Application of Prigogine-Flory-Patterson-Theory to Excess Molar Volumes of {Difuryl methane + (C₁-C₆)alkan-1-ol} Binary Mixtures at 298.15 K and Atmospheric Pressure

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The recently reported excess molar volume (V_m^E) data for {difuryl methane + (C₁-C₆) alkan-1-ol} binary mixtures as a function of composition at T = 298.15 K under atmospheric pressure have been used to test the applicability of Prigogine-Flory-Patterson theory. An analysis of each of the three contributions viz., interactional volume (V_{int}^E), free volume (V_{fv}^E) and characteristic pressure (V_{ps}^E) to V_m^E show that the V_{fv}^E contribution was small and as expected negative for all {difuryl methane + (C₁-C₆) alkan-1-ol} binary mixtures, exhibiting a decrease with the alka-1-ol chain length. The V_{ps}^E contribution was large and negative for mixtures containing methanol, ethanol and propan-1-ol and determined the overall experimental shape of V_m^E isotherms for {difuryl methane + (C₁-C₃) alkan-1-ol} binary mixtures. For {difuryl methane + (C₄-C₆) alkan-1-ol} binary mixtures, large and positive magnitudes of V_{ps}^E and V_{int}^E contributions are the most important in accounting for the experimental shapes of V_m^E isotherms. The correlation between the theoretical excess molar volumes (V_{PFP}^E) and experimental V_m^E data was satisfactory for {difuryl methane + (methanol or ethanol or hexan-1-ol)} binary mixtures and inadequate for {difuryl methane + (propan-1-ol, or butan-1-ol, or pentan-1-ol)} binary systems.

Keywords: Excess molar volume, Prigogine-Flory-Patterson, Difuryl methane, *n*-Alkanol.

INTRODUCTION

The Prigogine-Flory-Patterson (PFP) theory used for quantitative estimation of excess thermodynamic functions of binary liquid mixtures¹⁻⁵ has been described by Patterson and co-workers⁶⁻¹³. 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.

We are recently involved in systematic measurements of various thermophysical properties of {difuryl methane + alkan-1-ol} binary systems. Following our recent thermodynamics study of the binary mixtures containing difuryl methane¹⁴⁻¹⁶, the reported V_m^E data for {difuryl methane + (C₁-C₆) alkan-1-ol} binary mixtures at 298.15 K 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 {difuryl methane + (C₁-C₆) alkan-1-ol} binary mixtures.

EXPERIMENTAL

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 {difuryl methane + (C₁-C₆) alkan-1-ol} binary systems. According to the PFP theory, the expression for V_m^E which separates the three contributions is:

$$\begin{aligned} V_m^E / (x_1 V_1^* + x_2 V_2^*) = & [(\tilde{V}^{1/3} - 1) \tilde{V}^{2/3} \Psi_1 \theta_2 \chi_{12}] / [(4/3) \tilde{V}^{1/3} - 1] P_1^* \\ & (V_{int}^E \text{ term}) \\ & - [(\tilde{V}_1 - \tilde{V}_2)^2 [(14/9) \tilde{V}^{1/3} - 1] \Psi_1 \Psi_2] / [(4/3) \tilde{V}^{1/3} - 1] \tilde{V} \\ & (V_{fv}^E \text{ term}) \\ & + [(\tilde{V}_1 - \tilde{V}_2)(P_1^* - P_2^*) \Psi_1 \Psi_2] / (P_2^* \Psi_1 + P_1^* - P_2^*) \quad (1) \\ & (V_{ps}^E \text{ term}) \end{aligned}$$

where 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_{ps}^{E} term is the characteristic pressure contribution and is proportional to $(\tilde{V}_1 - \tilde{V}_2)(P_1^* - P_2^*)$ 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 eqn (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 by:

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

with the hard-core volume fraction, ϕ_1 and ϕ_2 for alkan-1-ol and difuryl methane 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^0 from the expression, $V_i^* = V_i^0 / \tilde{V}_i$ 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^{17,19}:

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

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 contributions²⁰. S_i value can also be estimated from van der Waals area and volume data for organic molecules²¹.

RESULTS AND DISCUSSION

The values of the various parameters of the pure components required in the PFP theory (Eqn. 1) obtained by using Flory formalism⁶⁻¹³ are listed in Table-1. The Flory interaction parameter, χ_{12} , required for the calculation of the theoretical excess molar volume, $V_{\text{PFP}}^{\text{E}}$, 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 {difuryl methane + (C₁-C₆) alkan-1-ol} binary mixtures was derived from the experimental V_m^{E} data¹⁴⁻¹⁶ at equimolar composition. The calculated values of the three PFP contributions to V_m^{E} together with the χ_{12} parameter at equimolar concentration for each binary systems are presented in Table-2. The interactional parameter, χ_{12} , for each of the {difuryl methane + (C₁-C₆) alkan-1-ol} binary mixtures has been used to calculate the $V_{\text{PFP}}^{\text{E}}$ values over the entire composition range. Fig. 1 shows the composition dependence of $V_{\text{PFP}}^{\text{E}}$, together with the three contributions ($V_{\text{int}}^{\text{E}}$, V_{fv}^{E} and V_{ps}^{E} terms), compared with the experimental V_m^{E} data for each of {difuryl methane + (C₁-C₆) alkan-1-ol} 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 $V_{\text{PFP}}^{\text{E}}$ over the entire composition range (Fig. 1) reveals that the interactional contribution, $V_{\text{int}}^{\text{E}}$ and the values of the Flory's interactional parameter χ_{12} are

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) AND 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)	C_p (JK ⁻¹ mol ⁻¹)	$10^4 \kappa_T$ (MPa ⁻¹)	S (nm ⁻¹)
Methanol	431.6	40.75	31.67	11.96 ^a	81.47 ^a	12.55 ^a	16.49 ^{b,c}
Ethanol	450.6	58.68	46.31	10.96 ^a	112.34 ^a	11.64 ^a	15.43 ^{b,c}
Propan-1-ol	458.1	75.16	60.24	10.04 ^a	143.84 ^a	10.17 ^a	14.89 ^{b,c}
Butan-1-ol	457.8	91.99	74.37	9.48 ^a	177.08 ^a	9.447 ^a	14.56 ^{b,c}
Pentan-1-ol	463.2	108.71	88.53	9.05 ^a	208.98 ^a	8.783 ^a	14.34 ^{b,c}
Hexan-1-ol	470.2	125.34	102.56	8.78 ^a	241.32 ^a	8.315 ^a	14.18 ^{b,c}
Difuryl methane	671.9	135.82	110.19	9.27 ^d	256.00 ^d	6.251 ^{d*}	12.02 ^b

^aReference 22, ^bReference 20, ^cReference 21, ^dReference 23, ^{d*}Calculated from κ_S data, Reference 23

TABLE-2
CALCULATED VALUES OF THE INTERACTIONAL PARAMETERS (χ_{12}) AND THE THREE CONTRIBUTIONS ($V_{\text{int}}^{\text{E}}$, V_{fv}^{E} AND V_{ps}^{E}) FROM THE PFP THEORY TO THE EXCESS MOLAR VOLUMES FOR {DIFURYL METHANE (2) + (C₁-C₆) ALKAN-1-OL(1)} BINARY MIXTURES AT $X_2 = 0.5$ AND 298.15 K

System	χ_{12}	$V_{\text{int}}^{\text{E}}$	V_{fv}^{E}	V_{ps}^{E}
Difuryl methane + methanol	-8.9884	-0.0774	-0.0199	-0.2579
Difuryl methane + ethanol	-5.4092	-0.0629	-0.0117	-0.2050
Difuryl methane + propan-1-ol	-0.4474	-0.0063	-0.0031	-0.1113
Difuryl methane + butan-1-ol	4.1079	0.0670	-0.0003	-0.0354
Difuryl methane + pentan-1-ol	5.8842	0.1071	-0.0004	0.0415
Difuryl methane + hexan-1-ol	6.4795	0.1283	-0.0020	0.0973

negative for each of the binary mixtures {difuryl methane + (C₁-C₃) alkan-1-ol} but were positive for {difuryl methane + (C₄-C₆) alkan-1-ol}. It is also noticeable that the sequence of the algebraic value of each of the parameters V_m^E term and χ_{12} falls in the order: hexan-1-ol > pentan-1-ol > butan-1-ol > propan-1-ol > ethanol > methanol. The interactional contribution, $V_m^{E_{int}}$ or the Flory interaction parameter χ_{12} , when negative,

Fig. 1. Excess molar volume, V_m^E , as a function of the mole fraction of difuryl methane (x_2), for {difuryl methane + (C₁-C₆) alkan-1-ol} systems at 298.15 K. (a) {difuryl methane + methanol}; (b) {difuryl methane + ethanol}; (c) {difuryl methane + propan-1-ol}; (d) {difuryl methane + butan-1-ol}; (e) {difuryl methane + pentan-1-ol}; (f) {difuryl methane + hexan-1-ol}. (•) Experimental points^{14,15,16}; dotted line, free volume contribution ($V_m^{E_{fv}}$); dashed line, interactional contribution ($V_m^{E_{int}}$); dotted-dashed line, characteristic pressure contribution ($V_m^{E_{ps}}$); solid line, total excess molar volume predicted by the PFP theory ($V_m^{E_{PFP}}$)

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 created¹³.

The free volume contributions, V_{fv}^{E} , are negative for all the {difuryl methane + (C₁-C₆) alkan-1-ol} binary mixtures, as would be expected. It is also observed that the magnitude of negative V_{fv}^{E} term decreases with increasing chain length of the alkan-1-ol, suggesting that as the chain length increases, the contribution of the V_{fv}^{E} term to the experimental V_{m}^{E} decreases. This observation may suggest that as the carbon chain length in alcohols increases, interstitial accommodation becomes poorer due to steric factors and thus dispersive interactions become more important, which contributes to an increase in the positive magnitude of the V_{m}^{E} isotherms from butan-1-ol to hexan-1-ol. Because of the smaller magnitude of the V_{fv}^{E} term, its contribution the experimental V_{m}^{E} values is minimal except to a limited degree for the {difuryl methane + (C₁-C₃) alkan-1-ol} binary mixtures (Fig. 1 a, b and c). Inspection of Table-1 further shows that the characteristic pressure P_2^* for difuryl methane was greater than P_1^* for the alkan-1-ol in each of these binary mixtures. Fig. 1 shows that the contribution arising from the $V_{\text{p}^*}^{\text{E}}$ term was large and negative for {difuryl methane + (C₁-C₄) alkan-1-ol} binary mixtures as a consequence of a large negative ($P_1^* - P_2^*$) and a positive ($\tilde{V}_1 - \tilde{V}_2$) terms. Thus the large negative contributions due to $V_{\text{p}^*}^{\text{E}}$ and $V_{\text{int}}^{\text{E}}$ terms in the {difuryl methane + (C₁-C₃) alkan-1-ol} mixtures largely determined the experimentally observed negative V_{m}^{E} data for these systems. For the {difuryl methane + butan-1-ol} binary system (Fig. 1 d), the large and positive $V_{\text{int}}^{\text{E}}$ term predominates over the relatively smaller negative $V_{\text{p}^*}^{\text{E}}$ and V_{fv}^{E} terms. The $V_{\text{int}}^{\text{E}}$ and $V_{\text{p}^*}^{\text{E}}$ contributions are large and positive for the {difuryl methane + (C₅-C₆) alkan-1-ol} binary mixtures (Figs. 1e and f) and determine the overall shapes of the experimental V_{m}^{E} isotherms. The large positive $V_{\text{int}}^{\text{E}}$ and $V_{\text{p}^*}^{\text{E}}$ suggest predominance of dispersive intermolecular interactions due to the dissociation of the hydrogen bonds in (C₅, C₆) alkan-1-ols and weak difuryl methane : (C₅, C₆) alkan-1-ol, dipole-dipole intermolecular interactions. From the results of the model calculations presented in Fig. 1 it can be inferred that the PFP theory gives a fairly good description of excess molar volumes for the {difuryl methane + (methanol, or ethanol, or hexan-1-ol)} binary systems. It can also be observed that the correlation between $V_{\text{PFP}}^{\text{E}}$ and the experimental V_{m}^{E} for the {difuryl methane + (propan-1-ol, or butan-1-ol, or pentan-1-ol)} binary mixtures was inadequate. 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.

Conclusion

It may be concluded that the interactional, $V_{\text{int}}^{\text{E}}$ and characteristic pressure $V_{\text{p}^*}^{\text{E}}$ contributions are the most important in describing the sign of the V_{m}^{E} experimental data for {difuryl methane + (C₁-C₆) alkan-1-ol} binary mixtures at 298.15 K. The V_{fv}^{E} contribution for each of {difuryl methane + (C₁-C₆) alkan-1-ol} binary mixtures was a small negative in comparison to the magnitudes of the $V_{\text{int}}^{\text{E}}$ and $V_{\text{p}^*}^{\text{E}}$ terms and rapidly decreased in magnitude with the alkan-1-ol chain length. It can also be observed that the PFP theory reproduces the main features of the experimental data by using only one adjustable parameter, χ_{12} to describe V_{m}^{E} for the {difuryl methane + (methanol or ethanol or hexan-1-ol)} binary mixtures over the entire composition range. It can further be inferred that quantitative agreement is only achieved for the {difuryl methane + (methanol or hexan-1-ol)} systems. For the {difuryl methane + (propan-1-ol or butan-1-ol or pentan-1-ol)} binary systems, which exhibit sigmoidal shaped experimental V_{m}^{E} isotherms, the PFP correlation is inadequate.

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