

Excess Molar Volume of Ternary Liquid Mixture at Temperature 298.15 K

Manish Tiwari¹, Ghan Shyam Gupta¹, V. K.Pandey² and Rajeev K.Shukla^{3*}

¹*Department of Physical Science, Faculty of Science & Environment,
M.G.C.G. Vishwavidyalaya, Chitrakoot, Satna, India*

²*Department of Chemistry DBS College, Kanpur, India*

³*Department of Chemistry VSSD College, Kanpur-208002, India
email* rkshuklavssd@gmail.com*

Abstract- Densities were measured for some oxygenated ternary system at 298.15K and atmospheric pressure and further compared with the theoretical results obtained from two models (Bertrand- Acree- Bruchfield and Flory). The properties were fitted to the Redlich-Kister polynomial equation to estimate the binary coefficients and standard errors. The excess volume was computed to study the nature and extent of the molecular interactions in the ternary mixtures. Testing of the models for the ternary system showed that a fair agreement is achieved between experimental and theoretical results when they are compared. Conclusively, both theoretical models were consistent with the experimental results.

Index Terms -Bertrand- Acree-Bruchfield , Excess volume, Flory model , Redlich-Kisterand Ternary liquid mixture

1. INTRODUCTION

The studies of excess thermodynamic properties are of considerable interest in understanding the intermolecular interactions in liquid mixtures. The practical importance of liquid mixtures rather than single component liquid systems, has gained much importance during the last two decades in assessing the nature of molecular interactions and investigating the physico-chemical behavior of systems. Thermodynamic investigation of liquid mixtures consisting of polar and non-polar components is considerable importance in understanding intermolecular interactions between the component molecules. Knowledge of excess volume is very useful in predicting the behaviour of attraction forces in liquid mixtures. Excess volume of binary mixtures has been experimentally determined by various workers[1-3]. But for many practical purposes it is necessary to predict the properties of multi component liquid mixtures from the properties of pure components and from the data of binary systems. Marsh[4] outlined the techniques for measuring the excess functions of liquid mixtures as well as properties of the aliphatic hydrocarbons and complex organic mixtures in terms of various equation of state, interaction parameters and chemical equilibrium. Rastogi[5] independently reviewed the thermodynamic properties of ternary mixtures and their molecular interactions. Lark[6] et al developed a new batch dilatometer and determined the ternary volume effect. The

experimental excess molar volumes were compared with the predictions obtained using the Flory[7-8] and these models were found to describe, in a qualitative way, the variation of the magnitude of the excess molar volume with the length of alkanol chain. A critical review of various properties of multi component systems has been given by Rowlinson & Swinton[9]. In most of the theories, properties of the multi component system are determined with the help of the properties of their binaries[10-11] but only Flory's statistical theory[7-8]¹⁵⁻¹⁶ can be successfully utilized to predict the properties of the multi component system from those of the pure components. Most of the work on excess volume for binary systems has been carried out by Mc Glasson[12], Patterson[13-14], Benson[15], Street[16]. For these reasons, we measured densities of ternary and binary mixtures of tetrahydrofuran, 2-propanol, and 2,2,4-trimethylpentane at temperature 298.15 K and atmospheric pressure. Present study involves the theoretical study (using the predictive model of Bertrand- Acree-Bruchfield and Flory theory), of excess volume for ternary liquid mixtures: Tetrahydrofuran + 2-Propanol + 2,2,4-Trimethyl pentane and their contributory binaries: Tetrahydrofuran + 2-Propanol), Tetrahydrofuran + 2,2,4-Trimethyl pentane and 2-Propanol + 2,2,4-Trimethyl pentane binary systems. The values of excess volumes, V^E were evaluated and fitted to the Redlich-Kister polynomial[17] to derive the binary coefficients and standard errors. Some

oxygenated compounds are usually added to gasoline to improve the octane number and reduce pollution. The present work is concerned with the oxygenated compounds of the type either cyclic ether or aliphatic alcohol and the

alkenes liquid that generally appears in gasoline. From the viewpoint of association, cyclic ethers can be regarded as an intermediate case between alkanes (inert compounds) and alkanols (highly self-associated compounds).

2. THEORETICAL

2.1 Flory theory

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

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

where, \tilde{P} , \tilde{v} and \tilde{T} are the reduced parameters of the pressure volume and temperature respectively which are given by

$$\tilde{P} = \frac{P}{P^*} = \frac{2Pv^{*2}}{S\eta}, \quad \tilde{T} = \frac{T}{T^*} = \frac{2v^*CKT}{S\eta}, \tag{2}$$

$$\tilde{v} = \frac{v}{v^*} = \frac{V}{V^*} \tag{2}$$

The reduced equation of state at zero pressure is;

$$V^{1/3} = \left[\frac{\alpha T}{3(1 + \alpha T)} + 1 \right] \tag{3}$$

where $V=rv$ is the molar volume and α is the coefficient of thermal expansion at $P=0$. Thus the reduced and characteristic volumes and temperatures can be computed with the help of the experimental value of α , using Eq.(2) and (3).

In the light of above relations, the excess volume of ternary liquid mixture can be obtained by the equation as;

$$\tilde{v} - \tilde{v}_0 = v^E = \frac{v^E}{x_1v_1^* + x_2v_2^* + x_3v_3^*} \tag{4}$$

where \tilde{v}_0 is the ideal reduce volume and it is given as

$$\tilde{v}_0 = \psi_1 \tilde{v}_1 + \psi_2 \tilde{v}_2 + \psi_3 \tilde{v}_3 \tag{5}$$

substitution of Eq.(5) in eq.(4) directly gives the excess volume of ternary system with slight rearrangement which can be represented as

$$V^E = (x_1v_1^* + x_2v_2^* + x_3v_3^*)[\tilde{v} - (\psi_1 \tilde{v}_1 + \psi_2 \tilde{v}_2 + \psi_3 \tilde{v}_3)] \tag{6}$$

where V^E is the excess molar volume and \tilde{v} is the reduced volume of the ternary liquid mixtures which is given on assuming that the volume reduction parameters of the ternary mixtures to be linear in mole fraction as;

$$\tilde{v} = \frac{V}{x_1v_1^* + x_2v_2^* + x_3v_3^*}, \tag{7}$$

$$V = \frac{M_1x_1 + M_2x_2 + M_3x_3}{\rho_m} \tag{7}$$

The above mentioned equation have been utilized for the computation of excess volume of ternary liquid mixtures. Pandey et al [18] have formulated the equations for characteristic pressure and reduced temperature of mixture which are as below;

$$\tilde{T} = T/T^* = \frac{T}{P^* / (\frac{\psi_1 P_1^*}{T_1^*} + \frac{\psi_2 P_2^*}{T_2^*} + \frac{\psi_3 P_3^*}{T_3^*})} \tag{8}$$

where P^* is the characteristic pressure of ternary system and can be expressed as ;

$$P^* = [\psi_1 P_1^* + \psi_2 P_2^* + \psi_3 P_3^* - (\psi_1 \theta_2 X_{12} + \psi_2 \theta_3 X_{23} + \psi_3 \theta_1 X_{31})] \tag{9}$$

Here X_{12} , X_{23} , X_{31} are the interaction parameters which have been computed on using the following equations by adopting familiar Berthelot relationship i.e. $\eta_{ij} = (\eta_{ii} \eta_{jj})^{1/2}$.

The application of above relation makes it possible to predict the excess volume, using V^E as a second approach of Flory theory to evaluate the volume of mixing in the multi component liquid mixture.

2.2 Bertrand-Acree-Bruchfield Model:

Bertrand, Acree and Coworkers[10-11] have developed a predictive equation, based on a model ternary system for the studies of the thermo-chemical properties of solute in simple binary solvents. This equation obeys the general mixing equation,

$$\Delta Z_{123}^{ex} = (n_1\Gamma_1 + n_2\Gamma_2 + n_3\Gamma_3)^{-1} (n_1\Gamma_1 n_2\Gamma_2 A_{12} + n_1\Gamma_1 n_3\Gamma_3 A_{13} + n_2\Gamma_2 n_3\Gamma_3 A_{23}) \quad (10)$$

where Z_{ij} represents any extensive thermodynamic property described in the terms of interaction parameters A_{ij} and weighting factors Γ_i . This equation leads to a very good predictive form, for combining the properties of binary systems. Review of Eq. (10) reveals that for systems obeying this equation, the properties of the contributing binary systems would obey (per mole of ternary solution) the following equation:

$$\Delta Z_{ij}^{-ex} = X_i^* X_j^* \Gamma_i \Gamma_j A_{ij} / (X_i^* \Gamma_i + X_j^* \Gamma_j) \quad (11)$$

But these can be evaluated only in a relative sense (Γ_i/Γ_j) rather than absolutely. However a method for the calculation of the ratio of raw weighting factors has been given by Bertrand et al¹⁸. Here ratio is calculated for each binary combination of the components of the multi component system, which are then combined to normalize the weighting factors to an average value of 100 b

$$\Gamma_i = (100/N) [(\Gamma_1^{raw} / \Gamma_i^{raw}) + (\Gamma_2^{raw} / \Gamma_i^{raw}) + \dots + (\Gamma_N^{raw} / \Gamma_i^{raw})] \quad (12)$$

These calculations become meaningless if, the ratio of raw weighting factors calculated has a negative value, or an abnormally high or low value, and in such cases molar volumes for weighting factors have to be used. In such cases, weighted mole fractions become equivalent to volume fraction. If we reasonably modify this approach in the light of the above findings then $\phi_1, \phi_2 \dots \phi_n$ can be used in the place of weighted mole fractions, and the equations takes up the following form:

$$\Delta Z_{12\dots N}^E = \sum_{i=1}^N \sum_{j>1}^N (X_i + X_j)(\phi_i + \phi_j)(\Delta Z_{ij}^E) \quad (13)$$

Where X_i and X_j are the mole fractions of multi component system, and ϕ_i and ϕ_j are their respective volume fractions and (ΔZ_{ij}^E) can be more appropriately taken as the experimental excess property of the constituent binary combinations at the same molar ratio of the components as in the multi component system.

In the subsequent studies Eq. (10) has been employed to determine the excess volume of ternary system, for which Eq.(13) takes the following form:

$$\Delta V_{123}^E = \sum_{i=1}^3 \sum_{j>1}^3 (X_i + X_j)(\phi_i + \phi_j)(\Delta V_{ij}^E) \quad (14)$$

Results so obtained were compared with the experimental findings, and with the results of Flory theory which utilize the properties of single components to predict the thermodynamic properties of multi component liquid mixtures.

3. TABLES AND FIGURES

Table. 1: Thermal expansion coefficient(α), isothermal compressibility (β_T), molar volume(V), densities (ρ) and viscosities(η) of pure components for comparisons at 298.15

| Components | $10^4 \alpha / K^{-1}$ | β_T / TPa^{-1} | $V_m / cm^3 mol^{-1}$ | $\rho / g.cm^{-3}$ | |
|-------------------------|------------------------|----------------------|-----------------------|--------------------|--------------------|
| | | | | Exp | Lit* ¹⁸ |
| tetrahydrofuran | 11.4643 | 90.4397 | 81.75 | 0.88237 | 0.8829 |
| 2-propanol | 10.4832 | 96.1425 | 76.50 | 0.78116 | 0.7812 |
| 2,2,4-trimethyl pentane | 10.8773 | 101.1729 | 166.44 | 0.68795 | 0.6878 |

Table 2. Binary coefficients of the Redlich–Kister Equation and standard deviations ($\Delta\delta$) of V^E for the binary systems at 298.15 K

| | A0 | A1 | A2 | A3 | $\Delta\delta$ |
|-----------------------------|--------|--------|--------|---------|----------------|
| $V^E / cm^3 \cdot mol^{-1}$ | 0.7547 | 0.1712 | 0.0644 | -0.0072 | 0.0012 |

Tetrahydrofuran + 2-Propanol

| | | | | | |
|---|--|---------|--------|--------|--------|
| | Tetrahydrofuran + 2,2,4-Trimethylpentane | | | | |
| $v^E / \text{cm}^3 \cdot \text{mol}^{-1}$ | 0.4766 | -0.5690 | 0.1754 | 0.3050 | 0.0018 |
| | 2-Propanol + 2,2,4-Trimethylpentane | | | | |
| $v^E / \text{cm}^3 \cdot \text{mol}^{-1}$ | 2.1563 | -0.9141 | 0.1610 | 0.2627 | 0.0029 |

Table 3. Experimental densities (ρ_{exp}) excess molar volume (v^E) and theoretical excess molar volume (v^E_{Flory}) for binary mixtures at 298.15 K

| x_1 | $\rho_{\text{exp/g.cm}^{-3}}$ | v^E $\text{cm}^3 \text{mole}^{-1}$ | $v^E_{\text{Flory/}}$ $\text{cm}^3 \text{mole}^{-1}$ | x_1 | $\rho_{\text{exp/g.cm}^{-3}}$ | v^E $\text{cm}^3 \text{mole}^{-1}$ | $v^E_{\text{Flory/}}$ $\text{cm}^3 \text{mole}^{-1}$ |
|---|-------------------------------|---|---|--|-------------------------------|---|---|
| Tetrahydrofuran + 2-Propanol | | | | 0.6000 | 0.6000 | 0.090 | 0.086 |
| 0.0500 | 0.7863 | 0.020 | 0.024 | 0.6500 | 0.6500 | 0.075 | 0.071 |
| 0.1000 | 0.7913 | 0.048 | 0.054 | 0.7000 | 0.7000 | 0.063 | 0.059 |
| 0.1500 | 0.7963 | 0.077 | 0.081 | 0.7500 | 0.7500 | 0.051 | 0.047 |
| 0.2001 | 0.8013 | 0.103 | 0.107 | 0.8000 | 0.8000 | 0.040 | 0.038 |
| 0.2500 | 0.8063 | 0.124 | 0.129 | 0.8500 | 0.8500 | 0.029 | 0.026 |
| 0.3000 | 0.8113 | 0.144 | 0.153 | 0.9000 | 0.9000 | 0.018 | 0.016 |
| 0.3500 | 0.8163 | 0.159 | 0.167 | 0.9500 | 0.9500 | 0.011 | 0.007 |
| 0.4000 | 0.8213 | 0.173 | 0.180 | 2-Propanol + 2,2,4-Trimethylpentane | | | |
| 0.4500 | 0.8263 | 0.184 | 0.189 | 0.0500 | 0.6808 | 0.190 | 0.193 |
| 0.5000 | 0.8312 | 0.191 | 0.201 | 0.1000 | 0.6825 | 0.314 | 0.325 |
| 0.5500 | 0.5500 | 0.191 | 0.200 | 0.1501 | 0.6845 | 0.395 | 0.411 |
| 0.6000 | 0.6000 | 0.189 | 0.193 | 0.2000 | 0.6867 | 0.456 | 0.471 |
| 0.6500 | 0.6500 | 0.183 | 0.189 | 0.2500 | 0.6891 | 0.506 | 0.526 |
| 0.7000 | 0.7000 | 0.172 | 0.180 | 0.3000 | 0.6918 | 0.542 | 0.555 |
| 0.7500 | 0.7500 | 0.157 | 0.164 | 0.3500 | 0.6948 | 0.559 | 0.567 |
| 0.8000 | 0.8000 | 0.134 | 0.138 | 0.4000 | 0.6980 | 0.562 | 0.572 |
| 0.8500 | 0.8500 | 0.107 | 0.112 | 0.4500 | 0.7015 | 0.554 | 0.562 |
| 0.9000 | 0.9000 | 0.071 | 0.086 | 0.5000 | 0.7053 | 0.535 | 0.542 |
| 0.9500 | 0.9500 | 0.035 | 0.041 | 0.5500 | 0.7095 | 0.511 | 0.522 |
| Tetrahydrofuran + 2,2,4-Trimethylpentane | | | | 0.6000 | 0.7140 | 0.479 | 0.484 |
| 0.0500 | 0.6926 | 0.026 | 0.022 | 0.6500 | 0.7191 | 0.436 | 0.446 |
| 0.1001 | 0.6977 | 0.041 | 0.038 | 0.7000 | 0.7246 | 0.388 | 0.393 |
| 0.1500 | 0.7030 | 0.076 | 0.071 | 0.7500 | 0.7307 | 0.332 | 0.339 |
| 0.2000 | 0.7086 | 0.102 | 0.099 | 0.8000 | 0.7374 | 0.276 | 0.282 |
| 0.2500 | 0.7146 | 0.123 | 0.117 | 0.8500 | 0.7448 | 0.211 | 0.222 |
| 0.3000 | 0.7210 | 0.143 | 0.141 | 0.9000 | 0.7530 | 0.147 | 0.152 |
| 0.3500 | 0.7278 | 0.152 | 0.149 | 0.9500 | 0.7622 | 0.071 | 0.084 |
| 0.4000 | 0.7351 | 0.151 | 0.150 | | | | |
| 0.4500 | 0.7430 | 0.144 | 0.141 | | | | |
| 0.5000 | 0.7513 | 0.132 | 0.127 | | | | |
| 0.5500 | 0.5500 | 0.104 | 0.101 | | | | |

Table 4. Experimental densities (ρ_{exp}) excess molar volume (v^E) and theoretical excess molar volumes (v^E_{Flory} v^E_{BOB}) for the Tetrahydrofuran + 2-Propanol + 2,2,4-Trimethylpentane at 298.15 K

| x_1 | x_2 | ρ | v^E cm^3mole^{-1} | v^E_{Flory} cm^3mole^{-1} | v^E_{BAB} cm^3mole^{-1} |
|--------|--------|--------|--------------------------|----------------------------------|--------------------------------|
| 0.0500 | 0.9000 | 0.7758 | 0.104 | 0.114 | 0.099 |
| 0.0501 | 0.7999 | 0.7580 | 0.242 | 0.262 | 0.237 |
| 0.0500 | 0.7000 | 0.7436 | 0.382 | 0.401 | 0.376 |
| 0.0500 | 0.6000 | 0.7318 | 0.477 | 0.496 | 0.471 |
| 0.0500 | 0.5001 | 0.7220 | 0.531 | 0.567 | 0.524 |
| 0.0500 | 0.4000 | 0.7138 | 0.567 | 0.583 | 0.553 |
| 0.0500 | 0.3000 | 0.7069 | 0.545 | 0.555 | 0.531 |
| 0.0500 | 0.2000 | 0.7011 | 0.474 | 0.496 | 0.461 |
| 0.0500 | 0.1000 | 0.6965 | 0.304 | 0.317 | 0.293 |
| 0.0500 | 0.0500 | 0.6944 | 0.210 | 0.218 | 0.201 |
| 0.1000 | 0.8500 | 0.7806 | 0.131 | 0.151 | 0.126 |
| 0.1000 | 0.7500 | 0.7623 | 0.290 | 0.312 | 0.281 |
| 0.1000 | 0.6500 | 0.7477 | 0.387 | 0.393 | 0.373 |
| 0.1000 | 0.5500 | 0.7358 | 0.462 | 0.475 | 0.451 |
| 0.1000 | 0.4500 | 0.7258 | 0.512 | 0.522 | 0.501 |
| 0.1000 | 0.3499 | 0.7174 | 0.526 | 0.533 | 0.512 |
| 0.1000 | 0.2500 | 0.7103 | 0.500 | 0.517 | 0.489 |
| 0.1000 | 0.1501 | 0.7045 | 0.399 | 0.407 | 0.387 |
| 0.1000 | 0.0500 | 0.6997 | 0.214 | 0.224 | 0.201 |
| 0.2000 | 0.7500 | 0.7901 | 0.186 | 0.201 | 0.172 |
| 0.2000 | 0.6500 | 0.7712 | 0.314 | 0.322 | 0.304 |
| 0.2000 | 0.5500 | 0.7561 | 0.391 | 0.407 | 0.382 |
| 0.2000 | 0.4500 | 0.7437 | 0.436 | 0.444 | 0.413 |
| 0.2000 | 0.3500 | 0.7334 | 0.450 | 0.462 | 0.438 |
| 0.2000 | 0.2500 | 0.7246 | 0.446 | 0.460 | 0.432 |
| 0.2000 | 0.1501 | 0.7174 | 0.363 | 0.376 | 0.351 |
| 0.2000 | 0.0500 | 0.7112 | 0.235 | 0.243 | 0.221 |
| 0.3000 | 0.6500 | 0.7995 | 0.237 | 0.245 | 0.222 |
| 0.3000 | 0.5500 | 0.7801 | 0.324 | 0.334 | 0.316 |
| 0.3000 | 0.4500 | 0.7645 | 0.381 | 0.397 | 0.372 |
| 0.3000 | 0.3500 | 0.7516 | 0.400 | 0.416 | 0.392 |
| 0.3001 | 0.2500 | 0.7409 | 0.390 | 0.397 | 0.378 |
| 0.3000 | 0.1500 | 0.7320 | 0.322 | 0.331 | 0.312 |
| 0.3000 | 0.0500 | 0.7243 | 0.241 | 0.261 | 0.231 |
| 0.4000 | 0.5500 | 0.8091 | 0.256 | 0.262 | 0.241 |
| 0.4000 | 0.4500 | 0.7891 | 0.320 | 0.332 | 0.304 |
| 0.4000 | 0.3500 | 0.7729 | 0.353 | 0.364 | 0.341 |
| 0.3999 | 0.2501 | 0.7596 | 0.346 | 0.351 | 0.334 |
| 0.4000 | 0.1500 | 0.7484 | 0.317 | 0.326 | 0.302 |
| 0.4000 | 0.0500 | 0.7393 | 0.208 | 0.217 | 0.199 |
| 0.5000 | 0.4500 | 0.8187 | 0.265 | 0.271 | 0.251 |
| 0.5000 | 0.3500 | 0.7981 | 0.309 | 0.318 | 0.299 |
| 0.5000 | 0.2500 | 0.7814 | 0.304 | 0.312 | 0.291 |
| 0.5000 | 0.1501 | 0.7677 | 0.271 | 0.292 | 0.262 |
| 0.5000 | 0.0500 | 0.7564 | 0.173 | 0.181 | 0.161 |
| 0.6000 | 0.3500 | 0.8284 | 0.247 | 0.253 | 0.234 |
| 0.6000 | 0.2500 | 0.8077 | 0.255 | 0.262 | 0.243 |

| | | | | | |
|--------|--------|--------|-------|-------|-------|
| 0.6000 | 0.1500 | 0.7901 | 0.225 | 0.241 | 0.214 |
| 0.6000 | 0.0500 | 0.7761 | 0.140 | 0.146 | 0.135 |
| 0.7000 | 0.2500 | 0.8385 | 0.190 | 0.203 | 0.183 |
| 0.7000 | 0.1500 | 0.8165 | 0.196 | 0.214 | 0.187 |
| 0.6999 | 0.0500 | 0.7990 | 0.118 | 0.123 | 0.109 |
| 0.8000 | 0.1500 | 0.8484 | 0.136 | 0.149 | 0.124 |
| 0.8000 | 0.0500 | 0.8260 | 0.090 | 0.103 | 0.086 |
| 0.8999 | 0.0501 | 0.8585 | 0.052 | 0.074 | 0.051 |

3. RESULTS AND DISCUSSION

Rastogi has noted that the strength of interaction between two components is weakened by the third component showing nearly ideal behaviour of a ternary system. The extent of weakening of interaction can be assessed roughly by the expression,

$$E_{12}^{liq}/E_{12}^{vacuum} = 1 - \frac{E_3(E_1 + E_2 + E_3)}{(E_1 + E_3)(E_2 + E_3)} P_3^w K \quad (15)$$

where E_{12}^{liq} denotes the interaction between 1 and 2 in the presence of component 3. E_{12}^{vacuum} denotes the interaction between 1 and 2 in vacuum and $P_3^w = P_3 N_0/M_3$. The validity of equation for a number of ternary system has shown that percent decrease in E_{12}^{vacuum} is quite significant. The experimental basis of the change in the interaction parameters in ternary system with respect to binary system can be expressed by;

$$V^E = V_{123}^E - \frac{1}{2}(x_1 + x_2)V_{12}^E + (x_2 + x_3)V_{23}^E + (x_3 + x_1)V_{31}^E \quad (16)$$

where V^E is the measure of change of interaction in ternary system showing the weakening of interactions.

Here, we present the results of experimental and theoretical excess volume for ternary liquid mixtures along with their contributory binaries with the use of Flory theory and Bartrand-Acree-Bruchfield (BAB) predictive model. Parameters for the pure components are collected from the literature [19] and presented in Table 1.

The excess volume (V^E) were represented mathematically by the Redlich-Kister equation for correlating the experimental data,

$$y = x_1(1 - x_1) \sum_{i=0}^p A_i (2x_1 - 1)^i \quad (17)$$

where (y) refers to (V^E), x_1 is the mole fraction and A_i is the coefficients. The values of coefficients A_i were determined by a multiple regression analysis based on the least squares method and are summarized along with the standard deviations between the experimental and fitted values of the respective function in Table 2. The standard deviation is defined by.

$$\sigma = \left[\sum_{i=1}^m (y_{exp_i} - y_{cal_i})^2 / (m - p) \right]^{1/2} \quad (18)$$

where (m) is the number of experimental points and (p) is the number of adjustable parameters. For the case the highest value of (σ) corresponds to 2.2986 for toluene + cyclohexane while the lowest value of (σ) corresponds to 0.0050 for cyclohexane + pentane respectively. The excess volumes for binary and ternary systems, computed from the Flory and BAB models are presented in Tables 3&4. A close perusal of Tables (3&4) reveal that the increase in the mole fraction of the second and third component of given binary and ternary liquid mixtures almost increases the excess volume and thereafter decreases. Similar trend is observed for all the liquid mixtures. It can be observed from Tables (3&4) that values of excess volume predicted from Flory and BAB theories are in close agreement both in magnitude and sign except in few places.

The molar excess volumes, V^E , were calculated from density data according to the following equation;

$$V^E = \sum_{i=1}^N x_i M_i (1/\rho - 1/\rho_i) \quad (19)$$

where x_i , M_i , and ρ_i are the mole fraction, molar mass. In the ternary mixture of Tetrahydrofuran + 2-Propanol + 2,2,4-Trimethylpentane, the V^E values are positive at all compositions. The uncertainty of excess molar volumes was estimated to be less than $1 \cdot 10^{-3} \text{ cm}^3 \cdot \text{mol}^{-1}$. The values of V^E vary from $0.011 \text{ cm}^3 \cdot \text{mol}^{-1}$ to $0.562 \text{ cm}^3 \cdot \text{mol}^{-1}$. The excess molar volume $V^E(x)$ 0.5 increases in the order: $0 < \text{tetrahydrofuran} + 2,2,4\text{-trimethylpentane} < \text{tetrahydrofuran} + 2\text{-propanol} < 2\text{-propanol} + 2,2,4\text{-trimethylpentane}$. The dependence of V^E on both composition and temperature for the present mixtures may be explained as a balance between positive contributions (hydrogen bond rupture or dispersive interaction). In our systems, the observed V^E are positive, and the predominant contribution to the positive V^E is most likely from the breaking of these two kinds of interactions upon mixing. Larger V^E values in the mixtures of 2,2,4-trimethylpentane with 2-propanol than those with tetrahydrofuran lead us to

believe that the contribution to the V^E values from the cleavage of the H-bond between 2-propanol molecules is greater than that of the O-O interaction between tetrahydrofuran molecules.

The plots of V^E with mole fraction, x_i , for the binary mixtures of the excess volume can be interpreted in three areas, namely physical, chemical, and structural effects. The physical contributions comprising of dispersion forces and non-specific physical (weak) interactions, and the chemical contributions involve breaking up of the associates present in the pure liquids, resulting in positive V^E values. The structural effects arises due to specific interactions such as formation of H-bonding, charge – transfer (donor–acceptor) complexes, and strong dipole–dipole interactions between the component molecules of the mixture, were resulting in negative V^E values. In present investigation physical effects are prevailing in all the ternary mixtures except in few places.

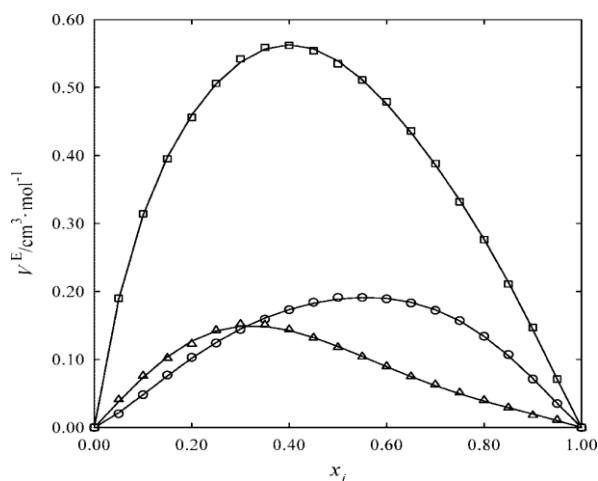


Fig. 1. Variation of excess molar volume V^E with mole fraction x_i for the binary systems at T 98.15 K: O, tetrahydrofuran + 2-propanol, Δ , tetrahydro furan + 2,2,4-trimethylpentane, \square , 2-propanol + 2, 2,4-trimethylpentane.

4 CONCLUSION

Prediction of the thermodynamic and transport properties of liquid mixture depends largely on the extent of interactions involved in the liquid mixture. A good correlation between the theoretical and experimental values clearly point out towards the consideration of all the possible interactions present. The magnitude of such properties gives the measure of various interactions which may be associated with a particular system. Structural chemistry is related to

the interactions involved in the liquid systems. Nature and type of bonding associated with the structure can readily be studied through the study of interactions.

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