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Studies of viscosities of dilute solutions of alkylamines in non-electrolyte solvents: IV. Alkylamines in 1,4-dioxane and oxolane at 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 1,4-dioxane and oxolane (tetrahydrofuran) have been measured at 303.15 K. 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 $\Delta\eta$ for alkylamine solutions are negative in dioxane while positive in oxolane, and their magnitude increases with the increase in concentration of alkylamine. The values of excess Gibbs energy of activation ΔG^{*E} of viscous flow, based on Eyring's theory of absolute reaction rates, are negative for alkylamine solutions in 1,4-dioxane, while positive for alkylamine solutions in oxolane solutions. The results have been analyzed in terms of Herskovits and Kelly equation and Nakagawa equation. The values of viscosity increment ν in Herskovits and Kelly equation and the coefficient B'_{int} in Nakagawa equation are negative for the investigated alkylamine solutions in dioxane, while opposite is the case for oxolane.

1. Introduction

The thermodynamic and transport properties of dilute solutions provide information about solute–solute and solute–solvent interactions, and can be used for the development of molecular models for describing the thermodynamic behaviour of solutions. 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 [1–7]. It has been reported that cyclic ethers interact with alkylamines in their mixtures [8–17]. Different volumetric effects are observed upon mixing because of the extent of interactions varies in 1,4-dioxane–amine and oxolane–amine systems. 1,4-Dioxane is considered as a non-associating molecule while oxolane as an associating component. The formation of hydrogen bonding is assumed between the weak proton donor amine group of primary or secondary group and unshared electron pairs on the oxygen atom of ether. In earlier paper [6], 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 1,4-dioxane ($C_4H_8O_2$) and oxolane (C_4H_8O) at 303.15 K. As the viscosity behaviour in dilute solution is also very sensitive to predict solute–solute and solute–solvent interactions [1,2,7,18,19], we in this paper report viscosity behaviour of dilute solutions of same seven alkylamines in 1,4-dioxane and oxolane. 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 [18] and Nakagawa equation [20].

2. Experimental

The viscosities η were measured with a modified calibrated suspended level Ubbelohde viscometer [21]. The viscometer was designed so as to reduce surface tension effects to negligible values [22]. 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 [23]. 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 liquid or liquid mixture and the arithmetic mean was taken for the calculations. The densities ρ required to convert kinematic viscosities into dynamic viscosities η were taken from earlier reported work [6]. The details of the experimental procedure have been described earlier [1,3].

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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)	
	Expt.	Lit.	Obs.	Lit.
$C_3H_7NH_2$	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]
$C_4H_8O_2$	1.02230	1.0223[b,j] 1.02229[k] 1.02234[l]	1.0750	1.087[b]
C_4H_8O	0.87290	0.8730[b]	0.3260	0.325[b]

[a] [24].
[b] [23].
[c] [25].
[d] [26].
[e] [27].
[f] [28].
[g] [29].
[h] [30].
[i] [16].
[j] [31].
[k] [32].
[l] [33].

All the solutions were prepared by mixing known masses of pure liquids 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 different 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. 1,4-Dioxane ($C_4H_8O_2$, Merck AR) and oxolane (C_4H_8O, Galaxo AR) of purity better than 99.5 mol% were used after further purification and drying by standard procedures [23]. Both the cyclic ethers were refluxed for several hours over sodium metal pieces till free from peroxide and finally fractionally distilled over sodium. Immediately before use samples were dried over molecular sieve 0.4 nm (Fluka) and fractionally distilled twice. The measured values of density and viscosities were compared with the literature values in Table 1.

3. Theoretical

3.1. Herskovits and Kelly equation

In general for interpreting viscosity data the following relation

$$\eta/\eta_S^o = 1 + Bm + Dm^2 \tag{1}$$

has commonly been used [19], 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, whereas 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 [18] 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)

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

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

Recently, Matsubayashi and Nakahara [34] have extended the conformal solution theory (ECS) [35] to the dynamic problem through the first-order perturbation theory, theoretically derived the formula about concentration dependence of dynamical properties, and shown the validity of their ECS theory for binary regular mixtures containing benzene. According to the ECS theory, a dynamic property η for binary solution is written as the following:

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

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 [36,37] can be rewritten as

$$\eta/\eta_S^o = 1 + B'c + D'c^2 \tag{4}$$

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

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

From Eq. (5), the B' Jones-Dole coefficient is the first partial differential coefficient by molarity at $c = 0$, i.e.

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

Eq. (3) can be rearranged to

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

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

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

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

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

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

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

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

3.2.2. *Division of B′ coefficient*

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

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

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.

It is proposed that $B'_{\text{int}} = B' - B'_{id}$, namely

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

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

4. Results

The 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 1,4-dioxane and oxolane at 303.15 K are presented in Tables 2 and 3. The densities were taken from our earlier work [6] for converting kinematic viscosities to dynamic viscosities.

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

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

On the basis of the theory of absolute reaction rates [38], the excess Gibbs energy of activation ΔG^{*E} of viscous flow has been calculated from

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

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

Table 2
Densities and viscosities for alkylamine solutions in 1,4-dioxane at 303.15 K.

Solute	m (mol kg^{-1})	x_s	ρ^a (g cm^{-3})	η (mPa s)
$C_3H_7NH_2$	0.1086	0.0095	1.01934	1.0600
	0.2456	0.0212	1.01571	1.0427
	0.3295	0.0282	1.01353	1.0284
	0.4780	0.0404	1.00977	1.0140
	0.5767	0.0484	1.00734	0.9987
	0.7164	0.0594	1.00390	0.9852
	0.8321	0.0683	1.00115	0.9693
	1.0278	0.0830	0.99657	0.9504
	1.1161	0.0895	0.99457	0.9395
$C_4H_9NH_2$	0.1085	0.0095	1.01903	1.0604
	0.2365	0.0204	1.01526	1.0458
	0.3679	0.0314	1.01147	1.0320
	0.4745	0.0401	1.00849	1.0200
	0.5834	0.0489	1.00547	1.0075
	0.7574	0.0626	1.00081	0.9893
	0.8872	0.0725	0.99745	0.9764
	1.0040	0.0813	0.99447	0.9652
	1.1157	0.0895	0.99170	0.9543
$(C_3H_7)_2NH$	0.0998	0.0087	1.01816	1.0625
	0.2282	0.0197	1.01299	1.0499
	0.3410	0.0292	1.00857	1.0391
	0.4787	0.0405	1.00342	1.0270
	0.6261	0.0523	0.99804	1.0122
	0.7266	0.0602	0.99456	1.0005
	0.8461	0.0694	0.99045	0.9902
	0.9821	0.0796	0.98603	0.9801
	1.1489	0.0919	0.98073	0.9661
$(C_4H_9)_2NH$	0.1225	0.0107	1.01634	1.0651
	0.2369	0.0204	1.01103	1.0534
	0.3608	0.0308	1.00550	1.0405
	0.4533	0.0384	1.00152	1.0312
	0.5940	0.0497	0.99573	1.0191
	0.7122	0.0590	0.99103	1.0060
	0.8855	0.0724	0.98442	0.9937
	0.9669	0.0785	0.98149	0.9865
	1.1382	0.0911	0.97551	0.9766
$(C_2H_5)_3N$	0.1590	0.0138	1.01532	1.0540
	0.2697	0.0232	1.01065	1.0420
	0.4098	0.0349	1.00494	1.0180
	0.5388	0.0453	0.99987	0.9980
	0.6616	0.0551	0.99517	0.9800
	0.8419	0.0691	0.98859	0.9550
	0.9909	0.0803	0.98341	0.9320
	1.1350	0.0909	0.97857	0.9140
	1.2695	0.1006	0.97422	0.8940
$(C_3H_7)_3N$	0.1093	0.0095	1.01635	1.0598
	0.2293	0.0198	1.01011	1.0451
	0.3509	0.0300	1.00406	1.0319
	0.4408	0.0374	0.99977	1.0225
	0.5919	0.0496	0.99286	1.0073
	0.7147	0.0592	0.98758	0.9934
	0.8383	0.0688	0.98237	0.9807
	0.9836	0.0798	0.97663	0.9694
	1.1511	0.0921	0.97034	0.9571
$(C_4H_9)_3N$	0.1229	0.0107	1.01440	1.0621
	0.2173	0.0188	1.00865	1.0500
	0.3227	0.0276	1.00256	1.0330
	0.4476	0.0379	0.99571	1.0233
	0.5768	0.0484	0.98895	1.0081
	0.7655	0.0632	0.97972	0.9912
	0.8789	0.0719	0.97460	0.9804
	1.0282	0.0831	0.96830	0.9659
	1.1794	0.0941	0.96243	0.9569

[a] Taken from Ref. [6].

Table 3
Densities and viscosities for alkylamine solutions in oxolane at 303.15 K.

Solute	x_s	m (mol kg^{-1})	ρ^a (g cm^{-3})	η (mPa s)
$C_3H_7NH_2$	0.1123	0.0080	0.87160	0.3280
	0.2842	0.0201	0.86963	0.3315
	0.3986	0.0279	0.86836	0.3329
	0.5609	0.0389	0.86657	0.3353
	0.7487	0.0512	0.86454	0.3395
	0.8957	0.0607	0.86294	0.3412
	1.0016	0.0674	0.86182	0.3436
	1.1388	0.0759	0.86042	0.3453
	1.3767	0.0903	0.85808	0.3513
$C_4H_9NH_2$	0.1429	0.0102	0.87108	0.3290
	0.2304	0.0163	0.87000	0.3312
	0.5054	0.0352	0.86667	0.3360
	0.5880	0.0407	0.86571	0.3398
	0.7153	0.0490	0.86426	0.3442
	0.8391	0.0571	0.86287	0.3481
	1.0092	0.0678	0.86101	0.3510
	1.2698	0.0839	0.85822	0.3549
	1.4071	0.0921	0.85681	0.3619
$(C_3H_7)_2NH$	0.1794	0.0128	0.86996	0.3320
	0.2850	0.0201	0.86828	0.3350
	0.4155	0.0291	0.86626	0.3388
	0.5881	0.0407	0.86365	0.3437
	0.7109	0.0488	0.86187	0.3491
	0.9435	0.0637	0.85862	0.3545
	1.0507	0.0704	0.85717	0.3574
	1.1980	0.0795	0.85524	0.3640
	1.3568	0.0891	0.85322	0.3717
$(C_4H_9)_2NH$	0.1402	0.0100	0.87039	0.3333
	0.2993	0.0211	0.86766	0.3417
	0.4313	0.0302	0.86548	0.3498
	0.5953	0.0412	0.86290	0.3567
	0.7592	0.0519	0.86039	0.3648
	0.8997	0.0609	0.85835	0.3735
	1.0274	0.0690	0.85654	0.3806
	1.2011	0.0797	0.85423	0.3912
	1.3805	0.0905	0.85195	0.4015
$(C_2H_5)_3N$	0.1482	0.0106	0.87024	0.3270
	0.3064	0.0216	0.86751	0.3293
	0.4546	0.0317	0.86504	0.3307
	0.5880	0.0407	0.86287	0.3315
	0.7856	0.0536	0.85978	0.3361
	0.8993	0.0609	0.85807	0.3349
	1.0564	0.0708	0.85577	0.3376
	1.2402	0.0821	0.85317	0.3386
	1.4181	0.0928	0.85074	0.3410
$(C_3H_7)_3N$	0.1317	0.0094	0.87020	0.3305
	0.2429	0.0172	0.86804	0.3364
	0.3465	0.0244	0.86607	0.3397
	0.4545	0.0317	0.86408	0.3447
	0.5811	0.0402	0.86181	0.3523
	0.6842	0.0470	0.86004	0.3577
	0.8378	0.0570	0.85751	0.3607
	0.9371	0.0633	0.85595	0.3681
	1.1141	0.0744	0.85328	0.3753
$(C_4H_9)_3N$	0.1637	0.0117	0.86928	0.3385
	0.3071	0.0217	0.86631	0.3517
	0.4107	0.0288	0.86427	0.3637
	0.5836	0.0404	0.86100	0.3764
	0.7131	0.0489	0.85868	0.3894
	0.9025	0.0611	0.85553	0.4036
	1.1253	0.0751	0.85216	0.4181
	1.2042	0.0799	0.85102	0.4323
	1.3105	0.0863	0.84958	0.4444

[a] Taken from Ref. [6].

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

System	A_1	A_2	A_3	σ (mPa s)
In 1,4-dioxane				
$C_3H_7NH_2$	1.0750	−1.5967	1.0021	0.0016
$C_4H_9NH_2$	1.0744	−1.3895	0.5392	0.0006
$(C_3H_7)_2NH$	1.0744	−1.2349	0.5654	0.0012
$(C_4H_9)_2NH$	1.0770	−1.2482	1.4123	0.0016
$(C_2H_5)_3N$	1.0768	−1.6274	−1.9398	0.0019
$(C_3H_7)_3N$	1.0746	−1.5057	2.3993	0.0011
$(C_4H_9)_3N$	1.0763	−1.5267	2.6409	0.0018
In oxolane				
$C_3H_7NH_2$	0.3263	0.2145	0.6161	0.0006
$C_4H_9NH_2$	0.3256	0.3341	0.5159	0.0015
$(C_3H_7)_2NH$	0.3268	0.3566	1.4666	0.0012
$(C_4H_9)_2NH$	0.3265	0.6675	1.7539	0.0008
$(C_2H_5)_3N$	0.3257	0.1632	0.0075	0.0008
$(C_3H_7)_3N$	0.3254	0.6059	0.8985	0.0013
$(C_4H_9)_3N$	0.3260	1.1636	1.9406	0.0030

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

System	A_1	A_2	A_3	σ (mPa s)
In 1,4-dioxane				
$C_3H_7NH_2$	−1.477	0.60	2.9	0.002
$C_4H_9NH_2$	−1.457	6.08	−44.7	0.001
$(C_3H_7)_2NH$	−1.340	7.08	−52.5	0.002
$(C_4H_9)_2NH$	−0.793	−9.92	85.1	0.001
$(C_2H_5)_3N$	−1.247	−8.73	45.7	0.002
$(C_3H_7)_3N$	−1.519	6.34	−33.0	0.002
$(C_4H_9)_3N$	−1.129	−7.09	73.8	0.003
In oxolane				
$C_3H_7NH_2$	0.808	−2.05	27.1	0.002
$C_4H_9NH_2$	0.837	6.48	−33.1	0.005
$(C_3H_7)_2NH$	1.505	−7.28	86.9	0.003
$(C_4H_9)_2NH$	2.282	−0.76	42.0	0.002
$(C_2H_5)_3N$	0.267	7.24	−54.4	0.003
$(C_3H_7)_3N$	1.371	21.26	−173.2	0.005
$(C_4H_9)_3N$	3.201	22.27	−148.1	0.012

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

$$\psi=\sum_{i=1}^{m} P_i x_s^i \tag{19}$$

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 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 1,4-dioxane				
$C_3H_7NH_2$	−0.858	0.33	5.8	0.002
$C_4H_9NH_2$	−0.930	6.36	−46.7	0.001
$(C_3H_7)_2NH$	−0.846	7.77	−57.6	0.002
$(C_4H_9)_2NH$	−0.507	−10.82	92.8	0.001
$(C_2H_5)_3N$	−0.597	−9.33	48.8	0.002
$(C_3H_7)_3N$	−1.154	6.89	−36.0	0.002
$(C_4H_9)_3N$	−1.304	−7.65	79.4	0.003
In oxolane				
$C_3H_7NH_2$	0.240	−0.78	9.6	0.000
$C_4H_9NH_2$	0.155	2.09	−10.6	0.002
$(C_3H_7)_2NH$	0.343	−2.46	29.0	0.001
$(C_4H_9)_2NH$	0.333	−0.14	12.9	0.001
$(C_2H_5)_3N$	0.086	2.27	−17.1	0.001
$(C_3H_7)_3N$	0.181	6.88	−55.9	0.001
$(C_4H_9)_3N$	0.209	7.03	−46.5	0.004

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 1,4-dioxane			
$C_3H_7NH_2$	−926	−434	4.0
$C_4H_9NH_2$	−1198	1925	3.2
$(C_3H_7)_2NH$	−758	2919	5.1
$(C_4H_9)_2NH$	−599	−6213	8.0
$(C_2H_5)_3N$	−76	−13427	6.4
$(C_3H_7)_3N$	−1066	3841	3.2
$(C_4H_9)_3N$	−1362	−4487	7.2
In oxolane			
$C_3H_7NH_2$	1729	304	5.2
$C_4H_9NH_2$	1566	5946	11.3
$(C_3H_7)_2NH$	2829	418	10.3
$(C_4H_9)_2NH$	4401	478	6.1
$(C_2H_5)_3N$	1324	3129	7.2
$(C_3H_7)_3N$	3754	10010	11.5
$(C_4H_9)_3N$	7742	−2724	19.3

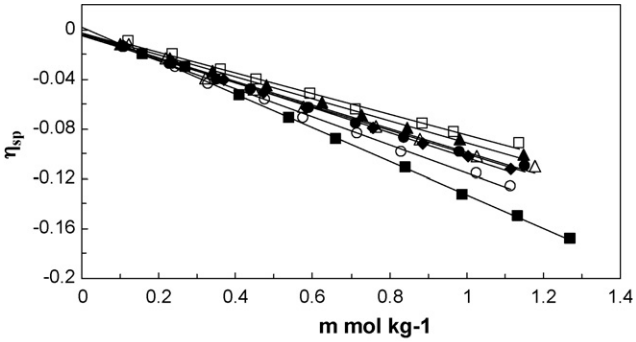

Fig. 1. Specific viscosities of $C_3H_7NH_2$ (○), $C_4H_9NH_2$ (♦), $(C_3H_7)_2NH$ (▲), $(C_4H_9)_2NH$ (□), $(C_2H_5)_3N$ (■), $(C_3H_7)_3N$ (●), and $(C_4H_9)_3N$ (△) in 1,4-dioxane at 303.15 K, linear curve for $(\eta - \eta_S^o)/\eta_S^o$ versus m (—).

5. Discussion

5.1. Alkylamine solutions in 1,4-dioxane

The dependence of $(\eta - \eta_S^o)/\eta_S^o$ on m, $\Delta\eta$ and ΔG^{*E} on x_s is shown in Figs. 1–3. The viscosity η of all amines solutions in 1,4-dioxane decreases with the increase in amine molality (Table 2) as a result the values of $(\eta - \eta_S^o)/\eta_S^o$ and ΔG^{*E} are small negative for all alkylamines in 1,4-dioxane and their magnitude increases with the increase in concentration of amine. In general plots of $(\eta - \eta_S^o)/\eta_S^o$, $\Delta\eta$ and ΔG^{*E} in Figs. 1–3 are almost linear for amine solutions in 1,4-dioxane. The alkylamine molecules possess significant dipole moment (0.78–1.37 D) and 1,4-dioxane molecules have small dipole moment (0.45 D [23]). The primary and secondary amines are also self-associated through H-bonding. The magnitude and sign of $(\eta - \eta_S^o)/\eta_S^o$ are based on the difference between the viscosity of solute and solvent apart from molecular interaction and therefore it will be discussed in terms of Herskovits–Kelly and Nakagawa equations in latter sections.

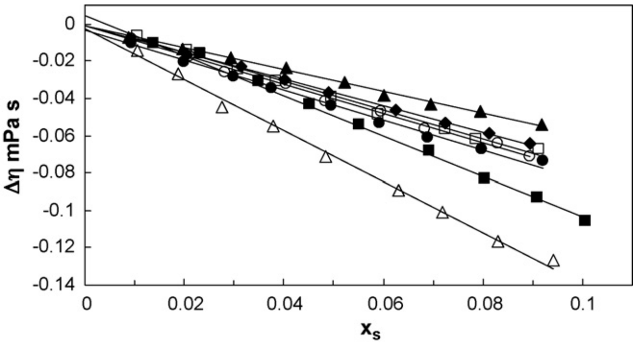

Fig. 2. Viscosity deviations of $C_3H_7NH_2$ (○), $C_4H_9NH_2$ (♦), $(C_3H_7)_2NH$ (▲), $(C_4H_9)_2NH$ (□), $(C_2H_5)_3N$ (■), $(C_3H_7)_3N$ (●), and $(C_4H_9)_3N$ (△) in 1,4-dioxane at 303.15 K, linear curve for $\Delta\eta$ versus x_s (—).

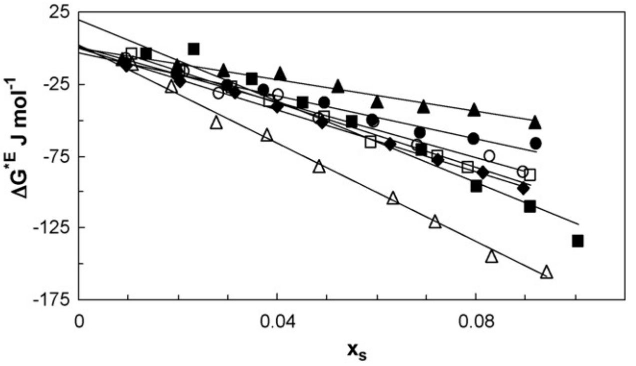

Fig. 3. Excess Gibbs energy of activation of viscous flow of $C_3H_7NH_2$ (○), $C_4H_9NH_2$ (♦), $(C_3H_7)_2NH$ (▲), $(C_4H_9)_2NH$ (□), $(C_2H_5)_3N$ (■), $(C_3H_7)_3N$ (●), and $(C_4H_9)_3N$ (△) in 1,4-dioxane at 303.15 K, linear curve for ΔG^{*E} versus x_s (—).

The over all behaviour of $\Delta\eta$ and ΔG^{*E} can be envisaged as a resultant of opposite effects: (i) disruption of ether–ether (solvent–solvent) interactions, (ii) break down of dipolar and or H-bonding self-association in amines (solute–solute interaction), and (iii) alkylamine–dioxane cross-association (solute–solvent interaction). The disruption of associated structure (effects (i) and (ii)) reduces the cohesive forces between the molecules, thereby increasing the mobility. On the other hand, enhanced dipole–dipole and cross-association between unlike components (effect (iii)) increases the cohesive forces, as a result mobility is reduced. From the large positive equimolar excess enthalpy H_m^E 1603 J mol^{-1} for 1,4-dioxane + cyclohexane at 298.15 K [39], 1595 J mol^{-1} for 1,4-dioxane + hexane at 303.15 K [40] and 1642 J mol^{-1} for 1,4-dioxane + heptane at 298.15 K [41], respectively, it is clear that the ether–ether interactions are quite strong. Though, our present study is concerned with dilute amine solutions, yet the ether–ether interactions will not be negligible, but the contribution will be of small extent only. In order to arrive at certain meaningful conclusions about the solute–solute and solute–solvent interactions in the present solutions, it will be interesting to compare present viscosity behaviour with that obtained for amines solution in cyclohexane [1]. The values of $\Delta\eta$ and ΔG^{*E} for amine solutions in both the solvents: 1,4-dioxane and cyclohexane are negative. Generally, the values of primary and secondary amine solutions in 1,4-dioxane are less negative as compared to cyclohexane solutions, where as with tri-n-alkylamines, almost similar behaviour is observed. The reductions in negative values of $\Delta\eta$ and ΔG^{*E} for primary and secondary amines in 1,4-dioxane as compared to cyclohexane solutions may be attributed to the enhanced dipole–dipole interactions and cross-association between unlike components. However, the over all negative values of $\Delta\eta$ and ΔG^{*E} and positive excess partial molar volumes [3] definitely suggest that the dispersive interaction due to disruption of ether–ether interactions, the breaking of dipolar order in amine as well as in 1,4-dioxane and the disruption of H-bonding in primary and secondary amines dominate over the enhanced dipole–dipole and cross-association between the unlike components. The latter interaction is based on the picture that the H-atom of the amine interacts as a proton donor to unshared electron pairs of the oxygen atom of the ether molecules. The similar assumption has been done previously for n-butylamine + 1,4-dioxane mixture [15,42]. The smaller positive values of excess molar enthalpy, Gibbs energy, and volumes

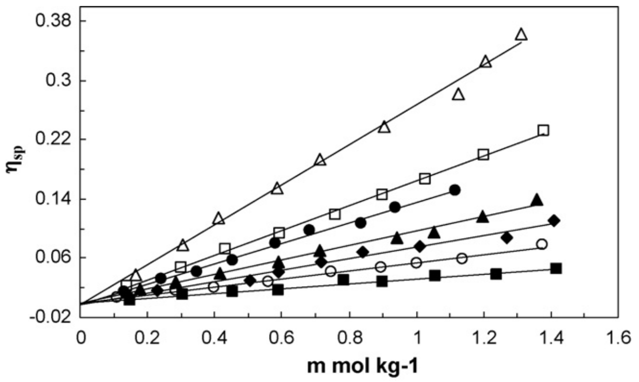

Fig. 4. Specific viscosities of $C_3H_7NH_2$ (○), $C_4H_9NH_2$ (♦), $(C_3H_7)_2NH$ (▲), $(C_4H_9)_2NH$ (□), $(C_2H_5)_3N$ (■), $(C_3H_7)_3N$ (●), and $(C_4H_9)_3N$ (△) in oxolane at 303.15 K, linear curve for $(\eta - \eta_S^o)/\eta_S^o$ versus m (—).

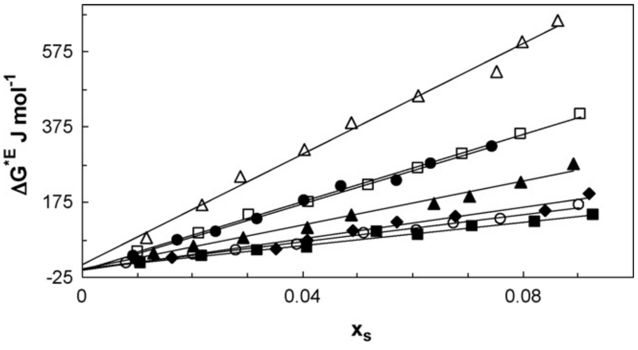

Fig. 6. Excess Gibbs energy of activation of viscous flow of $C_3H_7NH_2$ (○), $C_4H_9NH_2$ (♦), $(C_3H_7)_2NH$ (▲), $(C_4H_9)_2NH$ (□), $(C_2H_5)_3N$ (■), $(C_3H_7)_3N$ (●), and $(C_4H_9)_3N$ (△) in THF at 303.15 K, linear curve for ΔG^{*E} versus x_s (—).

for primary and secondary amine in 1,4-dioxane compared to that in cyclohexane or n-hexane [10,12–15,42–44] also corroborate the above interpretation.

In case of tri-n-alkylamine, the 1,4-dioxane molecules also act as an order breaker for the amines [45]. Larger negative values of $\Delta\eta$ and ΔG^{*E} for tri-n-alkylamine + 1,4-dioxane compared to primary or secondary amine + 1,4-dioxane may be attributed to dominant contribution because of disruption of dipolar orders in like molecules compared to the operation of weak dipole–dipole (amine–ether) interactions. This is well supported by large positive equimolar excess molar enthalpy H_m^E of tri-n-butylamine + 1,4-dioxane (1754 J mol^{-1} [11]) and 1,4-dioxane + cyclohexane (1603 J mol^{-1} [39]). Letcher and Domanska [11] reported that tri-n-alkylamine–1,4-dioxane association is presumably very weak.

5.2. Alkylamine solutions in oxolane

The dependence of $(\eta - \eta_S^o)/\eta_S^o$ on m, $\Delta\eta$ and ΔG^{*E} on x_s is shown in Figs. 4–6. The viscosity η of all amines solutions in oxolane increases with the increase in amine molality (Table 3) and the values of $(\eta - \eta_S^o)/\eta_S^o$, $\Delta\eta$ and ΔG^{*E} are large positive for all alkylamines and plots in Figs. 4–6 are linear with composition m or x_s. The over all behaviour of $\Delta\eta$ and ΔG^{*E} is a result of opposite effects (i) disruption of ether–ether (solvent–solvent) interactions, (ii) break down of dipolar and or H-bonding self-association in amines (solute–solute interaction), and (iii) amine–ether cross-association (solute–solvent interaction). As in amine–dioxane solutions, the contribution due to disruption of ether–ether (solvent–solvent) interactions though quite strong (H_m^E (x = 0.5) = 750, 740 and 791 J mol^{-1} for oxolane + cyclohexane [39], + n-hexane [40] and +n-heptane [41] at 298.15 K, respectively), but will contribute only marginally, as the solutions under study are dilute. The over all positive values of $\Delta\eta$ and ΔG^{*E} suggest qualitatively that the dipole–dipole interactions (μ for oxolane = 1.75 D and for amines 0.78–1.37 D [23]) and cross-association between amine and oxolane components dominate over the dispersive ether–ether interactions, breaking of dipolar order of amine as well as of oxolane and the disruption of H-bonding in primary and secondary amines. In the cross-association the H-atom of the amine interacts with O-atom of the oxolane molecules. Apparently, the present viscosity behaviour suggests that the specific interactions between amines and oxolane are stronger compared to amine–dioxane.

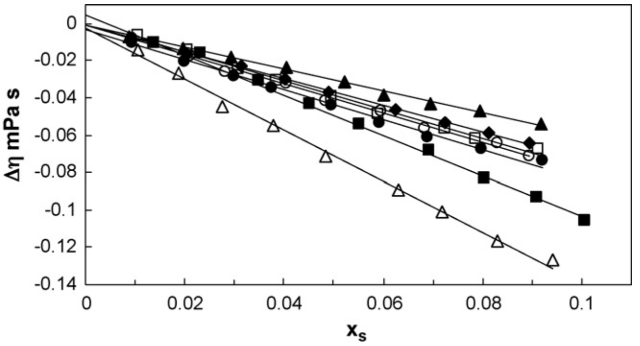

Fig. 5. Viscosity deviations of $C_3H_7NH_2$ (○), $C_4H_9NH_2$ (♦), $(C_3H_7)_2NH$ (▲), $(C_4H_9)_2NH$ (□), $(C_2H_5)_3N$ (■), $(C_3H_7)_3N$ (●), and $(C_4H_9)_3N$ (△) in THF at 303.15 K, linear curve for $\Delta\eta$ versus x_s (—).

It is an accepted procedure to estimate the strength of interaction from excess molar enthalpy H_m^E or partial molar excess enthalpy $H_{m,i}^{E,\infty} \cdot H_m^E$ of alkylamines + ethers has been investigated by Letcher and coworkers [11,13–15]. The amine–ether interactions for $C_4H_9NH_2$, $(C_4H_9)_2NH$, and $(C_4H_9)_3N$ with $C_4H_8O_2$ and C_4H_8O were estimated by subtracting sum of partial molar excess enthalpy of amine in hydrocarbon and ether in hydrocarbon from the partial molar excess enthalpy of amine in ether. The partial molar excess enthalpy was obtained from molar excess enthalpy data of amine + ether, amine + hydrocarbon and ether + hydrocarbon data from the literature [11,13,14,39,40,44]. These are summarized in Table 8. It was observed from last column of Table 8 that interaction energy for $(C_4H_9)_3N$–C_4H_8O is somewhat more negative than that for $(C_4H_9)_3N$–$C_4H_8O_2$, indicating that specific interactions in $(C_4H_9)_3N$–C_4H_8O were stronger than that in $(C_4H_9)_3N$–$C_4H_8O_2$. Reverse were the observations for $C_4H_9NH_2$ and $(C_3H_7)_2NH$ amines with $C_4H_8O_2$ and C_4H_8O systems. For these latter amines, the interactions are supposed to be stronger with 1,4-dioxane compared to oxolane. Similar were the findings by Letcher et al. [11,13–15] for amine–ether interactions. Thus, the predicted extent of specific interactions from the viscosity results for tri-n-butylamine–ether solutions are in agreement with the H_m^E results, but not so for n-butylamine and di-n-butylamine. It has been noted earlier [46–48] also that the viscosity behaviour not only depends on molecular interactions but also depends upon the size and the shape of molecules. Thus it may be inferred that it is difficult to estimate quantitatively the strength of interaction from viscosity behaviour alone.

5.3. On Herskovits and Kelly equation

Table 9 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 1,4-dioxane and oxolane. The values of partial spe-

Table 8
Limiting values of excess molar enthalpy of amine in ether, amine in hydrocarbon and ether in hydrocarbon, and amine–ether interaction.

Amine + ether	$H^{E,\infty}_{m,\text{amine}}$ in ether (kJ mol^{-1}) (A)	$H^{E,\infty}_{m,\text{amine}}$ in hydrocarbon (kJ mol^{-1}) (B)	$H^{E,\infty}_{m,\text{ether}}$ in hydrocarbon (kJ mol^{-1}) (C)	Amine–ether interaction (kJ mol^{-1}) A – (B + C)
$C_4H_9NH_2 + C_4H_8O_2$	2.34[a]	6.56[b]	7.42[c]	−11.64
$C_4H_9NH_2 + C_4H_8O$	8.79[d]	6.56[b]	4.58[e]	−8.87
$(C_4H_9)_2NH + C_4H_8O_2$	3.47[f]	1.41[g]	7.42[c]	−5.36
$(C_4H_9)_2NH + C_4H_8O$	0.71[h]	1.41[g]	4.57[c]	−5.26
$(C_4H_9)_3N + C_4H_8O_2$	8.75[i]	1.04[j]	8.21[k]	−0.49
$(C_4H_9)_3N + C_4H_8O$	3.87[l]	1.04[j]	3.37[m]	−0.54

[a] From H^E_m of $C_4H_9NH_2 + C_4H_8O_2$ [13].
[b] From H^E_m of $C_4H_9NH_2$ + cyclohexane [44].
[c] From H^E_m of $C_4H_8O_2$ + n-hexane [40].
[d] From H^E_m of $C_4H_9NH_2 + C_4H_8O$ [13].
[e] From H^E_m of C_4H_8O + n-hexane [40].
[f] From H^E_m of $(C_4H_9)_2NH + C_4H_8O_2$ [14].
[g] From H^E_m of $(C_4H_9)_2NH$ + n-hexane [44].
[h] From H^E_m of $(C_4H_9)_2NH + C_4H_8O$ [14].
[i] From H^E_m of $(C_4H_9)_3N + C_4H_8O_2$ [11].
[j] from H^E_m of $(C_4H_9)_3N$ + cyclohexane [44].
[k] From H^E_m of $C_4H_8O_2$ + cyclohexane [39].
[l] From H^E_m of $(C_4H_9)_2NH + C_4H_8O$ [11].
[m] From H^E_m of C_4H_8O + cyclohexane [39].

cific 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 −0.084 to −0.130 for alkylamines in 1,4-dioxane and from 0.027 to 0.253 in oxolane. The values of viscosity increment $\nu = 1000B/M_s\bar{v}_s\rho$ are negative for amine solutions in 1,4-dioxane while positive for oxolane. On the basis of Einstein model of sphere in a continuum [49], the viscosity increment ν should be equal to 2.5. The values of viscosity increment ν are not only far different than 2.5 but also have negative values in 1,4-dioxane. The deviation of *B* coefficient and related viscosity increments from the Einstein [49] and Guth–Simha [50] values may be attributed to the nature of solvent in terms structure forming and structure breaking and deviation of solute particle from sphericity. Lower values of ν were also found for homologous series of non-electrolytes in polar and non-polar solvents [1,2,19,51].

5.4. *On Nakagawa equation*

We estimated the B', B'_{id} and B'_{int} coefficients from the η_{int} values (Table 10) using Eqs. (13)–(15). The values of B' Jones-Dole coefficient for alkylamines are from −0.091 to −0.139 dm^3 mol^{-1} in 1,4-dioxane, from 0.040 to 0.324 in oxolane. 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 1,4-dioxane while positive in case of oxolane. Since it is well known that weak interaction occurs in case of amine and dioxane while strong interaction between amine and oxolane. The negative values of B'_{int} for all the amine solutions in dioxane clearly indicate disruption of local-order of amines by addition of dioxane molecules. The positive values of B'_{int} for all amine solutions in oxolane are result of specific interactions between alkylamine and oxolane. The interpretation based on the relative magnitude of B'_{int} derived from the ECS theory is consistent with the partial molar volume and the heat of solution [6].

Table 9
B and *D* coefficients and standard deviations σ estimated from Eq. (2) and the values of partial specific volume $\bar{v}_s$, viscosity increment $\nu = 10^3 B/(M_s\bar{v}_s\rho)$ and $10^6 D/(M_s\bar{v}_s\rho)^2$.

System	*B*	*D*	σ	$\bar{v}_s$	ν	$\frac{10^6 D}{(M_s\bar{v}_s\rho)^2}$
In 1,4-dioxane						
$C_3H_7NH_2$	−0.130	0.016	0.004	1.42	−1.51	2.17
$C_4H_9NH_2$	−0.120	0.020	0.004	1.38	−1.17	1.89
$(C_3H_7)_2NH$	−0.109	0.020	0.005	1.38	−0.77	0.99
$(C_4H_9)_2NH$	−0.084	−0.001	0.005	1.35	−0.47	−0.03
$(C_2H_5)_3N$	−0.121	−0.012	0.005	1.38	−0.85	−0.59
$(C_3H_7)_3N$	−0.127	0.029	0.003	1.35	−0.64	0.74
$(C_4H_9)_3N$	−0.111	0.012	0.007	1.32	−0.44	0.19
In oxolane						
$C_3H_7NH_2$	0.055	−0.001	0.003	1.40	0.76	−0.19
$C_4H_9NH_2$	0.065	0.009	0.006	1.38	0.74	1.17
$(C_3H_7)_2NH$	0.097	0.000	0.005	1.36	0.81	0.00
$(C_4H_9)_2NH$	0.159	0.004	0.004	1.33	1.06	0.18
$(C_2H_5)_3N$	0.027	0.005	0.005	1.38	0.22	0.34
$(C_3H_7)_3N$	0.116	0.023	0.009	1.34	0.69	0.82
$(C_4H_9)_3N$	0.253	0.014	0.014	1.31	1.20	0.31

Table 10
Regular terms of viscosities η_{int}, viscosity B', B'_{id}, B'_{int} parameters.

System	η_{int}	B'	B'_{id}	B'_{int}
In 1,4-dioxane				
$C_3H_7NH_2$	−0.867	−0.127	−0.058	−0.070
$C_4H_9NH_2$	−0.800	−0.115	−0.051	−0.064
$(C_3H_7)_2NH$	−0.675	−0.102	−0.048	−0.054
$(C_4H_9)_2NH$	−0.796	−0.091	−0.027	−0.064
$(C_2H_5)_3N$	−0.992	−0.139	−0.060	−0.080
$(C_3H_7)_3N$	−0.972	−0.117	−0.039	−0.078
$(C_4H_9)_3N$	−1.504	−0.113	0.007	−0.121
In oxolane				
$C_3H_7NH_2$	0.243	0.068	0.007	0.062
$C_4H_9NH_2$	0.239	0.090	0.030	0.061
$(C_3H_7)_2NH$	0.328	0.121	0.038	0.083
$(C_4H_9)_2NH$	0.389	0.202	0.103	0.099
$(C_2H_5)_3N$	0.154	0.040	0.001	0.039
$(C_3H_7)_3N$	0.360	0.159	0.068	0.091
$(C_4H_9)_3N$	0.439	0.324	0.213	0.111

6. Conclusions

The viscosities η, specific viscosities $(\eta - \eta^o_S)/\eta^o_S$, and viscosity deviations $\Delta\eta$ of dilute solutions of seven alkylamines in 1,4-dioxane and oxolane were determined. The molecular interpretation of possible cross-association between amine and ether is based on the picture that the hydrogen atom of the amine group interacts as a proton donor with the oxygen of the ether molecules. The tri-n-alkylamine-ether association seems to be very weak.

The values of B-coefficient and viscosity increment ν for alkylamines in Herskovits and Kelly equation are negative in 1,4-dioxane and positive in oxolane. The values of B'_{int} in Nakagawa equation are negative for all amine solutions in 1,4-dioxane while positive in case of oxolane.

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