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Densities, viscosities, refractive indices and excess properties of aniline and *o*-anisidine with 2-alkoxyethanols at 303.15 K

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ABSTRACT

Densities, viscosities and refractive indices have been measured for the binary mixtures of aromatic amines such as aniline and *o*-anisidine with 2-alkoxyethanols like 2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol at 303.15 K. The excess properties are excess molar volume (V^E), deviation of viscosity (η^E), deviation of refractive index (Δn_D), excess molar refraction (R_m^E) and excess Gibbs free energy (ΔG^{*E}) for the six binary mixtures that were calculated and the values are fitted with Redlich–Kister polynomial equation. The measured refractive index values are analyzed by different theoretical mixing rules and the standard deviations are predicted. From the values of excess properties of the binary mixtures and its deviations indicate that a strong specific type of interaction is formed between the amino group (–NH_2) of aniline and *o*-anisidine with hydroxyl group (–OH) of 2-alkoxyethanols. The strength of interaction is in the following order: aniline > *o*-anisidine in 2-alkoxyethanols (2-BE > 2-EE > 2-ME). Further the hydrogen bonding interaction of anilines with 2-alkoxyethanols is confirmed by FT-IR spectra.

1. Introduction

The information about physical and thermodynamic properties of liquid mixtures is most important in the field of molecular modelling and drug designing [1–3]. The physico-chemical properties like densities, viscosities and refractive indices of liquid and liquid mixtures are used to identify the behaviour of molecules and its nature of structure making/breaking effect in the systems. Nowadays the knowledge of refractive index at different temperatures of liquid mixtures gives the type and nature of interaction. Also it can be useful in engineering calculations. Volumetric studies in binary mixtures have been undertaken in order to gain information about intermolecular interactions between the donor-acceptor types of molecules [4–7]. Thermodynamic properties of binary liquid mixtures formed by one or two components associated through hydrogen bonds are important from both theoretical and process design aspects [8]. In this present work the molecular interactions are studied for aromatic amines with alcohols (i.e.) aniline and *o*-anisidine with 2-alkoxyethanols like 2-methoxyethanol ($C_2H_8O_2$), 2-etoxyethanol ($C_4H_{10}O_2$) and 2-butoxyethanol ($C_6H_{14}O_2$). The major use of aniline is to act as a precursor in indigo colour, the blue of blue jeans in the dye industry. Drugs are prepared from its derivatives. *o*-Anisidine is mainly used in the manufacture of dyes for tattooing and coloration of paper. 2-Alkoxyethanols are used as a solvent for many different purposes such as varnishes, dyes, and resins. 2-Alkoxyethanols are a very interesting class of solvent having ether, i.e. oxygen (–O–) and hydroxyl (–OH–) group and is noted for its donating and accepting ability. In this present work the compounds are different in nature, because the alkoxyethanols are aliphatic and the anilines are aromatic type. The alkoxyethanols are having a common (OH) group and anilines having (NH_2) group. In this way we identify the possible interactions between (NH_2) group of aniline with hydroxyl group (–OH) of 2-alkoxyethaol. This type of interaction studies (N–H…O–H) plays an important role in biological and drug synthesis applications. Redlich–Kister polynomial equation is used to identify the standard deviations in the experimental and theoretical values of the binary liquid mixtures. Seven different theoretical mixing rules are used in this present study [15], by calculating the average deviations in experimental and theoretical values of refractive indices. FT-IR studies are also carried out for the identification of hydrogen bonding interactions between liquid mixtures.

2. Materials and methods

All compounds used in this work were supplied by Loba (purity ≫ 99%) chemicals and were used as such without further purification. The purity of chemicals was checked by comparing their densities with literature values. The binary mixtures were prepared using airtight stoppered bottles (due to evaporation) and weight of the empty bottle was measured by digital electronic balance (Anamad, M-300DR) with accuracy ±0.001 g. The weights were measured at least three times for accuracy of the composition of mixtures. The density values of liquid and liquid mixtures were measured using a double armed pycnometer which has a bulb volume of 10 mL. The pycnometer

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Table 1
Experimental and literature values of pure components at 303.15 K.

Compounds	Experimental			Literature		
	ρ g cm^{-3}	η mPa s	n_D	ρ g cm^{-3}	η mPa s	n_D
Aniline	1.0139	3.7462	1.5855	1.0131 [10]	3.7701 [11]	1.5855 [12]
o-Anisidine	1.0917	4.9236	1.5705	1.0923 [10]	—	1.574 [14]
2-Methoxyethanol	0.9553	1.9678	1.4005	0.9558 [9]	1.9911 [13]	1.3983 [9]
2-Ethoxyethanol	0.9205	1.8447	1.4060	0.9212 [9]	2.1001 [13]	1.4065 [9]
2-Butoxyethanol	0.8922	2.8227	1.4170	0.8923 [9]	2.8227 [14]	1.4150 [9]

was calibrated with freshly prepared double distilled water. A digital electronic balance was used in the density measurements. The viscosities of pure and binary liquid mixtures were measured using an Ostwald's viscometer and it was calibrated with double distilled water. The measurement of flow time of the solution between the two points of the viscometer was performed at least five times for each solution and the result was averaged. The time flow was measured using digital stop watch with an accuracy of ± 0.01 s. The viscometer was fitted vertically in the thermostat at constant temperature. For all the measurements, temperature was controlled by circulating water bath through an ultra thermostat (Concord) with an accuracy of ± 0.01 K. The uncertainty in density, viscosity and refractive index measurements was within ± 0.0001 g cm^{-3}, $\pm 2\times10^{-4}$ mPa s and ± 0.0001. FT-IR measurements were measured at equimolar ratio of each molecule and diluted with CCl_4. The formation of hydrogen bonds in the binary mixtures was studied in the 400–4000 cm^{-1}region with a Shimadzu FT-IR spectrometer.

3. Result and discussions

Table 1 contains the experimental and literature values of aniline, *o*-anisidine and 2-alkoxyethanols at 303.15 K. A perusal of Tables 2 and 3 provides the experimental values of density, viscosity and refractive index of the binary liquid mixtures of aniline and *o*-anisidine (2-methoxyaniline) with 2-alkoxyethanols at 303.15 K. As the concentration of aniline and *o*-anisidine increases in the binary mixtures, the values of densities, viscosities and refractive indices also

Table 2
Experimental values of density (ρ), viscosity (η), refractive index (n_D), molar refraction (R_m) and polarizability (α) of aniline + 2-alkoxyethanol binary mixtures at 303.15 K.

Mole fraction X_2	Density ρ g cm^{-3}	Viscosity η mPa s	Refractive index n_D	Molar refraction R_m (m^3 mol^{-1})	Polarizability $\alpha\times10^{-26}$ cm mol^{-1}
Aniline + 2-methoxyethanol					
0.0000	0.9553	1.9678	1.4005	19.3314	0.7666
0.0881	0.9637	2.1559	1.4165	20.2256	0.8021
0.1786	0.9731	2.3514	1.4335	21.1575	0.8390
0.2716	0.9815	2.5549	1.4510	22.1427	0.8781
0.3671	0.9895	2.7568	1.4685	23.1544	0.9182
0.4652	0.9965	2.9551	1.4865	24.2272	0.9608
0.5661	1.0022	3.1293	1.5045	25.3529	1.0054
0.6700	1.0056	3.2843	1.5235	26.6039	1.0550
0.7768	1.0093	3.4368	1.5435	27.9170	1.1071
0.8867	1.0119	3.5913	1.5640	29.2710	1.1608
1.0000	1.0134	3.7462	1.5855	30.7076	1.2178
Aniline + 2-ethoxyethanol					
0.0000	0.9205	2.1081	1.4060	24.0479	0.9537
0.1062	0.9364	2.2661	1.4230	24.5940	0.9753
0.2109	0.9499	2.3937	1.4400	25.1796	0.9985
0.3142	0.9627	2.5226	1.4575	25.7865	1.0226
0.4162	0.9741	2.7395	1.4750	26.4104	1.0474
0.5167	0.9841	2.9396	1.4925	27.0508	1.0727
0.6160	0.9925	3.1144	1.5110	27.7603	1.1009
0.7139	1.0002	3.2772	1.5295	28.4744	1.1292
0.8105	1.0063	3.4350	1.5480	29.2145	1.1586
0.9059	1.0125	3.5948	1.5665	29.9331	1.1871
1.0000	1.0139	3.7462	1.5855	30.7076	1.2178
Aniline + 2-butoxyethanol					
0.0000	0.8922	2.8227	1.4170	33.3074	1.3209
0.1380	0.9114	2.9991	1.4385	33.0720	1.3115
0.2648	0.9273	3.1559	1.4585	32.8465	1.3026
0.3818	0.9422	3.2868	1.4770	32.5645	1.2914
0.4900	0.9559	3.4001	1.4945	32.2718	1.2798
0.5903	0.9685	3.4859	1.5120	32.0264	1.2701
0.6837	0.9798	3.5534	1.5285	31.7750	1.2601
0.7708	0.9901	3.6136	1.5440	31.5177	1.2499
0.8522	1.0007	3.6656	1.5588	31.2278	1.2384
0.9284	1.0100	3.7069	1.5725	30.9439	1.2271
1.0000	1.0139	3.7462	1.5855	30.7076	1.2178

Table 3
Experimental values of density (ρ), viscosity (η), refractive index (n_D), molar refraction (R_m) and polarizability (α) of *o*-anisidine + 2-alkoxyethanol binary mixtures at 303.15 K.

Mole fraction of anisidine X_2	Density ρ g cm^{-3}	Refractive index n_D	Viscosity η mPa s	Molar refraction R_m cm^3 mol^{-1}	Polarizability $\alpha\times10^{-26}$ cm mol^{-1}
o-Anisidine + 2-methoxyethanol					
0.0000	0.9553	1.4005	1.9678	19.3314	0.7323
0.0724	0.9703	1.4080	2.2250	20.2154	0.7779
0.1494	0.9861	1.4135	2.5072	21.0488	0.8231
0.2314	1.0012	1.4210	2.8080	22.0420	0.8752
0.3190	1.0158	1.4295	3.1323	23.1581	0.9329
0.4127	1.0300	1.4420	3.4780	24.5497	1.0028
0.5131	1.0436	1.4595	3.7944	26.2987	1.0884
0.6211	1.0563	1.4845	4.0827	28.5667	1.1966
0.7376	1.0680	1.5115	4.3433	31.1189	1.3180
0.8635	1.0796	1.5410	4.6140	33.9833	1.4549
1.0000	1.0917	1.5705	4.9236	37.0375	1.6035
o-Anisidine + 2-ethoxyethanol					
0.0000	0.9205	1.4060	2.1081	24.0479	0.8779
0.0875	0.9398	1.4190	2.2001	24.9960	0.9316
0.1775	0.9588	1.4310	2.5468	25.9184	0.9855
0.2701	0.9776	1.4435	2.9081	26.8951	1.0426
0.3653	0.9955	1.4560	3.2675	27.9143	1.1020
0.4633	1.0129	1.4700	3.6025	29.0513	1.1669
0.5643	1.0297	1.4875	3.9169	30.4171	1.2420
0.6683	1.0456	1.5075	4.1799	31.9698	1.3256
0.7755	1.0612	1.5280	4.4356	33.5899	1.4136
0.8860	1.0768	1.5485	4.6809	35.2454	1.5050
1.0000	1.0917	1.5705	4.9236	37.0375	1.6035
o-Anisidine + 2-butoxyethanol					
0.0000	0.8922	1.4170	2.8227	33.3074	1.1785
0.1150	0.9153	1.4355	3.2101	33.8885	1.2300
0.2262	0.9371	1.4535	3.5385	34.4418	1.2800
0.3338	0.9585	1.4705	3.8468	34.9152	1.3271
0.4380	0.9795	1.4870	4.1160	35.3404	1.3727
0.5390	0.9998	1.5025	4.3339	35.7033	1.4156
0.6369	1.0190	1.5170	4.4944	36.0276	1.4559
0.7318	1.0376	1.5310	4.6290	36.3222	1.4946
0.8238	1.0563	1.5445	4.7414	36.5720	1.5319
0.9132	1.0742	1.5575	4.8387	36.8028	1.5678
1.0000	1.0917	1.5705	4.9236	37.0375	1.6035