

Modeling of excess molar volumes of [difurylmethane + (acetonitrile or propionitrile or benzonitrile)] binary Mixtures using the Prigogine – Flory – Patterson theory

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Abstract: The recently reported experimental excess molar volume data for {difuryl methane + (acetonitrile or benzonitrile or propionitrile)} binary mixtures as a function of composition at $T = 298.15\text{ K}$ under atmospheric pressure, have been used to test the applicability of Prigogine-Flory-Patterson theory. Analysis of each of the three contributions to the experimental excess molar volume *vis.* the interactional, the free volume and the characteristic pressure terms, show that the interactional and the free volume contributions were negative for all three {difuryl methane + (acetonitrile or benzonitrile or propionitrile)} binary mixtures. The characteristic pressure contribution was negative for {difuryl methane + (acetonitrile or propionitrile)} and positive for (difuryl methane + benzonitrile). The relatively large magnitude of the interactional contribution which arises from dipole-dipole interactions between difurylmethane and the nitrile molecule determined the overall experimental shape of the excess molar volume isotherms for {difuryl methane + (acetonitrile or benzonitrile or propionitrile)} binary mixtures. The correlation between the theoretical and experimental excess molar volumes data was satisfactory for each of the three binary systems.

Keywords: Excess Molar Volume, Prigogine-Flory-Patterson, Difurylmethane, Acetonitrile, Benzonitrile, Propionitrile

1. Introduction

The Prigogine-Flory-Patterson (PFP) theory used for quantitative estimation of excess thermodynamic functions of binary liquid mixtures [1-5] has been described in detail by Patterson and co-workers [6-13]. The PFP theory is widely used with the aim of establishing the relative importance of different contributions that give rise to the experimentally observed values of the excess thermodynamic functions. The PFP theory considers excess thermodynamic properties of binary mixtures to be the sum of three contributions. The excess molar volumes, V_m^E , can thus be expressed as a sum of the interactional term calculated from the interactional parameter, χ_{12} the free volume contribution and P^* contribution which originates from the differences in the internal pressures and the reduced volumes of the pure components.

Following our recent thermodynamics study of the binary systems containing difurylmethane, (DFM) with acetonitrile

(ACN) or benzonitrile (BCN) or propionitrile (PCN)} binary mixtures at 298.15 K, the reported V_m^E data [11] have been used in this paper to test the applicability of the PFP theory. To the best of our knowledge, the PFP theory has not yet been tested on V_m^E data for {DFM + (ACN or BCN or PCN)} binary mixtures.

2. Prigogine-Flory-Patterson Theory

Although the basic concepts and equations involved in the PFP theory have been reported in literature, for the sake of completeness we include here some of the relevant equations for the calculation of the theoretical excess molar volume, V_{PFP}^E for each of the {DFM + (C₁-C₆) alkan-1-ol} binary systems. According to the PFP theory, for a binary mixture that comprise of molecules that differ in the number of segments (isometric portions), r , each containing s interacting sites, the expression for V_m^E separates the three contributions as follows:

$$\begin{aligned}
 V_m^E / (x_1 V_1^* + x_2 V_2^*) &= [(\tilde{V}^{1/3} - 1) \tilde{V}^{2/3} \Psi_1 \theta_2 \chi_{12}] / [(4/3) \tilde{V}^{-1/3} - 1] P^*_{11} \\
 &\quad (V_{int}^E \text{ term}) \\
 -[(\tilde{V}_1 - \tilde{V}_2)^2 ((14/9) \tilde{V}^{-1/3} - 1) \Psi_1 \Psi_2] &/ [(4/3) \tilde{V}^{-1/3} - 1] \tilde{V} \\
 &\quad (V_{fv}^E \text{ term}) \\
 +[(\tilde{V}_1 - \tilde{V}_2)(P^*_{11} - P^*_{22}) \Psi_1 \Psi_2] &/ (P^*_{22} \Psi_1 + P^*_{11} \Psi_2) \quad (1) \\
 &\quad (V_{P^*}^E \text{ term})
 \end{aligned}$$

where 1 and 2 subscripts refer to the two pure components and the V_{int}^E term is the interactional contribution which arises from any difference in the chemical natures of the two components in the binary mixture and is proportional to the Flory parameter, χ_{12} . The free volume term, V_{fv}^E , arises from dependence of the reduced volume upon the reduced temperature as a result of the difference in the degree of thermal expansion between the two components in the mixture. The V_{fv}^E term is a measure of geometrical effects which include size, shape and conformation of unlike molecules in the binary mixture. Since the two unlike components in the binary mixture always have different free volumes, there is always a net decrease in volume during the mixing process resulting in a net negative V_{fv}^E value. The $V_{P^*}^E$ term is the characteristic pressure contribution and is proportional to $(\tilde{V}_1 - \tilde{V}_2)(P^*_{11} - P^*_{22})$ and can bear either sign depending on the relative magnitude of P^*_i and \tilde{V}_i (or the isobaric thermal expansivity, α_i) of unlike components in the binary mixture [10,13]. The reduced volume \tilde{V}_i for each pure component i at a specific temperature T was calculated from the corresponding value of the isobaric thermal expansivity, α_i :

$$\tilde{V}_i = [(1 + (4/3) \alpha_i T) / (1 + \alpha_i T)]^3 \quad (2)$$

The reduced volume \tilde{V} of the binary solution mixture in equation (1) is calculated from:

$$\tilde{V} = \Psi_1 \tilde{V}_1 + \Psi_2 \tilde{V}_2 \quad (3)$$

Where the molecular contact energy fraction Ψ_i of component i is expressed:

$$\Psi_1 = 1 - \Psi_2 = \phi_1 P_1^* / (\phi_1 P_1^* + \phi_2 P_2^*), \quad (4)$$

with the hard-core volume fraction, ϕ_1 and ϕ_2 for alkan-1-ol and DFM respectively, calculated from:

$$\phi_1 = (1 - \phi_2) = x_1 V_1^* / (x_1 V_1^* + x_2 V_2^*) \quad (5)$$

The characteristic volume V_i^* of component i is calculated from the molar volume V_i^o from the expression, $V_i^* = V_i^o / \tilde{V}_i$, and the characteristic pressure P^*_i of component i is expressed by:

$$P^*_i = T \tilde{V}_i^2 \alpha_i / \kappa_{T,i} \quad (6)$$

where $\kappa_{T,i}$ is the isothermal compressibility of pure component i , obtained from the isentropic compressibility $\kappa_{S,i}$ from the thermodynamic relation [17,18]:

$$\kappa_{T,i} = \kappa_{S,i} + \alpha^2 V_m T / C_{p,m} \quad (7)$$

where $C_{p,m}$ is the isobaric heat capacity. The molecular surface fraction of solute component 2 is given by:

$$\theta_2 = \phi_2 S_2 / [\phi_1 S_1 + \phi_2 S_2] \quad (8)$$

where S_i is the molecular surface/volume ratio for the component i which is determined by Bondi's method of molecular group contributions [20]. S_i value can also be estimated from van der Waals area and volume data for organic molecules [21].

3. Experimental

Acetonitrile (ACN), propionitrile (PCN) and benzonitrile (BCN) were purchased from Aldrich and the claimed purity was more than 99.5 mass%. The purity of the chemicals was assessed by measuring their densities. There was close agreement between the experimental and values cited in literature. Water required for the densimeter calibration was first deionised by means of ion exchange resins and then doubly distilled over KMnO_4 under a nitrogen atmosphere. Its conductivity was always less than $1.0 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$. Difuryl methane (DFM) was prepared as described elsewhere [12] and its purity was confirmed by $^1\text{H-NMR}$, density measurements and elemental analyses. All purified organic liquids were stored in brown glass bottles and fractionally distilled shortly before use. The [DFM + (ACN or PCN or BCN)] binary mixtures were prepared by weighing appropriate amounts of the purified DFM and nitrile on a Sartorius Super-micro balance (Fabr.-Nr., $\Delta m = \pm 0.000001 \text{ g}$) by syringing each component into Teflon stoppered flasks in order to minimize preferential evaporation. Pure components were separately degassed by ultrasound shortly before sample preparations. This procedure eliminated possible changes in mixture composition that could occur during the degassing of already prepared binary mixtures. All mixtures were completely miscible over the entire composition range. The uncertainty in solution composition expressed as mole fraction was less than 8×10^{-5} . The density measurements of pure liquid and mixtures were performed at atmospheric pressure at 298.15 K by means of a vibrating-tube densimeter (Anton Paar, model 4500, resolution $1 \times 10^{-5} \text{ g.cm}^{-3}$). A sample volume of not more than 1.0 cm^3 was needed to fill the densimeter cell and thermal equilibrium was attained quickly. The temperature of the sample was controlled electrically by means of a built-in thermostat (a semiconductor Peltier element and a resistance thermometer temperature control system) and was measured with an accuracy of $\pm 0.01 \text{ K}$. The densimeter was calibrated after each set of four sample measurements to offset. A linear relation between the density of the fluid and the square of the vibrating period τ , ($\rho = A + B\tau^2$), was assumed. Buoyancy corrections to the weight were made by taking into account the air density, the barometric pressure, and the relative humidity. Under such conditions quadruplet density measurements of each sample were reproducible to within $\pm 1 \times 10^{-5} \text{ g.cm}^{-3}$.

4. Results and Discussion

The values of the various parameters of the pure components (DFM, ACN, BCN and PCN) required in the PFP theory (Equation 1) obtained by using Flory formalism [6-13] are listed in Table 1. The Flory interaction parameter, χ_{12} , required for the calculation of the theoretical excess molar volume, V_m^E , is usually evaluated using experimental values of the excess molar enthalpies H^E . Since H^E values of mixing for these binary systems are presently not known, the value of χ_{12} parameter for each of {DFM + (ACN or BCN or PCN)} binary mixtures was derived from the experimental V_m^E data [11] at equi-molar composition. The calculated values of the three PFP contributions to V_m^E together with the χ_{12} parameter at equimolar concentration for each of {DFM + (ACN or BCN or PCN)} binary systems are presented in Table 2. The interactional parameter, χ_{12} for each of the {DFM + (ACN or BCN or PCN)} binary mixtures has been used to calculate the V_m^E values over the entire composition range. Figure 1 shows the composition dependence of V_m^E , together with the three contributions (V_{int}^E , V_{fv}^E and $V_{p^*}^E$ terms), compared with the experimental V_m^E data for each of {DFM + (ACN or BCN or PCN)} binary mixtures at 298.15 K. Study of the data presented in Table 2 as well as an analysis of each of the three theoretical contributions to the calculated V_m^E over the entire composition range (Figure 1) reveals that the interactional contribution, V_{int}^E , and the values of the Flory's interactional parameter χ_{12} are negative for each of three binary mixtures. It is also noticeable that the sequence of the algebraic value of each of the parameters V_{int}^E term and χ_{12} falls in the order: BCN > ACN > PCN and BCN > PCN > ACN respectively. The interactional contribution, V_{int}^E or the Flory interaction parameter χ_{12} , when negative, shows the existence of specific intermolecular interactions whereas positive values of each of these two functions indicates a predominance of dispersion forces when a binary mixture is created [13]. The sequence of the algebraic values observed for the function, V_{int}^E , for the three binary systems is identical to that reported for experimental excess molar volumes, V_m^E [11].

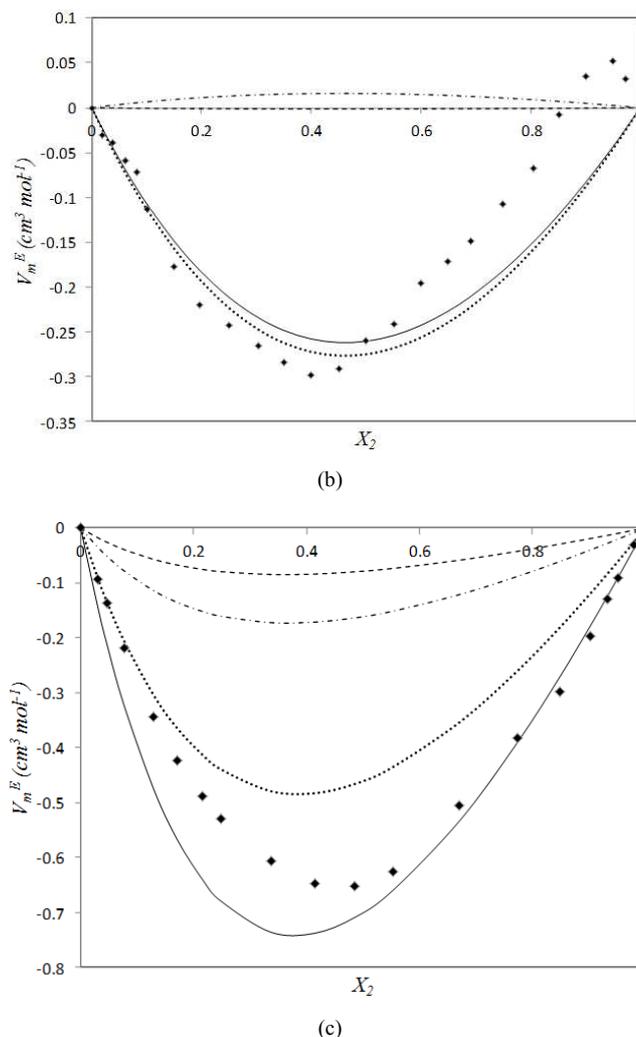
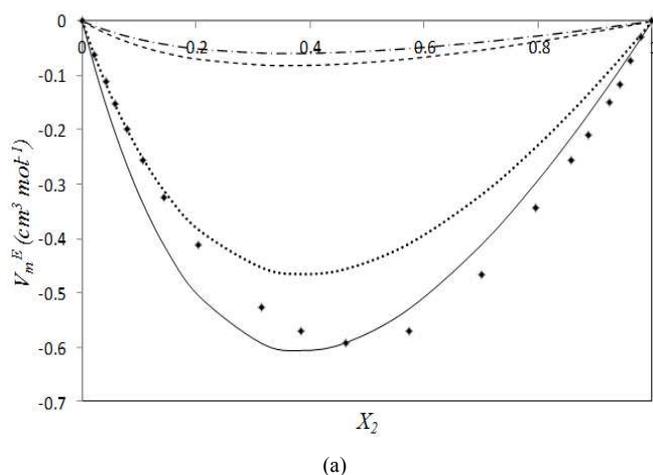


Figure 1. Excess molar volume, V_m^E , as a function of the mole fraction of DFM (x_2), for {DFM + (C_1 – C_6) alkan-1-ol} systems at 298.15 K. (a) (DFM + ACN); (b) (DFM + BCN); (c) (DFM + PCN). (♦) Experimental points [14]; dotted line, interactional contribution (V_{int}^E); dashed line, free volume contribution (V_{fv}^E); dotted-dashed line, characteristic pressure contribution ($V_{p^*}^E$); solid line, total excess molar volume according to PFP theory (V_{PFP}^E).

The free volume contributions, V_{fv}^E , are negative for all the three {DFM + (ACN or BCN or PCN)} binary mixtures, as would be expected. It is also observed that the algebraic value of the V_{int}^E term falls in the order: BCN > ACN > PCN. This trend also reflects the order of contribution of the geometrical interstitial accommodation to the experimental V_m^E data. Inspection of Table 2 and Figure 1 shows that the negative magnitude of the V_{fv}^E term is very small for (DFM + BCN) in comparison to {DFM + (ACN or PCN)} binary mixtures. Because of the small magnitude of the V_{fv}^E term for (DFM + BCN), its contribution to the experimental V_m^E data is minimal. Table 1 further shows that the characteristic pressure P_2^* for DFM was greater than P_1^* for the nitriles (ACN or BCN or PCN). The value of the reduced volume, \tilde{V}_1 for component 1 calculated, for ACN, BCN, PCN was 1.31858, 1.22372, 1.30777, while \tilde{V}_2 for component 2 (DFM) of each binary system was 1.23254 respectively. Figures 1a and b illustrate that the contribution arising from the $V_{p^*}^E$ term was negative for {DFM + (ACN or PCN)} binary mixtures as a

consequence of a large negative ($P^*_1 - P^*_2$) and a positive ($\tilde{V}_1 - \tilde{V}_2$) terms which contributed negatively to the experimental V_m^E data. For the (DFM + BCN) binary system (Fig. 1 c), the large negative ($P^*_1 - P^*_2$) and a small negative ($\tilde{V}_1 - \tilde{V}_2$) magnitudes result in a positive $V_{P^*}^E$ term since this term is proportional to $(P^*_1 - P^*_2)(\tilde{V}_1 - \tilde{V}_2)$. The positive $V_{P^*}^E$ contribution may account for the sigmoidal behaviour in the experimental V_m^E in the mole fraction range $0.85 \leq x_2 \leq 1.00$. From Table 2 and Figure 1, it can be observed that for each of the two {DFM + (ACN or BCN)} binary systems, the sequence of the algebraic value of the three contributions falls in the order: $V_{P^*}^E > V_{fv}^E > V_{int}^E$, while that for (DFM + BCN) it is $V_{fv}^E > V_{P^*}^E > V_{int}^E$. Comparing of the magnitude and sign of

the three contributing terms, (V_{fv}^E , $V_{P^*}^E$ and V_{int}^E), it was evident that the interaction parameter, V_{int}^E , was the most dominant in determining the magnitude of the calculated $V_{m, PFP}^E$ and the experimental V_m^E values. From the results of the model calculations presented in Figure 1 it can be inferred that the PFP theory gives a good description of excess molar volumes for the three {DFM + (ACN or BCN or PCN)} binary systems. Patterson and co-workers postulated that the discrepancies between theory and experimental values arise from additional factors that occur during mixing [12,13] since the PFP theory does not consider all the possible interactions existing in a binary mixture.

Table 1. Properties and parameters of pure components used in the PFP theory calculations: Characteristic pressure P^* , characteristic volume V^* , molar volume V^0 , thermal expansion coefficient α , isothermal compressibility κ_T , surface volume ratio S .

Component	$P^*(J.cm^{-3})$	$V^0(cm^3.mol^{-1})$	$V^*(cm^3.mol^{-1})$	$10^4\alpha(K^{-1})$	$X_T(JK^{-1}.mol^{-1})$	$10^4\kappa_T(MPa^{-1})$	$S(nm^{-1})$
DFM	671.669	135.818	110.193	9.270	256.00	6.251	12.015
ACN	642.285	52.848	40.096	13.680	91.46	11.041	15.192
BCN	622.592	103.081	84.236	8.854	190.29	6.349	12.422
PCN	601.930	70.918	54.228	13.088	119.70	11.087	14.663

Table 2. Calculated values of the interactional parameters χ_{12} and the three contributions (V_{int}^E , V_{fv}^E and $V_{P^*}^E$) from the PFP theory to the excess molar volumes for {DFM + (ACN or BCN or PCN)} binary mixtures at ($x = 0.5$), 298.15 K and atmospheric pressure.

System	χ_{12}	V_{int}^E	V_{fv}^E	$V_{P^*}^E$
DFM + ACN	-46.345	-0.4532	-0.07714	0.05598
DFM + BCN	-16.323	-0.2749	-0.00135	0.01589
DFM + PCN	-33.972	-0.4604	-0.07846	0.16125

4. Conclusions

The calculations based on the PFP theory showed that the theory adequately predicted the main features of the experimental excess molar volume, V_m^E , for {DFM + (ACN or PCN)} but failed to give a good prediction at high concentrations of DFM in the (DFM + BCN) binary system. The PFP model predicts that for each of the, {DFM + (ACN or BCN or PCN)} binary systems, the magnitude of interactional contribution, V_{int}^E , which arises from the dipole-dipole intermolecular interactions, largely determined the negative values of experimental V_m^E data. The negative magnitude of the free volume contribution, V_{fv}^E , for the three binary systems was in the order: PCN > ACN >> BCN. The internal pressure term, $V_{P^*}^E$, was negative for {DFM + (ACN or PCN)} and positive for (DFM + BCN) binary systems. In essence, the PFP theory accurately reproduces the main features of experimental V_m^E results. The deviations can be attributed to the fact that the theory does not take into consideration all the factors that arise when mixing two solutions.

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