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Densities, speeds of sound, isentropic compressibilities, refractive indices and viscosities of binary mixtures of tetrahydrofuran with hydrocarbons at 303.15 K

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Abstract

Isentropic compressibilities, Rao's molar sound functions, molar refractions, excess isentropic compressibilities, excess molar volumes, viscosity deviations and excess Gibbs energies of activation of viscous flow for seven binary mixtures of tetrahydrofuran (THF) with cyclohexane, methylcyclohexane, *n*-hexane, benzene, toluene, *p*-xylene and propylbenzene over the entire range of composition at 303.15 K have been derived from experimental densities, speeds of sound, refractive indices and viscosities. The excess partial molar volumes of THF in different solvents have been estimated. The experimental results have been analyzed in terms of the Prigogine–Flory–Patterson theory.

Keywords: Binary liquid mixtures; Hydrocarbon; Isentropic compressibility; Refractive index; Speed of sound; Tetrahydrofuran; Viscosity

1. Introduction

The interaction between cyclic ethers and linear or cyclic alkanes as well as aromatic hydrocarbons have been subject of many investigations and, particularly, much attention has been paid to the analysis of the thermodynamic properties of these kinds of liquid mixtures [1–4]. Such study of cyclic ethers in polar and non-polar solvents is not only of interest to analyze the structures of the mixtures but also important for many industrial processes as cyclic ethers are excellent solvents of polymers and their application in polymer synthesis [5]. As a part of our systematic studies on the thermodynamic, transport and acoustic properties of liquid mixtures containing cyclic ethers, in previous papers [6–8], speeds of sound, isentropic compressibilities, viscosities and related mixing functions for binary mixtures of *p*-dioxane with a variety of solvents have been reported. As an extension of our studies, in this paper, we report densities, speeds of sound, isentropic compressibilities, refractive indices, viscosities and related mixing functions for binary mixtures of tetrahydrofuran (THF) with cyclohexane, methylcyclohexane, *n*-hexane, benzene, toluene, *p*-xylene and propylbenzene.

2. Experimental

The speeds of sound u in pure liquids and in binary mixtures were measured with a multi frequency ultrasonic interferometer supplied by Mittal Enterprise, New Delhi. In the present work, a steel cell fitted with a quartz crystal of 2 MHz frequencies was employed. The refractive indices n_D were measured using the Research refractometer RL_3 made in Poland. The viscosities η were measured with a modified suspended-level Ubbelohde viscometer [9]. The viscometer was designed so as to reduce surface tension

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Table 1
Densities, refractive indices, speeds of sound, viscosities, thermal expansion coefficients and heat capacities for pure liquids at 303.15 K

Liquids	ρ (kg m^{-3})	n_D	u (m s^{-1})	η (mPa s)	α° (kK^{-1})	C_P° (J mol^{-1} K^{-1})
Tetrahydrofuran	876.70	1.4028	1255	0.438	1.243[a]	125.9[a]
	876.7[b]	1.4028[c]	1255[d]	0.438[c]		
Cyclohexane	769.28	1.4210	1228	0.820	1.233[e]	158.0[e]
	769.18[f]	1.4214[c]	1229.1[g]	0.820[c]		
Methylcyclohexane	760.31	1.4200	1194	0.641	1.187[e]	187.0[e]
	760.31[c]	1.41804[c]	1193[g]	0.639[c]		
n-Hexane	650.45	1.3704	1054	0.278	1.398[c]	198.0[h]
	650.56[c]	1.36966[c]	1053.7[i]	0.278[c]		
Benzene	868.29	1.4951	1277	0.560	1.233[e]	136.8[e]
	868.29[e]	1.49472[c]	1277[j]	0.562[c]		
Toluene	857.60	1.4910	1282	0.520	1.084[e]	158.4[e]
	857.55[c]	1.49133[c]	1283.2[e]	0.520[c]		
p-Xylene	852.30	1.4909	1290	0.570	1.013[k]	181.7[d]
	852.25[c]	1.49068[c]		0.567[l]		
Propylbenzene	853.30	1.4878	1308	0.750	0.968[l]	210.6[l]
	853.8[l]	1.4828[l]		0.746[l]		

[a] Ref. [16].
[b] Ref. [14].
[c] Ref. [13].
[d] Ref. [15].
[e] Ref. [19].
[f] Ref. [17].
[g] Ref. [18].
[h] Ref. [21].
[i] Ref. [20].
[j] Ref. [22].
[k] Derived from density data [24].
[l] Ref. [23].

effects to negligible values [10]. A water-circulating thermostat with an accuracy of ±0.02 K was used for controlling the temperature for the speed of sound, refractive index and viscosity measurements. The densities ρ were measured with an Anton Paar vibrating tube digital densimeter (model DMA 60/602) with a thermostat-bath controlled to ±0.01 K. The details of the apparatus and procedures have been described in previous publications [11,12].

Mixtures were prepared by mixing known masses of pure liquids in narrow-mouth ground-glass-stoppered bottles. All the mass measurements were performed on a Mettler AE 163, Switzerland. The possible error in the mole fraction is estimated to be $\pm 1\times10^{-4}$. The errors in values of ρ, u, n_D and η were estimated to be less than 0.02 kg m^{-3}, 1 m s^{-1}, 0.0002 units and 0.002 mPa s, respectively. The isentropic compressibilities determined from the relation $\kappa_S=1/(u^2\rho)$ are believed to be reliable to ±1 T Pa^{-1}.

Cyclohexane (Merck, Bombay, >99 mol%), methylcyclohexane (BDH, AR), *n*-hexane (Fluka), benzene (Merck, >99 mol%), toluene (Merck, >99 mol%), *p*-xylene (Merck, >99 mol%) and propylbenzene (Merck, >99 mol%) were used after further purification by standard procedures [13]. THF (Merck, >99 mol%) was refluxed for several hours over sodium metal pieces till free from peroxide and finally fractionally distilled over sodium [13]. Immediately before use all liquid samples were dried over a molecular sieve type 0.4 nm from Fluka and fractionally distilled twice. The purity of liquid samples tested by gas–liquid chromatography was better than 99.8 mol% for all samples. The pure component properties ρ, n_D, u and η along with literature values [13–24] are given in Table 1.

3. Results

The results for the densities, speeds of sound, refractive indices, viscosities, isentropic compressibilities, Rao's molar sound functions and molar refraction for binary mixtures over the entire range of composition at 303.15 K are given in Table 2.

Rao's molar sound functions R [25] and molar refractions R_m were obtained from the relations

$$R = u^{1/3}V \tag{1}$$

$$R_m = \left[\left(n_D^2-1\right)/\left(n_D^2+2\right)\right]V \tag{2}$$

where $V=\sum(x_iM_i)/\rho$ in which x_i and M_i are the mole fraction and molecular weight of component i. The values of R and R_m were uncertain within ±0.3%.

Excess molar volumes V^E for each mixture were calculated from equation

$$V^E = \sum(x_iM_i)/\rho - \sum(x_iM_i/\rho_i) \tag{3}$$