Indian Journal of Chemistry
Vol. 62, July 2023, pp. 735-745
DOI: 10.56042/ijc.v62i7.3733

Volumetric and acoustic studies of binary liquid mixtures of propylene glycol monopropyl ether + *n*-alkylamine at 288.15, 298.15 and 308.15 K

Amalendu Pal*[a] & Anil Kumar[b]
[a] Department of Chemistry, Kurukshetra University, Kurukshetra 136 119, Haryana, India
[b] Department of Chemistry, Arya P. G. College, Panipat 132 103, Haryana, India
E-mail: palchem21@gmail.com, kumar_anilab@rediffmail.com

Received 15 November 2022; accepted (revised) 14 June 2023

The densities, *ρ*, and the speeds of sound, *u,* for binary liquid mixtures containing propylene glycol monopropyl ether (PGMPE) and *n*- butylamine (BA), dibutylamine (DBA) or tributylamine (TBA) have been measured as a function of composition using a vibrating tube densimeter and sound analyzer Anton-Paar model DSA-5000 at temperatures 288.15, 298.15 and 308.15 K and atmospheric pressure. From these data excess molar volumes, V_m^E , the thermal expansion coefficient, α^E, and deviations in isentropic compressibility, $\Delta\kappa_{s,}$ have been calculated.. The V_m^E values are negative over the whole mole fraction range for the systems propylene glycol monopropyl ether + *n*-butylamine, and dibutylamine, and positive for the system propylene glycol monopropyl ether + tributylamine. whereas the $\Delta\kappa_s$ values are negative over the entire range of composition for all mixtures with the exception of tributylamine. Also, in the present study, thermophysical parameters such as apparent molar volume ,$v_{\Phi,i}$, and apparent molar isentropic compressibility, $K_{\varphi,i}$ are studied for the PGMPE with BA, DBA or TBA. The results reveal the dominance of ether – BA or DBA as compared to ether –TBA interactions which are found to increase with elevation of temperature but decrease with increasing the chain length of alkylamine. Further, the deviation of the speeds of sound u^D from their ideal values u^{id} in an ideal mixture have been calculated for all measured values of mole fraction x_1. Sign and magnitude of V_m^E, $\Delta\kappa_s$ and u^D with respect to the composition and temperature have been used to analyze the mixing behavior of the components.

Keywords: Excess volume, Ultrasonic speed, Prpopylene glycol monopropyl ether, *n*-Alkylamine

Molecular interactions present between the various components in a mixture provide useful information about the mixing patterns that exist among solutions. Thus experimental data on some of the properties associated with liquid and liquid mixtures like density and ultrasonic speed find extensive application in solution theory and molecular dynamics[1]. Thermodynamic, acoustic and transport properties of binary liquid mixtures containing alkoxyethanols with *n*-alkylamines[2], alkylacetates[3] or 1-alkanols[4] and alkoxypropanols with *n*-alkylamines[5-7], 1-alkanols[8-11] or amides[12] have been intensely studied in our lab., especially in terms of evaluation of various thermodynamic properties and functions that give a better understanding of the molecular interactions. Some work on the density and the speed of sound studies of binary mixtures of esters with alkoxypropanols[13,14] has been reported. However, an understanding of mixing behaviour of propylene glycol monopropyl ether with butylamine, dibutylamine and tributylamine still needs to be developed in terms of interactions, arrangements and their strength. As a part of our continuing work, here, in the present study, we report new experimental density and speed of sound data for the mixtures of propylene glycol monopropyl ether (PGMPE) with *n*-butylamine (BA), dibutylamine (DBA) or tributylamine (TBA) with over the whole composition at temperatures of 288.15, 298.15 and 308.15 K and atmospheric pressure. The liquids were selected on the basis of their industrial use. The aim of this work is to provide a set of data for the characterization of molecular interactions of the

---

List of symbols: a_i : Coefficients in the smoothing Eqs. (8) and (10) ($m^3\ mol^{-1}$); V : Molar volume of mixture (m^3); V_i^* : Molar volume of component i (=1, 2) (m^3); V_m^E : Molar excess volume; x_i : Mole fraction of component i (= 1, 2); M_i : Molecular weight of component i (=1, 2); k : Number of coefficients in Eqs. (8) and (10); R : Gas constant (=8.31441 $JK^{-1}Mol^{-1}$); T : Absolute temperature; u : Speed of sound; u^* : Speed of sound of pure component; *Greek letters*: α : Isobaric thermal expansivity; ρ : Solution density (kg m^{-3}); ρ^*: Density of pure component (kgm^{-3}); σ : Standard deviation in Eqs. (8) and (10); κ_S: Isentropic compressibility; *Superscripts*: E : Excess property; *Subscripts*: i : Grade of coefficient in eqs.(9) and (10); 1,2: Represents the component of binary mixtures; m : Molar property.

oxygen (-O-) and hydroxyl (-OH) groups of alkoxypropanol with the amine (-NH) group of alkylamines and to study the composition – temperature dependent behavior of these mixtures.

Experimental Section

Materials

Propylene glycol monopropyl ether (PGMME) (Aldrich, mass fraction >99 mol%) were used without further purification. Butylamine (S.D.Fine chemical, minimum assay (GLC), 98 mol%), dibutylamine (Merck – Schuchardt, GC >99 mol%), and tributylamine (S.D.Fine, chemical, minimum assay (GLC), 99 mol%) were stored over sodium hydroxide pellets for several days and fractionally distilled twice[15,16]. The middle fraction of the distillate was used. Prior to measurements, all liquids were stored in dark bottles over 0.4 nm molecular sieve to reduce water content, and were partially degassed at low pressure. The purity of the final samples were checked by comparing the densities, and speeds of sound at 298.15 ± 0.01 K with their corresponding literature values[16-26] in Table 1.

Apparatus and procedures

Densities and speeds of sound of both pure liquids and their binary mixtures were measured simultaneously and automatically , using an Anton Paar (model DSA 5000) vibrating tube digital densimeter instrument thermostated by a built-in solid state thermostat within ± 1 × 10^{-2} K. The apparatus was also tested with the density of a known molality of aqueous NaCl using the data given by Pitzer *et al.*[27]. The sensitivity of the instrument corresponded to a precision in density and speed of sound measurements of ± 1 × 10^{-3} kg m^{-3} and ± 1 × 10^{-2} m s^{-1}. The reproducibility of the density and speed of sound estimates was found to be within ± 5 × 10^{-3} kg m^{-3} and ± 5 × 10^{-2} m s^{-1}, respectively. The reproducibility of the results was confirmed by performing the measurements in triplicate. Before each series of measurements, the instrument was pre-calibrated with doubly distilled, deionized, degassed water, and dry air for the temperature range investigated.

The binary mixtures were prepared by mass and were kept in special airtight stoppered glass bottles to avoid evaporation. The weighing were done on an

Table 1 — Observed and literature values of densities ρ^* (kg m^{-3}); isobaric thermal expansion α_p^*(k K^{-1}); speed of sound u^* (m s^{-1}) of pure liquid components at different temperatures.

Components	T (K)	ρ^* x10^{-3} (kg m^{-3})		α_p^* (kK^{-1})	u^* (m s^{-1})	
		obs.	lit.		obs.	lit.
Propylene glycol monopropyl ether	288.15	0.89032			1282.6	
	298.15	0.88115	0.8813 (Ref. 17)		1245.6	
	308.15	0.87183			1208.8	
Butylamine	288.15	0.74359		1.257 (Ref. 23)	1294.3	
	298.15	0.73402	0.73323 (Ref. 18) 0.73325 (Ref. 19)		1248.8	1250 (Ref. 18) 1249.8 (Ref. 22)
	308.15	0.72453	0.73335 (Ref. 21) 0.72339 (Ref. 20)		1204.1	
Dibutylamine	288.15	0.76927		0.78 (Ref. 25)	1290.6	
	298.15	0.76095	0.75770 (Ref. 24)		1250.4	1248 (Ref. 18)
	308.15	0.75259	0.75595 (Ref. 18)		1210.6	1206 (Ref. 18)
Tributylamine	288.15	0.78140			1283.8	
	298.15	0.77394	0.77367 (Ref. 26)	0.990 (Ref. 21)	1245.7	1246.9 (Ref. 22)
	308.15	0.76645	0.77378 (Ref. 16) 0.76695 (Ref. 18)		1208.2	

Afcoset electronic balance (India, Model ER-182A) with a precision of ± 0.01 mg. The probable error in the mole fraction was estimated to be less than $\pm 1 \times 10^{-4}$. All the molar quantities were based on the IUPAC relative atomic mass table[28].

Results and Discussion

Density and speed of sound

The experimental results of the density, ρ, and speed of sound, u, of binary mixtures of PGMPE with BA, DBA, and TBA, over the whole composition range expressed as the mole fraction, x_1, of PGMPE ($0 \leq x_1 \leq 1$) at different temperatures are listed in Table 2.

The excess molar volumes, V_m^E, were calculated by using the following relation:

$$V_m^E = \Sigma\, x_i M_i (\rho^{-1} - \rho^{*\,-1}) \qquad \text{...(1)}$$

where ρ and ρ_i^* are the density of the mixture and density of pure component i, respectively; x_i and M_i are the mole fraction and molar mass of component i in the mixture, respectively.

Table 2 — Excess molar volume $V_m^E \times 10^6$ ($m^3\ mol^{-1}$) of binary mixtures at different temperatures.

x_1	$\rho \cdot 10^{-3}$/ ($kg\ m^{-3}$)	$V_m^E \times 10^6$ ($m^3\ mol^{-1}$)	u ($m\ s^{-1}$)	u^D ($m\ s^{-1}$)	κ_s ($T\ Pa^{-1}$)	$\Delta\kappa_s$ ($T\ Pa^{-1}$)
$C_3H_7[O(CH_2)_3]OH$ (1) + $C_4H_9NH_2$ (2) 288.15 K						
0.0122	0.74655	-0.074	1294.9	0.79	798.856	-1.955
0.0713	0.75989	-0.335	1296.7	3.49	782.655	-8.853
0.1134	0.76886	-0.488	1297.7	5.12	772.332	-12.774
0.1610	0.77855	-0.638	1298.8	6.90	761.428	-16.656
0.2003	0.78627	-0.751	1299.6	8.25	753.024	-19.427
0.2828	0.80183	-0.981	1300.5	10.26	737.390	-23.695
0.4142	0.82372	-1.160	1300.4	11.81	717.904	-26.261
0.5000	0.83568	-1.080	1299.7	12.12	708.392	-25.440
0.5906	0.84677	-0.875	1298.2	11.63	700.731	-22.749
0.7124	0.86060	-0.580	1295.0	9.70	692.882	-17.509
0.8941	0.88159	-0.455	1288.8	5.25	682.908	-9.536
0.9409	0.88624	-0.361	1286.6	3.48	681.650	-6.450
$C_3H_7[O(CH_2)_3]OH$ (1) + $C_4H_9NH_2$ (2) 298.15 K						
0.0122	0.73699	-0.077	1249.4	0.65	869.230	-3.563
0.0713	0.75037	-0.350	1253.0	4.50	848.833	-11.455
0.1134	0.75936	-0.509	1254.8	6.47	836.379	-16.351
0.1610	0.76902	-0.657	1256.4	8.25	823.771	-20.665
0.2003	0.77693	-0.797	1257.5	9.50	813.958	-23.822
0.2828	0.79262	-1.047	1259.4	11.71	795.440	-28.901
0.4142	0.81489	-1.276	1260.7	13.46	772.107	-32.212
0.5000	0.82703	-1.215	1260.8	13.84	760.653	-31.427
0.5906	0.83802	-0.986	1259.8	13.11	751.869	-27.939
0.7124	0.85149	-0.625	1257.4	11.06	742.803	-21.478
0.8941	0.87208	-0.424	1251.3	5.44	732.354	-10.616
0.9409	0.87686	-0.342	1249.2	3.45	730.812	-6.994
$C_3H_7[O(CH_2)_3]OH$ (1) + $C_4H_9NH_2$ (2) 308.15 K						
0.0122	0.72745	-0.072	1204.4	0.22	947.666	-1.569
0.0713	0.74085	-0.356	1207.1	2.56	926.367	-9.986
0.1134	0.74985	-0.521	1209.5	4.71	911.620	-15.864
0.1610	0.75967	-0.695	1211.8	6.74	896.423	-21.324
0.2003	0.76761	-0.844	1213.6	8.32	884.521	-25.411

(*Contd.*)

Table 2 — Excess molar volume $V_m^E \times 10^6$ ($m^3 mol^{-1}$) of binary mixtures at different temperatures. (*Contd.*)

x_1	$\rho \cdot 10^{-3}$/ ($kg\ m^{-3}$)	$V_m^E \times 10^6$ ($m^3 mol^{-1}$)	u ($m\ s^{-1}$)	u^D ($m\ s^{-1}$)	κ_s ($T\ Pa^{-1}$)	$\Delta\kappa_s$ ($T\ Pa^{-1}$)
0.2828	0.78346	-1.122	1216.9	11.17	861.933	-32.219
0.4142	0.80560	-1.335	1220.5	14.11	833.307	-37.325
0.5000	0.81763	-1.253	1221.7	14.91	819.434	-36.816
0.5906	0.82861	-1.015	1222.0	14.80	808.179	-33.648
0.7124	0.84221	-0.660	1220.5	12.79	797.084	-26.488
0.8941	0.86286	-0.452	1214.3	5.88	785.973	-12.535
0.9409	0.86755	-0.353	1211.8	3.21	784.953	-7.482
$C_3H_7[O(CH_2)_3]OH$ (1) + $(C_4H_9)_2NH$ (2) 288.15 K						
0.0424	0.77510	-0.374	1291.0	0.67	774.087	-3.049
0.1448	0.78841	-1.003	1291.5	1.84	760.430	-8.484
0.2158	0.79707	-1.244	1291.8	2.63	751.818	-11.176
0.3225	0.80934	-1.352	1291.9	3.48	740.306	-13.439
0.4210	0.82035	-1.290	1291.5	3.82	730.823	-13.979
0.5050	0.82981	-1.179	1290.8	3.77	723.275	-13.573
0.6100	0.84199	-1.012	1289.7	3.52	714.029	-12.424
0.7149	0.85468	-0.830	1288.3	3.01	704.957	-10.573
0.8153	0.86724	-0.625	1286.9	2.52	696.259	-8.272
0.9059	0.87871	-0.38	1285.3	1.77	688.883	-5.232
0.9690	0.88657	-0.145	1284.1	1.19	684.052	-2.514
$C_3H_7[O(CH_2)_3]OH$ (1) + $(C_4H_9)_2NH$ (2) 298.15 K						
0.0424	0.76723	-0.487	1250.7	0.46	833.236	-3.612
0.1448	0.78058	-1.151	1251.6	1.76	817.808	-9.898
0.2158	0.78897	-1.349	1252.2	2.65	808.336	-12.785
0.3225	0.80095	-1.416	1252.9	3.81	795.356	-15.465
0.4210	0.81182	-1.341	1253.0	4.35	784.582	-16.273
0.5050	0.82120	-1.224	1252.5	4.24	776.239	-15.743
0.6100	0.83328	-1.050	1251.7	3.95	765.964	-14.413
0.7149	0.84584	-0.858	1250.5	3.39	755.918	-12.250
0.8153	0.85837	-0.659	1249.3	2.63	746.435	-9.426
0.9059	0.86990	-0.431	1247.8	1.64	738.313	-5.879
0.9690	0.87762	-0.177	1246.7	0.91	733.111	-2.618
$C_3H_7[O(CH_2)_3]OH$ (1) + $(C_4H_9)_2NH$ (2) 308.15 K						
0.0424	0.75921	-0.582	1210.7	0.16	898.597	-3.934
0.1448	0.77270	-1.305	1211.7	1.31	881.452	-10.844
0.2158	0.78088	-1.471	1212.5	2.22	871.068	-13.860
0.3225	0.79255	-1.492	1213.3	3.19	857.111	-16.301
0.4210	0.80325	-1.399	1213.6	3.65	845.275	-17.000
0.5050	0.81255	-1.278	1213.5	3.70	835.738	-16.631
0.6100	0.82456	-1.105	1213.2	3.59	823.973	-15.448
0.7149	0.83701	-0.906	1212.7	3.29	812.386	-13.425
0.8153	0.84940	-0.696	1212.0	2.80	801.461	-10.644
0.9059	0.86071	-0.442	1210.6	1.59	792.760	-6.362
0.9690	0.86831	-0.176	1209.2	0.33	787.642	-2.069

(*Contd.*)

Table 2 — Excess molar volume $V_m^E \times 10^6$ ($m^3 mol^{-1}$) of binary mixtures at different temperatures. (*Contd.*)

x_1	$\rho \cdot 10^{-3}$/ ($kg\ m^{-3}$)	$V_m^E \times 10^6$ ($m^3\ mol^{-1}$)	u ($m\ s^{-1}$)	u^D ($m\ s^{-1}$)	κ_s ($T\ Pa^{-1}$)	$\Delta\kappa_s$ ($T\ Pa^{-1}$)
			$C_3H_7[O(CH_2)_3]OH$ (1) + $(C_4H_9)_3N$ (2) 288.15 K			
0.0635	0.78537	0.004	1282.1	-1.66	774.608	1.550
0.1019	0.78788	0.006	1281.3	-2.43	773.105	2.216
0.1994	0.79468	0.011	1279.7	-3.95	768.407	3.388
0.3032	0.80262	0.027	1278.0	-5.57	762.831	4.699
0.4053	0.81132	0.035	1276.7	-6.77	756.189	5.578
0.4943	0.81975	0.037	1276.0	-7.38	749.234	5.886
0.6079	0.83185	0.030	1275.4	-7.84	739.030	6.082
0.7011	0.84312	0.020	1275.7	-7.42	728.809	5.517
0.8120	0.85839	0.009	1277.1	-5.85	714.275	4.082
0.8798	0.86892	0.004	1278.5	-4.34	704.075	2.918
0.9547	0.88179	0.003	1280.7	-1.99	691.417	1.326
0.9823	0.88692	0.001	1281.9	-0.74	686.131	0.442
			$C_3H_7[O(CH_2)_3]OH$ (1) + $(C_4H_9)_3N$ (2) 298.15 K			
0.0635	0.77776	0.031	1243.4	-2.29	831.635	2.678
0.1019	0.78015	0.057	1242.7	-2.99	830.021	3.407
0.1994	0.78664	0.118	1240.8	-4.88	825.696	5.421
0.3032	0.79433	0.160	1239.0	-6.68	820.080	7.243
0.4053	0.80285	0.173	1237.6	-8.07	813.214	8.500
0.4943	0.81113	0.169	1236.8	-8.86	805.955	9.083
0.6079	0.82304	0.155	1236.5	-9.15	794.677	9.035
0.7011	0.83415	0.130	1237.1	-8.54	783.333	8.117
0.8120	0.84932	0.085	1238.9	-6.73	767.107	6.033
0.8798	0.85982	0.052	1240.7	-4.92	755.542	4.224
0.9547	0.87269	0.013	1243.4	-2.21	741.171	1.799
0.9823	0.87779	0.003	1244.7	-0.90	735.326	0.706
			$C_3H_7[O(CH_2)_3]OH$ (1) + $(C_4H_9)_3N$ (2) 308.15 K			
0.0635	0.77004	0.083	1205.8	-2.42	893.170	3.367
0.1019	0.77232	0.129	1204.8	-3.43	892.016	4.734
0.1994	0.77856	0.226	1202.7	-5.57	887.960	7.510
0.3032	0.78603	0.289	1200.6	-7.72	882.601	10.167
0.4053	0.79432	0.316	1199.1	-9.26	875.576	11.895
0.4943	0.80242	0.314	1198.3	-10.11	867.895	12.663
0.6079	0.81415	0.283	1198.1	-10.38	855.676	12.538
0.7011	0.82513	0.240	1198.9	-9.64	843.163	11.251
0.8120	0.84013	0.167	1201.0	-7.62	825.216	8.523
0.8798	0.85056	0.110	1203.2	-5.48	812.118	5.923
0.9547	0.86334	0.044	1206.2	-2.55	796.122	2.775
0.9823	0.86844	0.018	1207.8	-0.98	789.351	1.115

The isentropic compressibilities, κ_s have been calculated from the relation:

$$\kappa_s = -V^{-1} (\delta V/\delta P)_S = (\rho u^2)^{-1} \qquad ...(2)$$

The deviations of the isentropic compressibility, $\Delta\kappa_s$, and excess molar thermal expansivities, α^E were calculated from experimental *u* and *ρ* values, as follows:

$$\Delta\kappa_s = \kappa_s - \kappa_s^{id} \qquad ...(3)$$

where κ_s^{id} are the volume fraction weighted average with the following equation[29-31]:

$$\kappa_s^{\,id} = \Sigma\,(\kappa^*_{s,i})\,\phi_i \qquad ...(4)$$

$$\alpha^E = \alpha - \Sigma\,\phi_i\,\alpha^*_{p,i} \qquad ...(5)$$

where ϕ_i (= $x_iV_{m,i}/\Sigma\, x_iV_{m,i}$) is the volume fraction. $V_{m,i}$ is the molar volume of component *i* and $\alpha^*_{p,i}$ is the isobaric expansivity.

The deviation of the speeds in ideal mixture was calculated from

$$u^D = u - u^{id} \qquad ...(6)$$

Numerous approximate ideal mixing rules have been used in literature[32-34] to estimate ideal speed of sound u^{id}. In so far as the Newton –Laplace equation is valid, the ideal ultrasonic speed u^{id} may be expressed[35] correctly in terms of thermodynamic properties of an ideal mixtures:

$$u^{id} = [\kappa_s^{\,id}.\Sigma\,\phi_i\,\rho_i^*\,]^{-\frac{1}{2}} \qquad ...(7)$$

where $\kappa_s^{\,id}$ can be obtained according to Eq.(4).

The calculated values of V_m^E, $\Delta\kappa_s$ and u^D of the binary mixtures as included in Table 2, at each temperature, were fitted to a Redlich–Kister polynomial equation:

$$F(x) = x_1x_2\,\Sigma_{i=0}\, a_i\,(x_1 - x_2)^i\,. \qquad ..(8)$$

where if *F(x)* ($\Delta\kappa_s$) is the deviation in isentropic compressibility, the composition is in volume fraction, if *F(x)* (V_m^E) is the excess molar volume, the composition is in mole fraction, and if *F(x)* (u^D) is the deviation in speed of sound, the composition is in volume fraction. Values of coefficients a_i of Eq. (8), evaluated by using the method of least squares with all points weighted equally along with the standard deviations, *σ(F(x))*are listed in Table 3.

Experimental results for V_m^E are plotted against x_1 , $\Delta\kappa_s$ and u^D are plotted against ϕ_1 alongwith the smoothed V_m^E, $\Delta\ \kappa_s$ and u^D values at 298.15 K by using Eq. 8 as in Fig. 1, Fig. 2, and Fig. 3.

The volume or theoretical expansion coefficient *α* of the mixture at a particular composition was calculated

Table 3 — Coefficients a_i of Eq. (8) and standard deviations σ of binary mixtures at different temperatures.

	T/K	a_0	a_1	a_2	a_3	a_4	σ
			$C_3H_7[O(CH_2)_3]OH$ (1) + $C_4H_9NH_2$ (2)				
$V_m^E \times 10^6$	288.15	-4.3292	3.3314	4.1662	-5.2753	-7.9518	0.005
($m^3\ mol^{-1}$)	298.15	-4.8539	3.4043	5.6932	-4.8881	-8.9210	0.005
	308.15	-5.0155	3.7369	5.0079	-5.5654	-7.9220	0.005
u^D ($m\ s^{-1}$)	288.15	48.1481	7.8646	-2.7903	14.2936	20.8822	0.17
	298.15	54.5101	10.3122	3.1369	2.9606	13.6952	0.15
	308.15	56.9849	25.7471	7.5247	4.2295	-17.8700	0.11
$\Delta\kappa_s$	288.15	-101.8125	43.3780	15.7968	-41.2555	-59.3314	0.13
($T\ Pa^{-1}$)	298.15	-125.3973	48.5866	25.8583	-26.4233	-73.9951	0.16
308.15		-147.1611	42.6726	19.1299	-44.0350	-20.0226	0.18
			$C_3H_7[O(CH_2)_3]OH$ (1) + $(C_4H_9)_2NH$ (2)				
$V_m^E \times 10^6$	288.15	-4.7464	3.0322	-3.2509	-0.6470	0.7420	0.004
($m^3\ mol^{-1}$)	298.15	-4.9366	3.1035	-3.0771	0.3992	-1.8656	0.003
	308.15	-5.1489	3.0541	-3.6956	1.9386	-2.5648	0.002
u^D ($m\ s^{-1}$)	288.15	14.8717	-6.5434	0.2462	11.8534	10.4176	0.16
	298.15	16.7384	-7.2707	1.0619	12.4873	-0.9097	0.12
	308.15	14.5276	-1.9831	11.5632	6.2180	-22.1372	0.08
$\Delta\kappa_s$	288.15	-54.7594	16.1563	-10.7959	-16.8102	-13.0989	0.19
($T\ Pa^{-1}$)	298.15	-63.6176	17.1316	-9.8987	-13.6488	-16.1419	0.15
	308.15	-66.5804	13.1839	-29.7142	-3.5839	7.9812	0.17
			$C_3H_7[O(CH_2)_3]OH$ (1) + $(C_4H_9)_3N$ (2)				
$V_m^E \times 10^6$	288.15	0.1493	--0.0372	-0.3073	0.0460	0.2434	0.001
($m^3\ mol^{-1}$)	298.15	0.6776	-0.1853	0.1729	0.1210	-0.6330	0.001
	308.15	1.2516	-30.3800	0.0654	0.1125	-0.1638	0.001
u^D ($m\ s^{-1}$)	288.15	-31.0718	5.0723	3.2774	4.2502	-10.3381	0.11
	298.15	-36.3050	7.5671	4.5064	6.2082	-15.7446	0.19
	308.15	-41.0764	9.8789	2.9318	5.1607	-14.4734	0.16
$\Delta\kappa_s$	288.15	23.8413	6.3150	2.6213	-6.0414		0.12
($T\ Pa^{-1}$)	298.15	36.6474	7.6815	-4.8178	-10.4136	14.7748	0.12
	308.15	51.0651	8.7178	6.3736	-7.4732	20.1194	0.13

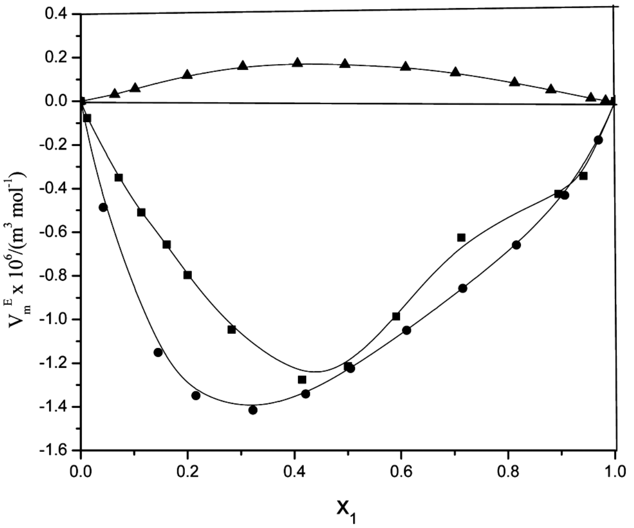

Fig. 1 — Excess molar volumes ($V_m{}^E$) for $x_1C_3H_7[O(CH_2)_3]OH + x_2C_4H_9NH_2$, (■); + x_2 $(C_4H_9)_2NH$, (●); + x_2 $(C_4H_9)_3N$, (▲) at 298.15 K. The solid curves have been drawn from Eq.(8).

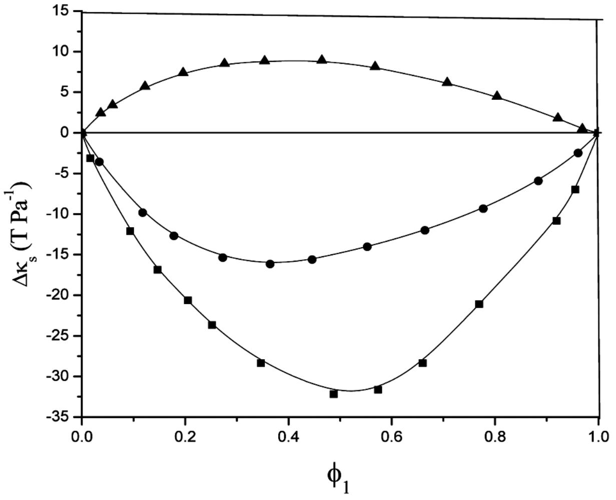

Fig. 2 — Composition dependence of values of deviation in isentropic compressibilities ($\Delta\kappa_{s,}$) for $\phi_1C_3H_7[O(CH_2)_3]OH + \phi_2C_4H_9NH_2$, (■); + ϕ_2 $(C_4H_9)_2NH$, (●); + ϕ_2 $(C_4H_9)_3N$, (▲) at 298.15 K. The solid curves have been drawn from Eq.(8).

for our systems by adding the contributions of the expansivities of each component in the mixtures:

$$\alpha = - 1/\rho[\ \delta\rho/\delta T] \qquad ...(9)$$

In Fig. 4, *α* plots are shown for different mixtures at 298.15 K. We note that a sharp decrease in *α* is shown for the PGMPE+BA or DBA systems as the concentration of ether increases.

From Fig. 1 and Table 2, it can be seen that the $V_m{}^E$ values are negative over the entire mole fraction range at all temperatures investigated for each binary system under study, except for PGMPE+TBA, which exhibits positive $V_m{}^E$ values for PGMPE overall concentrations in the ether-rich region.

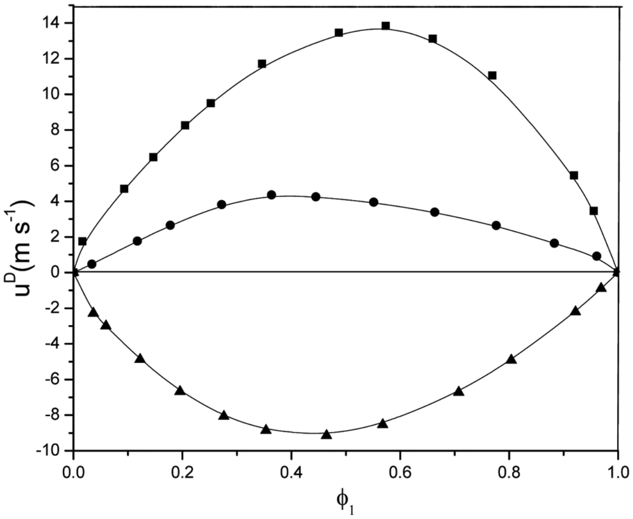

Fig. 3 — Composition dependence of values of deviation in speeds of sound (u^D) for $\phi_1C_3H_7[O(CH_2)_3]OH + \phi_2C_4H_9NH_2$, (■); + ϕ_2 $(C_4H_9)_2NH$, (●); + ϕ_2 $(C_4H_9)_3N$, (▲) at 298.15 K. The solid curves have been drawn from Eq.(8).

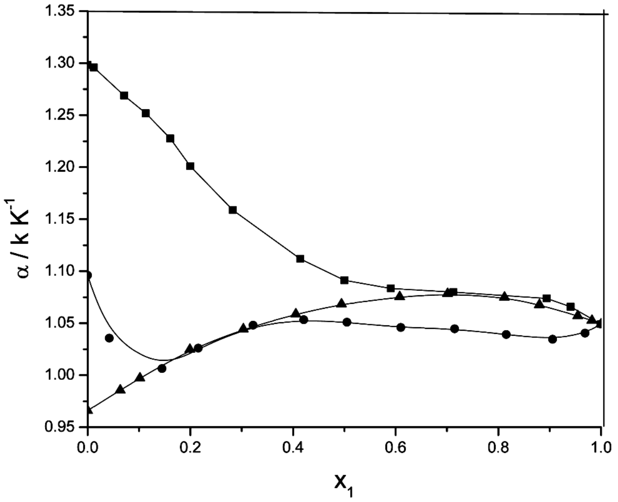

Fig. 4 — Thermal expansion coefficient, α for $x_1C_3H_7[O(CH_2)_3]OH + x_2C_4H_9NH_2$, (■); + x_2 $(C_4H_9)_2NH$,(●); + x_2 $(C_4H_9)_3N$,(▲) at 298.15 K.

The measured speeds of sound u were fitted to a polynomial of type:

$$Y(x) = \sum_{i=0}^{k} a_i x_1{}^i \qquad ...(10)$$

by the method of least – squares with each point weighted equally. The values of coefficients a_i and standard deviations σ are summarized in Table 4. For each mixture, experimental results for u, together with smoothed curves of them are shown in Fig. 5.

Table 4 — Coefficients a_i of Eq. (10) and standard deviations σ of binary mixtures at different temperatures.

	T/K	a_0	a_1	a_2	a_3	a_4	σ
				$C_3H_7[O(CH_2)_3]OH$ (1) + $C_4H_9NH_2$ (2)			
u (m s^{-1})	288.15	1294.3910	36.6899	-57.4663	10.3707		0.12
	298.15	1248.8310	62.2848	-103.4946	66.2621	-27.8677	0.18
	308.15	1203.6070	53.6907	-8.8204	-63.5217	23.5594	0.16
				$C_3H_7[O(CH_2)_3]OH$ (1) + $(C_4H_9)_2NH$ (2)			
u (m s^{-1})	288.15	1290.4720	11.3954	-24.2499	5.9032		0.10
	298.15	1250.1560	11.7117	-3.6716	-27.8531	15.9171	0.14
	308.15	1209.9420	17.0312	-28.1703	24.2705	-14.5092	0.19
				$C_3H_7[O(CH_2)_3]OH$ (1) + $(C_4H_9)_3N$ (2)			
u (m s^{-1})	288.15	1283.0010	-15.1011	-11.6855	26.2652		0.11
	298.15	1244.5660	-18.0063	-9.2915	28.1995		0.05
	308.15	1207.2030	-22.8402	-4.7265	28.9914		0.08

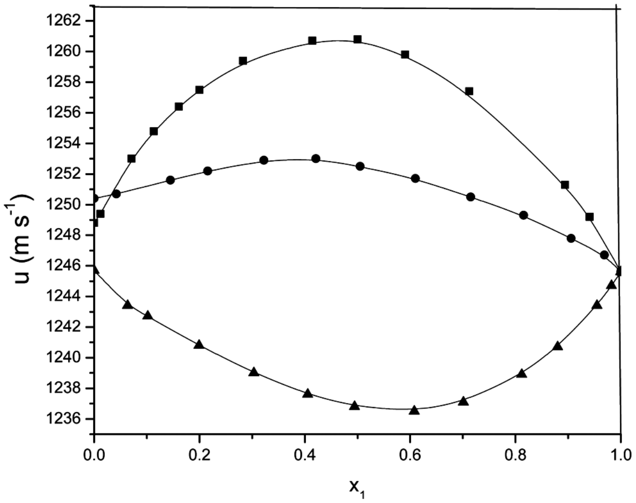

Fig. 5 — Composition dependence of experimental values of speeds of sound (u) for $x_1C_3H_7[O(CH_2)_3]OH$ + $x_2C_4H_9NH_2$, (■); + x_2 $(C_4H_9)_2NH$, (●); + x_2 $(C_4H_9)_3N$, (▲) at 298.15 K. The solid curves have been drawn from Eq.(10).

Excess molar volume

From Fig. 1, it can be seen that V_m^E is negative over the entire range of x_1 for mixtures containing butylamine and dibutylamine and is positive with the tributylamine. In fact, we observe similar characterization for V_m^E as in mixtures of dipropylene glycol monomethyl ether and dipropylene glycol monobutyl ether with alkylamines[6,7], but with a marked decrease in the algebraic value of V_m^E for both butylamine and dibutylamine with each addition of the *n*-alkyl chain length in the dipropylene glycol monomethyl ether to dipropylene glycol monobutyl ether. However,the V_m^E here is less positive for mixtures with tributylamine. The behavior of these mixtures is very complex and overall values of V_m^E are attributable to the results of several contraction and expansion processes which proceed simultaneously when amine – ether molecules are formed. The following effect can be considered: (1) disruption of liquid order on mixing, and unfavorable interactions between unlike molecules producing a positive contribution to V_m^E, (ii) contraction due to molecular volume and free volume[26] difference of unlike molecules, and (iii) contraction due to possible association through intermolecular hydrogen bond formation N---H-O and N-H---O between amine and ether producing a negative contribution to V_m^E.

The V_m^E values were found to decrease in the sequence from temperature 288.15 K to 308.15 K : tributylamine > dibutylamine > butylamine. This behavior may be compared with the negative H^E results for (a primary or a secondary amine + an alkanol)[36-38], which are due to strong intermolecular interaction between the NH group of the amine molecule and the OH group of the alkanol molecule. The presence of etheric oxygen (-O-) enhances the ability of the -OH group of the alkoxypropanol to form hydrogen bonds with the nitrogen atom in butylamine or dibutylamine molecules, leading to more negative V_m^E values for propylene glycol monopropyl ether – butylamine or dibutylamine mixtures. Again, due to electron donating inductive effect of the alkyl group, the strength of bonding with butylamine or dibutylamine increases as the aliphatic chain length of alkoxypropanol[6,7] increases, resulting in lower V_m^E values for the molecules with higher alkyl chain length. It is suggested[29] that unshared electron pair on oxygen atom in ether is weaker than the unshared pair of electrons on the nitrogen atom in amine molecule. Thus, the observed very large negative values of V_m^E can be accounted only by considering predominance of an energetically favored[33,39] cross bonding N---H-O compared to N-H---O over the rupture of the hydrogen bonds present in pure alkoxypropanol and amine. A similar effect on

H^E for (butylamine or dibutylamine + straight chain ether)[39,40]: with secondary amine H_m^E much more positive indicating less association than between the secondary butylamine and the ether.

Speed of sound and compressibility

From Fig. 2 and Table 2, it is seen that $\Delta\kappa_s$, is negative for butylamine and dibutylamine, and positive for tributylamine over the whole mole fraction range at different temperatures. Also, the behavior of excess molar volume seems to be consistent with a minimum value of $\Delta\kappa_s$, and a maximum value for u^D with propylene glycol monopropyl ether with butylamine. This is normal because u is generally higher when the structure has high rigidity. For the same value of x_1, V_m^E increases towards the positive direction for each amine, as the alkyl chain length of alkoxypropanol decreases. Although $\Delta\kappa_s$ is negative, that is, the mixture is less compressible than the corresponding ideal mixture, suggesting that there may be strong intermolecular hydrogen bonding with butylamine and dibutylamine. As the ether is added to amines, thereby causing a breakdown of self - associated ether, or both contribute to a denser packing of all the molecules through hydrogen bonding, the speed of sound increases and $\Delta\kappa_s$ decreases. However, both V_m^E and $\Delta\kappa_s$, are positive for tributylamine and u^D is likewise positive to negative from butylamine to tributylamine, indicating when the mixtures are created 'excess free volume' increase and is higher in mixtures containing propylene glycol monopropyl ether with tributylamine. This shows that interstitial accommodation plays an important role by influencing the $\Delta\kappa_s$ and u^D of liquid mixtures containing alkylamines. So, the molecular size and shape of the components are equally important factor here. We have suggested earlier[7] that the volume behavior of dipropylene glycol monomethyl ether or dipropylene glycol monobutyl ether + *n*-alkylamine is the result of several opposing effects; the present results for $\Delta\ \kappa_s$, and u^D supports this suggestion.

Further, from IR measurements of earlier paper[5,7] we have confirmed that there is existence of strong interaction due to the cross bonding of N---H-O between unlike molecules. The cross bonding decreases in the order butylamine > dibutylamine > tributylamine same as found both with dipropylene glycol monomethyl ether or dipropylene glycol monobutyl ether and alkylamines[5]. This supports with trends of the behavior of the V_m^E values of present studies.

Apparent molar volume

The apparent molar volume, $V_{\phi.1}$, and apparent molar compressibility, $K_{\phi.1}$, properties of a solute component ether (1) in *n*-alkylamine (2) defined in term of mole fraction concentration units, are calculated from the following relations[35,36]:

$$V_{\varphi.1} = V_1^{\ *} + \frac{V_m^E}{X_1} \qquad \text{...(11)}$$

$$K_{\varphi.1} = K_{\varphi.1}^{\ *} + \frac{\Delta K_{s,m}}{x_1} \qquad \text{...(12)}$$

where $V_1^{\ *}$ and $K_{\phi.1}^{\ *}$ are the molar volume and molar isentropic compressibility ($K^*_{S,m,1}$) respectively. Simple graphical extrapolation of $V_{\varphi.1}$ and $K_{\varphi.1}$ to $x_1 = 0$ ($x_2 = 1$) and of $V_{\phi.2}$ and $K_{\phi.2}$ to $x_2 = 0$ ($x_1 = 1$) gives values of $V_{\phi,1}^0 \, or \, V_{\phi,2}^0$ and $K_{\phi,1}^0 \, or \, K_{\phi,2}^0$ at infinite dilution, represented by $\overline{V}_{\phi,1}^{O}$ or $\overline{V}_{\phi,2}^{O}$ and $\overline{K}_{\phi,1}^{O}$ or $\overline{K}_{\phi,2}^{O}$

Partial molar volumes and partial molar isentropic compressibilities at infinite dilution and at different temperatures are listed in Table 5. Inspection of Table 5 shows that as in case of butylamine and dibutylamine , the $\overline{V}_{\phi,1}^{O}$ values are somewhat smaller than the corresponding $V_1^{\ *}$ values, which shows that molar volumes of the components in the mixture are somewhat less than in pure state indicating contraction in volume upon mixing. In addition, the difference in values (= $\overline{V}_{\phi,1}^{O}$ - $V_1^{\ *}$) tends to become less as temperature increases. The differences in values (= $\overline{V}_{\phi,1}^{O}$ - $V_1^{\ *}$) are also found to be negative for butylamine and dibutylamine and positive for tributylamine indicating towards the contraction to expansion in volume on mixing than in pure state. Further, Table 5 shows that the differences in $\overline{K}_{\phi,1}^{O}$ and $K_{\varphi.1}^{\ *}$ are largely negative for PGMPE + BA or DBA as compared to PGMPE + TBA at each temperature. It indicates that the strength of interactions in these mixtures follows the order TBA < DBA< BA. Again , the difference between $\overline{K}_{\phi,2}^{O}$ and $K_{\varphi.2}^{\ *}$ in Table 6 are also found to be negative, demonstrating lower compressibilities and a denser packing of molecules in the mixtures PGMPE + BA or DBA at all temperatures.

Table 5 — Values of V_1^*, $\overline{V_{\phi,1}}^0$ and $\overline{K_{\phi,1}}^0$ for (PGMPE + *n*-alkylamine) systems at different temperatures.

PGMPE(1) + Butylamine (2)	*288.15 K*	*298.15 K*	*308.15 K*
$V_1^* \times 10^6$ (m^3 mol^{-1})	132.724	134.116	135.549
$K^*_{S,m,1}$ (mm^3 mol^{-1} MPa^{-1})	88.995	97.599	107.236
$\bar{K}^0_{\phi,1}$ (mm^3 mol^{-1} MPa^{-1})	88.940	97.604	107.264
$\overline{V}^0_{\phi 1} \times 10^6$ (m^3 mol^{-1})	126.172	127.304	128.725
PGMPE(1) + Dibutylamine (2)			
$V_1^* \times 10^6$ (m^3 mol^{-1})	132.734	134.116	135.549
$K^*_{S,m,1}$ (mm^3 mol^{-1} MPa^{-1})	88.995	97.599	107.236
$\bar{K}^0_{\phi,1}$ (mm^3 mol^{-1} MPa^{-1})	89.502	97.306	106.080
$\overline{V}^0_{\phi 1} \times 10^6$ (m^3 mol^{-1})	122.464	121.062	119.902
PGMPE(1) + Tributylamine (2)			
$V_1^* \times 10^6$ (m^3 mol^{-1})	132.734	134.116	135.549
$K^*_{S,m,1}$ (mm^3 mol^{-1} MPa^{-1})	88.995	97.599	107.236
$\bar{K}^0_{\phi,1}$ (mm^3 mol^{-1} MPa^{-1})	90.382	98.205	106.654
$\overline{V}^0_{\phi 1} \times 10^6$ (m^3 mol^{-1})	132.816	134.600	136.962

Table 6 — Values of V_2^*, $\overline{V_{\phi,2}}^0$ and $\overline{K_{\phi,2}}^0$ for (PGMPE + *n*-alkylamine) systems at different temperatures.

PGMPE(1) + Butylamine (2)	*288.15 K*	*298.15 K*	*308.15 K*
$V_2^* \times 10^6$ (m^3 mol^{-1})	98.358	99.640	100.946
$K^*_{S,m,2}$ (mm^3 mol^{-1} MPa^{-1})	76.960	87.045	96.096
$\bar{K}^0_{\phi,2}$ (mm^3 mol^{-1} MPa^{-1})	79.945	87.040	94.946
$\bar{V}^0_{\phi,2} \times 10^6$ (m^3 mol^{-1})	90.902	92.385	93.126
PGMPE(1) + Dibutylamine (2)			
$V_2^* \times 10^6$ (m^3 mol^{-1})	168.011	169.848	171.734
$K^*_{S,m,2}$ (mm^3 mol^{-1} MPa^{-1})	131.122	142.760	155.703
$\bar{K}^0_{\phi,2}$ (mm^3 mol^{-1} MPa^{-1})	134.006	143.662	156.180
$\bar{V}^0_{\phi,2} \times 10^6$ (m^3 mol^{-1})	162.965	163.990	165.404
PGMPE(1) + Tributylamine (2)			
$V_2^* \times 10^6$ (m^3 mol^{-1})	237.206	239.493	241.833
$K^*_{S,m,2}$ (mm^3 mol^{-1} MPa^{-1})	184.187	199.415	216.150
$\bar{K}^0_{\phi,2}$ (mm^3 mol^{-1} MPa^{-1})	184.384	199.304	215.880
$\bar{V}^0_{\phi,2} \times 10^6$ (m^3 mol^{-1})	237.260	239.503	242.924

Conclusions

In this work density and speed of sound for the binary mixtures of PGMPE with *n*-alkylamines at different temperatures have been measured and results have been interpreted in terms of excess molar volume and deviations in isentropic compressibilities. The excess molar volume has been found to be negative for butyl amine and dibutylamine and is positive for tributylamine with PGMPE, which indicates that the mixtures have been found to have greater contraction than the pure components. Molecules of pure components are strongly interacting forming intermolecular hydrogen bond as in case of butylamine and dibutylamine as compared to TBA. This is also supported by the compressibility results. As the temperature is lowered ,the intermolecular interaction in PGMPE + alkylamines also decreases, hence resulting in an increase in $\Delta\kappa_{s,}$ and V_m^E values. The trends of isentropic compressibility with composition for PGMPE with alkylamines shifts from negative to positive values indicating that interactions are becoming weaker between PGMPE and tributylamine.

Acknowledgement

One of the authors (AK) is thankful to UGC, New Delhi for providing Minor Research Project.

References

1 Mchaweh A, Alsaygh A, Nasrifar K & Moshfeghian M, *Fluid Phase Equilib*, 224 (2004) 157.
2 Pal A & Bhardwaj R K, *J Chem Eng Data*, 46 (2001) 933.
3 Pal A & Bhardwaj R K, *J Indian Chem Soc*, 78 (2001) 18.
4 Pal A & Dass G, *J Chem Eng Data*, 45 (2000) 693.
5 Pal A, Kumar A & Kumar H, *J Chem Thermodyn*, 38 (2006) 1227.
6 (a) Pal A & Bhardwaj R K, *Z Phys Chem*, 216 (2002) 1033; (b) Pal A & Bhardwaj R K, *Indian J Chem*, 41A (2002) 706.
7 (a) Pal A & Gaba R, *J Indian Chem Soc*, 84 (2007) 661; (b) Pal A & Gaba R, *J Mol Liq*, 144 (2009) 50; (c) Pal A & Gaba R, *Fluid Phase Equilib*, 267 (2008) 99.
8 Pal A & Kumar H, *J Chem Thermodyn*, 36 (2004) 173.
9 Pal A & Kumar H, *J Indian Chem Soc*, 80 (2003) 824.
10 Pal A & Kumar H, *Indian J Phys*, 78 B (2004) 1319.
11 Pal A & Kumar A, *J Mol Liq*, 123 (2006) 146.
12 Pal A & Kumar A, *J Chem Eng Data,* 50 (2005) 856.
13 Pal A, Kumar H, Maan R & Sharma H K, *Indian J Chem,* 52A (2013) 1391.
14 (a) Pal A, Kumar H, Maan R & Sharma H K, *J Chem Eng Data*, 58 (2013) 225; (b) Pal A, Kumar H, Maan R & Sharma H K, *J Mol Liq*, 188 (2013) 96.
15 Letcher T M & Bayles J W, *J Chem Eng Data*, 16 (1971) 266.
16 Letcher T M, *J Chem Thermodyn*, 4 (1972) 159.
17 Su-Chen K, I-Hung P & Chen-Hsiun T, *J Chem Eng Data*, 46 (2001) 1392.
18 Oswal S L, Oswal P, Gardas R L, Patel S G & Shinde R G, *Fluid Phase Eqilib*, 216 (2004) 33.
19 Dominguez M, Rodriguez S, Lopez M C, Royo F M & Urieta J S, *J. Chem. Eng. Data*, 41 (1995) 37.
20 Kinnart C M, Kinnart W J, Checinska – Majak D & Cwiklinska A, *J Mol Liq*, 10 (2004) 19.
21 Oswal S L & Patel S G, *J Chem Soc Faraday Trans*, 90 (1994) 1083.
22 Goralaski P, Wasiak M & Bald A, *J Chem Eng Data*, 47 (2002) 83.
23 Mohren S, Heintz A, *Fluid Phase Equilib*, 133 (1997) 247.
24 Riddick J A, Bunger W B & Sakano T K, *Organic Solvents, Physical Properties and Methods of Purification*, 4th Edn, (Wiley Interscience, New York), 1986.
25 Reimann R & Heintz A, *J Sol Chem*, 20 (1991) 29.
26 (a) Letcher T M & Domanska U, *J Chem Thermodyn*, 26 (1994) 553; (b) Letcher T M & Domanska U, *J Chem Thermodyn*, 26 (1994) 1241.
27 Pitzer K S, Peiper J C & Busey R H, *J Phys Chem*, 13 (1984) 1.
28 IUPAC, *Commission on atomic weights and isotopic abundances 1985*, *Pure Appl Chem*, 58 (1986) 1677.
29 Benson G C & Kiyohara O, *J Chem Thermodyn*, 11 (1979) 1061.
30 Douheret G, Lajoi P, Davis M I, Ratliff J L, Ulloa J & Hoiland H, *J Chem Soc, Faraday Trans 1*, 91 (1995) 2291.
31 Douheret G & Viallard A, *J Chim Phys,* 80 (1983) 809.
32 Nath J, *J Chem Thermodyn,* 30 (1998) 885.
33 Papaioannou D & Panayiotou C G, *J Chem Eng Data*, 39 (1994) 457.
34 Douheret G, Pal A & Davis M I, *J Chem Thermodyn*, 22 (1990) 99.
35 Mehta S K & Chauhan R K, *J Solution Chem,* 26 (1997) 295.
36 Hawrylak B, Gracie K & Palepu R, *J Sol Chem,* 27 (1998) 17.
37 Tussel-langer E, Garcia Alonso J M, Villamanan Olfos M A & Lichtenthaler R N, *J Sol Chem,* 40 (1991) 153.
38 Pradhan S D, *Proc Indian Acad Sci - Chem Sci,* 90 (1981) 261.
39 Funke H, Wetzel M & Heintz A, *Pure Appl Chem,* 61 (1989) 1429.