Theoretical Estimation of Surface Tension for Binary Mixtures at Different Temperatures

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(Received on: February 14, 2018)

ABSTRACT

Theoretical estimation of surface tensions for benzyl alcohol + benzene binary system at 298.15, 303.15 and 313.15 K and atmospheric pressure over the whole concentration range has been done from the experimental data of density and surface tension. Prigogine-Flory-Patterson model (PFP), Ramaswamy and Anbananthan (RS), model derived by Glinski, Sanchez equation, Goldsack relation and Eberhart models were utilized to predict the associational behavior of weakly interacting liquids. The measured properties were fitted to Redlich-Kister polynomial relation to estimate the binary coefficients and standard errors. Furthermore, McAllister multi body interaction model was also used to correlate the binary properties. These non-associated and associated models were compared and tested for different systems showing that the associated processes yield fair agreement between theory and experiment as compared to non-associated processes.

Keywords: Surface Tension, Prigogine-Flory-Patterson, McAllister, Sanchez, Eberhart, GoldSacks.

INTRODUCTION

Prediction of surface tension is of out standing importance in many scientific and technological areas such as liquid-liquid extraction, gas absorption, distillation, condensation, environmental sciences, material sciences, process simulation, molecular dynamics¹,² etc and play a significant role in several industries³ such as paints, detergents, agrochemicals and petroleum. As a fundamental parameter, surface tension is the single most accessible
experimental parameter that describes the thermodynamic state and contains at least implicit information on the internal structure of a liquid interface. Apart from this theoretical interest, a detailed understanding of the behavior of a vapor-liquid interface, such as enrichment of one component in a liquid surface is important for modeling a distillation process.

In the present work, we present the theoretical results of surface tension for benzyl alcohol + benzene binary liquid mixtures at 298.15, 303.15 and 313.15 K and atmospheric pressure over the whole concentration range. These data were analyzed in terms of associated models of Ramaswamy and Anbananthan (RS) model\(^4\) & model derived by Glinski\(^5\) and non-associated models of Prigogine-Flory-Patterson (PFP) model\(^6\-8\), Sanchez model\(^9\), Goldsack model\(^10\) and Eberhart Model\(^11\). Associated models are based on the association constant as an adjustable parameters whereas non-associated are based on the additivity of liquids. For that purposes, we selected the liquids containing poor interacting properties. From these results, deviations in surface tension, \(\Delta\sigma\) were calculated and fitted to the Redlich-Kister polynomial equation\(^12\) to derive the binary coefficients and the standard errors. An attempt has also been made to correlate the experimental data with the McAllister multi body interaction model\(^13\) which is based on Eyrings theory of absolute reaction rates.

**THEORETICAL**

Ramaswamy and Anbananthan\(^4\) proposed the model based on the assumption of linearity of acoustic impedance with the mole fraction of components. Further it is assumed, that any equilibrium physical property such as viscosity, refractive index, surface tension etc can be predicted. Further Glinski\(^5\) assumed that when solute is added to solvent the molecules interact according to the equilibrium as:

\[
A + B = AB
\]

and the association constant \(K_{ab}\) can be defined as:

\[
K_{ab} = \frac{[AB]}{[A][B]}
\]

where \(A\) is amount of solvent and \(B\) is amount of solute in the liquid mixture.

By applying the condition of linearity with composition

\[
\sigma_{obs} = x_A\sigma_A + x_{AB}\sigma_{AB}
\]

where \(x_A, x_{AB}, \sigma_A\) and \(\sigma_{AB}\) and \(\sigma_{obs}\) are the mole fraction of \(A\), mole fraction of associate \(AB\), surface tension of \(A\), surface tension of associate \(AB\) and observed surface tension respectively. The component \(AB\) can not be obtained in its pure form. Following simplifications have been made, firstly, concentration term should be replaced by activities for concentrated solution and second, there are also molecules of non associated components in the liquid mixture. The eq (4) takes the form,

\[
\sigma_{obs} = [x_A\sigma_A + x_B\sigma_B + x_{AB}\sigma_{AB}]
\]

Now, assuming any value of surface tension in the pure component \(AB\), \(\sigma_{AB}\), it is possible to compare the surface tension calculated using eq (5) with the experimental values.
On changing both the adjustable parameters \( K_{as} \) and \( \sigma_{AB} \) gradually, one can get different values of the sum of squares of deviations,

\[
S = \sum (\sigma_{obs} - \sigma_{cal})^2 \tag{6}
\]

where \( \sigma_{obs} \) and \( \sigma_{cal} \) are the observed and calculated equilibrium properties respectively.

The minimum value of \( S \) can be obtained theoretically by a pair of the fitted parameters. But we found that for some \( K_{as} \) and \( \sigma_{AB} \), the value of \( S \) is high and changes rapidly, and for others, it is low and changes slowly when changing the fitted parameters. In such cases, the value of \( \sigma_{AB} \) should not be much lower than the lowest observed surface tension of the system or much higher than the highest one. Quantitatively, it should be reasonable to accept the pair of adjustable parameters \( K_{as} \) and \( \sigma_{AB} \) which has the physical sense and which reproduces the experimental physical property satisfactorily.

On inspecting the results obtained from Ramaswamy and Anbananthan model, Glisnki\(^5\) suggested the equation assuming additivity with the volume fraction, \( \phi \) as;

\[
\sigma_{cal} = \frac{\sigma_1 \sigma_2}{\phi_1 \sigma_2 + \phi_2 \sigma_1} \tag{7}
\]

where \( \sigma_{cal} \) is the theoretical surface tension of binary liquid mixture, \( \phi_1, \phi_2 \) are the volume fractions of component 1 and 2 and \( \sigma_1 \) and \( \sigma_2 \) are the surface tensions of pure component liquids.

The original cell model of Prigogine\(^7\) for spherical chain molecules uses a dependence of the configurational energy on volume equivalent to the the Lennard-Jones (6, 12) energy-distance relation i.e. Flory and collaborators\(^6\) used the cell partition function of Hirschfelder and Eyring and a simple Van der Waals energy-volume relation, by putting \( m=3, n\to\infty \) so that the Flory equations for the mixing functions and partial molar quantities may be obtained from the general corresponding states equations given by making this particular choice of \((m,n)\).

Patterson\(^8\) et al. have drawn attention to the close connection between the Flory theory and corresponding state theory of Prigogine employing a simple cell model of the liquid state. The equation of state for the materials conforming to the principle of corresponding states can be expressed in a universal form through the use of suitable characteristic values i.e. (reduction parameters) \( P^*, V^*, T^* \) for the pressure, volume and temperature respectively.

In order to extend corresponding state theory to deal with the surface tension, Patterson and Rastogi\(^8\) used the reduction parameters as,

\[
\sigma^* = k^{1/3} P^{2/3} T^{1/3} \tag{8}
\]

called the characteristic surface tension of the liquid. Here \( k \) is the boltzmann constant. Paterson and Rastogi extended the simple cell model theory of the surface tension of spherical molecules by Prigogine and Saraga\(^{15}\) to the case of chain molecules. With a particular choice \( m, n \) potential, Flory equation takes the form,

\[
\tilde{\sigma}(\tilde{V}) = [M \tilde{V}^{-5/3} - (\tilde{V}^{-1/3} - 1.0) \ln(\tilde{V}^{-1/3} - 0.5)] \tag{9}
\]

Thus on the basis of flory theory, surface tension of liquid mixture is given by,
The relationship between surface tension $\sigma$, isothermal compressibility, $\beta_T$, and density, $\rho$ of a liquid was obtained by Sanchez as;

$$\sigma(\beta_T / \rho)^{1/2} = A_0^{1/2}$$

(11)

and applied successfully to binary liquids, assuming the following approximations as;

$$\beta_T = \sum_{i=1}^{2} \varphi_i \beta_{T_i} \quad \text{and} \quad \rho = \sum_{i=1}^{2} \varphi_i \rho_i$$

(12)

Above expressions yield the final equation for the surface tension of binary liquids as;

$$\sigma = \sum_{i=1}^{2} x_i A_i^{1/2} \frac{\sum_{i=1}^{2} \varphi_i \rho_i}{\sum_{i=1}^{2} \varphi_i \beta_{T_i}}$$

(13)

where $A_i$ is defined as;

$$A_i = \sigma_i^2 (\beta_{T_i} / \rho_i)$$

(14)

all the notations used in the equations have their usual significance as described by Sanchez.

Goldsack and Sarvas used the mole fraction and volume fraction statistics to obtain the expression surface tension and applied to various systems as;

$$x_i, S = x_{i,B} \left[ (\sigma - \sigma_i) \frac{A_i}{R_T} \right] = 1$$

(15)

where $x_i$, $S$ and $x_i$, $B$ are the mole fraction of the component in surface and bulk phase respectively and $A_i$ is the molar surface area of the component for binary liquids, the resulting equation is given by,

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

(16)

Where $A_1=A_2=A$ and the volume of $A$ is obtained from the relation

$$A = A \left( \frac{3}{4\pi} \right)^{2/3} N^{1/3} V_i^{2/3}$$

(17)

where $N$ is the Avogadro number and $V_i$ is the molar volume of the component.

Eberhart assumed that the surface tension of binary liquids is a linear function of surface layer mole fractions as;

$$\sigma = y_1 \sigma_1 + y_2 \sigma_2$$

(18)

Using a semi-empirical constant, $S$, which is defined as the surface enrichment factor for the component having the lower surface tension,

$$S = \left( \frac{y_2}{y_1} \right) / \left( x_2 / x_1 \right)$$

(19)

where $y_1$ and $y_2$ are surface mole fractions and $x_1$ and $x_2$ are bulk mole fractions and where $y_1+y_2=1$ and $x_1+x_2=1$, $\sigma$ can be expressed in terms of bulk liquid composition of the mixture.
RESULTS & DISCUSSION

Pure component results and comparison with literature values\textsuperscript{14} are provided in Table 1. The reported uncertainty ($\pm 1.9 \times 10^{-4}$ N.m$^{-1}$) is the highest uncertainty found from all the data points. The mixture data are presented in Tables 4-5.

The results of fittings obtained from the models were utilized properly. The calculations were performed using a computer program which allows fittings easily both the adjustable parameters simultaneously or the parameters were changed manually.

We constructed the data sheet in a computer program with association constant $K_\text{as}$ and $C_{A,B}$ as the fitted parameters. On changing these parameters, the equilibrium concentrations of species [A], [B] and [AB] will change and the surface tension can be computed. The difference between experimental and theoretical values for surface tension is used to obtain the sum of squares of deviation. The values of surface tension in pure associate can be treated as a fitted one with the value of $K_\text{as}$.

Values of thermal expansion coefficient ($\alpha$) and isothermal compressibility needed in the PFP model were obtained from the equation which have already been tested in many cases\textsuperscript{16}.

The mixing function $\Delta \sigma$ can be represented mathematically by Redlich-Kister polynomial equation for correlating the experimental data. The values of coefficients were determined by a multiple regression analysis based on the least square method and are summarized along with the standard deviations between the experimental and fitted values of the respective function in Table 2.

Multibody interaction model of McAllister\textsuperscript{13} is widely used for correlating the surface tension viscosity of liquid mixtures with mole fraction. The coefficients $a, b$, and $c$ were calculated using the least square procedure and the results of estimated parameters and standard deviation between the calculated and experimental values are presented in Table 3. It is observed that four body model is correlated the mixture surface tension to a significantly higher degree of accuracy for all the systems than the three body model.

Mixture data are presented in Table 4-5. With the increase of mole fraction, the values of surface tension obtained from all the models decrease at all temperatures except at few places. The absolute average deviations (AAD) in surface tension obtained from different models are provided in Table 4. It is observed that all the equations are equally good and provide fairly good results. Higher deviation values in PFP model (eq 19) can be explained as the model was developed for non-electrolyte $\gamma$-meric spherical chain molecules and the system under investigation have interacting and associating properties. Moreover, the expression used for the computation of $\alpha$ and $\beta_T$ are also empirical in nature.

Results of surface tension obtained from different models along with percent deviation are reported in Table 5. A careful perusal of the results clearly indicates the close proximity of our results with the experimental findings.

In all the cases, theoretical surface tension computed from various models agrees well with the experimental value except PFP model. Close comparison of results indicate that in all

\[
\sigma = \left( x_1 \sigma_1 + x_2 \sigma_2 \right) / \left( x_1 + Sx_2 \right)
\]
the plots, the trend is almost similar and negative. Sometimes positive deviations are also observed which indicate strong molecular interactions between mixing molecules. These deviations are much prevalent as the composition of polar group increases as evidenced in figures. The negative deviations are usually explained quantitatively by the fact that surface layer of the liquid is enriched in the component of lower surface tension, thereby minimizing the Gibbs free energy of the mixture. Similar results have been presented earlier by many workers in recent past.

Table 1 Comparison of density ($\rho$) and Surface tension ($\sigma$) with literature data for pure components at 298.15, 303.15, and 313.15 K

<table>
<thead>
<tr>
<th>Components</th>
<th>T/K</th>
<th>$\alpha$ x $10^3$ K</th>
<th>$\beta$ x $10^{12}$ Pa</th>
<th>V/ cm$^3$ mole$^{-1}$</th>
<th>$\rho_{exp}$/ g.cm$^{-3}$</th>
<th>$\sigma_{exp}$/ mN.m$^{-1}$</th>
<th>$\sigma_{lit}$/ mN.m$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>298.15</td>
<td>1.218023</td>
<td>94.60978</td>
<td>89.3196</td>
<td>0.8732</td>
<td>28.02</td>
<td>28.20</td>
</tr>
<tr>
<td></td>
<td>303.15</td>
<td>1.21875</td>
<td>94.77915</td>
<td>89.9366</td>
<td>0.8680</td>
<td>27.38</td>
<td>27.56</td>
</tr>
<tr>
<td></td>
<td>313.15</td>
<td>1.24239</td>
<td>100.4023</td>
<td>91.1329</td>
<td>0.8575</td>
<td>26.79</td>
<td></td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>298.15</td>
<td>1.015504</td>
<td>54.82925</td>
<td>103.8210</td>
<td>1.0412</td>
<td>28.02</td>
<td>28.20</td>
</tr>
<tr>
<td></td>
<td>303.15</td>
<td>1.021907</td>
<td>55.872</td>
<td>104.2413</td>
<td>1.0376</td>
<td>27.38</td>
<td>27.56</td>
</tr>
<tr>
<td></td>
<td>313.15</td>
<td>1.063372</td>
<td>62.95392</td>
<td>107.9780</td>
<td>1.0366</td>
<td>26.79</td>
<td></td>
</tr>
</tbody>
</table>

a Ref. 14

Table 2 Coefficients of the Redlich-Kister equation and standard deviations ($\sigma$) for surface tension of binary liquid mixtures at various temperatures.

<table>
<thead>
<tr>
<th>Benzene+Benzyl alcohol</th>
<th>$\Delta \sigma$/mN.m$^{-1}$</th>
<th>T</th>
<th>$A_0$</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$A_3$</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>298.15</td>
<td>12.7894</td>
<td>10.0663</td>
<td>10.0663</td>
<td>0.3097</td>
<td>0.1998</td>
<td></td>
</tr>
<tr>
<td></td>
<td>303.15</td>
<td>17.1911</td>
<td>7.0611</td>
<td>-8.9754</td>
<td>3.8436</td>
<td>0.1620</td>
<td></td>
</tr>
<tr>
<td></td>
<td>313.15</td>
<td>7.5755</td>
<td>4.4203</td>
<td>-2.5178</td>
<td>-1.4961</td>
<td>0.1122</td>
<td></td>
</tr>
</tbody>
</table>

Table 3 Parameters of McAllister Three body and Four body Interaction Models and Standard Deviations ($\sigma$) for Surface Tension of Binary Liquid Mixtures at Various Temperatures

<table>
<thead>
<tr>
<th>Component</th>
<th>McAllister Three Body ($\sigma$/m N.m$^{-1}$)</th>
<th>McAllister Four Body ($\sigma$/m N.m$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene+Benzyl alcohol</td>
<td>$\text{Temp}$</td>
<td>$a$</td>
</tr>
<tr>
<td></td>
<td>298.15</td>
<td>42.1778</td>
</tr>
<tr>
<td></td>
<td>303.15</td>
<td>39.5465</td>
</tr>
<tr>
<td></td>
<td>313.15</td>
<td>34.0128</td>
</tr>
</tbody>
</table>

Table 4 Comparison of absolute average deviation values obtained from various liquid state models.

<table>
<thead>
<tr>
<th>Component liquids</th>
<th>$\text{Temp}$ (K)</th>
<th>$\sigma_{Eq.5}$/mN.m$^{-1}$</th>
<th>$\sigma_{Eq.10}$/mN.m$^{-1}$</th>
<th>$\sigma_{Eq.25}$/mN.m$^{-1}$</th>
<th>$\sigma_{Eq.29}$/mN.m$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene+Benzyl alcohol</td>
<td>298.15</td>
<td>2.91</td>
<td>3.08</td>
<td>3.46</td>
<td>3.15</td>
</tr>
<tr>
<td></td>
<td>303.15</td>
<td>2.91</td>
<td>3.09</td>
<td>2.86</td>
<td>3.15</td>
</tr>
<tr>
<td></td>
<td>313.15</td>
<td>1.33</td>
<td>3.37</td>
<td>1.85</td>
<td>1.94</td>
</tr>
</tbody>
</table>

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Table 5 Experimental densities (ρ), experimental surface tensions (σexp), theoretical surface tension from PFP model (σeq,19), Sanchez method (σeq,22), Goldsack model (σeq,22), Eberhart model (σeq,29), RS model (σeq,5), Glinski model (σeq,10) of binary liquid mixtures and their percent deviations (% Δσ) at various temperatures.

CONCLUSION

In this work, theoretical results of surface tension for benzyl alcohol + benzene binary liquid mixtures at different temperatures have been provided by utilizing associated and non-associated models. Associated models are based on the association constant as an adjustable parameters where as non-associated are based on the additivity of liquids. Conclusively, associated process give more reliable results as compared to non-associated processes and

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helpful in deducing the internal structure of associates through the fitted values of surface tension in a hypothetical pure associate and observed dependence of concentration on composition of a mixture.

REFERENCES