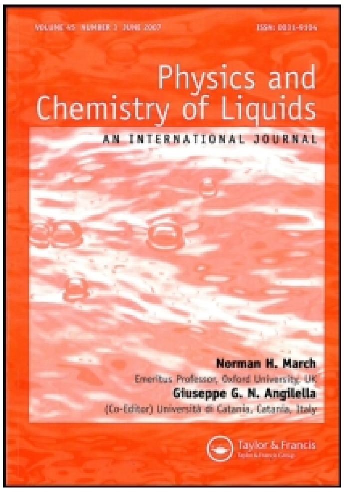

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Surface thermodynamic behaviour of binary liquid mixtures of benzene+1,1,2,2-tetrachloroethane at different temperatures: an experimental and theoretical study

Anwar Ali[a]; Mohd Tariq[a]
[a] Department of Chemistry, Jamia Millia Islamia (Central University), New Delhi-110025, India

To cite this Article Ali, Anwar and Tariq, Mohd(2008) 'Surface thermodynamic behaviour of binary liquid mixtures of benzene+1,1,2,2-tetrachloroethane at different temperatures: an experimental and theoretical study', Physics and Chemistry of Liquids, 46: 1, 47 — 58

To link to this Article: DOI: 10.1080/00319100701344628

URL: http://dx.doi.org/10.1080/00319100701344628

Physics and Chemistry of Liquids
Vol. 46, No. 1, February 2008, 47–58

Surface thermodynamic behaviour of binary liquid mixtures of benzene + 1,1,2,2-tetrachloroethane at different temperatures: an experimental and theoretical study

ANWAR ALI* and MOHD TARIQ

Department of Chemistry, Jamia Millia Islamia (Central University),
New Delhi – 110025, India

(*Received 11 July 2006; in final form 17 March 2007*)

Surface tensions, σ, of pure benzene, 1,1,2,2-tetrachloroethane and those of their binary liquid mixtures over the whole composition range at 298.15, 308.15 and 313.15 K have been measured. The experimental σ data have been correlated against temperature and concentration using standard relations. The measured values have been used to calculate various useful thermodynamic parameters, viz., deviation in surface tension, $\Delta\sigma$, surface entropy, S^s, and surface enthalpy, H^s. The sign and magnitude of these parameters were discussed in terms of molecular interactions between the component molecules of the liquid mixtures. A number of empirical, semi-empirical and statistical models and theories such as Aurebach, Sanchez, Goldsach–Sarvas volume fraction statistics, Brock and Bird relation, Sudgen's relation and Flory–Patterson–Rastogi model have been used to compute theoretically the values of surface tension. Moreover, deviation in surface tension, $\Delta\sigma$ has also been calculated using HSIS and HSEG theories and found to be qualitatively correct.

Keywords: Surface tension; Liquid mixtures; Semi-empirical relations; Statistical methods

1. Introduction

In continuation of our investigations [1–3] on bulk thermodynamic and transport behaviour of liquid mixtures, here, we present the experimental surface tension, σ, of pure benzene, 1,1,2,2-tetrachloroethane (TCE) and those of their binary liquid mixtures over the whole composition range at 298.15, 308.15 and 313.15 K. The surface tension of a liquid mixture is not a simple function of the surface tension of the pure components, because in a mixture the composition of the surface is not the same as that of the bulk [4]. Surface tension of mixtures is an important physical property in mass transfer processes such as liquid–liquid extraction, gas absorption, distillation and condensation, and also a property that represents changes in molecular interactions and could thus be used as a means of interpreting behaviour of binary mixtures [5]. The binary system of benzene with TCE is of considerable interest from the viewpoint of the

---

*Corresponding author. Email: anwar_jmi@yahoo.co.in

Physics and Chemistry of Liquids
ISSN 0031-9104 print/ISSN 1029-0451 online © 2008 Taylor & Francis
DOI: 10.1080/00319100701344628

existence of specific interactions between the components in the liquid state. These considerations led us to undertake the present study.

For these reasons, the surface parameters viz. surface enthalpy, H^s, surface entropy, S^s, and deviation in surface tension, $\Delta\sigma$ of the above binary mixtures at the studied temperatures have been obtained. Apart from the experimental work, we have also evaluated the theoretical values of surface tension of the present mixtures using Aurebach method [6], Brock and Bird relation [7], Sudgen's equation [8], Flory–Patterson–Rastogi model [9], Sanchez relation [10] and volume fraction statistics of Goldsach and Sarvas [11].

Moreover, deviations in surface tensions, $\Delta\sigma$, have been estimated by using the theories of Hildebrand and Scott [12] for ideal solutions (HSIS) and their extension of Guggenheim's ideal solution equation (HSEG) [13] valid for systems containing molecules of significantly different size.

2. Experimental

The chemicals used were supplied by Merck and s. d. Fine Chem Ltd. Their mass purities were benzene (Merck, >99.5%) and 1,1,2,2-tetrachloroethane (SD Fine Chem, >99.5%). Prior to use both chemicals were dried over molecular sieves (Sigma Union Carbide 0.4 nm). All mixtures were prepared by mass using a Precisa XB 220 A (Swiss make) electronic balance having a precision of $\pm 1\times10^{-4}$ g. Mixtures were stored in glass stoppered flasks to avoid contamination and evaporation. The accuracy in mole fraction was estimated to be within ±0.0001.

The surface tension of the samples were measured by the ring-detachment method using a De Nuoy tensiometer (SD Hardsons Ltd.) with a precision of $\pm 0.01\,\mathrm{mN\,m^{-1}}$. The platinum–iridium ring was thoroughly cleaned and flame dried before each measurement. The torsion balance was calibrated with ethanol, and triple distilled water. All solutions were thermostated with a precision of ±0.02 K using a constant stirrer water bath (Julabo, Germany). At least three readings were taken for each sample.

The corresponding densities were measured at 298.15 K using a single stem pycnometer having a bulb capacity of $8\times10^{-6}\,\mathrm{m^3}$, with an accuracy of $\pm 0.3\,\mathrm{kg\,m^{-3}}$. The ultrasonic speeds were measured at 298.15 K using single crystal variable path ultrasonic interferometer (Mittal Enterprises), operating at 2 MHz. The accuracy in measured ultrasonic speed was up to ±0.5%. Moreover, for comparison, measured values of pure components along with the literature values are given in table 1. It is clear from the table that our values are in good agreement with those reported earlier [14–18].

Table 1. Comparison of experimental values of surface tension, σ, density, ρ, and ultrasonic speed, u of pure components with literature values at 298.15 K.

	Benzene		1,1,2,2-tetrachloroethane	
Property	Experimental	Literature	Experimental	Literature
σ ($\mathrm{mN\,m^{-1}}$)	28.0	28.22[a]	35.50	35.58[a]
ρ ($\mathrm{kg\,m^{-3}}$)	873.4	873.598[b]	1586.7	1586.6[d]
u ($\mathrm{m\,s^{-1}}$)	1303.5	1304.0[c]	1153.5	1153.0[e]

[a][14], [b][15], [c][16], [d][17], [e][18].

3. Results and discussion

Table 2 lists the measured surface tension, σ of pure benzene, TCE and those of their binary mixtures over the whole composition range at 298.15, 308.15 and 313.15 K. At all compositions surface tension, σ decreased linearly with increasing temperature (table 2). The surface tensions of binary mixtures were correlated with temperature by the expression proposed by Jasper [19]:

$$\sigma\ (\mathrm{mN\,m^{-1}}) = K_1 - K_2 t \tag{1}$$

where K_1 and K_2 are fitting coefficients, the values of which are reported in table 3, and t is temperature in °C.

For a given temperature, the surface tension of the studied binary mixture decreases with increase of the benzene mole fraction (table 2). Connors and Wright [20] proposed an equation of the following type to describe the effect of composition on the surface tension of a mixture. This equation has been used successfully by many

Table 2. Values of experimentally measured surface tensions of the binary liquid mixtures at different temperatures.

	$\sigma/(\mathrm{mN\,m^{-1}})$		
x_1	298.15 K	308.15 K	313.15 K
0.0000	35.50	34.35	33.65
0.1222	34.39	33.30	32.65
0.1956	33.60	32.55	31.94
0.3028	32.60	31.52	30.89
0.3862	31.80	30.73	30.15
0.4960	30.75	29.65	29.10
0.5936	29.90	28.81	28.25
0.6890	29.10	28.00	27.43
0.8079	28.10	27.00	26.44
0.9020	27.50	26.40	25.90
1.0000	28.00	26.75	26.15

Table 3. Values of surface tension parameters K_1 ($\mathrm{mN\,m^{-1}}$) and K_2 ($\mathrm{mN\,m^{-1}\,K^{-1}}$) for the binary liquid mixture as a function of composition.

x_1	K_1	K_2
0.0000	38.57	0.1221
0.1222	37.28	0.1150
0.1956	36.36	0.1096
0.3028	35.44	0.1131
0.3862	34.54	0.1096
0.4960	33.50	0.1100
0.5936	32.65	0.1099
0.6890	31.88	0.1111
0.8079	30.87	0.1106
0.9020	30.17	0.1071
1.0000	31.09	0.1236

Table 4. Values of surface tension parameters a and b for the binary liquid mixtures at different temperatures.

T (K)	a	b
298.15	0.1948	0.1860
308.15	4.3213	0.4243
313.15	3.8728	0.2436

Table 5. Values of coefficients A_p of Redlich–Kister polynomial equation (4) along with standard deviations for the liquid mixtures at different temperatures.

	$\Delta\sigma$ (mN m^{-1})					
T (K)	A_0	A_1	A_2	A_3	A_4	s
298.15	−4.1562	2.2762	−0.0040	8.3492	−8.8123	0.0173
308.15	−3.7123	2.4185	0.4618	7.1584	−7.7525	0.0177
313.15	−3.3098	2.6131	−1.2130	6.1532	−4.0455	0.0206

workers [21–23]:

$$\sigma = \sigma_1 - \left(1 + \frac{bx_1}{1 - ax_1}\right) x_2(\sigma_1 - \sigma_2) \tag{2}$$

where σ_1 and σ_2 are the surface tensions of pure components 1 and 2, x_1 and x_2 are mole fractions of benzene and TCE, respectively, and a and b are adjustable parameters. σ is the surface tension of the mixture. The values of a and b obtained at each temperature are listed in table 4.

The deviations of surface tension of a liquid mixture from linearity reflect changes of structure and cohesive forces during the mixing process. Thus, surface tension deviation, $\Delta\sigma$, were calculated from our measurements according to the following equation:

$$\Delta\sigma = \sigma - x_1\sigma_1 - x_2\sigma_2 \tag{3}$$

The surface tension deviations were correlated by means of the Redlich–Kister polynomial [24]:

$$\Delta\sigma = x_1x_2 \sum_{p=0}^{4} A_p(x_1 - x_2)^p \tag{4}$$

The results of the Redlich–Kister fit of $\Delta\sigma$ together with coefficients A_p and standard deviations s are given in table 5 while its variation with mole fraction x_1 at different temperatures are graphically shown in figure 1.

It is clear from figure 1 that the $\Delta\sigma$ values are negative over the entire composition range and show minima in benzene-rich region ($x_1 \sim 0.8$) at all the three studied temperatures. It is to be emphasized that the influence of the solute/solvent for the present system on the surface behaviour is less marked as compared to the volumetric and compressibility behaviour [25] which were strongly correlated with the structures of solute/solvent.

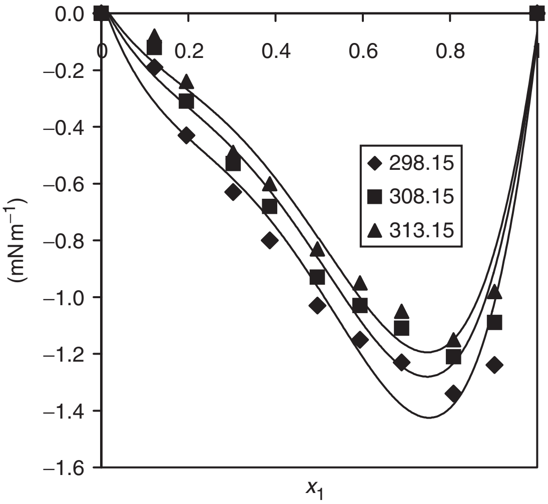

Figure 1. Surface tension deviations of binary liquid mixtures at various temperatures.

Thermodynamic parameters of the surface of these solutions were obtained by the following equations. Variation of surface entropy per unit area [26], due to the interface formation is:

$$S^{\mathrm{s}} = -\frac{\mathrm{d}\sigma}{\mathrm{d}T} \tag{5}$$

and the surface enthalpy per unit area is:

$$H^{\mathrm{s}} = \sigma - T\left(\frac{\mathrm{d}\sigma}{\mathrm{d}T}\right) \tag{6}$$

These equations were extensively used by many workers [27–29] to investigate the surface thermodynamics of various binary mixtures. The surface entropies and enthalpies of benzene + TCE mixtures calculated from equations (5) and (6) were drawn in figures 2 and 3 against mole fraction x_2 of TCE, respectively.

It is clear from figure 2 that surface entropy of the mixtures are less than those of the pure liquids, and show typical variation with mole fraction x_2 of TCE. Such a typical behaviour of surface entropy has also been reported by Azizian *et al.* [5,22] for the systems ethylene glycol + cyclohexanol/cyclopentanol. The surface enthalpies of the above system decreases rapidly at low concentration of TCE ($x_2 < 0.2$) and then it increases slowly by increasing TCE concentration. No significant effect of temperature is observed on surface enthalpy. It is clear from figures 2 and 3 that the trends of variation of both parameters i.e. S^{s} and H^{s} are almost similar, and thereby support each other.

3.1. *Theoretical analysis*

3.1.1. Surface tension prediction. In recent years, successful attempts have been made to predict theoretically the surface tensions [30–32] and deviations in surface

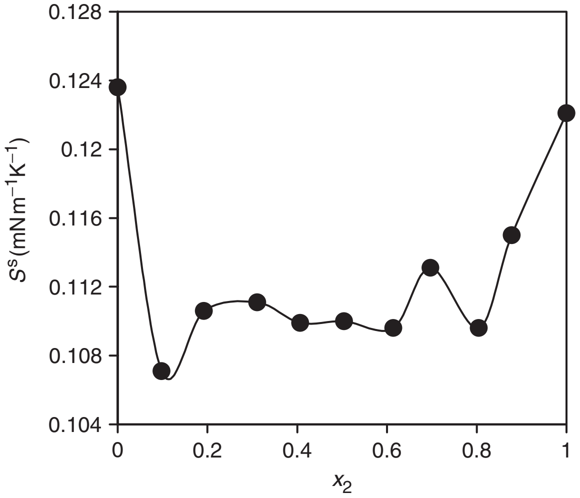

Figure 2. Plots of surface entropy *vs.* mole fraction of TCE.

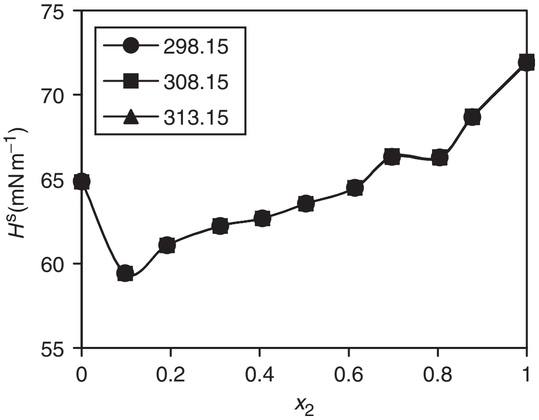

Figure 3. Plots of surface enthalpy *vs.* mole fraction of TCE at various temperatures.

tension [33–35] of liquid mixtures using various empirical, semi-empirical and statistical theories. As an extension, here we present six different surface tension predictive models and relations taken from the literature for this purpose.

The first relation we tested is the Aurebach relation [6], the equation for which can be written as,

$$\sigma = 6.4 \times 10^{-3} \rho u^{3/2}. \tag{7}$$

Using measured density, ρ and ultrasonic speed, u of pure liquids and liquid mixtures at 298.15 K, surface tension of the system under investigation has been calculated at 298.15 K by making use of equation (7).

Sanchez relation [10] has been applied successfully to binary liquid mixtures to deduce the value of surface tension of liquid mixtures:

$$\sigma = \sum_{i=1}^{2}\left(x_i A_i^{1/2}\right)\left[\sum_{i=1}^{2}\left(\frac{\phi_i \rho_i}{\phi_i \beta_{Ti}}\right)\right]^{1/2} \tag{8}$$

where β_{Ti} and ρ_i are the isothermal compressibility and density of pure liquids. ϕ_i and x_i are the volume fraction and mole fraction of the ith component. A_i is defined as:

$$A_i = \sigma_i^2\left(\frac{\beta_{Ti}}{\rho_i}\right). \tag{9}$$

Goldsach and Sarvas [11] used the mole fraction and volume fraction statistics to obtain the following expression for the surface tension of non-electrolyte solutions and applied this equation to obtain surface tension of various organic liquid mixtures,

$$\sigma = -\left(\frac{RT}{A}\right)\ln[x_1 \exp(-\sigma_1 A/RT) + x_2 \exp(-\sigma_2 A/RT)] \tag{10}$$

where A is the molar surface area, and can be obtained as:

$$A = 1.02 \times 10^8 \sum_{i=1}^{2}(V_i)^{2/3}. \tag{11}$$

Another theoretical expression we analyzed is Sudgen's equation [8] who introduces a parameter called parachor as,

$$[P_i] = \sigma_i^{1/4}\left(\frac{M_i}{\rho_i}\right) \tag{12}$$

where M_i is the molar mass of the pure component i, ρ_i its density and $[P_i]$ is the parachor, which is a characteristic of the liquid substance. Assuming that the parachor is additive with respect to mole number [36], σ can be obtained for a binary mixture as:

$$\sigma = \left\{[P_1]\frac{x_1}{M_1} + [P_2]\frac{x_2}{M_2}\right\}^4 \cdot \rho^4 \tag{13}$$

where $[P_1]$ and $[P_2]$ are the parachors for benzene and TCE, respectively, and ρ is the density of the mixture.

The extension of the principle of corresponding states given by Patterson and Rastogi [9] together with the Flory's theory [37–39] can be used to evaluate the surface tensions of pure liquids and their mixtures. The surface tension is given by the expression:

$$\sigma = \sigma^* \tilde{\sigma}(\tilde{v}) \tag{14}$$

where σ^* is the characteristic surface tension and $\tilde{\sigma}(\tilde{v})$ is the reduced surface tension. The characteristic surface tension can be calculated from the equation:

$$\sigma^* = k^{1/3} P^{*2/3} T^{*2/3} \tag{15}$$

where k is the Boltzman constant, P^* and T^* are the characteristic pressure and temperature, respectively.

The reduced surface tension can be defined as:

$$\tilde{\sigma}(\tilde{v}) = M\tilde{v}^{5/3} - \left(\frac{\tilde{v}^{1/3} - 1}{\tilde{v}^2}\right) \ln\left(\frac{\tilde{v}^{1/3} - 0.5}{\tilde{v}^{1/3} - 1}\right) \tag{16}$$

where, $\tilde{v}$ is the reduced volume and M is the fraction of nearest neighbours that a molecule loses on moving from the bulk of the liquid to the state surface. The most suitable value for the parameter M is 0.29 [40].

Another theoretical model we analyzed is due to Brock and Bird [7], which obtains the surface tension of pure components only from the values of critical parameters. The Brock and Bird expression for a binary mixture reads:

$$\sigma = \left(P_{\mathrm{C}m}^2 T_{\mathrm{C}m}\right)^{1/3} \left(-0.951 + \frac{0.432}{Z_{\mathrm{C}m}}\right) (1 - T_{\mathrm{r}m})^{11/9}. \tag{17}$$

In this expression, $P_{\mathrm{C}m}$, $T_{\mathrm{C}m}$, $Z_{\mathrm{C}m}$ and $T_{\mathrm{r}m}$, are the critical pressure, critical temperature, critical compressibility factor and reduced temperature respectively, for the mixture. These parameters are defined as [32,39]:

$$P_{\mathrm{C}m} = x_1 P_{\mathrm{C}1} + x_2 P_{\mathrm{C}2} \tag{18}$$

$$T_{\mathrm{C}m} = x_1 T_{\mathrm{C}1} + x_2 T_{\mathrm{C}2} \tag{19}$$

$$Z_{\mathrm{C}m} = \frac{P_{\mathrm{C}m} V_{\mathrm{C}m}}{R T_{\mathrm{C}m}} \tag{20}$$

where,

$$V_{\mathrm{C}m} = x_1 V_{\mathrm{C}1} + x_2 V_{\mathrm{C}2} \tag{21}$$

and

$$T_{\mathrm{r}m} = \frac{T}{T_{\mathrm{C}m}} \tag{22}$$

$P_{\mathrm{C}i}$, $T_{\mathrm{C}i}$ and $V_{\mathrm{C}i}$ are the critical pressure, critical temperature and critical volume of the ith component of the mixture. The values of which can be obtained from the literature [36].

The parameters for pure components used in these relations are listed in table 6. A close perusal of table 7 reveals that Sanchez method provides fairly good agreement in theory and experiment followed by Brock–Bird, Goldsach–Sarvas, Flory–Paterson–Rastogi, Aurebach and Sudgen's relation.

The Aurebach relation is based on ultrasonic speed and density measurements of the same mixtures, and, thus, the values obtained follows the density and ultrasonic behaviour. The parameter parachor, $[P_i]$ introduced by Sudgen has also been calculated by using density and, thereby, follows the same behaviour. Some other workers [33–35] also arrived at the same conclusions about Sudgen's method. Further, if $[P_i]$ were calculated using a recently proposed statistical mechanical method by Escobedo and Mansoori [30] or by using group's contribution described elsewhere [36], these discrepancies may further be minimized.

Table 6. Values of characteristic, Flory and pure component parameters at 298.15 K.

Parameter	Benzene	1,1,2,2-tetrachloroethane
V ($10^6\,\mathrm{m^3\,mol^{-1}}$)	89.50	105.63
$\tilde{V}$	1.2917	1.2473
α ($10^3\,\mathrm{K^{-1}}$)	1.223	0.998
β_T ($\mathrm{T\,Pa^{-1}}$)	967.0	617.0
P^* ($10^6\,\mathrm{J\,cm^{-3}}$)	648.0	774.0
V^* ($10^6\,\mathrm{m^3\,mol^{-1}}$)	69.14	84.69
T^* (K)	5237	4709
T_C (K)	562.05	661.15
P_C (MPa)	4.895	5.841
V_C ($\mathrm{cm^3\,mol^{-1}}$)	256.0	331.5
C_p ($\mathrm{J\,mol^{-1}\,K^{-1}}$)	136.0	162.3

The values of surface tension using the Flory–Patterson–Rastogi model are a bit higher than our experimental values. The possible reason for this difference is that the corresponding state treatment of liquid mixtures used in equation (16) considers the molecules of a mixture as equivalent to a single component. Also, the value of M which is the fractional decrease in the number of neighbours of a cell in the surface phase compared to the bulk phase depends on the temperature and pressure and, thus, can have values other than 0.29, as suggested by Patterson and Rastogi [9]. This might be the reason for the observed discrepancies. Similar conclusions were also drawn at by Pandey *et al.* [32].

Therefore, it is obvious that statistical approaches give better results than the empirical ones. Thus, the present work emphasizes the relative validity of these theories/models and their ability to reproduce the experimental data.

3.1.2. Estimation of deviation in surface tension. The first theory we analyzed for the estimation of deviation in surface tension, $\Delta\sigma$ of binary liquid mixtures is the Hildebrand and Scott ideal solution theory (HSIS) [12], which is based on Guggenheim's ideal solution equation [13]. It assumes that, the bulk liquid and the surface layer, form ideal solution and it must be applied when the size of the molecules in the mixture is similar. The equation for HSIS model can be written as [12,41]:

$$\Delta\sigma = -\frac{A_x}{2RT}(\sigma_1 - \sigma_2)^2 x_1 x_2 \tag{23}$$

where $\Delta\sigma$ is the surface tension deviation as defined in equation (3), R is the gas constant and T the absolute temperature, A_x is the molar surface area and can be defined as:

$$A_x = x_1 A_1 + x_2 A_2. \tag{24}$$

The molar surface area of the pure components can be deduced by the method described elsewhere [41,42], which assumes that the molecules in the liquid are close packed spheres and is given by the relation:

$$A_i = (V_i N)^{1/3} \tag{25}$$

Table 7. Measured surface tension, σ_{exp}, and theoretical surface tension, σ_{theo} of binary liquid mixtures from various methods and their percentage deviations at 298.15 K.

		σ_{theo}						Percentage deviations					
X_1	σ_{exp}	Aurebach	Goldsach–Sarvas	Sanchez	Sudgen	Flory	Brock and Bird	Aurebach	Goldsach–Sarvas	Sanchez	Sudgen	Flory	Brock and Bird
0.0000	35.50	39.78	35.50	35.50	35.29	31.99	20.78	−12.07	0.00	0.00	0.59	9.90	41.46
0.1222	34.39	39.43	29.52	35.01	40.85	32.26	22.84	−14.66	14.17	−1.82	−18.78	6.19	33.60
0.1956	33.60	39.25	29.18	34.67	43.66	32.43	24.06	−16.81	13.16	−3.20	−29.96	3.48	28.39
0.3028	32.60	38.61	28.86	34.11	46.82	32.68	25.83	−18.43	11.46	−4.63	−43.61	−0.24	20.76
0.3862	31.80	37.65	28.69	33.61	48.30	32.87	27.20	−18.38	9.79	−5.69	−51.90	−3.37	14.47
0.4960	30.75	35.60	28.51	32.87	48.70	33.13	28.97	−15.78	7.30	−6.88	−58.37	−7.74	5.78
0.5936	29.90	33.36	28.38	32.12	47.46	33.36	30.53	−11.58	5.09	−7.43	−58.72	−11.57	−2.11
0.6890	29.10	31.36	28.27	31.31	44.78	33.59	32.03	−7.76	2.89	−7.60	−53.90	−15.42	−10.06
0.8079	28.10	29.10	28.15	30.17	39.59	33.88	33.86	−3.56	−0.19	−7.38	−40.89	−20.55	−20.49
0.9020	27.50	27.62	28.07	29.17	34.29	34.10	35.27	−0.44	−2.09	−6.06	−24.68	−24.02	−28.26
1.0000	28.00	26.31	28.00	28.00	28.09	34.34	36.71	6.05	0.00	0.00	−0.30	−22.62	−31.10
Average percentage deviations (APD)								−10.31	5.60	−4.61	−34.59	−7.82	4.77

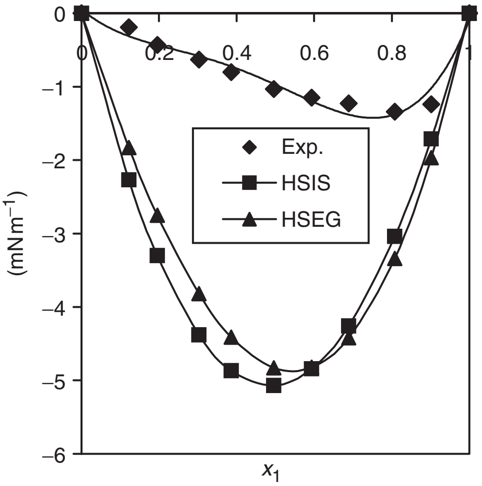

Figure 4. Experimental and theoretical surface tension deviations of binary liquid mixtures at 298.15 K.

where N is the Avogadro's number and V_i the molar volume of the pure component, i, obtained experimentally from the molar mass of the compound and its density. The obtained $\Delta\sigma$ values using HSIS model are presented in figure 4.

Another theoretical expression we analyzed for the estimation of $\Delta\sigma$ is HSEG, which is based on Guggenheim's ideal solution equation [13] and applicable to mixtures where the size of the molecules is different as in our case. The expression for the HSEG model can be written as [12,43]:

$$\sigma = Y_1\sigma_1 + Y_2\sigma_2 - \frac{(\sigma_1 - \sigma_2)^2}{2RT}(Y_1A_2 + Y_2A_1)Y_1Y_2 \tag{26}$$

where the parameter Y_i gives the relationship between the surface molar area, A_i for the molecule i and the total molar surface area. Thus, Y_i is defined by the following expression:

$$Y_i = \frac{x_iA_i}{x_1A_1 + x_2A_2}. \tag{27}$$

To obtain $\Delta\sigma$ from the HSEG model, we applied equation (3) to the σ values obtained from equation (26). The corresponding $\Delta\sigma$ values are plotted in figure 4, along with the experimental values and those obtained using HSIS models at 298.15 K.

It is clear from the figure 4 that neither HSIS nor HSEG models reproduce the form of experimental curves; both are symmetrical, while the experimental curve is asymmetrical. Although, these two models predict the sign of $\Delta\sigma$ correctly, but quantitatively $\Delta\sigma$ values predicted by the HSIS and HSEG models are much lower than the measured ones. The reason for the observed difference in $\Delta\sigma$ values may be that these two equations (HSIS and HSEG) are a good approximation for mixtures of quasispherical molecules [43,44]. Another reason for the observed discrepancies may be in the calculation of molar surface area A_i using equation (25), as there are other approaches in the literature for the calculation of A_i. For instance, Paquette [44,45] suggests a relation to calculate molar surface area using molar and critical volume. Another method to calculate A_i is the modified UNIFAC method, which assigns a given molar surface area to each functional group of the molecule [45,46]. By making use of these methods, the difference observed in the theoretical and experimental $\Delta\sigma$ values can be reduced.

References

[1] A. Ali, S. Hyder, M. Tariq. *Int. J. Thermophys*., **26**, 1537 (2005).
[2] A. Ali, A.K. Nain, D. Chand, R. Ahmad. *Phys. Chem. Liq*., **43**, 205 (2005).
[3] A. Ali, M. Tariq. *J. Mol. Liq*., **128**, 115 (2006).
[4] A. Villares, B. Giner, H. Artigas, C. Lafuente, F.M. Royo. *J. Solution Chem*., **34**, 205 (2005).
[5] S. Azizian, N. Bashavard. *J. Coll. Int. Sci*., **282**, 428 (2005).
[6] R. Aurebach. *Experimentia*, **4**, 473 (1948).
[7] J.R. Brock, R.B. Bird. *AIChE J*., **1**, 74 (1965).
[8] S. Sudgen. *J. Chem. Soc*., **125**, 1177 (1924).
[9] D. Patterson, A.K. Rastogi. *J. Phys. Chem*., **74**, 1067 (1970).
[10] I.C. Sanchez. *J. Chem. Phys*., **79**, 405 (1984).
[11] D.E. Goldsach, C.D. Sarvas. *Can. J. Chem*., **59**, 2968 (1981).
[12] J.H. Hildebrand, R.L. Scott. *Solubility of Nonelectrolytes*, Reinhold Pub. Corp., New York (1950).
[13] E.A. Guggenheim. *Mixtures*, Oxford University Press, London (1950).
[14] *CRC Hand Book of Chemistry and Physics*, 81st Edn, CRC Press Inc., Boca Raton, Florida (2000–2001).
[15] R.D. Peralta, R. Infante, G. Cortez, A. Cisneros, J. Wisniak. *Thermochim. Acta*, **398**, 39 (2003).
[16] M.I. Aralaguppi, T.M. Aminabhavi, S.B. Horogoppad, R.H. Balundgi. *J. Chem. Eng. Data*, **37**, 298 (1992).
[17] J.A. Riddick, W.B. Bunger, T.K. Sakano. *Organic Solvents: Physical Properties and Methods of Purification*, 4th Edn, Wiley Interscience, New York (1986).
[18] J. Nath, A.P. Dixit. *J. Chem. Eng. Data*, **29**, 322 (1984).
[19] J.J. Jasper. *J. Phys. Chem. Ref. Data*, **1**, 841 (1972).
[20] K.A. Connors, J.L. Wright. *Anal. Chem*., **6**, 194 (1989).
[21] S. Azizian, N. Bashavard. *Colloids Surf. A*, **240**, 69 (2004).
[22] G. Vazquez, E. Alvarez, J.M. Navaza, R. Rendo, E. Romer. *J. Chem. Eng. Data*, **42**, 57 (1999).
[23] B.C. Hoke Jr, J.C. Chen. *J. Chem. Eng. Data*, **36**, 322 (1991).
[24] O. Redlich, A.T. Kister. *Ind. Eng. Chem*., **40**, 345 (1948).
[25] J. Nath, A.D. Tripathi. *J. Chem. Eng. Data*, **28**, 263 (1983).
[26] A.A. Adamson. *Physical Chemistry of Surfaces*, 5th Edn, Wiley, New York (1990).
[27] J. Glinski, G. Chavepeyer, J.K. Platten. *Chem. Phys*., **272**, 119 (2001).
[28] D.G. Diaz, J.M. Navaza. *J. Chem. Eng. Data*, **49**, 1408 (2004).
[29] S. Azizian, M. Hemmati. *J. Chem. Eng. Data*, **48**, 662 (2003).
[30] J. Escobedo, G.A. Mansoori. *AIChE J*., **44**, 2324 (1998).
[31] Z. Li, B.C.Y. Lu. *Can. J. Chem. Eng*., **79**, 402 (2001).
[32] J.D. Pandey, N.K. Soni, V.K. Singh, V. Sanguri. *Phys. Chem. Liq*., **39**, 1763 (2001).
[33] M.D. Perez, L. Segade, C. Franjo, O. Cabeza, E. Jiminez. *Fluid Phase Equilib*., **232**, 9 (2005).
[34] E. Jiminez, M. Cabanas, L. Segade, S.G. Garbel, H. Casas. *Fluid Phase Equilib*., **180**, 151 (2001).
[35] E. Rilo, S. Freire, L. Segade, O. Cabeza, C. Franjo, E. Jiminez. *J. Chem. Thermodyn*., **25**, 839 (2003).
[36] R.C. Reid, J.M. Prausnitz, B.E. Poling. *The Properties of Gases and Liquids*, McGraw Hill, New York (1987).
[37] P.J. Flory, R.A. Orwell, A. Vrij. *J. Am. Chem. Soc*., **86**, 2507 (1964); **86**, 3515 (1964).
[38] P.J. Flory. *J. Am. Chem. Soc*., **87**, 1833 (1965).
[39] A. Abe, P.J. Flory. *J. Am. Chem. Soc*., **87**, 1838 (1965).
[40] J.D. Pandey, N. Pant. *J. Am. Chem. Soc*., **104**, 3299 (1982).
[41] S.K. Suri, V. Ramakrishnan. *J. Phys. Chem*., **72**, 3073 (1968).
[42] T.P. Hoar, D.A. Melford. *Trans. Faraday Soc*., **53**, 315 (1957).
[43] R.L. Schmidt, J.C. Randell, H.L. Clever. *J. Phys. Chem*., **70**, 3912 (1966).
[44] S. Nath. *J. Coll. Int. Sci*., **209**, 116 (1999).
[45] J. Tojo, C. Torres-Marchal, P. Rasmussen. *Chem. Eng. Sci*., **44**, 782 (1989).
[46] B.L. Larsen, P. Rasmussen, A. Fredeslund. *Ind. Eng. Chem. Res*., **26**, 2274 (1987).