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Excess Volumes and Excess Isentropic Compressibilities of Binary Liquid Mixtures of Trichloroethylene with Esters at 303.15 K

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Abstract Exces volumes, V^{E}, and excess isentropic compressibilities, κ_S^{E}, have been reported as a function of composition for binary liquid mixtures of trichloroethylene with ethyl acetate, *n*-propyl acetate, and *n*-butyl acetate at 303.15 K. Isentropic compressibilities are calculated using measured sound speeds and density data for pure components and for binary mixtures. Excess volumes and excess isentropic compressibilities are found to be negative for the three systems studied over the entire composition range at 303.15 K, whereas these values become more negative with an increase of carbon chain length. The results are discussed in terms of intermolecular interactions between unlike molecules.

Keywords Density · Excess isentropic compressibility · Excess volume · Intermolecular interactions · Sound speed · Trichloroethylene

1 Introduction

Trichloroethylene is a non-flammable liquid and commonly used as an industrial solvent. It is mainly used as a degreasing agent in metal fabricating operations. It had a multitude of uses in many other industries such as dry cleaning, textile, electronics, leather, and rubber. Acute and chronic inhalation exposure to trichloroethylene can affect the human nervous system. Liver, kidney, immunological, and developmental effects have also been reported in humans. In this concern, physical properties of liquid mixtures containing trichloroethylene are required in most calculations where

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mixing is an important factor in many practical problems concerning mass transport applications.

Studies on molecular interactions in terms of thermodynamic and physical properties of liquid mixtures containing trichloroethylene as a common component have been reported [1–3]. A survey of the literature revealed that the excess volumes, V^{E}, and excess isentropic compressibilities, κ_S^{E}, have not been studied earlier for the present three systems. However, the excess volumes have been reported for 1,1,1-trichloroethane with ketones and ester systems [4]. Hence, in the present paper, the main purpose is to study the solution behavior of trichloroethylene with ethyl acetate, *n*-propyl acetate, and *n*-butyl acetate at 303.15 K. Further, the effect of chain length on the molecular interactions is discussed.

2 Materials and Methods

Trichloroethylene, ethyl acetate, *n*-propyl acetate, and *n*-butyl acetate (S. D. Fine, India) were purified by the standard methods described in the literature [5]. The water content of solvents used in this work was measured using an Analab (MicroAqua Cal 100) Karl Fischer Titrator and Karl Fisher reagent from Merck. The purity of the samples was ascertained by comparing the measured densities and sound speeds with those reported in the literature [5–9], and the data are given in Table 1 along with CAS number and water content.

Densities of the pure liquids and their mixtures were measured by using a Rudolph Research analytical digital densimeter (DDM-2911 model), and these measurements were carried out by carefully filling the sample in the U tube of the instrument with the help of a medical syringe. We have also ensured that there is no bubble formation during the measurement since cell should be air-free. The density was measured automatically at the specified temperature with an uncertainty of 0.00005 g·cm^{-3}. The sound speeds, u, were measured using an ultrasonic interferometer at a fixed frequency of 2 MHz, and the values were accurate to 0.3 %. The sound speed is calculated by using the relation, $u = \nu\lambda$, where ν is the frequency and λ is the wavelength. The wavelength can be computed from the relation, $d = n\lambda/2$, where d is the total distance moved by the reflector.

3 Results and Discussion

The excess volume data were calculated from the densities of pure liquids and their mixtures using the following equation:

$$V^{\mathrm{E}} = \left[x_1 M_1 + x_2 M_2\right]/\rho_{\mathrm{m}} - \left[x_1 M_1/\rho_1 + x_2 M_2/\rho_2\right], \tag{1}$$

where x_1 and x_2 are mole fractions, M_1 and M_2 are molecular weights, ρ_1 and ρ_2 are densities of components 1 and 2, respectively, and ρ_{m} is the density of the mixture. The uncertainty in the excess volume measurement is 0.005 cm^3·mol^{-1}.

The experimental speed of sound (u) and density (ρ) data were used to compute the isentropic compressibility (κ_s) by using the equation,

Table 1 Densities and sound speeds, molar heat capacity, C_p, and thermal expansion coefficient, α, of pure components at 303.15 K

Components	CAS number	Density ($kg \cdot m^{-3}$)		Sound speed ($m \cdot s^{-1}$)		Water content (%)	Cp ($J \cdot mol^{-1} \cdot K^{-1}$)	α (kK^{-1})
		Present work	Literature	Present work	Literature			
Trichloro ethylene	79-01-6	1450.90	1447.10 [7]	1016	1013 [8]	0.045	122.4 [11]	1.121 [11]
Ethyl acetate	141-78-6	888.75	888.50 [5]	1126	1122 [9]	0.038	171.2 [12]	1.390 [12]
n-Propyl acetate	109-60-4	876.55	877.16 [5]	1148	1149 [9]	0.029	198.4 [12]	1.320 [12]
n-Butyl acetate	123-86-4	871.07	871.29 [5]	1170	1176 [9]	0.056	232.0 [12]	1.160 [12]

$$\kappa_s = u^{-2}\rho^{-1}. \tag{2}$$

The isentropic compressibility is dependent on the ultrasonic speed. This quantity is considered as a thermodynamic property if a negligible amount of ultrasonic absorption of the acoustic waves of low frequency and of low amplitude is observed.

The corresponding excess isentropic compressibility (κ_s^{E}) was calculated employing the following relations [10]:

$$\kappa_s^{\mathrm{E}} = \kappa_s - \kappa_s^{\mathrm{id}}, \tag{3}$$

where κ_s^{id} is the ideal value of the isentropic compressibility and was calculated from the following equation [10]:

$$\kappa_s^{\mathrm{id}} = \sum_{i=1}^{2} \varphi_i \left[\kappa d + T V_i \left(\alpha_i^2\right)/C_{p,i}\right] - \left\{T\left(\sum_{i=1}^{2} x_i V_i\right)\left(\sum_{i=1}^{2} \varphi_i \alpha_i\right)^2 \Big/ \sum_{i=1}^{2} x_i C_{p,i}\right\} \tag{4}$$

Here, $C_{p,i}$ and α_i are the molar heat capacity and the thermal expansion coefficient of the ith component, respectively. The values of $C_{p,i}$ and α_i were obtained and evaluated from the literature [11,12].

Densities, sound speeds, excess volumes, isentropic compressibilities, and excess isentropic compressibilities for the three binary systems are given in Table 2.

The excess volumes and excess isentropic compressibilities are plotted as a function of mole fraction and volume fraction, respectively, in Figs. 1 and 2.

Excess volumes and excess isentropic compressibilities are negative in all the systems over the whole range of mole fraction. The variation of V^{E} with mole fraction is almost symmetrical in the systems, trichloroethylene with *n*-propyl acetate and n-butyl acetate, whereas in the system of trichloroethylene with ethyl acetate, the values are skewed toward the trichloroethylene-rich region. The excess properties may be explained in terms of (a) the loss of dipolar association in pure components, (b) specific interactions between unlike components, and (c) the difference in size and shape of the components. The negative V^{E} and κ_S^{E} indicate that the effect due to specific interactions between unlike components is dominant over the effect due to loss of dipolar association.

The algebraic values of V^{E} and κ_S^{E} for the three systems fall in the sequence:

n-butyl acetate < *n*-propyl acetate < ethyl acetate

This order is in agreement with the order in molar polarizabilities [5] (ethyl acetate: 61.65 $\mathrm{cm^3 \cdot mol^{-1}}$; *n*-propyl acetate: 72.30 $\mathrm{cm^3 \cdot mol^{-1}}$; *n*-butyl acetate: 78.82 $\mathrm{cm^3 \cdot mol^{-1}}$) of non-common components. This is expected because the non-common component with higher polarizability interacts strongly with trichloroethylene, and hence, V^{E} and κ_S^{E} values are more negative in such mixtures.

Table 2 Mole fraction, x, volume fraction, ϕ, density, ρ, sound speed, u, excess volume, V^{E}, isentropic compressibility, κ_S, and excess isentropic compressibility, κ_S^{E}, of trichloroethylene binary mixtures at 303.15 K

x	ϕ	ρ (kg·m^{-3})	u (m·s^{-1})	V^{E} (cm^3·mol^{-1})	κ_S (TPa^{-1})	κ_S^{E} (TPa^{-1})
x Trichloroethylene + (1 − x) ethyl acetate						
0.0000	0.0000	888.75	1126	0	887	0
0.1325	0.1224	957.65	1105	−0.007	855	−5
0.2099	0.1953	998.68	1094	−0.013	837	−8
0.3674	0.3466	1083.99	1073	−0.034	801	−10
0.4158	0.3940	1110.76	1067	−0.045	791	−10
0.5484	0.5259	1185.16	1051	−0.062	764	−8
0.6854	0.6655	1263.95	1037	−0.078	736	−6
0.8354	0.8226	1352.10	1025	−0.064	704	−3
0.8995	0.8910	1390.34	1021	−0.046	690	−2
1.0000	1.0000	1450.90	1016	0	668	0
x Trichloroethylene + (1 − x) n-propyl acetate						
0.0000	0.0000	876.55	1148	0	866	0
0.1419	0.1139	942.22	1126	−0.031	837	−5
0.2337	0.1916	987.22	1112	−0.069	819	−8
0.3640	0.3079	1054.63	1097	−0.128	788	−12
0.4555	0.3940	1104.47	1081	−0.154	775	−13
0.5827	0.5204	1177.08	1063	−0.139	752	−10
0.6735	0.6158	1231.75	1055	−0.119	729	−8
0.7713	0.7238	1293.35	1046	−0.079	707	−3
0.8922	0.8654	1374.05	1027	−0.029	689	−2
1.0000	1.0000	1450.90	1016	0	668	0
x Trichloroethylene + (1 − x) n-butyl acetate						
0.0000	0.0000	871.07	1170	0	839	0
0.1739	0.1251	944.38	1145	−0.105	808	−11
0.2500	0.1846	979.14	1135	−0.131	793	−15
0.3658	0.2814	1035.81	1120	−0.176	770	−16
0.4722	0.3779	1092.05	1097	−0.191	761	−14
0.5724	0.4762	1149.11	1080	−0.184	746	−9
0.6942	0.6065	1224.71	1060	−0.165	727	−5
0.7761	0.7018	1279.91	1052	−0.148	706	−3
0.9126	0.8764	1380.34	1027	−0.076	687	−2
1.0000	1.0000	1450.90	1016	0	668	0

Uncertainty in density is 0.00005 g·cm^{-3}, sound speed is 0.3 %, and excess volume is 0.005 cm^3·mol^{-1}

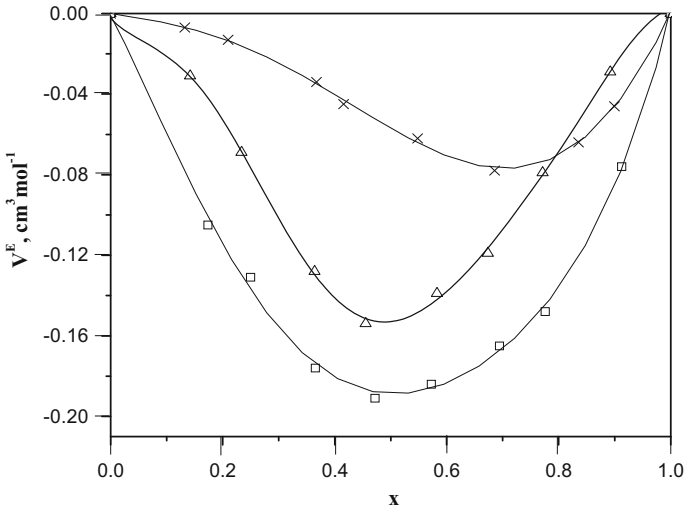

Fig. 1 Excess volumes versus mole fraction of trichloroethylene for the systems trichloroethylene + ethyl acetate (×), trichloroethylene + *n*-propyl acetate (△), and trichloroethylene + *n*-butyl acetate (□)

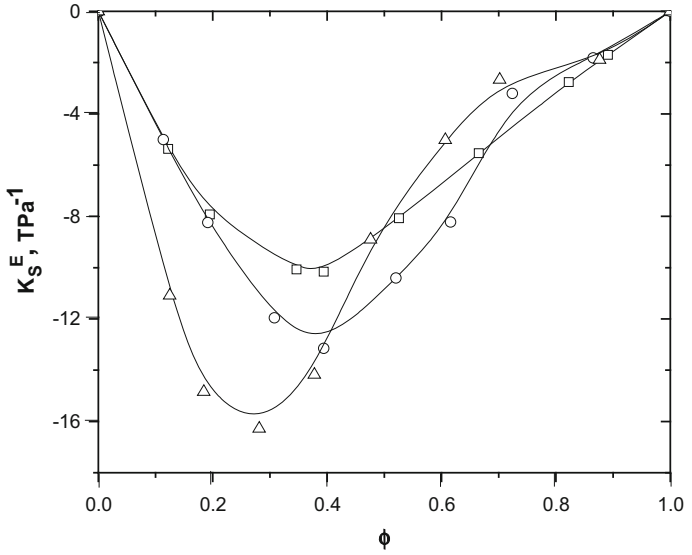

Fig. 2 Excess isentropic compressibility versus volume fraction of trichloroethylene for the systems trichloroethylene + ethyl acetate (□), trichloroethylene + *n*-propyl acetate (o), and trichloroethylene + *n*-butyl acetate (△)

4 Conclusions

The density and sound speed for three binary mixtures of trichloroethylene with ethyl acetate, *n*-propyl acetate, and *n*-butyl acetate at 303.15 K were measured. From the precise experimental density and sound-speed data, excess volumes, V^{E}, and excess

isentropic compressibilities, κ_S^E, were computed. These derived properties were found to be negative over the entire composition range which can be ascribed to specific interactions between unlike molecules. The computed data and the plots of excess properties were discussed in terms of intermolecular interactions.

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