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Densities of {poly(ethylene glycol) + water} over the temperature range (283.15 to 363.15) K

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ABSTRACT

Densities of {poly(ethylene glycol) [PEG] + water} prepared with PEG average molar mass (200, 400, 600, and 1500) $g \cdot mol^{-1}$ have been measured over the entire composition range over the temperature range (283.15 to 363.15) K at 10 K intervals using a density meter based on electromagnetically-induced oscillations of a U-shaped glass tube and an inbuilt Peltier thermostat. The density *versus* temperature data of (PEG + water) at each composition for all PEGs were fit to a simple quadratic equation: $\rho/(g \cdot cm^{-3}) = \rho_0/(g \cdot cm^{-3}) + a(T/K) + b(T/K)^2$. Fits were observed to be satisfactory at each composition for all four (PEG + water). The excess molar volumes of (PEG + water) are observed to be negative and significant over the entire composition range for all four (PEG + water). Irrespective of the temperature, the maximum absolute excess molar volumes are observed in the water-rich region of the mixture and are found to decrease with increasing temperature. This is attributed to the presence of strong interactions within the (PEG + water). Specifically, it is proposed to be due to the H-bonding interactions between the PEG and the water molecules within the mixtures.

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1. Introduction

Volatile organic compounds (VOCs) are among the foremost contributors towards the growing environmental pollution. As plausible greener alternatives to these VOCs [1–7], polymers and aqueous polymer systems are gaining widespread acceptance. In this context, poly(ethylene glycols) [PEGs] have found immense industrial importance and have become an increasingly popular class of chemicals of major investigations [7]. While PEGs of low average molar mass (average molar mass < 1000) are usually liquid at ambient conditions and may be used as solvents, their physicochemical properties are restricted. Water mixtures of PEG rather than neat PEGs may provide substantially improved physicochemical properties for many industrial applications [8]. Most importantly, the key physicochemical properties of (PEG + water) can be tuned with the amount of water present.

Prior to widespread applications of (PEG + water), a study of the properties of these relatively benign systems is essential. Among key physicochemical properties, density has enormous importance as far as various industrial applications are concerned. It is worthwhile to mention some earlier attempts by other research groups to investigate the density of (PEG + water) at varying temperatures. Eliassi *et al.* have reported the density of PEGs (PEG400, PEG4000, and PEG6000) within the temperature range (283.15 to 328.15) K [9]. The Rahbari-Sisakht group studied temperature-dependent density and viscosity of PEGs (PEG200, PEG300, PEG6000) from $T = (293.15$ to $338.15)$ K [10]. Another temperature-dependent density measurement was performed on the (PEG4000 + water) from $T = (308$ to $338)$ K and the results were discussed in terms of molecular interactions occurring within the mixture [11]. Recently, Perumalsamy *et al.* have also used PEG4000 to find the effect of phase compositions, molar mass, and temperature on density, viscosity, and (liquid + liquid) equilibrium of aqueous two-phase PEG system [12]. Densities of the (PEG400 + water) and those of PEG2000 and PEG10000 were presented by Müller and Rasmussen over the temperature range (298.15 to 328.15) K, and 328.15 K, respectively [13]. A few other research groups have also reported the densities of (PEG + water) prepared using a different PEG average molar mass in varying temperature ranges [14,15]. Although the densities of (PEG + water) have been reported by many researchers as mentioned, the temperature ranges of these measurements are rather limited. Further, the average molar mass of PEGs is also restricted in these studies.

Here, we report the densities of (PEG + water) prepared using PEG average molar mass (200, 400, 600, and 1500) $g \cdot mol^{-1}$ over the entire composition range within the temperature range (283.15 to 363.15) K in 10 K intervals. For this purpose, we have used a density meter which is based on electromagnetically-induced oscillations of a U-shaped glass tube having built-in Peltier thermostat controller. The standard deviations associated with the density measurement are $\leqslant 5 \cdot 10^{-5}\ g \cdot cm^{-3}$.

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2. Experimental

2.1. Materials

The PEGs of average molar mass (200, 400, 600, and 1500) $g \cdot mol^{-1}$ were obtained in highest purity from Central Drug House, New Delhi. Doubly-distilled deionised water was obtained from Millipore, Milli-Q Academic water purification system. Ethanol (mass fraction purity 0.999) was obtained from Merck.

TABLE 1
Comparison of experimental densities (ρ) of {PEG400 (1) + water (2)} with the literature values at different temperatures (X is the mole fraction). Literature values are from reference [14].

X_1	$\rho/(g \cdot cm^{-3})$					
	T = 303.15 K		T = 313.15 K		T = 323.15 K	
	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
0.000 (0.0000)[a]	0.9957	0.9957	0.9923	0.9922	0.9880	0.9880
0.005 (0.0050)[a]	1.0114	1.0114	1.0075	1.0075	1.0025	1.0025
0.019 (0.0190)[a]	1.0447	1.0448	1.0393	1.0394	1.0333	1.0332
0.029 (0.0291)[a]	1.0618	1.0616	1.0555	1.0557	1.0489	1.0486
0.043 (0.0431)[a]	1.0784	1.0781	1.0712	1.0710	1.0638	1.0635
0.063 (0.0634)[a]	1.0934	1.0931	1.0856	1.0850	1.0776	1.0768
0.095 (0.0951)[a]	1.1047	1.1041	1.0964	1.0964	1.0881	1.0877
1.000 (1.0000)[a]	1.1181	1.1180	1.1098	1.1097	1.1015	1.1017

[a] Mole fraction of PEG400 in reference [14].

2.2. Method

The (PEG + water) containing different average molar mass PEG were prepared by mass using Adventurer Ohaus AR2130 balance having a precision of ±1 mg. Densities of the (PEG + water) were measured in triplicate using a Mettler Toledo, DE45 delta range density meter. The measurements were performed at 10 K intervals over the temperature range (283.15 to 363.15) K. The uncertainty associated with temperature was measured to within ±0.1 K. The density measurement of the above mentioned density meter is based on electromagnetically-induced oscillations of a U-shaped glass tube. The densities of the solutions with known density values measured using this system showed relative errors of ⩽0.05% in measured densities [16]. Table 1 presents a comparison of densities of (PEG400 + water) measured by our instrumentation with those available in the literature [14]. It is clear that the two values are in good agreement. The average deviation in density being $2.083 \cdot 10^{-4}\ g \cdot cm^{-3}$ or 0.02% between our data and prior published data. The uncertainty associated with mixture composition is ⩽5%.

TABLE 2
Densities ($\rho/g \cdot cm^{-3}$) for the mixture of {poly(ethylene glycol) [PEG] (1) + water (2)} from T = (283.15 to 363.15) K as a function of mass fraction (W_1) of PEG.

T/K	$100W_1$										
	0	10	20	30	40	50	60	70	80	90	100
						PEG200					
283.15	0.9997	1.0158	1.0331	1.0510	1.0691	1.0865	1.1031	1.1147	1.1242	1.1298	1.1327
293.15	0.9982	1.0136	1.0299	1.0468	1.0638	1.0802	1.0961	1.1070	1.1163	1.1218	1.1246
303.15	0.9957	1.0106	1.0262	1.0422	1.0583	1.0737	1.0888	1.0995	1.1084	1.1138	1.1166
313.15	0.9923	1.0066	1.0217	1.0370	1.0522	1.0667	1.0814	1.0918	1.1005	1.1059	1.1086
323.15	0.9880	1.0018	1.0164	1.0311	1.0457	1.0599	1.0738	1.0838	1.0925	1.0979	1.1006
333.15	0.9831	0.9989	1.0114	1.0261	1.0406	1.0546	1.0686	1.0785	1.0872	1.0925	1.0953
343.15	0.9776	0.9914	1.0058	1.0204	1.0348	1.0489	1.0627	1.0725	1.0811	1.0865	1.0892
353.15	0.9716	0.9852	0.9995	1.0140	1.0284	1.0424	1.0561	1.0658	1.0744	1.0797	1.0824
363.15	0.9651	0.9784	0.9926	1.0070	1.0213	1.0351	1.0488	1.0585	1.0669	1.0722	1.0749
						PEG400					
283.15	0.9997	1.0170	1.0353	1.0540	1.0733	1.0919	1.1087	1.1210	1.1272	1.1335	1.1351
293.15	0.9982	1.0147	1.0321	1.0497	1.0678	1.0853	1.1012	1.1129	1.1191	1.1251	1.1265
303.15	0.9957	1.0114	1.0280	1.0447	1.0618	1.0784	1.0934	1.1047	1.1108	1.1167	1.1181
313.15	0.9923	1.0075	1.0234	1.0393	1.0555	1.0712	1.0856	1.0964	1.1025	1.1083	1.1098
323.15	0.9880	1.0025	1.0181	1.0333	1.0489	1.0638	1.0776	1.0881	1.0941	1.1001	1.1015
333.15	0.9831	0.9977	1.0132	1.0279	1.0437	1.0585	1.0719	1.0814	1.0888	1.0947	1.0962
343.15	0.9776	0.9922	1.0075	1.0223	1.0379	1.0526	1.0659	1.0754	1.0828	1.0887	1.0901
353.15	0.9716	0.9860	1.0013	1.0159	1.0315	1.0461	1.0593	1.0686	1.0760	1.0819	1.0833
363.15	0.9651	0.9791	0.9943	1.0088	1.0243	1.0388	1.0519	1.0612	1.0686	1.0744	1.0758
						PEG600					
283.15	0.9997	1.0170	1.0354	1.0547	1.0743	1.0933	1.1100	1.1226	1.1306	1.1344	Solid
293.15	0.9982	1.0148	1.0322	1.0504	1.0688	1.0866	1.1023	1.1143	1.1221	1.1259	1.1271
303.15	0.9957	1.0115	1.0281	1.0454	1.0627	1.0796	1.0945	1.1060	1.1136	1.1176	1.1186
313.15	0.9923	1.0076	1.0234	1.0399	1.0564	1.0724	1.0865	1.0977	1.1052	1.1090	1.1102
323.15	0.9880	1.0029	1.0182	1.0340	1.0487	1.0649	1.0784	1.0892	1.0966	1.1006	1.1019
333.15	0.9831	0.9980	1.0133	1.0291	1.0447	1.0598	1.0734	1.0840	1.0913	1.0952	1.0965
343.15	0.9776	0.9924	1.0077	1.0234	1.0390	1.0539	1.0674	1.0780	1.0852	1.0892	1.0904
353.15	0.9716	0.9863	1.0014	1.0170	1.0324	1.0474	1.0608	1.0712	1.0785	1.0824	1.0836
363.15	0.9651	0.9794	0.9945	1.0099	1.0253	1.0401	1.0534	1.0638	1.0710	1.0749	1.0761
						PEG1500					
283.15	0.9997	1.0173	1.0359	1.0557	1.0752	1.0952	1.1112	1.1249	Solid	Solid	Solid
293.15	0.9982	1.0149	1.0326	1.0511	1.0694	1.0882	1.1032	1.1161	1.1200	Solid	Solid
303.15	0.9957	1.0118	1.0284	1.0462	1.0635	1.0811	1.0953	1.1077	1.1130	Solid	Solid
313.15	0.9923	1.0078	1.0237	1.0407	1.0571	1.0738	1.0873	1.0991	1.1064	1.1094	Solid
323.15	0.9880	1.0030	1.0183	1.0346	1.0501	1.0660	1.0789	1.0902	1.0976	1.1008	1.1067
333.15	0.9831	0.9981	1.0134	1.0295	1.0450	1.0608	1.0736	1.0849	1.0923	1.0954	1.1040
343.15	0.9776	0.9926	1.0078	1.0238	1.0392	1.0549	1.0677	1.0789	1.0862	1.0894	1.0920
353.15	0.9716	0.9864	1.0015	1.0174	1.0328	1.0483	1.0610	1.0722	1.0795	1.0826	1.0852
363.15	0.9651	0.9795	0.9945	1.0104	1.0256	1.0412	1.0537	1.0648	1.0720	1.0751	1.0774

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