Indian Journal of Pure & Applied Physics
Vol. 52, January 2014, pp. 24-29

Viscometric, volumetric and acoustic properties of binary mixtures of a nuclear extractant with monocarboxylic acids (C_1-C_3) at 303.15 K

B Dalai[a], S K Dash[b]* & S K Singh[c]

[a]Department of Physics, Eastern Academy of Science and Technology, Bhubaneswar, Odisha 754 001, India

[b]DESM, Regional Institute of Education (NCERT), Bhubaneswar, Odisha 751 022, India

[c]Institute of Minerals and Materials Technology (CSIR), Bhubaneswar, Odisha 751 013, India

E-mail: *skdash59@yahoo.com*

Received 25 April 2013; revised 9 September 2013; accepted 25 October 2013

Experimental values of density (ρ), viscosity (η) and ultrasonic velocity (u) of the binary liquid mixtures of a nuclear extractant-di (2-ethyl hexyl) phosphoric acid (D2EHPA) and monocarboxylic acids *viz.* acetic acid, propionic acid and n-butyric acid over entire composition range of D2EHPA at 303.15 K are reported. Experimental data are used to assess the excess molar volume and deviation in isentropic compressibility, ultrasonic velocity and viscosity. These properties are used to interpret molecular interactions among component liquids. The values of excess/deviation functions have been fitted to a Redlich-Kister type polynomial equation to derive binary coefficients and estimate standard error. Furthermore, mixture viscosities are correlated with some single parameter viscosity models and relative merits of these models are discussed.

Keywords: Viscosity, Density, Ultrasonic velocity, Binary mixtures, Dipole-dipole interaction

1 Introduction

Ultrasonic[1,2], volumetric[3] and viscometric[4,5] properties of binary liquid mixtures have been investigated by a number of researchers over the past several years. Nuclear energy industry demands data on physical and chemical properties of a wide variety of liquid mixtures (i.e. polar-polar or polar-apolar) using extractants[6], *viz.* methyl isobutyl ketone (MIBK); tri-n-butyl phosphate (TBP), acetyl acetone (HAA), tri-n-octylphosphine oxide (TOPO), di(2-ethyl hexyl) phosphoric acid (D2EHPA) etc as one of the component of the mixture. D2EHPA is employed in combination with various polar or apolar synergistic reagents for extraction of uranium from its ore using Dapex procedure[7]. It has been used for recovery of chromium (III) ions by solvent extraction and separation of indium and gallium from sulphate solution[8]. Extraction efficacy is found to depend not only on the extractant but also on the nature of the stripping reagent and their physico-chemical behaviour with respect to their relative concentration. Again, addition of modifier with extractant facilitates extraction rate for greater dispersal and more rapid phase disengagement[9]. The present study of D2EHPA with monocarboxylic acids (C_1-C_3) is aimed at evaluation of excess molar volume (V^E) and deviations in ultrasonic velocity (Δu), viscosity ($\Delta\eta$) and isentropic compressibility ($\Delta\beta_s$) in order to study the molecular interaction in the mixture and identify a suitable modifier. Excess/deviation properties are graphically plotted with molefraction (X_2) of D2EHPA and found to be negative or positive depending on the nature of system and molecular interactions between the components of the liquid mixture. Furthermore, the suitability of some theoretical models, viz. Grunberg-Nissan[10], Katti-Chaudhri[11], Hind *et al*[12]. and Tamura-Kurata[13] using our experimental data has also been assessed.

2 Experimental Details

Di (2-ethyl hexyl) phosphoric acid (D2EHPA) and monocarboxylic acids viz. acetic acid, propionic acid and n-butyric acid used in this investigation were of AR grade and procured from E. Merck Chemicals Ltd, India. These chemicals were further purified and redistilled (purity ≥99%) before use, employing standard techniques[14,15]. Purity of these chemicals has been verified by comparing measured values of densities and viscosities with literature values[16,17].

All chemicals were kept in airtight bottles and adequate precautions were taken to avoid contamination and evaporation during mixing. The required properties of the mixture were measured on the same day of sample preparation. All mixtures were prepared by mass measurement using a digital balance (Shimadzu corporation, Kyoto, Japan, Model: BL 220H) with an uncertainty of $\pm 10^{-6}$ kg. Possible error in the molefraction was estimated to be around $\pm 10^{-4}$. All measurements for each sample were made thrice at temperature 303.15 K and average values were reported. Densities of pure liquids and their mixtures were determined with a pycnometer of 25 ml capacity, calibrated with doubly distilled water and benzene with an uncertainty of ± 0.02 kg m^{-3}. Ostwald viscometer having a bulb capacity 25 ml was employed and the same amount of liquid (25 ml) was taken for all viscosity measurements with an uncertainty of ± 0.003 mPa s. Viscometer with the sample was allowed to stand for 20 min in a glass walled water bath to obtain thermal equilibrium at the experimental temperature. During measurements of flow time, the caps of the limbs were removed. Flow time measurements were done with the help of a pre-calibrated RACER stopwatch of least count 0.01 s. Ultrasonic velocity of sample was measured by using a single-crystal variable path ultrasonic interferometer (Mittal Enterprises, India, model: F-81) operating at 2 MHz with an uncertainty of ± 0.5 ms^{-1}. It had been calibrated with water and benzene before measurement of sample under study. The working principle used in the measurement of ultrasonic velocity through a medium is based on accurate determination of wavelength of ultrasonic waves of known frequency produced by a quartz crystal in the measuring cell. Temperature of the sample was controlled thermally by circulating water through the jacket of the double-walled cell. In all measurements, temperature was maintained within ±0.1 K by an electronically controlled thermostatic water bath.

3 Results and Discussion

The density (ρ) and viscosity (η) values of pure liquids are reported in Table 1. Experimental values of ultrasonic velocity (u), density (ρ), viscosity (η) and calculated values of isentropic compressibility (β_s) over entire molefraction range of D2EHPA have been reported in Table 2. The values of excess molar volume (V^E), deviation in viscosity ($\Delta\eta$), ultrasonic velocity (Δu) and isentropic compressibility ($\Delta\beta_s$) have been calculated using following relations[18-21] and are shown in Figs 1-4.

Table 1 — Experimental density (ρ) and viscosity (η) values for pure liquids with literature values

Components	ρ (kg m^{-3})		η (mPa s)	
	Expt.	Lit.[a]	Expt.	Lit.[a]
acetic acid	1034.0	1044.6	0.884	1.056
propionic acid	981.8	988.2	0.868	1.030
n-butyric acid	950.1	952.8	1.296	1.426
D2EHPA	961.3	975.0	19.288	40.000[b]

[a] Ref. [16] at 298 K

[b] Ref. [17] at 293 K

Table 2 — Experimental values of ultrasonic velocity (u), density (ρ), viscosity (η) and calculated values of isentropic compressibility (β_s) of monocarboxylic acids + D2EHPA at 303.15 K

Molefraction X_2	U m s^{-1}	ρ kg m^{-3}	η mPa s	$\beta_s \times 10^{10}$ m^{2}N^{-1}
acetic acid (1) + D2EHPA (2)				
0.0000	1095	1034.0	0.884	8.066
0.0796	1129	1008.6	1.574	7.778
0.1382	1150	998.8	2.292	7.571
0.2186	1174	990.7	3.386	7.324
0.3103	1196	984.2	4.872	7.103
0.3968	1214	979.3	6.604	6.929
0.4788	1228	975.5	8.198	6.798
0.5297	1236	973.6	9.118	6.723
0.6234	1249	970.5	11.092	6.605
0.6891	1258	968.5	12.578	6.524
0.7384	1264	967.5	13.668	6.469
0.8068	1272	965.7	15.202	6.400
0.8905	1281	964.1	16.884	6.321
0.9592	1288	962.5	18.494	6.263
1.0000	1293	961.3	19.288	6.222
propionic acid (1) + D2EHPA (2)				
0.0000	1121	981.8	0.868	8.105
0.0668	1150	978.9	1.394	7.724
0.1278	1171	976.6	1.986	7.467
0.2286	1200	973.8	3.022	7.131
0.3182	1220	971.9	4.286	6.913
0.4677	1245	968.9	6.968	6.659
0.5096	1251	968.2	7.792	6.600
0.5879	1261	966.8	9.486	6.505
0.6584	1268	965.7	11.008	6.440
0.7068	1272	964.9	12.082	6.405
0.7594	1276	964.1	13.304	6.371
0.8140	1280	963.4	14.496	6.335
0.8783	1285	962.5	16.078	6.292
0.9378	1289	961.9	17.588	6.257
1.0000	1293	961.3	19.288	6.222
n-butyric acid (1) + D2EHPA (2)				
0.0000	1174	950.1	1.296	7.637
0.0532	1185	952.6	1.784	7.476
0.1098	1198	954.3	2.592	7.301
0.1892	1215	956.1	3.578	7.085
0.2612	1227	956.8	4.602	6.942
0.3278	1238	957.5	5.698	6.814
0.4066	1248	958.2	7.172	6.701
0.5002	1257	958.8	8.886	6.601
0.6095	1266	959.5	11.212	6.503
0.6884	1272	959.9	12.896	6.439
0.7405	1276	960.2	14.014	6.396
0.8096	1281	960.5	15.378	6.345
0.8811	1283	960.8	16.806	6.323
0.9342	1289	961.0	17.792	6.263
1.0000	1293	961.3	19.288	6.222

$$V^E = \sum_{i=1}^{2} X_i M_i \left(\rho^{-1} - \rho_i^{-1}\right) \qquad \dots (1)$$

$$\Delta\eta = \eta - \sum_{i=1}^{2} X_i \eta_i \qquad \dots (2)$$

$$\Delta u = u - \sum_{i=1}^{2} X_i u_i \qquad \dots (3)$$

$$\Delta\beta_s = \beta_s - \sum_{i=1}^{2} X_i \beta_{si} \qquad \dots (4)$$

where ρ_l, M_i, X_i, η_l, u_i and β_{si} are the density, molecular weight, molefraction, viscosity, ultrasonic velocity and isentropic compressibility of i^{th} component in the mixture, respectively.

From Table 2, it is observed that the values of ultrasonic velocity (u) and viscosity (η) increase nonlinearly in all mixtures with increase in D2EHPA molefraction while density (ρ) decreases nonlinearly in all mixtures under study except n-butyric acid mixture. Values of β_s show a nonlinear decreasing trend with increasing molefraction of D2EHPA in all the three mixtures.

According to the model proposed by Eyring and Kincaid[21] and findings of Rathnam *et al*[3]., the trend of variation of ultrasonic velocity and isentropic compressibility is opposite, which corroborates our findings. D2EHPA molecules are bigger in size as compared to the acid molecules used in this study. As such intramolecular voids in D2EHPA molecules can accommodate acid molecules due to large difference in their molar volumes ($V_{\text{D2EHPA}} = 3.3354\times10^{-4}$ m^3 mol^{-1}, $V_{\text{acetic acid}} = 5.8027\times10^{-5}$ m^3 mol^{-1}, $V_{\text{propionic acid}} = 7.5372\times10^{-5}$ m^3 mol^{-1} and $V_{\text{n-butyric acid}} = 9.2622\times10^{-5}$ m^3 mol^{-1}).

The deviation in the physical property from its ideal behaviour is a measure of the degree of interaction[19] between component molecules of the binary liquid mixture. In the present study, deviation of Δu is positive (Fig. 1) with a maximum at nearly equimolar concentration range. This indicates increasing strength of interaction[3,22] between component molecules of binary mixtures resulting in formation of molecular aggregates and more compact structures. In our study, the increasing trend of Δu (max.) with D2EHPA as common component has been obtained in the order:

propionic acid > acetic acid > n-butyric acid.

A correlation between the sign of $\Delta\eta$ and V^E has been observed by Fort *et al*[24]. for the binary system which reveals that $\Delta\eta$ is positive when V^E is negative and vice versa. However, in our study the trend of variation of $\Delta\eta$ (Fig. 2) and V^E (Fig. 3) does not follow the above general principle in all mixtures. Therefore, apart from the strength of specific or dispersion forces, the molecular size and shape of the components probably play a significant role.

According to Rastogi *et al*[2]., the observed excess property is a combination of interactive and a non-interactive part. Non-interactive part in the form of size effect can be comparable to the interactive part and may be sufficient to reverse the trend set by the latter. Based on this theory, the observed negative values of $\Delta\eta$ may be due to smaller size of monocarboxylic acid molecules as compared to that

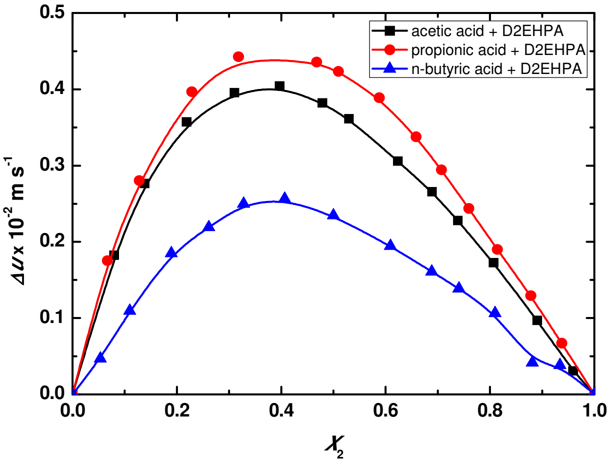

Fig. 1 — Deviation in ultrasonic velocity (Δu) versus molefraction (X_2) of D2EHPA

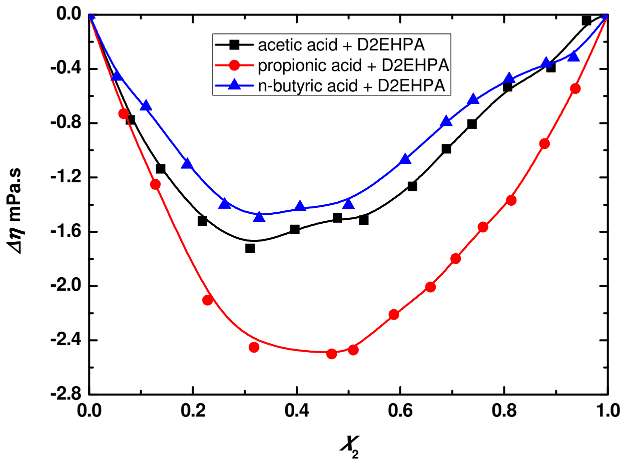

Fig. 2 — Deviation in velocity ($\Delta\eta$) versus molefraction (X_2) of D2EHPA

of D2EHPA. However, from Fig. 3, it is observed that V^E is negative for acetic and propionic acid over entire molefraction range of D2EHPA while it is positive for n-butyric acid. The observed trend of variation of excess molar volume[3,19] may be explained in terms of two opposing effects, (i) breaking of molecular order on mixing and the difference in molecular size between components of liquid mixture, and (ii) packing of larger sized molecules leading to interstitial voids that may be filled by smaller molecules and dipolar interaction as well as H-bonds between unlike molecules. However, the actual volume change depends upon the relative strength of these two effects. Mixing of D2EHPA with monocarboxylic acids may induce mutual dissociation of the H-bonded structures present in monocarboxylic acids with subsequent formation of new H-bonds (P = O---H – O) between phosphoryl group of D2EHPA and hydroxyl group of acids resulting in negative values of V^E in acetic acid (1) and propionic acid (1) with D2EHPA (2) mixtures. The large negative value of V^E for propionic acid with D2EHPA is probably due to more positive inductive effect on propionic acid, which increases electron density on the oxygen atom, resulting in an energetically favoured cross bonding[23], giving rise to a diol.

The positive values of V^E (Fig. 3) in n-butyric acid + D2EHPA mixtures indicates weak interaction[3] between components of the mixture, may be due to increase in size of the alkyl group in n-butyric acid as affected by the steric factor. Increase in number of methyl group in butyric acid restricts closer approach of D2EHPA and therefore, butyric acid molecules are increasingly hindered due to switching mechanism[25], resulting in positive value of V^E. The magnitude of relatively stronger interaction in response to the variation of V^E with D2EHPA as common component increases in the order: propionic acid > acetic acid > n-butyric acid.

In our study, $\Delta\beta_s$ (Fig. 4) is negative for entire range of composition in all binary mixtures, reaching minimum at about 0.4 molefraction of D2EHPA with maximum deviation in propionic acid mixture. Magnitude of $\Delta\beta_s$ (max.) increases in the order identical to Δu (max.) and V^E (max.).

The negative values of $\Delta\beta_s$ indicate that the liquid mixture is less compressible than the pure liquids forming the complex and molecules in the mixture are more tightly bound than in pure liquids. This corroborates the presence of relatively stronger molecular interaction, possibly through hydrogen bonding[1,4] between unlike molecules.

The excess/deviation functions have been fitted to a Redlich-Kister type polynomial equation[26] as given by:

$$\Delta Y = (1 - X_2) X_2 \sum_{j=0}^{4} a_j (1 - 2X_2)^j \qquad \ldots (5)$$

where a_j and j are the equation coefficients and the degree of polynomial expansion, respectively.

In each case, optimum numbers of coefficients a_j were determined from an examination of the variation of standard deviation (σ) as given by:

$$\sigma(\Delta Y) = \left[\sum \left(\Delta Y_{\exp} - \Delta Y_{cal} \right)^2 / (n - m) \right]^{1/2} \qquad \ldots (6)$$

where n represents the number of experimental data points and m is the number of a_j coefficients

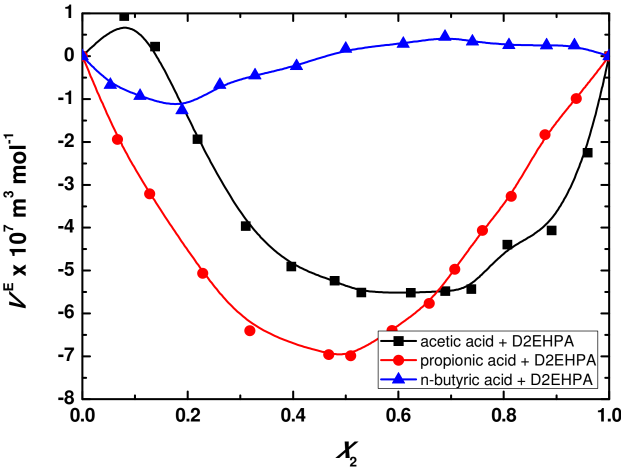

Fig. 3 — Excess volume (V^E) versus molefraction (X_2) of D2EHPA

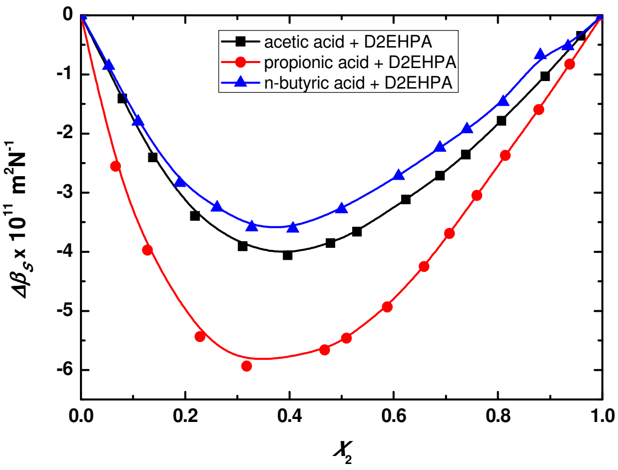

Fig. 4 — Deviation in isentropic compressibility ($\Delta\beta_s$) versus molefraction (X_2) of D2EHPA

Table 3 — Coefficients a_j along with standard deviation, (σ) for all three binary mixtures

ΔY	a_0	a_1	a_2	a_3	a_4	$\sigma(\Delta Y)$
acetic acid (1) + D2EHPA (2)						
$\Delta u \times 10^{-2}$ ms^{-1}	1.4928	-0.8002	0.4189	-0.1745	-0.1559	0.0004
$\Delta\eta$ mPa s	–6.0577	3.9619	–1.1725	0.9339	0.4426	0.0049
$V^E \times 10^7$ m^3 mol^{-1}	–21.9566	–2.6597	3.1798	–44.9283	7.4394	0.0426
$\Delta\beta_s \times 10^{11}$ m^{2}N^{-1}	–15.0804	8.1728	–4.1338	–3.4800	6.5452	0.0027
propionic acid (1) + D2EHPA (2)						
$\Delta u \times 10^{-2}$ ms^{-1}	1.7169	–0.7597	0.1759	–0.2579	0.1881	0.0003
$\Delta\eta$ mPa s	–9.8423	4.0529	–1.8402	–4.1009	1.7614	0.0017
$V^E \times 10^7$ m^3 mol^{-1}	–27.9241	5.4215	8.4253	3.2675	–2.4703	0.0105
$\Delta\beta_s \times 10^{11}$ m^{2}N^{-1}	–22.1477	11.6218	–4.1009	4.7703	–3.4293	0.0041
n-butyric acid (1) + D2EHPA (2)						
$\Delta u \times 10^{-2}$ ms^{-1}	0.9423	–0.5534	0.1184	0.3086	–0.5279	0.0003
$\Delta\eta$ mPa s	–5.5004	4.6396	2.6569	–3.5652	–4.8229	0.0072
$V^E \times 10^7$ m^3 mol^{-1}	8.0107	–4.0327	3.9457	2.3089	–2.4295	0.0139
$\Delta\beta_s \times 10^{11}$ m^{2}N^{-1}	–12.5420	7.8569	–2.7452	–4.5054	7.5794	0.0076

Table 4 — Adjustable parameters and standard deviations in correlating viscosities of the binary mixtures

Binary mixture of D2EHPA (2) with	Grunberg-Nissan		Katti-Chaudhri		Hind *et al.*		Tamura-Kurata	
	d_{12}	σ	W_{vis}/RT	σ	η_{12}	σ	C	σ
acetic acid (1)	2.9744	0.0207	4.3497	0.0069	7.0477	0.0290	1.1312	0.0263
propionic acid (1)	2.3770	0.0121	3.3818	0.0204	5.1523	0.0380	–0.4637	0.1851
n-butyric acid (1)	2.4033	0.0271	3.2060	0.0323	7.6283	0.0091	3.2192	0.0779

considered.

The coefficients and standard deviation are presented in Table 3. Standard deviations estimated using Redlich-Kister polynomial equation are found to be small enough which is in agreement with the order of accuracy of our experimental data.

4 Viscosity Mixture Models

Experimentally determined viscosity values of liquid mixtures have been correlated with the following theoretical models:

Grunberg-Nissan[10],

$$\eta = \exp\left(X_1 \ln\eta_1 + X_2 \ln\eta_2 + X_1 X_2 d_{12}\right) \quad \ldots (7)$$

where X_1 and X_2 are the molefraction of pure components (monocarboxylic acids and D2EHPA), respectively and d_{12} is an adjustable parameter which represents a measure of intermolecular interactions between unlike molecules of binary mixtures.

Katti-Chaudhri[11],

$$\ln\eta V = X_1 \ln\eta_1 V_1 + X_2 \ln\eta_2 V_2 + X_1 X_2 \left(W_{vis}/RT\right) \quad \ldots (8)$$

where W_{vis} is an interaction term.

Hind *et al* [12].,

$$\eta = X_1^2\eta_1 + X_2^2\eta_2 + 2X_1X_2\eta_{12} \quad \ldots (9)$$

where η_{12} is an attributed to unlike pair interaction.

Tamura-Kurata [13],

$$\eta = X_1\varphi_1\eta_1 + X_2\varphi_2\eta_2 + 2(X_1X_2\varphi_1\varphi_2)^{1/2}C \quad \ldots (10)$$

where (ϕ_1 and ϕ_2) and (η_1 and η_2) are the volume fraction and viscosities of pure components, respectively and C is an adjustable parameter.

The values of interaction parameters calculated from the Eqs (7-10) together with standard deviations are presented in Table 4. Calculated values of viscosity of acetic acid (1)+D2EHPA (2) system based on Katti-Chaudhri equation produces best fitting to experimental values, since it gives smallest deviations. Similarly, Grunberg-Nissan and Hind *et al.* equations give better fit for correlating mixture viscosities of propionic acid (1) + D2EHPA (2) and n-butyric acid (1)+D2EHPA (2) systems, respectively.

5 Conclusions

Trends of deviation/excess properties indicate the presence of molecular interaction in the present binary mixtures under study. It may be qualitatively inferred that the interaction between unlike molecules is mainly due to hydrogen bonding through highly polar lone pair oxygen atom of phosphoryl group of D2EHPA and hydrogen atom of hydroxyl group of monocarboxylic acids. Results of excess molar volume and the deviation of isentropic compressibility, viscosity and ultrasonic velocity show that molecular interaction is relatively stronger in propionic acid mixture in comparison with other two mixtures. It is suggested that propionic acid may be used as an effective modifier with D2EHPA in the solvent extraction process. Furthermore, different theoretical models have been tested with the experimental data of viscosity in all binary mixtures under study. This indicates that these models have limited utility; probably Katti-Chaudhri equation is more suitable to smaller molecules while Grunberg-Nissan and Hind *et al.* equations to bigger molecules.

Acknowledgement

The authors are grateful to the Director, Institute of Minerals and Materials Technology (CSIR), Bhubaneswar for providing necessary facilities to carry out the research work. One of our authors (S K Dash) is thankful to the University Grants Commission (UGC), India, for the award of the research project no. PSO-019/10-11 (ERO).

References

1 Ali A & Nabi F, *J Disp Sc Tech*, 31 (2010) 1326.
2 Rastogi R P, Nath J & Misra J, *J Phys Chem*, 71 (1967) 1277.
3 Rathnam M V, Sayed R T, Bhanushali K R & Kumar M S S, *J Mol Liq*, 166 (2012) 9.
4 Nabi F, Jesudason C G, Malik M A & Al-Thabaiti S A, *Chem Eng Comm*, 200 (2013) 77.
5 Awasthi A & Awasthi A, *Thermochim Acta*, 537 (2012) 57.
6 Singh S K, Dhami P S, Tripathi S C & Dakshinamoorthy A, *Hydrometallurgy*, 95 (2009) 170.
7 Lemire A E, Janzen A F & Marat K, *Inorg Chim Acta*, 110 (1985) 237.
8 Lee M S, Ahn J G & Lee E C, *Hydrometallurgy*, 63 (2002) 269.
9 Dalai B, Dash S K, Singh S K, Swain N & Swain B B, *Phys Chem Liq*, 50 (2012) 242.
10 Grunberg L & Nissan A H, *Nature*, 164 (1949) 799.
11 Katti P K & Chaudhri M M, *J Chem Eng Data*, 9 (1964) 442.
12 Hind R K, McLaughlin E & Ubbelohde A R, *Trans Faraday Soc*, 56 (1960) 328.
13 Tamura M & Kurata M, *Bull Chem Soc Jpn*, 25 (1952) 32.
14 Riddick J A, Bunger W B & Sokano T K, *Organic Solvents: Physical properties and methods of Purification,* 4th edn, (Wiley-Interscience, New York), 1986.
15 Vogel A I, *Text book of practical organic chemistry*, (Longmann Green, London), 1989.
16 Haynes W M & Lide D R, *CRC handbook of chemistry and physics*, 92nd ed. (CRC Press, Boca Raton), 2011.
17 Koekemoer L R, Badenhorst M J G & Everson R C, *J Chem Eng Data*, 50 (2005) 587.
18 Pal A & Kumar B, *J Mol Liq*, 163 (2011) 128.
19 Ali A, Abida & Hyder S, *Phys Chem Liq*, 42 (2004) 411.
20 Pradhan S K, Dash S K, Moharana L & Swain B B, *Indian J Pure & Appl Phys*, 50 (2012) 161.
21 Nadh M L, Mohan T M, Krishna T V & Kumar C R S, *Indian J Pure & Appl Phys*, 51 (2013) 406.
22 Kincaid J F & Eyring H, *J Chem Phys*, 6 (1938) 620.
23 Oswal S L, Gheewala D B, Prajapati K D, Gardas R L, Ghael N Y & Ijardar S P, *Thermochim Acta*, 426 (2005) 141.
24 Fort R J & Moore W R, *Trans Faraday Soc*, 62 (1966) 1112.
25 Hassion F X & Cole R H, *J Chem Phys*, 23 (1955) 1756.
26 Redlich O & Kister A T, *Ind Eng Chem*, 40 (1948) 345.