



Densities and some related properties of the binary systems of methanol with isomeric xylenes between 303.15 and 323.15 K

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ARTICLE INFO

Article history:

Received 30 September 2010

Received in revised form 12 January 2011

Accepted 20 January 2011

Available online 25 January 2011

Keywords:

Densities

Excess molar volumes

Apparent molal volumes

Partial molar volumes

Thermal expansivities

Methanol and xylenes

ABSTRACT

Densities ρ for the systems of methanol + *o*-xylene, + *m*-xylene and + *p*-xylene in the whole range of composition were measured at an interval of 5 K in the range of 303.15 K to 323.15 K. From experimental ρ , excess molar volumes V_m^E , apparent molal volumes ϕ_v , partial molar volumes \bar{V}_i , thermal expansivities α and excess thermal expansivities α^E were calculated. V_m^E values plotted against the mole fraction of methanol show two lobes, one small positive in the xylene-rich region and the other is larger and negative in the methanol-rich region. The positive V_m^E has been interpreted in terms of dissociation of associated methanol molecules, whereas, negative V_m^E is due to their re-association, in conjunction with partial accommodation of the xylenes into structural networks of methanol.

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1. Introduction

Studies on thermo-physical and thermodynamic properties of binary mixtures have great importance in theoretical as well as applied fields. In theoretical level, it provides deep understanding about the types of interaction or forces acting in the mixing up of different species and also shows the appearance of a new phenomenon, which is completely absent in their pure state. It has been observed that mixing up different liquids gives rise to solutions that generally do not behave ideally. The relevant deviations from ideality are expressed by different thermodynamic variables, particularly by their excess values. Excess thermodynamic properties of mixtures thus become useful in the study of intermolecular interactions as well as structures. In particular, they reflect the interactions that take place intermolecularly as solute–solute, solute–solvent, and solvent–solvent species. In the applied field, physical and chemical properties of liquid mixtures are often required for technological process designing. The chemical or process engineers, in particular, seek knowledge about physical properties of the systems especially in the fluid phase essential for designing industrial equipments. Thus, the importance of data of thermo-physical and thermodynamic properties of binary liquid mixtures appears to be increasing gradually

in industrial process designing, in biological and other industrial applications.

As a part of our continuing research on volumetric and viscometric properties of non-aqueous solutions [1–5] of alkanols, here we report on volumetric properties of binary systems of methanol + isomeric xylenes (*ortho*-, *meta*- and *para*-xylenes). The present investigation mainly involves aspects relating to excess molar volumes V_m^E , apparent molal volumes ϕ_v , partial molar volumes \bar{V}_i , thermal expansivities α and excess thermal expansivities α^E , all being estimated from the measured ρ values of the systems over the entire range of composition between 303.15 K and 323.15 K. This would enable us to get information regarding forces acting between the alkanol and aromatic hydrocarbons as well as to see the effect of positional variation of substituents in the aromatic hydrocarbons. So far we know data similar to the present systems are yet to be reported.

2. Experimental section

2.1. Materials

The chemicals used in this experiment were of stated purity: methanol (E. Merck, D-6100 Darmstadt, F.R. GERMANY, and GLC >98%), *o*-xylene (E. Merck, D-6100 Darmstadt, F.R. GERMANY, and GC >99%), *m*-xylene and *p*-xylene (ALDRICH-Chemical Co. Inc, U.S.A, and GC >99%). All were used without further purification. The purity of these chemicals is further checked by comparing their measured density values with the available literature data as shown in Table 1.

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Table 1
Comparison of experimental densities ρ of pure liquids with literature values between 303.15 K and 323.15 K.

T/K	Methanol		o-xylene		m-xylene		p-xylene	
	$\rho/\text{kg m}^{-3}$							
	This work	lit.	This work	lit.	This work	lit.	This work	lit.
303.15	782.2	781.9 ^a 781.7 ^d 782.0 ^f	870.9	871.31 ^b 870.66 ^k 871.36 ^g	855.3	855.3 ^h 855.74 ^b 855.87 ^g	852.5	852.35 ^k 852.47 ^b
308.15	777.4	777.2 ^c 776.9 ^d 777.1 ^e	866.6	867.05 ^b	851.2	851.45 ^b	848.1	848.12 ^b
313.15	773.1	772.4 ^a 772.6 ^f 772.4 ⁱ	862.5	862.79 ^b	846.9	847.17 ^b 847.1 ⁱ	843.9	843.77 ^b 843.41 ^m
318.15	768.1	767.6 ^c 767.6 ^e	858.3	858.53 ^b	842.5	842.88 ^b	839.5	839.42 ^b
323.15	763.2	762.8 [*]	854.0	853.79 ^m	838.4	838.9 ^j 838.25 ^k	835.1	834.90 ^k

^aRef. [13], ^bRef. [15], ^cRef. [18], ^dRef. [19], ^eRef. [20], ^fRef. [21], ^gRef. [22], ^hRef. [23], ⁱRef. [24], ^jRef. [25], ^kRef. [26], ^lRef. [27], ^mRef. [28].

^{*}Extrapolated values of ref. [18].

2.2. Apparatus and procedures

Densities of pure liquids and their binary mixtures were measured by using a 10 cm³ bi-capillary pycnometer previously calibrated with doubly distilled water. All weighings were made by a digital balance (College B 204-S, METTLER TOLEDO) with an accuracy of ± 0.0001 g. In the whole study a thermostatically controlled water bath capable of maintaining the temperature constant up to ± 0.05 K was used.

Binary solutions of methanol + o-xylene, + m-xylene and + p-xylene were prepared by the method of mass. The mass of each component used was later converted into its mole fraction. Special care was taken to prevent evaporation and the introduction of moisture. The accuracy in the mole fraction was estimated as $\pm 10^{-4}$, whereas, calculated uncertainty in measured density was ± 0.12 kg m⁻³.

2.3. Theory/calculation

Excess molar volume V_m^E at any composition was calculated from measured ρ by using the equation [6]:

$$V_m^E = x_1 M_1 (1/\rho - 1/\rho_1) + x_2 M_2 (1/\rho - 1/\rho_2) \quad (1)$$

where M_1 and M_2 are the molar masses, x_1 and x_2 are the mole fractions, ρ_1 and ρ_2 are the densities of pure components 1 and 2, respectively and ρ represents the density of the mixture.

The apparent molal volume of the each component can also be calculated from the density data. As for example, at molality m the apparent molal volume $\phi_{v,1}$ is equated as [7]:

$$\phi_{v,1} = 1000 (\rho_1 - \rho) / m \rho \rho_1 + M_2 / \rho \quad (2)$$

where all the terms have their usual significances.

The average isobaric thermal expansivities α of pure liquids and of their binary mixtures have been calculated by using the equation [8,9]:

$$\alpha = -(\partial \ln \rho / \partial T)_p \quad (3)$$

So that slope of the plot of $\ln \rho$ vs. T yields the α value at a particular composition.

Excess thermal expansivities α^E of all the solutions have been obtained by following equation [9]:

$$\alpha^E = \alpha - (x_1 \alpha_1 + x_2 \alpha_2) \quad (4)$$

where α is the observed thermal expansivity of the mixture and α_1 and α_2 are those of pure components 1 and 2, respectively.

3. Results and discussion

Densities ρ of the three systems measured at 303.15, 308.15, 313.15, 318.15 and 323.15 K within the range of composition, $0 \leq x_1 \leq 1$, where, x_1 represents the mole fraction of methanol, are summarized in Tables 2–4. The variation in densities of the three systems as a function of mole fraction of methanol is represented by Fig. 1. As Fig. 1 shows, order of densities of pure xylenes is: o-xylene > m-xylene > p-xylene. Also for all systems ρ vs. x_1 curves show essentially similar variational patterns; densities decreasing with the increasing concentration of methanol. However, rate of decrement is found to be enhanced with increasing x_1 , particularly in the methanol-rich region and in the whole range of composition, order of increasing ρ follows: methanol + o-xylene > + m-xylene > + p-xylene.

Excess molar volumes V_m^E for the systems of methanol + o-xylene, + m-xylene and p-xylene at different temperatures estimated by Eq. (1) are listed in Tables 2–4 and graphically represented by Figs. 2–4, respectively. Fig. 5 is the comparative diagram of V_m^E vs. x_1 at 303.15 K. At a particular temperature all the V_m^E values have been fitted to the four-parameter Redlich–Kister equation [10] of the following form:

$$Y^E = x_1 x_2 \sum_{i=0}^n A_i (1 - 2x_1)^i \quad (5)$$

where Y^E represents V_m^E and A_i is the regression coefficient.

Figs. 2–4 exhibit the following characteristics:

- In the xylene-rich region, V_m^E are found to be small positive, whereas, in the methanol-rich region these are large and negative, extending over a wide range of composition.
- In all cases, rise of temperature increases the region and height of positive V_m^E but decreases the region and magnitude of negative V_m^E , i.e., V_m^E/dT are positive for all the systems.

As Fig. 5 shows, small positive V_m^E having a maximum in the methanol-poor region follow the order: methanol + p-xylene > + m-xylene > + o-xylene, whereas, negative V_m^E with a minimum in the methanol-rich region vary as: methanol + m-xylene > + p-xylene > + o-xylene. These trends are in good agreement with those of Bhardwaj et al. [11] observed for isomeric butanols + isomeric xylenes and Diaz et al. [12] for n-heptane + isomeric xylenes.

V_m^E for the present systems are not significantly large, particularly positive V_m^E in the methanol-poor region. Here, pure methanol which generally exists in associated form is thought to be dissociated, giving rise to expansion in volume, and hence, the positive V_m^E . As the concentration of alkanol increases, molecules become increasingly associated forming its structural networks, especially in the methanol-rich region. At this stage, probably $-\text{CH}_3$ group of the xylenes enters into the structural networks of methanol, resulting into overall contraction of the volume of the solution which is manifested by its large negative V_m^E . This type of behavior has already been observed for the systems of toluene + isomeric pentanols and m-xylene + isomeric propanols and termed as due to 'partial interstitial accommodation' effect [3,5]. Another factor, that is likely to cause volume contraction, may be considered as the large size difference between methanol and the xylenes. As the ratio of molar volumes of methanol and a xylene is approximately 1:3, smaller methanol molecules may tend to fit themselves into void spaces left by the much larger xylenes. Consequently, it contributes negatively to V_m^E , especially in the xylene-rich region. As this negative effect is also significant in the xylene-rich region, positive V_m^E is affected thereby. As a result the existing positive lobe due to dispersion effect becomes smaller for all the systems. Such a behavior has also been reported by Shukla et al.

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