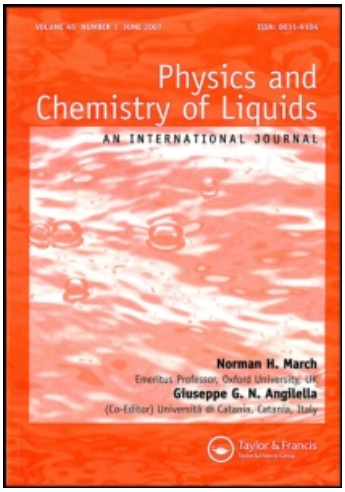

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Volumetric and optical study of molecular association in binary mixtures of dimethyl sulphoxide with carboxylic acid

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Volumetric and optical study of molecular association in binary mixtures of dimethyl sulphoxide with carboxylic acid

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Density and refractive index have been measured for the binary mixture of dimethyl sulphoxide (DMSO) with propanoic acid and *n*-butyric acid at three temperatures, 293, 303 and 313 K, over the entire composition range. Excess parameters such as excess molar volume (V^{E}) and molar refraction deviation (ΔR_{m}) have been calculated from the measured density and refractive index to study the molecular association between the component molecules. The V^{E} and ΔR_{m} values of these mixtures were fitted to the Redlich–Kister polynomial equation. Both excess parameters were plotted against the mole fraction of DMSO over the whole composition range. The values of V^{E} and ΔR_{m} have been found to be negative for both mixtures over the entire composition range, which suggests the presence of strong intermolecular interaction. The experimental refractive data of these mixtures were also used to test the validity of the empirical relations for the refractive index.

Keywords: density; refractive index; excess molar volume; molar refraction deviation

1. Introduction

The refractive index of a medium is a quantitative measure of the response of the medium to the electromagnetic radiation. The refractive index is an important property of liquid and liquid mixtures and is often needed for many physico-chemical applications involving multiphase systems. Since this property is closely related to the orientation, ordering and strength of the constituent atomic oscillators of a given medium, it is expected that the variation of the refractive index of the mixture with temperature and composition can give a valuable insight into the molecular re-arrangement due to mixing. Since the re-arrangement at molecular level due to mixing causes definite contraction or expansion of the liquid, the variation in density is observed. The variation in density produces a significant change in the refractive index. Gladstone and Dale [1] gave a simple formula for the estimation of the refractive index of a binary mixture from the properties of the pure components. Using these factors, many researchers [2–4] have studied and measured the refractive index and density of pure liquids and liquid mixtures.

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The investigations of excess thermodynamic properties of mixtures are found to be highly useful in understanding the intermolecular interactions. The interaction studies are mostly done in terms of excess thermodynamic functions. These functions are found to be sensitive not only to the intermolecular forces but also to the difference in size and shape of the molecules. Properties such as molar volume and refractive index, their deviation from ideality and variation with temperature and composition of binary mixtures are useful for design engineering processes in chemical and biological industries and to test theories of solutions [5].

Ali *et al.* [6] have carried out intermolecular interaction studies on binary mixtures of dimethyl sulphoxide (DMSO) with alcohols. DMSO is a versatile compound used as a solvent and plasticiser, and in biological processes involving both plants and animals [7]. It is highly polar, strongly associated aprotic solvent due to −S=0 groups in molecules [8,9]. DMSO has a large dipole moment and dielectric constant ($\mu = 3.96$ D and $\varepsilon = 46.6$ at 298.15 K) [10].

Carboxylic acids are used as a chemical constituent in paints, ink formation, pesticides, cosmetics, plastic and rubber. DMSO is also used as a natural colourant for food and nutraceutical products. Electronegative substituent near the carboxyl group acts to increase the acidity.

In continuation of our ongoing research programme concerning the physico-chemical properties of binary liquid mixtures, we report the excess molar volume (V^{E}) and molar refraction deviation (ΔR_{m}) for the binary mixture of DMSO with propanoic acid (PA) and butyric acid at temperatures 293, 303 and 313 K, over the entire composition range. The aim of this study is to analyse the disruption of self-association in PA and *n*-butyric acid (BA), and breaking of dipole–dipole interaction of DMSO along with the interaction between −S=O group of DMSO and −COOH group of PA and BA, respectively. Various empirical and semiempirical mixing rules for refractive indices have also been applied to these binary mixtures.

2. Experimental details

Refractive indices of the liquids under investigation were measured using an Abbe's refractometer supplied by the Optics Technologies, New Delhi, at 293, 303 and 313 K, which could measure refractive indices in the range of 1.300–1.700 with an accuracy of ±0.001 unit. Temperature was controlled by circulating water around the prism of refractometer from thermostatically controlled and adequately stirred water bath (accuracy ±0.1°C). The sample mixture was directly injected into the prism assembly of the instrument by means of an air-tight hypodermic syringe. An average of four to five measurements were taken for each sample mixture.

Density of the liquids was measured by a single-limbed pyknometer, with a bulb of volume ~8.0 mL. The pyknometer stem, with a uniform fine bore, had 0.01 mL uniform graduations over it. A certain mass of solution is allowed to expand at the desired temperature and the densities were calculated from the fixed mass and the volume at various temperatures.

Mixtures were prepared by weighing the liquids in specially designed ground glass stoppered weighing bottle taking extreme precaution to minimise preferential evaporation. A Sartorius (BP 121 S) single pan balance having a stated precision of 0.1 mg was used throughout. The maximum possible error in the mole fraction

is estimated to be ±0.0001. The samples were kept in tightly sealed bottles to minimise the absorption of atmospheric moisture.

The chemicals used were obtained from Ranbaxy and Merck Chemicals Ltd. All the chemicals were purified by a standard procedure [11]. The purities of all the chemicals were ascertained by constancy of their boiling points during final distillation. The values agreed well within the precision of experimental error.

3. Theory

The excess molar volume (V^{E}) and molar refraction deviation (ΔR_{m}) values were determined using the following relation:

$$V^{\mathrm{E}} = \left(\frac{x_1 M_1 + x_2 M_2}{\rho_{\mathrm{m}}}\right) - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2}\right) \tag{1}$$

$$\Delta R_m = \left(\frac{n^2_{\exp t} - 1}{n^2_{\exp t} + 2}\right) V_{\mathrm{m}} - \sum_i \left[\left(\frac{n_i^2 - 1}{n_i^2 + 2}\right) V_i \cdot \phi_i\right], \tag{2}$$

where M, ρ, n_{m}, ϕ and x represent the molecular weight, density, refractive index, volume refraction and mole fraction of the mixture, respectively. The subscript 1, 2 and m represent the pure components and mixture, respectively.

The value of V^{E} and ΔR_{m} were fitted to Redlich–Kister [12] polynomial equation:

$$Y^{\mathrm{E}} = x_1(1 - x_1) \sum_{i=1}^{5} A_{i(2x_1-1)}^{i-1}, \tag{3}$$

where Y^{E} is the excess parameter. The value of coefficient A_i of Equation (3) together with the standard deviation (SD), σ (Y^{E}), are calculated by:

$$\sigma(Y^{\mathrm{E}}) = \left[\frac{\sum (Y^{\mathrm{E}}_{\mathrm{obs}} - Y^{\mathrm{E}}_{\mathrm{cal}})^2}{(m - n)}\right]^{1/2}, \tag{4}$$

where m is the total number of experimental points and n is the number of A_i coefficients considered ($n = 5$ in this calculation).

4. Results

The experimental values of the refractive index (n_{m}), excess molar volume (V^{E}) and molar refractive deviation (ΔR_{m}) at three temperatures, namely $T = 293$, 303 and 313 K, are given in Tables 1 and 2 for DMSO + PA and DMSO + BA mixtures, respectively. The values of A_i along with the SD $\sigma(Y^{\mathrm{E}})$ (calculated using Equations (3) and (4)) are given in Table 3. The values of V^{E} and ΔR_{m} are plotted against the mole fraction of DMSO (x_1) and shown in Figures 1 and 2, respectively.

Table 1. Refractive index (n_m), excess molar volume (V^E) and molar refraction deviation (ΔR_m) for DMSO + PA mixture.

x_1	ρ_m (g cm^{-3})	n_m	V^E (cm^3 mol^{-1})	ΔR_m
$T = 293$ K				
0.0000	0.9980	1.3870	0.0000	0.0000
0.0955	1.0214	1.3970	−1.0091	−0.1543
0.1917	1.0402	1.4070	−1.6373	−0.2362
0.2891	1.0500	1.4150	−1.6156	−0.2491
0.3875	1.0645	1.4250	−1.8959	−0.2740
0.4867	1.0727	1.4330	−1.7405	−0.2735
0.5874	1.0802	1.4410	−1.5264	−0.2679
0.6888	1.0888	1.4500	−1.3775	−0.2508
0.7917	1.0958	1.4590	−1.1126	−0.2135
0.8953	1.1063	1.4710	−1.0640	−0.1373
1.0000	1.1010	1.4770	0.0000	0.0000
$T = 303$ K				
0.0000	0.9869	1.3780	0.0000	0.0000
0.0955	1.0105	1.3890	−1.0330	−0.1264
0.1917	1.0291	1.4000	−1.6468	−0.1755
0.2891	1.0410	1.4090	−1.7565	−0.1970
0.3875	1.0544	1.4190	−1.9506	−0.2144
0.4867	1.0626	1.4280	−1.7766	−0.2071
0.5874	1.0701	1.4360	−1.5425	−0.1954
0.6888	1.0787	1.4460	−1.3747	−0.1724
0.7917	1.0856	1.4550	−1.0818	−0.1280
0.8953	1.0959	1.4660	−1.0027	−0.0971
1.0000	1.0921	1.4720	0.0000	0.0000
$T = 313$ K				
0.0000	0.9753	1.3740	0.0000	0.0000
0.0955	0.9998	1.3860	−1.1175	−0.1032
0.1917	1.0196	1.3980	−1.8223	−0.1347
0.2891	1.0307	1.4070	−1.8676	−0.1627
0.3875	1.0446	1.4170	−2.0908	−0.1894
0.4867	1.0527	1.4250	−1.8965	−0.1806
0.5874	1.0616	1.4340	−1.7426	−0.1750
0.6888	1.0688	1.4430	−1.4661	−0.1462
0.7917	1.0769	1.4530	−1.2369	−0.1047
0.8953	1.0858	1.4640	−1.0524	−0.0489
1.0000	1.0817	1.4690	0.0000	0.0000

5. Discussion

It may qualitatively be explained that the mixing of DMSO with carboxylic acid will induce (1) the breaking up of hydrogen bonds (in the carboxylic acid molecules) and loss of dipolar association (in DMSO molecules), (2) the possibility of formation of hydrogen bonds between −S=0 group of DMSO and −COOH group of carboxylic acid $(-S=O\cdots H-O-\overset{\overset{O}{\|}}{C})$, dipole–dipole interaction between unlike molecules and (3) interstitial accommodation of component molecules into each other's structure. The first effect leads to expansion in volume, hence positive deviation in V^E and ΔR_m,

Table 2. Refractive index (n_m), excess molar volume (V^E) and molar refraction deviation (ΔR_m) for DMSO + butyric acid mixture.

x_1	ρ_m (g cm^{-3})	n_m	V^E (cm^3 mol^{-1})	ΔR_m
$T = 293$ K				
0.0000	0.9586	1.3980	0.0000	0.0000
0.1115	0.9886	1.4080	−1.5792	−0.2864
0.2200	1.0059	1.4160	−1.8890	−0.3680
0.3261	1.0242	1.4250	−2.2338	−0.4199
0.4294	1.0365	1.4310	−2.0434	−0.4664
0.5302	1.0506	1.4390	−1.9722	−0.4558
0.6283	1.0608	1.4450	−1.5995	−0.4432
0.7247	1.0788	1.4550	−1.7596	−0.4138
0.8187	1.0881	1.4620	−1.2910	−0.3287
0.9104	1.0996	1.4700	−0.9723	−0.2414
1.0000	1.1010	1.4770	0.0000	0.0000
$T = 303$ K				
0.0000	0.9485	1.3940	0.0000	0.0000
0.1115	0.9794	1.4040	−1.6802	−0.3022
0.2200	0.9964	1.4110	−1.9660	−0.4194
0.3261	1.0132	1.4190	−2.1777	−0.4754
0.4294	1.0274	1.4260	−2.1346	−0.5117
0.5302	1.0407	1.4340	−1.9889	−0.4981
0.6283	1.0515	1.4400	−1.6427	−0.4892
0.7247	1.0693	1.4490	−1.7849	−0.4679
0.8187	1.0779	1.4560	−1.2461	−0.3789
0.9104	1.0885	1.4640	−0.8565	−0.2665
1.0000	1.0921	1.4720	0.0000	0.0000
$T = 313$ K				
0.0000	0.9381	1.3900	0.0000	0.0000
0.1115	0.9690	1.3990	−1.7212	−0.3556
0.2200	0.9877	1.4070	−2.1643	−0.4643
0.3261	1.0037	1.4150	−2.3049	−0.5039
0.4294	1.0185	1.4220	−2.3020	−0.5530
0.5302	1.0310	1.4290	−2.0876	−0.5457
0.6283	1.0423	1.4360	−1.7743	−0.5283
0.7247	1.0601	1.4450	−1.9042	−0.5055
0.8187	1.0678	1.4510	−1.2999	−0.4230
0.9104	1.0791	1.4590	−0.9418	−0.3225
1.0000	1.0817	1.4690	0.0000	0.0000

and the other two effects lead to contraction in volume, resulting in negative deviation in V^E and ΔR_m.

Figure 1 shows that V^E values are negative for both mixtures at all three temperatures studied here, which suggest the presence of a strong intermolecular interaction between unlike molecules. This is in accordance with the view proposed by Fort and Moore [13] that liquids of different molecular size usually mix with negative V^E. Molar volumes for DMSO, PA and butyric acid at 293 K are 70.97, 74.27 and 91.91 cm^3 mol^{-1}, respectively. Large negative values of V^E for DMSO + butyric acid mixture as compared to DMSO + PA mixture may be due

Table 3. The values of coefficients A_i for V^E and ΔR_m and SD $\sigma(Y^E)$ for binary mixture at varying temperatures.

Parameters	Temperature (K)	A_1	A_2	A_3	A_4	A_5	$\sigma(Y^E)$
DMSO + PA							
V^E ($cm^3 mol^{-1}$)	293	−10.2555	−1.0509	8.6608	−3.7345	−22.8723	0.1053
	303	−8.4558	−1.8078	1.4056	−3.6052	−17.2325	0.0992
	313	−10.061	−2.2055	3.6079	−3.5905	−16.8211	0.1034
ΔR_m	293	−1.094	−0.0715	−0.8461	−0.3472	−0.1799	0.0053
	303	−0.8337	−0.0278	0.5629	−0.3253	−1.8826	0.0031
	313	−0.6542	0.1158	−0.1592	−0.824	−0.213	0.0043
DMSO + butyric acid							
V^E ($cm^3 mol^{-1}$)	293	−6.9447	−2.0246	3.302	3.1606	−16.5998	0.0966
	303	−7.1343	0.0092	9.7241	−0.7044	−25.4948	0.068
	313	−7.1622	1.0626	7.1298	−2.842	−23.264	0.072
ΔR_m	293	−1.8101	0.6304	0.8792	−1.2333	−4.1905	0.0073
	303	−2.0158	−0.0896	−0.7328	0.1525	−1.638	0.0067
	313	−2.2082	−0.1492	−0.404	0.2731	−3.1694	0.0099

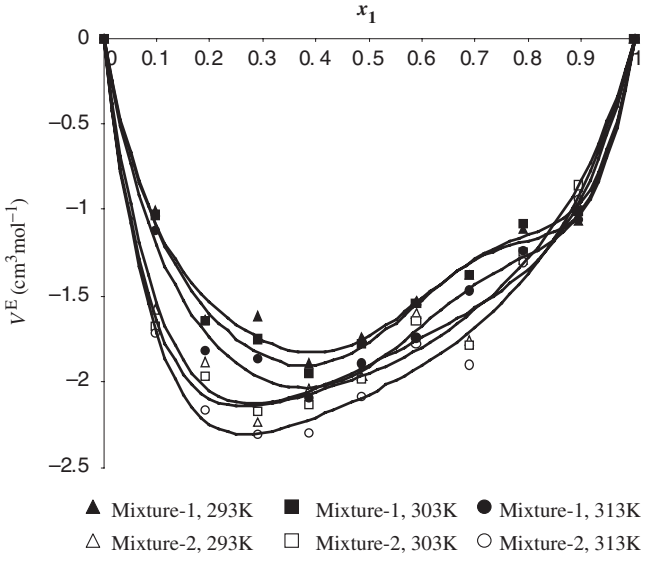

Figure 1. Excess molar volume (V^E) against mole fraction of DMSO (x_1) for DMSO + PA (Mixture 1) and DMSO + butyric acid mixture (Mixture 2).

to the large molar volume difference between DMSO and butyric acid than between DMSO and PA, which would allow a more favourable packing of butyric acid molecules into the space created by DMSO molecules. Similar trends in V^E with composition have been reported by earlier researchers [5,14,15] for binary mixtures of anisole + alkyl benzene, tetrahydrofuran (THF) + 1-propanol and THF + methanol/*o*-cresol.

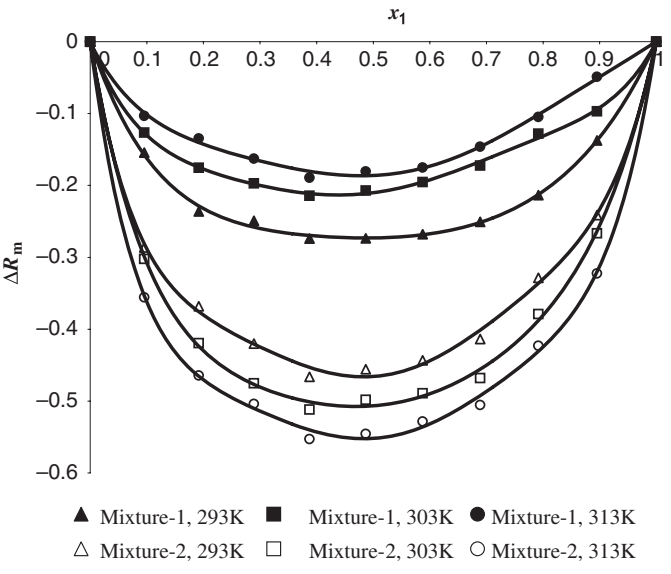

Figure 2. Molar refraction deviation ΔR_m against mole fraction of DMSO (x_1) for DMSO + PA mixture (Mixture 1) and DMSO + butyric acid mixture (Mixture 2).

The molar refraction deviation, ΔR_m, represents the electronic perturbation due to orbital mixing of two components [16,17]. ΔR_m gives the strength of interaction in the mixture and is a sensitive function of wavelength, temperature and mixture composition. Figure 2 shows that ΔR_m values are negative for both the mixtures over the entire composition range. The negative values of ΔR_m suggest that the structure-making effect is predominant in these systems. This decreases the free space between the molecules in the mixtures due to increased interaction, which would in turn provide negative deviation in molar refraction. The mixing of DMSO with carboxylic acid tends to break the associates present in the carboxylic acid molecules and there is a possibility of hydrogen bonding between the oxygen atom of DMSO and the hydrogen atom of carboxylic acid molecules. The observed negative value of ΔR_m in both the mixtures indicates the presence of a strong intermolecular interaction through hydrogen bonding between the unlike molecules. Al-Kandary *et al.* [5] and Gupta *et al.* [14] have also reported similar behaviour of ΔR_m in binary mixtures of anisole with alkyl benzene and THF with alkanols, respectively.

Further refractive index data of these binary mixtures were correlated using the empirical/semiempirical equation proposed by Lorentz–Lorentz (L–L), Gladstones–Dale (G–D), Arago–Biot (A–B), Eykman (Eyk), Oster (Os), Heller (H), Weiner (W) and Newton (Nn) as reported in our earlier work [18]. The average percentage deviation (APD) in the calculated values of refractive indices using different relations is given in Table 4. A good agreement has been found between the experimental and calculated values of refractive index with maximum APD of −0.36 at 293 K for DMSO + PA mixture and −0.46 at 313 K for DMSO + butyric acid mixture using Eykman's relation. The correlation with these equations showed the suitability of all these relations for representing the mixing refractive indices

Table 4. APD of various theoretical mixing rules used for the evaluation of refractive index (n_m) at varying temperatures.

Temperature (K)	A–B	G–D	Nn	H	W	L–L	Eyk	Os
DMSO + PA								
293	0.15561	0.11561	0.12603	0.18600	0.16383	0.18587	−0.36316	0.09572
303	0.23675	0.23675	0.20419	0.27002	0.024571	0.26973	−0.27270	0.17333
313	0.31894	0.31894	0.28589	0.35268	0.32802	0.35224	−0.22336	0.25506
DMSO + butyric acid								
293	0.19953	0.19953	0.17694	0.22337	0.20596	0.22281	−0.35548	−0.02688
303	0.13890	0.13890	0.11672	0.16231	0.14522	0.16161	−0.40852	−0.08529
313	0.10989	0.10989	0.08730	0.13372	0.11632	0.13291	−0.46407	−0.11642

of the binary mixtures of DMSO + PA/butyric acid. The mixing rules proposed by Newton's and Oster's relations are found to be more suitable for the prediction of our data.

6. Conclusion

The values of excess molar volume and molar refraction deviation were found to be negative for both the mixtures, which suggest the presence of strong intermolecular interaction through hydrogen bonding between the unlike molecules. Newton's and Oster's relations were found to be more suitable for the theoretical prediction of refractive index.

References

[1] J.H. Gladstone and T.P. Dale, Phil. Trans. **153**, 317 (1863).
[2] C.C. Wang, H.W. Chen, and C.H. Tu, J. Chem. Eng. Data **50**, 1687 (2005).
[3] S. Parveen, S. Singh, D. Shukla, K.P. Singh, M. Gupta, and J.P. Shukla, Acta Phys. Pol. A **6**, 111 (2009).
[4] A.H. Al Dujali, A.A. Yaseen, and A.M. Awwad, J. Chem. Eng. Data **45**, 647 (2000).
[5] J.A. Al Kandary, A.S. Al Jimaz, and A.H.M. Abdul-Latif, J. Chem. Eng. Data **51**, 99 (2006).
[6] A. Ali, K. Tewari, A.K. Nain, and V. Chakravortty, Phys. Chem. Liq. **38**, 459 (2000).
[7] M. Madhusudan and B.L. Tambe, J. Phys. Chem. **98**, 7090 (1994).
[8] G.A. Kerstov, *Thermodynamics of Solvation* (Ellis Horwood Limited, England, 1991).
[9] I.I. Vaisman and B.L. Tembe, J. Am. Chem. Soc. **114**, 7889 (1992).
[10] Y. Marcus, *Introduction of Liquid State Chemistry* (Wiley Intersciences, New York, 1997).
[11] D.D. Perin and W.L.F. Armarego, *Purification of Laboratory Chemicals*, 3rd ed. (Pergamon Press, Oxford, 1988).
[12] O. Redlich and A.T. Kister, Ind. Eng. Chem. **40**, 345 (1948).
[13] R.J. Fort and W.R. Moore, Trans. Faraday Soc. **61**, 2102 (1965).
[14] M. Gupta, I. Vibhu, and J.P. Shukla, Phys. Chem. Liq. **41**, 575 (2003).

[15] S. Parveen, S. Singh, D. Shukla, K.P. Singh, M. Gupta, and J.P. Shukla, Appl. Acoust. **70**, 507 (2009).
[16] T.M. Aminabhavi, S.K. Raikar, and R.H. Balundgi, Ind. Eng. Chem. Res. **32**, 931 (1993).
[17] C.J.F. Bottcher, *Theory of Electronic Polarization* (Elsevier, Amsterdam, 1952).
[18] A. Mishra, I. Vibhu, R.K. Singh, M. Gupta, and J.P. Shukla, Phys. Chem. Liq. **45**, 93 (2007).