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Excess Molar Quantities of Binary Mixture of Dipropyl amine with Aliphatic Alcohols at 298.15 K

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ABSTRACT

Refractive indices (n_D), viscosities (η) and densities (ρ) were deliberated for the binary mixtures created by dipropyl amine with 1-octanol, 1-heptanol, 1-hexanol, 1-pentanol and tert-pentyl alcohol at temperature 298.15 K over the perfect installation extent. The function of Redlich-Kister were used to calculate and renovated of the refractive index deviations (Δn_D), viscosity deviations (η^E), excess molar Gibbs free energy (ΔG^{*E}) and excess molar volumes(V_m^E). The standard errors and coefficients were respected by this function. The values of Δn_D, η^E, V_m^E and ΔG^{*E} were plotted against mole fraction of dipropyl amine. In all cases the obtained η^E, ΔG^{*E}, V_m^E and Δn_D values were negative at 298.15K. Effect of carbon atoms number in the chain of alcohol and hydroxyl groups' position on molecular interactions in these mixtures has also been discussed.

Keywords: Binary system, Aliphatic alcohols, Dipropylamine, Viscosity, Refractive index, Density and Excess properties.

INTRODUCTION

The familiarity of the excess parameters of organic liquid blends is salutary in industrial enforcements and is highly significant for understanding the molecular interactions between the components this as well assist to develop theoretical patterns[1-3]. The experimental conclusions are adduced in this paper for the binary system of dipropyl amine with 1-alkanols and tert-pentyl alcohol at 298.15 K. These conclusions expose the cross-association between alkanol and amine molecules down the identical conditions[4-6]. Also the conclusions display the steric hindrance of methyl groups. Alcohols are polar and self-associated through hydrogen bonding in the state alcohols are multilateral solvents used in the division of saturated and unsaturated hydrocarbons and in medicinal synthesis and serve as solvents for numerous polymers[7]. A survey of the literature detects sundry on the excess properties of binary mixtures including amines and alcohols[8-13]. The thermodynamic properties of multicomponent systems are some major parameters for the layout and optimization of

chemical process. Although many surveys on density and viscosity have been recorded[14-15].

Alcohols are highly paramount solvents in a numeral of processing procedures and have sundry enforcements as reagents or solvents, hand sanitizers, antifreeze, and antiseptics as well as keeper in learning and métier[16]. Amines are compounds contain on basic nitrogen atom carried a lone pair. Derivatives of ammonia are known amines, which contains one or more hydrogen atoms have been replaced by substituent such as an alkyl or aryl group. Amines are highly paramount several enforcement for example; dipropyl amine is a secondary amine whose belongs to the class of dialkyl amines. It is multilateral medium with a diversity of enforcements. Most paramount enforcements are found in the field of agricultural chemicals; however, also substantial volumes are wasted for the produce of other non- agricultural chemicals.

EXPERIMENTAL

Liquid materials

The following liquid materials were used are:

Name of material	Chemical formula	Purity	Name of company
Dipropyl amine	$C_6H_{15}N$	99%	Aldrich & Co
1-Pentanol	$C_5H_{12}O$	99%	Aldrich & Co
1-Hexanol	$C_6H_{14}O$	98%	Aldrich & Co
1-Heptanol	$C_7H_{16}O$	98%	Aldrich & Co
1-Octanol	$C_8H_{18}O$	99%	Aldrich & Co
tert-Pentyl alcohol	$C_5H_{12}O$	98%	Aldrich & Co

Chemicals

Table 1: Comparison of experimental, viscosities (η), densities (ρ) and refractive index (n_D) of pure liquids with literature data at 298.15 K.

Liquid	η(mpas)		ρ(g.cm^{-3})		n_D	
	Experimental	Literature	Experimental	Literature	Experimental	Literature
Dipropyl amine	0.51734	0.50685[17]	0.73825	0.73133[18]	1.40362	1.40184[19]
				0.73564[19]		
				0.7333[62]		
1-Pentanol	3.5411	3.53441[21]	0.81084	0.81083[24]	1.40812	1.40781[24]
		3.53241[22]		0.81076[25]		1.40823[26]
		3.34785[23]		0.81072[22]		1.40953[27]
1-Hexanol	4.59242	4.59324[28]	0.81503	0.81523[28]	1.41775	1.41589[31]
		4.59112[29]		0.8152[23]		
1-Heptanol	5.94435	5.94432[32]	0.81876	0.81873[32]	1.41987	1.42254[33]
		6.00162[28]		0.81879[28]		1.42262[32]
1-Octanol	7.66058	7.59812[28]	0.82165	0.82172[33]	1.42645	1.42835[34]
		7.66153[32]		0.82182[29]		1.42823[24]
tert-Pentyl alcohol	3.52642	3.53346[35]	0.80447	0.804337[35]	1.40186	1.40237[35]
		3.54825[36]		0.80507[36]		1.40246[24]

Density measurement

Densities of pure components and liquid-liquid mixtures were measured with an Anton paar digital densimeter (Model DMA 60/602) with an accuracy of ± 10^{-5} g.cm^{-3}. Air and double distilled water used for the calibration of the densimeter. At least three times for each composition in experimental were generally repeated and the results were treatment.

Viscosities measurements

By using a suspended-level ubbelohde viscometer in a bath controlled to ± 0.01 K at 298.15 K was determined the viscosities. To give the final values the experimental were repeated at least three times and the results were corrected.

Refractive index measurements

By using a digital Abbe refractometer (Model: BOE 32400) were determined the refractive

indices of pure components and their liquid-liquid mixtures. The measuring refractive indices of double distilled water and toluene were used to calibrate the refractometer at 298.15 K.

RESULTS AND DISCUSSION

Table 2 shows experimental viscosities, densities, refractive indices, deviation in viscosity, excess volumes, refractive index deviation and excess molar Gibbs free energy for five binary systems dipropyl amine with some alcohols and tert-pentyl alcohol at 298.15 K.

The excess molar volumes (V_m^E) were matured from density data according to:

$$V_m^E = \sum_{i=1}^{N} X_i M_i (\rho^{-1} - \rho_i^{-1}) \quad (1)$$

Where ρ_i, X_i and Mi are the density, mole fraction and molar mass of the component i, ρ is the density of mixtures, n is the number of components.

Table 2: Densities ρ, viscosities η, refractive index n_D, excess molar volumes V_m^E, viscosity deviations η^E, excess molar Gibbs free energy ΔG^{*E} and refractive index deviation Δn_D of dipropylamine and alcohols at 298.15 K

Dipropylamine + 1-pentanol							
X_1	ρ(g cm^{-3})	V_m^E (cm^3 .mole^{-1})	n_D	Δn_D (cm^3 mole^{-1})	η(map.s)	η^E (mpa.s)	ΔG^{*E} (kj.mole^{-1})
0.0000	0.81084	0.0000	1.40812	0.0000	3.53411	0.0000	0.0000
0.1023	0.80304	-0.18339	1.40711	-0.18198	2.79173	-0.03923	-0.09073
0.1989	0.79666	-0.48158	1.40699	-0.26683	2.20124	-0.09125	-0.21509
0.2760	0.79223	-0.72726	1.40685	-0.31225	1.84520	-0.11953	-0.28256
0.3698	0.78665	-1.01336	1.40678	-0.33301	1.52964	-0.12685	-0.29865
0.5020	0.78081	-1.66832	1.40606	-0.35115	1.17818	-0.13389	-0.31529
0.5976	0.77225	-1.42027	1.40562	-0.33262	0.99412	-0.11998	-0.28187
0.7824	0.75485	-0.60369	1.40392	-0.28168	0.71839	-0.08981	-0.21178
0.8134	0.75349	-0.40939	1.40388	-0.24816	0.69255	-0.06687	-0.15615
0.9432	0.74247	-0.16618	1.40364	-0.08815	0.55995	-0.02998	-0.07103
1.0000	0.73825	0.0000	1.40362	0.0000	0.51734	0.0000	0.0000
Dipropylamine + 1-hexanol							
X_1	ρ(g cm^{-3})	V_m^E (cm^3 .mole^{-1})	n_D	Δn_D (cm^3 mole^{-1})	η(mpa.s)	η^E (mpa.s)	ΔG^{*E} (kj.mole^{-1})
0.0000	0.81503	0.0000	1.41775	0.0000	4.59242	0.0000	0.0000
0.0963	0.80805	-0.16181	1.41362	-0.19308	3.53586	-0.05118	-0.12509
0.2067	0.80005	-0.32685	1.41081	-0.27377	2.62279	-0.10884	-0.26817
0.3192	0.79223	-0.52383	1.40882	-0.32114	2.00411	-0.13225	-0.32562
0.4009	0.78705	-0.73774	1.40722	-0.35613	1.61593	-0.16914	-0.41689
0.5104	0.77992	-1.41890	1.40565	-0.36436	1.21287	-0.21698	-0.53538
0.5983	0.77449	-1.20197	1.40471	-0.34233	1.02298	-0.19532	-0.48182
0.6842	0.76421	-0.55365	1.40412	-0.29843	0.89202	-0.14478	-0.35668
0.8032	0.75448	-0.38876	1.40364	-0.21049	0.69967	-0.12779	-0.31525
0.9134	0.74543	-0.19249	1.40363	-0.09603	0.57572	-0.08216	-0.20294
1.0000	0.73825	0.0000	1.40362	0.0000	0.51734	0.0000	0.0000

Dipropylamine + 1-heptanol

X_1	ρ(g cm^{-3})	V_m^E (cm^3 .mole^{-1})	n_D	Δn_D (cm^3 mole^{-1})	η(mpas)	η^E (mpas)	ΔG^{*E} (kj.mole^{-1})
0.0000	0.81876	0.0000	1.41987	0.0000	5.94435	0.0000	0.0000
0.0918	0.81244	-0.14637	1.41465	-0.28905	4.24546	-0.11246	-0.27867
0.2033	0.80468	-0.32199	1.41185	-0.37162	2.96688	-0.19857	-0.49199
0.3095	0.79715	-0.47790	1.40976	-0.40419	2.01857	-0.32441	-0.80383
0.4166	0.78984	-0.69812	1.40773	-0.42831	1.38273	-0.44126	-1.09342
0.5059	0.78488	-1.09271	1.40615	-0.43801	1.05941	-0.48957	-1.21323
0.5860	0.77599	-0.66799	1.40509	-0.41849	0.93833	-0.41537	-1.02926
0.6974	0.76545	-0.40583	1.40408	-0.35380	0.79445	-0.30986	-0.76772
0.8259	0.75399	-0.24066	1.40377	-0.21445	0.65932	-0.18256	-0.45231
0.9069	0.74666	-0.12423	1.40365	-0.11902	0.58778	-0.09965	-0.24689
1.0000	0.73825	0.0000	1.40362	0.0000	0.51734	0.0000	0.0000

Dipropylamine + 1-octanol

X_1	ρ(g cm^{-3})	V_m^E (cm^3 .mole^{-1})	n_D	Δn_D (cm^3 mole^{-1})	η(mpa.s)	η^E (mpa.s)	ΔG^{*E} (kj.mole^{-1})
0.0000	0.82165	0.0000	1.42645	0.0000	7.66058	0.0000	0.0000
0.0976	0.81505	-0.10235	1.42141	-0.33971	4.25221	-0.32561	-0.80490
0.1991	0.80812	-0.23419	1.41911	-0.43279	2.81785	-0.46351	-1.14490
0.3014	0.80105	-0.39128	1.41705	-0.46881	1.86003	-0.60318	-1.48977
0.3975	0.79421	-0.53960	1.41001	-0.49983	1.32479	-0.68352	-1.68810
0.4982	0.78679	-0.68898	1.40825	-0.52734	0.9438	-0.75121	-1.85559
0.5987	0.77784	-0.59433	1.40701	-0.49186	0.84889	-0.58632	-1.44708
0.6954	0.76799	-0.31784	1.40567	-0.44746	0.74136	-0.46115	-1.13748
0.8011	0.75794	-0.20262	1.40441	-0.35821	0.65756	-0.29622	-0.72999
0.8984	0.74848	-0.10811	1.40388	-0.20527	0.60956	-0.10979	-0.26966
1.0000	0.73825	0.0000	1.40362	0.0000	0.51734	0.0000	0.0000

Dipropylamine + tert-pentyl alcohol

X_1	ρ(g cm^{-3})	V_m^E (cm^3 .mole^{-1})	n_D	Δn_D (cm^3 mole^{-1})	η(mpa.s)	η^E (mpa.s)	ΔG^{*E} (kj.mole^{-1})
0.0000	0.80447	0.0000	1.40186	0.0000	3.52642	0.0000	0.0000
0.0910	0.79747	-0.05195	1.40281	-0.09327	2.92724	-0.01157	-0.02320
0.1967	0.79155	-0.13254	1.40305	-0.20991	2.35395	-0.02669	-0.05580
0.3056	0.78334	-0.35867	1.40315	-0.29535	1.86591	-0.04998	-0.11036
0.3724	0.77989	-0.55792	1.40329	-0.32221	1.61414	-0.06672	-0.15061
0.5036	0.77138	-0.63133	1.40342	-0.34182	1.2476	-0.07248	-0.16422
0.5924	0.76454	-0.45953	1.40344	-0.32979	1.06688	-0.05853	-0.13031
0.7093	0.75625	-0.28299	1.40348	-0.27930	0.87032	-0.03778	-0.08127
0.7991	0.74998	-0.11369	1.40358	-0.21097	0.74207	-0.02485	-0.05208
0.9111	0.7433	-0.04679	1.4036	-0.10506	0.60699	-0.01082	-0.02208
1.0000	0.73825	0.0000	1.40362	0.0000	0.51734	0.0000	0.0000

The values of excess molar volumes are shown in Figure 1.

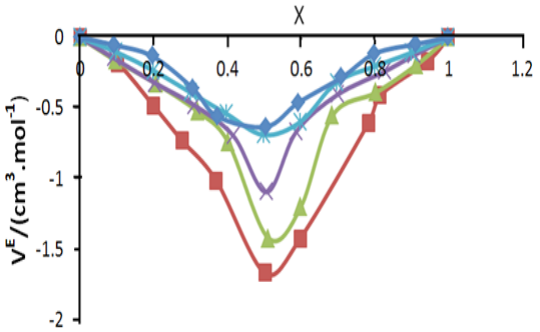

Fig. 1. Curves of excess molar volumes (V^E)Vs mole fraction (X_1) for the binary mixtures of dipropylamine+1-pentanol (□), 1-hexanol (Δ), 1-heptanol (×), 1-octanol (*) and tert-pentyl –alcohol(♦), at 298.15K

The excess molar volumesV_m^E, inspected in project were all negative over the whole range of dipropylamine composition at 298.15 K. These are shown in Fig. 1. This may suggest that volume construction takes place onto mixing dipropylamine with alcohols due to the cross-association between these various molecules[37].

And the negative values are attributable mainly to the association between amine and alcohols intermolecular hydrogen bonds between the –OH groups in alcohols and the nitrogen atoms in the amine. The strength of the associations arising from interactions between the unlike molecules was stronger than the strength of the association between like molecules[38]. The magnitude of the volume contraction follows the sequence of:

1-pentanol > 1-hexanol > 1-heptanol > 1-octanol > ter-pentyl alcohol

The viscosity deviations (η^E) for two compound mixtures can be calculated as:

$$\eta^E = \eta - \sum_{i=1}^{N} X_i \eta_i \quad (2)$$

Where η_i is the absolute viscosity of pure component i and η is the absolute viscosity of the mixtures. The (η^E) values are also graphically represented as a function of mole fraction at 298.15 K in Figure 2.

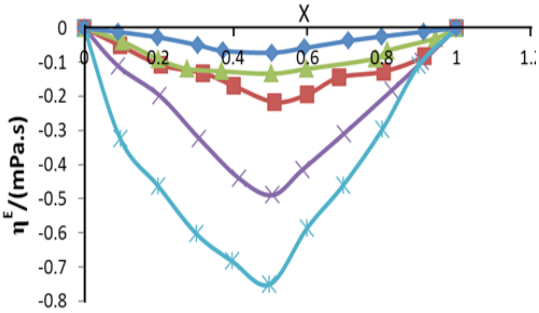

Fig. 2.Curves of viscosity devation (η^E)Vs mole fraction (X_1) for the binary mixtures of dipropylamine+1-hexanol (□), 1-pentanol (Δ), 1-heptanol (×), 1-octanol (*) and tert-pentyl –alcohol(♦), at 298.15K

Excess molar Gibbs free energy of activation of viscous flow was acquired by using:

$$\Delta G^{*E} = RT\,[\ln(\eta_m V_m) - (X_1 \ln \eta_1 V_1) - (X_2 \ln \eta_2 V_2)] \quad (3)$$

Where R is the universal constant of gases, T is a Kelvin temperature, X_1, X_2 represent mole fraction of component 1 and 2, V_1, V_2 are the molar volumes of component 1 and 2, and η_1, η_2 and η_m are the viscosity of component 1, 2 and viscosity of mixture respectively.

V_m is obtained from equation:

$$V_m = (X_1 V_1 + X_2 V_2)/\rho_m \quad (4)$$

The values excess molar Gibbs free energy is shown in Figure 3.

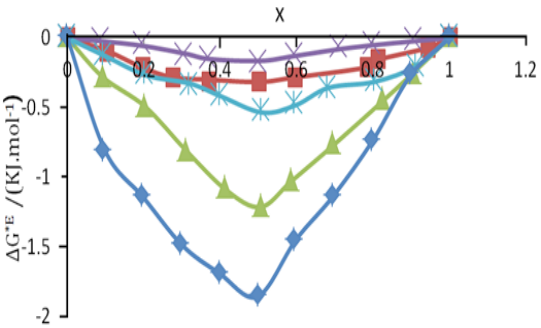

Fig. 3. Curves of excess molar Gibbs free energy (ΔG^{*E}) Vs mole fraction (X_1) for the binary mixtures of dipropylamine+1-pentanol(□),1-heptanol (Δ), tert-pentylalcohol(×), 1-hexanol (*) and 1-octanol(♦), at 298.15K

The viscosity deviations (η^E), Fig. 2 and excess molar Gibbs energy (ΔG^{*E}), Fig. 3 are negative over the whole mole fraction range at 298.15 K. These results can be attributed to the laceration of hydrogen bonded between dipropylamine and alcohols which overtake on

dipole-dipole molecular interaction between them and become less positive as the length of alkanol chain increased. The necessitation values of deviation in viscosity and excess molar Gibbs free energy for binary liquid mixtures fall in the order:

1-octanol >1-heptanol >1-hexanol >1-pentanol >ter-pentyl alcohol by Brocos *et al.,*[36] were calculated the deviation of refractive index (Δn_D) from the volume fraction average:

$$\Delta n_D = n_D - \sum_{i=1}^{N} \varphi_i n_{Di} \quad (5)$$

$$\varphi_i = X_i V_i / \sum_{i=1}^{N} X_i V_i) \quad (6)$$

Where φ_i, n_D, and n_{Di} are the volume fraction, refractive index of mixture, the density of the mixture and refractive index of pure component i respectively. V and V_i are the molar volume of the mixture and molar volume of pure component i respectively. The values of Δn_D are shown in Figure 4.

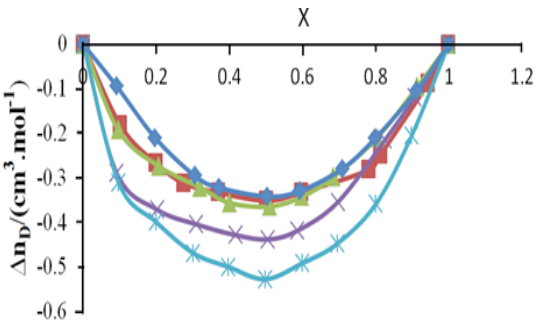

Fig. 4. Curves of refractive index devation (Δn_D) Vs mole fraction (X_1) for the binary mixtures of dipropylamine+1-pentanol (□), 1-hexanol (△), 1-heptanol (×), 1-octanol (*) and tert-pentyl –alcohol(♦), at 298.15K

The values of refractive index deviation (Δn_D) for the system containing dipropylamine and alcohols are negative values, Fig. 4. These values are due to hetero association of unlike molecules which give rise to formation of cross complexes where O-H-N bonds of the mixtures are stronger than O-H-O and N-H-N bonds of the single component solvents. In case of dipropylamine-ter-pentyl alcohol mixtures (Δn_D) give lowest negative values such behavior may be explained qualitatively by crowdies of methyl groups around the active site of alcohol (OH) and (Δn_D) for these binary mixtures follows the sequence of:

1-octanol >1-heptanol >1-hexanol >1-pentanol > ter-pentyl alcohol

The ΔG^{*E}, η^E, n_D, and V_m^E values were fitted to a Redlich-Kister- type [39] polynomial equation:

$$Y = X_i X_j \sum_{k=0}^{p} A_k (X_i - X_j)^k \quad (7)$$

Where Y is ΔG^{*E}, η^E, n_D, and V_m^E and p is a degree of polynomial expansion. Standard deviations were calculated by means of the equation:

Table 3: Parameters standard deviation of equation 7 and 8 for dipropylamine + alkanols at 298.15 K

System		A_o	A_1	A_2	σ
Dipropylamine+1-octanol		-2.44097	0.148396	2.795911	0.06421
	η_E	-2.75230	1.038491	0.885666	0.04509
	ΔG^{*E}	-6.79637	2.575367	2.195665	0.07098
	Δn_D	-2.01773	0.415549	-1.36639	0.01812
Dipropylamine+1-heptanol		-3.21208	0.172151	3.680239	0.08654
	η^E	-1.80056	0.009326	1.257793	0.04814
	ΔG^{*E}	-4.46177	0.023272	3.117813	0.07580
	Δn_D	-1.71089	0.636926	-0.755443	0.03860
Dipropylamine+1-hexanol		-4.29573	-0.866775	5.620885	0.11518
	η^E	-0.755944	-0.159739	0.096060	0.03269
	ΔG^{*E}	-1.86389	-0.396231	0.23781	0.05147
	Δn_D	-1.42871	-0.159739	-0.300361	0.02524
Dipropylamine+1-pentanol		-5.85815	-0.674100	7.409172	0.0017
	η^E	-0.536023	0.060830	0.044138	0.00783
	ΔG^{*E}	-1.26255	0.145386	0.110340	0.01223
	Δn_D	-1.38495	0.057135	-0.751003	0.02726
Dipropylamine+ter-pentyl alcohol		-2.28249	0.304666	3.523535	0.07039
	η^E	-0.272259	0.0374112	0.272345	0.01882
	ΔG^{*E}	-0.612963	0.087126	0.676092	0.02966
	Δn^D	-1.38513	0.002102	0.194445	0.01812

$$\delta = [\sum \frac{(X^{E}_{Cal} - X^{E}_{Exp})^2}{m-n}]^{0.5} \quad (8)$$

Where (m) is a number of data points and (n) are a number of estimated parameters. Values of these coefficients and the standard deviation are given in Table 3.

CONCLUSION

The densities, viscosities and refractive index of liquid-liquid mixtures of dipropylamine with 1-octanol, 1-heptanol, 1-hexanol, 1-pentanol and tert-pentyl alcohol at 298.15K were measured. The V_m^E, Δn_D, ΔG^{*E} and η^E were acquired from experimental data and were correlated using Redlich-Kister Polynomial equation. The results assure what has been formerly announced that in the solvents systems investigated, the negative values are attributable to stronger hydrogen bond formations between unlike molecules than those between like molecules and become less positive as the length of alkanol chain increased.

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