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Studies of viscosities of dilute solutions of alkylamines in non-electrolyte solvents
III. Alkylamines in butanols 303.15 K

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ABSTRACT

Viscosities η of dilute solutions of *n*-propylamine, *n*-butylamine, di-*n*-propylamine, di-*n*-butylamine, triethylamine, tri-*n*-propylamine, and tri-*n*-butylamine in 1-butanol and 2-butanol at 303.15 K have been measured. The specific viscosities $(\eta - \eta_S^o)/\eta_S^o$ and viscosity deviations $\Delta\eta$ have been calculated. The values of $(\eta - \eta_S^o)/\eta_S^o$ and $\Delta\eta$ are negative and their magnitude increases with the increase in concentration of alkylamine. The values of excess Gibbs energy of activation ΔG^{*E} of viscous flow determined based on Eyring's theory of absolute reaction rates are positive for alkylamine solutions in both the butanols. The strong solute–solvent interactions leading to the structure formation between butanol and alkylamine molecules through H-bondings are observed. The results have been further analyzed in terms of Herskovits and Kelly equation and Nakagawa equation. The values of viscosity increment (in Herskovits and Kelly equation and coefficient B'_{int} in Nakagawa equation are negative for all presently investigated alkylamine solutions.

1. Introduction

This laboratory is engaged in systematic investigations of thermodynamic and transport properties of dilute solutions involving important organic bases: primary, secondary and tertiary alkylamines in polar and non-polar solvents [1–5]. It has been reported that mixture containing associate components like alkanols and amines are highly non-ideal systems with large negative heat as well as volumetric effect [6–13]. In order to know the nature and extent of molecular interactions the partial molar properties of dilute solutions are of great significance [14,15]. The thermodynamic and transport properties of dilute solutions provide information about the molecular interactions between solute–solute and solute–solvent interactions, and can be used for the development of molecular models for describing the thermodynamic behaviour of solutions. In earlier paper [5] we have reported volumetric properties of dilute solutions of *n*-propylamine ($C_3H_7NH_2$), *n*-butylamine ($C_4H_9NH_2$), di-*n*-propylamine ($(C_3H_7)_2NH$), di-*n*-butylamine ($(C_4H_9)_2NH$), triethylamine ($(C_2H_5)_3N$), tri-*n*-propylamine ($(C_3H_7)_3N$), and tri-*n*-butylamine ($(C_4H_9)_3N$) in 1-butanol (1-C_4H_9OH) and 2-butanol (2-C_4H_9OH) at 303.15 K. The cross-associations through H-bonding between amine and alkanol molecules were observed. Compared to 1-butanol, the complex formation is relatively weak in case of 2-butanol solutions due to steric hindrance. As the viscosity behaviour in dilute solution is also very sensitive to predict solute–solute and solute–solvent interactions [16,17], we in this paper report viscosity behaviour of dilute solutions of same seven alkylamines in 1-butanol and 2-butanol. This study is expected to reveal some more interesting facts concerning the nature and different extent of interactions in amines. The results have also been analyzed in terms of Herskovits and Kelly equation [16] and Nakagawa equation [18].

2. Experimental

The viscosities η were measured with a modified calibrated suspended level Ubbelohde viscometer [19]. The viscometer was designed so as to reduce surface tension effects to negligible values [20]. The apparatus was submerged in a thermostatic bath at 303.15 K with a resolution of ±0.05 K and allowed to attain thermal equilibrium. The viscometer has been calibrated so as to determine the two constants C and B in the equation $\eta/\rho = Ct - B/t$, obtained by measuring the flow time t with pure water, benzene, toluene, cyclohexane and p-xylene [21]. The flow time of a definite volume of liquid through the capillary was measured with an accurate stopwatch with a precision of ±0.1 s. Four to five sets of readings for the flow times were taken for each pure solvent or solution and the arithmetic mean was taken for the calculations. The densities ρ

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Table 1
Comparison of experimental densities and viscosities of pure components at 303.15 K with the literature data.

Components	Density ($g\,cm^{-3}$)		Viscosity (mPa s)	
	Experimental	Literature	Observed	Literature
$C_3H_7NH_2$	0.70610	0.70615[a]	0.3527	0.350[b]
$C_4H_9NH_2$	0.72865	0.72848[c] 0.72849[e]	0.4442	0.4430[d] 0.456[b]
$(C_3H_7)_2NH$	0.73121	0.73019[f]	0.5118	0.4789[g]
$(C_4H_9)_2NH$	0.75228	0.75248[f] 0.75228[d]	0.7584	0.734[h] 0.7593[g]
$(C_2H_5)_3N$	0.71844	0.71845[b] 0.7185[i]	0.3296	0.3295[b] 0.3298[h]
$(C_3H_7)_3N$	0.74915	0.7484[a]	0.5977	0.595[h]
$(C_4H_9)_3N$	0.77021	0.7701[i] 0.77018[c]	1.1670	1.1663[h]
1- C_4H_9OH	0.80192	0.80191[j] 0.80193[l]	2.2550	2.2266[k] 2.271[b]
2- C_4H_9OH	0.79840	0.79841[b] 0.79825[j]	2.4710	2.4989[b] 2.743[m]

[a] [24].
[b] [21].
[c] [25].
[d] [22].
[e] [26].
[f] [27].
[g] [28].
[h] [29].
[i] [30].
[j] [31].
[k] [32].
[l] [33].
[m] [34].

required to convert kinematic viscosities into dynamic viscosities η were measured by Anton Paar vibrating-tube digital densimeter (model DMA 60/602) with thermostat bath controlled to ±0.01 K. The details of the experimental procedure have been described earlier [5,22,23].

All the solutions were prepared by mixing known masses of pure components in air tight, narrow-mouth ground stoppered bottles taking due precautions to minimize the evaporation losses. Eight to nine solutions up to 0.1 mol fraction of each alkylamine in both the solvents were prepared. The possible error in the mole fraction and molality is estimated to be less than $\pm 1 \times 10^{-4}$. The error in viscosity η was less than 2×10^{-3} mPa s.

n-Propylamine (Merck, Schuchardt), *n*-butylamine (Fluka AG), di-*n*-propylamine (Fluka AG), di-*n*-butylamine (Fluka AG), triethylamine (Sisco, extra pure), tri-*n*-propylamine (Fluka AG), and tri-*n*-butylamine (SRL, Bombay) of purity better than 99.0 mol% were refluxed over Na metal and distilled twice fractionally before use. 1-Butanol and 2-butanol (BDH AR) of purity better then 99.5 mol% were used after further purification and drying by standard procedures [21]. The measured values of densities and viscosities were compared with literature values in Table 1.

3. Theoretical

3.1. Herskovits and Kelly equation

In general for interpreting viscosity data the following relation

$$\frac{\eta}{\eta_S^o} = 1 + Bm + Dm^2 \qquad (1)$$

has commonly been used [17], where η/η_S^o is the relative viscosity, B a coefficient related to the size and shape of solute molecule and to solvation effects, where as the D coefficient includes solute–solute interactions and those solute–solvent interactions which arise with higher concentrations and are not accounted for by the Bm term.

Herskovits and Kelly [16] substituted molality in terms of volume faction ϕ_s as $m = 1000\,\phi_s/M_s\bar{v}_s\rho$ in Eq. (1) and obtained Eq. (2)

$$\frac{\eta}{\eta_S^o} = 1 + (10^3 B/(M_s\bar{v}_s\rho))\phi_s + (10^6 D/(M_s\bar{v}_s\rho)^2)\phi_s{}^2 \qquad (2)$$

where $\bar{v}_s$ is partial specific volume. The coefficients B and D of equation can be evaluated from the intercept and slope of $(\eta/\eta_S^o - 1)/m$ versus m plots.

3.2. Nakagawa equation

Matsubayashi and Nakahara [35] ‘extended the conformal solution theory (ECS) [36] to the dynamic problem through the first-order perturbation theory. They theoretically derived the formula about concentration dependence of dynamical properties, and the validity of their ECS theory was shown through the binary regular mixtures containing benzene. According to the ECS theory, a dynamic property η for binary solution is written as the following

$$\eta = x_s\eta_s^o + (1 - x_s)\eta_S^o + (1 - x_s)x_s\eta_{int} \qquad (3)$$

where η_s^o and η_S^o are viscosities of solute and solvent components and η_{int} is the interaction term for regular solution.

3.2.1. Derivation of B coefficients from η_{int} through ECS theory

For non-electrolyte solutions of higher concentrations, Jones–Dole equation [37,38] can be rewritten as

$$\frac{\eta}{\eta_S^o} = 1 + B'c + D'c^2 \qquad (4)$$

where c is the concentrations in mol dm^{-3} and B' and D' are adjustable parameters. Differentiating Eq. (4) by molarity c at constant temperature T and pressure P,

$$\left[\frac{\partial(\eta/\eta_S^o)}{\partial c}\right]_{T,P} = B' + 2D'c \qquad (5)$$

Form Eq. (5), the B′ coefficient is the first partial differential coefficient by molarity at $c = 0$. i.e.,

$$B' = \lim_{c\to 0}\left[\frac{\partial(\eta/\eta_S^o)}{\partial c}\right]_{T,P,c=0} \qquad (6)$$

Eq. (3) can be rearranged to

$$\frac{\eta}{\eta_S^o} = x_s\left(\frac{\eta_s^o}{\eta_S^o}\right) + (1 - x_s) + (1 - x_s)x_s\eta_{int}/\eta_S^o \qquad (7)$$

Since, the interaction term η_{int} is independent to the concentration for regular solution, we get the following equation by differentiating Eq. (7) by x_s at constant T and P.

$$\left[\frac{\partial(\eta/\eta_S^o)}{\partial x_s}\right]_{T,P} = \left(\frac{\eta_s^o}{\eta_S^o}\right) - 1 + (1 - 2x_s)\left(\frac{\eta_S^o}{\eta_{int}}\right) \qquad (8)$$

The mole fraction x_s and concentration c of solute in molarity are related with following relation

$$c = \frac{1000x_s\rho}{x_sM_s + (1 - x_s)M_S} \qquad (9)$$

The density ρ of solution can be expressed as power series of x_s, that is,

$$\rho = \sum_{i=o}^{n} A_i x_s^i \tag{10}$$

where A_i is fitting coefficient, in particular, ($A_o \equiv \rho_S$) means the neat solvent density. Substituting Eq. (10) to Eq. (9), and differentiating it by x_s at constant T and P, one obtains

$$\left[\frac{\partial c}{\partial x_s}\right]_{T,P} = \frac{1000\left[\sum_{i=1}^{n} A_i x_s^{i+1}(M_s - M_S) + \sum_{i=o}^{n}(i+1)A_i x_s^i M_S\right]}{[x_s M_s + (1 - x_s)M_S]^2} \tag{11}$$

Combination of Eqs. (8) and (11), and comparison with Eq. (6), gives

$$B' = \lim_{c\to 0}\left[\frac{\partial(\eta/\eta_S^o)}{\partial c}\right] = \lim_{c\to 0}\left[\frac{\partial(\eta/\eta_S^o)}{\partial x_s}\right] \Big/ \left[\frac{\partial c}{\partial x_s}\right] \tag{12}$$

$$B' = \frac{M_S\left[(\eta_s^o/\eta_S^o) - 1 + \eta_{int}/\eta_S^o\right]}{1000\rho_S} \tag{13}$$

3.2.2. Division of B′ coefficient

For an ideal solution, namely, $\eta_{int} = 0$, Eq. (13) is

$$B'_{id} = \frac{M_S\left[(\eta_s^o/\eta_S^o) - 1\right]}{1000\rho_S} \tag{14}$$

where B'_{id} is the contribution of ideal mixture for the B' coefficient, which is based on the difference between the viscosity of solute and of solvent. If η_s is larger than η_S, the B'_{id} coefficient is positive and vice versa. This finding implies that the B' coefficient is not characteristic for solute–solvent interaction. Hence, it is proposed that $B'_{int} = B' - B'_{id}$, namely

$$B'_{int} = \frac{M_S \eta_{int}}{1000\rho_S \eta_S} = K\eta_{int} \tag{15}$$

should be the interaction parameter instead of B', where $K = M_S/1000\rho_S\eta_S = 1/1000v_S\eta_S$ is the constant which is independent of the solution composition.

4. Results

The experimental, densities ρ and viscosities η of dilute solutions of $C_3H_7NH_2$, $C_4H_9NH_2$, $(C_3H_7)_2NH$, $(C_4H_9)_2NH$, $(C_2H_5)_3N$, $(C_3H_7)_3N$, and $(C_4H_9)_3N$ in 1-C_4H_9OH and 2-C_4H_9OH at 303.15 K are presented in Tables 2 and 3.

The experimental values of η are expressed by

$$\eta = \sum_{i=1}^{m} A_i x_s^{i-1} \tag{16}$$

The coefficients A_i obtained from a least squares fit with equal weights assigned to each point, are listed in Table 4 together with the standard deviations σ.

Since components used in the solution formation are both liquids and each one of them has dynamic viscosity. It would be appropriate to take into account viscosity of both the components in calculating viscosity deviations from a linear dependence on mole fraction. The viscosity deviations $\Delta\eta$ have been evaluated as

$$\Delta\eta = \eta - (x_s\eta_s^o + x_S\eta_S^o) \tag{17}$$

Table 2
Viscosities for alkylamine solutions in 1-butanol at 303.15 K.

Solute	m (mol kg^{-1})	x_s	ρ^* (g cm^{-3})	η (mPa s)
$C_3H_7NH_2$	0.1619	0.0119	0.80158	2.2138
	0.3046	0.0221	0.80125	2.1853
	0.4275	0.0307	0.80094	2.1599
	0.5845	0.0415	0.80055	2.1334
	0.6943	0.0489	0.80028	2.1134
	0.8960	0.0623	0.79978	2.0827
	1.0610	0.0729	0.79933	2.0531
	1.1109	0.0761	0.79921	2.0377
	1.2760	0.0864	0.79878	2.0131
$C_4H_9NH_2$	0.1457	0.0107	0.80162	2.2279
	0.2830	0.0205	0.80130	2.2049
	0.3843	0.0277	0.80106	2.1848
	0.5808	0.0413	0.80058	2.1546
	0.7106	0.0500	0.80026	2.1352
	0.8452	0.0590	0.79993	2.1157
	1.0536	0.0724	0.79940	2.0874
	1.2260	0.0833	0.79895	2.0592
	1.3374	0.0902	0.79867	2.0399
$(C_3H_7)_2$ NH	0.1370	0.0100	0.80142	2.2247
	0.2640	0.0192	0.80096	2.1958
	0.4699	0.0337	0.80019	2.1650
	0.5753	0.0409	0.79980	2.1450
	0.7035	0.0496	0.79933	2.1211
	0.8388	0.0585	0.79883	2.0981
	1.0188	0.0702	0.79818	2.0642
	1.1582	0.0791	0.79767	2.0404
	1.3643	0.0918	0.79694	2.0059
$(C_4H_9)_2NH$	0.1576	0.0115	0.80127	2.2299
	0.2477	0.0180	0.80089	2.2133
	0.3385	0.0245	0.80051	2.1982
	0.4782	0.0342	0.79994	2.1774
	0.5849	0.0416	0.79952	2.1632
	0.6889	0.0486	0.79911	2.1500
	0.8093	0.0566	0.79865	2.1338
	0.9120	0.0633	0.79826	2.1197
	1.5228	0.1014	0.79611	2.0305
$(C_2H_5)_3N$	0.1482	0.0109	0.80116	2.2234
	0.3064	0.0222	0.80034	2.1928
	0.4546	0.0326	0.79957	2.1621
	0.5880	0.0418	0.79890	2.1335
	0.7471	0.0525	0.79810	2.0976
	0.8993	0.0625	0.79736	2.0759
	1.0564	0.0726	0.79660	2.0522
	1.2402	0.0842	0.79572	2.0194
	1.4181	0.0951	0.79490	1.9908
$(C_3H_7)_3N$	0.1619	0.0119	0.80119	2.2249
	0.2673	0.0194	0.80070	2.2009
	0.4223	0.0304	0.79999	2.1783
	0.5620	0.0400	0.79937	2.1568
	0.7232	0.0509	0.79866	2.1335
	0.8871	0.0617	0.79796	2.1124
	1.0794	0.0741	0.79715	2.0846
	1.1762	0.0802	0.79675	2.0740
	1.2751	0.0863	0.79635	2.0595
$(C_4H_9)_3N$	0.1056	0.0078	0.80149	2.2447
	0.1995	0.0146	0.80109	2.2358
	0.3155	0.0228	0.80062	2.2259
	0.4693	0.0336	0.80002	2.2108
	0.6263	0.0444	0.79943	2.1971
	0.7020	0.0495	0.79916	2.1906
	0.8541	0.0595	0.79863	2.1778
	1.0578	0.0727	0.79795	2.1603
	1.3219	0.0892	0.79712	2.1385

* Taken from reference [5].

On the basis of the theory of absolute reaction rates [39], the excess Gibbs energy of activation ΔG^{*E} of viscous flow has been calculated from

$$\frac{\Delta G^{*E}}{RT} = \{\ln(\eta V/\eta_S^o V_S^o) - x_s \ln(\eta_s^o V_s^o/\eta_S^o V_S^o)\} \tag{18}$$

Table 3
Viscosities for alkylamine solutions in 2-butanol at 303.15 K.

Solute	m (mol kg^{-1})	x_s	ρ^* (g cm^{-3})	η (mPa s)
$C_3H_7NH_2$	0.1148	0.0084	0.79794	2.4391
	0.2577	0.0187	0.79735	2.4080
	0.4034	0.0290	0.79676	2.3769
	0.5894	0.0419	0.79601	2.3427
	0.6475	0.0458	0.79578	2.3289
	0.8257	0.0577	0.79508	2.3003
	0.9822	0.0679	0.79448	2.2766
	1.1085	0.0759	0.79399	2.2527
	1.2557	0.0851	0.79344	2.2239
$C_4H_9NH_2$	0.1381	0.0101	0.79783	2.4378
	0.2757	0.0200	0.79726	2.4102
	0.4237	0.0305	0.79665	2.3811
	0.5356	0.0382	0.79620	2.3644
	0.7262	0.0511	0.79545	2.3324
	0.8465	0.0590	0.79499	2.3126
	1.0474	0.0720	0.79423	2.2834
	1.2178	0.0828	0.79360	2.2598
	1.4233	0.0954	0.79285	2.2287
$(C_3H_7)_2$ NH	0.1289	0.0095	0.79783	2.4416
	0.2847	0.0207	0.79715	2.4112
	0.4493	0.0322	0.79644	2.3811
	0.5873	0.0417	0.79585	2.3584
	0.7095	0.0500	0.79532	2.3356
	0.8501	0.0593	0.79474	2.3129
	1.0231	0.0705	0.79402	2.2859
	1.2835	0.0869	0.79297	2.2506
	1.3405	0.0904	0.79274	2.2384
$(C_4H_9)_2NH$	0.1146	0.0084	0.79802	2.4461
	0.2439	0.0178	0.79757	2.4201
	0.3771	0.0272	0.79712	2.3984
	0.4423	0.0317	0.79690	2.3891
	0.5920	0.0420	0.79639	2.3692
	0.7130	0.0502	0.79599	2.3529
	0.8628	0.0601	0.79549	2.3322
	0.9566	0.0662	0.79519	2.3198
	1.1110	0.0761	0.79468	2.2987
$(C_2H_5)_3N$	0.1482	0.0109	0.79761	2.4358
	0.3064	0.0222	0.79678	2.4061
	0.4546	0.0326	0.79601	2.3803
	0.5880	0.0418	0.79533	2.3566
	0.7471	0.0525	0.79452	2.3304
	0.8993	0.0625	0.79377	2.3015
	1.0564	0.0726	0.79301	2.2762
	1.2402	0.0842	0.79213	2.2461
	1.4181	0.0951	0.79130	2.2166
$(C_3H_7)_3N$	0.1232	0.0091	0.79774	2.4484
	0.2757	0.0200	0.79695	2.4229
	0.4146	0.0298	0.79625	2.3999
	0.5621	0.0400	0.79552	2.3787
	0.7411	0.0521	0.79468	2.3519
	0.8822	0.0614	0.79404	2.3323
	0.9695	0.0670	0.79366	2.3171
	1.1517	0.0787	0.79287	2.2913
	1.3633	0.0918	0.79199	2.2643
$(C_4H_9)_3N$	0.1538	0.0113	0.79771	2.4562
	0.3007	0.0218	0.79705	2.4388
	0.4554	0.0327	0.79642	2.4233
	0.5935	0.0421	0.79594	2.4093
	0.7036	0.0496	0.79551	2.3987
	0.8296	0.0579	0.79509	2.3867
	0.9923	0.0685	0.79453	2.3716
	1.1389	0.0778	0.79403	2.3588
	1.3052	0.0882	0.79353	2.3445

* Taken from reference [5].

Table 4
Coefficients A_i of Eq. (16) along with standard deviation σ for viscosities.

System	A_1	A_2	A_3	σ (mPa s)
In 1-butanol				
$C_3H_7NH_2$	2.2513	−2.9580	2.6180	0.0037
$C_4H_9NH_2$	2.2536	−2.3970	0.6744	0.0023
$(C_3H_7)_2NH$	2.2520	−2.6185	−0.6514	0.0027
$(C_4H_9)_2NH$	2.2529	−2.0983	−0.8017	0.0024
$(C_2H_5)_3N$	2.2565	−3.0622	2.8642	0.0030
$(C_3H_7)_3N$	2.2536	−2.5841	4.1357	0.0022
$(C_4H_9)_3N$	2.2549	−1.2941	−0.1095	0.0003
In 2-butanol				
$C_3H_7NH_2$	2.4675	−3.1729	4.2484	0.0033
$C_4H_9NH_2$	2.4682	−2.9000	4.3579	0.0022
$(C_3H_7)_2NH$	2.4696	−2.8505	3.4959	0.0015
$(C_4H_9)_2NH$	2.4684	−2.6555	6.0392	0.0024
$(C_2H_5)_3N$	2.4680	−2.7075	0.7951	0.0020
$(C_3H_7)_3N$	2.4700	−2.3379	1.0297	0.0012
$(C_4H_9)_3N$	2.4718	−1.5106	0.7433	0.0006

Table 5
Coefficients P_i of Eq. (19) along with standard deviation σ for specific viscosities.

System	P_1	P_2	P_3	σ (mPa s)
In 1-butanol				
$C_3H_7NH_2$	−1.650	11.9	−84.7	0.0012
$C_4H_9NH_2$	−1.151	2.6	−15.6	0.0009
$(C_3H_7)_2NH$	−1.433	7.8	−60.3	0.0015
$(C_4H_9)_2NH$	−1.035	2.0	−13.8	0.0009
$(C_2H_5)_3N$	−1.247	−1.7	20.8	0.0014
$(C_3H_7)_3N$	−1.218	3.5	−10.7	0.0010
$(C_4H_9)_3N$	−0.587	0.4	−3.8	0.0002
In 2-butanol				
$C_3H_7NH_2$	−1.600	11.9	−81.1	0.0008
$C_4H_9NH_2$	−1.388	8.0	−44.7	0.0006
$(C_3H_7)_2NH$	−1.286	5.6	−31.6	0.0008
$(C_4H_9)_2NH$	−1.295	10.0	−65.2	0.0003
$(C_2H_5)_3N$	−1.357	8.2	−57.5	0.0012
$(C_3H_7)_3N$	−1.023	2.6	−16.4	0.0005
$(C_4H_9)_3N$	−0.525	−2.6	23.1	0.0005

Table 6
Coefficients P_i of Eq. (19) along with standard deviation σ for viscosity deviations.

System	P_1	P_2	P_3	σ (mPa s)
In 1-butanol				
$C_3H_7NH_2$	−1.815	26.6	−189.2	0.001
$C_4H_9NH_2$	−0.787	5.9	−35.4	0.002
$(C_3H_7)_2NH$	−1.455	17.8	−137.0	0.003
$(C_4H_9)_2NH$	−0.816	4.6	−31.9	0.002
$(C_2H_5)_3N$	−0.887	−3.9	46.7	0.003
$(C_3H_7)_3N$	−1.092	8.2	−25.7	0.002
$(C_4H_9)_3N$	−0.229	0.7	−6.4	0.000
In 2-butanol				
$C_3H_7NH_2$	−1.836	29.4	−200.9	0.002
$C_4H_9NH_2$	−1.409	19.9	−111.5	0.001
$(C_3H_7)_2NH$	−1.189	14.0	−80.0	0.002
$(C_4H_9)_2NH$	−1.457	24.3	−158.1	0.001
$(C_2H_5)_3N$	−1.224	20.6	−145.4	0.003
$(C_3H_7)_3N$	−0.655	6.8	−43.2	0.001
$(C_4H_9)_3N$	0.003	−6.2	56.0	0.001

where η and V are the viscosity and molar volume of the solution; and η_s^o and η_S^o are the viscosities and V_s^o and V_S^o are molar volumes of the pure solute and solvent, respectively. The values of $(\eta - \eta_S^o)/\eta_S^o$, $\Delta\eta$, and ΔG^{*E} have been fitted to the polynomial of the form

$$\psi = \sum_{i=1}^{m} P_i x_s^i \qquad (19)$$

The coefficients P_i of Eq. (19), obtained by the method of least squares with all points weighted equally, and the standard deviations σ are given in Tables 5–7.

Table 7
Coefficients P_i of Eq. (19) along with standard deviation σ for ΔG^{*E}.

System	P_1	P_2	σ (J mol^{-1})
In 1-butanol			
$C_3H_7NH_2$	732	7098	6.6
$C_4H_9NH_2$	1121	1216	3.1
$(C_3H_7)_2NH$	657	2384	6.1
$(C_4H_9)_2NH$	804	−818	3.9
$(C_2H_5)_3N$	1672	−961	4.3
$(C_3H_7)_3N$	1032	4218	2.8
$(C_4H_9)_3N$	1736	−2907	0.5
In 2-butanol			
$C_3H_7NH_2$	1110	9137	6.6
$C_4H_9NH_2$	985	7063	4.6
$(C_3H_7)_2NH$	1139	4696	3.1
$(C_4H_9)_2NH$	459	9843	4.2
$(C_2H_5)_3N$	2042	3782	5.5
$(C_3H_7)_3N$	1823	723	2.4
$(C_4H_9)_3N$	2068	−3971	1.4

5. Discussion

The viscosity η of all amines solutions in both the butanols decrease with increase in molality. The dependence of $(\eta - \eta_S^o)/\eta_S^o$ on m, $\Delta\eta$ and ΔG^{*E} on x_S is shown in Figs. 1–6. The values of $(\eta - \eta_S^o)/\eta_S^o$ and $\Delta\eta$ are negative and their magnitude increases with the increase in concentration of amine. The plots of $(\eta - \eta_S^o)/\eta_S^o$ versus m are almost linear for both the butanols. However, slopes of the curves are larger for 1-butanol than that for 2-butanol. Papaioannou et al. [6,40] studied the viscosity behaviour for propylamine + 1-butanol and butylamine + 1-butanol over the entire range of composition at 298.15 K and different pressures from

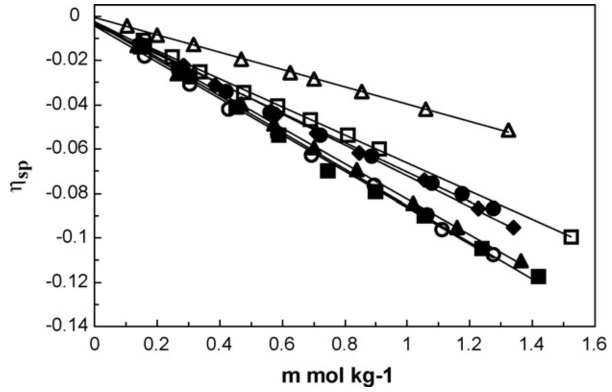

Fig. 1. Specific viscosities of $C_3H_7NH_2$ (○), $C_4H_9NH_2$ (♦), $(C_3H_7)_2NH$ (▲), $(C_4H_9)_2NH$ (□), $(C_2H_5)_3N$ (■), $(C_3H_7)_3N$ (●), and $(C_4H_9)_3N$ (△) in 1- C_4H_9OH at 303.15 K.

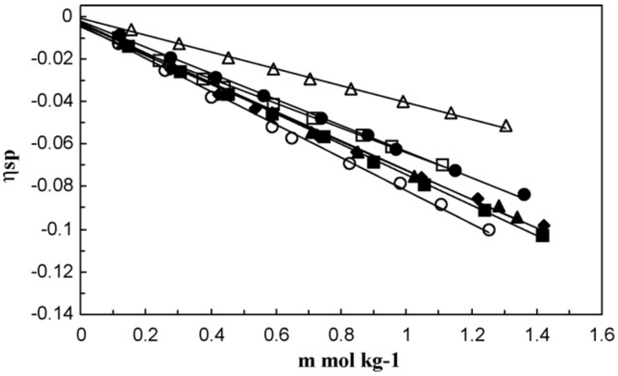

Fig. 2. Specific viscosities of $C_3H_7NH_2$ (○), $C_4H_9NH_2$ (♦), $(C_3H_7)_2NH$ (▲), $(C_4H_9)_2NH$ (□), $(C_2H_5)_3N$ (■), $(C_3H_7)_3N$ (●), and $(C_4H_9)_3N$ (△) in 2-C_4H_9OH at 303.15 K.

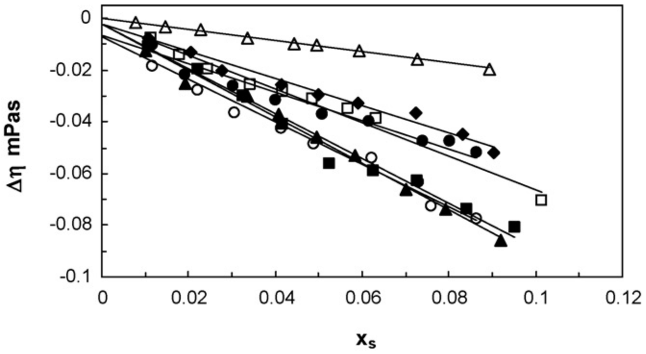

Fig. 3. Viscosity deviations of $C_3H_7NH_2$ (○), $C_4H_9NH_2$ (♦), $(C_3H_7)_2NH$ (▲), $(C_4H_9)_2NH$ (□), $(C_2H_5)_3N$ (■), $(C_3H_7)_3N$ (●), and $(C_4H_9)_3N$ (△) in 1-C_4H_9OH at 303.15 K.

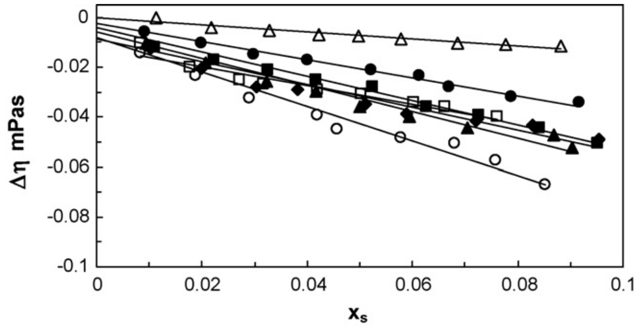

Fig. 4. Viscosity deviations of $C_3H_7NH_2$ (○), $C_4H_9NH_2$ (♦), $(C_3H_7)_2NH$ (▲), $(C_4H_9)_2NH$ (□), $(C_2H_5)_3N$ (■), $(C_3H_7)_3N$ (●), and $(C_4H_9)_3N$ (△) in 2-C_4H_9OH at 303.15 K.

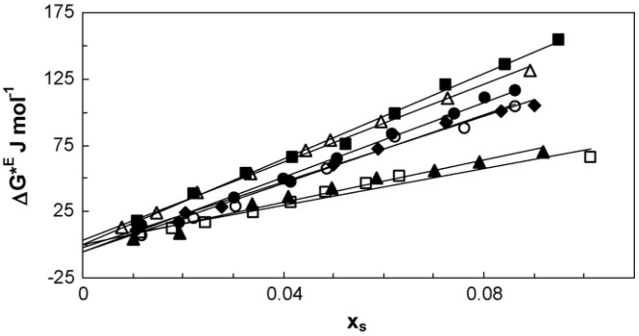

Fig. 5. Excess Gibbs energy of activation of viscous flow of $C_3H_7NH_2$ (○), $C_4H_9NH_2$ (♦), $(C_3H_7)_2NH$ (▲), $(C_4H_9)_2NH$ (□), $(C_2H_5)_3N$ (■), $(C_3H_7)_3N$ (●), and $(C_4H_9)_3N$ (△) in 1-C_4H_9OH at 303.15 K.

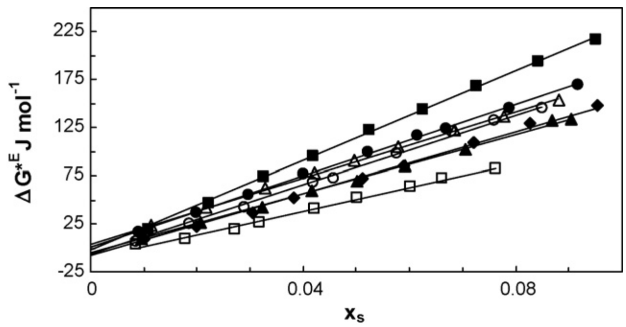

Fig. 6. Excess Gibbs energy of activation of viscous flow of $C_3H_7NH_2$ (○), $C_4H_9NH_2$ (♦), $(C_3H_7)_2NH$ (▲), $(C_4H_9)_2NH$ (□), $(C_2H_5)_3N$ (■), $(C_3H_7)_3N$ (●), and $(C_4H_9)_3N$ (△) in 2-C_4H_9OH at 303.15 K.

Table 8
B and D coefficients and standard deviations σ estimated from Eq. (2) and the values of partial specific volume $\bar{v}_s$, viscosity increment $\nu = 1000B/M_s\bar{v}_s\rho$ and $10^6D/(M_s\bar{v}_s\rho)^2$.

System	B	D	σ	$\bar{v}_s$	ν	$\frac{10^6D}{(M_s\bar{v}_s\rho)^2}$
In 1-butanol						
$C_3H_7NH_2$	−0.110	0.023	0.004	1.30	−1.78	6.03
$C_4H_9NH_2$	−0.083	0.010	0.002	1.29	−1.10	1.74
$(C_3H_7)_2NH$	−0.097	0.014	0.004	1.30	−0.92	1.25
$(C_4H_9)_2NH$	−0.074	0.007	0.002	1.30	−0.55	0.39
$(C_2H_5)_3N$	−0.095	0.009	0.002	1.33	−0.88	0.78
$(C_3H_7)_3N$	−0.088	0.017	0.003	1.30	−0.59	0.77
$(C_4H_9)_3N$	−0.043	0.003	0.001	1.28	−0.23	0.08
In 2-butanol						
$C_3H_7NH_2$	−0.108	0.026	0.004	1.36	−1.68	6.30
$C_4H_9NH_2$	−0.095	0.021	0.003	1.34	−1.21	3.42
$(C_3H_7)_2NH$	−0.090	0.016	0.002	1.32	−0.84	1.40
$(C_4H_9)_2NH$	−0.088	0.026	0.003	1.29	−0.66	1.46
$(C_2H_5)_3N$	−0.091	0.015	0.004	1.34	−0.84	1.29
$(C_3H_7)_3N$	−0.073	0.010	0.001	1.31	−0.49	0.44
$(C_4H_9)_3N$	−0.042	0.002	0.001	1.29	−0.22	0.05

Table 9
Regular terms of viscosities η_{int}, viscosity B', B'_{id}, B'_{int} parameters.

System	η_{int}	B'	B'_{id}	B'_{int}
In 1-butanol				
$C_3H_7NH_2$	−1.120	−0.124	−0.078	−0.046
$C_4H_9NH_2$	−0.637	−0.100	−0.074	−0.026
$(C_3H_7)_2NH$	−1.050	−0.116	−0.073	−0.043
$(C_4H_9)_2NH$	−0.726	−0.092	−0.062	−0.030
$(C_2H_5)_3N$	−0.981	−0.119	−0.079	−0.040
$(C_3H_7)_3N$	−0.799	−0.101	−0.068	−0.033
$(C_4H_9)_3N$	−0.226	−0.054	−0.045	−0.009
In 2-butanol				
$C_3H_7NH_2$	−1.057	−0.119	−0.080	−0.040
$C_4H_9NH_2$	−0.804	−0.106	−0.076	−0.030
$(C_3H_7)_2NH$	−0.773	−0.104	−0.075	−0.029
$(C_4H_9)_2NH$	−0.815	−0.096	−0.065	−0.031
$(C_2H_5)_3N$	−0.679	−0.106	−0.080	−0.026
$(C_3H_7)_3N$	−0.473	−0.088	−0.071	−0.018
$(C_4H_9)_3N$	−0.143	−0.054	−0.049	−0.005

1 to 79.8 bar. The viscosity deviations for butylamine + 1-butanol at 303.15, 313.15 and 323.15 K were also obtained by Weng [41]. The viscosity deviations are negative over the entire range of composition of these alkylamines in 1-butanol and magnitude of deviation decrease with rise in temperature and increases with increase in pressure. The observed large negative values of $(\eta - \eta_S^o)/\eta_S^o$ are resulted from strong solute–solvent interaction leading to the structure formation between butanol and amine molecules through H-bondings: $NH_2\cdots OH$ and $OH\cdots NH_2$ for primary amine, $NH\cdots OH$ and $OH\cdots NH$ for secondary amine, and $OH\cdots N$ for tertiary amine. Similar conclusions were drawn from the earlier volumetric studies of alkylamine solutions in butanols [42–47]. For both the butanol solutions, the values of ΔG^{*E} (Figs. 5 and 6) are positive. In case of 2-butanol ΔG^{*E} are more positive compared to 1-butanol. This supports that amine would form comparatively weak hydrogen-bonded complex with 2-butanol than that with the 1-butanol. French and Criss [48] and Lampreia and Barbosa [15] suggested stronger complex formation in case of primary amines in methanol than that in secondary amines. Present results also corroborate that the strength of complex formation decreases from primary to secondary to tertiary. This is also in agreement with the conclusions drawn by Spencer et al. [49], based on spectroscopic and enthalpic data for the formation of complexes between 1-butanol and diethyl- and butylamines. However, the negative values of viscosity deviations in the present amine solutions do not fully explain strong amine–alkanol interactions. According to Fort and Moore [50] strong solute–solvent specific interaction is expected to result in positive deviations in the viscosity. Nonetheless, on comparing the values of $\Delta\eta$ for amine solutions in butanols with that in cyclohexane [1], it was observed that the $\Delta\eta$ values are of smaller magnitude for former solutions. This is definitely a result of occurrence of solute–solvent specific interactions. It means that the strength of the intermolecular association is not the only factor influencing the viscosity deviations of liquid solutions. The molecular sizes and shapes and association of individual components are equally important factors. Thus, the viscosity deviations are functions of molecular interaction as well as of size and shape of molecules [6,45,51].

5.1. *On Herskovits and Kelly equation*

Table 8 gives that the values of coefficient B and D of Eq. (2), viscosity increment $\nu = 1000B/M_s\bar{v}_s\rho$ and the values of $10^6D/(M_s\bar{v}_s\rho)^2$ of $C_3H_7NH_2$, $C_4H_9NH_2$, $(C_3H_7)_2NH$, $(C_4H_9)_2NH$, $(C_2H_5)_3N$, $(C_3H_7)_3N$ and $(C_4H_9)_3N$ in 1-butanol and 2-butanol. The values of partial specific volume $\bar{v}_s$ of amines reported in V column have been derived from the measurements of densities of dilute solutions at number of concentrations of amines [1,2]. The values of B coefficient are in the range from −0.042 to −0.110 for alkylamines in 1-butanol and 2-butanol. The values of viscosity increment $\nu = 1000B/M_s\bar{v}_s\rho$ are negative for amine solutions in butanols. On the basis of Einstein model of sphere in a continuum [52], the viscosity increment η should be equal to 2.5. The values of viscosity increment η are not only far different than 2.5 but also have negative values. The deviation of B coefficient and related viscosity increments from the Einstein [52] and Guth–Simha [53] values may be attributed to the nature of solvent in terms of structure forming and structure breaking and deviation of solute particle from sphericity. Lower values of η were also found for homologous series of non-electrolytes in either high polar or non-polar solvents [17,54].

5.2. *On Nakagawa equation*

We estimated the B', B'_{id} and B'_{int} coefficients from the η_{int} values (Table 9) using Eqs. (13)–(15). The values of B' coefficient for alkylamines are from −0.124 to −0.054 in 1-butanol and 2-butanol. Since the B' coefficient also contains the contributions to the difference of viscosities for solute and solvent components and therefore, it is inappropriate to discuss the solute–solvent interaction in terms of B'. Solute–solvent interactions can be considered by the term B'_{int} defined by Eq. (15).

The values of B'_{int} are negative for all amine solutions in 1-butanol and 2-butanol. Since it is well known that strong cross association occurs between amine and alkanol, the values of B'_{int} should be positive. The interpretation based on the relative magnitude of B'_{int} derived from the ECS theory is inconsistent with the interactions present as amine–butanol does not form regular solution. Comparing the magnitude of B'_{int}, for corresponding amine solutions in cyclohexane [1] and the present values in butanols, it is observed that the magnitude of negative value of B'_{int} is reduced, which may point towards the presence of specific interactions between solute–solvent.

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