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Estimation of surface tension of ternary liquid systems by corresponding-states group-contributions method and Flory theory

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ABSTRACT

For the first time two-body interaction coefficients between any two molecules are considered to be non-identical. On this basis, various expressions involved in Flory theory have been deduced, and then utilized to compute surface tension of three ternary liquid mixtures. Prior to this, corresponding-states group-contributions method for the first time has been extended to three ternary liquid mixtures, viz. *n*-pentane + *n*-hexane + benzene, cyclohexane + *n*-heptane + toluene, 2,2,4-trimethyl pentane + cyclohexane + decane and some binary mixtures at 298.15 K. On comparing the computed values of surface tension by the present two approaches with experimental data, quite satisfactory results have been observed.

1. Introduction

The study of surface tension of multicomponent liquid systems is useful in the design of separation processes because its role is important in affecting significantly the mass and heat transfer at the interface. Such studies are also of considerable importance in biotechnology and environmental engineering. The experimental data on surface tension of multicomponent liquid mixtures are very scarce in the literature. Hence, the theoretical methods of their prediction are found to be very useful. Escobedo and Ali Mansoori [1] developed statistical method for estimating the surface tension of binary liquid mixtures and obtained excellent results for 55 binary liquid mixtures. They have also suggested that their model could be applied to muticomponent liquid mixtures. In the year 2000, Chunxi et al. [2] proposed a new surface tension equation based on the thermodynamic definition of surface tension and Wilson equation for the excess Gibbs free energy. The proposed relation was tested for 124 binary and 16 multicomponent systems with excellent agreement. Li and Lu [3] developed predictive method for surface tension of real mixtures on the basis of Davis theory and tested with the molecular dynamics simulation results for surface tension of Lennard–Jones fluid. The proposed model is found to be suitable for obtaining the molecular parameters from pure liquid surface tension values. Although Flory statistical theory has earlier [4,5] been applied successfully for estimating the surface tension of binary liquid mixtures. The proposed model was tested for nine ternary and four quaternary mixtures using molecular parameters of pure liquids and the adjustable binary parameters with 1.75 and 1.03 average percent deviation (APD) values, respectively.

A different approach for estimating the surface tension of multicomponent liquid systems has been advanced by Pandey et al. [6–11]. In this approach they have made theoretical formalism of the most widely used Flory's statistical theory, and applied quite successfully for estimating the surface tensions of ternary [6,8,11] and quaternary [7] liquid mixtures. In addition, they have also extended Brock–Bird corresponding-states model, Goldsack–Sarvas volume fraction statistics and Sanchez method to multicomponent systems [12–14]. In three of the above methods even surface tension values of pure liquids are not required. The entire approach requires only the values of thermal expansivity, isothermal compressibility and critical constants of pure components. In all the cases agreement with experimental surface tensions is invariably found to be quite good. Very recently Bahramian and Danesh [15] have developed an equation for predicting interfacial surface tension in multicomponent systems on the basis of lattice theory and regular solution model. The values predicted by this model were compared with semi-empirical equations.

Various models [1–3,15] proposed, during recent years, for predicting the surface tension of multicomponent systems, give

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excellent agreement with experimental values. But all these models involve complicated approach and need several input data for the estimation of surface tension. In most cases correlations of binary mixtures and pure liquids data are used, For instance, in Chunxi et al. [2] model several adjustable model parameters are required. Li and Lu [3] model also involves use of molecular parameter and adjustable parameters obtained from correlating surface tensions of binary mixtures. In Bahramian and Danesh [15] model, complicated procedure is involved since it is based on lattice theory and regular solution assumptions. Moreover, it is assumed that the excess surface area in the interface is zero, and it is proposed to use molecular surface area of a pure liquid instead of its partial molar value. In essence, we can say that all the models propose during recent past give excellent results for the surface tension of multicomponent systems but need many input data and several adjustable parameters obtained from binary and pure component data.

The purpose of the present work is two fold. Firstly, we shall apply the corresponding-states group-contribution method [14] for estimation of surface tensions of ternary liquid mixtures. Perhaps, this is our first attempt to extend the corresponding-states group-contributions method to multicomponent systems. In earlier approach [6–11] of applying Flory's statistical theory for computing the surface tension of multicomponent systems, only two-body interactions have been considered, and binary interaction coefficients between same two molecules are assumed to be equal, i.e. $X_{ij}=X_{ji}$. In case of ternary mixture *ijk*, it was assumed that $X_{ij}=X_{ji}$, $X_{jk}=X_{kj}$ and $X_{ik}=X_{ki}$. In a recent paper [16,17], we have modified the theory by considering $X_{ij}\neq X_{ji}$, $X_{jk}\neq X_{kj}$ and $X_{ik}\neq X_{ki}$. In this way, a number of thermodynamic properties, density (ρ), ultrasonic velocity (u), internal pressure (P_{int}), isothermal compressibility (β_{T}), isentropic compressibility (β_{S}) and thermal expansion coefficient (α) of ternary mixtures were calculated, and improvement in the results was achieved. Here, we shall apply the modified version of Flory theory for estimating the surface tensions of ternary liquid mixtures. A new estimative method [9,10], namely, corresponding-states group-contributions method was proposed for the estimation of surface tension of pure liquids by combining the corresponding-states theorem and group-contributions methods. Corresponding-states theorem and the group-contribution methods independently have been widely used for the estimation of a variety of physical properties of substances. In the present investigation, an effort has been made to apply corresponding-states group-contribution method to evaluate surface tension of three ternary liquid mixtures under consideration. Validity of the present two approaches (Flory theory and corresponding-states group-contributions method) has been examined by comparing computed values with the available experimental data. Present approaches are new, to the best of our knowledge, and for the first time they have been utilized in the present investigation. Three ternary liquid mixtures viz. *n*-pentane + *n*-hexane + benzene, cyclohexane + *n*-heptane + toluene, 2,2,4-trimethyl pentane + cyclohexane + decane at 298.15 K have been considered for the present investigation.

2. Theoretical

Surface tension (σ) of a liquid or a liquid mixture in terms of Flory theory is given by the expression:

$$\sigma = \sigma^*\,\tilde{\sigma}(\tilde{\upsilon}) \tag{1}$$

where characteristic (σ^*) and reduced $\tilde{\sigma}(\tilde{\upsilon})$ surface tensions are given by

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

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

The intermolecular energy (E_0) may be expressed as

$$-\frac{E_0}{\bar{r}N} = \frac{s}{2v}\left[\theta_1\eta_{11}+\theta_2\eta_{22}+\theta_3\eta_{33}-\theta_1\theta_2\ \Delta\eta_1 -\theta_2\theta_3\,\Delta\eta_2-\theta_3\theta_1\,\Delta\eta_3\right] \tag{4}$$

Interaction parameter (X_{ij}) is defined by

$$X_{ij} = \frac{s_i\,\Delta\eta_{ii}}{2v^{*2}}$$

Therefore, we get

$$X_{12} = \frac{s_1\,\Delta\eta_1}{2v^{*2}},\quad X_{23} = \frac{s_2\,\Delta\eta_2}{2v^{*2}},\quad X_{31} = \frac{s_3\,\Delta\eta_3}{2v^{*2}}$$

$$X_{13} = \frac{s_1\,\Delta\eta_1}{2v^{*2}},\quad X_{21} = \frac{s_2\,\Delta\eta_2}{2v^{*2}},\quad X_{32} = \frac{s_3\,\Delta\eta_3}{2v^{*2}}$$

Adding consecutive expressions, we find

$$\Delta\eta_1 = \frac{(X_{12}+X_{13})v^{*2}}{s_1},\quad \Delta\eta_2 = \frac{(X_{23}+X_{21})v^{*2}}{s_2},\quad \Delta\eta_3 = \frac{(X_{31}+X_{32})v^{*2}}{s_3} \tag{5}$$

Expressions for the characteristic pressure of pure components are

$$P_1^* = \frac{s_1\eta_{11}}{2v^{*2}},\quad P_2^* = \frac{s_2\eta_{22}}{2v^{*2}},\quad P_3^* = \frac{s_3\eta_{33}}{2v^{*2}}$$

or

$$\eta_{11} = \frac{2P_1^*v^{*2}}{s_1},\quad \eta_{22} = \frac{2P_2^*v^{*2}}{s_2},\quad \eta_{33} = \frac{2P_3^*v^{*2}}{s_3} \tag{6}$$

Using Eqs. (5) and (6), Eq. (4) becomes

$$-\frac{E_0}{\bar{r}N} = \frac{s}{2v}\left[\theta_1\frac{2P_1^*v^{*2}}{s_1}+\theta_2\frac{2P_2^*v^{*2}}{s_2}+\theta_3\frac{2P_3^*v^{*2}}{s_3} -\frac{\theta_1\theta_2(X_{12}+X_{13})v^{*2}}{s_1}-\frac{\theta_2\theta_3(X_{23}+X_{21})v^{*2}}{s_2} -\frac{\theta_3\theta_1(X_{31}+X_{32})v^{*2}}{s_3}\right] \tag{7}$$

Defining segment fractions

$$\theta_1 = \frac{\psi_1s_1}{s},\quad \theta_2 = \frac{\psi_2s_2}{s},\quad \theta_3 = \frac{\psi_3s_3}{s} \tag{8}$$

Incorporating Eqs. (8) into (7) we get

$$-\frac{E_0}{\bar{r}N} = \frac{v^{*2}}{2v}\left[\psi_1P_1^*+\psi_2P_2^*+\psi_3P_3^*-\psi_1\theta_2\left(\frac{X_{12}+X_{13}}{2}\right) -\psi_2\theta_3\left(\frac{X_{23}+X_{21}}{2}\right)-\psi_3\theta_1\left(\frac{X_{31}+X_{32}}{2}\right)\right] \tag{9}$$

Comparing above equation with energy expression given by

$$-\frac{E_0}{\bar{r}N} = \frac{P^*v^*}{\tilde{\upsilon}} \tag{10}$$

we find expressions for characteristic pressure, P^*, and characteristic temperature, T^*, involving all the six interaction parameters of liquid mixture as