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FT-IR study of excess thermodynamic properties of binary liquid mixtures of p-xylene with 1-alkanols at 303.15 K

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ABSTRACT

Excess volumes (V^E) and excess isentropic compressibilities (κ^E) have been determined at 303.15 K for the binary systems of p-xylene with 1-propanol, 1-butanol and 1-pentanol. Excess volumes exhibit an inversion sign for all binary systems. Further, isentropic compressibilities (κ) were also computed for the same 1-alkanols from precise speed of sound and density data. The excess isentropic compressibilities (κ^E) from ideal behavior were also computed and the data were negative in all the binary systems. The calculated excess functions were correlated with Redlich–Kister and Hwang polynomial equations and the experimental speed of sound data have been analyzed in terms of free length theory (FLT) and collision factor theory (CFT). The results were discussed in terms of intermolecular interactions between component molecules with the help of FT-IR spectral studies.

1. Introduction

Thermodynamic data is essential for many industrial applications such as in the oil and gas industries for flow assurance and oil recovery, in chemical industries for the design and separation processes, in pharmaceutical and polymer industries for solvent selection and emission control and recently in biotechnology for aggregation of proteins and several protein separations.

Volumetric and acoustic properties of binary liquid mixtures containing polar and self-associated components exhibit significant deviations from ideality due to difference in size of molecules and possible hydrogen bonding interaction between unlike molecules. A survey of the literature has shown that excess volume and sound speed data for the binary mixtures of aromatic hydrocarbons with 1-alkanols [1–4], chlorotoluenes [5], isoalkanols [6], esters [7], aliphatic hydrocarbons [8] and aliphatic and aromatic alcohols [9] were reported earlier.

This work forms a part of our systematic study on excess thermodynamic properties of liquid mixtures containing o- and m-xylenes [10]. In the present study, we report here new excess volume and excess isentropic compressibility data of the binary mixtures of p-xylene with 1-propanol, 1-butanol and 1-pentanol. The sound speed of binary liquid mixtures was computed theoretically at different mole fractions using free length theory (FLT) [11,12] and collision factor theory (CFT) [13]. Further, the present investigation emphasizes on the effect of addition of methyl group in toluene molecule that may influence both the sign and magnitude of excess volume and excess isentropic compressibility.

2. Experimental methods

2.1. Materials

In the present investigation all the liquids were used Analytical Reagent (AR) grade (procured from S.D. Fine Chemicals Ltd., and Merck) and their purities were as follows: p-xylene 99.5%, 1-propanol 99.5%, 1-butanol 99.5% and 1-pentanol 99.5%. Before the experimental measurements, all the liquids were purified as described in the literature [14]. The experimental density (ρ) and speed of sound (u) data of pure substances were compared with literature values [15–18] and were listed in Table 1.

2.2. Measurements

Densities of pure components were measured by using a bi-capillary type pycnometer which offered an accuracy of 1×10^{-5} g·cm^{-3} [19]. Excess volumes were measured using the dilatometer of the type described earlier [20,21]. The measured values of V^E were accurate to ± 0.003 cm^3 mol^{-1}. Speed of sound (u) measurements were performed by using single crystal ultrasonic interferometer (model F-05) from Mittal Enterprises, New Delhi, India, at 2 MHz frequency as described in the literature [22,23] and the data were accurate to $\pm 0.15\%$. A thermostatically controlled, well-stirred circulated water bath with ± 0.01 K was used for all the speed of sound (u) measurements

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Table 1
Density (ρ), speed of sound (u), thermal expansion coefficient (α) and heat capacity (C_p) data for pure components at 303.15 K.

Component	ρ (g·cm^{-3})		u (m·s^{-1})		α (kK^{-1})	C_p (J·mol^{-1}·k^{-1})
	Exp	Lit	Exp	Lit		
p-Xylene	0.85224	0.85226 [15]	1291	1289 [15]	1.056 [17]	183.7 [18]
1-Propanol	0.79556	0.79559 [16]	1190	1192 [16]	0.7684 [16]	147.8 [16]
1-Butanol	0.80203	0.80206 [16]	1225	1226 [16]	0.9476 [16]	177.1 [16]
1-Pentanol	0.80659	0.80656 [16]	1264	1262 [16]	0.8995 [16]	212.3 [16]

with an uncertainty of ± 0.5 m·s^{-1}. FT-IR spectra were recorded on a FT-IR spectrophotometer (JASCO FT-IR-4100, Japan; wave number range 7800–400 cm^{-1}; wavelength range 1282–25,000 nm). The device has a maximum resolution of 0.9 cm^{-1} and has 22,000/1 signal-to-noise ratio [17].

3. Results and discussion

3.1. Excess volumes (V^E)

The experimental excess volume (V^E) data for of the binary mixtures were incorporated in Table 2 and these were graphically represented in Fig. 1. These values were fitted to Redlich–Kister [24] and Hwang et al. [25] empirical relations:

Redlich–Kister equation is:

$$V^E/\mathrm{cm}^3\cdot\mathrm{mol}^{-1} = x_1(1-x_1)\left[a_0 + a_1(2x_1-1) + a_2(2x_1-1)^2\right]. \quad (1)$$

Hwang et al. equation is:

$$V^E/\mathrm{cm}^3\cdot\mathrm{mol}^{-1} = x_1x_2\left[b_0 + b_1x_1^3 + b_2x_2^3\right] \quad (2)$$

where a_0, a_1 and a_2 and b_0, b_1 and b_2 are adjustable parameters and $x_1$is the mole fraction of p-xylene. The values of parameters were obtained by the least-square method. The method of correlation of excess properties with Hwang et al. equation was described earlier [26]. The values of these adjustable parameters were given in Table 3 along with standard deviations σ (V^E).

The V^E data in Table 2 can be explained as follows: according to Treszczanowicz and Benson [27] the positive V^E values arise due to the breaking of hydrogen bonds in self-associated 1-alkanols and physical dipole–dipole interactions between 1-alkanol monomers and multimers. Negative contributions arise from changes in 'free volume' in the real mixture and presence of π-electrons in xylene molecule resulting in the formation of weak intermolecular complexes [28]. This may be due to the fact that, at lower mole fraction of p-xylene, the dissociation of 1-alkanol is of less importance and at higher mole fraction, the effect of the breaking of alkanol–alkanol H-bonds is proportionally very large [8,29]. However, V^E values for mixtures of p-xylene with 1-propanol, 1-butanol and 1-pentanol are algebraically smaller than those for mixtures of toluene with same 1-alkanols [3]. This shows that the addition of another methyl group in toluene has influenced the sign and magnitude of V^E.

Moreover, in the case of p-xylene and 1-alkanol mixtures, both the factors which are responsible for positive and negative V^E data compete with each other. Singh et al. reported the excess volumes at 298.15 K as a function of composition for the system 1-propanol + p-xylene by dilatometric method and they observed negative excess volume at higher mole fraction and positive excess volume at lower mole fraction of 1-propanol [30], and this comparison data was also graphically represented in Fig. 1. Similar behavior was also reported by Maurizio Fermeglla and Lapasin [31] for the system of 1-butanol + p-xylene and Tsierkezos et al. [32] for the system 1-pentanol + p-xylene at 298.15 K. In the present investigation, similar trend was observed in all the binary mixtures of p-xylene with 1-alkanols. According to Marcus [33], the molecules of 1-alkanols are associated through hydrogen bonding in pure state. When 1-alkanol is mixed with p-xylene, molecules would induce mutual dissociation of the hydrogen-bonded structures present in pure 1-alkanols with subsequent formation of weak hydrogen bonding (π–H) between π-electrons of the benzene ring of p-xylene and protons of 1-alkanols [34]. Further, the curves in

Table 2
Mole fraction of p-xylene (x_1), excess volumes (V^E) and predicted excess molar volumes in terms of Redlich–Kister and Hwang et al. at T = 303.15 K for the binary mixtures of p-xylene with 1-alkanols.

x_1	V^E (exp.)	V^E (Redlich–Kister)	V^E (Hwang et al.)
	cm^3·mol^{-1}		
p-Xylene (1) + 1-propanol (2)			
0.0625	−0.012	−0.012	−0.015
0.1053	−0.020	−0.021	−0.024
0.1704	−0.032	−0.033	−0.035
0.1931	−0.037	−0.037	−0.037
0.2420	−0.045	−0.043	−0.042
0.3126	−0.048	−0.047	−0.044
0.4306	−0.035	−0.035	−0.033
0.5122	−0.015	−0.015	−0.016
0.6106	0.015	0.017	0.014
0.6799	0.041	0.040	0.037
0.7524	0.061	0.060	0.059
0.7927	0.068	0.067	0.067
0.8426	0.070	0.070	0.071
0.8810	0.065	0.065	0.068
0.9408	0.043	0.043	0.047
p-Xylene (1) + 1-butanol (2)			
0.0529	−0.013	−0.009	−0.012
0.1008	−0.017	−0.016	−0.019
0.1527	−0.020	−0.023	−0.024
0.2109	−0.019	−0.027	−0.026
0.3208	−0.010	−0.024	−0.021
0.4001	−0.003	−0.012	−0.009
0.4526	0.006	0.000	0.001
0.5270	0.018	0.020	0.019
0.6009	0.033	0.042	0.039
0.6621	0.049	0.060	0.057
0.7316	0.065	0.075	0.073
0.7808	0.074	0.081	0.080
0.8227	0.078	0.081	0.082
0.8614	0.077	0.076	0.078
0.9327	0.055	0.050	0.053
p-Xylene (1) + 1-pentanol (2)			
0.0663	−0.005	−0.006	−0.009
0.1002	−0.010	−0.008	−0.011
0.1476	−0.011	−0.010	−0.012
0.2020	−0.009	−0.009	−0.009
0.2661	−0.003	−0.005	−0.002
0.3648	0.012	0.010	0.013
0.4270	0.026	0.024	0.026
0.4806	0.040	0.038	0.039
0.5524	0.058	0.058	0.057
0.6309	0.078	0.079	0.076
0.7083	0.092	0.093	0.091
0.7624	0.096	0.098	0.096
0.8120	0.094	0.096	0.096
0.9316	0.056	0.055	0.058