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Studies of viscosities of dilute solutions of alkylamine in non-electrolyte solvents

I. Aliphatic and aromatic hydrocarbons

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Abstract

Viscosities, η, of dilute solutions of *n*-propylamine, *n*-butylamine, di-*n*-propylamine, di-*n*-butylamine, tri-*n*-propylamine, and tri-*n*-butylamine in cyclohexane, benzene at 303.15 and 313.15 K and of triethylamine in *n*-heptane, cyclohexane, benzene, toluene, ethylbenzene and *p*-xylene at 303.15 K have been measured. The specific viscosities, $(\eta - \eta_S^0)/\eta_S^0$, and viscosity deviations, $\Delta\eta$, have been calculated. Based on Eyring's theory of absolute reaction rates, the values of excess Gibbs energy of activation, ΔG^{*E}, of viscous flow has been determined. The results have been analysed in terms of Herskovits and Kelly equation and Nakagawa equation.

Keywords: Alkylamines; Dilute solutions; Hydrocarbon; Specific viscosities; Herskovits and Kelly equation; Nakagawa equation

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1. Introduction

We are engaged in systematic studies of thermodynamic and transport properties of solutions involving alkylamine as they are important organic bases because of their strong electron donating capability. From studies of speed of sound, isentropic compressibility, and excess molar volume over the entire range of composition [1–5], it has been observed that alkylamine interacts with aromatic hydrocarbon. In order to know the nature and extent of solute–solute, and solute–solvent interactions, the partial molar properties of dilute solutions in non-polar, non-interacting solvent are of great significance [6–12]. Viscosity behaviour in dilute solution is very sensitive to predict solute–solute and solute–solvent interactions [13,14]. With this view in mind, in this paper we have reported viscosity behaviour of dilute solutions of alkylamine in variety of solvents. This study is expected to reveal some interesting facts concerning the nature and different extent of interactions in amines. The results have also been analysed in terms of Herskovits and Kelly equation [13] and Nakagawa equation [15].

2. Experimental

The viscosities, η, were measured with a modified calibrated suspended level Ubbelohde viscometer [16]. The viscometer was designed so as to reduce surface tension effects to negligible values [17]. The apparatus was submerged in a thermostatic bath at 303.15 or 313.15 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 [18]. 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 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 [1,19].

All the solutions were prepared by mixing known masses of pure liquids in air tight, narrow-mouth ground stoppered

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bottles taking due precautions to minimise 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 (PA) (Merck, Schuchardt), *n*-butylamine (BA) (Fluka AG), di-*n*-propylamine (DPA) (Fluka AG), di-*n*-butylamine (DBA) (Fluka AG), triethylamine (TEA) (Sisco, extra pure), tri-*n*-propylamine (TPA) (Fluka AG), and tri-*n*-butylamine (TBA) (SRL, Bombay), of purity better than 99.0 mol% were refluxed over Na metal and distilled twice fractionally before use. Cyclohexane (CHN) (Fluka AG), *n*-heptane (HEP) (Sisco, extra pure), benzene (BEN) (Merck, GR), toluene (TOL) (Galaxo, AR), ethyl benzene (EB) (Sisco extra pure) and *p*-xylene (pXY) (Galaxo, AR) of purity better then 99.5 mol% were used after further purification and drying by standard procedures [18]. 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

$$\frac{\eta}{\eta_{\mathrm{S}}^{0}} = 1 + Bm + Dm^{2} \tag{1}$$

has commonly been used [14], where $\eta/\eta_{\mathrm{S}}^{0}$ 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 [13] substituted molality in terms of volume faction ϕ_{s} as $m = 1000\phi_{\mathrm{s}}/M_{\mathrm{s}}\bar{v}_{\mathrm{s}}\rho$ in Eq. (1) and obtained the Eq. (2):

$$\frac{\eta}{\eta_{\mathrm{S}}^{0}} = 1 + \frac{1000B\phi_{\mathrm{s}}}{M_{\mathrm{s}}\bar{v}_{\mathrm{s}}\rho} + \frac{(1\times10^{6})D\phi_{\mathrm{s}}^{2}}{(M_{\mathrm{s}}\bar{v}_{\mathrm{s}}\rho)^{2}} \tag{2}$$

Table 1
Comparison of experimental densities and viscosity of pure liquids at 303.15 K with the literature data

Solvents	Temperature (K)	Density (g cm^{-3})		Viscosity (mPa s)	
		Obs.	Lit.	Obs.	Lit.
PA	303.15	0.70610	0.70615 [20]	0.3527	0.350 [18]
	313.15	0.69604	0.6960 [20]	0.3127	0.3087 [21]
BA	303.15	0.72865	0.72865 [22]	0.4442	0.4430 [19]
					0.456 [18]
					0.458 [23]
	313.15	0.71917	0.7182 [24]	0.3927	0.3852 [21]
			0.71917 [22]		0.398 [23]
DPA	303.15	0.73121	0.73019 [25]	0.5118	0.4789 [21]
	313.15	0.72615	0.7216 [20]	0.4233	0.4230 [21]
DBA	303.15	0.75228	0.75248 [24]	0.7584	0.734 [26]
					0.7593 [21]
	313.15	0.74344	0.74284 [26]	0.6649	0.64 [26]
			0.7431 [20]		0.6567 [21]
TEA	303.15	0.71844	0.71845 [18]	0.3296	0.3295 [18]
					0.3298 [27]
TPA	303.15	0.74915	0.7497 [28]	0.5977	0.595 [27]
	313.15	0.74041	0.7404 [20]	0.5378	0.5196 [21]
TBA	303.15	0.77021	0.7709 [20]	1.1670	1.1663 [27]
	313.15	0.76311	0.7612 [26]	0.9704	0.989 [27]
			0.7634 [20]		0.99 [26]
CHN	303.15	0.76910	0.76904 [29]	0.8183	0.820 [18]
			0.76915 [30]		
	313.15	0.75952	0.7595 [29]	0.7160	
BEN	303.15	0.86830	0.86829 [30]	0.5625	0.5621 [18]
	313.15	0.75952	0.85769 [29]	0.4921	
HEP	303.15	0.67518	0.67519 [18]	0.3753	0.3753 [18]
TOL	303.15	0.85753	0.85754 [18]	0.5190	0.5191 [18]
EB	303.15	0.85799	0.8581 [18]	0.5960	0.5963 [18]
pXY	303.15	0.85223	0.85225 [18]	0.5658	0.566 [18]

where $\bar{v}_\mathrm{s}$ is partial specific volume. The coefficients B and D of equation can be evaluated from the intercept and slope of $(\eta/\eta_\mathrm{S}^0 - 1)/m$ versus m plots.

3.2. Nakagawa equation

Recently, Matsubayashi and Nakahara [31] have extended the conformal solution theory (ECS) [32] 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

$$\eta = x_\mathrm{s}\eta_\mathrm{s}^0 + (1 - x_\mathrm{s})\eta_\mathrm{S}^0 + (1 - x_\mathrm{s})x_\mathrm{s}\eta_\mathrm{int} \tag{3}$$

where η_s^0 and η_S^0 are viscosities of solute and solvent components, respectively, 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 [33,34] can be rewritten as

$$\frac{\eta}{\eta_\mathrm{S}^0} = 1 + B'c + D'c^2 \tag{4}$$

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

$$\left[\frac{\partial(\eta/\eta_\mathrm{S}^0)}{\partial c}\right]_{T,P} = B' + 2D'c \tag{5}$$

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

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

Eq. (3) can be rearranged to

$$\frac{\eta}{\eta_\mathrm{S}^0} = x_\mathrm{s}\left(\frac{\eta_\mathrm{s}^0}{\eta_\mathrm{S}^0}\right) + 1 - x_\mathrm{s} + \frac{(1 - x_\mathrm{s})x_\mathrm{s}\eta_\mathrm{int}}{\eta_\mathrm{S}^0} \tag{7}$$

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:

$$\left[\frac{\partial(\eta/\eta_\mathrm{S}^0)}{\partial x_\mathrm{s}}\right]_{T,P} = \frac{\eta_\mathrm{s}^0}{\eta_\mathrm{S}^0} - 1 + (1 - 2x_\mathrm{s})\left(\frac{\eta_\mathrm{int}}{\eta_\mathrm{S}^0}\right) \tag{8}$$

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

$$c = \frac{1000x_\mathrm{s}\rho}{x_\mathrm{s}M_\mathrm{s} + (1 - x_\mathrm{s})M_\mathrm{S}} \tag{9}$$

The density ρ of solution can be expressed as power series of x_s [31], that is

$$\rho = \sum_{i=0}^{n} A_i x_\mathrm{s}^i \tag{10}$$

where A_i is fitting coefficient, in particular, $A_0 \equiv \rho_\mathrm{S}$ means the neat solvent density. Substituting Eq. (10) to Eq. (9), and differentiating it by x_s at constant T and P, one obtains

$$\left[\frac{\partial c}{\partial x_\mathrm{s}}\right]_{T,P} = \frac{1000\left[\sum_{i=1}^{n} A_i x_\mathrm{s}^{i+1}(M_\mathrm{s} - M_\mathrm{S}) + \sum_{i=0}^{n}(i + 1)A_i x_\mathrm{s}^i M_\mathrm{S}\right]}{[x_\mathrm{s}M_\mathrm{s} + (1 - x_\mathrm{s})M_\mathrm{S}]^2} \tag{11}$$

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

$$B' = \lim_{c\to 0}\left[\frac{\partial(\eta/\eta_\mathrm{S}^0)}{\partial c}\right] = \lim_{c\to 0}\left[\frac{\partial(\eta/\eta_\mathrm{S}^0)/\partial x_\mathrm{s}}{\partial c/\partial x_\mathrm{s}}\right] \tag{12}$$

$$B' = \frac{M_\mathrm{S}[(\eta_\mathrm{s}^0/\eta_\mathrm{S}^0) - 1 + (\eta_\mathrm{int}/\eta_\mathrm{S}^0)]}{1000\rho_\mathrm{S}} \tag{13}$$

3.2.2. Division of B' coefficient

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

$$B'_\mathrm{id} = \frac{M_\mathrm{S}[(\eta_\mathrm{s}^0/\eta_\mathrm{S}^0) - 1]}{1000\rho_\mathrm{S}} \tag{14}$$

where B'_id is the contribution of ideal mixture for the B' coefficient, which is based on the difference between the viscosities 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 a characteristic for solute–solvent interaction.

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

$$B'_\mathrm{int} = \frac{M_\mathrm{S}\eta_\mathrm{int}}{1000\rho_\mathrm{S}\eta_\mathrm{S}} = K\eta_\mathrm{int} \tag{15}$$

should be the interaction parameter instead of B', where $K = M_\mathrm{S}/1000\rho_\mathrm{S}\eta_\mathrm{S} = 1/1000v_\mathrm{S}\eta_\mathrm{S}$ is the constant which is independent of the solution composition.

4. Results

The experimental densities, ρ, and viscosities, η, of dilute solutions of PA, BA, DPA, DBA, TPA and TBA in cyclohexane and benzene at 303.15 and 313.15 K, and TEA in cyclohexane, *n*-heptane, benzene, toluene, ethylbenzene and *p*-xylene at 303.15 K are presented in Table 2.

The experimental values of η are expressed by

$$\eta = \sum_{i=1}^{m} A_i x_\mathrm{s}^{i-1} \tag{16}$$

Table 2
Properties of amine solution in different solvents

x_s	m (mol kg^{-1})	ρ (g cm^{-3}) (at 303.15 K)	η (mPa s) (at 303.15 K)	ρ (g cm^{-3}) (at 313.15 K)	η (mPa s) (at 313.15 K)
CHN + PA					
0.0076	0.0911	0.7685	0.8113	0.7589	0.7093
0.0076	0.0911	0.7685	0.8113	0.7582	0.6999
0.0169	0.2040	0.7678	0.8039	0.7574	0.6903
0.0282	0.3449	0.7669	0.7953	0.7568	0.6849
0.0365	0.4504	0.7662	0.7890	0.7559	0.6772
0.0483	0.6032	0.7653	0.7803	0.7553	0.6700
0.0570	0.7178	0.7646	0.7736	0.7547	0.6638
0.0652	0.8282	0.7640	0.7669	0.7540	0.6564
0.0747	0.9588	0.7633	0.7583	0.7532	0.6488
0.0859	1.1163	0.7625	0.7506		
CHN + BA					
0.0097	0.1159	0.7684	0.8095	0.7588	0.7083
0.0197	0.2391	0.7677	0.8005	0.7581	0.6998
0.0282	0.3450	0.7671	0.7907	0.7575	0.6925
0.0380	0.4699	0.7664	0.7823	0.7569	0.6831
0.0471	0.5877	0.7658	0.7702	0.7563	0.6749
0.0581	0.7331	0.7650	0.7580	0.7556	0.6646
0.0674	0.8587	0.7644	0.7469	0.7549	0.6553
0.0724	0.9268	0.7641	0.7374	0.7546	0.6487
0.0873	1.1366	0.7631	0.7267	0.7536	0.6370
CHN + DPA					
0.0114	0.1367	0.7683	0.8095	0.7587	0.7072
0.0213	0.2580	0.7677	0.8028	0.7580	0.6995
0.0321	0.3943	0.7669	0.7945	0.7573	0.6920
0.0414	0.5132	0.7663	0.7840	0.7567	0.6827
0.0509	0.6375	0.7657	0.7745	0.7561	0.6721
0.0622	0.7879	0.7650	0.7633	0.7553	0.6596
0.0727	0.9314	0.7643	0.7535	0.7547	0.6490
0.0811	1.0492	0.7638	0.7441	0.7542	0.6399
0.0919	1.2028	0.7631	0.7334	0.7535	0.6296
CHN + DBA					
0.0109	0.1314	0.7685	0.8102	0.7590	0.7072
0.0204	0.2475	0.7681	0.8023	0.7586	0.6959
0.0298	0.3653	0.7676	0.7945	0.7582	0.6867
0.0392	0.4844	0.7672	0.7871	0.7578	0.6761
0.0493	0.6160	0.7668	0.7755	0.7574	0.6665
0.0583	0.7357	0.7665	0.7665	0.7570	0.6583
0.0689	0.8799	0.7661	0.7585	0.7566	0.6494
0.0797	1.0284	0.7656	0.7491	0.7561	0.6406
0.0881	1.1474	0.7653	0.7420	0.7558	0.6327
CHN + TEA					
0.0102	0.1226	0.7683	0.8057		
0.0192	0.2320	0.7675	0.7913		
0.0299	0.3662	0.7666	0.7725		
0.0422	0.5236	0.7656	0.7556		
0.0498	0.6222	0.7650	0.7402		
0.0618	0.7827	0.7640	0.7264		
0.0712	0.9102	0.7634	0.7134		
0.0799	1.0314	0.7627	0.7009		
0.0895	1.1676	0.7621	0.6879		
0.0995	1.3125	0.7614	0.6772		
CHN + TPA					
0.0109	0.1307	0.7685	0.8118	0.7590	0.7082
0.0200	0.2426	0.7681	0.8071	0.7586	0.6992
0.0305	0.3738	0.7676	0.8005	0.7581	0.6899
0.0406	0.5024	0.7671	0.7936	0.7577	0.6808
0.0511	0.6396	0.7667	0.7874	0.7573	0.6730
0.0596	0.7526	0.7664	0.7784	0.7569	0.6664
0.0693	0.8845	0.7659	0.7721	0.7566	0.6605

Table 2 (*Continued*)

x_s	m (mol kg^{-1})	ρ (g cm^{-3}) (at 303.15 K)	η (mPa s) (at 303.15 K)	ρ (g cm^{-3}) (at 313.15 K)	η (mPa s) (at 313.15 K)
0.0787	1.0153	0.7655	0.7660	0.7562	0.6541
0.0878	1.1444	0.7652	0.7599	0.7558	0.6465
CHN + TBA					
0.0103	0.1237	0.7689	0.8168	0.7594	0.7154
0.0216	0.2623	0.7688	0.8160	0.7593	0.7139
0.0318	0.3900	0.7687	0.8153	0.7592	0.7132
0.0402	0.4980	0.7686	0.8141	0.7591	0.7121
0.0516	0.6463	0.7685	0.8132	0.7590	0.7111
0.0598	0.7554	0.7684	0.8121	0.7590	0.7102
0.0709	0.9067	0.7683	0.8113	0.7589	0.7090
0.0807	1.0431	0.7682	0.8100	0.7589	0.7078
0.0861	1.1190	0.7681	0.8086	0.7590	0.7065
HEP + TEA					
0.0097	0.0973	0.6755	0.3735		
0.0187	0.1907	0.6758	0.3719		
0.0300	0.3081	0.6763	0.3707		
0.0422	0.4397	0.6767	0.3687		
0.0484	0.5081	0.6769	0.3675		
0.0593	0.6292	0.6774	0.3663		
0.0702	0.7537	0.6778	0.3650		
0.0774	0.8374	0.6780	0.3639		
0.0888	0.9722	0.6785	0.3630		
0.0988	1.0943	0.6788	0.3622		
BEN + PA					
0.0079	0.1015	0.8671	0.5618	0.8564	0.4898
0.0186	0.2432	0.8654	0.5605	0.8548	0.4864
0.0280	0.3681	0.8639	0.5588	0.8534	0.4837
0.0366	0.4869	0.8626	0.5574	0.8521	0.4817
0.0470	0.6309	0.8609	0.5554	0.8505	0.4766
0.0579	0.7868	0.8592	0.5534	0.8488	0.4725
0.0659	0.9025	0.8579	0.5520	0.8476	0.4704
0.0759	1.0519	0.8564	0.5501	0.8460	0.4670
0.0844	1.1795	0.8550	0.5480	0.8446	0.4636
BEN + BA					
0.0094	0.1209	0.8668	0.5633	0.8561	0.4919
0.0195	0.2544	0.8652	0.5628	0.8546	0.4907
0.0284	0.3744	0.8638	0.5622	0.8533	0.4905
0.0380	0.5054	0.8623	0.5620	0.8518	0.4893
0.0480	0.6454	0.8607	0.5618	0.8503	0.4884
0.0588	0.8000	0.8591	0.5617	0.8487	0.4876
0.0669	0.9178	0.8578	0.5608	0.8475	0.4869
0.0764	1.0593	0.8563	0.5598	0.8460	0.4861
0.0859	1.2024	0.8548	0.5588	0.8446	0.4852
BEN + DPA					
0.0105	0.1359	0.8660	0.5622	0.8554	0.4915
0.0207	0.2709	0.8639	0.5617	0.8533	0.4902
0.0306	0.4041	0.8618	0.5610	0.8513	0.4897
0.0390	0.5190	0.8600	0.5607	0.8496	0.4890
0.0508	0.6849	0.8576	0.5602	0.8473	0.4880
0.0614	0.8372	0.8554	0.5588	0.8452	0.4872
0.0723	0.9980	0.8533	0.5575	0.8431	0.4861
0.0812	1.1315	0.8515	0.5554	0.8414	0.4851
0.0917	1.2926	0.8494	0.5542	0.8394	0.4839
BEN + DBA					
0.0108	0.1394	0.8657	0.5674	0.8551	0.4959
0.0201	0.2624	0.8635	0.5699	0.8530	0.4998
0.0300	0.3950	0.8612	0.5746	0.8508	0.5030
0.0390	0.5185	0.8592	0.5771	0.8489	0.5067
0.0487	0.6547	0.8571	0.5809	0.8467	0.5110
0.0593	0.8069	0.8549	0.5840	0.8445	0.5134
0.0689	0.9463	0.8528	0.5864	0.8426	0.5150

Table 2 (*Continued*)

x_s	m (mol kg^{-1})	ρ (g cm^{-3}) (at 303.15 K)	η (mPa s) (at 303.15 K)	ρ (g cm^{-3}) (at 313.15 K)	η (mPa s) (at 313.15 K)
0.0797	1.1076	0.8506	0.5907	0.8405	0.5177
0.0892	1.2533	0.8486	0.5931	0.8385	0.5198
BEN + TEA					
0.0102	0.1324	0.8659	0.5567		
0.0209	0.2734	0.8634	0.5513		
0.0311	0.4113	0.8610	0.5450		
0.0395	0.5272	0.8591	0.5386		
0.0501	0.6747	0.8568	0.5341		
0.0618	0.8435	0.8541	0.5287		
0.0712	0.9819	0.8520	0.5215		
0.0804	1.1194	0.8500	0.5162		
0.0919	1.2958	0.8475	0.5096		
0.1000	1.4217	0.8458	0.5041		
BEN + TPA					
0.0104	0.1344	0.8655	0.5599	0.8549	0.4902
0.0206	0.2694	0.8628	0.5574	0.8522	0.4877
0.0307	0.4051	0.8602	0.5552	0.8497	0.4859
0.0402	0.5369	0.8579	0.5532	0.8474	0.4836
0.0497	0.6702	0.8555	0.5515	0.8452	0.4818
0.0596	0.8111	0.8532	0.5487	0.8429	0.4793
0.0693	0.9537	0.8509	0.5467	0.8407	0.4772
0.0788	1.0955	0.8487	0.5453	0.8386	0.4760
0.0889	1.2496	0.8464	0.5429	0.8364	0.4738
TOL + TEA					
0.0120	0.1314	0.8555	0.5137		
0.0223	0.2477	0.8537	0.5093		
0.0311	0.3478	0.8522	0.5049		
0.0419	0.4742	0.8503	0.4993		
0.0488	0.5569	0.8491	0.4963		
0.0617	0.7137	0.8470	0.4911		
0.0685	0.7981	0.8458	0.4859		
0.0792	0.9329	0.8440	0.4823		
0.0916	1.0943	0.8420	0.4786		
0.1002	1.2090	0.8405	0.4755		
EB + TEA					
0.0108	0.1024	0.8564	0.5914		
0.0205	0.1975	0.8550	0.5873		
0.0302	0.2934	0.8535	0.5822		
0.0440	0.4340	0.8515	0.5755		
0.0503	0.4993	0.8507	0.5715		
0.0632	0.6359	0.8487	0.5666		
0.0710	0.7196	0.8476	0.5623		
0.0794	0.8124	0.8464	0.5569		
0.0941	0.9782	0.8442	0.5505		
0.1003	1.0496	0.8433	0.5476		
pXY + TEA					
0.0103	0.0977	0.8508	0.5611		
0.0206	0.1976	0.8493	0.5576		
0.0304	0.2956	0.8479	0.5525		
0.0426	0.4192	0.8461	0.5488		
0.0541	0.5385	0.8445	0.5433		
0.0665	0.6706	0.8427	0.5381		
0.0760	0.7750	0.8414	0.5342		
0.0846	0.8708	0.8402	0.5307		
0.0959	0.9990	0.8386	0.5253		
0.1075	1.1348	0.8369	0.5207		

Table 3
Coefficients A_i of Eq. (16) along with standard deviation σ for viscosity

System	Temperature (K)	A_1	A_2	A_3	σ (mPa s)
CHN + PA	303.15	0.8176	−0.7829	0.0042	0.0006
	313.15	0.7154	−0.8763	1.2241	0.0009
CHN + BA	303.15	0.8193	−0.9819	−1.2655	0.0021
	313.15	0.7165	−0.8458	−0.8933	0.0009
CHN + DPA	303.15	0.8188	−0.7508	−2.0416	0.0010
	313.15	0.7165	−0.7437	−2.3632	0.0012
CHN + DBA	303.15	0.8192	−0.8441	−0.4704	0.0012
	313.15	0.7159	−1.2020	2.5031	0.0005
CHN + TEA	303.15	0.8206	−1.6589	2.0824	0.0018
CHN + TPA	303.15	0.8186	−0.5754	−1.1745	0.0010
	313.15	0.7169	−0.9326	1.5747	0.0009
CHN + TBA	303.15	0.8182	−0.0846	−0.2585	0.0003
	313.15	0.7161	−0.0791	−0.3284	0.0002
HEP + TEA	303.15	0.3753	−0.1791	0.4592	0.0002
BEN + PA	303.15	0.5624	−0.0185	−3.7114	0.0006
	313.15	0.4918	−0.2356	−1.5112	0.0011
BEN + BA	303.15	0.5771	0.0222	−1.2267	0.0011
	313.15	0.5014	−0.0786	−0.1557	0.0002
BEN + DPA	303.15	0.5751	−0.1787	0.7136	0.0024
	313.15	0.5018	−0.0730	−0.3629	0.0004
BEN + DBA	303.15	0.5627	0.3994	−0.6627	0.0005
	313.15	0.4916	0.4501	−1.5022	0.0006
BEN + TEA	303.15	0.5624	−0.5506	−0.2884	0.0008
BEN + TPA	303.15	0.5753	−0.1849	0.2296	0.0003
	313.15	0.4982	−0.4132	2.5281	0.0020
TOL + TEA	303.15	0.5176	−0.7231	2.2363	0.0009
EB + TEA	303.15	0.5964	−0.4682	−0.2150	0.0006
pXY + TEA	303.15	0.5656	−0.4019	−0.1546	0.0004

Table 4
Coefficients A_i of Eq. (19) along with standard deviation σ for viscosity deviations

System	Temperature (K)	A_1	A_2	A_3	σ (mPa s)
CHN + PA	303.15	−0.4804	5.4349	−44.1758	0.0008
	313.15	−0.5407	2.6324	−7.7118	0.0010
CHN + BA	303.15	−0.4694	−4.7964	24.0101	0.0020
	313.15	−0.4416	−3.1550	16.4636	0.0008
CHN + DPA	303.15	−0.3942	−2.9255	4.0473	0.0011
	313.15	−0.4320	−2.1913	−4.3878	0.0015
CHN + DBA	303.15	−0.6254	−5.0548	33.9100	0.0009
	313.15	−0.7223	−9.0556	84.7150	0.0017
CHN + TEA	303.15	−0.7074	−8.1342	56.0054	0.0026
CHN + TPA	303.15	−0.3383	−1.1727	−2.2475	0.0012
	313.15	−0.5248	−6.1366	−62.3117	0.0016
CHN + TBA	303.15	−0.4675	2.3105	−20.7221	0.0004
	313.15	−0.3115	−1.2207	8.0193	0.0004
HEP + TEA	303.15	−0.1477	0.9662	−3.9558	0.0003
BEN + PA	303.15	0.1423	−2.4861	15.4963	0.0002

Table 4 (*Continued*)

System	Temperature (K)	A_1	A_2	A_3	σ (mPa s)
	313.15	−0.1074	−0.6662	0.3544	0.0006
BEN + BA	303.15	0.2098	−3.4938	24.0268	0.0007
	313.15	0.0774	−1.8194	13.8547	0.0003
BEN + DPA	303.15	0.0153	0.0338	−7.2785	0.0003
	313.15	0.1017	−3.0930	21.3322	0.0006
BEN + DBA	303.15	0.2601	−2.5400	14.9286	0.0005
	313.15	0.1658	1.9909	−26.9921	0.0007
BEN + TEA	303.15	−0.3232	−0.2541	0.2045	0.0009
BEN + TPA	303.15	−0.2978	0.9735	−5.7188	0.0003
	313.15	−0.2265	−1.1112	9.5526	0.0003
TOL + TEA	303.15	−0.2198	−2.0705	18.1553	0.0006
EB + TEA	303.15	−0.1329	−2.0593	12.3701	0.0006
PXY + TEA	303.15	−0.2143	1.2386	−9.4372	0.0006

Table 5
Coefficients A_i of Eq. (19) along with standard deviation σ for ΔG^{*E}

System	Temperature (K)	A_1	A_2	σ (J mol^{-1})
CHN + PA	303.15	−394.2	2599.7	3.9
	313.15	−1090.2	5628.7	4.0
CHN + BA	303.15	−1038.7	−10402.3	7.9
	313.15	−1178.5	−8347.7	4.3
CHN + DPA	303.15	−828.2	−9897.4	3.3
	313.15	−1040.0	−12705.4	4.7
CHN + DBA	303.15	−1728.1	−7367.3	5.2
	313.15	−2819.1	−5122.7	8.7
CHN + TEA	303.15	−1853.7	−7897.6	12.8
CHN + TPA	303.15	−394.8	−5897.0	3.2
	313.15	−1689.2	−2374.6	6.5
CHN + TBA	303.15	−95.7	−973.2	1.8
	313.15	79.9	−3634.0	1.1
HEP + TEA	303.15	−897.9	3462.7	1.5
BEN + PA	303.15	755.7	−4228.5	1.3
	313.15	−331.0	−3959.7	3.1
BEN + BA	303.15	886.8	−6017.4	3.3
	313.15	382.5	−3017.4	2.5
BEN + DPA	303.15	422.7	−3504.9	1.8
	313.15	647.3	−5497.9	3.5
BEN + DBA	303.15	1868.1	−6047.0	2.6
	313.15	1962.0	−5591.6	4.3
BEN + TEA	303.15	−830.5	−2979.5	3.8
BEN + TPA	303.15	−279.9	−126.1	1.1
BEN + TPA	313.15	−258.9	−2853.2	2.4
TOL + TEA	303.15	−972.4	−1260.5	6.4
EB + TEA	303.15	−345.0	−3448.1	2.9
pXY + TEA	303.15	−548.2	−121.6	2.6

The coefficients A_i obtained from a least-squares fit with equal weights assigned to each point are listed in Table 3 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

$$\Delta\eta = \eta - (x_s\eta_s^0 + x_S\eta_S^0) \qquad (17)$$

On the basis of the theory of absolute reaction rates [35], the excess Gibbs energy of activation ΔG^{*E} of viscous flow has been calculated from

$$\frac{\Delta G^{*E}}{RT} = \ln\left(\frac{\eta V}{\eta_S^0 V_S^0}\right) - x_s \ln\left(\frac{\eta_s^0 V_s^0}{\eta_S^0 V_S^0}\right) \qquad (18)$$

where η and V are the viscosity and molar volume of the solution, and η_s^0 and η_S^0 are the viscosities and V_s^0 and V_S^0 are molar volumes of the pure solute and solvent, respectively. The values of $\Delta\eta$ and ΔG^{*E} have been fitted to the polynomial of the form

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

The coefficients A_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 4 and 5.

5. Discussion

We have determined specific viscosities $(\eta - \eta_S^0)/\eta_S^0$, viscosity deviations $\Delta\eta$ and excess Gibbs energies of activation ΔG^{*E} of flow at 303.15 K as well as at 313.15 K for some solutions. The dependence of $(\eta - \eta_S^0)/\eta_S^0$ on m, $\Delta\eta$ and ΔG^{*E} on x_s is shown only at 303.15 K, since for other temperature the curves are similar. The values of $(\eta - \eta_S^0)/\eta_S^0$ are negative and their magnitude increases with increase in amine mole fraction except for BA and DBA solutions in benzene. In general plots of $(\eta - \eta_S^0)/\eta_S^0$ versus m are almost linear for solutions in cyclohexane and heptane (Fig. 1), while some curvature is observed for aromatic hydrocarbon solutions (Fig. 2). Values of slope of these curves depends on the size and shape of solute molecule and to solvation effects. The relative values of $\Delta\eta$ and ΔG^{*E} have been analysed in terms of solute–solute and solute–solvent interactions.

5.1. Amine solutions in aliphatic hydrocarbons

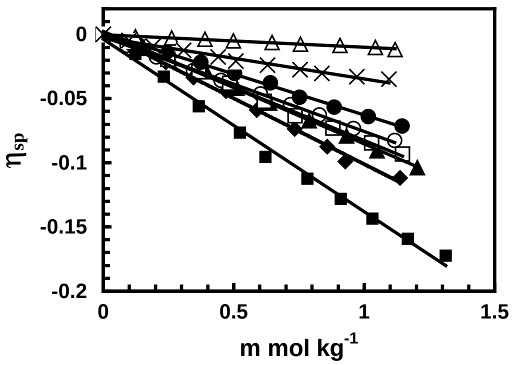

Fig. 1. Specific viscosities of PA (○), BA (◆), DPA (▲), DBA (□), TEA (■), TPA (●), and TBA (△) in CHN and TEA (×) in HEP at 303.15 K.

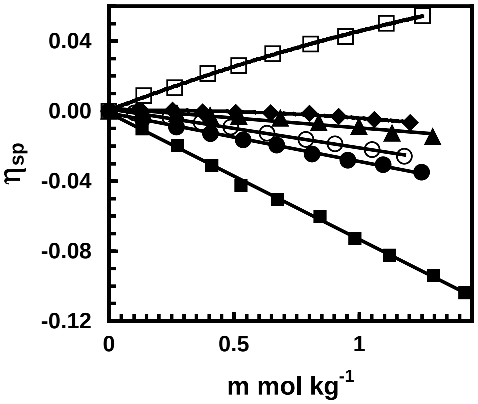

Fig. 2. Specific viscosities of PA (○), BA (◆), DPA (▲), DBA (□), TEA (■) and TPA (●) in BEN at 303.15 K.

The values of $\Delta\eta$ and ΔG^{*E} are negative and their magnitude increases with increase in amine mole fraction (Figs. 3 and 4). This viscosity behaviour may be explained by the fact that with the addition of cyclohexane molecules, the local-order in amine molecules due to self-association or dipole structure is disrupted. As a result, the cohesive forces of amine molecules are greatly reduced and hence have greater mobility. This loss of cohesive forces is the most in the case of primary amine molecules than that in secondary and than in the tertiary amines. The negative deviations of TEA in *n*-heptane are smaller compared to those observed for TEA in cyclohexane solutions. This is attributed to flexible chain structure of solvent *n*-heptane molecule.

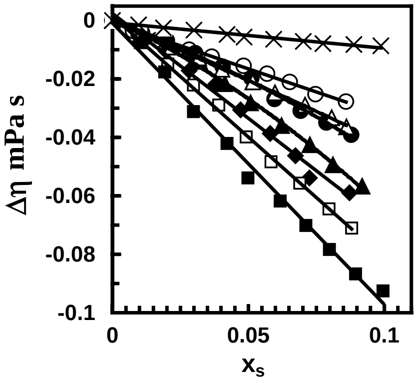

Fig. 3. Viscosity deviations of PA (○), BA (◆), DPA (▲), DBA (□), TEA (■), TPA (●), and TBA (△) in CHN and TEA (×) in HEP at 303.15 K.

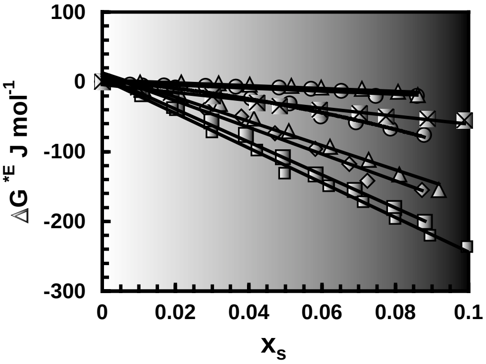

Fig. 4. Excess Gibbs energy of activation of viscous flow for PA (○), BA (◆), DPA (▲), DBA (□), TEA (■), TPA (●), and TBA (△) in CHN and TEA (×) in HEP at 303.15 K.

5.2. Amine solutions in aromatic hydrocarbons

The values of $\Delta\eta$ and ΔG^{*E} (Figs. 5 and 6) are either positive or negative but are of small magnitudes. On comparing the values of $\Delta\eta$ and ΔG^{*E} for amine solutions in benzene with that in cyclohexane, it was observed that $\Delta\eta$ and ΔG^{*E} are of smaller magnitude for benzene. These results indicate the occurrence of specific interactions between amine and benzene. Study of viscosity and excess enthalpy of amine + benzene mixtures over entire range of composition also predicted the specific interaction between unlike components [19,36,37].

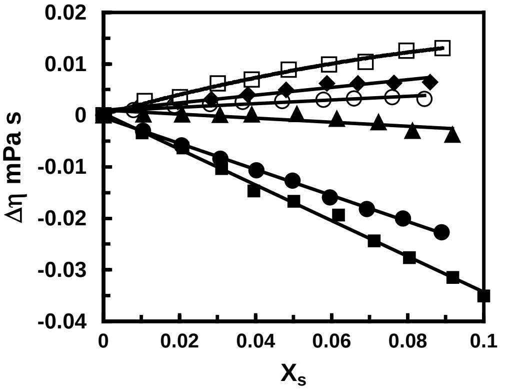

Fig. 5. Viscosity deviations of PA (○), BA (◆), DPA (▲), DBA (□), TEA (■) and TPA (●) in BEN at 303.15 K.

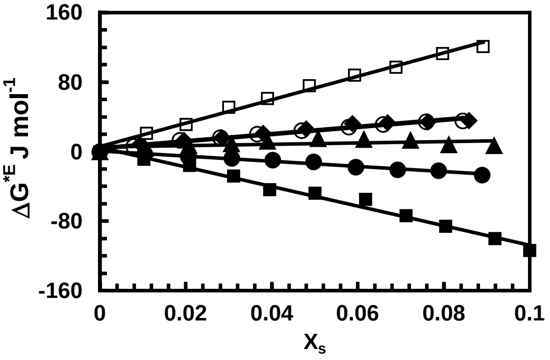

Fig. 6. Excess Gibbs energy of activation of viscous flow for PA (○), BA (◆), DPA (▲), DBA (□), TEA (■) and TPA (●) in BEN at 303.15 K.

The values of $\Delta\eta$ and ΔG^{*E} are small and negative for toluene, *p*-xylene, and ethyl benzene and are almost similar to the benzene solutions. Like benzene solutions, here also specific interactions of n–π-type may explain the results. The small difference in the viscosity behaviour may be due to alkyl substitution in benzene. Similar conclusions were reached from the heat of solutions [38,39].

5.3. On Herskovits and Kelly equation

Table 6 gives the values of coefficients *B* and *D* of Eq. (2), viscosity increment $\nu = 1000B/M_S\bar{v}_S\rho$ and the values of $10^6 D/(M_S\bar{v}_S\rho)^2$ of PA, BA, DPA, DBA, TPA and TBA in cyclohexane and benzene, and TEA in cyclohexane, *n*-heptane, benzene, toluene, ethylbenzene and *p*-xylene. The values of partial specific volume of amines reported in sixth column have been derived from the measurements of densities of dilute solutions at number of concentrations of amines [40,41]. The values of *B* coefficient are in the range −0.009 to −0.144 for alkylamines in cyclohexane, from −0.046 to 0.062 in benzene, and from −0.077 to −0.098 in alkyl benzene. It has been reported earlier that in benzene solutions the value of *B* coefficient depends on size of trialkylamine and decreases with decreasing chain length of tri-*n*-alkylamines from tridodecyl to tripropylamine [14]. The similar effect of chain length on *B* coefficient values was observed in the homologous series of some aliphatic acids, alcohols, amides, tetraalkylammonium salts and trialkylammonium hydrochloride [42–44] in polar and non-polar solvents. Thus, it will be useful to plot *B* coefficient values of trialkylamine series in benzene and see whether our values for TEA, TPA, and TBA lie on the same curve or not. It can be seen from the Fig. 7 that our values for TEA, TPA and TBA lies on the same curve. The values of *B* for different trialkylamine can be given by $8.0863 \times 10^{-3}C_n^2 - 0.003617C_n - 0.0917$ where C_n represent number of carbon in alkyl chain length.

The values of viscosity increment $\nu = 1000B/M_S\bar{v}_S\rho$ are negative for amine solutions in cyclohexane, while both positive and negative for benzene, toluene, ethyl benzene and *p*-xylene. On the basis of Einstein model of sphere in a con-

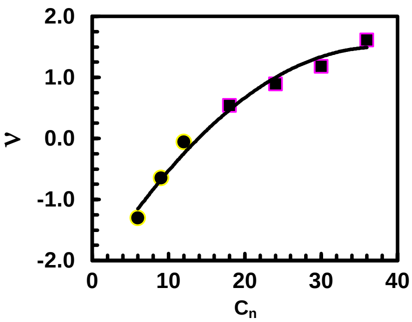

Fig. 7. Variation of viscosity increment ν with number of carbons C_n in alkylamine: this work (●); Ref. [14] (■).

Table 6
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	Temperature (K)	B	D	σ	$\bar{v}_s$	ν	$10^6D/(M_s\bar{v}_s\rho)^2$
CHN + PA	303.15	−0.090	0.016	0.003	1.5	−1.32	3.46
	313.15	−0.109	0.024	0.004	1.51	−1.61	5.23
CHN + BA	303.15	−0.092	−0.011	0.004	1.44	−1.13	−1.67
	313.15	−0.094	−0.006	0.002	1.46	−1.16	−0.91
CHN + DPA	303.15	−0.074	−0.012	0.003	1.4	−0.68	−1.01
	313.15	−0.085	−0.015	0.003	1.42	−0.78	−1.26
CHN + DBA	303.15	−0.077	−0.006	0.003	1.36	−0.57	−0.33
	313.15	−0.109	0.003	0.007	1.37	−0.81	0.17
CHN + TEA	303.15	−0.144	−0.003	0.008	1.43	−1.30	−0.32
CHN + TPA	303.15	−0.057	−0.005	0.002	1.35	−0.39	−0.22
	313.15	−0.096	0.007	0.006	1.37	−0.65	0.32
CHN + TBA	303.15	−0.012	0.003	0.001	1.31	−0.06	0.09
	313.15	−0.009	−0.003	0.001	1.33	−0.05	−0.09
HEP + TEA	303.15	−0.049	0.045	0.007	1.4	−0.51	1.73
BEN + PA	303.15	−0.014	−0.008	0.001	1.42	−0.19	−1.50
	313.15	−0.046	−0.003	0.002	1.43	−0.63	−0.57
BEN + BA	303.15	0.007	−0.011	0.003	1.38	0.08	−1.43
	313.15	−0.007	−0.005	0.002	1.39	−0.08	−0.66
BEN + DPA	303.15	−0.003	−0.006	0.001	1.37	−0.02	−0.41
	313.15	−0.002	−0.009	0.003	1.38	−0.02	−0.62
BEN + DBA	303.15	0.059	−0.013	0.003	1.35	0.39	−0.57
	313.15	0.062	−0.012	0.003	1.36	0.41	−0.53
BEN + TPA	303.15	−0.035	0.006	0.001	1.35	−0.21	0.21
	313.15	−0.031	0.001	0.001	1.36	−0.19	0.04
BEN + TEA	303.15	−0.077	0.003	0.003	1.39	−0.63	0.20
TOL + TEA	303.15	−0.080	0.007	0.003	1.38	−0.67	0.49
EB + TEA	303.15	−0.077	−0.002	0.004	1.37	−0.64	−0.21
pXY + TEA	303.15	−0.098	0.033	0.013	1.38	−0.67	0.71

tinuum [45], 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. The deviation of B coefficient and related viscosity increments from the Einstein [45] and Guth and Simha [46] 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 ν were also found for homologous series of non-electrolytes in non-polar solvents [14]. The values of ν for trialkylamine series (from tri-*n*-hexyl to tri-*n*-dodecyl amine) in benzene solutions were found to be 0.545–1.608 and were dependent on the hydrocarbon chain length [14]. If these results are extra plotted our values $\nu = 0.34$, -0.25 and -1.61 for TBA, TPA and TEA, respectively, lie on the linear curve.

5.4. On Nakagawa equation

We estimated B', B'_{id} and B'_{int} coefficients from the η_{int} values (Table 7) using Eqs. (13)–(15). The values of B' coefficient for alkylamine are from -0.202 to -0.016 in cyclohexane, from -0.094 to 0.067 in benzene and from -0.139 to -0.095 in alkyl benzene. Since the B' coefficient also contains the contributions to the difference of viscosities for solute and solvent components, 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 cyclohexane, which clearly indicates disruption of local-order of amines by addition of cyclohexane molecules. From the comparison of B'_{int}, for cyclohexane solutions and benzene solutions of amines, it is observed that negative value of B'_{int} is reduced or in some cases become positive, which may be attributed to specific interactions between amine and benzene. The specific interaction may be considered between the lone pair of electrons in N atom of amine and the π electrons of aromatic ring. In case of the benzene solutions where the values of B'_{int} are negative reveals that in these solutions dispersion interactions are dominating

Table 7
Regular terms of viscosities η_{int}, viscosity B', B'_{id}, B'_{int} parameters

System	Temperature (K)	η_{int}	B'	B'_{id}	B'_{int}
CHN + PA	303.15	−0.367	−0.111	−0.062	−0.049
	313.15	−0.460	−0.134	−0.062	−0.071
CHN + BA	303.15	−0.662	−0.139	−0.050	−0.088
	313.15	−0.573	−0.139	−0.050	−0.089
CHN + DPA	303.15	−0.563	−0.116	−0.041	−0.075
	313.15	−0.592	−0.137	−0.045	−0.092
CHN + DBA	303.15	−0.813	−0.117	−0.008	−0.109
	313.15	−1.085	−0.176	−0.008	−0.168
CHN + TEA	303.15	−1.023	−0.202	−0.065	−0.137
CHN + TPA	303.15	−0.426	−0.086	−0.029	−0.057
	313.15	−0.670	−0.131	−0.028	−0.104
CHN + TBA	303.15	−0.432	−0.016	0.041	−0.058
	313.15	−0.365	−0.017	0.039	−0.057
HEP + TEA	303.15	−0.116	−0.064	−0.018	−0.046
BEN + PA	303.15	0.008	−0.032	−0.034	0.001
	313.15	−0.150	−0.061	−0.033	−0.028
BEN + BA	303.15	0.183	0.008	−0.021	0.029
	313.15	0.032	−0.014	−0.020	0.006
BEN + DPA	303.15	−0.084	−0.023	−0.010	−0.013
	313.15	0.011	−0.012	−0.014	0.002
BEN + DBA	303.15	0.189	0.062	0.031	0.030
	313.15	0.190	0.067	0.032	0.035
BEN + TEA	303.15	−0.357	−0.094	−0.037	−0.057
BEN + TPA	303.15	−0.207	−0.029	0.004	−0.032
	313.15	−0.475	−0.080	0.007	−0.086
TOL + TEA	303.15	−0.484	−0.139	−0.039	−0.100
EB + TEA	303.15	−0.212	−0.099	−0.055	−0.044
pXY + TEA	303.15	−0.195	−0.095	−0.052	−0.043

over the solute–solvent specific interactions. The opposite is true when the values of B'_{int} are positive. 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.

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