Journal of Molecular Liquids 159 (2011) 230–235

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

Topological investigations of excess molar volumes and excess isentropic compressibilities of ternary mixtures containing 1-methyl pyrrolidin-2-one at 308.15 K

Y. Chhikara [a], J.S. Yadav [b], D. Sharma [c], V.K. Sharma [a,*]

[a] Department of Chemistry, Maharshi Dayanand University, Rohtak 124001, India
[b] Department of Chemistry, A.I.J.H.M. College, Rohtak 124001, Haryana, India
[c] P.D.M. College of Engineering for Women, Bhadurgarh, Haryana, India

ARTICLE INFO

Article history:
Received 19 October 2010
Received in revised form 13 December 2010
Accepted 28 January 2011
Available online 3 February 2011

Keywords:
Connectivity parameter of third degree
Excess molar volumes
Excess isentropic compressibilities
Speeds of sound

ABSTRACT

Excess molar volumes and speeds of sound, of 1-methyl pyrrolidin-2-one (i) + benzene or methyl benzene or cyclohexane (j) + propan-1-ol (k) ternary mixtures have been measured as a function of composition at 308.15 K using dilatometer and interferometer. The observed speeds of sound data have been utilized to calculate excess isentropic compressibilities of the studied mixtures. The observed excess molar volumes and excess isentropic compressibility values have been fitted to the Redlich–Kister equation to predict ternary adjustable parameters and standard deviations. The resulting data have also been analyzed in terms of Graph theory and Flory–Prigogine–Patterson theory. It has been observed that excess molar volumes and excess isentropic compressibility values determined by the Graph theory compare well with their corresponding experimental values.

1. Introduction

The structure of lactams is of great interest as they are related to many structural problems in molecular biology [1]. Self association of lactams serves as a model for the hydrogen bonding in nucleic acid amides. Thermodynamic studies of multicomponent liquid mixtures involving lactams are, therefore, required for gaining a better knowledge about molecular interactions in complex molecules of biological interest. The 1-methyl pyrrolidin-2-one, ε-caprolactam, is a dipolar aprotic compound. It has good thermal, chemical stability and low volatility. It is used as a solvent in various processes like extractive distillation and desulfurization of fuels [2]. It is also used for the production of nylon 6 which is polycaprolactum formed by ring opening polymerization. Thermodynamic properties of 1-methyl pyrrolidin-2-one + alkanol or aromatic hydrocarbon or cyclohexane mixtures are useful for the design and optimization of various industrial processes. Researchers [3–6] have reported thermodynamic properties of 1-methyl pyrrolidin-2-one (i) + alkanol (j) binary mixtures as a function of composition over a wide range of temperature. In recent studies, topology of constituents of mixture has been successfully utilized [7] to predict excess molar volumes, excess isentropic compressibilities of 1-methyl pyrrolidin-2-one (i) + propan-1-ol or propan-2-ol (j) binary mixtures. In continuation of our work on thermodynamic properties of mixtures containing 1-methyl pyrrolidin-2-one as one of the components, we report here excess molar volumes, V^E_{ijk} and speeds of sound data of 1-methyl pyrrolidin-2-one (i) + benzene or methyl benzene or cyclohexane (j) + propan-1-ol (k) ternary mixtures at 308.15 K. It would be of interest to see how Graph theory (which in turn involves the topology of a molecule) describes the excess molar volumes and excess isentropic compressibilities (determined by employing the speeds of sound data) of the studied (i + j + k) mixtures.

2. Experimental

1-methyl pyrrolidin-2-one [8a] (NMP) (Fluka, USA, 99%), benzene [8b] (A R Grade 99.7% Sisko), cyclohexane [8c] (A R Grade 98% Sisko), methyl benzene [8d] (A R Grade 99.5% Sisko) and propan-1-ol [8e] (A R Grade 99% Sisko) were purified by standard methods. The purities of the liquids were checked by measuring their densities with bicapillary pycnometer (with an accuracy of two parts in 10^5) at 298.15 ± 0.01 K. The resulting densities (reported in Table 1) agreed to within 0.05 kg m^{-3} with their corresponding literature values [9,10].

The excess molar volumes, V^E_{ijk}, for the ternary mixtures were measured in a three limbed dilatometer in the manner described elsewhere [11].The dilatometer was equilibrated in a constant temperature water bath at 308.15 ± 0.01 K. After attainment of thermal equilibrium, the change in liquid level of the dilatometer

* Corresponding author. Tel.: +91 9729071881.
E-mail address: v_sharmachem58@rediffmail.com (V.K. Sharma).

0167-7322/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.molliq.2011.01.018

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

Liquids	ρ (kg m^{-3})		u (m s^{-1})	
	Expt.	Lit.	Expt.	Lit.
1-methyl pyrrolidin-2-one	1028.3	1028.2 [10]	1546	1546.06 [10]
Benzene	873.56	873.60 [9]	1298	1298.9 [12]
Toluene	862.21	862.19 [9]	1303	1304.1 [13]
Cyclohexane	773.86	773.89 [9]	1255	1254.4 [14]
Propan-1-ol	799.63	799.60 [9]	1189*	1188.80* [15]

* Value at 308.15 K.

capillary was measured with a cathetometer that could be read to 10^{-5} m. The uncertainty in the measured V^E_{ijk} values is 0.5%.

The speeds of sound were determined at 2 MHz using a quartz crystal interferometer (Model-M 84, Mittal Enterprises, New Delhi, India). The measuring cell was a specially designed double-walled cell in which water was circulated to maintain the temperature at 308.15 ± 0.01 K. The uncertainty in measured sound speeds is 1 m s^{-1}. The speeds of sound values for the purified liquids at 298.15 ± 0.01 K (recorded in Table 1) compare well with their corresponding literature values [10,12–15].

3. Results and discussion

Excess molar volumes, V^E_{ijk}, and speeds of sound, u_{ijk}, data of NMP (i) + benzene or methyl benzene or cyclohexane (j) + propan-1-ol (k) ternary mixtures measured over the entire composition range at 308.15 K are recorded in Tables 2 and 3 respectively. The isentropic compressibilities, $(\kappa_S)_{ijk}$, for ternary mixtures were determined using

$$(\kappa_S)_{ijk} = \left(\rho_{ijk} u^2_{ijk}\right)^{-1}. \quad (1)$$

The densities, ρ_{ijk}, of the ternary mixtures were determined using excess molar volumes data via Eq. (2)

$$V^E_{ijk} = \sum_{i=i}^{k} x_i M_i \left(\rho_{ijk}\right)^{-1} - \sum_{i=i}^{k} x_i M_i (\rho_i)^{-1}, \quad (2)$$

where x_i, M_i and ρ_i are the mole fraction, molar mass, and density, respectively, of component (i) of the ($i+j+k$) ternary mixture.

The excess isentropic compressibilities, $(\kappa^E_S)_{ijk}$ for the investigated ternary mixtures were determined using

$$\left(\kappa^E_S\right)_{ijk} = (\kappa_S)_{ijk} - \kappa^{id}_S. \quad (3)$$

κ^{id}_S values were obtained as suggested by Benson and Kiyohara [16]

$$\kappa^{id}_S = \sum_{i=i}^{k} \varphi_i \left[\kappa_{S,i} + \frac{T v_i \alpha_i^2}{C_{p,i}}\right] - T\left(\sum_{i=i}^{k} x_i v_i\right) \frac{\left(\sum_{i=i}^{k} \varphi_i \alpha_i\right)^2}{\left(\sum_{i=i}^{k} x_i C_{p,i}\right)}, \quad (4)$$

where φ_i is the volume fraction of component (i) in the mixed state; $\kappa_{S,i}$, v_i, α_i and $C_{p,i}$ are isentropic compressibility, molar volume, thermal expansion coefficient and molar heat capacity respectively of pure component (i). The various parameters of pure components were determined using isothermal compressibility, κ_T reported in literature [17]. The κ_T values for those liquids which were not available in the literature were calculated by employing enthalpy of vaporization, ΔH_V values in the manner as suggested by Hildebrand [18]. The resulting $(\kappa_S)_{ijk}$ and $(\kappa^E_S)_{ijk}$ values for the ($i+j+k$) ternary mixtures are recorded in Table 3.

Table 2
Comparison of measured excess molar volumes, V^E_{ijk} values for the various ($i+j+k$) ternary mixtures at 308.15 K with the values predicted from the Graph theory and PFP theory; Also included are the various parameters $V^{(n)}_{ijk}$ (n = 0–2) along with their standard deviation, $\sigma(V^E_{ijk})$, interaction parameters χ'_{jk}, χ^{**}_{ij} etc., and connectivity parameter of third degree, $^3\xi_i$ ($i = i$ to k).

x_i	x_j	V^E_{ijk} (cm^3 mol^{-1})		
		(2Exptl)	(Graph)	(PFP)
1-methyl pyrrolidin-2-one (i) + benzene (j) + propan-1-ol (k)[a]				
0.0871	0.6033	−0.060	−0.012	−0.278
0.1074	0.5827	−0.050	−0.047	−0.304
0.1186	0.5605	−0.105	−0.103	−0.317
0.1450	0.5462	−0.147	−0.147	−0.342
0.1921	0.5177	−0.212	−0.212	−0.365
0.2012	0.4889	−0.269	−0.270	−0.384
0.2234	0.4607	−0.307	−0.303	−0.394
0.2556	0.4349	−0.360	−0.360	−0.406
0.2869	0.4031	−0.396	−0.396	−0.411
0.3051	0.3826	−0.410	−0.409	−0.411
0.3123	0.3717	−0.420	−0.417	−0.409
0.3316	0.3520	−0.418	−0.419	−0.407
0.3521	0.3307	−0.423	−0.423	−0.402
0.3771	0.3199	−0.450	−0.450	−0.400
0.3961	0.2940	−0.431	−0.432	−0.389
0.4142	0.2716	−0.411	−0.413	−0.378
0.4369	0.2505	−0.396	−0.398	−0.365
0.4515	0.2314	−0.368	−0.371	−0.351
0.4787	0.2101	−0.350	−0.348	−0.335
0.4921	0.1844	−0.291	−0.291	−0.312
0.5266	0.1624	−0.272	−0.253	−0.290
0.5432	0.1441	−0.236	−0.206	−0.270
0.5662	0.1744	−0.369	−0.327	−0.297
0.5891	0.2066	−0.498	−0.480	−0.319
0.6121	0.1901	−0.480	−0.450	−0.302
0.6429	0.1707	−0.452	−0.413	−0.280
0.7011	0.1517	−0.449	−0.420	−0.249
0.7316	0.1226	−0.380	−0.312	−0.215
1-methyl pyrrolidin-2-one (i) + methyl benzene (j) + propan-1-ol (k)[b]				
0.0621	0.6241	−0.046	−0.024	−0.125
0.0924	0.5964	−0.126	−0.119	−0.163
0.1001	0.5621	−0.141	−0.125	−0.171
0.1124	0.5794	−0.177	−0.177	−0.185
0.1331	0.5514	−0.224	−0.224	−0.206
0.1620	0.5141	−0.282	−0.281	−0.230
0.1878	0.5047	−0.341	−0.343	−0.250
0.2010	0.4861	−0.358	−0.360	−0.258
0.2362	0.4565	−0.414	−0.414	−0.276
0.2514	0.4434	−0.437	−0.434	−0.282
0.2781	0.4216	−0.467	−0.463	−0.292
0.2954	0.3920	−0.463	−0.460	−0.293
0.3011	0.4012	−0.485	−0.480	−0.298
0.3112	0.3761	−0.468	−0.466	−0.295
0.3341	0.3507	−0.472	−0.469	−0.296
0.3627	0.3191	−0.463	−0.463	−0.293
0.3911	0.3004	−0.469	−0.468	−0.292
0.4101	0.2871	−0.472	−0.467	−0.289
0.4416	0.2519	−0.436	−0.436	−0.277
0.4764	0.2316	−0.430	−0.425	−0.268
0.4920	0.2164	−0.413	−0.406	−0.260
0.5119	0.1806	−0.341	−0.346	−0.238
0.5241	0.1711	−0.331	−0.332	−0.232
0.5601	0.1511	−0.314	−0.302	−0.216
0.5969	0.1361	−0.307	−0.279	−0.202
0.6161	0.1021	−0.236	−0.202	−0.173
0.6340	0.1132	−0.278	−0.233	−0.180
0.6591	0.0921	−0.243	−0.184	−0.159
0.6703	0.2061	−0.589	−0.505	−0.239
0.7533	0.2003	−0.599	−0.571	−0.217
1-methyl pyrrolidin-2-one (i) + cyclohexane (j) + propan-1-ol (k)[c]				
0.0564	0.6851	0.557	0.579	−0.383
0.0924	0.6496	0.541	0.548	−0.463
0.1141	0.6279	0.529	0.530	−0.504
0.1344	0.6077	0.514	0.513	−0.538
0.1489	0.5891	0.503	0.508	−0.560
0.1621	0.5799	0.491	0.491	−0.577

(continued on next page)