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Volumetric, Optical, Acoustical and Viscometric Study of Molecular Association in Binary Mixtures of Butylamine with 1-Butanol and Tert-Butanol

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Density (ρ), refractive index (n), ultrasonic velocity (u), and viscosity (η) were measured for the binary mixtures formed by butylamine with 1-butanol and tert-butanol at temperatures 293, 303, and 313 K over the entire composition range. Excess molar volume $V_{\mathrm{m}}^{\mathrm{E}}$, molar refraction deviation ΔR_{m}, deviation in ultrasonic velocity Δu, viscosity deviation $\Delta\eta$, and excess Gibb's free energy of activation for viscous flow $\Delta G^{*\mathrm{E}}$ were derived from the experimental data and the computed results were fitted to the Redlich–Kister polynomial equation. The values of $V_{\mathrm{m}}^{\mathrm{E}}$, ΔR_{m}, Δu, $\Delta\eta$, and $\Delta G^{*\mathrm{E}}$ were plotted against the mole fraction of butylamine. The observed positive and negative values of excess parameters for both the mixtures were explained on the basis of intermolecular interactions present in these mixtures. The higher negative values of $V_{\mathrm{m}}^{\mathrm{E}}$ and ΔR_{m} and positive values of Δu, $\Delta\eta$, and $\Delta G^{*\mathrm{E}}$ for butylamine + 1-butanol mixture suggest that specific interactions are taking place in butylamine + 1-butanol mixture, while weak dipole-dipole induced forces and dispersive forces seem to be responsible for butylamine + tert-butanol mixture. Furthermore, different empirical relations were used to correlate the binary refractive indices. An excellent agreement was found between experimental and theoretical values.

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1. Introduction

The knowledge of the thermodynamic properties of organic liquid mixtures is very important for understanding the molecular interactions between the com-

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ponents. This also helps to evolve theoretical models and is useful in industrial applications [1–4]. Excess properties of liquid systems, such as excess molar volume, deviation in molar refraction are needed for the design of separation equipment and to test the theories of the solution [5]. In addition, excess properties provide information about the molecular interactions and macroscopic behaviour of fluid mixtures and can be used to test and to improve thermodynamical models for calculating and predicting the fluid phase equilibria. The knowledge of excess Gibb's free energy of activation for viscous flow helps in understanding the molecular orientation and to study the extent of intermolecular interaction between component molecules of the liquid mixtures. In recent years, there has been considerable upsurge in the theoretical and experimental investigation of the excess thermodynamic properties of binary liquid mixtures [6, 7].

Butylamine is commonly used as an intermediate for the production of pharmaceuticals, dyestuffs, emulsifying agents, insecticides, synthetic tanning agents, and rubber chemicals. Also, butylamine is used as a raw material for herbicides, corrosion inhibitors, vulcanization accelerators, and flotation agents.

Alcohols are self associated organic liquids and are widely used as basic organic compound for the synthesis of other organic compounds; *n*-butylalcohols have been administered to patients for the control of postoperative pain in otolaryngeal surgery and for an unexplained anti-haemorrhagic effect in those with far advanced cancer.

In order to examine molecular interactions in the mixture of butylamine with alcohols through excess properties viz. excess molar volume V_m^E, molar refraction deviation ΔR_m, deviation in ultrasonic velocity Δu, viscosity deviation $\Delta\eta$, and excess Gibb's free energy of activation for viscous flow $\Delta G^{*\mathrm{E}}$, we report here density (ρ), refractive index (n), ultrasonic velocity (u), and viscosity (η) of binary mixtures of butylamine with 1-butanol and tert-butanol over the entire composition range at temperatures 293, 303, and 313 K. Further, seven mixing rules for the prediction of refractive index proposed by Lorentz–Lorentz (L–L), Gladstone–Dale (G–D), Weiner (W), Heller (H), Arago–Biot (A–B), Newton (N), and Eykmen (Eyk) have been theoretically applied to these binary mixtures. A comparative study has been made between the experimental and theoretically calculated values of refractive indices at all the three temperatures. The results have been discussed in terms of average percentage deviation (APD).

2. Experimental section

The densities were measured using a pyknometer having a bulb volume of 8 ml and an internal diameter of the capillary of about 0.1 cm with an accuracy ±0.5%. The pyknometer was calibrated at 298 K with double distilled water and benzene. The pyknometer with the test solution was equilibrated in a thermostatically controlled water bath maintained at ±0.1 K of the desired temperature. An average of triplicate measurements was taken into account.

Refractive index was measured using Abbe's refractometer provided by Optics Technologies, Delhi. The refractometer was calibrated by measuring the refractive indices of triply distilled water and benzene at $T = 293$ K. The accuracy in the refractive index measurement was 0.001 units. Temperature was controlled by circulating adequately stirred water bath (accuracy ±0.1°C). The sample mixtures were directly injected into the prism assembly of the instrument by means of an air-tight hypodermic syringe. An average of four to five measurements was taken for each sample mixture.

The ultrasonic velocity of pure components and their mixtures were measured by variable path fixed frequency interferometer provided by Mittal Enterprises, New Delhi (Model-83). It consists of a high frequency generator and a measuring cell. The calibration of ultrasonic interferometer was done by measuring the velocity in AR grade benzene and carbon tetrachloride. Standard value of u for benzene and carbon tetrachloride were calculated from the literature value [8] of u at 298 K and $-\mathrm{d}u/\mathrm{d}t$. Our measured values of u agree closely with the literature values [8]. The maximum estimated error in ultrasonic velocity measurements has been found to be ±0.08%. The measured values of standard deviations of velocities have been found to be smaller than 0.12 m/s for the mixtures studied at various temperatures for fine measurements. The temperature was controlled by circulating water around the liquid cell from thermostatically controlled adequately stirred water bath (accuracy ±0.1°C).

The viscosity was measured by Ostwald's viscometer which was calibrated at 298 K with double distilled water and purified methanol using density and viscosity values from the literature [8]. The flow times were accurate to ±0.1 s, and the uncertainty in the viscosity measurements was within ±0.5%. An average of 3–4 flow times were taken to estimate the viscosity.

Mixtures were prepared by weighing the liquids in specially designed ground glass stopped bottles, taking extreme precautions to minimize preferential evaporation. A Sartorius (BP 121S) single pan balance having a stated precision of 0.1 mg was used throughout. The maximum possible error in the mole fraction is estimated to be ±0.0001. The chemicals used were obtained from Ranbaxy Fine Chemicals Limited. All the chemicals used were purified by standard procedure, discussed by Perrin and Armarego [9]. All the samples were kept in tightly sealed bottles to minimize the absorption of atmospheric moisture.

3. Results and discussion

The experimental values of ρ, n, u, and η at three temperatures viz. 293, 303, and 313 K are given in Tables I and II for butylamine + 1-butanol and butylamine + tert-butanol mixtures.

The experimental values of ρ, n, u, and η were used to calculate the values of $V_{\mathrm{m}}^{\mathrm{E}}$, ΔR_{m}, Δu, $\Delta\eta$, and $\Delta G^{*\mathrm{E}}$ using the standard relations

TABLE I

Density (ρ), refractive index (n), ultrasonic velocity (u), viscosity (η), excess molar volume $V_{\mathrm{m}}^{\mathrm{E}}$, molar refraction deviation ΔR_{m}, deviation in ultrasonic velocity Δu, viscosity deviation $\Delta\eta$, and excess Gibb's free energy of activation for viscous flow $\Delta G^{*\mathrm{E}}$ for mixture butylamine + 1-butanol with mole fractions of butylamine (x_1) at $T = 293$, 303, and 313 K.

x_1	ρ [g/cm^3]	n	u [m/s]	η [mPa s]	$V_{\mathrm{m}}^{\mathrm{E}}$ [cc/mol]	ΔR_{m}	Δu [m/s]	$\Delta\eta$ [mPa s]	$\Delta G^{*\mathrm{E}}$ [kJ/mol]
$T = 293$ K									
0.0000	0.8098	1.399	1286	2.8250	0.0000	0.0000	0.00	0.0000	0.000
0.1011	0.8029	1.399	1282	2.7285	–0.0600	–0.0496	0.19	0.1268	0.290
0.2025	0.7969	1.400	1279	2.6276	–0.1870	–0.0879	0.37	0.2500	0.571
0.3028	0.7915	1.401	1275	2.5339	–0.4110	–0.1217	0.51	0.3779	0.850
0.4032	0.7848	1.401	1272	2.3650	–0.4630	–0.1357	0.57	0.4307	1.053
0.5033	0.7780	1.401	1269	2.1510	–0.4780	–0.1416	0.62	0.4379	1.193
0.6032	0.7707	1.402	1265	1.9208	–0.4200	–0.1205	0.56	0.4284	1.290
0.7030	0.7632	1.402	1262	1.6457	–0.3160	–0.1047	0.45	0.3737	1.286
0.8020	0.7558	1.402	1258	1.3375	–0.2070	–0.0894	0.28	0.2842	1.151
0.9000	0.7484	1.403	1255	0.9978	–0.0760	–0.0391	0.15	0.1611	0.803
1.0000	0.7414	1.403	1251	0.6158	0.0000	0.0000	0.00	0.0000	0.000
$T = 303$ K									
0.0000	0.8017	1.392	1228	2.2970	0.0000	0.0000	0.00	0.0000	0.000
0.1011	0.7953	1.392	1227	2.2045	–0.1280	–0.0610	0.29	0.0855	0.264
0.2025	0.7893	1.393	1226	2.1168	–0.3000	–0.1047	0.46	0.1765	0.530
0.3028	0.7835	1.393	1224	2.0382	–0.4800	–0.1473	0.64	0.2744	0.798
0.4032	0.7769	1.393	1224	1.8997	–0.5460	–0.1846	0.70	0.3128	0.987
0.5033	0.7700	1.393	1222	1.7283	–0.5680	–0.1874	0.71	0.3177	1.116
0.6032	0.7628	1.394	1221	1.5458	–0.5300	–0.1719	0.69	0.3112	1.202
0.7030	0.7554	1.394	1220	1.3303	–0.4570	–0.1545	0.59	0.2714	1.192
0.8020	0.7480	1.394	1218	1.0910	–0.3561	–0.1215	0.46	0.2064	1.057
0.9000	0.7405	1.395	1216	0.8289	–0.2200	–0.0547	0.29	0.1170	0.728
1.0000	0.7324	1.395	1215	0.5358	0.0000	0.0000	0.00	0.0000	0.000
$T = 313$ K									
0.0000	0.7934	1.389	1189	1.8880	0.0000	0.0000	0.00	0.0000	0.000
0.1011	0.7872	1.389	1186	1.8014	–0.1770	–0.0740	0.46	0.0569	0.240
0.2025	0.7813	1.389	1182	1.7252	–0.3840	–0.1542	0.64	0.1247	0.491
0.3028	0.7752	1.390	1178	1.6587	–0.5570	–0.1940	0.79	0.2006	0.748
0.4032	0.7684	1.390	1174	1.5443	–0.6200	–0.2055	0.89	0.2286	0.925
0.5033	0.7614	1.390	1170	1.4071	–0.6510	–0.2108	0.96	0.2335	1.045
0.6032	0.7540	1.391	1166	1.2591	–0.6200	–0.1970	0.92	0.2274	1.119
0.7030	0.7466	1.391	1162	1.0884	–0.5540	–0.1813	0.84	0.1984	1.104
0.8020	0.7390	1.391	1158	0.9004	–0.4480	–0.1520	0.70	0.1509	0.972
0.9000	0.7314	1.392	1154	0.6960	–0.3300	–0.0810	0.47	0.0855	0.660
1.0000	0.7225	1.392	1150	0.4685	0.0000	0.0000	0.00	0.0000	0.000

$$V_{\mathrm{m}}^{\mathrm{E}} = \frac{x_1 M_1 + x_2 M_2}{\rho_{\mathrm{m}}} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2}\right), \tag{1}$$

$$\Delta R_{\mathrm{m}} = R_{\mathrm{m}}^{\mathrm{expt}} - R_{\mathrm{m}}^{\mathrm{id}}, \tag{2}$$

where

TABLE II

Density (ρ), refractive index (n), ultrasonic velocity (u), viscosity (η), excess molar volume V_m^E, molar refraction deviation ΔR_m, deviation in ultrasonic velocity Δu, viscosity deviation $\Delta\eta$, and excess Gibb's free energy of activation for viscous flow ΔG^{*E} for mixture butylamine + tert-butanol with mole fractions of butylamine (x_1) at T = 293, 303, and 313 K.

x_1	ρ [g/cm^3]	n	u [m/s]	η [mPa s]	V_m^E [cc/mol]	ΔR_m	Δu [m/s]	$\Delta\eta$ [mPa s]	ΔG^{*E} [kJ/mol]
T = 293 K									
0.0000	0.8018	1.396	1208	6.6250	0.0000	0.0000	0.00	0.0000	0.000
0.1012	0.7953	1.397	1213	3.3710	–0.0003	–0.0058	0.11	–2.6459	–1.060
0.2015	0.7890	1.398	1217	2.4141	–0.0006	–0.0138	0.21	–3.0000	–1.292
0.3026	0.7827	1.398	1221	1.8566	–0.0008	–0.0192	0.28	–2.9500	–1.347
0.4031	0.7765	1.399	1226	1.4827	–0.0009	–0.0221	0.34	–2.7200	–1.313
0.5032	0.7704	1.400	1230	1.2412	–0.0009	–0.0225	0.36	–2.3600	–1.166
0.6029	0.7645	1.400	1234	1.0820	–0.0009	–0.0205	0.36	–1.9200	–0.924
0.7026	0.7586	1.401	1239	0.9192	–0.0008	–0.0161	0.30	–1.4837	–0.744
0.7980	0.7586	1.402	1243	0.8050	–0.0006	–0.0097	0.23	–1.0246	–0.515
0.9012	0.7470	1.403	1247	0.7173	–0.0003	–0.0021	0.11	–0.4922	–0.200
1.0000	0.7414	1.403	1251	0.6158	0.0000	0.0000	0.00	0.0000	0.000
T = 303 K									
0.0000	0.7944	1.389	1180	5.5260	0.0000	0.0000	0.00	0.0000	0.000
0.1012	0.7877	1.390	1184	3.0631	–0.0003	–0.0068	0.14	–1.9639	–0.891
0.2015	0.7812	1.390	1187	2.2105	–0.0005	–0.0157	0.28	–2.3206	–1.123
0.3026	0.7748	1.391	1191	1.6560	–0.0006	–0.0220	0.36	–2.3740	–1.256
0.4031	0.7684	1.392	1195	1.4045	–0.0007	–0.0256	0.41	–2.1260	–1.080
0.5032	0.7622	1.392	1198	1.2752	–0.0007	–0.0265	0.43	–1.7563	–0.735
0.6029	0.7561	1.393	1202	1.1065	–0.0007	–0.0249	0.43	–1.4268	–0.506
0.7026	0.7500	1.393	1205	0.9783	–0.0006	–0.0209	0.36	–1.0555	–0.230
0.7980	0.7443	1.394	1208	0.8325	–0.0005	–0.0147	0.27	–0.7221	–0.077
0.9012	0.7383	1.395	1212	0.6678	–0.0003	–0.0057	0.15	–0.3670	–0.025
1.0000	0.7325	1.395	1215	0.5358	0.0000	0.0000	0.00	0.0000	0.000
T = 313 K									
0.0000	0.7871	1.385	1141	4.7960	0.0000	0.0000	0.00	0.0000	0.000
0.1012	0.7802	1.386	1142	2.9805	–0.0004	–0.0086	0.18	–1.3513	–0.625
0.2015	0.7734	1.387	1143	2.2640	–0.0007	–0.0189	0.30	–1.6139	–0.733
0.3026	0.7666	1.387	1144	1.6765	–0.0009	–0.0261	0.39	–1.7499	–0.902
0.4031	0.7600	1.388	1145	1.5416	–0.0010	–0.0302	0.46	–1.4419	–0.512
0.5032	0.7535	1.389	1146	1.3784	–0.0011	–0.0313	0.49	–1.1697	–0.197
0.6029	0.7472	1.389	1147	1.2170	–0.0010	–0.0295	0.50	–0.9031	0.082
0.7026	0.7409	1.390	1148	0.9894	–0.0009	–0.0248	0.41	–0.7080	0.147
0.7980	0.7350	1.391	1149	0.8258	–0.0007	–0.0177	0.30	–0.4724	0.253
0.9012	0.7287	1.391	1149	0.6088	–0.0004	–0.0073	0.17	–0.2629	0.084
1.0000	0.7227	1.392	1150	0.4685	0.0000	0.0000	0.00	0.0000	0.000

$$R_m^{\text{expt}} = \frac{n_m^2 - 1}{n_m^2 + 2}\frac{x_1 M_1 + x_2 M_2}{\rho_m}, \tag{2a}$$

and

$$R_m^{\text{id}} = \frac{n_1^2 - 1}{n_1^2 + 2}\frac{M_1}{\rho_1}\phi_1 + \frac{n_2^2 - 1}{n_2^2 + 2}\frac{M_2}{\rho_2}\phi_2, \tag{2b}$$

$$\Delta u = u - (x_1 u_1 + x_2 u_2), \tag{3}$$

$$\Delta \eta = \eta - (x_1 \eta_1 + x_2 \eta_2), \tag{4}$$

$$\Delta G^{*\mathrm{E}} = RT \left[\ln \left(\frac{\eta V_{\mathrm{m}}}{\eta_2 V_{\mathrm{m}2}} \right) - x_1 \ln \left(\frac{\eta_1 V_{\mathrm{m}1}}{\eta_2 V_{\mathrm{m}2}} \right) \right]. \tag{5}$$

Mixing rules for refractive index [10, 11] are listed below.

The Lorentz–Lorentz relation for refractive index is based on the change in the molecular polarizability with volume fraction

$$\frac{n_{\mathrm{m}}^2 - 1}{n_{\mathrm{m}}^2 + 2} \frac{1}{\rho_{\mathrm{m}}} = \frac{n_1^2 - 1}{n_1^2 + 2} \frac{w_1}{\rho_1} + \frac{n_2^2 - 1}{n_2^2 + 2} \frac{w_2}{\rho_2}. \tag{6}$$

Gladstone–Dale equation for predicting the refractive index of a binary mixture is as follows:

$$n_{\mathrm{m}} - 1 = \varphi_1 (n_1 - 1) + \varphi_2 (n_2 - 1). \tag{7}$$

Wiener's relation may be represented as

$$\frac{n_{\mathrm{m}}^2 - n_1^2}{n_{\mathrm{m}}^2 + 2n_1^2} = \frac{n_2^2 - n_1^2}{n_2^2 + 2n_1^2} \varphi_2. \tag{8}$$

Heller's relation is given by

$$\frac{n_{\mathrm{m}} - n_1}{n_1} = \frac{3}{2} \frac{m^2 - 1}{m^2 + 2} \varphi_2. \tag{9}$$

Arago–Biot, assuming volume additivity, proposed the following relation for refractive index of binary mixtures:

$$n_{\mathrm{m}} = \varphi_1 n_1 + \varphi_2 n_2. \tag{10}$$

Newton gave the following equation:

$$n_{\mathrm{m}}^2 - 1 = \varphi (n_1^2 - 1) + \varphi_2 (n_2^2 - 1). \tag{11}$$

Eykman's relation may be represented as

$$\frac{n_{\mathrm{m}}^2 - 1}{n_{\mathrm{m}} + 0.4} V_{\mathrm{m}} = \frac{n_1^2 - 1}{n_1 + 0.4} \frac{M_1 x_1}{\rho_1} + \frac{n_2^2 - 1}{n_2 + 0.4} \frac{M_2 x_2}{\rho_2}. \tag{12}$$

In Eqs. (1)–(12) M_i, ρ_i, n_i, u_i, η_i, ϕ_i, $V_{\mathrm{m}i}$, W_i, and x_i, respectively, represent molecular weight, density, refractive index, ultrasonic velocity, viscosity, volume fraction, molar volume, weight fraction, and mole fraction of the i-th component ($i = 1, 2$ for binary mixtures), ρ_{m}, n_{m}, u, η, and V_{m} are density, refractive index, ultrasonic velocity, viscosity, and molar volume of the mixtures. R is the universal gas constant and T is the absolute temperature. All the excess parameters are summarized in Tables I and II for butylamine + 1-butanol, butylamine + tert-butanol mixtures and are shown graphically in Figs. 1 to 5.

The values of $V_{\mathrm{m}}^{\mathrm{E}}$, ΔR_{m}, Δu, $\Delta \eta$, and $\Delta G^{*\mathrm{E}}$ for each mixture have been fitted to Redlich–Kister polynomial equation

$$Y^{\mathrm{E}} = x(1 - x) \sum_{i=1}^{5} a_i (1 - 2x)^{i-1}, \tag{13}$$

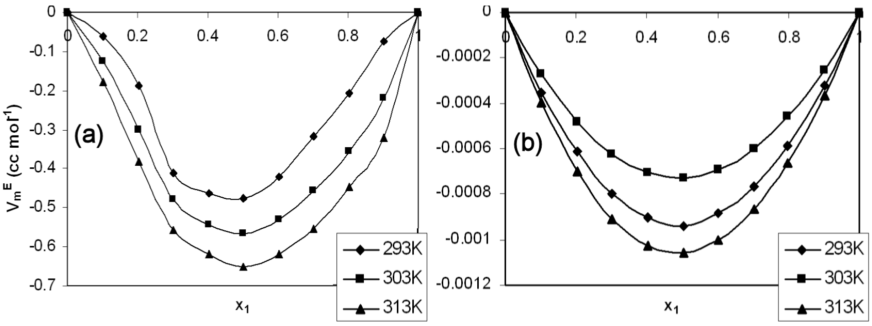

Fig. 1. (a) Excess molar volume $V_{\rm m}^{\rm E}$ as a function of butylamine (x_1) for butylamine + 1-butanol mixture at all the three temperatures. (b) As in (a), but for butylamine + tert-butanol mixture.

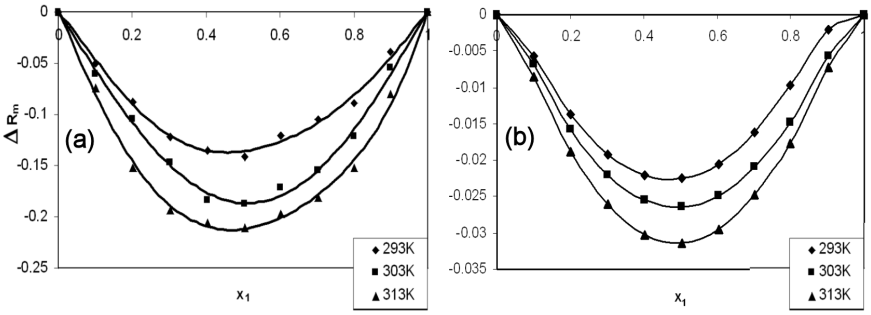

Fig. 2. (a) Molar refraction deviation $\Delta R_{\rm m}$ as a function of butylamine (x_1) for butylamine + 1-butanol mixture at all the three temperatures. (b) As in (a), but for butylamine + tert-butanol mixture.

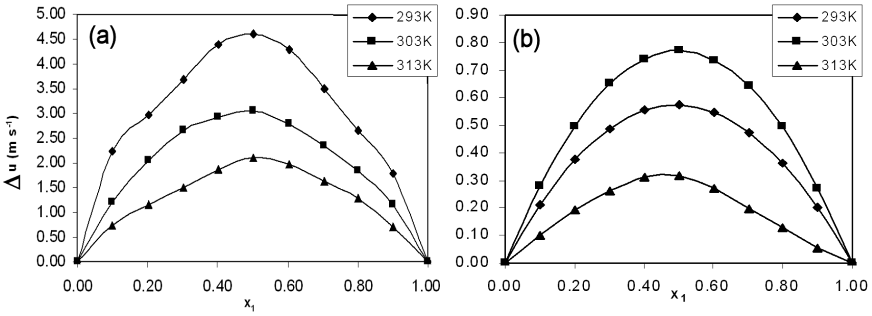

Fig. 3. (a) Deviation in ultrasonic velocity Δu as a function of butylamine (x_1) for butylamine + 1-butanol mixture at all the three temperatures. (b) As in (a), but for butylamine + tert-butanol mixture.

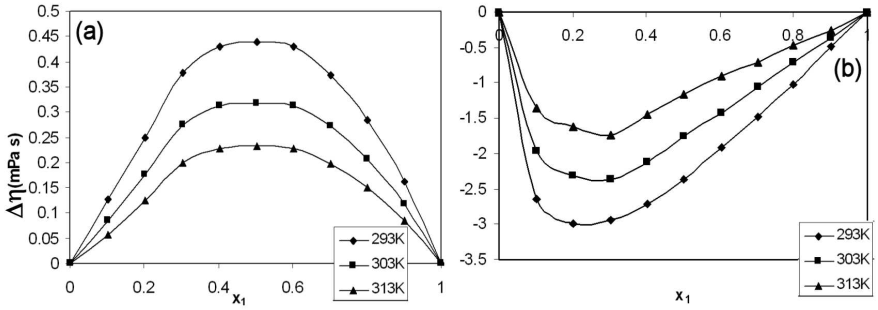

Fig. 4. (a) Viscosity deviation $\Delta\eta$ as a function of butylamine (x_1) for butylamine + 1-butanol mixture at all the three temperatures. (b) As in (a), but for butylamine + tert-butanol mixture.

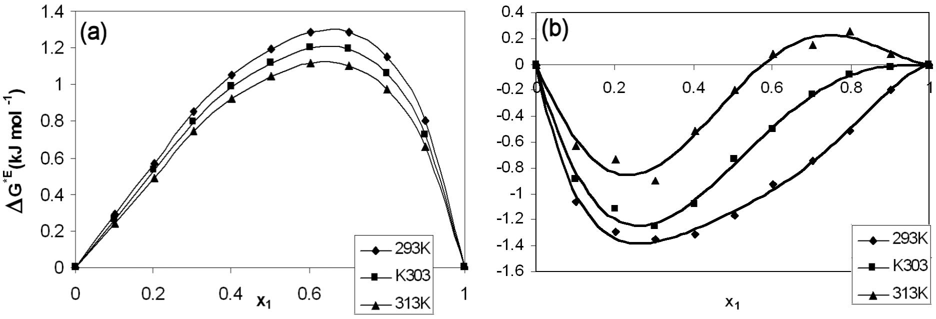

Fig. 5. Excess Gibb's free energy of activation for viscous flow $\Delta G^{*\mathrm{E}}$ as a function of butylamine (x_1) for butylamine + 1-butanol mixture at all the three temperatures. (b) As in (a), but for butylamine + tert-butanol mixture.

where Y^{E} refers to excess/deviation parameter. The values of the coefficients a_i were calculated by the method of least squares along with the standard deviation $\sigma(Y^{\mathrm{E}})$, which are given in Table III. The coefficient i is an adjustable parameter for the best fit of the excess functions.

The standard deviation values were obtained from

$$\sigma(Y^{\mathrm{E}}) = \left[\frac{\sum(Y_{\mathrm{expt}} - Y_{\mathrm{cal}})}{n-p}\right]^{1/2}, \tag{14}$$

where n is the total number of experimental points, p is the number of coefficients, Y_{expt} and Y_{cal} are the experimental and calculated excess parameters, respectively.

According to Fort and Moore [12], a negative excess molar volume $V_{\mathrm{m}}^{\mathrm{E}}$ is an indication of strong heteromolecular interaction in the liquid mixtures and is attributed to change-transfer, dipole–dipole interactions, and hydrogen bonding between the unlike molecules, while a positive sign indicates a weak interaction and is attributed to dispersive forces. The magnitudes of the contribution will vary

TABLE III

Adjustable parameters a_i with the standard deviations $\sigma(Y^{\mathrm{E}})$ for excess molar volume $V_{\mathrm{m}}^{\mathrm{E}}$, molar refraction deviation ΔR_{m}, deviation in ultrasonic velocity Δu, viscosity deviation $\Delta\eta$, and excess Gibb's free energy of activation for viscous flow $\Delta G^{*\mathrm{E}}$ for both the binary mixtures at temperature T.

Functions	a_1	a_2	a_3	a_4	a_5	$\sigma(Y^{\mathrm{E}})$
butylamine + 1-butanol						
$T = 293$ K						
$V_{\mathrm{m}}^{\mathrm{E}}$ [cc mol^{-1}]	–2.7352	0.1091	5.7878	0.0100	–4.2354	0.0185
ΔR_{m}	–0.3075	0.1167	–1.2200	–0.2893	1.4631	0.0026
Δu [m s^{-1}]	2.8128	0.6734	–3.0512	–0.6426	2.4812	0.0101
$\Delta\eta$ [mPa s]	1.7588	1.3502	–2.8873	–2.4902	4.1265	0.0062
$\Delta G^{*\mathrm{E}}$ [kJ mol^{-1}]	4.7663	–1.2483	–0.8438	– 3.6428	4.4870	0.0062
$T = 303$ K						
$V_{\mathrm{m}}^{\mathrm{E}}$ [cc mol^{-1}]	–2.2418	0.1183	0.7154	1.1997	–0.3612	0.0088
ΔR_{m}	–0.7517	–0.6084	1.4337	0.8919	2.5799	0.0031
Δu [m s^{-1}]	2.8396	0.0039	–0.6800	–0.0314	1.9891	0.0119
$\Delta\eta$ [mPa s]	1.2756	1.0935	–2.3223	–2.0557	3.2663	0.0051
$\Delta G^{*\mathrm{E}}$ [kJ mol^{-1}]	4.4550	–0.8614	–1.4084	–3.7104	4.7677	0.0067
$T = 313$ K						
$V_{\mathrm{m}}^{\mathrm{E}}$ [cc mol^{-1}]	–2.6484	–0.3158	0.4029	1.8694	0.6349	0.0079
ΔR_{m}	–0.8453	–0.9300	–1.4544	6.2933	8.2021	0.0416
Δu [m s^{-1}]	3.6083	–0.6669	0.6641	0.8993	2.7189	0.0076
$\Delta\eta$ [mPa s]	0.9348	0.8450	–1.8077	–1.6347	2.4777	0.0040
$\Delta G^{*\mathrm{E}}$ [kJ mol^{-1}]	4.1697	–0.7172	–1.5392	–3.4585	4.4195	0.0062
butylamine + tert-butanol						
$T = 293$ K						
$V_{\mathrm{m}}^{\mathrm{E}}$ [cc mol^{-1}]	–0.0038	0.0000	0.0004	–0.0001	–0.0004	0.0000
ΔR_{m}	–0.0933	0.0071	–0.0057	–0.0492	0.1289	0.0001
Δu [m s^{-1}]	1.2959	–0.2210	0.6007	0.3178	–1.1162	0.0047
$\Delta\eta$ [mPa s]	–9.3427	–8.2706	–9.4929	–10.3303	–4.9512	0.0307
$\Delta G^{*\mathrm{E}}$ [kJ mol^{-1}]	–4.5957	–3.5642	–4.5549	–3.6679	1.2399	0.0182
$T = 303$K						
$V_{\mathrm{m}}^{\mathrm{E}}$ [cc mol^{-1}]	–0.0029	–0.0002	0.0003	0.0001	–0.0002	0.0000
ΔR_{m}	–0.1091	0.0148	–0.0133	–0.0326	0.1170	0.0001
Δu [m s^{-1}]	1.8271	–0.9722	1.6243	1.3659	–3.0403	0.0050
$\Delta\eta$ [mPa s]	–7.1154	–13.3623	10.9313	3.6904	–31.1975	0.0363
$\Delta G^{*\mathrm{E}}$ [kJ mol^{-1}]	–3.5474	–5.2484	1.8237	– 1.0549	–6.4960	0.0384
$T = 313$ K						
$V_{\mathrm{m}}^{\mathrm{E}}$ [cc mol^{-1}]	–0.0042	–0.0006	0.0005	0.0006	– 0.0009	0.0000
ΔR_{m}	–0.1249	0.0031	–0.0116	– 0.0162	0.1068	0.0001
Δu [m s^{-1}]	1.8503	–0.0335	– 0.0769	0.1226	0.3475	0.0069
$\Delta\eta$ [mPa s]	–4.4301	–4.5759	–3.8543	–4.4739	–4.9215	0.0569
$\Delta G^{*\mathrm{E}}$ [kJ mol^{-1}]	–0.7821	–6.330	–0.2592	2.3868	–4.8700	0.0736

with the components and composition of the mixtures. In the present investigation, both the mixtures gave a negative magnitude of $V_{\mathrm{m}}^{\mathrm{E}}$, and they depict the presence of heteromolecular interaction, which support the Fort and Moore [12] observation. Wen-Lu Weng [13] and Papaioannou et al. [14] have also observed negative values of $V_{\mathrm{m}}^{\mathrm{E}}$ in the case of butylamine + 1-butanol mixture. The negative $V_{\mathrm{m}}^{\mathrm{E}}$ values of butylamine + 1-butanol observed in the present investigation have been found to be in good agreement with the values of $V_{\mathrm{m}}^{\mathrm{E}}$ reported earlier by Wen-Lu Weng [13] and Papaioannou et al. [14]. The negative values of $V_{\mathrm{m}}^{\mathrm{E}}$ indicate that volume contraction takes place upon mixing butylamine with 1-butanol/tert-butanol due to cross association between these dissimilar molecules [15]. The magnitude of the volume contraction follows the sequence of 1-butanol > tert-butanol. This is in agreement with the results reported by Ali and Nain [15] on binary mixtures of tetrahydrofuran (THF) with 1-butanol and tert-butanol which suggest that the excess values follow the same sequence, due to the steric hindrance produced by the presence of three methyl groups at 3^0 carbon atom in tert-butanol, as compared to one butyl group in 1-butanol. Molar refraction deviation ΔR_{m} as calculated from Eq. (2b) represents the electronic perturbation due to orbital mixing of two components [16]. R_{m} gives the strength of the interaction in mixture and is a sensitive function of wavelength, temperature, and mixture composition. Figure 2 shows that ΔR_{m} values are negative for both the mixtures at all the temperatures. The values of $V_{\mathrm{m}}^{\mathrm{E}}$ and ΔR_{m} support each other. The $V_{\mathrm{m}}^{\mathrm{E}}$ and ΔR_{m} values become more negative at higher temperature for both the mixtures, suggesting an increase in interaction between unlike molecules.

Deviation in ultrasonic velocity Δu, viscosity deviation $\Delta\eta$, and excess Gibb's free energy of activation for viscous flow $\Delta G^{*\mathrm{E}}$ can be used to detect the molecular interactions present in the binary mixture. Δu has been found to be positive for both the mixtures over the entire mole fraction range (Fig. 3). It is evident from Fig. 3 that in both the mixtures containing butylamine, Δu increases as a function of mole fraction of butylamine, attains maxima and then decreases. The values of Δu systematically become more positive with the rise in temperature suggesting that specific interaction increases due to enhanced thermal energy.

Figure 4 shows that viscosity deviation $\Delta\eta$ values are positive for butylamine + 1-butanol and negative for butylamine + tert-butanol mixtures. The positive values of Δn in butylamine + 1-butanol mixture can be explained on the basis of complex formation between unlike molecules through hydrogen bonding. The negative values of Δn for butylamine + tert-butanol may be attributed to the presence of weak dipole–dipole interaction due to predominance rupture of dipolar association of tert-butanol and steric hindrance produced by three methyl groups over the hydrogen bond formed between unlike molecules. Our positive values of $\Delta\eta$ in the case of butylamine + 1-butanol do not corroborate with the values of $\Delta\eta$ on the same mixtures reported earlier by Wen-Lu Weng [13] and Dominguez et al. [17]. However, all the excess parameters $V_{\mathrm{m}}^{\mathrm{E}}$, ΔR_{m}, and $\Delta\eta$ reported here by us are in conformity with each other. $\Delta\eta$ values are found to decrease with increasing temperature in the positive and negative directions in the cases of butylamine + 1-butanol and butylamine + tert-butanol mixtures, respectively.

Figure 5 shows that $\Delta G^{*\mathrm{E}}$ values are positive for butylamine + 1-butanol and negative for butylamine + tert-butanol mixtures, respectively. However, a smaller positive trend has been observed at a temperature of 313 K in butylamine rich region. The positive values of $\Delta G^{*\mathrm{E}}$ indicates the presence of strong interaction in butylamine + 1-butanol mixture, whereas negative $\Delta G^{*\mathrm{E}}$ values for butylamine + tert-butanol mixture may be assigned to the predominance of dispersive forces and also due to less acidic nature of tertiary alcohols than primary alcohols [18]. Gupta et al. [19] and Mialkowski et al. [20] have also reported similar variations in the $\Delta G^{*\mathrm{E}}$ values for binary mixtures of ether + alcohols and γ-butyrolactone + dimethylcarbonate.

TABLE IV

APD of theoretically calculated refractive indices from different semi-empirical relations at all the three temperatures.

Temp. [K]	L–L	G–D	W	H	A–B	N	Eyk
butylamine + 1-butanol							
293	–0.0786	0.00278	0.00280	0.00285	0.00279	0.00272	–0.07384
303	–0.11447	–0.00617	–0.00615	–0.00613	–0.00617	–0.06620	–0.10786
313	–0.1415	–0.01283	–0.01282	–0.01279	–0.01283	–0.01287	–0.13357
butylamine + tert-butanol							
293	0.00799	0.00800	0.00806	0.00820	0.00800	0.00781	0.00788
303	0.00587	0.00588	0.00593	0.00604	0.00589	0.00574	0.00579
313	0.00589	0.00591	0.00598	0.00612	0.00591	0.00592	0.00578

Further, seven empirical relations (Eqs. (6) to (12)) were used for the prediction of refractive indices. The refractive index data correlated with these semi-empirical equations for both the binary mixtures show an excellent agreement with the respective experimental values of refractive index (Table IV). It can be seen from Table IV that the correlation of these equations showed the suitability of all the seven relations for representing the mixing refractive indices of the binary mixtures of butylamine + 1-butanol/tert-butanol. The applicability of these semi-empirical relations for predicting refractive index has also been emphasized by others [10, 11].

4. Conclusions

The observed negative and positive values of various excess parameters for butylamine + 1-butanol system are attributed to the strong intermolecular interaction through H-bonding. The less negative values of $V_{\mathrm{m}}^{\mathrm{E}}$ and ΔR_{m} at all the three temperatures and small positive values of $\Delta G^{*\mathrm{E}}$ at 313 K for binary mixture of butylamine + tert-butanol are due to the weak specific interactions arising from induced dipole–dipole forces. However, dispersive forces may be responsible for negative values of $\Delta\eta$.

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