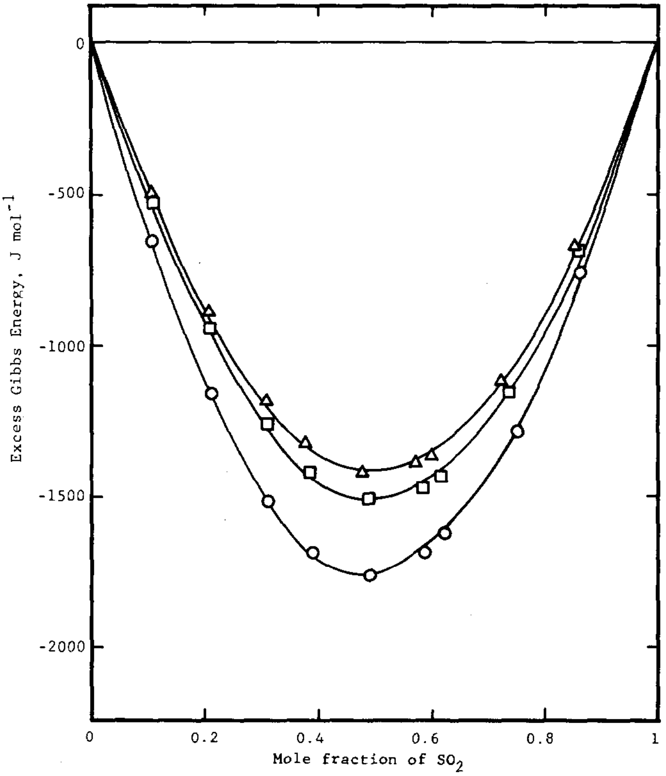

Fig. 1. Excess Gibbs energies for SO_2–acetone mixtures. Experimental points (△, −23.2°C; □, −35.8°C; ○, −45.6°C), data of Lorimer et al. [1]. Calculated (———).

temperature-dependent parameters were given by Renon et al. [8] in the simultaneous correlation of vapor–liquid equilibrium and excess enthalpy data. The parameters for benzene–n-pentane were taken from Gmehling et al. [11].

Mutual solubility data were used to obtain the energy parameters of paraffin–SO_2 mixtures by solving the relation for each component I with the Newton–Raphson technique.

$$(\gamma_I x_I)^{\mathrm{I}} = (\gamma_I x_I)^{\mathrm{II}} \tag{23}$$

where the superscripts I and II represent equilibrium phases.

Figures 1 and 2 show that the proposed association model gives a good representation of the excess Gibbs energies for mixtures of acetone, diethylaniline and ethylene glycol with SO_2.

Ternary mixtures of hydrocarbons with sulphur dioxide

Vapor–liquid equilibrium calculations were performed using the following equation for any component I.

$$\phi_I y_I P = \gamma_I x_I \phi_I^{s} P_I^{s} \exp\left[v_I^{L}(P - P_I^{s})/RT\right] \tag{24}$$

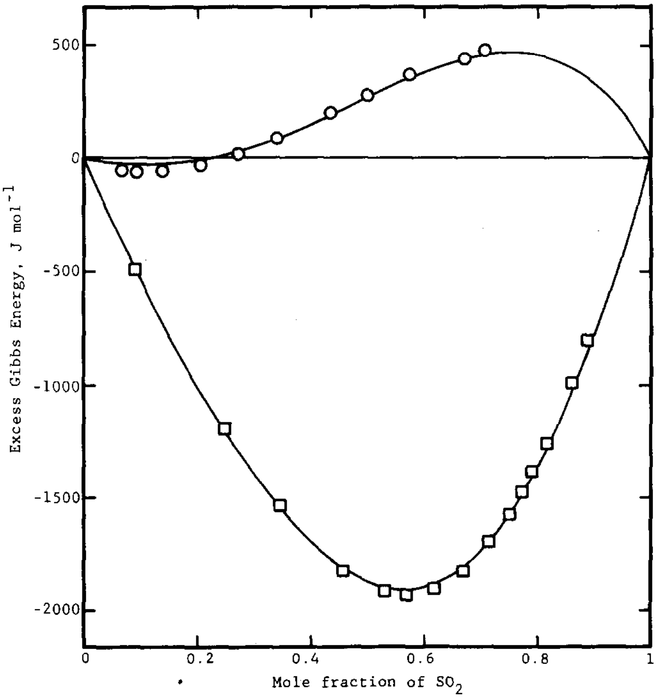

Fig. 2. Excess Gibbs energies for SO_2–diethylaniline and SO_2–ethylene glycol mixtures at 0°C. Experimental points (for diethylaniline, □; for ethylene glycol, ○), data of Foote and Fleischer [7]. Calculated (———).

where P is the total pressure, P_I^s is the vapor pressure of pure component I and y is the vapor-phase mole fraction. The fugacity coefficients, ϕ and ϕ_I^s, were calculated from the volume-explicit virial equation truncated after the second term. The second virial coefficients were estimated by the generalized method of Hayden and O'Connell [12]. The pure liquid molar volumes, v_I^L, were calculated using the modified Rackett equation [13]. The pure component vapor pressures were obtained from the Antoine equation [11,14]. Table 3 compares calculated values obtained from only the binary parameters with

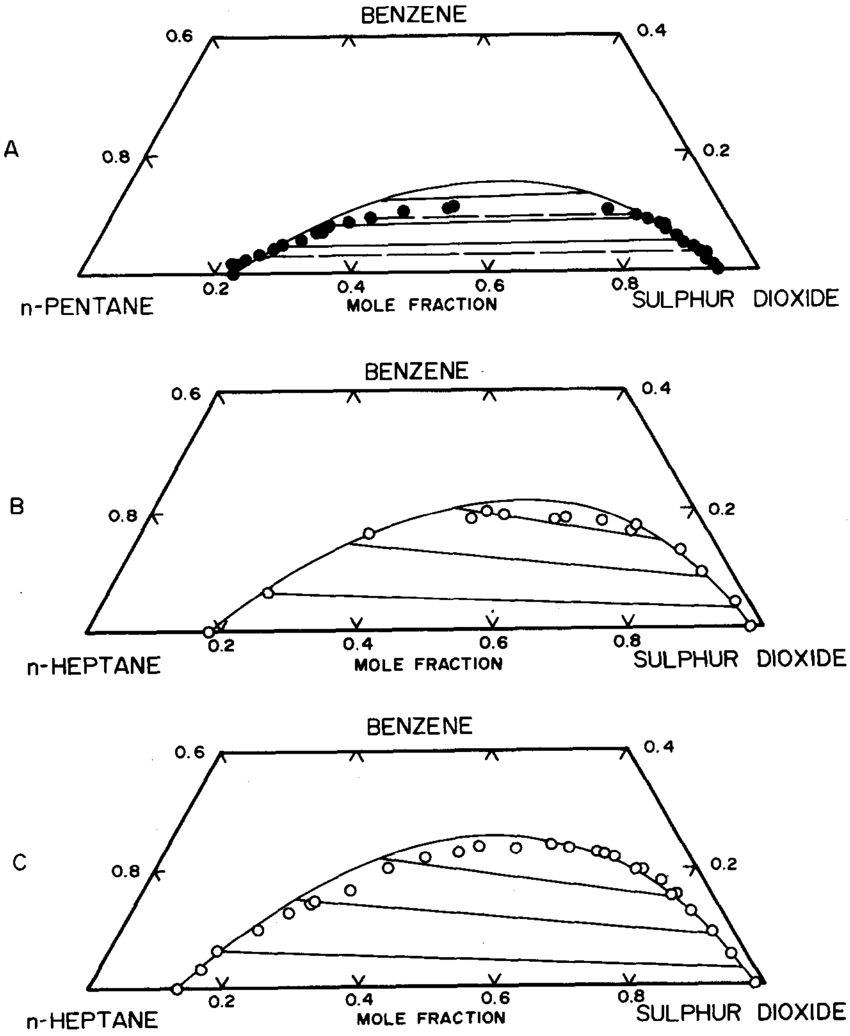

Fig. 3. Ternary liquid–liquid equilibria for mixtures of hydrocarbons with SO_2. Experimental: A, *n*-pentane–benzene–SO_2 at −17.8°C, (●— — —●) tie-line data of Bowden et al. [6]; B, *n*-heptane–benzene–SO_2 at −17.8°C, (○) solubility data of Satterfield et al. [9]; C, *n*-heptane–benzene–SO_2 at −28.9°C, (○) solubility data of Satterfield et al. [9]. Calculated (———).

TABLE 3

Comparison of calculated and experimental vapor–liquid equilibrium data for the ternary system *n*-pentane(1)–sulphur dioxide(2)–benzene(3) at −17.8°C

No.	Experimental						Deviations [a]			
	x_1	x_2	y_1	y_2	y_3	P (Torr)	Δy_1 ($\times 10^3$)	Δy_2 ($\times 10^3$)	Δy_3 ($\times 10^3$)	ΔP (Torr)
1	0.411	0.475	0.125	0.873	0.002	525.0	8.4	−8.5	0.1	6.7
2	0.414	0.464	0.124	0.874	0.002	520.5	6.6	−6.9	0.3	4.9
3	0.420	0.444	0.123	0.874	0.003	513.0	5.0	−4.6	−0.4	1.0
4	0.413	0.446	0.124	0.874	0.002	508.0	4.5	−5.2	0.7	2.6
5	0.431	0.416	0.128	0.868	0.004	501.0	8.5	−7.5	−1.0	−2.1
6	0.427	0.409	0.125	0.872	0.003	488.0	3.0	−3.4	0.4	2.2
7	0.449	0.380	0.130	0.866	0.004	481.5	6.6	−6.2	−0.4	−1.4
8	0.451	0.366	0.131	0.864	0.005	465.0	6.2	−5.2	−1.0	3.7
9	0.456	0.349	0.132	0.863	0.005	452.9	4.3	−3.7	−0.6	3.3
10	0.457	0.336	0.136	0.859	0.005	440.0	5.5	−5.2	−0.3	4.6
11	0.461	0.303	0.139	0.855	0.006	419.2	1.3	−1.1	−0.2	−4.1
12	0.452	0.301	0.144	0.850	0.006	406.0	4.7	−4.9	0.2	1.8
13	0.447	0.288	0.145	0.848	0.009	388.0	2.1	−2.0	−0.1	4.1
14	0.454	0.271	0.160	0.832	0.008	376.0	13.1	−12.6	−0.5	2.9
15	0.453	0.252	0.169	0.822	0.009	355.8	15.6	−15.1	−0.5	3.0
16	0.457	0.230	0.174	0.817	0.009	337.3	11.1	−11.7	−0.6	0.3
17	0.451	0.213	0.181	0.808	0.011	322.5	10.4	−10.4	0.0	−5.9
18	0.456	0.204	0.188	0.800	0.012	309.0	13.7	−13.2	−0.5	−0.2
19	0.449	0.195	0.183	0.804	0.013	302.5	3.2	−2.6	−0.6	−6.5

20	0.443	0.186	0.197	0.789	0.014	280.6	11.2	−10.7	−0.5	3.0
21	0.448	0.175	0.210	0.775	0.015	263.5	17.5	−16.7	−0.8	9.6
22	0.438	0.163	0.213	0.771	0.016	246.6	10.0	−10.0	0.0	9.3
23	0.433	0.155	0.223	0.758	0.019	235.5	14.9	−13.1	−1.8	9.6
24	0.428	0.122	0.263	0.712	0.025	196.0	20.8	−18.1	−2.7	9.6
25	0.429	0.096	0.277	0.695	0.028	176.0	−7.3	7.5	−0.2	−1.0
26	0.394	0.192	0.202	0.781	0.017	270.9	18.7	−16.8	−1.9	0.8
27	0.365	0.230	0.177	0.810	0.013	291.5	10.3	−10.4	0.1	6.8
28	0.342	0.280	0.158	0.828	0.014	325.5	12.0	−8.7	−3.3	8.6
29	0.312	0.338	0.151	0.838	0.011	365.5	17.4	−15.3	−2.1	3.0
30	0.293	0.386	0.130	0.862	0.008	393.5	2.4	−2.0	−0.4	2.1
31	0.245	0.473	0.125	0.869	0.006	428.5	6.4	−6.5	0.1	1.6
32	0.216	0.552	0.124	0.872	0.004	464.8	8.4	−9.1	0.7	−2.5
33	0.186	0.626	0.122	0.873	0.005	484.4	9.4	−8.1	−1.3	2.2
34	0.151	0.675	0.119	0.876	0.005	498.0	9.9	−8.4	−1.5	−5.3
35	0.136	0.719	0.117	0.880	0.003	510.0	5.5	−5.4	−0.1	−3.3
36	0.115	0.747	0.114	0.883	0.003	518.5	6.3	−6.2	−0.1	−10.0
37	0.103	0.786	0.114	0.883	0.003	523.0	5.5	−4.9	−0.6	−2.0
38	0.089	0.814	0.116	0.882	0.002	531.0	9.0	−9.2	0.2	−4.4
39	0.058	0.878	0.106	0.891	0.003	542.0	10.8	−9.3	−1.4	−3.8
40	0.781	0.054	0.325	0.661	0.014	200.5	10.6	−10.2	−0.4	5.0
41	0.860	0.032	0.404	0.584	0.012	176.0	9.3	−9.8	0.5	−2.9
Abs. arith. mean deviation							9.0	8.4	0.7	4.1

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[a] Calculated value – experimental one.

the experimental vapor–liquid equilibrium data of Bowden et al. [6] for the *n*-pentane–SO_2–benzene system at −17.8°C. Agreement is considered good.

The ternary activity coefficient equations were used with an algorithm developed by Null [15] to predict the binodal curve and tie lines for the normal paraffin–benzene–SO_2 systems. The predictions of the binodal curves shown in Fig. 3 were based only on binary information.

In conclusion, although more ternary experimental phase equilibrium data are needed to test the ability of the association model, the calculated results suggest that the model may be useful in the correlation and prediction of phase equilibria for SO_2 liquid mixtures.

NOTATION

a_{JI}	binary interaction parameter defined by $(g_{JI} - g_{II})/R$
G_{IJ}	coefficient defined by $\exp(-\alpha_{IJ}\tau_{IJ})$
g_{JI}	binary interaction parameter
h_A	molar enthalpy of chain association of SO_2
h_1	enthalpy of formation of chemical complex AB
K_A	equilibrium constant for linear association of SO_2
K_B	equilibrium constant for linear association of component B
K_1, K_2	equilibrium constants of formation of chemical complexes AB and A_2B
P	total pressure
P_I^s	saturation pressure of pure component I
R	universal gas constant
S	stoichiometric sum
T	absolute temperature
v_I^L	molar liquid volume of pure component I
x_I	liquid-phase mole fraction of component I
y_I	vapor-phase mole fraction of component I

Greek letters

α_{JI}	nonrandomness parameter of NRTL equation, $\alpha_{JI} = \alpha_{IJ}$
γ_I	activity coefficient of component I
τ_{JI}	coefficient as defined by $(g_{JI} - g_{II})/RT = a_{JI}/T$
ϕ_I	vapor-phase fugacity coefficient of component I
ϕ_I^s	vapor-phase fugacity coefficient of pure component I at system temperature T and pressure P_I^s

Subscripts

A,B,C	SO_2 and organic compounds
A_i,B_i	*i*-mers of SO_2 and component B

A_1,B_1,C_1	monomers of SO_2 and organic compounds B and C
AB,A_2B	chemical complexes between SO_2 and compound B

Superscripts

L	liquid
s	saturation
*	pure liquid

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