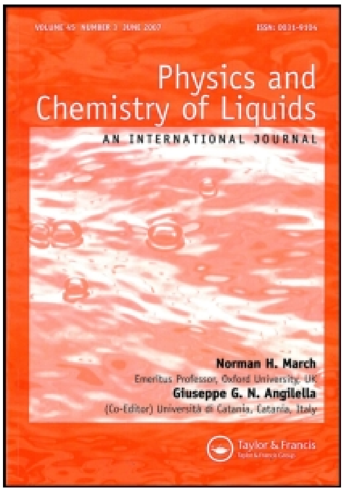

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A Study of Interactions in Binary Mixtures from Viscosity Measurements

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Viscosities for binary liquid mixtures of butylamine with benzene, toluene and isomeric xylenes have been measured at 303.15 K. Excess viscosity data have been obtained. The values of η^E are negative over entire composition range. This may be attributed to the dissociation of self associated butylamine by the aromatic hydrocarbons. Further, the study has been extended to investigate intermolecular interactions in terms of excess free energy of mixing, strength of interaction parameter and interaction energy between the components.

1 INTRODUCTION

In continuation to our studies on the binary liquid mixtures of butylamine as common component[1–4] we report here new viscosity data for mixtures of butylamine with benzene, toluene, *o*-xylene, *m*-xylene and *p*-xylene at 303.15 K. The present investigation has been undertaken to have an insight into self-association of the amine and structure breaking effect of aromatic hydrocarbons through viscosity measurement. Excess free energy of mixing ($\alpha\Delta F_m$) strength of interaction (d) and interaction energy (W_{vis}) have been evaluated and the interaction between unlike molecules have been discussed in terms of these parameters.

2 EXPERIMENTAL SECTION

Materials

Butylamine was dried over potassium hydroxide for 3 days then reflexed for 2 h and fractionally distilled.[5] The aromatic hydrocarbons were made thiophene-free as described by Vogel,[6] dried over calcium chloride and finally fractionally distilled over metallic sodium. The purity of the samples was checked by comparing the measured densities with those reported in the literature.[7,8] The densities were determined with a bicapillary pycknometer described by Rao and Naidu.[9] The data are given in Table I.

Viscosities

Viscosity of liquids and liquid mixtures were determined by using Ostwald viscometers. The accuracy of the viscometers was checked by measuring the viscosities of pure benzene and cyclohexane. The results show very good agreement with those reported in literature. Mixtures of various known compositions were prepared by weight. A constant volume of the mixture transferred into the viscometer and then inserted in a water thermostat controlled at 303.15 ± 0.01 K. The time of flow of the liquid through capillary was determined. Viscosity was then obtained from density, flow time and constants of the viscometers using the relation

$$\eta = k_v \rho t \qquad (1)$$

where k_v is viscometer constant and ρ and t are the density and flow time respectively. Densities for pure components was determined

TABLE I

Densities of pure component liquids

Component	T/K	Density ρ/g cm^{-3} Experimental	Literature
Butylamine	298.15	0.73450	0.73460
Benzene	303.15	0.86839	0.86836
Tolueno	303.15	0.85772	0.85766
o-Xylene	303.15	0.87161	0.87161
m-Xylene	303.15	0.85566	0.85565
p-Xylene	303.15	0.85231	0.85232

experimentally. In case of mixtures densities were obtained from excess volumes reported earlier[1] using the equation

$$\rho = \frac{xM_1 + (1-x)M_2}{V + V^E} \tag{2}$$

where x stands for mole fraction of butylamine, M_1 and M_2 are molecular weights of amine and hydrocarbons respectively. V and V^E stand for the molar volume and excess molar volume respectively.

Excess viscosities (η^E) of the mixtures were calculated by the relation suggested by Fort and Moor,[10]

$$\eta^E = \eta_m - [x\eta_A + (1-x)\eta_B] \tag{3}$$

where η_m is the viscosity of the mixture, η_A and η_B are the viscosities of amine and aromatic hydrocarbons respectively.

THEORETICAL ASPECTS

The following equations are used to calculate excess free energy of mixing ($\alpha\Delta F_m$), strength of interaction parameter (d) and interaction energy (W_{vis}) between the components.

Eyring[11] gave the following relation to calculate the excess free energy of mixing

$$\alpha\Delta F_m = -RT[\ln\eta_m - x\ln\eta_1 + (1-x)\ln\eta_2] \tag{4}$$

where R and T are gas constant and absolute temperature respectively.

The strength of interaction (d) between the components of the mixture was calculated by using the following relationship proposed by Kendall,[12]

$$\ln\eta_m = x\ln\eta_1 + (1-x)\ln\eta_2 + x(1-x)d \tag{5}$$

Katti and Chaudhuri[13] deduced the following expression to show the variation of viscosity with molar volume and composition

$$\ln\eta_m v = x\ln\eta_1 v_1 + (1-x)\ln\eta_2 v_2 + \frac{W_{\text{vis}}}{RT}x(1-x) \tag{6}$$

where W_{vis} represents the interaction energy between the components.

RESULTS AND DISCUSSION

The values of density (ρ), viscosity (η_m), excess viscosity (η^E), excess free energy of mixing ($\alpha\Delta F_m$), strength of interaction parameter (d) and interaction energy between the components (W_{vis}) for the systems of butylamine with aromatic hydrocarbons are given in Table II and

TABLE II

Values of density (ρ), viscosity of the mixture (η_m), excess viscosity (η^E), free energy of mixing ($\alpha\Delta F_m$), strength of interaction parameter (d) and strength interaction (W_{vis}) at 303.15 K

x	ρ (g cm^{-3})	η_m (cp)	η^E (cp)	$\alpha\Delta F_m$ (cal mol^{-1})	d	W_{vis} (cal mol^{-1})
			n-Butylamine + benzene			
0.0000	0.86839	0.562	—	—	—	—
0.0558	0.85948	0.536	−0.019	19.864	−0.002	−1.047
0.1165	0.84978	0.516	−0.032	24.711	−0.004	−2.543
0.2036	0.83640	0.494	−0.043	50.967	−0.014	−8.264
0.2875	0.82400	0.479	−0.049	58.726	−0.020	−12.028
0.3820	0.81054	0.465	−0.052	63.297	−0.025	−14.943
0.5164	0.79210	0.453	−0.048	60.755	−0.025	−15.173
0.5676	0.78512	0.451	−0.044	55.768	−0.023	−13.687
0.6631	0.77283	0.448	−0.035	45.321	−0.017	−10.125
0.7656	0.75982	0.447	−0.024	31.659	−0.009	−5.681
0.8602	0.74815	0.446	−0.014	18.097	−0.004	−2.176
0.9278	0.73996	0.444	−0.008	10.634	−0.001	−0.712
1.0000	0.73150	0.443	—	—	—	—
			n-Butylamine + toluene			
0.0000	0.85772	0.521	—	—	—	—
0.0685	0.84915	0.510	−0.006	6.814	−0.001	−0.435
0.1474	0.83903	0.497	−0.013	15.326	−0.003	−1.926
0.2553	0.82841	0.485	−0.017	22.217	−0.007	−3.997
0.3280	0.81692	0.474	−0.021	27.240	−0.010	−6.003
0.4247	0.80489	0.464	−0.024	30.001	−0.012	−7.331
0.5197	0.79307	0.457	−0.023	30.343	−0.013	−7.574
0.6107	0.78163	0.453	−0.020	26.140	−0.010	−6.213
0.6993	0.77041	0.449	−0.017	22.366	−0.008	−4.703
0.7946	0.75824	0.446	−0.013	17.581	−0.005	−2.869
0.8819	0.74695	0.445	−0.007	10.348	−0.002	−1.077
0.9407	0.73930	0.444	−0.004	5.001	−0.001	−0.279
1.0000	0.73150	0.443	—	—	—	—
			n-Butylamine + *o*-xylene			
0.0000	0.87161	0.680	—	—	—	—
0.0811	0.86174	0.648	−0.013	11.418	−0.001	−0.851
0.1509	0.85309	0.624	−0.020	19.296	−0.004	−2.472
0.2681	0.83818	0.587	−0.029	28.837	−0.009	−5.658
0.3574	0.82650	0.560	−0.035	39.105	−0.015	−8.982
0.4598	0.81272	0.535	−0.036	39.016	−0.016	−9.692
0.5460	0.80072	0.518	−0.033	38.642	−0.016	−9.579
0.6419	0.78710	0.499	−0.029	33.444	−0.013	−7.689
0.7306	0.77404	0.484	−0.023	27.858	−0.009	−5.482
0.8169	0.76092	0.469	−0.017	21.952	−0.006	−3.284
0.8974	0.74826	0.457	−0.010	13.033	−0.002	−1.200
0.9503	0.73971	0.450	−0.005	6.660	−0.001	−0.314
1.000	0.73150	0.443	—	—	—	—

TABLE II (*continued*)

x	ρ (g cm^{-3})	η_m (cp)	η^E (cp)	$\alpha\Delta F_m$ (cal mol^{-1})	d	W_{vis} (cal mol^{-1})
			n-Butylamine + *m*-xylene			
0.0000	0.85566	0.538	—	—	—	—
0.0824	0.84694	0.525	−0.005	6.055	−0.001	−0.458
0.1495	0.83925	0.516	−0.008	10.000	−0.002	−1.271
0.2739	0.82530	0.497	−0.015	17.649	−0.006	−3.510
0.3870	0.81209	0.484	−0.017	21.805	−0.009	−5.172
0.4543	0.80405	0.476	−0.109	22.950	−0.010	−5.690
0.5525	0.79201	0.469	−0.017	20.962	−0.009	−5.197
0.6484	0.77991	0.462	−0.014	19.035	−0.007	−4.340
0.7553	0.76862	0.457	−0.011	16.143	−0.005	−3.142
0.8160	0.75771	0.453	−0.008	12.047	−0.003	−1.809
0.8978	0.74632	0.448	−0.005	6.445	−0.001	−0.591
0.9469	0.73928	0.445	−0.003	0.964	−0.001	−0.049
1.0000	0.73150	0.443	—	—	—	—
			n-Butylamine + *p*-xylene			
0.0000	0.85231	0.564	—	—	—	—
0.0795	0.84391	0.545	−0.009	9.643	−0.001	−0.706
0.1507	0.83634	0.530	−0.016	18.046	−0.004	−2.409
0.2545	0.82508	0.511	−0.022	25.513	−0.008	−4.819
0.3628	0.81299	0.494	−0.026	30.903	−0.012	−7.108
0.4612	0.80164	0.481	−0.027	32.520	−0.013	−8.072
0.5562	0.79031	0.471	−0.026	31.759	−0.013	−7.831
0.6469	0.77913	0.464	−0.022	28.057	−0.011	−6.385
0.7338	0.76804	0.457	−0.018	23.006	−0.008	−4.518
0.8144	0.75739	0.451	−0.014	15.473	−0.004	−2.349
0.8979	0.74601	0.448	−0.008	9.730	−0.002	−0.904
0.9456	0.73934	0.444	−0.005	5.652	−0.001	−0.301
1.0000	0.73150	0.443	—	—	—	—

TABLE III

Values of the parameters a_0, a_1 and a_2 in Eq. (7) and the standard deviation, $\sigma(\eta^E)$ at 303.15 K

System	a_0 (cp)	a_1 (cp)	a_2 (cp)	$\sigma(\eta^E)$ (cp)
n-Butylamine + benzene	−0.188	0.124	−0.045	0.004
n-Butylamine + toluene	−0.095	0.014	0.016	0.002
n-Butylamine + *o*-xylene	−0.140	0.033	0.012	0.002
n-Butylamine + *p*-xylene	−0.106	0.027	0.005	0.001
n-Butylamine + *m*-xylene	−0.073	0.015	0.022	0.002

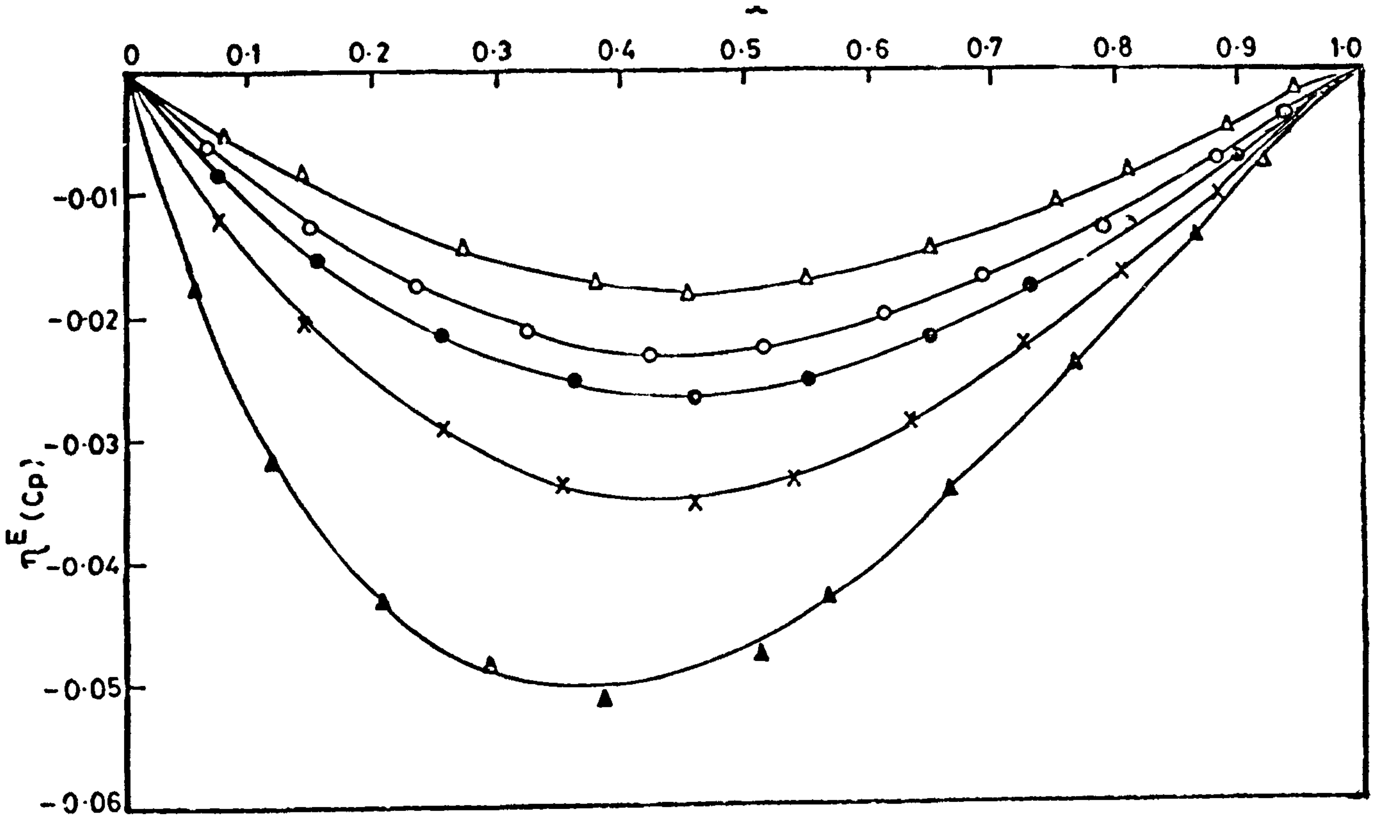

FIGURE 1 Values of η^E plotted against mole fraction of butylamine (x): Butylamine + Benzene (▼), + Toluene (○), + *o*-Xylene (×), + *m*-Xylene (▽) and + *p*-Xylene (●).

graphically presented in Figure 1. The dependence of η^E on composition may be expressed by an empirical equation of the form

$$\eta^E = x(1 - x)[a_0 + a_1(2x - 1) + a_2(2x - 1)^2] \tag{7}$$

where a_0, a_1 and a_2 are adjustable parameters. The values of the parameters, obtained by the least square method, are included in Table III along with the standard deviation, $\sigma(\eta^E)$.

Values of η^E are negative over the whole range of composition in all the systems. The negative values may be attributed to the depolymerization of self-associated butylamine by the aromatic hydrocarbons. According to Sohug and Chang[14] self association of butylamine through hydrogen bonding leads to the formation of linear trimers. The addition of hydrocarbons would, therefore, be expected to break-up of hydrogen bonds in amine trimers. This would contribute to reduction in flow time. The observed negative values of η^E are therefore in order.

The plots of η^E against mole fraction in Figure 1 show that the negative values of η^E at 0.5 mole fraction for the five systems fall in the order: Benzene > *o*-xylene > *p*-oxylene > toluene > *m*-xylene. This suggests that the value of η^E are influenced by the substitution of methyl groups in benzene ring and also by the position of the substitution.

The values of $\alpha\Delta F_m$ are positive and the values of d and W_{vis} are negative over the entire composition range for all the systems. The variation in these parameters is similar to that observed for η^E.

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