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Study of Volumetric and Viscometric properties on Non Aqueous–Non Electrolyte Liquid mixtures of Propanoic acid, N, N Dimethyl Aniline and N, N-Diethyl Aniline

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Abstract
Volumetric and viscometric properties on non aqueous–non electrolyte liquid mixtures were studied. The apparent molar volumes, standard partial molar volumes in dilute solutions, transfer apparent molar volumes at infinite dilution and viscosity B-coefficients were determined. Knowledge of the temperature dependence of excess properties of liquid mixtures provides valuable information on the nature of inter molecular interactions existing among the component molecules. The volumetric and viscometric study of molecular interactions in some non aqueous–non electrolyte liquid mixtures is presented in this chapter. These molecular interactions are studied at three different temperatures (303.15, 313.15 and 323.15 K). It was concluded that the behavior of volumetric and viscometric properties in studied ternary system is mainly determined by hydrophobic interactions.

Keywords: Propanoic acid, non electrolyte liquid mixtures, volumetric properties, viscometric properties

1. Introduction
The volumetric and viscometric study of non aqueous – non electrolyte liquid mixtures enables the determination of some useful thermodynamic and other properties that are highly sensitive to molecular interactions [1–4]. Pyridinium cationic surfactants have bactericidal activity against a wide range of Gram-positive and some Gram-negative organisms [5]. Propanoic acid (PpA) has immune-stimulating effect, e.g. important for defense against infections such as common cold. It also acts as inhibitor of histamine, a compound that is released during allergic reaction. As a powerful antioxidant it can neutralize pollutants and toxins. Ascorbic acid plays an important role for the synthesis of several important peptide hormones neurotransmitters and creatinine. The studies on partial molar volume and viscosity of cationic surfactants in aqueous vitamins solutions are rare [6, 7]. Volumetric and viscometric properties are important because they reflect the effects of solute–solute and solute–solvent interactions. Knowledge of the temperature dependence of excess properties of liquid mixtures provides valuable information on the nature of inter molecular interactions existing among the component molecules [8, 9, 10]. Thermodynamic properties of liquid acid-base mixtures were studied [8, 9, 10, 17], with propanoic acid as one component in binary mixtures. Study of volumetric and viscometric properties in propanoic acid with equimolar mixture of N,N-dimethyl formamide + methanol/ethanol/1-propanol is depicted in this paper. Previous literature shows that, [14, 15, 16, 18] studied the density and viscosity studies of binary mixtures of aniline+benzene and ternary mixtures of (aniline+benzene + N, N-dimethyl formamide) at 298.15, 303.15, 308.15, and 313.15 K. Intermolecular interaction studies in organic ternary liquid mixtures benzene, chlorobenzene and nitrobenzene with N,N-dimethyl formamide (DMF) in cyclohexane by ultrasonic velocity measurements was studied [19]. Densities, excess molar volumes, viscosity, and refractive indices studies of binary and ternary liquid mixtures of methanol (1) + ethanol (2) + 1,2-propanediol (3) at 81.5 kPa were carried out [11, 12, 13, 20]. The variations of the properties with composition as well as with temperature are discussed in terms of molecular interactions existing among the molecules of these mixtures.

Deviation/excess properties are fitted to Redlich-Kister type polynomial equation. The experimental viscosity data of all binary/equimolar liquid mixtures are correlated with the viscosity models such as Grunberg and Nissan, Hind *et al*., Katti and Chaudhrai, and Heric and Brewer. The volumetric and viscometric studies of molecular interactions in some non aqueous–non electrolyte liquid mixtures are presented in this paper. These molecular interactions are studied at three different temperatures (303.15, 313.15 and 323.15 K).

Materials and Methods

High purity and Analytical Reagent (AR) grade compounds of propanoic acid, N,N dimethyl aniline and N,N-diethyl aniline obtained from LOBA chemicals, India are used in the present study. All the chemicals are further purified by standard methods [21, 22], distillation, fractional distillation under reduced pressure and only middle fractions were collected. Finally, after purification method the purity of the propanoic acid, N, N-dimethyl aniline and N,N-diethyl aniline is found to be w = 0.997, w = 0.993 and w = 0.993 respectively. Before use, the chemicals were stored over 0.4 nm molecular sieves approximately for 72 hr to remove water content and degassed. Binary mixtures of propanoic acid with N,N-dimethyl aniline and N,N-diethyl aniline (PA+DMA and PA+DEA) are prepared by mass in air tight bottles over the entire composition range of propanoic acid (i.e. 0 to 100% of PA). The mass measurements are performed on a METTLER TOLEDO (Switzerland make) ABB5- S/FACT digital balance with an accuracy ±0.01mg. The uncertainty in the mole fraction is 10-4. Densities of pure liquids and their mixtures have been determined by using a 5 cm3 two stem double-walled Parker & Parker type pyknometer [23]. This pyknometer is calibrated with triply distilled water. An Ostwald viscometer has been used to determine the viscosity of the liquid mixture, which is calibrated as described by Subramanyam Naidu and Ravindra Prasad [24] using triply distilled water. The viscometer was also calibrated using benzene, CCl4 liquids etc at working temperatures. The length of one of the capillary tube of viscometers used in the present study is 8 cm and its diameter is 0.56 mm. The reproducibility in the measured parameters density and viscosity are 3 in 105 parts and ± 0.2% respectively.

The experiment is performed at three different temperatures 303.15, 313.15 and 323.15 K. The densities and viscosities measured at 303.15 K and 313.15 K for the pure liquids used in this investigation are compiled in Table 1 together with the literature data [8, 11, 13] available. These results are in good agreement with the reported data.

Table 1: Comparison of densities (*p*) and viscosities (*n*) of pure liquids with literatures data at 303.15 and 313.15 K

Component	temp. T/K	ρ/kg·m^{-3}		η/10^{-3}N·s·m^{-2}	
		present work	literature	present work	literature
Propanoic acid	303.15	982.1	982.0 [8]	0.950	0.9498[8]
	313.15	973.4	971.0 [8]	0.848	0.8453[8]
N,N-dimethyl aniline	303.15	948.0	948.0 [13]	1.174	1.173 [11]
	313.15	938.5	939.75 [11]	0.982	0.985 [11]
N,N-diethyl aniline	303.15	926.0	925.9 [13]	1.703	1.709 [13]
	313.15	917.7	918.0 [13]	1.402	1.402 [13]

Results and Discussion

The experimental values of densities (ρ) and viscosities (η) are reported in Tables 2 and 3 for DMA+PA and DEA+PA binary mixtures respectively. It has been observed that the density varies almost linearly with the concentration of propanoic acid as well as with temperature but the viscosity changes non-linearly showing maxima in all the systems studied at all temperatures investigated. This type of behaviour could be attributed to complex formation. The experimental values of density and viscosity are used to calculate the deviation/excess properties such as deviation in viscosity, Δη, excess molar volume, E Vm and excess Gibbs free energy of activation of viscous flow, ΔG*E. The deviation/excess properties are illustrated in Table 4. Generally, negative values of Δη indicate the presence of dispersion forces or mutual loss of specific interactions in like molecules operating in the systems arising due to weak intermolecular interactions and positive values of deviation in viscosity indicate strong specific interactions [25, 26]. The sign and magnitude of Δη depend on the combined effect of factors such as molecular size, shape, and intermolecular forces. In general ethyl groups are more +I effect than methyl groups. In DEA the ethyl groups are more electrons releasing than methyl groups of DMA on nitrogen atom. So, the nitrogen in DEA possesses more electron density than in DMA, therefore DEA is more favoured to accept the proton of the PA. Hence it is an appropriate reason to support the observed more positive Δη values in propanoic acid + N,N-diethyl aniline system.

Table 2: Experimental values of densities (*p*) and viscosities (*n*) with mole fraction ofpropanoic acid, X for N, N-diethyl aniline + propanoic acid binary system at 303.15 and 313.15 and 323.15 K

x	$T = 303.15$ K		$T = 313.15$ K		$T = 323.15$ K	
	ρ/kg·m^{-3}	η/10^{-3}N·s·m^{-2}	ρ/kg·m^{-3}	η/10^{-3}N·s·m^{-2}	ρ/kg·m^{-3}	η/10^{-3}N·s·m^{-2}
0.0000	948.0	1.174	938.5	0.982	930.7	0.826
0.1020	954.4	1.270	943.7	1.019	934.8	0.843
0.2054	959.8	1.329	949.1	1.058	939.7	0.869
0.3071	964.5	1.386	954.2	1.093	944.5	0.895
0.4092	969.3	1.446	959.2	1.124	949.1	0.920
0.5107	974.0	1.494	964.0	1.149	953.5	0.940
0.6178	978.6	1.545	968.6	1.151	958.0	0.944
0.7083	982.2	1.534	972.2	1.119	961.1	0.912
0.8023	985.3	1.457	975.3	1.060	963.5	0.864
0.8987	986.4	1.225	975.7	0.965	963.5	0.778
1.0000	982.1	0.950	973.4	0.848	961.4	0.706

The deviation of a physical and chemical property of the liquid mixture from the ideal behaviour is a measure of the interaction between molecules of the components of liquid mixtures and such type of deviation is generally attributed to dipole-dipole interactions and hydrogen bond between unlike molecules [27] respectively. The factors that are mainly responsible for the expansion of volume i.e. positive values of E Vm are: (i) breaking one or both of the components in a solution i.e. loss of dipolar association between the molecules (dispersion forces). (ii) The geometry of molecular structures which does not favour the fitting of molecules of one component into the voids created by the molecules of other component. (iii) Steric hindrance of the molecules. The negative values of E Vm are due to strong specific interactions such as (iv) association of molecules through the formation of hydrogen bond (or) association due to dipole-dipole interactions (or) association due to induced dipole-dipole interactions (v) accommodation of molecules due to larger differences in molar volumes.

Table 3: Experimental values of densities (*p*) and viscosities (*n*) with mole fraction ofpropanoic acid, X for N, N-diethyl aniline + propanoic acid binary system at 303.15 and 313.15 and 323.15 K

x	$T = 303.15$ K		$T = 313.15$ K		$T = 323.15$ K	
	ρ/kg·m^{-3}	η/10^{-3}N·s·m^{-2}	ρ/kg·m^{-3}	η/10^{-3}N·s·m^{-2}	ρ/kg·m^{-3}	η/10^{-3}N·s·m^{-2}
0.0000	926.0	1.703	917.7	1.402	912.8	1.049
0.1047	933.4	1.801	924.6	1.450	919.5	1.068
0.2096	942.1	2.040	932.8	1.590	926.4	1.173
0.3142	952.1	2.404	942.2	1.765	934.9	1.315
0.4164	963.8	2.910	953.7	2.118	944.3	1.555
0.5177	977.9	3.663	967.3	2.527	955.3	1.865
0.6097	989.1	4.040	977.5	2.880	965.3	2.100
0.7077	996.2	3.968	984.0	2.738	971.3	1.949
0.8123	995.0	3.260	982.7	2.086	974.7	1.510
0.9156	990.9	1.532	980.1	1.247	974.2	0.972
1.0000	982.1	0.950	973.4	0.848	961.4	0.706

The variation of excess molar volume in the present investigation is negative over the entire mole fraction range. Both the components of the liquid mixtures studied are polar molecules in nature. The observed negative E Vm values are due to the interaction between the proton of acid and lone pair of electrons on the nitrogen atom of aniline/resonant electron density on benzene ring of substituted aniline. Due to the large difference in molar volumes/masses of propanoic acid and substituted anilines accommodation of smaller molecules of one component into the voids created by the other component of molecules is also responsible for observed negative E Vm values. The above factors are responsible for the negative values of E Vm [28].

Table 4: Calculated values of deviation in viscosities, Δη, excess molar volumes, V Em and excess Gibbs free energy, ΔG^{*E}, with mole fraction of propanoic acid, X for all binary system at 303.15 and 313.15 and 323.15 K

N,N-dimethyl aniline+propanoic acid				*N,N*-diethyl aniline+propanoic acid			
x	V_m^E / $10^{-6}m^3.mol^{-1}$	Δη/ $10^{-3}N\cdot s\cdot m^{-2}$	ΔG^{*E}/ kJ.mol^{-1}	x	V_m^E / $10^{-6}m^3.mol^{-1}$	Δη/ $10^{-3}N\cdot s\cdot m^{-2}$	ΔG^{*E}/ kJ.mol^{-1}
			T =303.15 K				
0.0000	0.00	0.000	0.00	0.0000	0.00	0.000	0.00
0.1020	-0.55	0.1190	268.79	0.1047	-0.73	0.177	338.96
0.2054	-0.89	0.201	454.02	0.2096	-1.51	0.495	840.03
0.3071	-1.10	0.281	626.40	0.3142	-2.29	0.938	1428.44
0.4092	-1.25	0.364	794.98	0.4164	-3.10	1.521	2065.96
0.5107	-1.35	0.434	933.08	0.5177	-3.96	2.350	2784.62
0.6178	-1.36	0.510	1071.60	0.6097	-4.34	2.796	3150.72
0.7083	-1.31	0.519	1092.57	0.7077	-4.07	2.798	3233.22
0.8023	-1.16	0.463	1000.37	0.8123	-2.89	2.169	2879.75
0.8987	-0.80	0.253	599.88	0.9156	-1.51	0.519	1103.60
1.0000	0.00	0.000	0.00	1.0000	0.00	0.000	0.00
			T =313.15 K				
0.0000	0.00	0.000	0.00	0.0000	0.00	0.000	0.00
0.1020	-0.40	0.050	154.36	0.1047	-0.67	0.106	271.21
0.2054	-0.75	0.103	308.96	0.2096	-1.39	0.304	683.59
0.3071	-1.00	0.152	444.26	0.3142	-2.11	0.537	1115.45
0.4092	-1.19	0.197	563.42	0.4164	-2.93	0.947	1730.10
0.5107	-1.29	0.236	661.49	0.5177	-3.77	1.412	2312.60
0.6178	-1.30	0.252	703.33	0.6097	-4.08	1.816	2759.00
0.7083	-1.24	0.232	656.09	0.7077	-3.78	1.728	2739.68
0.8023	-1.09	0.186	537.39	0.8123	-2.60	1.135	2157.44
0.8987	-0.66	0.103	314.66	0.9156	-1.35	0.353	923.99
1.0000	0.00	0.000	0.00	1.0000	0.00	0.000	0.00
			T =323.15 K				
0.0000	0.00	0.000	0.00	0.0000	0.00	0.000	0.00
0.1020	-0.29	0.030	121.77	0.1047	-0.70	0.055	206.00
0.2054	-0.63	0.068	264.12	0.2096	-1.29	0.196	608.00
0.3071	-0.90	0.106	396.53	0.3142	-1.97	0.374	1049.00
0.4092	-1.09	0.143	519.66	0.4164	-2.61	0.649	1618.00
0.5107	-1.20	0.175	622.05	0.5177	-3.25	0.994	2209.72
0.6178	-1.24	0.192	675.08	0.6097	-3.67	1.260	2609.58
0.7083	-1.19	0.171	611.59	0.7077	-3.43	1.143	2496.83
0.8023	-1.01	0.134	492.24	0.8123	-2.80	0.740	1894.46
0.8987	-0.60	0.060	237.53	0.9156	-1.80	0.237	784.00
1.0000	0.00	0.000	0.00	1.0000	0.00	0.000	0.00

From the tables 3 and 4 it has been observed that as the temperature of the systems increases the negative excess molar volumes decrease indicating the decrease of interaction between the unlike molecules. The negative excess molar volumes follows the order N, N-diethyl aniline > N,N-dimethyl aniline hence the strength of interactions as follows, N,N-diethyl aniline > N,N-dimethyl aniline. The ΔG*E are found to be positive for both the systems and at all temperatures. These positive values are indicating the existing of strong interactions between the components of unlike molecules. As temperature increases these positive values are found to decrease which shows the decrease of interaction between constituent molecules. The values of deviation in viscosity and excess molar volume have been fitted to Redlich-Kister type polynomial [29] equation. The smaller standard deviation values show that the polynomial better fits the calculated properties. The partial molar volumes, 1 mV of component 1(PA) and, 2 mV of component 2 (DMA/DEA) in the mixtures over the entire composition range are calculated. The dynamic viscosities of the binary liquid mixtures have been calculated using various empirical relations like Grunberg and Nissan [30], Hind and Ubbelohde [31], Katti and Chaudari [32], Heric and Brewer [33] and the corresponding interaction parameters are also evaluated. Further the interaction parameter values are found to decrease with an increase of temperature for all the systems studied. These results are in good agreement with the results derived from the excess properties. Prolongo *et al* [34] reported positive values of interaction parameter corresponding to systems with negative excess molar volumes. This is in good agreement with our results. The estimated values of σ are smaller indicating that experimental values of viscosities are well correlated by all the viscosity models.

Conclusions

Densities and viscosities of binary mixtures of propanoic acid with N, N-dimethyl aniline and N, N-diethyl aniline are measured over the entire composition range at T=(303.15, 313.15, and 323.15) K. The deviations in viscosity, excess molar volumes are computed from the experimental results. These deviation/excess properties have been fitted to Redlich Kister type polynomial. These results indicate the presence of strong specific interactions such as interactions between proton of propanoic acid and lone pair of electrons on the nitrogen atom of aniline and due to the observed difference in molar volumes of propanoic acid and substituted aniline is responsible for the observed negative E Vm and positive Δη values in the present investigated systems. The strength of interactions follows the order N, N-diethyl aniline + propanoic acid > N, N-dimethyl aniline + propanoic acid. The strength of interactions was also studied with the variation of temperature. The experimental viscosity values are compared with the viscosity values obtained from different empirical relations and these are in good agreement with the experimental values.

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