

**DERIVED THERMODYNAMIC PROPERTIES OF [*o*-XYLENE OR *p*-XYLENE +
(ACETIC ACID OR TETRAHYDROFURAN)] AT DIFFERENT TEMPERATURES
AND PRESSURES**

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ABSTRACT. Thermal expansion coefficients α , their excess values α^E , isothermal coefficient of pressure excess molar enthalpy $(\partial H_m^E / \partial P)_{T,x}$, partial molar volumes \bar{V}_i and excess partial molar volumes \bar{V}_i^E , were calculated from experimental densities. The isothermal coefficients of pressure excess molar enthalpy $(\partial H_m^E / \partial P)_{T,x}$ for binary mixtures {*o*-xylene or *p*-xylene + acetic acid} at temperatures 313.15-473.15 K and pressure 0.2-2 MPa are negative and for binary mixtures {*o*-xylene or *p*-xylene + tetrahydrofuran (THF)} at temperatures 278.15 K to 318.15 K and pressure 81.5 kPa are negative and with increasing temperature become more negative. The excess thermal expansions coefficient α^E , for binary mixtures {*o*-xylene or *p*-xylene + acetic acid} at temperatures 313.15-473.15 K and pressure 0.2 MPa and 2 MPa are positive. The excess thermal expansions coefficient α^E for binary mixtures {*o*-xylene or *p*-xylene + tetrahydrofuran (THF)} at temperatures 278.15-318.15 K and pressure 81.5 kPa are positive and with increasing temperature become more positive. The excess molar volumes were correlated with a Redlich-Kister type equation.

KEY WORDS: Thermal expansion coefficients, Isothermal coefficient, Excess partial molar volumes

INTRODUCTION

This paper is a continuation of our earlier work related to the study of thermodynamic properties of binary and ternary mixtures [1-6]. Reliable data on phase behavior and thermodynamic excess properties of multi component fluid mixtures are necessary for the proper design of synthesis and separation processes of the chemical substances involved. Experimental determination of all these properties is time-consuming and involves great expense especially if the data have to be known at various state conditions and compositions. Therefore, the properties of multicomponent mixtures are often estimated from the corresponding data of the constituting binary mixtures, but the reliability of such estimation is always questionable and has to be tested. Numerous researches have done with binary and ternary mixtures of (*o*-, *m*-, *p*-) xylene and acetic acid with other component [7-18]. In this project we consider the experimental data for the binary mixtures {*o*-xylene or *p*-xylene + acetic acid} and {*o*-xylene or *p*-xylene + tetrahydrofuran (THF)} at different temperature and pressure [18-20]. The excess molar volumes [20] show that the V^E values are positive over the entire mole fraction range and are almost symmetrical with a maximum around $x = 0.4$ for the two binary mixtures. The values of V^E can be explained in terms of two opposing effects [18]: (1) expansion in volume owing to mutual loss of dipolar association and the difference in size and shape of the component molecules; (2) contraction in volume occurs owing to dipole-induced dipole and dipole-dipole interactions and donor-acceptor interactions between unlike molecules. The influence of methyl groups into benzene will increase the electron density and its donor capacity [18]; however

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steric hindrance among the atoms of acetic acid and the two bulky methyl groups hinders the proper orientation of acetic acid to interact with xylene, which results in a more positive excess volume. In addition, the dissociation of self-associated acetic acid also contributes to the increase in the excess volume. The molecules of THF are polar and those of the aromatic hydrocarbons (*o*-xylene, *m*-xylene, *p*-xylene) have large quadrupole moments [19], which lead to the molecular order in the pure state. On the other hand, there is the possibility of electron donor-acceptor type (or charge-transfer) interactions [20] between the highly electronegative oxygen of THF (acting as donor) and the π -electrons of the aromatic hydrocarbon molecules (acting as acceptor) is caused negative value of V^E . The observed negative V^E values suggest the presence of significant donor-acceptor interactions between THF and the aromatic hydrocarbon molecules in these mixtures. Recently, Yang *et al.* [20] has also reported similar types of donor-acceptor interactions between the oxygen atom of sulpholane and π -electrons of the aromatic hydrocarbons (*o*-xylene, *m*-xylene and *p*-xylene).

The more negative V^E values for THF + *p*-xylene that are observed are due to the fact that the THF molecules could approach more closely to the ring of *p*-xylene from two directions as compared to *o*- and *m*-xylene, showing a maximum interaction of the THF molecule with the former *p*-xylene than with the latter two xylene. This is in good agreement with the reported [21] trends in V^E for the DMSO + xylene.

The values of V^E increase with increasing temperature for the binary mixtures of *o*-xylene and *p*-xylene + tetrahydrofuran. The increase in V^E is attributed to the breaking of donor acceptor interactions between unlike molecules with a rise in temperature, leading to an expansion in volume, resulting in an increase in V^E values [19].

In this work we derived the properties such as (thermal expansion coefficients α and their excess values α^E , isothermal coefficient of pressure excess molar enthalpy $(\partial H_m^E / \partial P)_{T,x}$, partial molar volumes \bar{v}_i and partial excess molar volumes \bar{v}_i^E). The results provide valuable information for qualitatively analyzing the molecular interactions between molecules.

EXPERIMENTAL

The experimental densities and the excess molar volumes, V^E for all components and binary mixtures were used from Ref. [18] and Ref. [19].

RESULTS AND DISCUSSION

The variation of temperature, the excess molar volumes of all binary mixtures were fitted using a temperature-dependent Redlich-Kister expression [21]:

$$V^E = x_i x_j \sum_{p=0}^4 \left(\sum_{q=0}^2 A_{pq} T^q \right) (x_i - x_j)^p \quad (1)$$

where x_i and x_j are the mole fraction; A_{pq} are the temperature dependent parameters for the binary mixtures; and T is the absolute temperature. These parameters were obtained by the unweighted least-squares method. Standard deviations (σ) calculated by using the following relation:

$$\sigma(V) = \left[\frac{\sum (V_{\text{mexp},i}^E - V_{\text{mcal},i}^E)^2}{(n-k)} \right]^{1/2} \quad (2)$$

where n is the number of experimental data points and k is the number of A_{pq} parameters. The parameters A_{pq} for all binary mixtures and standard deviations (σ) are given in Table 1.

Table 1. Coefficients A_{pq} of equation 2 and standard deviations for the fits of the binary excess molar volumes in the temperatures range (278.15 to 318.15) K and 81.5 kPa, (313.15 to 473.15) K and 0.2, 0.4, 0.8, 1.2, 1.6 and 2 MPa.

| q | p | | | | | $\sigma(V_m^E)$ |
|---|-----------------------|------------------------|-----------|-----------------------|------------------------|-----------------|
| | 0 | 1 | 2 | 3 | 4 | |
| { <i>o</i> -Xylene (1) + Acetic acid (2)} $P = 0.2$ MPa | | | | | | |
| 0 | 17.4 | -0.110 | 0.000207 | 6.24 | -0.0304 | 0.0142 |
| 1 | 0.0000465 | -28.3 | 0.156 | -0.000205 | 6.64 | |
| 2 | -0.0439 | 0.0000723 | -8.98 | 0.0467 | -0.0000559 | |
| { <i>o</i> -Xylene (1) + Acetic acid (2)} $P = 0.4$ MPa | | | | | | |
| 0 | 18.3 | -0.115 | 0.000212 | 4.00 | -0.0188 | 0.0131 |
| 1 | 0.0000325 | -18.3 | 0.0970 | -0.000119 | 1.69 | |
| 2 | -0.0121 | 0.000022 | -15.3 | 0.0903 | -0.000130 | |
| { <i>o</i> -Xylene (1) + Acetic acid (2)} $P = 0.8$ MPa | | | | | | |
| 0 | 20.4 | -0.127 | 0.000227 | -0.370 | 0.00386 | 0.0180 |
| 1 | 4.09×10^{-6} | -21.2 | 0.118 | -0.000155 | 5.22 | |
| 2 | -0.0262 | 0.0000329 | -1.03 | 0.00533 | -6.27×10^{-6} | |
| { <i>o</i> -Xylene (1) + Acetic acid (2)} $P = 1.2$ MPa | | | | | | |
| 0 | 19.1 | -0.119 | 0.000216 | 4.90 | -0.0241 | 0.0137 |
| 1 | 0.0000407 | -19.9 | 0.113 | -0.000153 | -2.86 | |
| 2 | 0.0169 | -0.0000241 | -4.13 | 0.0175 | -0.0000165 | |
| { <i>o</i> -Xylene (1) + Acetic acid (2)} $P = 1.6$ MPa | | | | | | |
| 0 | 17.2 | -0.109 | 0.000202 | 9.42 | -0.0469 | 0.0167 |
| 1 | 0.0000695 | -14.0 | 0.0796 | -0.000106 | -3.17 | |
| 2 | 0.0179 | -0.0000253 | -9.81 | 0.0512 | -0.0000643 | |
| { <i>o</i> -Xylene (1) + Acetic acid (2)} $P = 2$ MPa | | | | | | |
| 0 | 18.81 | -0.116 | 0.000211 | 11.6 | -0.0568 | 0.0195 |
| 1 | 0.0000797 | -32.5 | 0.174 | -0.000225 | 0.322 | |
| 2 | -0.00475 | 0.0000109 | 8.92 | -0.0452 | 0.0000568 | |
| { <i>p</i> -Xylene (1) + Acetic acid (2)} $P = 0.2$ MPa | | | | | | |
| 0 | -2.50 | 0.010 | 0.0000261 | 3.59 | -0.0188 | 0.0118 |
| 1 | 0.0000354 | 1.58 | -0.00421 | 1.73×10^{-7} | -24.7 | |
| 2 | 0.139 | -0.000190 | -17.2 | 0.0844 | -0.0000946 | |
| { <i>p</i> -Xylene (1) + Acetic acid (2)} $P = 0.4$ MPa | | | | | | |
| 0 | 0.259 | -0.000433 | 0.0000324 | 4.22 | -0.0247 | 0.0170 |
| 1 | 0.0000481 | -0.369 | -0.0053 | 0.0000234 | -4.27 | |
| 2 | 0.0283 | -0.0000440 | -12.4 | 0.0628 | -0.0000776 | |
| { <i>p</i> -Xylene (1) + Acetic acid (2)} $P = 0.8$ MPa | | | | | | |
| 0 | 8.03 | -0.0429 | 0.0000887 | 0.836 | -0.00190 | 0.0297 |
| 1 | 0.0000130 | -13.8 | 0.0618 | -0.0000612 | -0.452 | |
| 2 | 0.00224 | -2.18×10^{-6} | 17.1 | -0.0873 | 0.000112 | |
| { <i>p</i> -Xylene (1) + Acetic acid (2)} $P = 1.2$ MPa | | | | | | |
| 0 | 4.8102 | -0.0261 | 0.0000664 | -3.038 | 0.0187 | 0.021 |
| 1 | -0.0000139 | 3.57 | -0.0279 | 0.0000547 | 4.07 | |
| 2 | -0.0211 | 0.0000278 | -2.19 | 0.0121 | -0.0000164 | |
| { <i>p</i> -Xylene (1) + Acetic acid (2)} $P = 1.6$ MPa | | | | | | |
| 0 | 5.97 | -0.0334 | 0.0000766 | 1.46 | -0.00465 | 0.022 |
| 1 | 0.0000162 | 7.62 | -0.0475 | 0.0000772 | -2.99 | |
| 2 | 0.0168 | -0.0000226 | -20.3 | 0.110 | -0.000145 | |
| { <i>p</i> -Xylene (1) + Acetic acid (2)} $P = 2$ MPa | | | | | | |
| 0 | 8.39 | -0.0464 | 0.0000931 | 2.97 | -0.0115 | 0.024 |

| | | | | | | |
|--|------------------------|------------|-----------|------------|------------------------|-------|
| 1 | 0.0000244 | -7.53 | 0.0317 | -0.0000252 | -3.39 | |
| 2 | 0.0177 | -0.0000225 | 0.151 | 0.00306 | -8.79×10 ⁻⁶ | |
| {}o-Xylene (1) + THF (2)} P = 81.5 kPa | | | | | | |
| 0 | -1.03 | -0.00315 | 0.0000154 | 0.253 | 0.00159 | 0.001 |
| 1 | -6.74×10 ⁻⁶ | -0.152 | -0.00341 | 0.0000147 | 0.991 | |
| 2 | -0.00779 | 0.0000149 | 0.401 | -0.00195 | 1.01×10 ⁻⁶ | |
| {}p-Xylene (1) + THF (2)} P = 81.5 kPa | | | | | | |
| 0 | -1.51 | -0.00399 | 0.0000213 | -0.0926 | 0.00361 | 0.001 |
| 1 | -9.94×10 ⁻⁶ | 2.24 | -0.0202 | 0.0000435 | 1.70 | |
| 2 | -0.012 | 0.0000213 | -2.86 | 0.0187 | -0.0000296 | |

Thermal expansion coefficient and their excess values

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

$$\rho(T) / g.cm^{-3} = \sum_{i=0}^4 a_i T^i \quad (3)$$

The thermal expansion coefficient α for pure components was obtained by analytical differentiation and presented in Table 2. The average uncertainty in the thermal expansion coefficient is estimated to be $\pm 5 \times 10^{-6} K^{-1}$. The basic expression relating the molar volume of a mixture and its excess molar volume is:

$$V = \sum_{i=1}^N x_i V_i + V_m^E \quad (4)$$

where V_i and x_i correspond to the molar volume and to the mole fraction concentration of component i . By differentiating equation (4):

$$\left(\frac{\partial V}{\partial T}\right)_{P,x_i} = \frac{\partial \left(\sum_{i=1}^N x_i V_i\right)}{\partial T} + \left(\frac{\partial V_m^E}{\partial T}\right)_{P,x_i} \quad (5)$$

And dividing by V and reversing the order of terms:

$$\alpha = 1/V \left[\left(\frac{\partial V_m^E}{\partial T}\right)_{P,x_i} + \frac{\partial \sum_{i=1}^N (x_i V_i)}{\partial T} \right] \quad (6)$$

We then obtain:

$$\alpha = V^{-1} \left[\left(\frac{\partial V_m^E}{\partial T}\right)_{P,x_i} + \sum_{i=1}^N \alpha_i x_i V_i \right] \quad (7)$$

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

$$\alpha^E = \alpha - \sum_{i=1}^n \phi_i \alpha_i \quad (8)$$

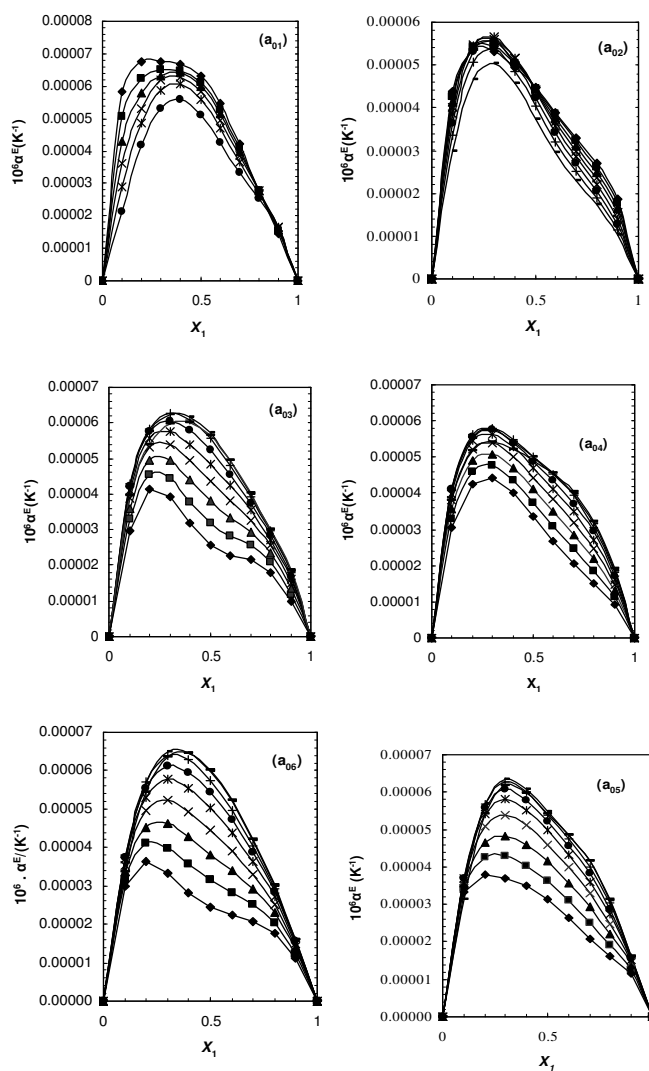
$$\text{where } \phi_i = x_i V_i / \sum_{i=1}^2 x_i V_i \quad (9)$$

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 no ideality of the mixture. The thermal expansion coefficient α and excess thermal expansion coefficient α^E are recorded in supplementary data and graphically represented in Figures (1 and 2).

Table 2. Thermal expansion coefficients (α) of the pure components at different temperatures and pressures.

| Component | T/K | 0.2 MPa | 0.4 MPa | 0.8 MPa | 1.2 MPa | 1.6 MPa | 2 MPa | 81.5 kPa |
|-------------------------------------|--------|---------|---------|---------|---------|---------|-------|----------|
| $10^4 \cdot \alpha / \text{K}^{-1}$ | | | | | | | | |
| <i>o</i> -Xylene | 278.15 | | | | | | | 9.55 |
| | 283.15 | | | | | | | 9.59 |
| | 288.15 | | | | | | | 9.64 |
| | 293.15 | | | | | | | 9.68 |
| | 298.15 | | | | | | | 9.73 |
| | 303.15 | | | | | | | 9.78 |
| | 308.15 | | | | | | | 9.83 |
| | 313.15 | 10.9 | 9.91 | 9.74 | 9.69 | 9.64 | 9.59 | 9.87 |
| | 318.15 | | | | | | | 9.92 |
| | 333.15 | 9.76 | 10.0 | 9.97 | 9.92 | 9.87 | 9.82 | |
| | 353.15 | 10.3 | 10.5 | 10.4 | 10.4 | 10.3 | 10.3 | |
| | 373.15 | 11.5 | 11.2 | 11.1 | 11.1 | 11.0 | 10.9 | |
| | 393.15 | 12.4 | 12.1 | 12.0 | 11.9 | 11.8 | 11.7 | |
| | 413.15 | 11.8 | 13.0 | 12.8 | 12.7 | 12.7 | 12.6 | |
| | 433.15 | | 13.8 | 13.7 | 13.6 | 13.5 | 13.4 | |
| | 453.15 | | 14.4 | 14.5 | 14.4 | 14.2 | 14.1 | |
| 473.15 | | | | | | | | |
| <i>p</i> -Xylene | 278.15 | | | | | | | 9.55 |
| | 283.15 | | | | | | | 10.0 |
| | 288.15 | | | | | | | 10.1 |
| | 293.15 | | | | | | | 10.1 |
| | 298.15 | | | | | | | 10.1 |
| | 303.15 | | | | | | | 10.2 |
| | 308.15 | | | | | | | 10.3 |
| | 313.15 | 9.35 | 10.0 | 9.90 | 9.87 | 9.83 | 9.81 | 10.3 |
| | 318.15 | | | | | | | 10.7 |
| | 333.15 | 11.2 | 10.9 | 10.9 | 10.9 | 10.9 | 10.9 | |
| | 353.15 | 12.2 | 12.0 | 12.0 | 12.0 | 12.0 | 12.0 | |
| | 373.15 | 12.9 | 13.2 | 13.2 | 13.1 | 13.1 | 13.1 | |
| | 393.15 | 14.2 | 14.3 | 14.3 | 14.3 | 14.2 | 14.2 | |
| | 413.15 | 17.0 | 15.4 | 15.4 | 15.3 | 15.3 | 15.3 | |
| | 433.15 | | 16.3 | 16.3 | 16.3 | 16.2 | 16.2 | |
| | 453.15 | | 16.9 | 17.1 | 17.0 | 17.0 | 16.9 | |
| 473.15 | | | 17.5 | 17.5 | 17.5 | 17.5 | | |
| Acetic acid | 278.15 | | | | | | | |
| | 283.15 | | | | | | | |
| | 288.15 | | | | | | | |
| | 293.15 | | | | | | | |
| | 298.15 | | | | | | | |
| | 303.15 | | | | | | | |
| | 308.15 | | | | | | | |
| | 313.15 | 9.90 | 10.3 | 10.4 | 10.4 | 10.3 | 10.3 | |
| | 333.15 | 11.3 | 11.2 | 11.1 | 11.1 | 11.0 | 11.0 | |
| | 353.15 | 12.1 | 12.0 | 11.9 | 11.8 | 11.8 | 11.7 | |
| | 373.15 | 12.7 | 12.8 | 12.7 | 12.6 | 12.6 | 12.5 | |
| | 393.15 | 13.5 | 13.6 | 13.7 | 13.6 | 13.5 | 13.5 | |
| 413.15 | 15.2 | 14.8 | 14.8 | 14.7 | 14.6 | 14.6 | | |
| 433.15 | | 16.5 | 16.3 | 16.2 | 16.1 | 15.9 | | |

| | | | | | | | | |
|-----------------|--------|--|------|------|------|------|------|------|
| | 453.15 | | 18.8 | 18.2 | 18.0 | 17.9 | 17.7 | |
| | 473.15 | | | 20.6 | 20.4 | 20.2 | 20.0 | |
| Tetrahydrofuran | 278.15 | | | | | | | 11.0 |
| | 283.15 | | | | | | | 11.0 |
| | 288.15 | | | | | | | 11.1 |
| | 293.15 | | | | | | | 11.2 |
| | 298.15 | | | | | | | 11.2 |
| | 303.15 | | | | | | | 11.3 |
| | 308.15 | | | | | | | 11.4 |
| | 313.15 | | | | | | | 11.4 |
| | 318.15 | | | | | | | 11.5 |



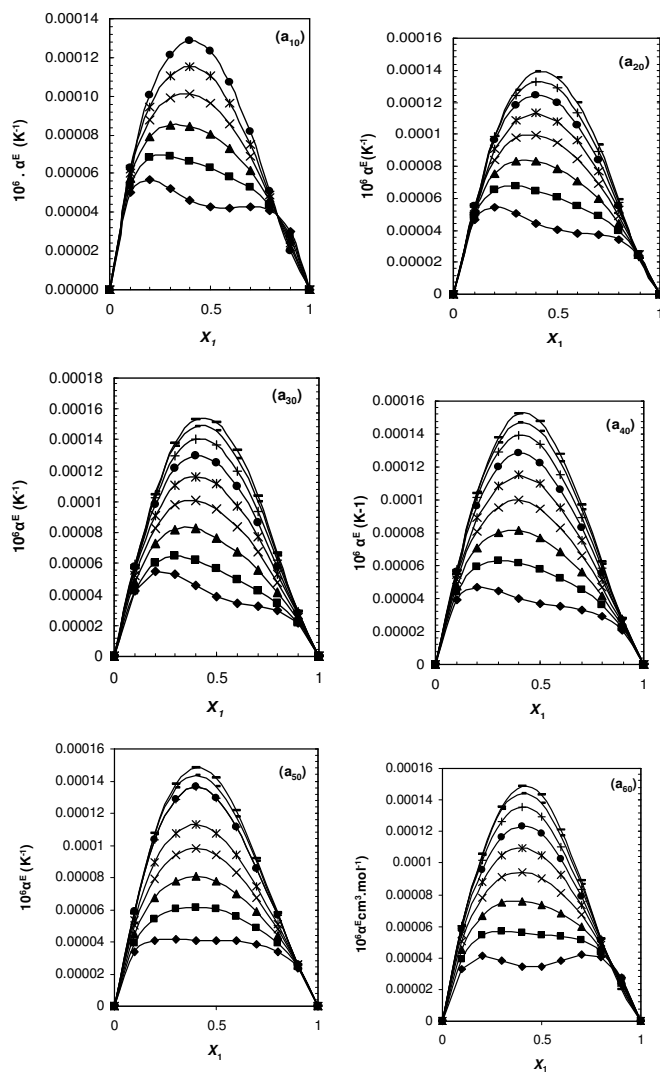


Figure 1. Excess thermal expansion coefficients against mole fraction for {*p*-xylene + acetic acid (a_{01} to a_{06})} and for {*o*-xylene + acetic acid {(a_{10} to a_{60})}}, at the temperatures 313.15 K (\diamond), 333.15 K (\blacksquare), 353.15 K (\blacktriangle), 373.15 K (\times), 393.15 K (\otimes), 413.15 K (\bullet), 433.15 K ($+$), 453.15 K ($-$), 493.15 K (\dashv) at pressures 0.2 MPa (a_{01} , a_{10}), 0.4 MPa (a_{02} , a_{20}), 0.8 MPa (a_{03} , a_{30}), 1.2 MPa (a_{04} , a_{40}), 1.6 MPa (a_{05} , a_{50}), 2 MPa (a_{06} , a_{60}).

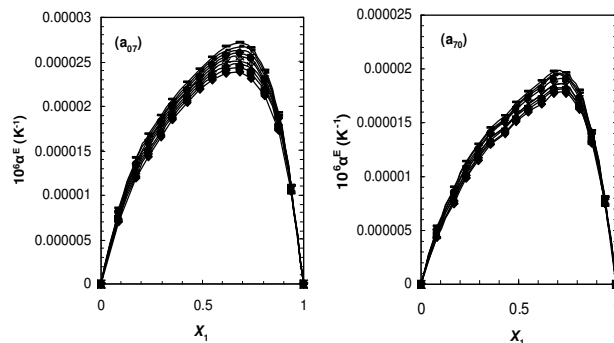


Figure 2. Excess thermal expansion coefficients against mole fraction for $\{p\text{-xylene} + \text{THF} (a_{07})$ and for $o\text{-xylene} + \text{THF} (a_{70})$, at the temperatures 278.15 K (\diamond), 283.15 K (\blacksquare), 288.15 K (\blacktriangle), 293.15 K (\times), 298.15 K (\mathcal{K}), 303.15 K (\bullet), 308.15 K ($+$), 313.15 K ($-$), 318.15 K (—) at pressure 81.5 kPa.

The excess thermal expansions coefficient α^E for binary mixtures $\{p\text{-xylene}, o\text{-xylene} + \text{acetic acid}\}$ at temperatures 313.15 K to 473.15 K and pressure 0.2 MPa to 0.4 MPa are positive and become more decreasing with increasing temperature (Figure 1).

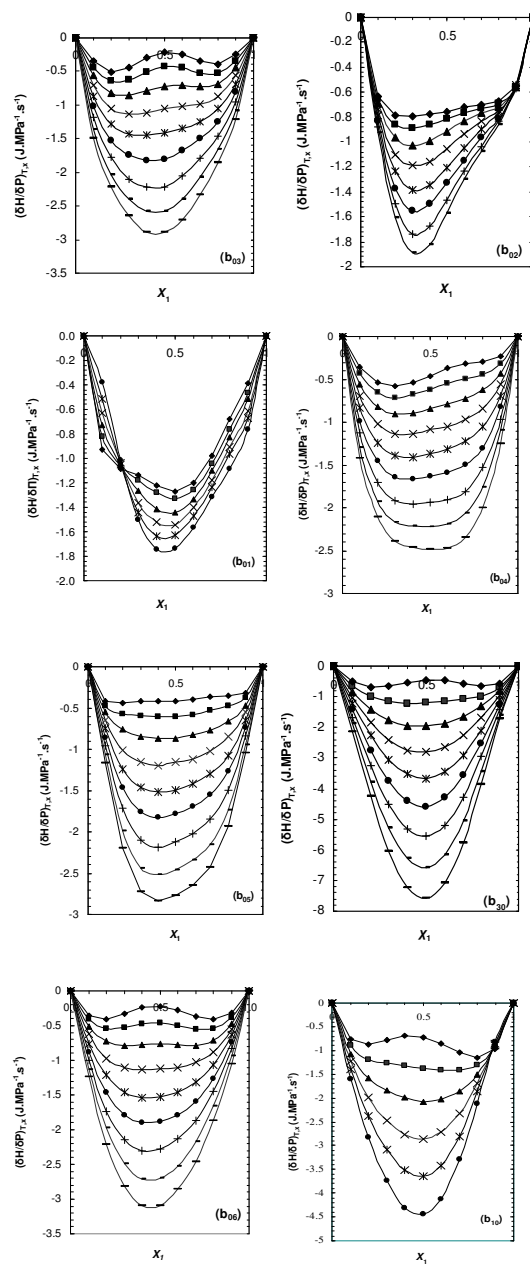
The excess thermal expansions coefficients α^E for binary mixtures $\{o\text{-xylene} \text{ or } p\text{-xylene} + \text{THF}\}$ at temperatures 278.15 K to 318.15 K and pressure 81.5 kPa are positive and become more positive with increasing temperature (Figure 2). The α^E values for all binary mixtures are positive over the entire concentration range. Thermal expansions coefficient is related to the fluctuation of cross term of enthalpy interaction and interaction volume of liquids and mixtures. The excess amount may reflect the molecular orientation and packing of mixtures. Molecular orientation effects are ascribed to shapes of molecules for nonpolar solvents and dipole moments, higher multipole moments, and special interactions such as hydrogen bonds for polar solvents.

Isothermal coefficient of pressure excess molar enthalpy

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

$$\left(\frac{\partial H_m^E}{\partial P}\right)_{T,x} = V_m^E - T \left(\frac{\partial V_m^E}{\partial T}\right)_{P,x} \quad (10)$$

This quantity represents the dependence of the excess molar enthalpy of mixing with pressure at fixed composition and temperature. The isothermal coefficients of pressure excess molar enthalpy $(\partial H_m^E / \partial P)_{T,x}$ for binary mixtures $\{o\text{-xylene} \text{ or } p\text{-xylene} + \text{acetic acid}\}$ at temperatures 313.15 K to 473.15 K and pressure 0.2 MPa to 2 MPa are negative and become more negative with increasing temperature (Figure 3) and for binary mixtures $\{o\text{-xylene} \text{ or } p\text{-xylene} + \text{THF}\}$ at temperatures 278.15 K to 318.15 K and pressure 81.5 kPa are negative and become more negative with increasing temperature (Figure 4). Negative values of $(\partial H_m^E / \partial P)_{T,x}$ for all binary mixtures are due to the presence of significant donor-acceptor interactions between THF and the aromatic hydrocarbon molecules in these mixtures.



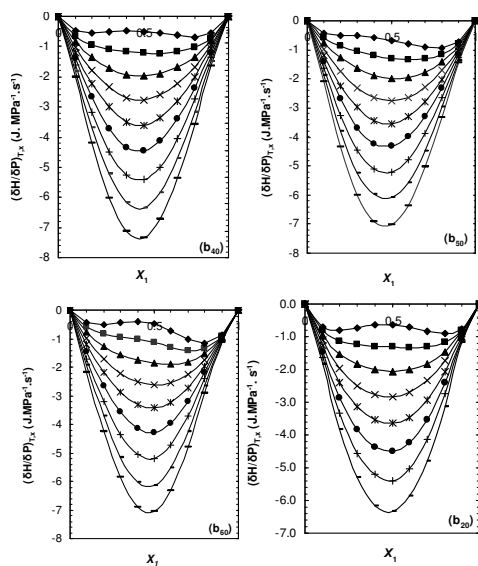


Figure 3. Isothermal coefficient of pressure excess molar enthalpy against mole fraction for $\{p$ -xylene + acetic acid $\{b_{01}$ to $b_{06}\}$ and for $\{o$ -xylene + acetic acid $\{b_{10}$ to $b_{60}\}$, at the temperatures 313.15 K (\diamond), 333.15 K (\blacksquare), 353.15 K (\blacktriangle), 373.15 K (\times), 393.15 K (\mathcal{K}), 413.15 K (\bullet), 433.15 K ($+$), 453.15 K ($-$), 493.15 K (\longleftarrow) at pressures 0.2 MPa (b_{01} , b_{10}), 0.4 MPa (b_{02} , b_{20}), 0.8 MPa (b_{03} , b_{30}), 1.2 MPa (b_{04} , b_{40}), 1.6 MPa (b_{05} , b_{50}), 2 MPa (b_{06} , b_{60}).

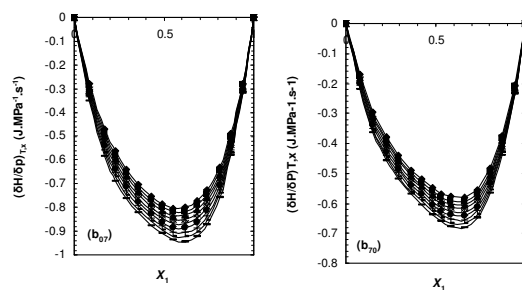


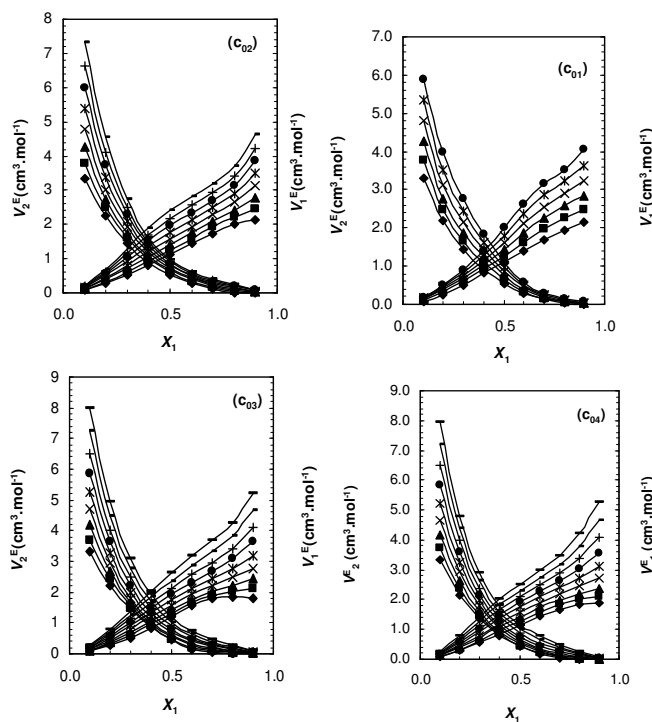
Figure 4. Isothermal coefficient of pressure excess molar enthalpy against mole fraction for $\{p$ -xylene + THF (b_{07}) and for $\{o$ -xylene + THF (b_{70}), at the temperatures 278.15 K (\diamond), 283.15 K (\blacksquare), 288.15 K (\blacktriangle), 293.15 K (\times), 298.15 K (\mathcal{K}), 303.15 K (\bullet), 308.15 K ($+$), 313.15 K ($-$), 318.15 K (\longleftarrow) at pressure 81.5kPa.

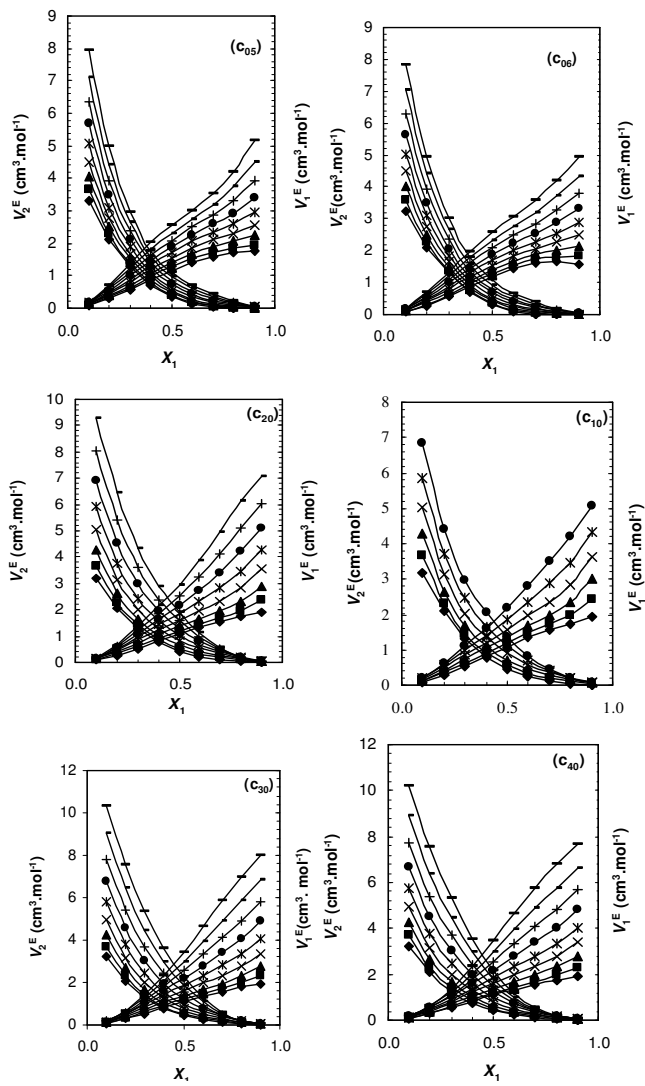
Excess partial molar volume

The excess partial molar volume \bar{V}_i^E of a component in a binary mixture can be determined from excess molar volume data using:

$$\bar{V}_i^E / (\text{cm}^3 \cdot \text{mol}^{-1}) = V_m^E + (1 - x_i) \left(\frac{\partial V_m^E}{\partial x_i} \right)_{x_j, p, T} \quad (11)$$

where $\left(\frac{\partial V_m^E}{\partial x_i} \right)_{x_j, p, T}$ is calculated from equation (1) using the parameters in Table 1. The average uncertainty in the partial excess molar volume is estimated to be $2 \times 10^{-2} \text{ cm}^3 \cdot \text{mol}^{-1}$. The excess partial molar volumes \bar{V}_i^E values of binary mixtures are recorded in supplementary data. The excess partial molar volumes \bar{V}_i^E for binary mixtures {*o*-xylene or *p*-xylene + acetic acid} at temperatures 313.15 K to 473.15 K and pressure 0.2 MPa to 2 MPa are shown in Figure 5 and for binary mixtures {*o*-xylene or *p*-xylene + THF} at temperatures 278.15 K to 318.15 K and pressure 81.5 kPa are shown Figure 6. The excess partial molar volumes \bar{V}_i^E for all binary mixtures in this study show that with increasing mole fraction of one component, the \bar{V}_i^E values are increased. With increase the mole fraction of one component in mixtures the possibility of electron donor-acceptor type (or charge-transfer) interactions between the mixture components are decreased, so the \bar{v}_i^E values are increased.





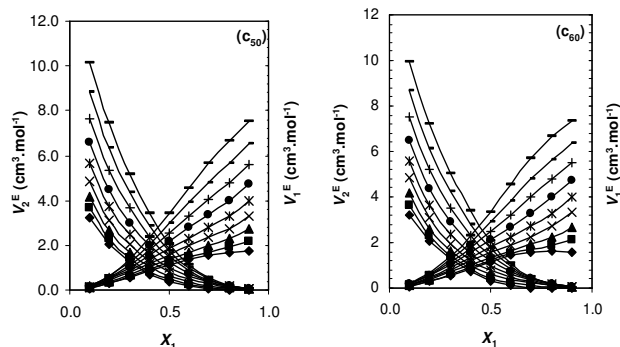


Figure 5. Excess partial molar volume against mole fraction for {*p*- xylene + acetic acid (c₀₁ to c₀₆)} and for {*o*- xylene + acetic acid {c₁₀ to c₆₀}}, at the temperatures 313.15 K (◇), 333.15 K (■), 353.15 K (▲), 373.15 K (×), 393.15 K (⋈), 413.15 K (●), 433.15 K (+), 453.15 K (-), 493.15 K (—) at pressures 0.2 MPa (b₀₁, b₁₀), 0.4 MPa (b₀₂, b₂₀), 0.8 MPa (c₀₃, c₃₀), 1.2 MPa (c₀₄, c₄₀), 1.6 MPa (c₀₅, c₅₀), 2 MPa (c₀₆, c₆₀).

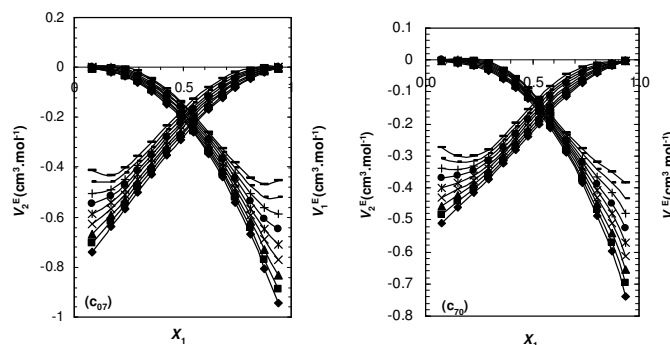


Figure 6. Excess partial molar volume against mole fraction for {*p*-Xylene + THF (c₀₇) and for *o*-xylene + THF (c₀₇), at the temperatures 278.15 K (◇), 283.15 K (■), 288.15 K (▲), 293.15 K (×), 298.15 K (⋈), 303.15 K (●), 308.15 K (+), 313.15 K (-), 318.15 K (—) at pressure 81.5 kPa.

CONCLUSIONS

In this work thermal expansion coefficients α , their excess values α^E , isothermal coefficient of pressure excess molar enthalpy $(\partial H_m^E / \partial P)_{T,x}$, partial molar volumes \bar{V}_i and excess partial molar volumes \bar{V}_i^E , were calculated from experimental densities. The results show that: (i) the excess thermal expansions coefficient α^E , for all binary mixtures at different temperatures and pressures are positive and with increasing temperature become more positive; (ii) the isothermal coefficients of pressure excess molar enthalpy $(\partial H_m^E / \partial P)_{T,x}$ for all binary mixtures at different temperatures and pressure are negative with increasing temperature become more negative; (iii) the excess partial molar volumes \bar{V}_i^E for all binary mixtures in this study show that with increasing mole fraction of one component, the \bar{V}_i^E values are increased. In the above binary

mixtures, expansions in volume and changing other calculated parameters are due to a decrease in the molecular order in the lattice.

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