

Thermodynamic and Excess Thermodynamic properties of Cyclic Liquid Mixtures

Ashish Kumar Singh

Department of Chemistry, VSSD College, Kanpur-208002, India

Abstract: Surface tension and excess volume for trimethyl benzene with tetrahydrofuran, tetra chloromethane, and diethyl solfoxide were theoretically predicted with the help of Flory model over the entire concentration range at 298.15 K which has immense sense of applicability in organic separation, synthesis as solvent and industries. Further; we found that computed results are in good agreement with the experimental findings. The results so obtained have been explained on the basis of packing effect and dipolar-dipolar interactions. An attempt has also been made to study the excess thermodynamic functions which measure the extent of molecular interactions involved in the liquid mixture.

Keywords: Surface Tension, Excess Molar Volumes, Flory model, Molecular Interaction and Excess Surface Tension

I. Introduction

Prediction of surface tension and excess molar volume is of out standing importance in many scientific and technological areas. As a fundamental parameter, surface tension is the single most accessible parameter that describes the thermodynamic state and contains implicit information on the internal structure of a liquid interface. The surface tension of liquid and liquid mixtures is often essential in design calculation involving interface mass transfer, heat transfer and separations. 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. The study of excess molar volume leads with the two structural aspects that is, size difference and interaction forces between molecules. Substantial amount of work [1-8] has been done and is still in progress on the measurements and theoretical interpretations of surface tension for liquids and liquid mixtures with the use of various models of liquid state.

In the present work, the Prigogine-Saraga cell model theory [9,10] of surface tension is then used together with the statistical mechanical theory of Flory [11-13]. The component liquids (six binaries) which are taken in the present work are (tetrahydrofuran+ 1,2,4-trimethyl benzene, tetrahydrofuran+1,3,5- trimethyl benzene, tetrachloromethane +1,2,4- trimethyl benzene, tetrachloromethane +1,3,5- trimethyl benzene, dimethyl solfoxide+ 1,2,4- trimethyl benzene and dimethyl solfoxide+ 1,3,5- trimethyl benzene over the entire concentration range at 298.15 K for the theoretical prediction of surface tension and excess molar volume which have immense sense of applicability in organic separation and synthesis as solvent. Further, we found that computed results are in good agreement with the experimental findings. The results so obtained have been explained on the basis of packing effect and dipolar-dipolar interactions. An attempt has also been made to study the excess thermodynamic functions i.e. excess volume and excess surface tension which measure the extent of molecular interactions involved in the liquid mixture.

II. Theoretical

The original cell model of Prigogine [9] 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. ,

$$\tilde{U}(\tilde{V}) = -2\tilde{V}^{-2} + \tilde{V}^{-4} \quad (1)$$

More generally for an (m, n) potential,

$$\tilde{U}(\tilde{V}) = \frac{(-n\tilde{V}^{-m/3} + m\tilde{V}^{-n/3})}{(n-m)} \quad (2)$$

This leads to the following equation of state,

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = (1 - b\tilde{V}^{-1/3})^{-1} + \frac{mn}{3(n-m)} (\tilde{V}^{-n/3} - \tilde{V}^{-m/3}) \quad (3)$$

where b is a packing factor and equals to $(m/n)^{1/(n-m)}$

Flory and collaborators used the cell partition function of Hirschfelder and Eyring and a simple Van der Waals energy- volume relation, $\tilde{U} = -\tilde{V}^{-1}$, by putting $m=3$, $n \rightarrow \infty$ 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 et al [14] 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 [14] used the reduction parameters as,

$$\sigma^* = k^{1/3} P^{*2/3} T^{*1/3} \tag{4}$$

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 to the case of chain molecules. A segment experiences an increase in the configurational energy equal to $-M \tilde{U}(\tilde{V})$ due to the loss of a fraction, M , of its nearest neighbors at the surface while moving from the bulk phase to the surface phase. It's most suitable value ranges from 0.25 to 0.29. In the present case the value of M is taken as 0.29 throughout the calculation. The cell partition function of a segment at the surface is increased due to the loss of constraining nearest neighbors in one direction, so that,

$$\frac{\Phi_{surface}}{\Phi_{bulk}} = \frac{(\tilde{V}^{-1/3} - 0.5b)}{(\tilde{V}^{-1/3} - b)} \tag{5}$$

Here b is a packing fraction given by,

$$b = \left(\frac{m}{n} \right)^{1/(n-m)}$$

and tends to unity when $n \rightarrow \infty$.

According to Prigogine and Saraga the reduced surface tension is given by,

$$\tilde{\sigma}(\tilde{V})^{2/3} = -M \tilde{U}(\tilde{V}) - T \ln \frac{(\tilde{V}^{-1/3} - 0.5b)}{(\tilde{V}^{-1/3} - b)} \tag{6}$$

The surface energy and entropy are given by,

$$\tilde{\sigma}_u = -M \tilde{U}(\tilde{V}); \quad \tilde{\sigma}_s = \ln \frac{(\tilde{V}^{-1/3} - 0.5b)}{(\tilde{V}^{-1/3} - b)} \tag{7}$$

With the particular (3,∞) choice of m,n potential or the Flory model, eq (7) takes the form as;

$$\tilde{\sigma}(\tilde{V}) = \left[M \tilde{V}^{-5/3} - \left(\frac{\tilde{V}^{-1/3} - 1.0}{\tilde{V}^2} \right) \ln \left(\frac{\tilde{V}^{-1/3} - 0.5}{\tilde{V}^{-1/3} - 1.0} \right) \right] \tag{8}$$

Thus on the basis of flory theory, surface tension of liquid mixture is given by the expression,

$$\sigma = \sigma^* \tilde{\sigma}(\tilde{V}) \tag{9}$$

The reduced equation of state derived from the resulting partition function is given by,

$$\frac{\tilde{P}\tilde{V}}{T} = \frac{\tilde{V}^{-1/3}}{\tilde{V}^{-1/3} - 1} - \frac{1}{\tilde{V}T} \tag{10}$$

The reduced quantities \tilde{P} , and \tilde{T} are given by,

$$\tilde{P} = \frac{P}{P^*} = \frac{2PV^*}{S\eta} \tag{11}$$

$$\tilde{T} = \frac{T}{T^*} = \frac{2V^* cKT}{S\eta} \quad (12)$$

$$\tilde{V} = \frac{V}{V^*} = \frac{V}{V^*} \quad (13)$$

Thus

$$P^* = cKT^* / V^* \quad (14)$$

where $V=rv$;is the molar volume. The isobar at zero pressure is;

$$T^* = -\frac{\tilde{T}\tilde{V}^{4/3}}{\tilde{V}^{1/3} - 1} \quad (16)$$

from which

$$\tilde{V} = \left[\frac{\alpha T}{(3 + 3\alpha T)} + 1 \right]^3 \quad (17)$$

where α is the thermal expansion coefficient at $p=0$ (or with out appreciable error at 1 atm. The temperature derivative of eq (11) at constant volume evaluated for $P=0$ gives,

$$P^* = \frac{\alpha}{\beta_T} T \tilde{V}^2 = \gamma T \tilde{V}^2 \quad (18)$$

where β_T and γ are the isothermal compressibility and the thermal pressure coefficient respectively. The quantities T^* , P^* , and V^* can be computed from α , β_T and V as prescribed by eq. (12) to (17).

The equation for excess molar volume according to Flory theory can be expressed as,

$$\tilde{V} - \tilde{V}_0 = V^E = \frac{V^E}{x_1 V_1^* + x_2 V_2^*} \quad (19)$$

The ideal reduced volume (\tilde{V}_0) is related to,

$$\tilde{V}_0 = \psi_1 V_1 + \psi_2 \tilde{V}_2 \quad (20)$$

and

$$V^E = (x_1 V_1^* + x_2 V_2^*) [\tilde{V} - (\psi_1 \tilde{V}_1 + \psi_2 \tilde{V}_2)] \quad (21)$$

All the notations used in the above equations have their usual significance as detailed out by Flory.

The excess surface tension can be expressed as,

$$\sigma^E = [\sigma_{cal} - \sigma_{idl}] \quad (22)$$

The characteristic and reduced parameters involved in the above equation have been evaluated from the knowledge of the reduced equation of state derived from the resulting partition function. The characteristic pressure of the mixture is given by,

$$P_{mix}^* = [\psi_1 P_1^* + \psi_2 P_2^* - (\psi_1 \theta_2 X_{12} + \psi_2 \theta_1 X_{21})] \quad (23)$$

where θ and ψ are the segment and the site fractions of their respective components and X_{ij} is the interaction parameters. The characteristic temperature of liquid mixture is expressed as

$$T_{mix}^* = \frac{P_{mix}^*}{\psi_1 P_1^* / T_1^* + \psi_2 P_2^* / T_2^*} \quad (24)$$

Assuming the volume fraction parameters of the liquid mixture to be linear in mole fraction of the component adopting familiar Berthelot relationship i.e. $\eta_{ij} = (\eta_{ii}\eta_{jj})^{1/2}$ for homopolar species, we have,

$$V_{mix}^* = x_1 V_1^* + x_2 V_2^* \quad (25)$$

and
$$\tilde{V}_{mix} = \frac{V_{mix}}{(x_1 V_1^* + x_2 V_2^*)} \quad (26)$$

where,
$$V_{mix} = \frac{M_1 x_1 + M_2 x_2}{\rho_{mix}} = \frac{M_{mix}}{\rho_{mix}} \quad (27)$$

The interaction parameter X_{12} , can be represented as,

$$x_{12} = P_1^* [1 - (P_2^* / P_1^*)^{1/2} (V_2^* / V_1^*)^{1/6}]^2 \quad (28)$$

For a spherical molecule, the segment and the site fraction of the binary liquid mixture is given by,

$$\psi_2 = \frac{x_2}{x_2 + x_1 (V_1^* / V_2^*)} \quad (29)$$

$$\psi_1 = [1 - \psi_2] \quad (30)$$

and site fraction
$$\theta_2 = \frac{\psi_2}{\psi_2 + \psi_1 (V_2^* / V_1^*)^{1/3}} \quad (31)$$

$$\theta_1 = [1 - \theta_2] \quad (32)$$

All the above equations have been used for the computation of surface tension of binary liquid mixture.

III. Figures and Tables

Table. 1 Parameters of Pure Components at 298.15 K.

| Liquids | $10^4 \alpha/K^{-1}$ | β_T/Tpa^{-1} | $V_m/cm^3 \cdot mol^{-1}$ | $\rho_{exp}/g \cdot cm^{-3}$ | $\rho_{lit}/g \cdot cm^{-3}$ | $\sigma_{exp}/m N \cdot m^{-1}$ | $\sigma_{lit}/m N \cdot m^{-1}$ |
|-------------------------------|----------------------|--------------------|---------------------------|------------------------------|------------------------------|---------------------------------|---------------------------------|
| 1,2,4- trimethylbenzene (TMB) | 11.168 | 81.445 | 137.893 | 0.8716 | 0.87174 ^a | 29.25 | 29.19 ^f |
| 1,3,5 trimethylbenzene (TMB) | 11.320 | 85.961 | 139.592 | 0.8610 | 0.86109 ^b | 28.09 | 27.54 ^f |
| Tetrahydrofurane (THF) | 11.464 | 90.440 | 81.752 | 0.8821 | 0.88197 ^c | 27.04 | 26.50 ^f |
| Tetrachloromethane (TCM) | 11.504 | 91.704 | 97.121 | 1.5838 | 1.58429 ^d | 26.76 | 26.43 ^f |
| Dimethylsulfoxide (DMSO) | 9.8922 | 50.134 | 71.316 | 1.0955 | 1.095560 ^e | 42.09 | 42.86 ^f |

^aref. 15 , ^bref. 16 , ^cref 17 , ^dref. 18 , ^eref. 19 , ^fref. 20

Table. 2 Density (ρ_m), Experimental and Theoretical Excess Molar Volume (V_{exp}^E & V_{theo}^E), Experimental and Theoretical Surface Tension (σ_{exp} & σ_{theo}) . Excess Theoretical Surface Tension (σ_{theo}^E) and Percent Deviation ($\% \Delta \sigma$) at 298.15 K for xTHF+ (1-x) 1,2,4-TMB

| x_1 | $\rho_m/g \cdot cm^{-3}$ | $V_{exp}^E/cm^3 \cdot mol^{-1}$ | $V_{theo}^E/cm^3 \cdot mol^{-1}$ | $\sigma_{exp}/m N \cdot m^{-1}$ | $\sigma_{theo}/m N \cdot m^{-1}$ | $\sigma_{theo}^E/m N \cdot m^{-1}$ | $\% \Delta \sigma/m N \cdot m^{-1}$ |
|--------|--------------------------|---------------------------------|----------------------------------|---------------------------------|----------------------------------|------------------------------------|-------------------------------------|
| 0.0988 | 0.8727 | -0.068 | 0.037 | 29.11 | 28.94 | -0.0149 | 0.585 |
| 0.2018 | 0.8737 | -0.106 | 0.070 | 29.00 | 28.73 | -0.0301 | 0.946 |
| 0.3003 | 0.8748 | -0.133 | 0.095 | 28.88 | 28.52 | -0.0438 | 1.240 |
| 0.3995 | 0.8758 | -0.156 | 0.113 | 28.73 | 28.32 | -0.0560 | 1.433 |
| 0.5002 | 0.8769 | -0.165 | 0.122 | 28.53 | 28.11 | -0.0656 | 1.458 |
| 0.6005 | 0.8779 | -0.159 | 0.123 | 28.29 | 27.92 | -0.0711 | 1.325 |

| | | | | | | | |
|--------|--------|---------|-------|-------|-------|---------|--------|
| 0.6986 | 0.8789 | -0.132 | 0.113 | 28.01 | 27.73 | -0.0705 | 1.013 |
| 0.7996 | 0.8800 | -0.0103 | 0.090 | 27.68 | 27.54 | -0.0612 | 0.504 |
| 0.9006 | 0.8810 | -0.042 | 0.053 | 27.34 | 27.37 | -0.0393 | -0.101 |

Table. 3 Density (ρ_m), Experimental and Theoretical Excess Molar Volume (V_{exp}^E & V_{theo}^E), Experimental and Theoretical Surface Tension (σ_{exp} & σ_{theo}) . Excess Theoretical Surface Tension (σ_{theo}^E) and Percent Deviation ($\% \Delta \sigma$) at 298.15 K for xTHF+ (1-x) 1,3,5-TMB

| x_1 | $\rho_m / \text{g.cm}^{-3}$ | $V_{\text{exp}}^E / \text{cm}^3 \cdot \text{mol}^{-1}$ | $V_{\text{theo}}^E / \text{cm}^3 \cdot \text{mol}^{-1}$ | $\sigma_{\text{exp}} / \text{mN.m}^{-1}$ | $\sigma_{\text{theo}} / \text{m N.m}^{-1}$ | $\sigma_{\text{theo}}^E / \text{m N.m}^{-1}$ | $\% \Delta \sigma / \text{m N.m}^{-1}$ |
|--------|-----------------------------|--|---|--|--|--|--|
| 0.1006 | 0.8631 | 0.003 | 0.0151 | 27.88 | 28.08 | -0.008 | -0.726 |
| 0.2021 | 0.8653 | 0.007 | 0.0563 | 27.72 | 27.92 | -0.032 | -0.710 |
| 0.3501 | 0.8684 | 0.013 | 0.0761 | 27.57 | 27.81 | -0.046 | -0.881 |
| 0.4000 | 0.8694 | 0.015 | 0.0904 | 27.44 | 27.71 | -0.057 | -0.981 |
| 0.5004 | 0.8716 | 0.018 | 0.0980 | 27.32 | 27.61 | -0.066 | -1.055 |
| 0.6010 | 0.8737 | 0.02 | 0.0980 | 27.23 | 27.51 | -0.071 | -1.032 |
| 0.7003 | 0.8758 | 0.019 | 0.0895 | 27.15 | 27.42 | -0.069 | -0.999 |
| 0.7989 | 0.8778 | 0.015 | 0.0717 | 27.09 | 27.34 | -0.059 | -0.925 |
| 0.9000 | 0.8800 | 0.008 | 0.0421 | 27.06 | 27.27 | -0.038 | -0.773 |

Table. 4 Density (ρ_m), Experimental and Theoretical Excess Molar Volume (V_{exp}^E & V_{theo}^E), Experimental and Theoretical Surface Tension (σ_{exp} & σ_{theo}) . Excess Theoretical Surface Tension (σ_{theo}^E) and Percent Deviation ($\% \Delta \sigma$) at 298.15 K for xTCM+ (1-x) 1,2,4-TMB

| x_1 | $\rho_m / \text{g.cm}^{-3}$ | $V_{\text{exp}}^E / \text{cm}^3 \cdot \text{mol}^{-1}$ | $V_{\text{theo}}^E / \text{cm}^3 \cdot \text{mol}^{-1}$ | $\sigma_{\text{exp}} / \text{mN.m}^{-1}$ | $\sigma_{\text{theo}} / \text{m N.m}^{-1}$ | $\sigma_{\text{theo}}^E / \text{m N.m}^{-1}$ | $\% \Delta \sigma / \text{m N.m}^{-1}$ |
|--------|-----------------------------|--|---|--|--|--|--|
| 0.0496 | 0.9069 | 0.055 | 0.013 | 29.13 | 29.03 | -0.0046 | 0.334 |
| 0.0996 | 0.9426 | 0.104 | 0.026 | 29.04 | 28.92 | -0.0091 | 0.415 |
| 0.1986 | 1.0131 | 0.208 | 0.050 | 28.89 | 28.70 | -0.0175 | 0.673 |
| 0.3001 | 1.0854 | 0.289 | 0.070 | 28.72 | 28.47 | -0.0251 | 0.881 |
| 0.4006 | 1.1569 | 0.359 | 0.086 | 28.50 | 28.24 | -0.0313 | 0.905 |
| 0.5987 | 1.2980 | 0.369 | 0.098 | 28.24 | 27.81 | -0.0373 | 1.540 |
| 0.6986 | 1.3692 | 0.309 | 0.093 | 27.89 | 27.59 | -0.0358 | 1.079 |
| 0.7985 | 1.4403 | 0.231 | 0.076 | 27.54 | 27.38 | -0.0301 | 0.590 |
| 0.9011 | 1.5134 | 0.121 | 0.046 | 27.13 | 27.17 | -0.0184 | -0.132 |

Table. 5 Density (ρ_m), Experimental and Theoretical Excess Molar Volume (V_{exp}^E & V_{theo}^E), Experimental and Theoretical Surface Tension (σ_{exp} & σ_{theo}) . Excess Theoretical Surface Tension (σ_{theo}^E) and Percent Deviation ($\% \Delta \sigma$) at 298.15 K for xTCM+ (1-x)1,3,5-TMB

| x_1 | $\rho_m / \text{g.cm}^{-3}$ | $V_{exp}^E / \text{cm}^3 \cdot \text{mol}^{-1}$ | $V_{theo}^E / \text{cm}^3 \cdot \text{mol}^{-1}$ | $\sigma_{exp} / \text{mN.m}^{-1}$ | $\sigma_{theo} / \text{m N.m}^{-1}$ | $\sigma_{theo}^E / \text{m N.m}^{-1}$ | $\% \Delta \sigma / \text{m N.m}^{-1}$ |
|--------|-----------------------------|---|--|-----------------------------------|-------------------------------------|---------------------------------------|--|
| 0.1009 | 0.9340 | 0.195 | 0.086 | 27.77 | 27.96 | -0.061 | -0.669 |
| 0.2014 | 1.0066 | 0.351 | 0.157 | 27.53 | 27.78 | -0.115 | -0.924 |
| 0.2994 | 1.0774 | 0.461 | 0.211 | 27.29 | 27.63 | -0.160 | -1.229 |
| 0.4007 | 1.1506 | 0.505 | 0.250 | 27.10 | 27.47 | -0.196 | -1.371 |
| 0.4998 | 1.2223 | 0.497 | 0.270 | 26.99 | 27.33 | -0.218 | -1.273 |
| 0.5995 | 1.2943 | 0.441 | 0.269 | 26.91 | 27.21 | -0.225 | -1.117 |
| 0.6988 | 1.3661 | 0.354 | 0.244 | 26.86 | 27.11 | -0.213 | -0.922 |
| 0.797 | 1.4371 | 0.257 | 0.195 | 26.83 | 27.03 | -0.176 | -0.742 |
| 0.9012 | 1.5124 | 0.145 | 0.112 | 26.81 | 26.98 | -0.106 | -0.628 |

Table. 6 Density (ρ_m), Experimental and Theoretical Excess Molar Volume (V_{exp}^E & V_{theo}^E), Experimental and Theoretical Surface Tension (σ_{exp} & σ_{theo}) . Excess Theoretical Surface Tension (σ_{theo}^E) and Percent Deviation ($\% \Delta \sigma$) at 298.15 K for xDMSO + (1-x)1,2,4-TMB

| x_1 | $\rho_m / \text{g.cm}^{-3}$ | $V_{exp}^E / \text{cm}^3 \cdot \text{mol}^{-1}$ | $V_{theo}^E / \text{cm}^3 \cdot \text{mol}^{-1}$ | $\sigma_{exp} / \text{mN.m}^{-1}$ | $\sigma_{theo} / \text{m N.m}^{-1}$ | $\sigma_{theo}^E / \text{m N.m}^{-1}$ | $\% \Delta \sigma / \text{m N.m}^{-1}$ |
|--------|-----------------------------|---|--|-----------------------------------|-------------------------------------|---------------------------------------|--|
| 0.1007 | 0.8942 | -0.066 | -0.051 | 28.48 | 28.25 | -1.990 | 0.802 |
| 0.2007 | 0.9166 | -0.128 | -0.093 | 28.77 | 28.14 | -3.191 | 2.192 |
| 0.3007 | 0.9390 | -0.163 | -0.125 | 28.81 | 28.23 | -4.190 | 2.015 |
| 0.3995 | 0.9611 | -0.184 | -0.147 | 29.10 | 28.60 | -4.897 | 1.724 |
| 0.501 | 0.9838 | -0.183 | -0.158 | 29.46 | 29.48 | -5.121 | -0.064 |
| 0.6012 | 1.0062 | -0.161 | -0.157 | 29.34 | 30.58 | -5.109 | -4.233 |
| 0.6992 | 1.0282 | -0.125 | -0.142 | 29.35 | 31.96 | -4.801 | -8.880 |
| 0.7992 | 1.0506 | -0.083 | -0.112 | 30.04 | 33.83 | -4.015 | -12.622 |
| 0.9013 | 1.0734 | -0.041 | -0.065 | 35.71 | 36.57 | -2.384 | -2.420 |

Table. 7 Density (ρ_m), Experimental and Theoretical Excess Molar Volume (V_{exp}^E & V_{theo}^E), Experimental and Theoretical Surface Tension (σ_{exp} & σ_{theo}) . Excess Theoretical Surface Tension (σ_{theo}^E) and Percent Deviation ($\% \Delta \sigma$) at 298.15 K for xDMSO+ (1-x)1,3,5-TMB

| x_1 | $\rho_m / \text{g.cm}^{-3}$ | $V_{exp}^E / \text{cm}^3 \cdot \text{mol}^{-1}$ | $V_{theo}^E / \text{cm}^3 \cdot \text{mol}^{-1}$ | $\sigma_{exp} / \text{mN.m}^{-1}$ | $\sigma_{theo} / \text{m N.m}^{-1}$ | $\sigma_{theo}^E / \text{m N.m}^{-1}$ | $\% \Delta \sigma / \text{m N.m}^{-1}$ |
|--------|-----------------------------|---|--|-----------------------------------|-------------------------------------|---------------------------------------|--|
| 0.1023 | 0.8850 | 0.047 | -0.061 | 27.30 | 27.554 | -1.798 | -0.929 |
| 0.1987 | 0.9076 | 0.084 | -0.109 | 26.92 | 27.556 | -2.942 | -2.363 |
| 0.3027 | 0.9320 | 0.108 | -0.149 | 26.70 | 28.076 | -3.660 | -5.154 |

| | | | | | | | |
|--------|--------|-------|--------|-------|--------|--------|--------|
| 0.401 | 0.9551 | 0.122 | -0.174 | 27.41 | 28.799 | -4.107 | -5.067 |
| 0.4999 | 0.9783 | 0.121 | -0.187 | 28.40 | 29.912 | -4.171 | -5.322 |
| 0.6003 | 1.0018 | 0.107 | -0.185 | 30.09 | 31.157 | -4.120 | -3.545 |
| 0.699 | 1.0250 | 0.086 | -0.168 | 32.05 | 32.732 | -3.719 | -2.128 |
| 0.8003 | 1.0487 | 0.063 | -0.132 | 34.77 | 34.799 | -2.857 | -0.084 |
| 0.8998 | 1.0720 | 0.032 | -0.077 | 37.92 | 37.155 | -1.685 | 2.017 |

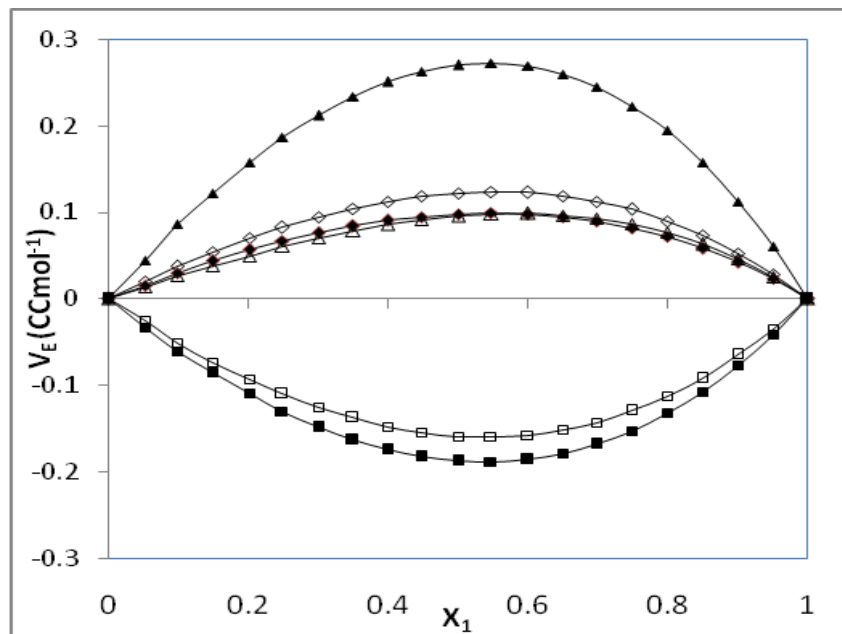


Figure 1 excess molar volume, V^E Δ , for x THF+(1-x) 1,2,4 TMB, \blacktriangle , x THF+(1-x) 1,3,5 TMB, \diamond , x TCM+(1-x) 1,2,4 TMB, \blacklozenge , x TCM+(1-x) 1,3,5 TMB, \square , x DMSO+(1-x) 1,2,4 TMB, \blacksquare , x DMSO+(1-x) 1,3,5 TMB at 298.15 K.

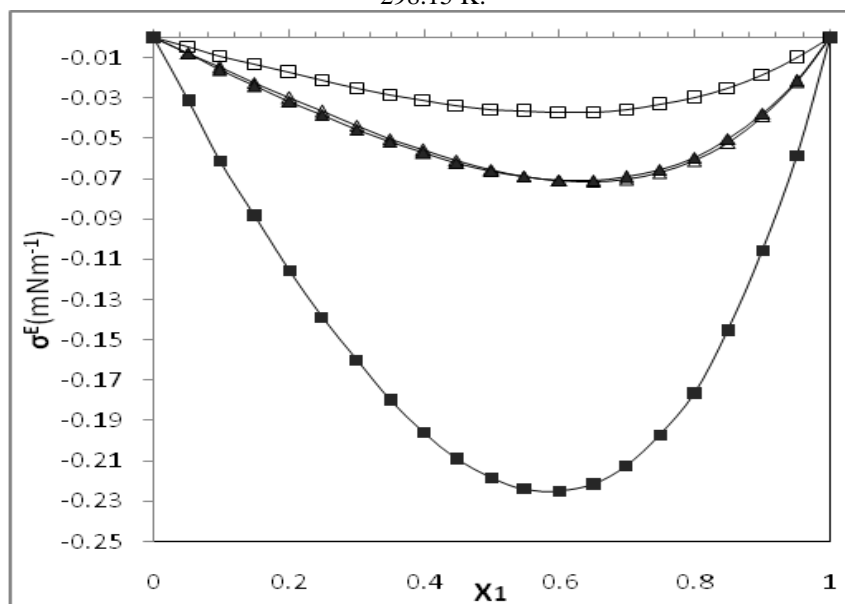


Figure 2 excess surface tension σ^E Δ , for x THF+(1-x) 1,2,4 TMB, \blacktriangle , x THF+(1-x) 1,3,5 TMB, \diamond , x TCM+(1-x) 1,2,4 TMB, \blacklozenge , x TCM+(1-x) 1,3,5 TMB at 298.15 K.

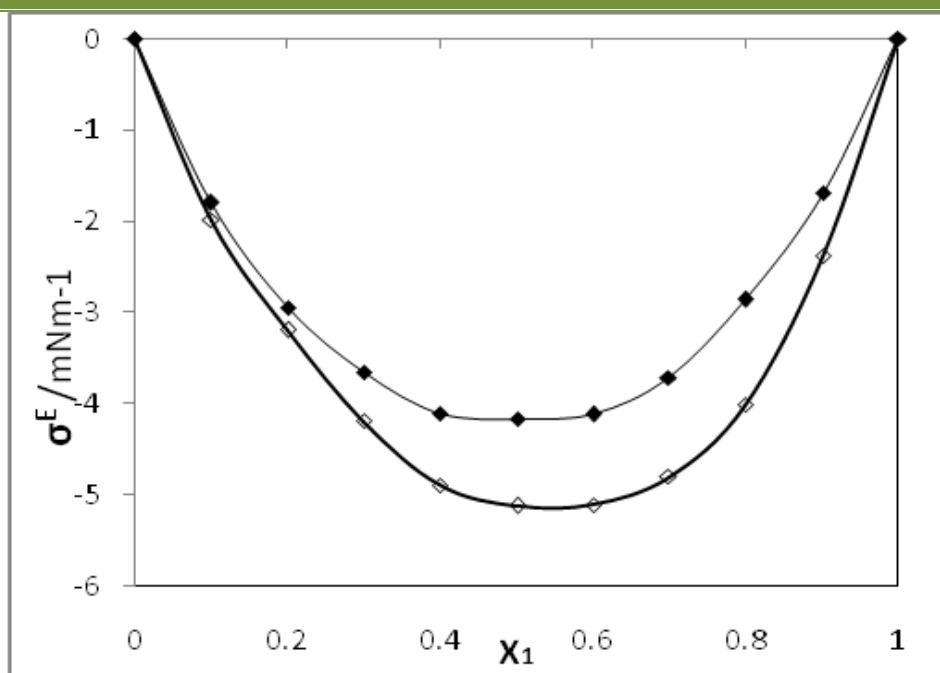


Figure 3 excess surface tension σ^E , \diamond , x DMSO+(1-x) 1,2,4 TMB, \blacklozenge , x DMSO+(1-x) 1,3,5 TMB at 298.15 K.

IV. Results and Discussion

Surface tension, excess surface tension and excess molar volume for six cyclic polar-non polar liquid mixtures namely [1] (tetrahydrofuran (THF)+ 1,2,4- trimethyl benzene (TMB), [2] tetrahydrofuran(THF) + 1,3,5- trimethyl benzene(TMB), [3] tetrachloromethane(TCM) +1,2,4- trimethyl benzene(TMB), [4] tetrachloromethane(TCM) +1,3,5- trimethyl benzene(TMB), [5] dimethyl solfoxide(DMSO) + 1,2,4- trimethyl benzene(TMB) and [6] dimethyl solfoxide (DMSO)+ 1,3,5- trimethyl benzene(TMB), have been predicted over the whole composition range at 298.15 K. All the measured data needed for computation have been taken from the experimental work of P.Chuanrong et.al. [7]. The theoretical results obtained are in good agreement both in magnitude and sign as compared with the experiment. Values of excess molar volume (V^E) are listed in TABLES 2-7 and graphically presented in Fig.1. TABLES 2-7 also list the surface tension and excess surface tension (σ^E) for six binary mixtures (THF+1,2,4 TMB, THF+ 1,3,5 TMB, TCM+ 1,2,4 TMB, TCM+1,3,5 TMB, at 298.15 K) and graphically presented in Fig. 2. Fig.3 presents the excess surface tension data for DMSO+1,2,4 TMB and DMSO+1,3,5 TMB. Parameters of pure component liquids are presented in TABLE 1.

A careful look on the Fig.1 shows that the values of excess molar volume for THF+1,2,4 TMB, THF+1,3,5 TMB, TCM+ 1,2,4 TMB and TCM+1,3,5 TMB are positive and negative for DMSO+1,2,4 TMB and DMSO+1,3,5 TMB respectively. Figs.2&3 show that the values of excess surface tension (σ^E) for all the six binary mixture are negative. The magnitude of both the theoretical values (V^E & σ^E) for all the binary mixtures except DMSO are very close to experimental findings indicating that all the binary mixtures are weak interacting, although they are polar in nature up to some extent.

The V^E values for THF and TCM are small positive and σ^E values for all the liquid components are negative. The possible reason may be that there are no strong intermolecular forces between them because 1, 3, 5 TMB is a symmetrical non-polar molecule conversely, a little stronger forces will exist with the 1, 2, 4 TMB because 1, 2, 4 TMB is weakly polar symmetrical molecule, so the values are negative. Negative values of σ^E can be explained on the basis of dipolar-dipolar interactions. During mixing, structure of the component liquid changes, possibly owing to the packing effect hence positive values of V^E are observed.

Gibbs enrichment of a mixture surface by the component of lower surface tension is well known. The normal results show a lowering of mixture surface tension, which results in a negative deviation from a linear function of bulk mole fraction. The minimum percent deviation ($\% \Delta \sigma$) is found to be -0.064 and maximum percent deviation is found to be -12.22 for the system DMSO+1, 2, 4 TMB.

Flory theory was derived for γ -meric spherical non-polar chain molecule but its applicability to cyclic non-polar-polar liquid mixtures have been carried out successfully. Conclusively, it can be stated that PFP model can be suitable for any system having weak interacting liquids irrespective of the structural orientations.

V. Conclusion

In many technological areas, prediction of surface tension and excess molar volume plays important role to study the thermodynamic state and internal structure of molecules. In the present work six polar-non polar cyclic liquid binary mixtures were theoretically studied from the experimental work of P. Chuanrong et al. It is observed that theoretical results are much consistent with the experimental findings. Furthermore, excess thermodynamic properties (excess molar volume, V^E , and excess surface tension, σ^E) have also been studied and predicted the nature and extent of molecular interactions involved in liquid mixtures. Negative and Positive deviations in the values of V^E and σ^E are explained on the basis of dipolar-dipolar interaction and packing effect.

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