Journal of Molecular Liquids 155 (2010) 8–15

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Thermodynamic and acoustic properties for binary and ternary mixtures of cyclic ethers with industrially important solvents at 308.15 K

Satish Kumar [a], Wonsub Lim [a], Younghee Lee [a], Jaibir S. Yadav [b], Dimple Sharma [b], V.K. Sharma [b], Il Moon [a,*]

[a] Department of Chemical and Bimolecular Engineering, Yonsei University 262-Seongsanoo, Seodaemun-gu, Seoul 120-749, Republic of Korea
[b] Department of Chemistry, Maharshi Dayanand University, Rohtak-124001, India

ARTICLE INFO

Article history:
Received 13 December 2009
Received in revised form 2 April 2010
Accepted 9 April 2010
Available online 24 April 2010

Keywords:
Speed of sound
Cyclic ethers
Graph theory
Interaction parameters

ABSTRACT

Speeds of sound data, u_{ijk} of 1,3-dioxolane or 1,4-dioxane(i) + benzene or toluene (j) + formamide or N,N-dimethylformamide (k) ternary mixtures and their sub-binary mixtures, u_{ij} of *1,3-dioxolane or 1,4-dioxane* (i) + benzene or toluene or *formamide* or *N,N-dimethylformamide* (j); benzene or toluene (i) + formamide or N,N-dimethylformamide (j) have been measured using a quartz crystal interferometer as a function of composition at 308.15 K. The experimental data have been utilized to evaluate excess isentropic compressibilities of binary, $(\kappa_S^E)_{ij}$ and ternary, $(\kappa_S^E)_{ijk}$ mixtures and the same have been fitted to Redlich–Kister equation to predict binary and ternary adjustable parameters along with standard deviations. $(\kappa_S^E)_{ij}$ and $(\kappa_S^E)_{ijk}$ data have also been analyzed in terms of Graph and Flory theories. It has been observed that predicted $(\kappa_S^E)_{ij}$ and $(\kappa_S^E)_{ijk}$ values by Graph theory compare well with their corresponding experimental values.

1. Introduction

Specific molecular interactions in liquid mixtures can be deduced from the measurements of excess properties like excess molar volumes, excess molar enthalpies, excess Gibb's free energies and excess isentropic compressibilities etc. The systematic investigations of these excess properties are therefore of great importance and have attracted the attention of researchers in the past decades. These properties provide an important tool to extract information about (i) state of aggregation of components in pure as well as in mixed state and (ii) molecular interactions among the constituents of mixtures.

Further, topological methods occupy an eminent place in the field of prediction of excess properties of chemical compounds. One of the current tendencies in chemical and biological investigations is the prediction of physico-chemical and biological properties of chemical compounds and drugs from their structures [1–6]. The fundamental basis of these investigations is molecular graph of a molecule (in which atoms are represented by dots and chemical bonds by lines) that describes the topology of a molecule which provides total information contained in that molecule [7–9]. In our earlier publications [10,11] we have employed Graph theory based on connectivity parameter of third degree of a molecule (which in turn depends upon its topology) to evaluate excess isentropic compressibilities of binary and ternary mixtures. In present study, we report here speeds of sound data of 1,3-dioxolane or 1,4-dioxane (i) + benzene or toluene (j) + formamide or N,N-dimethylformamide (k) ternary and their sub-binary mixtures.

2. Experimental

1,3-dioxolane (Fluka USA 99%), 1,4-dioxane (AR Grade 99% s.d. fine-chem) formamide (FA) (AR Grade 99% s.d. fine-chem), N,N-dimethylformamide (DMF) (AR Grade 99.5% s.d. fine-chem), benzene (AR Grade 99.7% RANKEM), toluene (AR Grade 99.5% Sisco) were purified by standard methods [12]. The purities of the purified liquids were checked by measuring their densities (recorded in Table 1) at 298.15 ± 0.01 K and these agreed to within $\pm 5\times10^{-3}$ kg m^{-3} with their corresponding literature values [13–16].

Speeds of sound at 2 MHz for various binary and ternary mixtures were determined at 308.15 K ± 0.01 K using a variable path ultrasonic interferometer (Model M 81, Mittal Enterprises, and India) and a measuring cell. Water from the thermostat was circulated through the cell to maintain the temperature of the study. The speed of sound values for the purified liquids at 308.15 ± 0.01 K (recorded in Table 1) compare well with their corresponding literature values [17–19]. The uncertainties in measurement of speed of sound values are ± 1 m/s.

3. Results and discussion

Speeds of sound, u_{ijk} data of 1,3-dioxolane or 1,4-dioxane (i) + benzene or toluene (j) + FA or DMF (k) ternary and u_{ij} data of their sub-binary 1,3-dioxolane or 1,4-dioxane (i) + benzene or toluene or FA or DMF (j); benzene or toluene (i) + FA or DMF (j) mixtures were

* Corresponding author. Tel.: +82 2 2123 2761.
E-mail addresses: vatssatish@yahoo.co.in (S. Kumar), ilmoon@yonsei.ac.kr (Il Moon).

0167-7322/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.molliq.2010.04.007

Table 1
Comparison of densities, ρ and speeds of sound of pure liquids along with their literature values at 298.15 K and 308.15 K respectively.

Liquids	T (K)	ρ (g cm^{-3})		u (m s^{-1})	
		Expt.	Lit.	Expt.	Lit.
1, 3-dioxolane	298.15	1.05885	1.05881 [13]		
	298.15			1338	1338.8 [17]
1, 4-dioxane	298.15	1.02792	1.02797 [13]		
	308.15			1324	1325 [18]
Benzene	298.15	0.87360	0.87362 [14]		
	308.15			1259	1260 [14]
Toluene	298.15	0.86219	0.86220 [14]		
	308.15			1261	1262 [14]
Formamide	298.15	1.12926	1.12918 [15]		
	308.15			1580	1580.5 [19]
N, N-dimethylformamide	298.15	0.94445	0.94447 [16]		
	308.15			1464	1465 [16]

measured over entire mole fraction range at 308.15 K and are reported in Tables 2 and 3. The isentropic compressibilities for binary $(\kappa_S^E)_{ij}$ and ternary $(\kappa_S^E)_{ijk}$ mixtures were determined by using Eqs. (1) and (2)

$$(\kappa_S)_{ij} = \left(\rho_{ij} u_{ij}^2\right)^{-1} \tag{1}$$

$$(\kappa_S)_{ijk} = \left(\rho_{ijk} u_{ijk}^2\right)^{-1} \tag{2}$$

The density, ρ_{ij} and ρ_{ijk} of various binary and ternary mixtures were calculated by employing their molar excess volumes data available in literature [20–22] via Eqs. (3) and (4)

$$V_{ij}^E = \sum_{i=i}^{j} x_i M_i \left(\rho_{ij}\right)^{-1} - \sum_{i=i}^{j} (x_i M_i)(\rho_i)^{-1} \tag{3}$$

$$V_{ijk}^E = \sum_{i=i}^{k} x_i M_i \left(\rho_{ijk}\right)^{-1} - \sum_{i=i}^{k} x_i M_i (\rho_i)^{-1} \tag{4}$$

where x_i, M_i, ρ_i etc. are the mole fraction, molecular mass and density of pure component (i) in binary or ternary mixtures. Excess isentropic compressibilities, $(\kappa_S^E)_{ij}$ and $(\kappa_S^E)_{ijk}$ for the binary $(i+j)$ and ternary $(i+j+k)$ mixtures were determined using Eqs. (5) and (6)

$$\left(\kappa_S^E\right)_{ij} = \kappa_S - \sum_{i=i}^{j} \phi_i (\kappa_S)_i \tag{5}$$

$$\left(\kappa_S^E\right)_{ijk} = \kappa_S - \sum_{i=i}^{k} \phi_i (\kappa_S)_i \tag{6}$$

where ϕ_i and $(\kappa_S)_i$ i are the volume fraction and isentropic compressibility of the component (i). Such $(\kappa_S^E)_{ij}$ and $(\kappa_S^E)_{ijk}$ values for binary and ternary mixtures are recorded in (Tables 2 and 3), and $(\kappa_S^E)_{ijk}$ values are plotted in Figs. 1–4. $(\kappa_S^E)_{ij}$ values for binary mixtures were fitted to Eq. (7)

$$\left(\kappa_S^E\right)_{ij} = x_i x_j \left[\sum_{n=0}^{2} \kappa_S^{(n)} (2x_i - 1)^n\right] \tag{7}$$

$\kappa_S^{(n)}$ $(n=0\text{–}2)$ etc. are parameters characteristics of $(i+j)$ binary mixtures and were evaluated by least squares method. Such parameters along with standard deviations, $\sigma(\kappa_S^E)_{ij}$, are defined by

$$\sigma\left(\kappa_S^E\right)_{ij} = \left[\sum \left(\kappa_{s(\text{exptl.})}^E - \kappa_{s(\text{calc.eq.7})}^E\right)^2 / (m-n)\right]^{0.5} \tag{8}$$

Table 2
Comparison of speed of sound, u_{ijk}, isentropic compressibilities $(\kappa_S^E)_{ijk}$ and excess isentropic compressibilities $(\kappa_S^E)_{ijk}$ for various $(i+j+k)$ ternary mixtures at 308.15 K with values evaluated from Graph theory, Flory theory; also included are various parameters $(\kappa_S^{(n)})_{ijk}$ $(n=0\text{–}2)$ along with standard deviation $\sigma(\kappa_S^E)_{ijk}$, interaction parameters χ_{ij}, etc and $({}^3\xi_i)$.

				$(\kappa_S^E)_{ijk}$ (T Pa^{-1})		
x_i	x_j	u_{ijk} (m s^{-1})	$(\kappa_S)_{ijk}$	(Exptl.)	(Graph)	(Flory)
1, 3-dioxolane (i) + benzene (j) + formamide (k)						
0.0819	0.8524	1311	658.7	−53.5	−53.6	−42.4
0.1128	0.8012	1326	637.9	−66.0	−66.0	−43.2
0.1439	0.7512	1339	620.4	−75.5	−75.6	−44.2
0.1725	0.6856	1362	592.0	−91.7	−93.5	−43.7
0.1987	0.2101	1496	439.3.	−99.5	−96.8	6.9
0.2613	0.1555	1470	448.8	−77.0	−73.9	−4.8
0.2829	0.0997	1461	447.5	−56.3	−51.8	3.3
0.3330	0.1320	1446	463.1	−65.7	−62.7	−15.6
0.3550	0.2020	1437	479.2	−82.4	−82.4	−30.8
0.4035	0.2036	1420	492.0	−77.4	−78.5	−41.8
0.4708	0.2489	1388	522.4	−72.0	−76.6	−59.7
0.5408	0.1201	1385	508.9	−49.8	−49.8	−62.8
0.5960	0.2690	1336	568.7	−46.6	−49.3	−82.9
0.7103	0.1111	1340	546.9	−32.6	−35.5	−95.6
0.8205	0.1280	1305	581.9	−16.5	−16.5	−115.1
$(\kappa_S^{(0)})_{ijk} = -1.5$; $(\kappa_S^{(1)})_{ijk} = -2.5$; $(\kappa_S^{(2)})_{ijk} = 5.3$; $\sigma(\kappa_S^E)_{ijk} = 0.3$						
$\chi_{ij}^* = 37.6$; $\chi_{jk}^* = -307.3$; $\chi_{ik}^* = -32.5$; $\chi'_{kk} = -375.7$,						
$({}^3\xi_i) = 0.601$; $({}^3\xi_j) = 0.666$; $({}^3\xi_k) = 0.440$						
1, 3-dioxolane (i) + toluene (j) + formamide (k)						
0.1804	0.2400	1513	438.5	−93.0	−110.3	2.2
0.2056	0.1824	1498	439.0	−76.2	−76.2	6.8
0.2567	0.2195	1453	474.1	−82.2	−52.3	−13.8
0.2680	0.1337	1452	460.8	−60.0	−33.4	−2.0
0.2875	0.0850	1448	455.8	−44.7	−44.7	3.2
0.3402	0.1134	1432	472.6	−52.2	−70.2	−16.9
0.4172	0.1766	1407	502.3	−61.4	−38.2	−45.2
0.4617	0.0945	1402	493.2	−44.4	−25.8	−44.4
0.4728	0.0449	1400	485.9	−31.2	−28.5	−39.9
0.4906	0.2176	1380	529.5	−58.4	−43.0	−64.6
0.5320	0.1101	1383	512.2	−43.0	−38.2	−62.5
0.6890	0.1231	1342	549.6	−32.0	−27.7	−9.4
0.7626	0.1010	1308	575.4	−24.1	−13.9	−106.2
0.8612	0.0814	1328	559.5	−13.5	−13.5	−22.4
$(\kappa_S^{(0)})_{ijk} = -2.6$; $(\kappa_S^{(1)})_{ijk} = -10{,}250.0$; $(\kappa_S^{(2)})_{ijk} = 15.3$; $\sigma(\kappa_S^E)_{ijk} = 0.4$						
$\chi_{ij}^* = 65.3$; $\chi_{jk}^* = -104.2$; $\chi_{ik}^* = -61.4$; $\chi'_{kk} = -1631.0$						
$({}^3\xi_i) = 0.601$; $({}^3\xi_j) = 0.666$; $({}^3\xi_k) = 0.440$						
1, 4-dioxane (i) + benzene (j) + N, N-dimethylformamide(k)						
0.1649	0.4739	1445	526.9	−103.3	−113.0	5.2
0.2046	0.3922	1450	517.8	−95.8	−95.8	7.4
0.2438	0.3114	1440	519.4	−77.5	−74.1	−14.7
0.2871	0.3536	1448	513.9	−94.5	−87.4	−10.4
0.3240	0.2376	1415	531.5	−52.0	−52.0	−5.5
0.3618	0.1540	1382	550.6	−15.2	−24.0	14.1
0.4058	0.1943	1392	542.3	−35.1	−37.5	−11.8
0.5078	0.4458	1356	577.0	−61.3	−94.4	−73.6
0.5307	0.1564	1373	549.9	−24.7	−24.7	−43.2
0.5529	0.3370	1401	534.3	−82.2	−81.2	−75.5
0.5674	0.0776	1341	567.6	6.9	3.2	−38.4
0.6242	0.2391	1392	534.5	−63.3	−56.1	−80.3
0.7302	0.1162	1356	552.5	−22.4	−16.8	−90.7
0.8136	0.1010	1344	557.8	−17.5	−17.5	−108.8
$(\kappa_S^{(0)})_{ijk} = -1520.0$; $(\kappa_S^{(1)})_{ijk} = -12{,}000.1$; $(\kappa_S^{(2)})_{ijk} = 10{,}200.9$; $\sigma(\kappa_S^E)_{ijk} = 0.4$						
$\chi_{ij}^* = -221.1$; $\chi_{jk}^* = 13.2$; $\chi_{ik}^* = 85.3$; $\chi'_{kk} = -810.9$,						
$({}^3\xi_i) = 0.801$; $({}^3\xi_j) = 0.666$; $({}^3\xi_k) = 0.589$						
1, 4-dioxane(i) + toluene(j) + N,N-dimethylformamide(k)						
0.0893	0.6777	1377	598.3	−66.1	−78.3	−30.0
0.1342	0.5937	1393	577.4	−73.2	−73.2	−26.6
0.1792	0.5095	1399	566.4	−69.7	−62.0	−22.9
0.2242	0.4251	1386	570.9	−50.1	−46.7	−18.7
0.2694	0.3405	1358	587.8	−17.4	−29.4	−14.3
0.3114	0.3794	1379	569.6	−45.5	−45.5	−35.3
0.4028	0.1696	1312	613.0	40.2	19.6	−19.0
0.4812	0.2904	1367	567.0	−36.4	−36.4	−66.8
0.5151	0.4475	1396	551.0	−85.8	−58.9	−93.5
0.6128	0.0829	1316	592.8	30.6	28.0	−69.3
0.6440	0.2441	1365	566.8	−52.2	−36.1	−101.8

(continued on next page)