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Journal of Saudi Chemical Society

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ORIGINAL ARTICLE

The theoretical study of effect of temperature on the physicochemical parameters for binary mixtures of vinyl acetate and benzyl acetate, + *o*-xylene, + *m*-xylene and + *p*-xylene

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Abstract In this work we used the Flory theory of liquid mixtures for determining the thermal parameters such as excess thermal expansion coefficients α^E, and isothermal coefficient of pressure excess molar enthalpy $(\partial H_m^E/\partial P)_{T,x}$, of the binary mixtures formed by vinyl acetate and benzyl acetate + *o*-xylene, or *m*-xylene, or *p*-xylene at (303.15 and 313.15) K. From these data the acoustical parameters such as available volume (V_a), isothermal (K^l), isobaric (K), and isochoric acoustical parameters ($K^{l/l}$), isochoric temperature coefficient of the internal pressure (X), and Moelwyn-Hughes parameter (C_1), have been calculated. The excess thermal expansion coefficient α^E, for the binary mixtures of benzyl acetate + *o*-xylene and vinyl acetate + *m*-xylene are negative in $x = 0.2434$ and $x = 0.9602$, respectively, and positive for all mole fractions and increase with increasing temperatures from (303.15 and 313.15) K. The isothermal coefficient of pressure excess molar enthalpy, $(\partial H_m^E/\partial P)_{T,x}$, for vinyl acetate + *o*-xylene, + *p*-xylene and benzyl acetate + *m*-xylene, + *p*-xylene are negative and decrease with increasing temperatures from (303.15 and 313.15) K. The isothermal coefficient of pressure excess molar enthalpy, $(\partial H_m^E/\partial P)_{T,x}$, for a binary mixture of benzyl acetate + *o*-xylene is positive and increases with increasing temperatures from (303.15 and 313.15) K.

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Peer review under responsibility of King Saud University.

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1. Introduction

Following the previous researches about excess parameters of other mixtures (Rezaei-Sameti et al., 2009, 2010a,b,c and Rezaei-Sameti and Rakhshi, 2011; Iloukhani and Rakhshi, 2009, 2011), in this project we used the experimental data (Rathnam et al., 2010), of the binary mixtures formed by

{vinyl acetate and benzyl acetate + o-xylene, or m-xylene, or p-xylene} at 303.15 and 313.15 K for study the thermodynamic and acoustical parameters of binary mixtures. These parameters are useful for understanding the nature of molecular systems and physico-chemical behavior in liquid mixtures. The non-rectilinear behavior of the above-mentioned properties of liquid mixtures with changing mole fractions is attributed to the difference in size of the molecules and strength of interactions. Here, we have reported thermal expansion coefficients, α, excess thermal expansion coefficient, α^E, and isothermal coefficient of pressure excess molar enthalpy, $(\partial H_m^E/\partial P)_{T,x}$, available volume ($V_a$), isothermal ($K'$), isobaric ($K$), and isochoric acoustical parameters (K''), isochoric temperature coefficient of the internal pressure (X), and Moelwyn-Hughes parameter (C_1) in combination with other mixing properties, provide valuable information for qualitatively analyzing the molecular interactions between molecules. The excess thermal expansion coefficients, α^E, and isothermal

Table 1 Flory and related parameters of pure components in the temperature range (303.15 and 313.15 K).

|	T/K	$10^4\alpha[K^{-1}]$	ρ/g cm^{-3}[10]	V^*/(cm^3.mol^{-1})	T^*/K^{-1}	$\widetilde{V}$	$\widetilde{T}$
Vinyl acetate	303.15	11.397	0.9191	73.2129	4966.7581	1.2794	0.0610
	313.15	14.950	0.9071	70.0951	4455.3156	1.3540	0.0703
Benzyl acetate	303.15	4.508	1.0476	50.9811	8939.1489	1.1251	0.0339
	313.15	7.212	1.0415	48.2492	6535.3152	1.1958	0.0479
o-xylene	303.15	7.924	0.8715	100.9869	6089.8319	1.2065	0.0498
	313.15	11.034	0.8633	96.1323	5130.2775	1.2974	0.0610
m-xylene	303.15	8.093	0.8553	102.5783	6011.8421	1.2102	0.0504
	313.15	11.225	0.8471	97.6750	5085.9394	1.2833	0.0616
p-xylene	303.15	8.575	0.8521	102.0702	5807.8545	1.2208	0.0522
	313.15	11.766	0.8435	97.2695	4968.2729	1.2941	0.0630
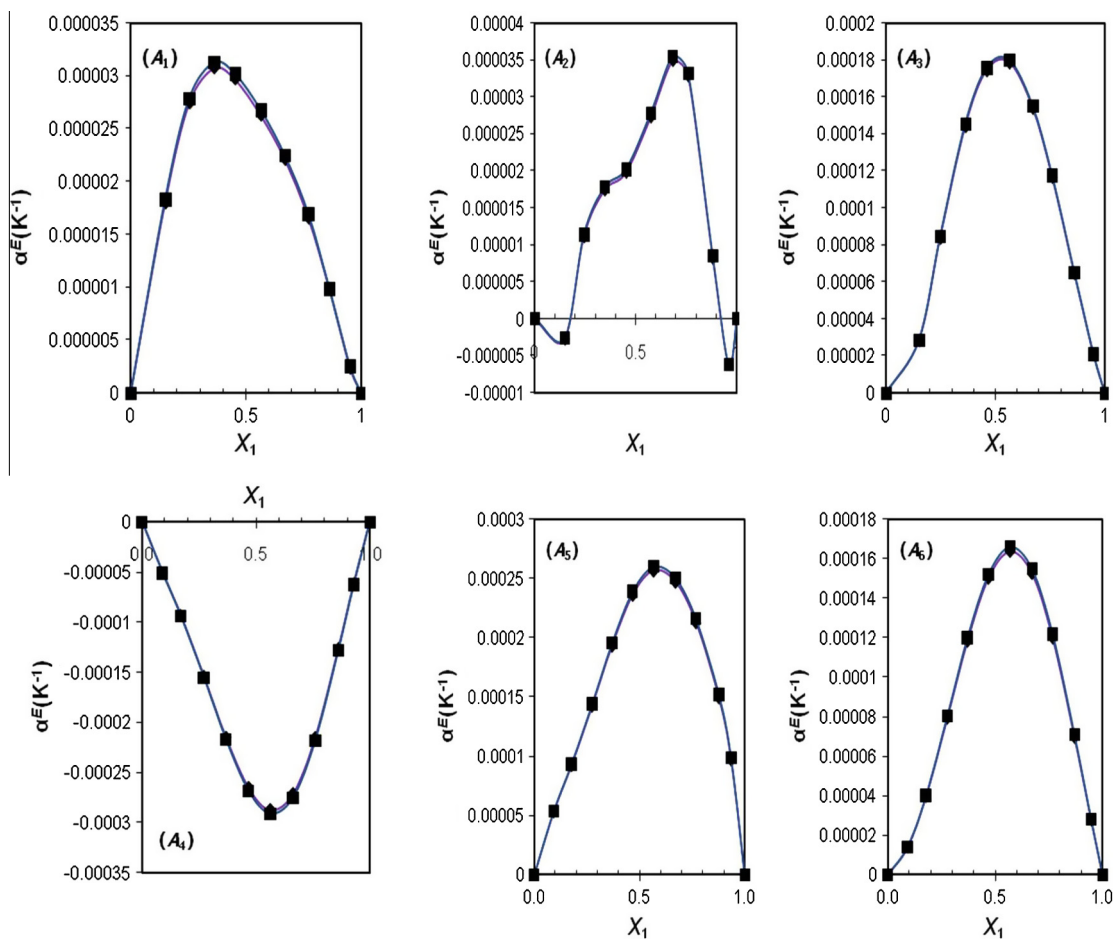
Figure 1 Plot of excess thermal expansion coefficients α^E, against mole fraction for {(A_1); vinyl acetate + o-xylene, (A_2); vinyl acetate + m-xylene, (A_3); vinyl acetate + p-xylene, (A_4); benzyl acetate + o-xylene, (A_5); benzyl acetate + m-xylene, (A_6); benzyl acetate + p-xylene} at 303.15 K (♦) and 313.15 K (■).

coefficient of pressure excess molar enthalpy, $(\partial H_m^E/\partial P)_{T,x}$, of the binary mixtures have been fitted to the Redlich-Kister (Iloukhani et al., 2011) the result are gathered in the Supplementary data.

2. Results and discussion

2.1. Thermal expansion coefficient and their excess values

The temperature dependence of density of the pure components was fitted to the equation:

$$\rho(T)/(\text{g.cm}^{-3}) = \sum_{i=0}^{4} A_i T^i \tag{1}$$

The thermal expansion coefficient, α, as in the case of pure components was obtained by analytical differentiation of the density fitting equation:

$$\alpha = -\rho^{-1}\left(\frac{\partial \rho}{\partial T}\right)_p \tag{2}$$

The thermal expansion coefficients of the pure components at different temperature are presented in Table 1. The average

uncertainty in the thermal expansion coefficient is estimated to be $\pm 5 \times 10^{-6} \text{K}^{-1}$.

The basic expression relating the molar volume of a mixture and its excess molar volume is (Rezaei-Sameti et al., 2010a,b,c):

$$V = \sum_{i=1}^{N} x_i V_i + V_m^E \tag{3}$$

where V_i and x_i correspond to the molar volume and to the mole fraction concentration of component i. By differentiating Eq. (3) we then obtain:

$$\alpha = V^{-1}\left[\left(\frac{\partial V_m^E}{\partial T}\right)_{P,x_i} + \sum_{i=1}^{N} \alpha_i x_i V_i\right] \tag{4}$$

Where α and α_i are the thermal expansion coefficients of the mixture and a pure component, respectively. From this expression, the excess thermal expansion coefficient can be rewritten as:

$$\alpha^E = \alpha - \sum_{i=1}^{n} \phi_i \alpha_i \tag{5}$$
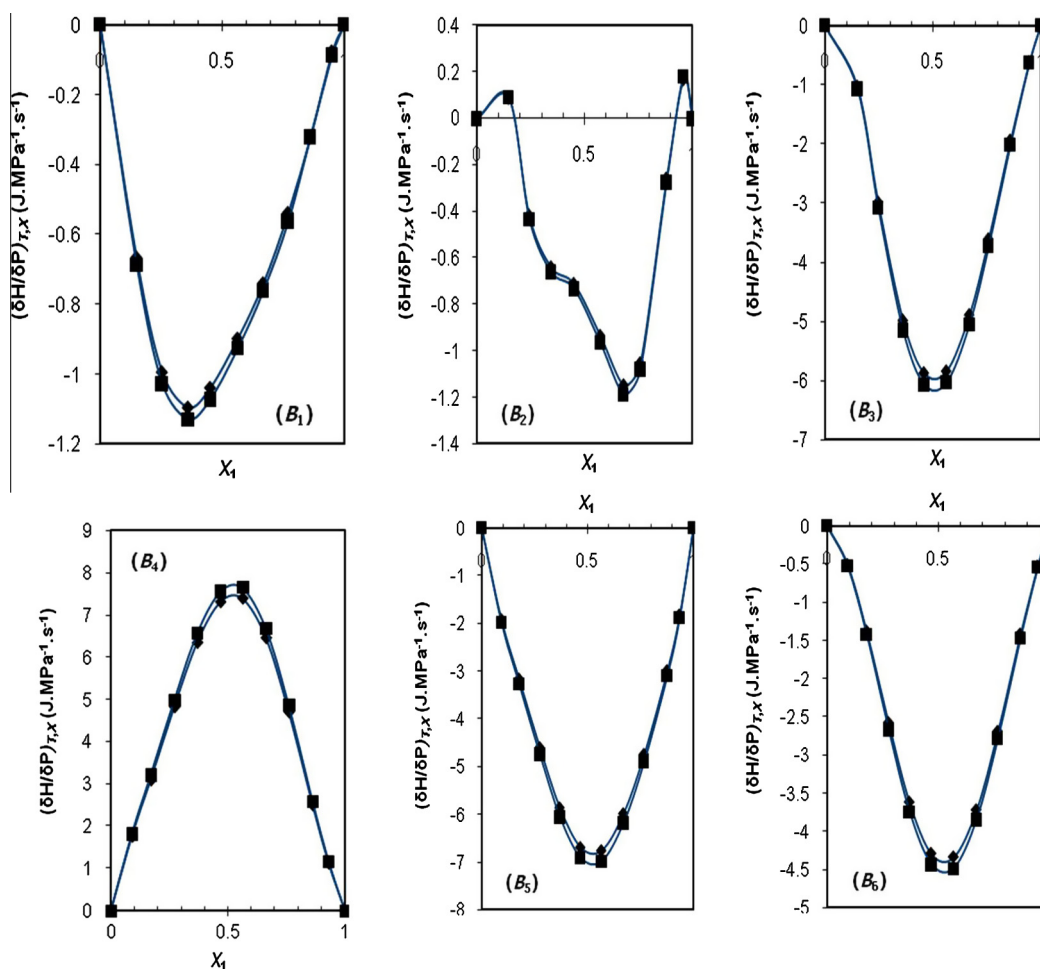
where

Figure 2 Plot of isothermal coefficient of pressure excess molar enthalpy $(\partial H_m^E/\partial P)_{T,x}$, against mole fraction for {(B_1); vinyl acetate + o-xylene, (B_2); vinyl acetate + m-xylene, (B_3); vinyl acetate + p-xylene, (B_4); benzyl acetate + o-xylene, (B_5); benzyl acetate + m-xylene, (B_6); benzyl acetate + p-xylene} at 303.15 K ($\blacklozenge$) and 313.15 K ($\blacksquare$).

$$\phi_i = x_i V_i / \sum_{i=1}^{2} x_i V_i \qquad (6)$$

And ϕ_i is the volumetric fraction of the components of the mixture. This property can be described as the variation of density with temperature due to the non ideality of the mixture. The thermal expansion coefficient α and excess thermal expansion coefficient α^E, are for all binary mixtures represented in Fig. 1 and gathered in the Supplementary data. The excess thermal expansion coefficient α^E, for vinyl acetate + o-xylene + p-xylene and benzyl acetate + m-xylene, + p-xylene are positive and increase with increasing temperatures from (303.15 and 313.15) K. The excess thermal expansion coefficient α^E, for binary mixture of benzyl acetate + o-xylene are negative and decrease with increasing temperatures from (303.15 and 313.15) K and vinyl acetate + m-xylene are negative in x = 0.2434, x = 0.9602 and positive for all mole fractions and increase with increasing temperatures from (303.15 to 313.15) K.

2.2. Isothermal coefficient of pressure excess molar enthalpy

The isothermal coefficient of pressure excess molar enthalpy can be derived accurately from volumetric measurements by the application of the following expression:

$$\left(\frac{\partial H_m^E}{\partial P}\right)_{T,x} = V_m^E - T\left(\frac{\partial V_m^E}{\partial T}\right)_{P,x} \qquad (7)$$

This quantity represents the dependence of the excess molar enthalpy of mixing with pressure at fixed composition and temperature.

The isothermal coefficient of pressure excess molar enthalpy, $(\partial H_m^E / \partial P)_{T,x}$, for all binary mixtures represented in Fig. 2 and gathered in the Supplementary data. The isothermal coefficient of pressure excess molar enthalpy, $(\partial H_m^E / \partial P)_{T,x}$, for vinyl acetate + o-xylene, + p-xylene and benzyl acetate + m-xylene, + p-xylene are negative and decrease with increasing temperatures from (303.15 to 313.15) K. The isothermal coefficient of pressure excess
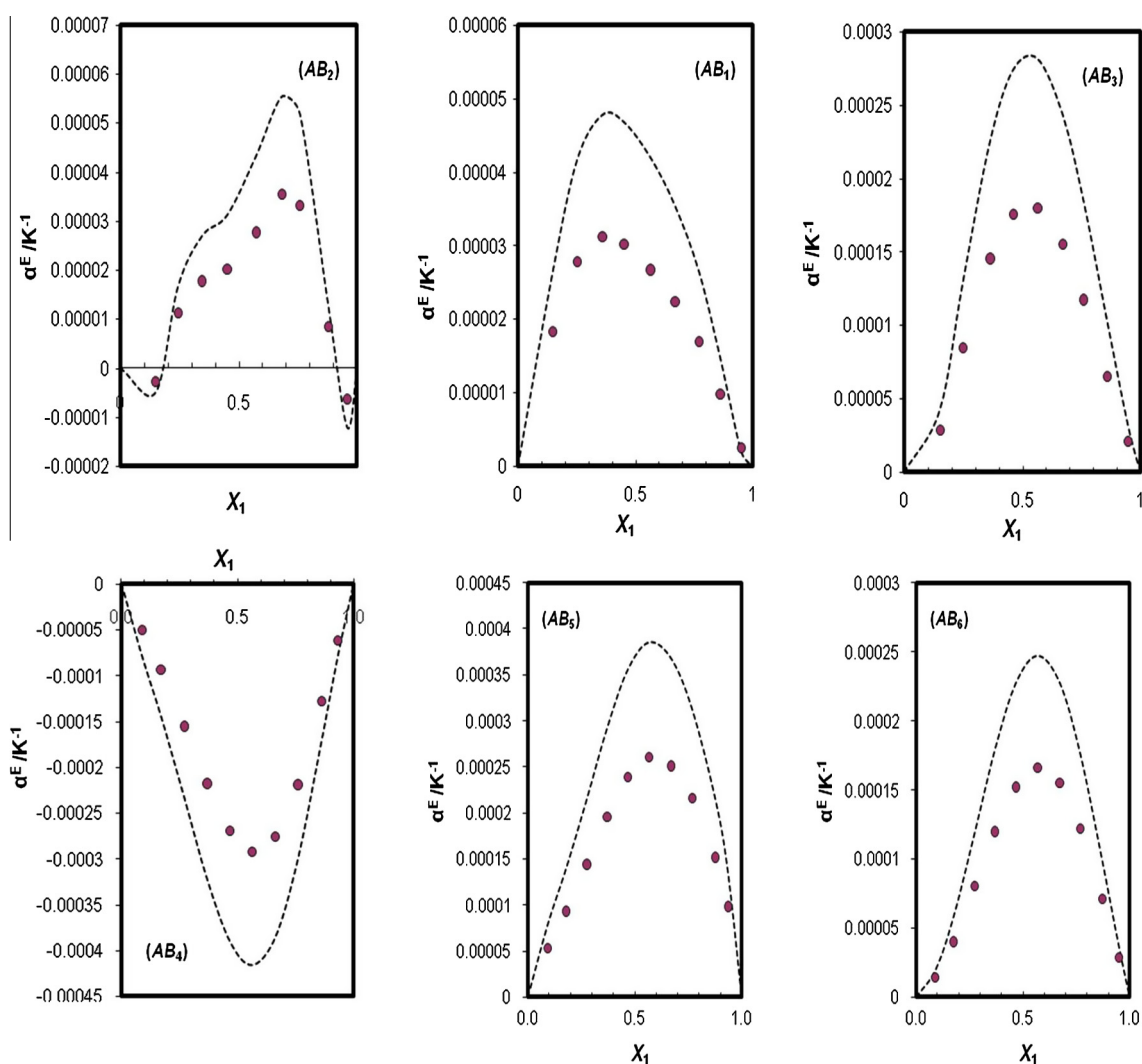

Figure 3 Plot of excess thermal expansion coefficients α^E, against mole fraction for {(AB_1); vinyl acetate + o-xylene, (AB_2); vinyl acetate + m-xylene, (AB_3); vinyl acetate + p-xylene, (AB_4); benzyl acetate + o-xylene, (AB_5); benzyl acetate + m-xylene, (AB_6); benzyl acetate + p-xylene} 313.15 K. (o) Experimental; (……) calculated by using Flory theory.

molar enthalpy, $(\partial H_m^E/\partial P)_{T,x}$, for a binary mixture of benzyl acetate + o-xylene is positive and increases with increasing temperatures from (303.15 and 313.15) K and vinyl acetate + m-xylene are positive in $x = 0.2434$, $x = 0.9602$ and negative for all mole fractions and decrease with increasing temperatures from (303.15 and 313.15) K. In the present study the molecules of both vinyl acetate and benzyl acetate are polar, while the aromatic hydrocarbons chosen have large quadruple moments hence molecular order in their pure state. However on mixing these aromatic hydrocarbons with the ester composition there is a change in the molecular order of the hydrocarbons, causing the positive excess molar volumes. Likewise, the observed negative excess molar volumes may be due to the presence of donor–acceptor interactions. The electronegative oxygen of an ester molecule is acting as the donor and the π-electrons of aromatic hydrocarbons are acting as acceptors. In addition the position of the (–CH$_3$) groups on the aromatic ring plays a dominant role in deciding the magnitude of V^E and also the order of interactions between the molecules of the mixture composition. The different behavior of V^E and its magnitude as observed in the present study reflect partially the type of interactions taking place in the mixture.

2.3. Flory model

In the present study the value of the reduced volume for the liquids and their mixtures $\widetilde{V}$ was determined for α values of the mixtures using the Flory (Flory, 1965; Flory et al., 1964a,b; Prigogine, 1957) model that has been commonly employed to analyze the molar volume of the mixture and the excess molar volume parting from the equation of state in function of the reduced variables:

$$\frac{\widetilde{P}\widetilde{V}}{\widetilde{T}} = \left[\frac{\widetilde{V}^{\frac{1}{3}}}{\widetilde{V}^{\frac{1}{3}} - 1}\right] - \left[\frac{1}{\widetilde{V}\widetilde{T}}\right] \tag{8}$$

The isothermal coefficient of pressure excess molar enthalpy, $(\partial H_m^E/\partial P)_{T,x}$, and excess thermal expansion coefficient α^E, according to the Flory model are calculated, comparison between theoretical and experimental results for $(\partial H_m^E/\partial P)_{T,x}$, and α^E for binary mixtures are graphically represented in Figs. 3 and 4 and gathered in the Supplementary data. The results show good agreement between experimental and theoretical data.
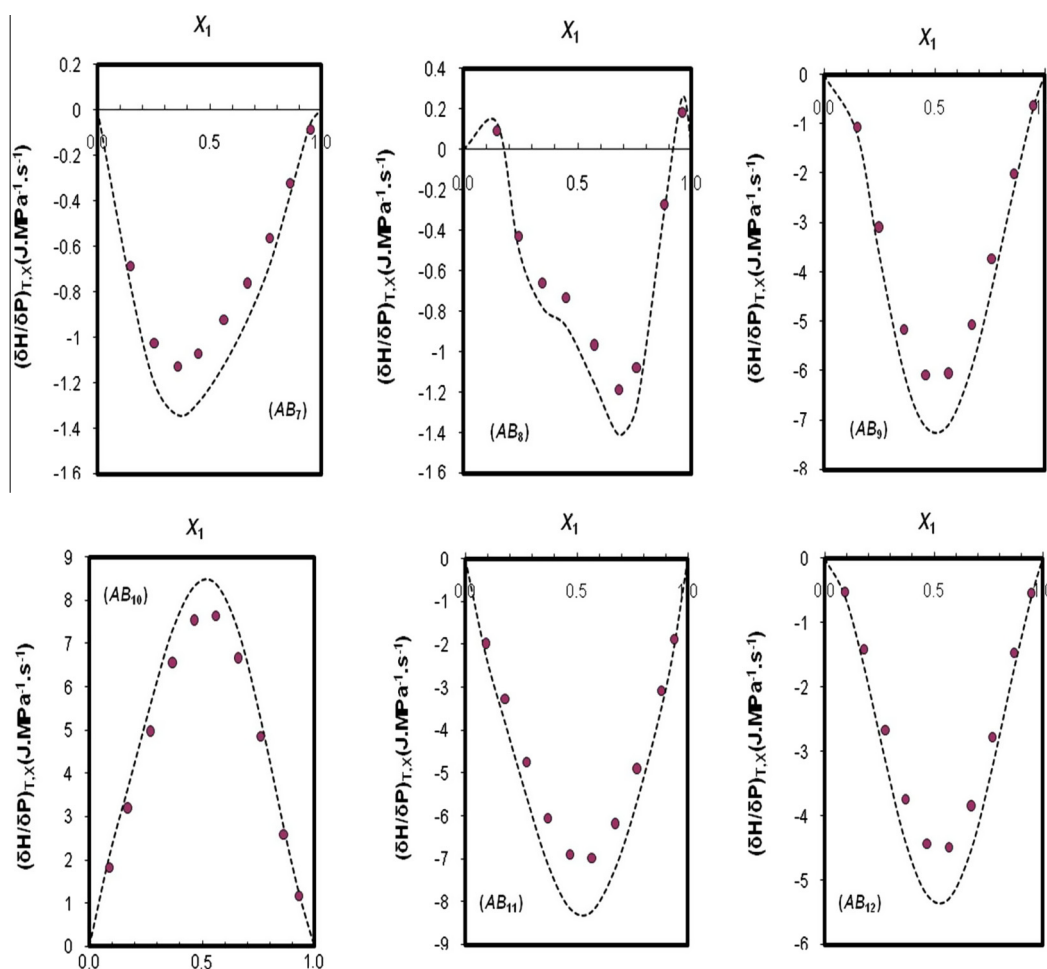

Figure 4 Plot of isothermal coefficient of pressure excess molar enthalpy $(\partial H_m^E/\partial P)_{T,x}$, against mole fraction for $\{(AB_8)$; vinyl acetate + o-xylene, (AB_9); vinyl acetate + m-xylene, (AB_{10}); vinyl acetate + p-xylene, (AB_{11}); benzyl acetate + o-xylene, (AB_{12}); benzyl acetate + m-xylene, (AB_{13}); benzyl acetate + p-xylene$\}$ 313.15 K. (o) Experimental; (......) calculated by using Flory theory.

2.4. Thermo acoustical parameters (TAP)

The thermo acoustical method (Bhatia et al., 2010) has also been employed to obtain the available volume, V_a using the relation,

$$V_a = V_T\left[\frac{1}{K^/ + 1}\right] = V_T\left[\frac{1}{K^{//} + K}\right]$$

(9)

Where $K^/$, K, $K^{//}$ and V_T are known as the isothermal, isobaric, isochoric acoustical parameters, molar volumes at temperature T, respectively, and can be expressed by the relations,

Table 2 Physical properties of pure liquid components in the temperature range (303.15 and 313.15 K).

| Compound	T (K)	$K^/$	K	$K^{//}$	X	S^*
Vinyl acetate	303.15	5.080	3.344	1.736	0.509	1.461
	313.15	4.529	3.047	1.482	0.451	1.624
Benzyl acetate	303.15	8.726	5.416	3.309	0.631	1.182
	313.15	6.303	4.031	2.272	0.574	1.301
o-Xylene	303.15	6.086	3.908	2.178	0.566	1.320
	313.15	5.080	3.334	1.736	0.509	1.461
m-Xylene	303.15	6.015	3.868	2.147	0.563	1.327
	313.15	5.043	3.323	1.719	0.506	1.469
p-Xylene	303.15	5.830	3.763	2.067	0.555	1.347
	313.15	4.944	3.269	1.675	0.497	1.491
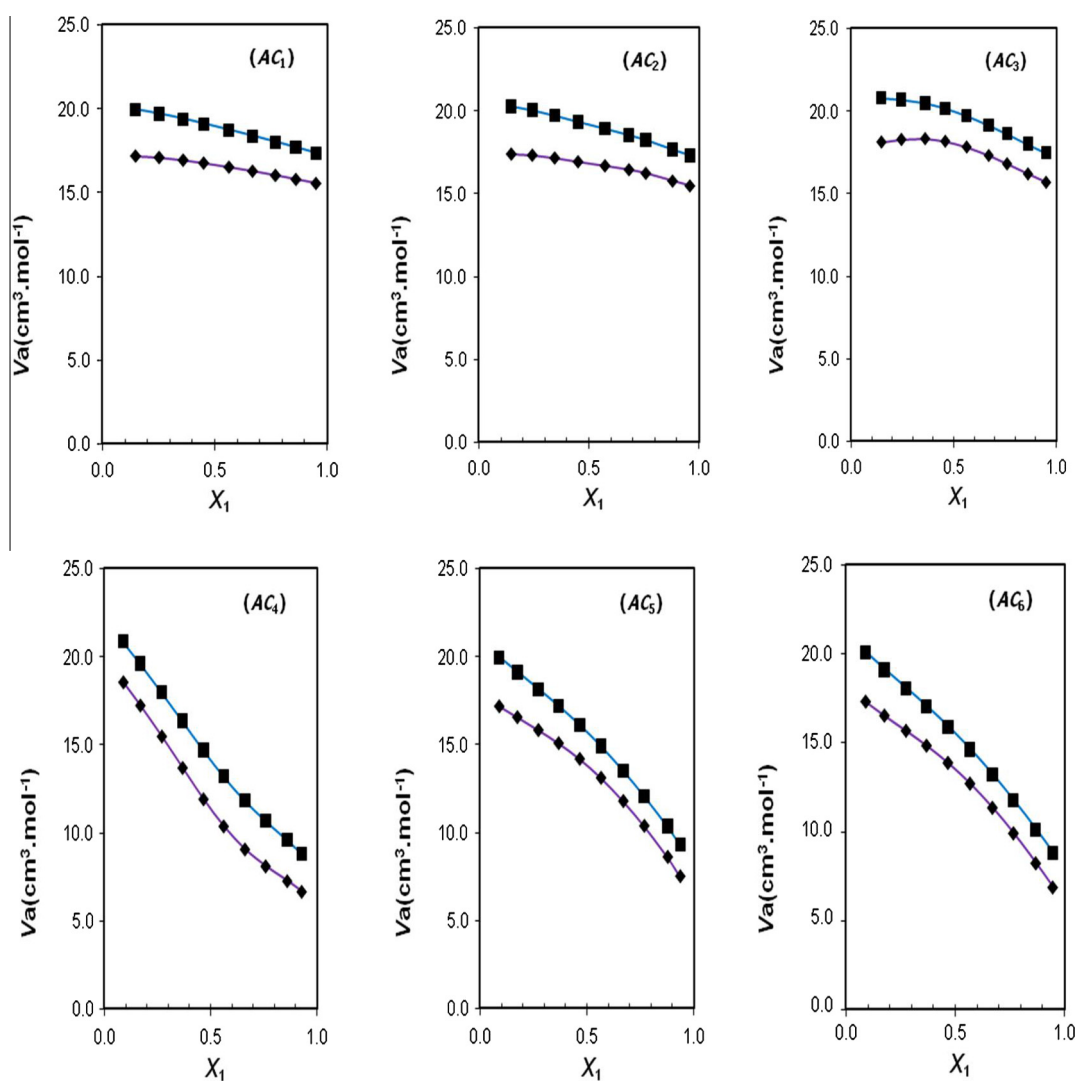
Figure 5 Plot of available volume, V_a, against mole fraction for {(AC_1); vinyl acetate + o-xylene, (AC_2); vinyl acetate + m-xylene, (AC_3); vinyl acetate + p-xylene, (AC_4); benzyl acetate + o-xylene, (AC_5); benzyl acetate + m-xylene, (AC_6); benzyl acetate + p-xylene} at 303.15 K (♦) and 313.15 K (■).

$$K^{/} = K + K^{//} = \frac{1}{2}\left[3 + \frac{S^*(1 + \alpha T) + X}{\alpha T}\right] \qquad (10)$$

$$K^{//} = 1 + \frac{X}{2\alpha T} \qquad (11)$$

$$K = \frac{1}{2}\left[1 + \frac{S^*(1 + \alpha T)}{\alpha T}\right] \qquad (12)$$

$$S^* = 1 + \frac{4\alpha T}{3} \qquad (13)$$

X is known as the isochoric temperature coefficient of the internal pressure and can be expressed as,

$$X = 2\left[\frac{1 + \alpha T}{(\widetilde{V}C_1)}\right] \qquad (14)$$

where $\widetilde{V}$ represents the reduced molar volume and determined with Flory Theory and C_1 is the Moelwyn-Hughes parameter and can be expressed as:

$$C_1 = \frac{13}{3} + \frac{1}{\alpha T} + \frac{4\alpha T}{3} \qquad (15)$$

Value of the isothermal ($K^{/}$), isobaric (K), isochoric acoustical parameters ($K^{//}$), available volume (V_a), isochoric temperature coefficient of the internal pressure (X), Moelwyn-Hughes parameter (C_1), for the pure components and binary mixtures are listed Table 2 and graphically represented in Fig. 5 and all other calculated data gathered in the Supplementary data. The results show that the available volume (V_a) for all these binary mixtures decrease with increase the mole fraction of solute may be due to the presence of donor–acceptor interactions and the electronegative oxygen of an ester molecule is acting as the donor and the π-electrons of the aromatic hydrocarbons acting as acceptors.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jscs.2011.09.004.

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