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Measurements and theoretical analysis of excess enthalpies and excess volumes of methyl methacrylate+*n*-alkanes (*n*-pentane, *n*-hexane, *n*-heptane, *n*-decane and *n*-dodecane)

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Abstract

Excess molar enthalpies (H_m^E) and excess molar volumes (V_m^E) have been measured for liquid binary mixtures of methyl methacrylate (MMA)+*n*-alkanes (*n*-pentane, *n*-hexane, *n*-heptane, *n*-decane and *n*-dodecane). The H_m^E and V_m^E values are positive over the whole composition range and vary quasi-regularly with the increase in carbon chain length of *n*-alkanes. The Flory (F) and Prigogine–Flory–Patterson (PFP) theories of solution thermodynamics have been used to analyze the H_m^E and V_m^E data. The key parameter needed for the analysis is the interaction parameter χ_{12} and has been treated as an adjustable parameter to be fitted to the H_m^E and V_m^E values of the binary mixtures. We have applied Flory as well as Patterson models to evaluate the single value for χ_{12} over 50 data points.

The H_m^E and V_m^E values are split into interactional, free volume and P^* contributions by using PFP theory. The free volume contributions to H_m^E and V_m^E data are found to be smaller and mostly negative. The interactional contribution calculated from PFP theory is not only in sign agreement but also close to measured H_m^E values. The interactional contribution to V_m^E values are always large and positive. The free volume and P^* effects are found to be dominant and balance the over estimation of interactional term in MMA+*n*-pentane, +*n*-hexane and +*n*-heptane. The P^* contribution, however, becomes positive in MMA+higher *n*-alkanes (>*n*-heptane).

Keywords: Excess molar enthalpies; Excess molar volumes; Methyl methacrylate+*n*-alkanes binary mixtures

1. Introduction

Studies on thermodynamic behaviour of liquid binary mixtures of acrylic ester+*n*-alkanes are of great utility from the practical as well as theoretical point of view. The production of higher homologues of acrylic esters is done by the transesterification reactions in which a methyl ester is reacted with an alcohol of the desired chain characteristics in an inert medium consisting of a simple aliphatic or aromatic hydrocarbons. Studies involving the measurements of various thermophysical properties of mixtures consisting of the binary pairs: acrylic ester+*n*-alkanes/aromatic hydrocarbons, acrylic ester+alcohols and alcohol+*n*-alkanes/aromatic hydrocarbons and the knowledge of various excess or mixing functions for these mixtures are of great help in optimizing the process parameters needed for an efficient design of the transesterification process at the industrial scale. The calculated binary coefficients for the mathematical representation of excess or deviation functions of

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the above three types of binary mixtures are also useful in the simulation of the respective functions for the ternary mixtures consisting of acrylic ester+alcohol+*n*-alkanes/aromatic hydrocarbons. From the theoretical point of view, the excess functions: excess enthalpies, excess volumes and viscosity deviations etc. can be qualitatively and quantitatively analyzed to understand the molecular interactions in both binary and ternary mixtures. Besides, these experimentally derived quantities can be used to test the solution theories.

A perusal of the literature shows that studies on binary mixtures of acrylic esters+*n*-alkanes are scarce in comparison to the wide and extensive measurements especially of excess volumes, excess enthalpies and vapour–liquid equilibrium on aliphatic alkyl alkanoate+*n*-alkanes [1–3]. The excess volumes and enthalpies of the later mixtures are found to show large deviations from ideal mixing values. These deviations are usually accounted by taking into consideration the weakening of COO–COO interactions, the changes in free volume accompanying the mixing of unlike components and the possibility of geometrical fitting of one component into another.

The changes in enthalpies, volumes and viscosities upon mixing these binary components are thus dependent on the net sum of several of these contributions. The thermodynamic properties of binary mixtures can also be explained in terms of Flory theory [4–7]. This theory was initially applied to simple hydrocarbon mixtures and further extended to systems of non-polar molecules differing in size and shape. An improvement to this theory was proposed by Patterson and coworkers [8–10] and considers excess thermodynamic properties of binary mixtures to be the sum of three contributions. The excess molar volumes can be expressed as: an interactional term calculated from the interactional parameter, χ_{12}, a free volume contribution arising out of the difference in the degrees of thermal expansion between the pure components and a P^* contribution which originates from the differences in the internal pressures and reduced volumes of the pure components. Similarly, the excess molar enthalpies have been split into a free volume and an interactional contribution.

We are involved in systematic measurements of various thermophysical properties of binary mixtures of acrylic esters+non-polar and as well as polar solvents. We have previously reported the excess volumes, excess isentropic compressibilities, excess dielectric functions for alkyl methacrylates+*n*-hexane or +*n*-heptane and excess volumes, relative permittivities and excess viscosities of an acrylic ester+*n*-alkanes (*n*-pentane–*n*-dodecane) [11–14]. The present study reports the excess molar enthalpies H_m^E (at 298.15 K) and excess molar volumes V_m^E (at 298.15 and 308.15 K) for the binary mixtures of MMA+*n*-alkanes (*n*-pentane, *n*-hexane, *n*-heptane, *n*-decane and *n*-dodecane). The Flory and Prigogine–Flory–Patterson (PFP) theories are used to predict the V_m^E and H_m^E data. The predicted excess molar enthalpies and excess volumes have been compared with the experimental data. The excess functions have been further analyzed in terms of PFP theory to ascertain various thermodynamic contributions.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA) was a Fluka purris grade chemical. It contained 5.0×10^{-5} mass fraction of hydroquinone monomethyl ether as stabilizer. The purity of MMA is stated to be >0.995 on mole fraction basis and it is used as such without any further treatment. *n*-Pentane was purchased from May and Baker, UK. *n*-Hexane and *n*-heptane were reagent grade chemicals procured locally. *n*-Decane and *n*-dodecane were procured from Alfa Biochem, India. *n*-Pentane was stored over activated molecular sieves of 0.3 nm from Fluka and filtered before use. *n*-Hexane was treated several times with concentrated sulfuric acid, then by 0.1 M potassium permanganate in 10% sulfuric acid, as well as 10% NaOH solutions. After a final washing with distilled water, it was dried over sodium wire and finally distilled. *n*-Heptane was shaken twice with concentrated sulfuric acid and then with water and a dilute aqueous solution of potassium hydroxide. It was finally distilled after allowing it to stand over KOH for 24 h. *n*-Decane and *n*-dodecane were shaken with concentrated sulfuric acid and then with an aqueous solution of 0.5 mol dm^{-3} sulfuric acid. The samples were then washed with an aqueous solution of sodium carbonate, then with water and dried with anhydrous magnesium sulfate. The substances were then fractionated by distillation. The purified hydrocarbons were stored over 0.3 nm molecular sieves. The chromatographically checked mole fraction purity of all the *n*-alkanes was found to be better than 0.995.

2.2. Methods

The binary mixtures for density measurements were prepared in hermetically sealed glass vials. The composition of mixtures has been expressed in mole fraction terms using the measured mass of each of the liquid. The mass measurements accurate to ±0.01 mg were made using a single pan balance Dhona 100 DS, Dhona, India.

A Parr 1451 solution calorimeter was used to measure excess molar enthalpies. The calorimeter consists of a glass dewar mixing chamber with a rotating sample cell, a thermistor probe, and a specially designed temperature measuring bridge, all assembled in a compact cabinet. Temperature changes can be plotted directly using a strip chart recorder and can be read to an accuracy of ±0.001 K.

The measuring cell serves the purpose of both the sample holder and agitator. It was closed with a detachable Teflon disk. The liquid sample can be added to the cell from a pipette inserted through the top stem. Excellent thermal insulation was provided by the fully silvered glass dewar which serves as mixing chamber. The flask can contain 90–120 cm^3 of solution. Temperatures were measured with a glass sheathed thermistor probe, combined with a special bridge designed for linear response over the range from 293.15 to 303.15 K, with bridge adjusted to that of a 100 μV change representing a temperature change of exactly 0.001 K. The output of the bridge is connected to a strip chart recorder, allowing the temperature change to be measured within an accuracy of 1%. The experimental error of excess molar enthalpies ${H_\mathrm{m}}^\mathrm{E}$ was estimated to be less than 1% by comparison of our results on binary mixtures of benzene+carbon tetrachloride and toluene+chlorobenzene with the literature data. The compositions reported are accurate to 0.01%. Typical measurement involves the addition of the components in the dewar mixing chamber and measuring the resulting temperature change by means of the thermistor probe. At the start of experiment, one of the liquids was held in a sealed glass rotating cell in thermal contact with the other component. When the system comes to thermal equilibrium, the contents of the rotating cell were mixed with the surrounding liquid. The temperature changes due to the mixing process were sensed by the thermistor and recorded on the strip chart recorder.

Densities of pure liquids and their mixtures were measured with an high precision vibrating tube digital densimeter (Anton Paar DMA 5000). The temperature within the oscillating tube was controlled to an accuracy of ±0.001 K by in-built integrated Pt 100 thermometers. The instrument was calibrated with air, double distilled and freshly degassed water at 293.15, 313.15 and 333.15 K during every session. The densities of all the mixtures belonging to a given system (including pure components) were measured during one session. The experimental precision (reproducibility of measured densities during a session) was better than three units in the sixth decimal place. The accuracy of the measurements was judged from the values of the density for a given pure compound measured in different sessions. The values varied from session to session and this variation may be ascribed to the possible effects of hygroscopicity over a long period of time and occasional use of solvents from different manufacturer's lot. However, the variation hardly occurred beyond one unit in the fifth decimal place. The binary mixtures were prepared shortly before the density measurements and the pure components were remeasured together with the mixtures. We believe that this procedure would cancel any systematic errors in the computation of excess volumes.

3. Theory

The detailed description of Flory theory and its refinement by Prigogine and coworkers have been given in detail in the original papers [5–10]. For convenience, a pertinent summary of equations used in this work is given below. In the Flory model, the excess molar volume is given exactly by

$${V_\mathrm{m}}^\mathrm{E} = \frac{[(xV^*)_1 + (xV^*)_2[(\Phi\tilde{v})_1 + (\Phi\tilde{v})_2]^{7/3}(\tilde{T} - \tilde{T}^0)]}{(4/3) - [(\Phi\tilde{v})_1 + (\Phi\tilde{v})_2]^{1/3}} \tag{1}$$

where V^* and $\tilde{v}$ are the hard core and reduced volumes, x and Φ the mole and segment fractions of pure MMA (1) and n-alkane (2) components. $\tilde{T}$ and $\tilde{T}^0$ are the reduced and ideal reduced temperatures of the mixture, respectively. The reduced temperature $\tilde{T}$ is defined as

$$\tilde{T} = \frac{(\Phi P^* \tilde{T})_1 + (\Phi P^* \tilde{T})_2}{(\Phi P^*)_1 + (\Phi P^*)_2 - \Phi_1 \theta_2 \chi_{12}} \tag{2}$$

where P^* is the characteristic pressure, calculated from the thermal expansion coefficient α_i, isothermal compressibility κ_i and reduced volume $\tilde{v}_i$ of respective components by the relation

$$P_i^* = \left(\frac{\alpha_i}{\kappa_i}\right) T (\tilde{v}_i)^2 \tag{3}$$

The reduced volume for pure substance i is defined in terms of the thermal expansion coefficient α_i,

$$\tilde{v}_i = \left[\frac{[1 + (4/3)\alpha_i T)]}{(1 + \alpha_i T)}\right]^3 \tag{4}$$

At zero pressure, the reduced volume and temperature satisfy the reduced equation of state

$$\tilde{T}_i = \left(\frac{\tilde{v}_i^{1/3} - 1}{\tilde{v}_i^{4/3}}\right) \tag{5}$$

Similarly, the ideal reduced temperature for the mixture can be calculated using the ideal reduced volume for the mixture $\tilde{v}^0$

$$\tilde{v}^0 = (\Phi \tilde{v})_1 + (\Phi \tilde{v})_2 \tag{6}$$

PFP theory gave the following expression for ${V_\mathrm{m}}^\mathrm{E}$ in terms of the three contributions:

$$\begin{aligned}
&\frac{{V_\mathrm{m}}^\mathrm{E}}{(xV^*)_1 + (xV^*)_2} \\
&\quad = \frac{(\tilde{v}^{1/3} - 1)\tilde{v}^{2/3} \Psi_1 \theta_2 \chi_{12}}{[(4/3)\tilde{v}^{-1/3} - 1]P_1^*} \quad \text{(interactional term)} \\
&\quad - \frac{(\tilde{v}_1 - \tilde{v}_2)^2((14/9)\tilde{v}^{-1/3} - 1)\psi_1 \psi_2}{[(4/3)\tilde{v}^{-1/3} - 1]\tilde{v}} \\
&\quad (\tilde{v} \text{ curvature}) \\
&\quad + \frac{(\tilde{v}_1 - \tilde{v}_2)(P_1^* - P_2^*)\psi_1 \psi_2}{P_2^* \psi_1 + P_1^* \psi_2} \quad (P^* \text{ effect})
\end{aligned} \tag{7}$$

The term χ_{12} in Eqs. (2) and (7) is the interactional parameter. The terms ϕ, θ and Ψ are the segment fraction, site fraction and the contact energy fraction, respectively, and are given by,

$$\Phi_1 = (1 - \Phi_2) = \frac{(xV^*)_1}{[(xV^*)_1 + (xV^*)_2]} \tag{8}$$

$$\theta_1 = (1 - \theta_2) = \frac{\Phi_1}{[\Phi_1 + (\Phi S)_2 / S_1]} \tag{9}$$

and the ratio $S_1/S_2 = (V_1^*/V_2^*)^{1/3}$

$$\Psi_1 = (1 - \Psi_2) = \frac{(\Phi P^*)_1}{[(\Phi P^*)_1 + (\Phi P^*)_2]} \tag{10}$$

In the Flory model the excess molar enthalpy is given by

$$\begin{aligned}
{H_\mathrm{m}}^\mathrm{E} = {} & (xP^*V^*)_1(\tilde{v}_1^{-1} - \tilde{v}^{-1}) + (xP^*V^*)_2(\tilde{v}_2^{-1} - \tilde{v}^{-1}) \\
& + \frac{x_1 V_1^* \theta_2 \chi_{12}}{\tilde{v}}
\end{aligned} \tag{11}$$

where

$$\tilde{v} = \tilde{v}^0 + \tilde{v}^\mathrm{E} \tag{12}$$

and

$$\tilde{v}^\mathrm{E} = (\tilde{v}^0)^{7/3}\left[\tfrac{4}{3} - (\tilde{v}^0)^{1/3}(\tilde{T} - \tilde{T}^0)\right] \tag{13}$$

PFP theory separates the excess molar enthalpies into a free volume contribution and an interaction contribution. The free volume contribution is given by

$$\frac{{H_\mathrm{m}}^\mathrm{E}(\text{f.v.})}{(xU^*)_1 + (xU^*)_2} = \tilde{C}_p(\tilde{T}_\mathrm{u})[(\Psi \tilde{T})_1 + (\Psi \tilde{T})_2 - \tilde{T}_\mathrm{u}] \tag{14}$$

where $\tilde{T}_\mathrm{u}$ is an average reduced temperature of binary mixture, appropriate to the reduced configurational energy $\tilde{U}$ and is defined as

$$\tilde{U}(\tilde{T}_\mathrm{u}) = \Psi_1 \tilde{U}(\tilde{T}_1) + \psi_2 \tilde{U}(\tilde{T}_2) \tag{15}$$

The reduced heat capacity $\tilde{C}_p$ for the pure components and for the mixture is calculated from a knowledge of the reduced volume of the pure or mixture components by

$$\tilde{C}_p^{-1} = (\tfrac{4}{3})\tilde{v}^{-1/3} - 1 \tag{16}$$

$\tilde{U}$ is defined as

$$\tilde{U} = -\tilde{v}^{-1} \tag{17}$$

and $U_i^* = P_i^* V_i^*$

Table 1
Physico-chemical data of pure components at 298.15 K

	α (k K^{-1})	V_T (cm^3 mol^{-1})	V^*	$\tilde{v}$	P^* (J mol^{-1})	$\tilde{T}$	C_p (J mol^{-1})	U^*
MMA	1.286	106.7833	81.9204	1.3035	627	0.0649	191.1	51364
n-Pentane	1.643	116.1911	85.0531	1.3661	431	0.0723		36658
n-Hexane	1.409	131.5880	99.2443	1.3259	430	0.0677	195.3	39995
n-Heptane	1.267	147.4875	113.4519	1.3000	435	0.0644	224.7	49352
n-Decane	1.156	195.9565	153.2347	1.2788	488	0.0615	314.6	74779
n-Dodecane	1.030	228.5789	182.3089	1.2538	476	0.0579	376.0	86779

The interactional contribution is given by

$$\frac{H_\mathrm{m}{}^\mathrm{E}(\text{interact.})}{(xU^*)_1+(xU^*)_2}=\frac{[-\tilde{U}(\tilde{T}_\mathrm{u})+\tilde{T}_\mathrm{u}\tilde{C}_p(\tilde{T}_\mathrm{u})]\chi_{12}\Psi_1\theta_2}{P_1^*} \qquad (18)$$

The various characteristic and reduced parameters of pure components needed for estimating the $V_\mathrm{m}{}^\mathrm{E}$ and $H_\mathrm{m}{}^\mathrm{E}$ of binary mixtures are calculated by appropriate relations and are given in Table 1.

4. Results

The experimentally measured excess molar enthalpies and excess molar volumes are given in Tables 2 and 3, respectively. The $V_\mathrm{m}{}^\mathrm{E}$ and $H_\mathrm{m}{}^\mathrm{E}$ values are also fitted to an equation of type

$$H_\mathrm{m}{}^\mathrm{E}(\mathrm{J\,mol^{-1}}) \quad \text{or} \quad V_\mathrm{m}{}^\mathrm{E}(\mathrm{cm^3\,mol^{-1}}) = x_1(1-x_1)\sum_{i=0}^{n} a_i(2x_1-1)^i \qquad (19)$$

where x_1 is the MMA mole fraction and a_i are the coefficients. The values of the coefficients are estimated by regression analysis based on least-squares method. The summary of the analysis along with the standard deviation σ between experimental and fitted values are given in Table 4.

The analysis of excess molar enthalpies and excess molar volumes of binary mixtures in terms of Flory and PFP theories is primarily based on the estimation of the interaction parameter, χ_{12}. χ_{12} is considered as an adjustable parameter. χ_{12} is estimated from the fit of experimental $V_\mathrm{m}{}^\mathrm{E}$ to Eqs. (1) and (2) for the Flory model and to Eq. (7) for the PFP theory. Similarly, χ_{12} can also be calculated from the fit of experimental

Table 2
Experimental excess molar enthalpies $H_\mathrm{m}{}^\mathrm{E}$ (in J mol^{-1}) of MMA+*n*-alkanes at 298.15 K

x_1	$H_\mathrm{m}{}^\mathrm{E}$
MMA (1)+*n*-pentane	
0.0375	243
0.0788	474
0.1236	684
0.1778	888
0.2239	1023
0.2728	1130
0.3450	1231
0.4189	1271
0.4432	1272
0 4943	1257
0.5415	1222
0.5807	1180
0.6439	1088
0.6993	982
0.7513	864
0.8023	728
0.8552	566
0.8971	422
0.9541	201
MMA (1)+*n*-hexane	
0.0366	207
0.0978	518
0.1533	756
0.2153	972
0.2587	1093
0.3946	1309
0.4769	1332
0.5467	1295
0.5944	1244
0.6767	1109
0.7500	942
0.8011	800
0.8682	578
0.9158	394
0.9711	147
MMA (1)+*n*-heptane	
0.420	243

Table 2 (*Continued*)

x_1	H_m^E
0.0737	408
0.1035	548
0. 1370	690
0.2118	952
0.2619	1087
0.3267	1218
0.3803	1291
0.4269	1330
0.4566	1343
0.5000	1346
0.5664	1317
0.5958	1290
0.6616	1200
0.7073	1112
0.7581	989
0.8041	854
0.8519	689
0.9022	490
0.9434	297
0.9757	133
MMA (1)+*n*-decane	
0.0335	186
0.0725	383
0.1142	571
0.1553	737
0.1880	856
0.2212	965
0.2540	1063
0.2894	1158
0.3199	1230
0.3481	1290
0.3774	1344
0.4044	1387
0.4704	1461
0.5261	1489
0.5778	1484
0.6267	1449
0.6751	1383
0.7250	1281
0.7707	1155
0.8184	988
0.8530	844
0.8872	681
0.9159	529
0.9399	390
0.9228	249
0.9822	122
MMA (1)+*n*-dodecane	
0.0476	277
0.0937	518
0.1399	733
0.1799	899
0.2204	1048
0.2492	1142
0.2742	1216
0.3373	1372
0.3817	1457
0.4237	1528
0.4710	1563
0.5084	1582
0.5439	1586
0.5853	1573
0.6245	1543
0.6670	1489
0.7126	1405
0.7562	1295
0.8038	1141
0.8477	962
0.8851	779
0.9181	591
0.9453	415
0.9697	241

Table 3
Experimental excess molar volumes, V_m^E of MMA+*n*-alkanes at 298.15 and 308.15 K

x_1	$V_m^E (cm^3 mol^{-1})$	
	T=298.15 K	T=308.15 K
MMA+*n*-pentane		
0.0598	0.0525	
0.1277	0.9940	
0.2642	0.1723	
0.3488	0.2125	
0.4851	0.2746	
0.4885	0.2761	
0.5521	0.3013	
0.6715	0.3294	
0.8034	0.2986	
0.8528	0.2592	
0.9560	0.1040	
MMA+*n*-heptane		
0.0445	0.1111	0.1581
0.1446	0.3331	0.4217
0.2470	0.5183	0.5929
0.3472	0.6551	0.6948
0.4492	0.7444	0.7513
0.5026	0.7688	0.7650
0.5484	0.7765	0.7680
0.6449	0.7488	0.7446
0.7636	0.6229	0.6417
0.8320	0.4980	0.5295
0.9452	0.1948	0.2213

Table 3 (*Continued*)

x_1	V_m^E(cm^3 mol^{-1})	
	T=298.15 K	T=308.15 K
MMA+n-dodecane		
0.0564	0.3037	0.3390
0.1552	0.6428	0.7078
0.2588	0.8286	0.8985
0.3551	0.9201	0.9842
0.4503	0.9770	1.0347
0.4999	0.9999	1.0557
0.5535	1.0195	1.0747
0.6605	1.0294	1.0873
0.7569	0.9668	1.0273
0.8548	0.7652	0.8196
0.9548	0.3169	0.3424
MMA+n-hexane		
0.0554	0.0846	0.1201
0.1541	0.2280	0.2922
0.2770	0.3866	0.4517
0.3232	0.4381	0.4993
0.4494	0.5477	0.5991
0.4978	0.5747	0.6247
0.5521	0.5931	0.6435
0.6509	0.5879	0.6439
0.7542	0.5186	0.5814
0.8497	0.3831	0.4433
0.9522	0.1472	0.1770
MMA+n-decane		
0.0542	0.2351	0.2687
0.1522	0.5305	0.5897
0.2613	0.7223	0.7831
0.3551	0.8153	0.8736
0.4542	0.8687	0.9316
0.5013	0.8816	0.9506
0.5551	0.8866	0.9657
0.6582	0.8612	0.9641
0.7529	0.7776	0.8977
0.8551	0.5826	0.6960
0.9538	0.2356	0.2904

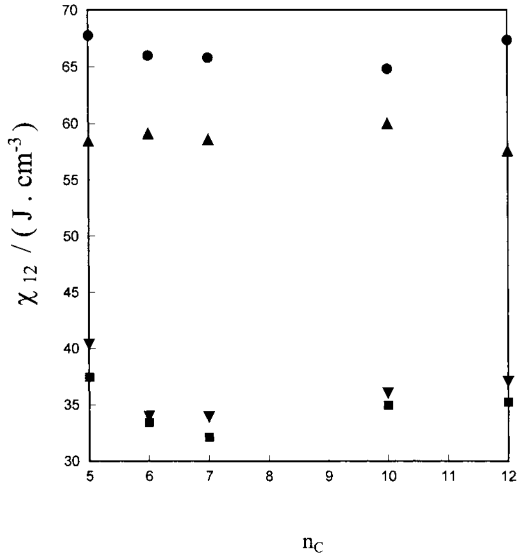

Fig. 1. Variation of interaction parameter χ_{12}, with the number of carbons in n-alkanes at 298.15 K. χ_{12} calculated from the fits of (●) H_m^E(Flory), (▲) H_m^E(Patt.), (▼) V_m^E(Flory) and (■) V_m^E(Patt.).

H_m^E values to Eq. (11) for the Flory model and Eq. (14) and (20) for the PFP theory. All the fits were done over the whole mole fraction range and using more than 50 data points. These data points were obtained by using the coefficients of Table 4 and Eq. (19). The final values for χ_{12} were chosen such that they minimize the $\sigma(H_m^E)$ and $\sigma(V_m^E)$ over all the points. The interaction parameter χ_{12} as evaluated by both the formulations from the fits of H_m^E and V_m^E at 298.15 K, is plotted as a function of the number of carbons in n-alkane in Fig. 1. It can be seen from the figure that no definite trend in variation of χ_{12} on the carbon chain length of n-alkane is observed. Furthermore, the χ_{12} values obtained from the fits of H_m^E are larger than those derived from the fits of experimental V_m^E data. The values of $\chi_{12}(H_m^E)$ and $\chi_{12}(V_m^E)$ obtained from Flory and Patterson models were used in calculating the H_m^E(Interact.) over the whole mole fraction range. Similarly, the values of $\chi_{12}(H_m^E)$ and $\chi_{12}(V_m^E)$ were used to calculate the V_m^E(Flory) and V_m^E(Interact.) at 298.15 K. Eq. (14) was used to evaluate the H_m^E(f.v.) contribution. Similarly, the second and third terms on the right-hand side of Eq. (7) were employed to calculate the V_m^E(f.v.) and $V_m^E(P^*)$ contributions for all the binary mixtures over the whole composition range. Then the final values of H_m^E and V_m^E were taken as the sum of the individual contributions, i.e. H_m^E(Cal.) $=H_m^E$(Interact.)$+H_m^E$(f.v.) and V_m^E(Cal.) $=V_m^E$(Interact.)$+V_m^E$(f.v.)$+V_m^E(P^*)$.

The experimental and theoretically obtained H_m^E and V_m^E values (for both the models) at equimolar composition are summarized in Tables 5 and 6. The deviations, δH_m^E and δV_m^E values are also given in the last four columns of the table. A perusal of data presented in Tables 5 and 6 reveals that the theoretical equimolar excess enthalpies as evaluated using the

Table 4
Parameters a_i and standard deviation σ for mathematical representation of $V_m{}^E$(cm^3 mol^{-1}) and $H_m{}^E$(J mol^{-1}) of binary mixtures by Eq. (19)

Mixture		T=298.15 K					T=308.15 K			
		a_0	a_1	a_2	a_3	σ	a_0	a_1	a_2	σ
MMA+n-pentane	$V_m{}^E$	1.1237	0.8360	0.7056	–	0.0001	–	–	–	–
	$H_m{}^E$	5013	−1158	759	–	0.2	–	–	–	–
MMA+n-hexane	$V_m{}^E$	2.3030	0.8993	0.1432	–	0.0001	2.5027	0.8779	0.7242	0.0001
	$H_m{}^E$	5292	1325	1862	528	0.6	–	–	–	–
MMA+n-heptane	$V_m{}^E$	3.0719	0.6399	0.1498	–	0.0001	3.0583	0.3310	1.1593	0.0001
	$H_m{}^E$	5388	−253	506	–	0.4	–	–	–	–
MMA+n-decane	$V_m{}^E$	3.5254	0.3943	1.1769	–	0.0001	3.8007	0.7074	2.6064	0.0001
	$H_m{}^E$	5920	971	511	−369	0.6	–	–	–	–
MMA+n-dodecane	$V_m{}^E$	3.9997	0.8405	3.1164	–	0.0001	4.2227	0.7892	3.6173	0.0001
	$H_m{}^E$	6315	813	947	336	0.6	–	–	–	–

$\chi_{12}(H_m{}^E)$ value following PFP approach agreed to ±5.5% with the experimental values. The $\chi_{12}(H_m{}^E)$ value obtained from the Flory model and the $\chi_{12}(H_m{}^E)$ values from Flory and PFP approaches predicted the equimolar $H_m{}^E$ values with larger deviations (≈30–45%). Similarly, the equimolar $V_m{}^E$ values as calculated by using the $\chi_{12}(H_m{}^E)$ values from Flory and PFP theories, are approximately close to experimentally measured values. It is surprising to note that the use of $\chi_{12}(H_m{}^E)$ obtained by the models produced not only large variations in the magnitude of $V_m{}^E$ but also are not even in sign agreement with the experimental values.

The variation of experimental $H_m{}^E$ values as a function of MMA mole fraction at 298.15 K is shown in Fig. 2. The theoretically predicted $H_m{}^E$ values using the $\chi_{12}(H_m{}^E)$ value following PFP theory are also shown as dotted lines in the figure. The $H_m{}^E$ values for MMA+n-alkanes and +n-heptane mixture are also reported in the literature by Luo et al. [15]. Our observed $H^E_{m0.5}$ values of 1323 and 1347 J mol^{-1} are 16 and 11.5% more than the values of 1137 and 1207 J mol^{-1} for the same mixtures and at the same temperature reported by Luo et al. The comparison of our $H_m{}^E$ values for these mixtures over the whole mole fraction range with those reported by Luo et al. revealed average absolute deviations of 11.6 and 9.8%. However, it may be noted that our $H^E_{m0.5}$ values are 1323 and 1347 J mol^{-1}, while those reported by Luo et al. are 1137 and 1207 J mol^{-1} for the same mixtures and both, however, show larger deviations from the theoretically calculated values. We could not find the $H_m{}^E$ data for the rest of the mixtures in the literature for comparison of our values.

The experimental excess molar volumes $V_m{}^E$ of all the five binary mixtures are graphically shown as a

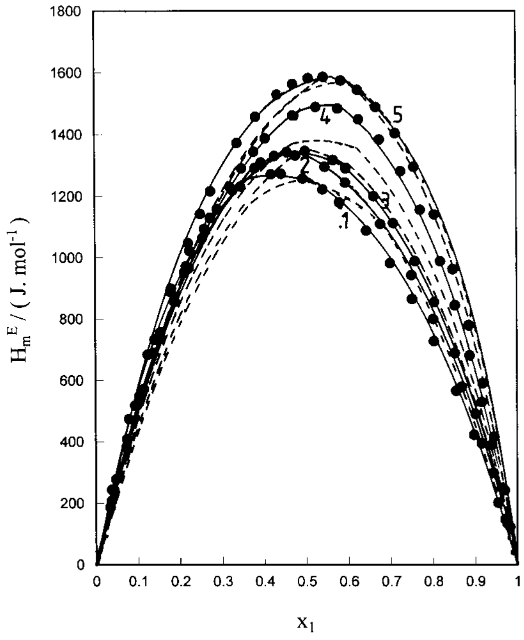

Fig. 2. Excess molar enthalpies $H_m{}^E$ at 298.15 K for the binary mixtures of MMA+n-pentane (1), +n-hexane (2), +n-heptane (3), +n-decane (4) and +n-dodecane (5). (●) Experimental values; (—) calculated from Eq. (19) with parameters from Table 4; (- - -) estimated using $\chi_{12}(H_m{}^E)$ from PFP model.

Table 5
Flory and PFP calculated contributions to the H_m^E(J mol^{-1}) data at equimolar composition along with the deviations between experimental and calculated values at 298.15 K

Mixtures	H_m^E (Exp.)	H_m^E(Interact.)				H_m^E(f.v)	H_m^E (Cal.)=H_m^E(Interact.)+H_m^E(f.v)				δH_m^E H_m^E (Exp.)−H_m^E(Cal.)			
		Flory		Patt.			Flory		Patt.		Flory		Patt.	
		$\chi(H_m^E)$	$\chi(V_m^E)$	$\chi(H_m^E)$	$\chi(V_m^E)$		$\chi(H_m^E)$	$\chi(V_m^E)$	$\chi(H_m^E)$	$\chi(V_m^E)$	$\chi(H_m^E)$	$\chi(V_m^E)$	$\chi(H_m^E)$	$\chi(V_m^E)$
MMA+*n*-pentane	1253	1488	890	1283	822	−14	1474	876	1269	808	−221	377	−16	445
MMA+*n*-hexane	1323	1488	769	1332	754	2	1490	771	1334	756	−167	552	−11	567
MMA+*n*-heptane	1347	1584	820	1400	773	1	1585	821	1401	774	−240	526	−54	573
MMA+*n*-decane	1480	1689	943	1562	910	−7	1682	936	1555	903	−202	544	−75	577
MMA+*n*-dodecane	1579	1824	1007	1558	954	−17	1807	990	1541	937	−228	589	38	642

Table 6

Flory and PFP calculated contributions to the V_m^E(cm^3 mol^{-1}) data at equimolar composition along with the deviations between experimental and calculated values at 298.15 K

Mixtures	V_m^E (Exp.)	V_m^E(Flory)		V_m^E(Interact.)		V_m^E(Patt.)		V_m^E(Cal.) (a+b+c)		δV_m^E (V_m^E (Exp.)$-V_m^E$ (Cal.))			
		$\chi(H_m^E)$	$\chi(V_m^E)$	$\chi(H_m^E)$(a)	$\chi(V_m^E)$(a)	V_m^E(f.v)(b)	V_m^E(P^*)(c)			Flory		Patt.	
										$\chi(H_m^E)$	$\chi(V_m^E)$	$\chi(H_m^E)$	$\chi(V_m^E)$
MMA+*n*-pentane	0.2809	0.9871	0.3391	1.3942	0.8943	−0.1169	−0.4842	0.7931	0.2932	−0.7026	−0.0582	−0.5122	−0.0123
MMA+*n*-hexane	0.5758	1.3152	0.5733	1.3950	0.7906	−0.0181	−0.1902	1.1867	0.5823	−0.7394	0.0025	−0.6109	−0.0065
MMA+*n*-heptane	0.7680	1.2604	0.6612	1.1234	0.6185	−0.0001	0.0293	1.1526	0.6477	−0.4924	0.1068	−0.3846	0.1203
MMA+*n*-decane	0.8814	1.5681	0.9363	1.3521	0.7886	−0.0235	0.1764	1.5050	0.9415	−0.6867	−0.0549	−0.6236	−0.0601
MMA+*n*-dodecane	0.9999	1.7252	1.0712	1.2598	0.5806	−0.1194	0.4111	1.5515	0.8723	−0.7253	−0.0713	−0.5516	0.1276

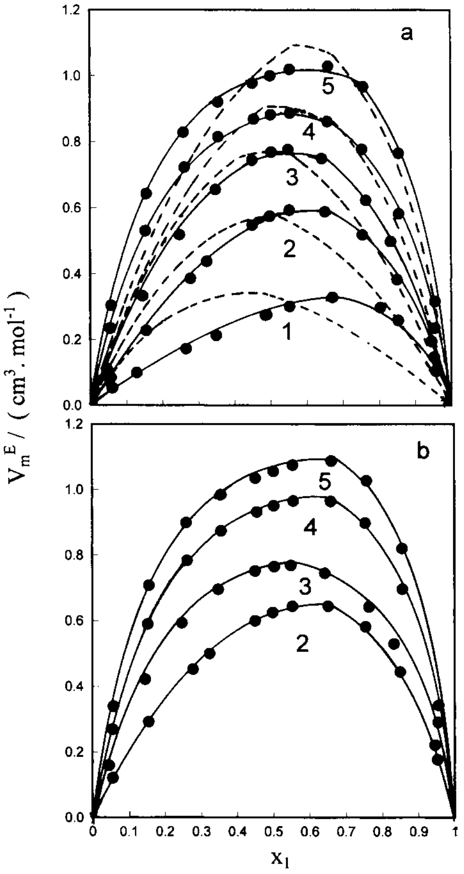

Fig. 3. Excess molar volumes V_m^E at (a) 298.15 K and (b) 308.15 K for binary mixtures of MMA+n-pentane (1), +n-hexane (2), +n-heptane (3), +n-decane (4) and +n-dodecane (5). (●) Experimental values; (—) calculated from Eq. (19) with parameters from Table 4; (- - -) estimated using $\chi_{12}(V_m^E)$ from Flory model.

function of MMA mole fraction in parts (a) and (b) of Fig. 3. Our observed $V_{m0.5}^E$ values of 0.5758 and 0.7680 cm^3 mol^{-1} for MMA+n-hexane and +n-heptane at 298.15 K are in excellent agreement with the equimolar V_m^E of 0.5750 and 0.7685 cm^3 mol^{-1} of Luo et al. [15]. The theoretically calculated V_m^E values using the $\chi_{12}(H_m^E)$ value estimated from Flory model are also shown as dotted lines in part (a) of Fig. 3. It can be seen from the figure that the Flory model predicted V_m^E values closely at the equimolar composition while the predictions are only approximate in the ester-low as well as ester-rich regions.

5. Discussion

The excess molar enthalpies H_m^E (Fig. 2) and excess molar volumes V_m^E (Fig. 3) are positive over the entire range of composition. Both the quantities in the equimolar composition increase quasi-regularly with the increase in carbon chain length in n-alkanes. The endothermicity observed in H_m^E values for all the mixtures indicates the decrease in the high energetic COO–COO dipole interactions among ester species in presence of n-alkanes. The weakening of these interactions leads to a volume expansion and hence these mixtures are characterized by large and positive excess volumes. These observations are qualitatively similar to the H_m^E and V_m^E results of simple alkyl ester+n-alkanes [16–18]. An attempt is also made to account for the reasons that lead to the large discrepancies between experimental and calculated H_m^E and V_m^E values using Flory and Patterson models. The splitting of H_m^E and V_m^E values into various terms, namely, interactional, free volume (f.v.) and P^* can be done using the Flory and Patterson equations. The columns 3–6 of upper part of Table 4 show the interactional contributions as calculated by different χ_{12} values from both the models and column 7 gives the free volume contribution to the H_m^E. A close examination of these columns reveals that the H_m^E(Interact.) terms are always positive. The large positive H_m^E(Interact.) for MMA+n-alkanes mixtures can be attributed to the possible endothermic effects that may arise due to the weakening of dipolar interactions in ester molecules upon mixing with n-alkanes. The H_m^E(f.v.) term is in general either negative or very small positive in MMA+n-hexane and +n-heptane. The negative H_m^E(f.v.) in particular and highly diminished positive values in general indicate the absence of any specific interactions in these mixtures. A perusal of the last four columns of the upper part of the table further shows that both Flory model and PFP model (using $\chi_{12}(V_m^E)$ value) predicted the H_m^E values poorly with mean deviations between the experimental and calculated values as large as 20–35%.

The contributions, V_m^E(Interact.), V_m^E(f.v) and $V_m^E(P^*)$ for all the five binary mixtures are listed in columns 5, 6, 7 and 8, respectively. The usage of $\chi_{12}(H_m^E)$ obtained from both Flory and PFP models results in large and positive V_m^E(Interact.) values. In contrast, the V_m^E(f.v.) term is small and negative in all the mixtures. The $V_m^E(P^*)$ term, however, is negative for MMA+n-pentane and +n-hexane and becomes increasingly positive from MMA+n-heptane to MMA+n-dodecane mixtures. The sum of the individual contributions, i.e. V_m^E(Interact.)($\chi(V_m^E)$), V_m^E(f.v.) and $V_m^E(P^*)$ listed in columns 6, 7 and 8 agree with the experimental values with deviations ranging from 0.003 to 0.10 cm^3 mol^{-1}. It can also be seen from columns 11 and 13 that usage of $\chi_{12}(H_m^E)$ from both models predicted the V_m^E values with large negative deviations.

A perusal of H_m^E(Interact.) contributions as given in columns 3–6 in the upper part of Tables 5 and 6 reveals that the H_m^E(Interact.) values calculated using the $\chi_{12}(V_m^E)$ are far smaller than the H_m^E (Exp.) values. Since H_m^E(f.v.) values are too small and even negative, it is the H_m^E(Interact.) values which contribute predominantly to the observed values. Hence the role of H_m^E(f.v.) is less important in the net enthalpy changes in these mixtures. The reasonable agreement found between experimental H_m^E values on one hand and predicted values obtained by combining H_m^E(Interact.)($\chi(H_m^E)$)(Patt.) and H_m^E(f.v.) on the other indicates that the interactional term in H_m^E does depend strongly on the destruction of dipolar association in ester rather than on the dispersive force interactions between unlike molecules. The predicted V_m^E values by using the $\chi_{12}(V_m^E)$ (Flory model) and the net V_m^E values calculated by combining V_m^E(Interact.)(χV_m^E)(Patt.), V_m^E(f.v.) and $V_m^E(P^*)$ are in good agreement with the experimental V_m^E data. The $\chi_{12}(V_m^E)$ values are almost 1.5–2 times less than $\chi_{12}(H_m^E)$. The large χ_{12} values calculated from the fit of H_m^E data are perhaps responsible for the over estimation of V_m^E(Interact.) in Flory as well as Patterson models. The very fact that the net combined values of V_m^E(Interact.), V_m^E(f.v.) and $V_m^E(P^*)$ are close to V_m^E experimental data shows that not only weakening of dipolar association in ester species, but also the free volume changes upon mixing and the difference in internal pressures and reduced volumes of both the pure components equally contribute to the observed V_m^E values.

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