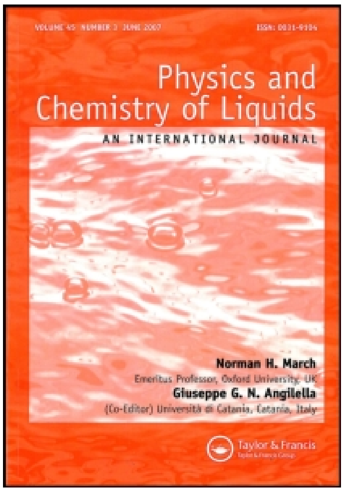

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Excess Molar Volumes and Densities of Multi-Component Liquid Systems At 298.15 K: A Comparison with Flory's Statistical Theory

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EXCESS MOLAR VOLUMES AND DENSITIES OF MULTI-COMPONENT LIQUID SYSTEMS AT 298.15 K: A COMPARISON WITH FLORY'S STATISTICAL THEORY

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Densities were measured over entire range of composition for three ternary liquid systems viz. Toluene + *n*-heptane + *n*-hexane (I), Cyclohexane + *n*-heptane + *n*-hexane (II) and *n*-hexane + *n*-heptane + *n*-decane (III), at 298.15 K. The experimental excess molar volumes for three ternary liquid systems have been evaluated from measured values of densities. The theoretical predictions of excess molar volumes of these systems were carried out with the help of Flory's statistical theory. The theoretically computed values of excess molar volume were compared with the experimentally evaluated values. An excellent agreement has been observed. Intermolecular interactions have also been studied on the basis of excess molar volume.

Keywords: Flory's statistical theory; Multi-component systems; Intermolecular interactions

1 INTRODUCTION

For many years, the chemical industry has recognised the importance of thermodynamic and physical properties in design calculations involving chemical separations, fluid flow and heat transfer. The development of flow calorimeters, continuous dilution dilatometer and vibrating tube densimeter has enabled the experimental determinations of excess enthalpies, heat capacities and excess volume of nonelectrolyte liquid mixtures with convenience and accuracy. But even with today's modern instrumentation, experimental measurements of thermodynamic properties become progressively more difficult and time consuming with each additional component beyond binary mixtures. To address this problem researchers have turned to predictive methods, as a way to generate desired quantities. Numerous equations have been derived for predicting the properties of ternary and high order multi-component systems from binary and pure component experimental data. However, very few investigations have been carried out on multi-component systems [1–8]. Recently [9,10] a general equation for estimating the excess thermodynamic and other physico-chemical properties of multi-component

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systems from their contributory binary combinations have been developed and applied to various multi-component systems. But only Flory's statistical theory [11,12] can be successfully used to predict the properties of the multi-component systems from those of pure components. Most of the work on excess volumes for binary systems has been carried out by McGlashan *et al.* [13], Patterson and Van [14], Benson and Zhang [15], Marsh and Ewing [16] and Roux-Desgranges *et al.* [17]. Experimental measurements of excess volumes of binary liquid mixtures are still in progress [18–20].

In the present work, Flory's statistical theory has been used for the prediction of excess volumes of three ternary liquid systems, viz. Toluene + *n*-heptane + *n*-hexane (I), Cyclohexane + *n*-heptane + *n*-hexane (II) and *n*-hexane + *n*-heptane + *n*-decane (III). Experimental excess volumes have been evaluated from measured density values. The comparative study of experimental and theoretical values of excess molar volumes have also been carried out to derive information about solute–solvent or molecular interactions.

2 THEORY

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

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

where $\tilde{P}$, $\tilde{V}$ and $\tilde{T}$ are the reduced pressure, volume and temperature, respectively. These are given by

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

$$\tilde{T} = T/T^* = \frac{2V^*CkT}{S\eta} \tag{3}$$

$$\tilde{V} = v/v^* = V/V^* \tag{4}$$

The reduced equation of state at zero pressure is

$$T^* = \frac{T}{\tilde{T}} = \frac{T\tilde{V}^{4/3}}{\tilde{V}^{1/3} - 1} \tag{5}$$

$$\tilde{V}^{1/3} = \left(\frac{\alpha T}{3(1+\alpha T)} + 1\right) \tag{6}$$

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 calculated using the experimental value of α on the basis of Eqs. (5) and (6).

While predicting the surface tension of ternary liquid mixtures, Pandey and Pant [21] extended the Flory theory and defined an element (or segment) as an arbitrary chosen portion of the molecule, and again defined the segment as well as site fractions of molecule by the relations

$$\psi_2 = X_2/[X_2 + X_3(V_3^*/V_2^*) + X_1(V_1^*/V_2^*)] \tag{7}$$

$$\psi_3 = X_3/[X_3 + X_2(V_2^*/V_3^*) + X_1(V_1^*/V_3^*)] \tag{8}$$

$$\psi_1 = [1 - \psi_2 - \psi_3] \tag{9}$$

$$\theta_2 = \psi_2/[\psi_2 + \psi_3(V_2^*/V_3^*)^{1/3} + \psi_1(V_2^*/V_1^*)^{1/3}] \tag{10}$$

$$\theta_3 = \psi_3/[\psi_3 + \psi_2(V_3^*/V_2^*)^{1/3} + \psi_1(V_3^*/V_1^*)^{1/3}] \tag{11}$$

$$\theta_1 = (1 - \theta_2 - \theta_3) \tag{12}$$

where ψ_1, ψ_2, ψ_3 and θ_1, θ_2, θ_3 are the segment and site fractions of Components 1–3.

In the light of the above relations, the excess volumes of ternary liquid mixture can be obtained using the equation

$$\tilde{V}\tilde{V} - \tilde{V}_0 = \tilde{V}^E \frac{V^E}{X_1V_1^* + X_2V_2^* + X_3V_3^*} \tag{13}$$

where $\tilde{V}_0$ is the ideal reduced volume given by

$$\tilde{V}_0 = \psi_1\tilde{V}_1 + \psi_2\tilde{V}_2 + \psi_3\tilde{V}_3 \tag{14}$$

Substitution of Eq. (14) into Eq. (13) gives the excess volume of the ternary liquid system which can be written as

$$V^E = (X_1V_1^* + X_2V_2^* + X_3V_3^*)[\tilde{V} - (\psi_1\tilde{V}_1 + \psi_2\tilde{V}_2 + \psi_3\tilde{V}_3)] \tag{15}$$

where V^E is the excess molar volume and $\tilde{V}$ is the reduced volume of ternary liquid mixture. Assuming the volume reduction parameters of the ternary system to be linear in mole fraction, one obtains

$$\tilde{V} = \frac{V}{X_1V_1^* + X_2V_2^* + X_3V_3^*} \tag{16}$$

where V is the molar volume of the liquid mixture, given by

$$V = \frac{M_1X_1 + M_2X_2 + M_2X_3}{\rho_m} \tag{17}$$

where ρ_m is the density of the mixture.

Excess volumes and reduced excess volumes are correlated with the equation as mentioned below. This equation can also be used to predict excess volume from the knowledge of the reduced excess volume, $\tilde{V}^E$, i.e.

$$V^E = (X_1 V_1^* + X_2 V_2^* + X_3 V_3^*)\tilde{V}^E \tag{18}$$

where $\tilde{V}^E$ is given by

$$\tilde{V}^E = \tilde{V}^{07/3}(4/3 - \tilde{V}^{01/3})^{-1}(\tilde{T} - \tilde{T}^0) \tag{19}$$

From Eq. (5), $\tilde{T}$ and $\tilde{V}$ are co-related with each other.

Pandey and Pant [21] have formulated the equations for the characteristic pressure and reduced temperature of the mixture given by

$$\tilde{T} = T/T^* = \frac{T}{P^*} \bigg/ \left(\frac{\psi_1 P_1^*}{T_1^*} + \frac{\psi_2 P_2^*}{T_2^*} + \frac{\psi_3 P_3^*}{T_3^*}\right) \tag{20}$$

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

$$P^* = [\psi_1 P_1^* + \psi_2 P_2^* + \psi_3 P_3^* - (\psi_1 \theta_2 X_{12} + \psi_2 \theta_3 X_{23} + \psi_3 \theta_1 X_{31})] \tag{21}$$

where X_{12}, X_{23} and X_{31} are the interaction parameters obtained from Eqs. (22)–(24) by adopting the familiar Berthelot relationship, $\eta_{ij} = (\eta_{ij}\eta_{ij})^{1/2}$.

$$X_{12} = P_1^*[1 - (P_2^*/P_1^*)^{1/2}(V_2^*/V_1^*)^{1/6}]^2 \tag{22}$$

$$X_{23} = P_2^*[1 - (P_3^*/P_2^*)^{1/2}(V_3^*/V_2^*)^{1/6}]^2 \tag{23}$$

$$X_{31} = P_3^*[1 - (P_1^*/P_3^*)^{1/2}(V_1^*/V_3^*)^{1/6}]^2 \tag{24}$$

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

3 EXPERIMENTAL

All the organic liquids used were of analytical grade, obtained from BDH chemicals Ltd. UK. These chemicals were further purified by double distillation. Densities of pure liquids and their ternary mixtures were measured using a densimeter (Anton-Paar DMA 602 HT-DMA60) at 298.15 K. The precision of the measured densities is estimated to be better than ±0.2 kg/m^3. Measured values of density have been compared with those reported in literature[a].

4 RESULTS AND DISCUSSION

A careful study of the resulting expression reveals that the computation of the excess volumes of ternary liquid mixtures can be studied by Flory's theory in two different ways, first by calculating the excess volume (V^E) directly from characteristic and reduced volumes and segment fraction using thermal expansion coefficient (α) only and secondly by calculating V^E using Eq. (18) in terms of V^E, considering all the interaction parameters on the basis of theoretical and experimental studies. The validity of the proposed theory has been tested for three ternary liquid systems containing *n*-alkanes. The required experimental density data have been generated in our laboratory [5].

Table I lists the values of the reduced and characteristic parameters of the pure components along with density and molecular weight values, while Tables II–IV records the experimental and computed values of excess volumes of ternary liquid systems. Figures 1–3 show the comparison between experimental and computed values of excess volume for the three ternary systems at 298.15 K.

A close perusal of Tables II–IV and Figs. 1–3 reveals that the theoretical excess volume has been found to exhibit excellent agreement both in sign and magnitude with the experimental values for Systems (I)–(III). In all three mixtures, the values of excess volumes are all negative passing through minima, indicating strong interaction between component molecules.

Here, we illustrate the validity of the extended form of Flory's theory with the help of the first method described above, using the experimental values of three ternary liquid systems (I)–(III).

The study of the excess volume leads to the two important structural aspects that can be assessed by the relation

$$V^E = V^E_{\text{size}} + V^E_{\text{int}} \tag{25}$$

V^E_{size} is associated with the size difference of molecules while V^E_{int} with the interaction forces between molecules. Theoretical studies of the molecular interactions in ternary liquid mixtures are very complicated due to the involvement of three body effects. However, in the multi-component system it appears that the contributions of three body interactions are less efficient and contribute very little to the energy of systems under investigation. That is why the results obtained by considering two-body interactions are found to be excellent. It is supported by the experimental study of

TABLE I Parameters of the pure component liquids at 298.15 K

Component liquids	*Mol wt.*	*Density*[a] (g/cm^3)	*Molar vol.*	$\alpha \times 10^3$ (K^{-1})	$\tilde{V}$ (cm^3 mol^{-1})	V^* (cm^3 mol^{-1})
n-hexane	86.18	0.6548	131.53	1.3897	1.3224	99.4706
n-heptane	100.21	0.6790	147.56	1.2589	1.2985	113.6375
n-decane	142.29	0.7260	195.94	1.0500	1.2579	155.7700
Cyclohexane	84.16	0.7736	108.79	1.2150	1.2902	84.2920
Toluene	92.15	0.8626	106.81	1.0740	1.2627	84.5867

[a] CRC Handbook of Chem. and Phys. 78th ed., CRC Press, Boca Raton, New York, 1997–1998.

TABLE II Theoretical and experimental excess molar volumes and densities of ternary liquid system: toluene (X_1) + n-heptane (X_2) + n-hexane (X_3) at 298.15 K

X_1	X_2	ρ (gcm^{-3})	V^E_{exptl} (cm^3 mol^{-1})	V^E_{theor} (cm^3 mol^{-1})
0.1210	0.1838	0.7506	−1.2273	−1.1972
0.1459	0.2011	0.7529	−1.1780	−1.1580
0.1698	0.2170	0.7570	−1.1607	−1.1407
0.1929	0.2358	0.7635	−1.1827	−1.1630
0.2160	0.2544	0.7682	−1.1761	−1.0981
0.2390	0.2726	0.7733	−1.1758	−1.0651
0.2641	0.2875	0.7791	−1.1796	−1.1796
0.2849	0.3000	0.7835	−1.1751	−1.1431
0.3088	0.3222	0.7849	−1.1158	−1.1603
0.3330	0.3391	0.7938	−1.1673	−1.0819
0.3559	0.3553	0.8000	−1.1819	−1.1568
0.3760	0.3735	0.8036	−1.1669	−1.1432
0.3983	0.3908	0.8089	−1.1694	−1.1540
0.4204	0.3974	0.8188	−1.2358	−1.1986
0.4439	0.4045	0.8324	−1.3530	−1.2780

TABLE III Theoretical and experimental excess molar volumes and densities of ternary liquid system: cyclohexane (X_1) + n-heptane (X_2) + n-hexane (X_3) at 298.15 K

X_1	X_2	ρ (gcm^{-3})	V^E_{exptl} (cm^3 mol^{-1})	V^E_{theor} (cm^3 mol^{-1})
0.1189	0.1823	0.6832	−0.2210	−0.2140
0.1440	0.2012	0.6863	−0.2214	−0.2186
0.1650	0.2202	0.6897	−0.2352	−0.2252
0.1879	0.2379	0.6922	−0.2288	−0.2248
0.2062	0.2484	0.6943	−0.2270	−0.2231
0.2346	0.2729	0.6979	−0.2269	−0.2229
0.2564	0.2903	0.6999	−0.2132	−0.2132
0.2799	0.3073	0.7036	−0.2272	−0.2212
0.3031	0.3266	0.7072	−0.2387	−0.2367
0.3249	0.3424	0.7098	−0.2360	−0.2361
0.3487	0.3599	0.7129	−0.2375	−0.2304
0.3700	0.3776	0.7157	−0.2383	−0.2363
0.3933	0.3948	0.7190	−0.2320	−0.2321
0.4143	0.4030	0.7217	−0.2466	−0.2426
0.4364	0.4103	0.7240	−0.2400	−0.2390

the molecular interactions expressed in terms of $V^E_{(a)}$, the volume of mixing, assuming the additivity of binary contributions. This can be expressed by the relation

$$V^E_{(a)} = 1/2\left[\sum_{i=1-4}^{j=4-1} (X_i + X_j) V^E_{ij}\right] \tag{26}$$

Where X_i and X_j are the mole fractions of their respective components and V^E_{ij} is the volume of mixing of corresponding binary mixtures. Consideration of two-body interactions is also supported theoretically by the BAB equation [9,10]. In this equation, properties of multi-component systems can be estimated with the help of the properties

TABLE IV Theoretical and experimental excess molar volumes and densities of ternary liquid system: n-hexane (X_1) + n-heptane (X_2) + n-decane (X_3) at 298.15 K

X_1	X_2	ρ (gcm^{-3})	V^E_{exptl} (cm^3 mol^{-1})	V^E_{theor} (cm^3 mol^{-1})
0.1735	0.2759	0.7167	−0.0840	−0.0824
0.2199	0.3692	0.7130	−0.0772	−0.0762
0.2260	0.3185	0.7128	−0.1321	−0.1310
0.2759	0.3158	0.7105	−0.1369	−0.1329
0.3813	0.3524	0.7074	−0.1605	−0.1691
0.3378	0.4849	0.7071	−0.1891	−0.2436
0.3464	0.5192	0.7050	−0.2475	−0.3035
0.3563	0.2797	0.7047	−0.3035	−0.3626
0.3569	0.4377	0.7046	−0.3049	−0.3029
0.3676	0.3504	0.7029	−0.3033	−0.3030
0.3854	0.5504	0.7022	−0.4677	−0.4577
0.4019	0.5429	0.7007	−0.4007	−0.4024
0.4069	0.3878	0.6980	−0.4723	−0.4628
0.4258	0.5421	0.6964	−0.4477	−0.4426
0.4500	0.5179	0.6947	−0.4043	−0.4039
0.4737	0.4943	0.6937	−0.4820	−0.4819

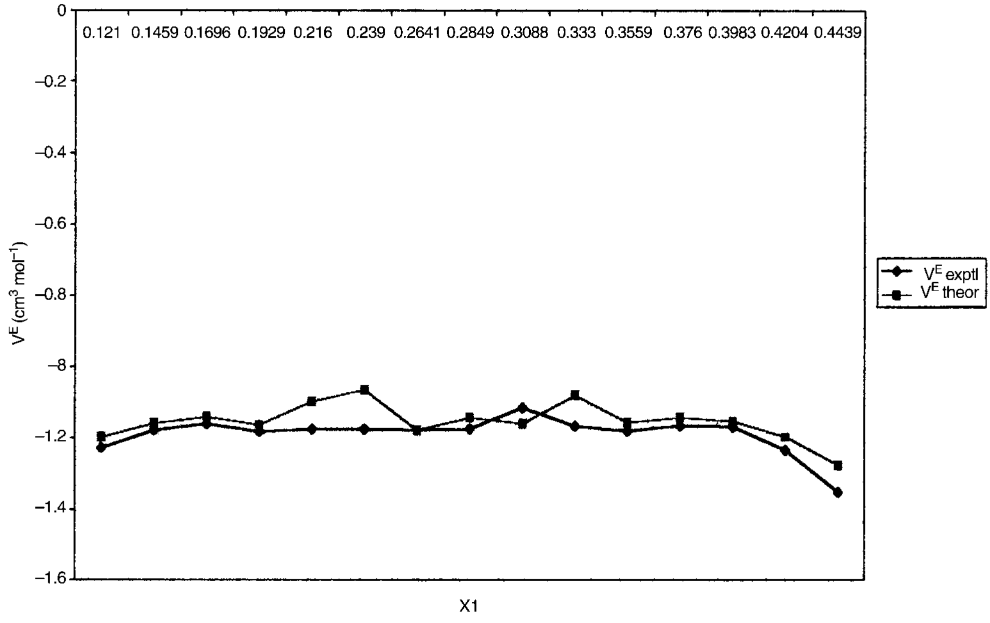

FIGURE 1 Comparison between experimental and theoretical excess molar volumes *vs* mole fraction (X_1) for ternary liquid system: toluene (X_1) + n-heptane (X_2) + n-hexane (X_3) at 298.15 K.

of their contributory binaries. Thus only two-body interactions are taken into consideration during the derivation of the proposed method, neglecting three-body interactions. Exhaustive study of the excess volume of multi-component systems reveals that the strength of interactions between two components is weakened by the addition of third component. A rough estimate of the extent of weakening of interactions has been discussed in detail by Rastogi [22] and Margenau and Kastner [23]. The

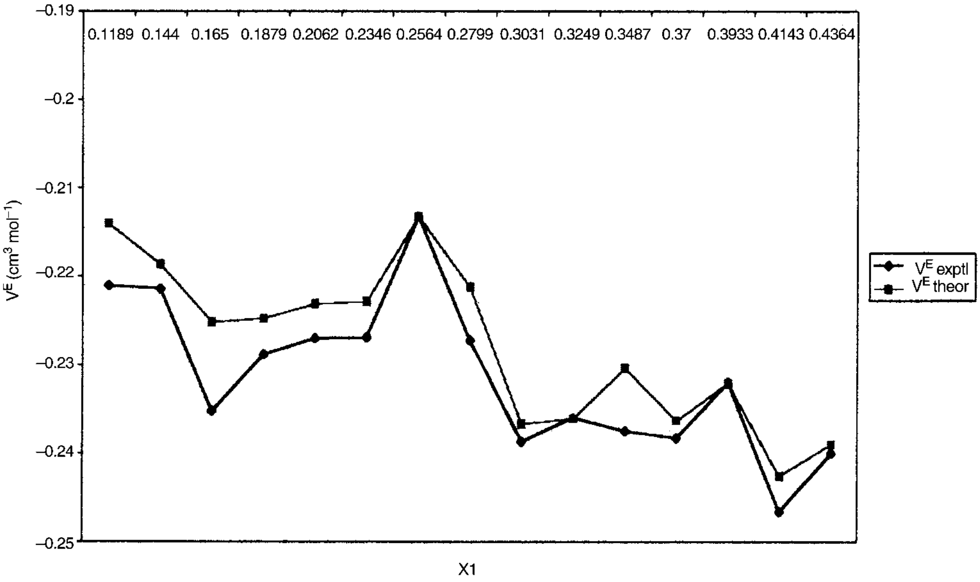

FIGURE 2 Comparison between experimental and theoretical excess molar volumes *vs* mole fraction (X_1) for ternary liquid system: cyclohexane (X_1) + n-heptane (X_2) + n-hexane (X_3) at 298.15 K.

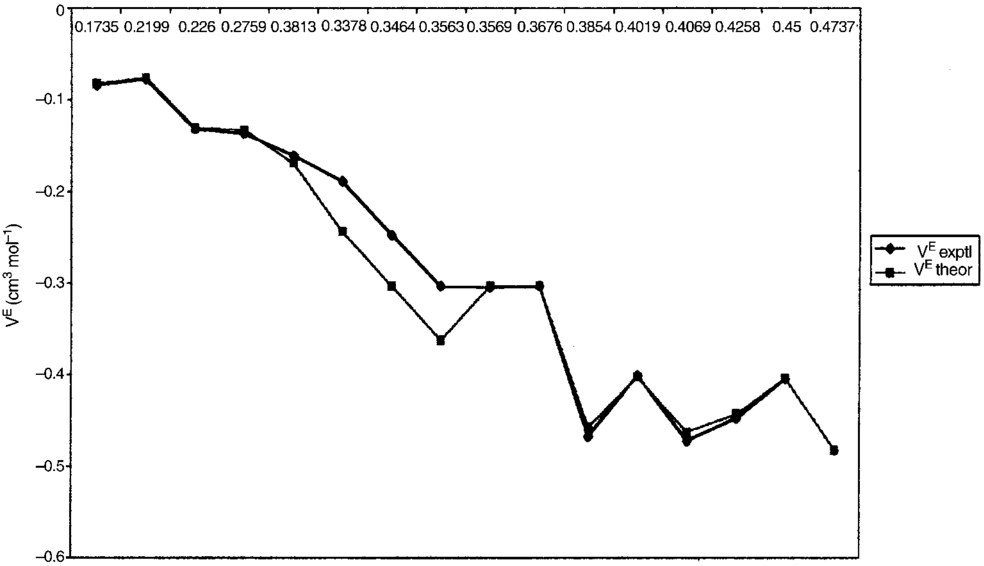

FIGURE 3 Comparison between experimental and theoretical excess molar volumes *vs* mole fraction (X_1) for ternary liquid system: n-hexane (X_1) + n-heptane (X_2) + n-decane (X_3) at 298.15 K.

change in the interactions of a ternary liquid mixture relative to a binary is given by the relation

$$\Delta V^E = V_{123}^E - 1/2 V_{(a)}^E \tag{27}$$

Thus, a ternary liquid system appears to be a fairly typical example of the extent of weakening of interactions proportional to the number of components.

The second structural aspect of the study of excess volume is V_{size}^E, which is defined by the expression

$$V_{\text{size}}^E = \left[\sum_{i=1}^{i=4} (V_i^* - V_{ii}^{**}) X_i \right] [1 - (9RT/\pi)(V^\circ / W_m)]^{-1} \tag{28}$$

where the interaction energy W_m is given by

$$W_m = N^2 \sum_{i=1}^{i=4} \gamma \in_i^* \gamma_i^{*3} X_i \tag{29}$$

The physical significance of the notations used and their evaluation is defined by Kiyohara and Arakawa [24]. It is evident that the difference in the sign of V^E seems to reflect the superposition of the size effect upon one another, which causes contraction. Most probably contraction may arise from the disruption by the mixing process of an expanded dipole-dipole structure of the pure liquid components. Increased disorder in breaking the ordered structure is more important than the loss or gain in the free volume. It was found that the magnitude of the excess volume depends exclusively on $\theta_2 X_{12}$ relative to $\sum_{i=1}^{i=3} \psi_1 P^*$, because a positive value of X_{12} increases $\tilde{T}$ for the mixture, making $\tilde{V} > \tilde{V}^\circ$ and hence $V^E > 0$. The difference in the molecular sizes, the nature of intermolecular interactions, and the *r*-meric relationship seem to play a vital role in determining the excess volume of a mixture. Inconsistency in the experimental as well as theoretical results may arise from several factors that may be equal or greater significance than the size difference, such as molecular shape, viz., the modes of molecular energy and the mechanism of flow. The interactions involving more than three bodies might be more appropriate when the value of $(V_i/V_j)^{1/3} \approx 1.5$ is used. The study of excess volume data is associated with steric hindrance, but its contribution is not observable in the case of linear alkanes as detailed out by Delmas and Ngugen [25].

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

$$\Delta E_{12,\text{liq}} / \Delta E_{12,\text{vacuum}} = 1 - \frac{\Delta E_3 (\Delta E_1 + \Delta E_2 + \Delta E_3)}{(\Delta E_1 + \Delta E_3)(\Delta E_2 + \Delta E_3)} P_3^W K \tag{30}$$

where $\Delta E_{12,\text{liq}}$ denotes the interaction between 1 and 2 in the presence of component 3. $\Delta E_{12,\text{vacuum}}$ denotes the interaction between 1 and 2 in vacuum and $P_3^w = P_3 \rho_3 N_0 / M_3$. The validity of Eq. (30) for a number of ternary systems has shown that the percentage decrease in $E_{12,\text{vacuum}}$ is quite significant.

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