Journal of Molecular Liquids 178 (2013) 178–184

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Liquids

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

Densities, refractive indices and excess properties of binary mixtures of dimethylsulphoxide with some poly(ethylene glycol)s at different temperatures

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ARTICLE INFO

Article history:
Received 15 September 2012
Received in revised form 1 November 2012
Accepted 2 December 2012
Available online 16 December 2012

Keywords:
Density
Refractive index
Dimethylsulphoxide
Poly(ethylene glycol)

ABSTRACT

The densities, ρ and refractive indices, n_D of binary mixtures of dimethylsulphoxide (DMSO) with poly(ethylene glycol) 200 (PEG200), poly(ethylene glycol) 300 (PEG300) and poly(ethylene glycol) 400 (PEG400) over the entire composition range were measured at temperatures (298.15, 303.15, 308.15, and 313.15 K) and at atmospheric pressure. From the experimental data, the excess molar volumes, V_m^E and excess refractive indices, n_D^E were calculated. The partial molar volumes, $\overline{V}^{\circ\infty}_{m,1}$ and $\overline{V}^{\circ\infty}_{m,2}$ of the components at infinite dilution and excess partial molar volumes, $\overline{V}^{\circ E,\infty}_{m,1}$ and $\overline{V}^{\circ E,\infty}_{m,2}$ of the components at infinite dilution have been calculated. The V_m^E values were negative and n_D^E were positive for all the three systems at each investigated temperatures. The results indicate the presence of specific interactions between DMSO and PEG molecules. The negative deviations in V_m^E values follow the order: PEG200 < PEG300 < PEG400. It is observed that V_m^E and n_D^E values depend upon the chain length of PEG molecules. Further, the refractive indices of these binary mixtures were calculated theoretically from the refractive index data of pure components and densities of the mixtures by using various empirical and semi-empirical relations and the results were compared with the experimental findings.

1. Introduction

Polymers and their aqueous or non-aqueous mixtures had always been the subject of interest of the researchers due to their anomalous behaviour in their physical properties. Consistent efforts are being made to understand their solution behaviour with respect to their solution structure (chain length and conformation of polymer molecules) and various other types of interactions [1–4]. Volumetric properties provide significant information for the characterization of molecular interactions which result from an interplay of solute–solute, solvent–solvent, solute–solvent and structural effects [5,6]. Refractive index is the most fundamental property of the polymers and the measurement of which is affected by the molecular intrinsic electromagnetic fields determined from the molecular sizes and the intermolecular forces of interactions [7–9]. In continuation to our ongoing research [10–13] on binary and ternary liquid mixtures, here we report the results of our study on the mixtures of dimethylsulphoxide (DMSO) with poly(ethylene glycol) 200 (PEG200), poly(ethylene glycol) 300 (PEG300) and poly(ethylene glycol) 400 (PEG400) over the entire composition range at different temperatures.

DMSO was chosen because it is a versatile compound having wide range of applicability as a solvent in chemical and biological processes involving both plants and animals [14]. It is highly polar (dipole moment = 3.96 D at 298.15 K) [15] and strongly associated aprotic solvent due to S=O group [16] in the molecule. The DMSO molecules associate in chains with parallel dipole moments, while neighbouring DMSO molecules from adjacent chains are oriented with anti-parallel dipole moments [17,18] in pure state, as reported by Bertagnolli et al. [17] using X-ray and neutron scattering, and also confirmed by Vaisman and Berkowitz [18] using molecular dynamics simulation. Poly(ethylene glycol)s have been chosen because of their benign nature and consequent wide range of applications especially in cosmetic and pharmaceutical industry but not limited to these only [2,3]. Therefore, the volumetric and optical properties of DMSO + PEG's binary mixtures will be an interesting platform to investigate the interplay of intermolecular interactions (H-bonding together with the dispersion forces) arising from the bond polarizability and propagating electromagnetic field of polymer molecules. Literature survey indicates that investigations have been carried out on the binary mixtures of DMSO with some PEGs using excess molar enthalpies at 308.15 K [4], densities and viscosities at 308.15 K [3] and densities and viscosities at different temperatures [4]. However, a systematic study on DMSO + PEG200, PEG300 and PEG400 mixtures from the point of view of their volumetric and optical properties at varied temperatures still lacks in literature.

In the present paper, the densities, ρ and refractive indices, n_D of binary mixtures of dimethylsulphoxide (DMSO) with poly(ethylene glycol) 200 (PEG200), poly(ethylene glycol) 300 (PEG300) and poly(ethylene glycol) 400 (PEG400) over the entire composition range were

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http://dx.doi.org/10.1016/j.molliq.2012.12.002

measured at temperatures (298.15, 303.15, 308.15, and 313.15 K) and at atmospheric pressure. From the experimental data, the excess molar volumes, V_m^E and excess refractive indices, n_D^E have been calculated. The partial molar volumes, $\overline{V}_{m,1}^{\circ\infty}$ and $\overline{V}_{m,2}^{\circ\infty}$ and excess partial molar volumes, $\overline{V}_{m,1}^{\circ E,\infty}$ and $\overline{V}_{m,2}^{\circ E,\infty}$ of the components at infinite dilution have also been calculated. The variations of V_m^E and n_D^E with composition and temperature of the mixtures have been discussed in terms of molecular interaction in these mixtures.

2. Experimental

2.1. Materials

DMSO (CDH, India, purity > 99.5%) was used as such without purification and PEG200, PEG300 and PEG400 (S.D. Fine-Chem Ltd., India, purity > 99%) were dried over phosphoric anhydride under reduced pressure at 60 °C [19]; the mass fraction purities as determined by gas chromatography are: DMSO > 0.995, PEG200 > 0.994, PEG300 > 0.993 and PEG400 > 0.993. Before use, the chemicals were stored over 0.4 nm molecular sieves for 72 h to remove water content, if any, and were degassed at low pressure. The M_n value of the polymers was determined using Hitachi ELITE LaChrom chromatograph equipped with L-2490 refractive index detector and Waters Styragel HR3 and HR4 columns in series. The chromatograph was calibrated with polystyrene standards and tetrahydrofuran was used as eluent. The M_n value together with the polydispersity index is tabulated in Table 1. The mixtures were prepared by mass and were kept in special airtight stopper glass bottles to avoid evaporation. The weighings were done by using an electronic balance (Model: GR-202, AND Japan) with a precision of ±0.01 mg. The uncertainty in the mole fraction was estimated to be less than $\pm 1\cdot 10^{-4}$.

2.2. Density and refractive index measurements

The densities of pure liquids and their binary mixtures were measured by using a single-capillary pycnometer (Borosil glass) and having a bulb capacity of ~10 mL. The capillary, with graduated marks, had a uniform bore and could be closed by a well-fitting glass cap. The marks on the capillary were calibrated by using triply distilled water. The reproducibility of density measurement was within ± 0.02 $kg\cdot m^{-3}$. The refractive indices of pure liquids and their binary mixture were measured using a thermostated Abbe refractometer. The refractometer was calibrated by measuring the refractive indices of triply distilled water and toluene at various temperatures. The values of refractive index were obtained using sodium D light. The temperature of the test liquids between the prisms of refractometer during the measurements was maintained to an accuracy of ±0.01 K by circulating water through the jacket around the prisms from an electronically controlled thermostatic water bath and the temperature was measured with a digital thermometer connected with the prism jacket. The uncertainty in refractive index measurements was within ±0.0001. The temperature of the test liquids during the measurements was maintained to an uncertainty of ±0.01 K in an electronically controlled thermostatic water bath (JULABO, Model: ME-31A, Germany). The reliability of experimental measurements of ρ and n_D was ascertained by comparing the experimental data of pure liquids with the corresponding literature [1,20–26] values at various temperatures (Table 1) and the agreement between the values is found good.

Table 1
Comparison of the experimental and literature values of density, ρ and refractive index, n_D at different temperatures.

Liquid	M_n	PD	T/K	ρ/kg m^{-3}		n_D	
				Expt.	Lit.	Exp.	Lit.
DMSO	–	–	298.15	1095.52	1095.37 [20]	1.4776	1.4770 [21]
			303.15	1090.62	1091.1 [21]	1.4757	1.4748 [21]
			308.15	1085.73	1085.9 [21,22]	1.4739	1.4730 [21]
					1086.1 [23]	1.4720	
			313.15	1080.86	1081.2 [22]		–
PEG200	192	1.137	298.15	1121.12	1120.98 [1]	1.4588	1.4585 [1]
			303.15	1117.18	1117.2 [1]	1.4575	1.4570 [1]
			308.15	1113.21		1.4561	
			313.15	1109.23	1108.98 [1]	1.4547	1.4547 [24]
PEG300	279	1.158	298.15	1121.84		1.4619	
			303.15	1117.77		1.4609	
			308.15	1113.69	1113.58 [25]	1.4596	1.4599 [26]
			313.15	1109.60		1.4584	
PEG400	361	1.189	298.15	1122.35	1122.49 [1]	1.4649	1.4650 [1]
			303.15	1118.35	1118.31 [1]	1.4637	1.4638 [1]
			308.15	1114.34	1114.89 [3]	1.4625	
			313.15	1110.33	1109.92 [24]	1.4614	1.4607 [24]

3. Results and discussion

3.1. Excess properties

The experimental values of the densities, ρ and refractive indices, n_D of the binary mixtures of DMSO with PEG200, PEG300 and PEG400 over the entire composition range, expressed in mole fraction, x_1 of DMSO at different temperatures are listed in Tables 2–4. The excess molar volumes, V_m^E and excess refractive indices, n_D^E for the binary mixtures were calculated by using the following relations

$$V_m^E = x_1M_1(1/\rho - 1/\rho_1) + x_2M_2(1/\rho - 1/\rho_2) \quad (1)$$

$$n_D^E = n_D - n_D^{id} \quad (2)$$

and

$$n_D^{id} = \left[\phi_1\left(n_{D,1}\right)^2 + \phi_2\left(n_{D,2}\right)^2\right]^{1/2} \quad (3)$$

where M is the molar mass, ϕ is the volume fraction, the subscripts 1 and 2 refer to the pure DMSO and PEG, respectively. The values of V_m^E and n_D^E are also included in Tables 2–4. The ϕ was calculated using the relation

$$\phi_i = x_iV_i / \sum_{i=1}^{2} x_iV_i. \quad (4)$$

The excess molar volumes, V_m^E and excess refractive indices, n_D^E were fitted to Redlich–Kister [27] type polynomial equation

$$Y^E = x_1x_2\sum_{i=0}^{k} A_i(2x_1 - 1)^i \quad (5)$$

where Y^E is V_m^E or n_D^E; k is the number of A_i coefficients considered. In case of n_D^E, volume fraction ϕ has been used in place of x in Eq. (5). The adjustable parameters, A_i have been obtained by using least-square regression analysis with all the points weighted equally. The parameters, A_i of V_m^E and n_D^E for the mixtures and corresponding standard deviations, σ at all investigated temperatures, respectively are listed in Table 5. The variations of V_m^E with mole fraction, x_1 of DMSO and of n_D^E with volume fraction, ϕ of DMSO along with the smoothed V_m^E and n_D^E values calculated by using Eq. (5) at 298.15 K are presented graphically in Figs. 1 and 2.

Fig. 1 indicates that the V_m^E values are negative over the whole composition range for all the three systems at each investigated temperature and the magnitude of the negative deviations in V_m^E follows the sequence: PEG400 > PEG300 > PEG200. This suggests a contraction in volume on moving from PEG200 to PEG400 thereby indicating