International Journal of Thermophysics, Vol. 13, No. 4, 1992

Viscosity of Binary Mixtures. II. *n*-Butyl, *n*-Hexyl, *n*-Octyl, *n*-Decyl, and *n*-Dodecylamine with Benzene and *n*-Hexyl, *n*-Decyl, and *n*-Dodecylamine with Cyclohexane

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Received January 22, 1992

Viscosities of eight binary systems of *n*-butylamine, *n*-hexylamine, *n*-octylamine, *n*-decylamine, and *n*-dodecylamine with benzene and *n*-hexylamine, *n*-decylamine, and *n*-dodecylamine with cyclohexane have been measured at 303.15 K with an Ubbelohde suspended level viscometer. Based on Eyring's theory, values of excess Gibbs energy of activation ΔG^{*E} of viscous flow have been calculated. Deviations of viscosities from linear dependence on the mole fraction and values of ΔG^{*E} are attributed to H-bonding and to the size of alkylamine molecules. The free volume theory of Prigogine–Flory–Patterson in combination with the work of Bloomfield–Dewan has been used to estimate the excess viscosity $\Delta \ln \eta$ and the terms corresponding to enthalpy, entropy, and free volume contributions for 10 binary mixtures containing *n*-butyl, *n*-hexyl, *n*-octyl, *n*-decyl, and *n*-dodecylamine with benzene and cyclohexane.

KEY WORDS: activation energy; alkylamines; benzene; binary liquids; butylamine; cyclohexane; decylamine; dodecylamine; Eyring's theory; hexylamine; octylamine; Prigogine–Flory–Patterson–Bloomfield–Dewan theory; viscosity.

1. INTRODUCTION

We are engaged in a systematic study of the thermodynamic, acoustic, and transport properties of binary liquid mixtures containing alkylamines. In a previous paper [1], we reported the viscosities of six binary mixtures of *n*-butyl, di-*n*-butyl, tri-*n*-butyl, *n*-octyl, di-*n*-octyl, and tri-*n*-octylamine with cyclohexane. It was observed that H-bonding in and size of alkylamine molecules have considerable effects on the viscosities of binary mixtures.

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0195-928X/92/0700-0629$06.50/0

Amines are known to interact with aromatic hydrocarbons [2–10]. To gain further insight into molecular interactions and to check the Prigogine–Flory–Patterson–Bloomfield–Dewan (PFPBD) theory [11–15], in this paper we report the viscosities of binary mixtures containing primary amines *n*-butyl, *n*-hexyl, *n*-octyl, *n*-decyl, and *n*-dodecylamines with benzene and *n*-hexyl, *n*-decyl, and *n*-dodecylamine with cyclohexane at 303.15 K.

2. EXPERIMENTAL

The methods and techniques used to determine the viscosities η and densities ρ have been described in previous papers [1, 8]. Kinematic viscosity (η/ρ) measurements were made with a modified Ubbelohde suspended level viscometer. Four or five sets of readings for flow time were taken for each pure liquid or liquid mixture at a constant temperature of 303.15 ± 0.02 K. The arithmatic mean was taken for the purpose of calculations. The viscometer was calibrated using doubly distilled water, benzene, cyclohexane, and *n*-hexadecane [16, 17]. The densities ρ at 303.15 K of the pure components and mixtures required for converting kinematic viscosities to absolute viscosities were determined with a glass pycnometer of approximately 12-cm^3 capacity. The errors in η and ρ are estimated to be 0.4 and 0.02%, respectively.

Samples of *n*-butylamine ($C_4H_9NH_2$), *n*-hexylamine ($C_6H_{13}NH_2$), *n*-octylamine ($C_8H_{17}NH_2$), and cyclohexane (C_6H_{12}) were from Fluka AG of stated purity better than 99%; *n*-decylamine ($C_{10}H_{21}NH_2$) and *n*-dodecylamine ($C_{12}H_{25}NH_2$) were from Sisco Research Laboratory Ltd., Bombay, of research grade. All amines were kept over sodium and frac-

Table I. Density and Refractive Index of the Pure Liquids Used

Liquid	Temp. (K)	ρ, density (kg · m^{-3})		η_D, refractive index	
		Expt.	Lit.	Expt.	Lit.
Benzene	298.15	873.62	873.60 [16]	1.4971	1.49792 [16]
Cyclohexane	298.15	773.90	773.89 [16]	1.4242	1.42354 [16]
Butylamine	298.15	733.23	733.08 [2] 734.52 [18]	1.3997	1.3987 [16]
Hexylamine	303.15	757.60	756.50 [19]	1.4160	1.4160 [20]
Octylamine	298.15	779.35	778.90 [20]	1.4271	1.4271 [20]
Decylamine	303.15	786.10		1.4356	1.4349 [20]
Dodecylamine	303.15	794.70	791.20 [19]	1.4397	1.4401 [20]

tionally distilled twice. C_6H_{12} was dried over a 4-Å molecular sieve and fractionally distilled twice over sodium wire. AnalaR benzene (C_6H_6) from British Drug Houses Ltd., Poole, was treated with H_2SO_4 to remove thiophene. It was washed properly with distilled water, kept over anhydrous calcium chloride, and dried over sodium wire prior to distillation and then it was kept over a 4-Å molecular sieve.

The purity of the liquids was checked with gas–liquid chromatography and from the measurement of density and refractive index, which compared well with the accepted literature values [2, 16–20] as shown in Table I.

3. RESULTS AND DISCUSSION

3.1. General

The measured viscosities η of the eight binary mixtures $C_6H_6+C_4H_9NH_2$, $C_6H_6+C_6H_{13}NH_2$, $C_6H_6+C_8H_{17}NH_2$, $C_6H_6+C_{10}H_{21}NH_2$, $C_6H_6+C_{12}H_{25}NH_2$, $C_6H_{12}+C_6H_{13}NH_2$, $C_6H_{12}+C_{10}H_{21}NH_2$, and $C_6H_{12}+C_{12}H_{25}NH_2$ over the entire range of mole fractions at 303.15 K are listed in Table II. The viscosity values in Table II are represented by a polynomial equation:

$$\eta=\sum_{i=0}^{m} A_i x_1^i \tag{1}$$

and the parameters A_i obtained from a least-squares fit are given in Table III, together with the standard deviations σ. Figure 1 shows the viscosities as a function of the mole fractions x_1 of the first component.

It can be seen from Table II that $C_6H_{12}+C_6H_{13}NH_2$ and $C_6H_6+C_6H_{13}NH_2$ are the two mixtures which show minima. From the smoothing Eq. (1), it can be shown that these occur at about 0.45 and 0.85 mole fractions x_1 of the first component in $C_6H_{12}+C_6H_{13}NH_2$ and $C_6H_6+C_6H_{13}NH_2$, respectively.

Figure 1 also indicates that the viscosities show negative deviations from a linear dependence on x_1 for all the present binary mixtures. The negative deviations, which entail a loss of cohesive energy upon mixing the pure liquids, may be associated with the destruction of H-bonding that is present in the primary amines.

3.2. Activation Energy of Viscous Flow

On the basis of the theory of absolute reaction rates [21], the excess Gibbs energy of activation ΔG^{*E} of viscous flow may be calculated from [22]

$$\Delta G^{*E}=RT[\ln(\eta V/\eta_2^0 V_2^0)-x_1\ln(\eta_1^0 V_1^0/\eta_2^0 V_2^0)] \tag{2}$$

Table II. Viscosity of Benzene + Alkylamines and Cyclohexane + Alkylamines at 303.15 K (x_1 Is the Mole Fraction of the First Component Named)

(1) x_1	(2) η (mPa·s)	(3) x_1	(4) η (mPa·s)	(5) x_1	(6) η (mPa·s)	(7) x_1	(8) η (mPa·s)
$C_6H_6+C_4H_9NH_2$		$C_6H_6+C_6H_{13}NH_2$		$C_6H_6+C_8H_{17}NH_2$		$C_6H_6+C_{10}H_{21}NH_2$	
0.0000	0.4443	0.0000	0.7290	0.0000	1.1687	0.0000	1.7661
0.0974	0.4454	0.1050	0.6977	0.1044	1.0990	0.2011	1.4636
0.1974	0.4466	0.2983	0.6450	0.3007	0.9459	0.3988	1.1738
0.5007	0.4542	0.4918	0.6006	0.4980	0.7915	0.4963	1.0426
0.6051	0.4738	0.5946	0.5814	0.5970	0.7318	0.5993	0.9230
0.7995	0.5056	0.6955	0.5639	0.6967	0.6798	0.7973	0.7207
0.9004	0.5322	0.7954	0.5506	0.7998	0.6239	1.0000	0.5621
1.0000	0.5621	0.8997	0.5490	0.8990	0.5891		
		1.0000	0.5621	1.0000	0.5621		
$C_6H_6+C_{12}H_{25}NH_2$		$C_6H_{12}+C_6H_{13}NH_2$		$C_6H_{12}+C_{10}H_{21}NH_2$		$C_6H_{12}+C_{12}H_{25}NH_2$	
0.0000	2.6576	0.0000	0.7290	0.0000	1.7661	0.0000	2.6576
0.2072	2.1219	0.1064	0.7192	0.2056	1.5618	0.2093	2.3100
0.4348	1.5625	0.2992	0.7005	0.3987	1.3614	0.3927	1.9485
0.5228	1.3750	0.4953	0.7021	0.5065	1.2394	0.5029	1.7094
0.6046	1.1891	0.5974	0.7073	0.5875	1.1590	0.6032	1.4916
0.7998	0.8357	0.6964	0.7145	0.7947	0.9708	0.8037	1.1164
1.0000	0.5621	0.7966	0.7200	1.0000	0.8195	1.0000	0.8195
		0.8980	0.7541				
		1.0000	0.8195				

Table III. Parameters A_i in Eq. (1) and Standard Deviations σ for the Viscosity of Binary Mixtures at 303.15 K

Mixtures	A_0	A_1	A_2	A_3	A_4	A_5	σ
$C_6H_6+C_4H_9NH_2$	0.4454	−0.0217	0.0286	0.1016	—	—	0.0031
$C_6H_6+C_6H_{13}NH_2$	0.7290	−0.3014	−0.0124	0.4543	−0.7403	0.4329	0.0008
$C_6H_6+C_8H_{17}NH_2$	1.1687	−0.5714	−1.1198	2.2281	−1.6455	0.5020	0.0040
$C_6H_6+C_{10}H_{21}NH_2$	1.7662	−1.4519	−0.5085	1.2713	−0.5152	—	0.0023
$C_6H_6+C_{12}H_{25}NH_2$	2.6576	−2.6117	0.0117	0.5046	—	—	0.0057
$C_6H_{12}+C_6H_{13}NH_2$	0.7290	−0.0738	−0.3569	1.6665	−2.4054	1.2602	0.0042
$C_6H_{12}+C_{10}H_{21}NH_2$	1.7663	−0.9270	−0.4013	0.3823	—	—	0.0040
$C_6H_{12}+C_{12}H_{25}NH_2$	2.6574	−1.3615	−1.6136	1.1384	—	—	0.0061

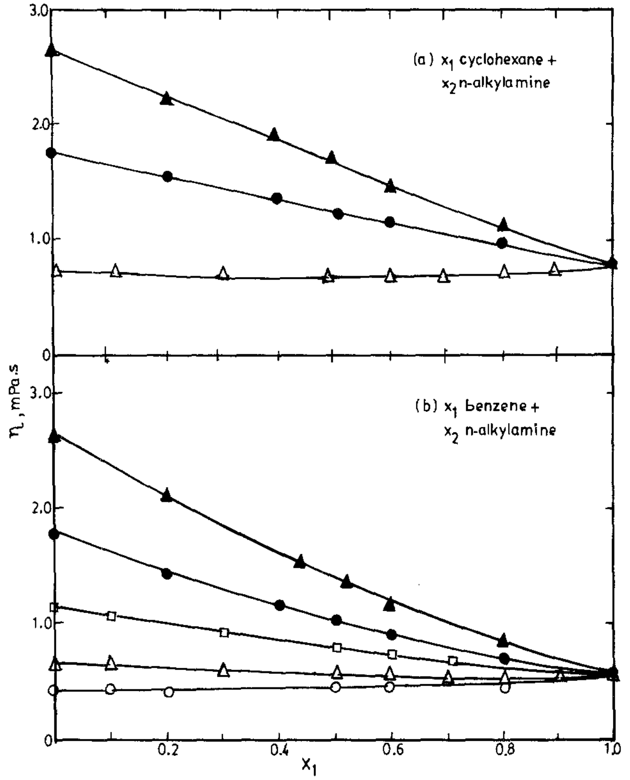

Fig. 1. Composition dependence of the viscosity of (a) cyclohexane + alkylamine and (b) benzene + alkylamine at 303.15 K. Alkylamine: (○) $C_4H_9NH_2$; (△) $C_6H_{13}NH_2$; (□) $C_8H_{17}NH_2$; (●) $C_{10}H_{21}NH_2$; (▲) $C_{12}H_{25}NH_2$. Solid curves were calculated from Eq. (1).

where η and V are the viscosity and molar volume of the mixture, and η_i and V_i are the viscosity and molar volume of the pure component i, respectively. The values of $\Delta G^{*E}/RT$ were fitted to the Redlich–Kister equation,

$$\Delta G^{*E}/RT = x_1 x_2 \sum_{i=0}^{m} B_i (1 - 2x_1)^i \qquad (3)$$

The parameter B_i and standard deviations σ are listed in Table IV, which also includes maximum values of excess Gibbs energy of activation $\Delta G^{*E}_{\max}$ of flow along with corresponding mole fractions. Figure 2 shows the dependence of ΔG^{*E} on the mole fraction x_1 of benzene or cyclohexane for

Table IV. Parameters B_i in Eq. (3), Standard Deviations σ, $\Delta G^{*E}_{\max}$, and Corresponding Mole Fraction x_1 for Binary Mixtures at 303.15 K

Mixture	B_0	B_1	B_2	σ	$\Delta G^{*E}_{\max}$ ($J \cdot mol^{-1}$)	x_1	Label in Fig. 3
$C_6H_6 + C_4H_9NH_2$	−0.3339	0.0634	0.0924	0.007	−231	0.50	1
$C_6H_6 + C_6H_{13}NH_2$	−0.1710	0.2052	−0.1617	0.003	−144	0.79	2
$C_6H_6 + C_8H_{17}NH_2$	0.1173	0.2360	0.0357	0.005	117	0.30	3
$C_6H_6 + C_{10}H_{21}NH_2$	0.4944	0.0355	0.0671	0.002	307	0.50	4
$C_6H_6 + C_{12}H_{25}NH_2$	1.0440	−0.1065	−0.0328	0.005	674	0.52	5
$C_6H_{12} + C_6H_{13}NH_2$	−0.3483	0.2824	−0.2212	0.007	−244	0.80	7
$C_6H_{12} + C_{10}H_{21}NH_2$	0.3452	0.0769	0.0089	0.003	227	0.40	9
$C_6H_{12} + C_{12}H_{25}NH_2$	0.8940	0.0437	−0.0528	0.004	565	0.50	10
$C_6H_{12} + C_4H_9NH_2$[a]					−319	0.58	6
$C_6H_{12} + C_8H_{17}NH_2$[a]					−126	0.80	8

[a] From Ref. 1.

all the binary mixtures. The values of ΔG^{*E} are estimated to be accurate to $\pm 25\ J \cdot mol^{-1}$ for the present binary mixtures.

The values of ΔG^{*E} for $C_6H_{12} + C_4H_9NH_2$ and $C_6H_{12} + C_8H_7NH_2$, reported in part I of this series [1], have also been used along with the results reported in this paper for the comprehensive analysis. In the series of binary mixtures both of benzene + alkylamine and of cyclohexane + alkylamine, the values of ΔG^{*E} increase as the size of the alkyl chain in alkylamine increases. The values of ΔG^{*E} for the mixtures containing *n*-butyl and *n*-hexylamine are negative, while those for the mixtures containing *n*-decyl and *n*-dodecylamines are positive. Both positive and negative values of ΔG^{*E} are observed for the mixtures containing *n*-octylamine, positive values for the mixtures rich in octylamine composition, and negative values otherwise. Thus, there is a prominent effect of molecular size, molecular shape, and self-association of amine molecules on the values of ΔG^{*E}.

The negative values of ΔG^{*E} at all mole fractions for $C_6H_6 + C_4H_9NH_2$, $C_6H_6 + C_6H_{13}NH_2$, $C_6H_{12} + C_4H_9NH_2$ [1], and $C_6H_{12} + C_6H_{13}NH_2$ and at higher mole fractions of *n*-octylamine for $C_6H_6 + C_8H_{17}NH_2$ and $C_6H_{12} + C_8H_{17}NH_2$ [1] are attributable to the destruction of the H-bonded-associated structure of the amines by the addition of either cyclohexane or benzene. The increasing positive values of ΔG^{*E} for the series from octylamine to dodecylamine through decylamine are due to the large size and cohesive energy difference between the two components of the mixtures.

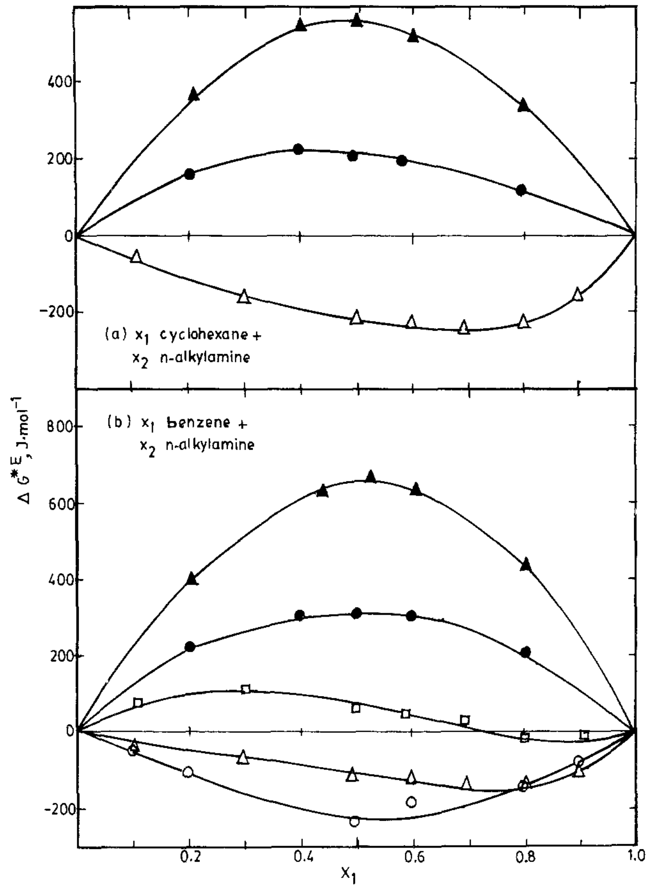

Fig. 2. Variation of ΔG^{*E} with composition for (a) cyclohexane + alkylamine and (b) benzene + alkylamine at 303.15 K. Symbols as in the legend to Fig. 1.

To see the effect of size on the excess Gibbs energy of activation of flow, as carried out in part I [1], the ΔG^{*E}_{max} (Table IV) are plotted against the values $(V_2^{1/2} - V_1^{1/2})^2$ in Fig. 3, where V is the molar volume. ΔG^{*E}_{max} is shown to be an increasing function of $(V_2^{1/2} - V_1^{1/2})^2$.

It can be seen from Table IV that the absolute values of ΔG^{*E}_{max} are higher for the benzene + alkylamine mixtures than the corresponding cyclohexane + alkylamine mixtures. This can be attributed to the N–π interaction between the lone pair of electrons of nitrogen in amine and π-electrons in benzene. This view is consistent with the analysis of excess enthalpies and excess volumes data for benzene + alkylamines [2–5].

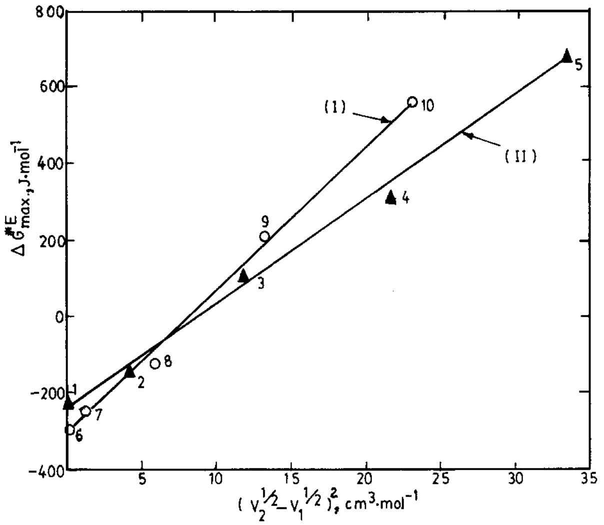

Fig. 3. $\Delta G^{*E}_{\max}$ versus the difference in molar volumes of the two components as $(V_2^{1/2}-V_1^{1/2})^2$. Cyclohexane + alkylamine (I); benzene + alkylamine (II). System corresponding to the numbers are given in Table IV.

4. THEORETICAL ANALYSIS

4.1. PFPBD Theory

The excess viscosities $\Delta \ln \eta$

$$\Delta \ln \eta = \ln(\eta/\eta_2^0) - x_1 \ln(\eta_1^0/\eta_2^0) \tag{4}$$

of a number of mixtures have recently been analyzed [1, 15, 23, 24] using PFPBD theory [11–14]. Previously [1], we used the PFPBD theory to estimate the excess viscosities of cyclohexane + tri-*n*-alkylamine mixtures. It was observed that for the mixtures different in size, the contribution because of size difference, to the overall excess viscosity, is quite significant and is shown to be an increasing function of $(V_2^{*1/2} - V_1^{*1/2})^2$, where V^* is the core volume. It is interesting to extend the calculations to estimate the excess viscosity for binary mixtures of primary alkylamines with benzene and cyclohexane. Following Bloomfield and Dewan [14], the theoretical excess viscosity $\Delta \ln \eta_{\text{th}}$ is composed of three contributory terms as

$$\Delta \ln \eta_{\text{th}} = \ln \eta_{\text{H}} + \ln \eta_{\text{S}} + \ln \eta_{\text{fv}} \tag{5}$$

Table V. Flory's Reduction Parameters of the Pure Components at 303.15 K

Component	$\tilde{V}$	V^*	P^*	S
Cyclohexane	1.2975	84.33	533	0.93
Benzene	1.2975	69.33	623	1.00
Butylamine	1.3137	76.43	582	1.14
Hexylamine	1.2651	105.65	528	1.02
Octylamine	1.2443	133.92	521	0.94
Decylamine	1.2320	162.42	500	0.88
Dodecylamine	1.2241	190.54	502	0.84

where

$$\ln \eta_{\mathrm{H}} = -H^{\mathrm{E}}/RT \tag{6}$$

$$\ln \eta_{\mathrm{S}} = S^{\mathrm{E}}/R \tag{7}$$

and

$$\ln \eta_{\mathrm{fv}} = 1/(\tilde{V}-1) - \sum_i x_i/(\tilde{V}_i - 1) \tag{8}$$

The terms $\ln \eta_{\mathrm{H}}$, $\ln \eta_{\mathrm{S}}$, and $\ln \eta_{\mathrm{fv}}$ in Eq. (5) are enthalpy, entropy, and free volume contributions, respectively, to $\Delta \ln \eta_{\mathrm{th}}$.

The values of the Flory reduction parameters $\tilde{V}$, V^*, and P^* and the surface-to-volume ratio S for the pure components used in the present work are listed in Table V. The terms $\ln \eta_{\mathrm{H}}$, $\ln \eta_{\mathrm{S}}$, and $\ln \eta_{\mathrm{fv}}$ in Eq. (5)

Table VI. Values of $H^{\mathrm{E}}_{\mathrm{exp}}$, $V^{\mathrm{E}}_{\mathrm{exp}}$, $X_{12}(H^{\mathrm{E}})$, and $X_{12}(V^{\mathrm{E}})$ for Equimolar Mixtures of Alkylamines with Benzene and Cyclohexane at 303.15 K

Mixture	$H^{\mathrm{E}}_{\mathrm{exp}}$ $(\mathrm{J \cdot mol^{-1}})^a$	$X_{12}(H^{\mathrm{E}})$ $(\mathrm{J \cdot cm^{-3}})$	$V^{\mathrm{E}}_{\mathrm{exp}}$ $(\mathrm{cm^3 \cdot mol^{-1}})^b$	$X_{12}(V^{\mathrm{E}})$ $(\mathrm{J \cdot cm^{-3}})$
$C_6H_6 + C_4H_9NH_2$	584	28.5	0.25	17.1
$C_6H_6 + C_6H_{13}NH_2$	585	26.6	0.33	14.1
$C_6H_6 + C_8H_{17}NH_2$	612	26.9	0.35	13.7
$C_6H_6 + C_{10}H_{21}NH_2$	645	27.6	0.42	13.6
$C_6H_6 + C_{12}H_{25}NH_2$	686	28.6	0.54	20.9
$C_6H_{12} + C_4H_9NH_2$	1131	53.2	0.71	38.0
$C_6H_{12} + C_6H_{13}NH_2$	937	38.2	0.69	36.8
$C_6H_{12} + C_8H_{17}NH_2$	888	33.4	0.57	32.2
$C_6H_{12} + C_{10}H_{21}NH_2$	840	30.5	0.58	31.3
$C_6H_{12} + C_{12}H_{25}NH_2$	826	29.3	0.66	37.7

[a] From Refs. 10 and 28.

[b] From Ref. 29.

were evaluated adopting a procedure similar to that described by Delmas and co-workers [15, 23, 24]. For this purpose, knowledge of the contact interaction parameter X_{12} and reduced volume $\tilde{V}_{12}$ for the mixture is essential. X_{12} can be obtained from any of the thermodynamic properties at a single composition of the mixture [12, 25–27]. In the present work, we have made two types of calculations, one using equimolar $H^{\mathrm{E}}_{\mathrm{exp}}$ and the other equimolar $V^{\mathrm{E}}_{\mathrm{exp}}$, to derive the parameters $X_{12}(H^{\mathrm{E}})$ and $X_{12}(V^{\mathrm{E}})$. The compatible values of $X_{12}(V^{\mathrm{E}})$ and $X_{12}(H^{\mathrm{E}})$ and values of $V^{\mathrm{E}}_{\mathrm{exp}}$ and $H^{\mathrm{E}}_{\mathrm{exp}}$ used in the present work are given in Table VI. Using $X_{12}(V^{\mathrm{E}})$ and $X_{12}(H^{\mathrm{E}})$ given in Table VI, the theoretical excess viscosity $\Delta \ln \eta_{\mathrm{th}}$ and the difference $\delta = \Delta \ln \eta_{\mathrm{exp}} - \Delta \ln \eta_{\mathrm{th}}$ were determined in each case and are reported in columns 7 and 8 in Table VII. In addition, the different contributions in Eq. (5), $\ln \eta_{\mathrm{H}}$, $\ln \eta_{\mathrm{S}}$, and $\ln \eta_{\mathrm{fv}}$ of equimolar mixtures are also presented in columns 3 to 5 in Table VII. Figure 4 compares the PFPBD

Table VII. Enthalpic, Entropic, and Free Volume Contributions to the Excess Viscosity and Comparison Between Theoretical and Experimental Excess Viscosity

(1) Mixture	(2) Property used	(3) $\ln \eta_{\mathrm{H}}$	(4) $\ln \eta_{\mathrm{S}}$	(5) $\ln \eta_{\mathrm{fv}}$	(6) $\Delta \ln \eta_{\mathrm{th}}$	(7) $\Delta \ln \eta_{\mathrm{exp}}$	(8) δ^{a}
$C_6H_6 + C_4H_9NH_2$	V^{E}	−0.138	0.038	−0.043	−0.144	−0.096	0.048
	H^{E}	−0.232	0.064	−0.070	−0.234	−0.096	0.138
$C_6H_6 + C_6H_{13}NH_2$	V^{E}	−0.121	0.026	−0.015	−0.110	−0.066	0.044
	H^{E}	−0.232	0.055	−0.045	−0.222	−0.066	0.156
$C_6H_6 + C_8H_{17}NH_2$	V^{E}	−0.121	0.003	0.044	−0.074	−0.020	0.054
	H^{E}	−0.243	0.044	0.003	−0.196	−0.020	0.176
$C_6H_6 + C_{10}H_{21}NH_2$	V^{E}	−0.121	0.002	0.081	−0.038	0.043	0.081
	H^{E}	−0.256	0.034	0.050	−0.172	0.043	0.215
$C_6H_6 + C_{12}H_{25}NH_2$	V^{E}	−0.195	0.009	0.121	−0.065	0.148	0.213
	H^{E}	−0.272	0.026	0.105	−0.141	0.148	0.289
$C_6H_{12} + C_4H_9NH_2$	V^{E}	−0.320	0.089	−0.093	−0.324	−0.130[b]	0.194
	H^{E}	−0.149	0.129	−0.130	−0.452	−0.130[b]	0.322
$C_6H_{12} + C_6H_{13}NH_2$	V^{E}	−0.358	0.088	−0.082	−0.352	−0.099	0.253
	H^{E}	−0.372	0.092	−0.086	−0.366	−0.099	0.267
$C_6H_{12} + C_8H_{17}NH_2$	V^{E}	−0.339	0.067	−0.027	−0.298	−0.037[b]	0.261
	H^{E}	−0.352	0.071	−0.030	−0.312	−0.037[b]	0.275
$C_6H_{12} + C_{10}H_{21}NH_2$	V^{E}	−0.342	0.054	−0.022	−0.266	+0.038	0.304
	H^{E}	−0.334	0.052	−0.024	−0.258	0.038	0.220
$C_6H_{12} + C_{12}H_{25}NH_2$	V^{E}	−0.426	0.061	0.063	−0.302	0.150	0.452
	H^{E}	−0.328	0.038	0.084	−0.206	0.150	0.356

[a] $\delta = \Delta \ln \eta_{\mathrm{exp}} - \Delta \ln \eta_{\mathrm{th}}$.
[b] From Ref. 1.

estimates of excess viscosities with the experimental estimates at all mole fractions.

4.2. Different Contributions to Excess Viscosity

It can be seen from Table VII that the term $\ln \eta_H$ for all 10 binary mixtures formed from each of five alkylamines (butyl, hexyl, octyl, decyl, and dodecyl) with cyclohexane and with benzene is negative. The magnitude of $\ln \eta_H$ is large and represents a quite significant contribution to the total excess viscosity $\Delta \ln \eta_{th}$. The variation of $\ln \eta_H$ with the alkyl chain length of amine molecules is not much but shows a slight increase in magnitude with the chain length.

The term $\ln \eta_S$ is small but positive for all 10 binary mixtures. The free volume term $\ln \eta_{fv}$ has both signs. It is negative for cyclohexane + butylamine, cyclohexane + hexylamine, cyclohexane + octylamine, benzene + butylamine, and benzene + hexylamine and positive for cyclohexane + decylamine, cyclohexane + dodecylamine, benzene + octylamine, benzene + decylamine, and benzene + dodecylamine mixtures. Thus, as the chain length of alkylamine increases, the $\ln \eta_{fv}$ term varies gradually and changes in sign from small negative to small positive.

4.3. Excess Viscosity

4.3.1. Benzene + Alkylamine Mixtures

From study of Fig. 4 and Table VII, it is observed that the agreement between the experimental and the estimated excess viscosity from the

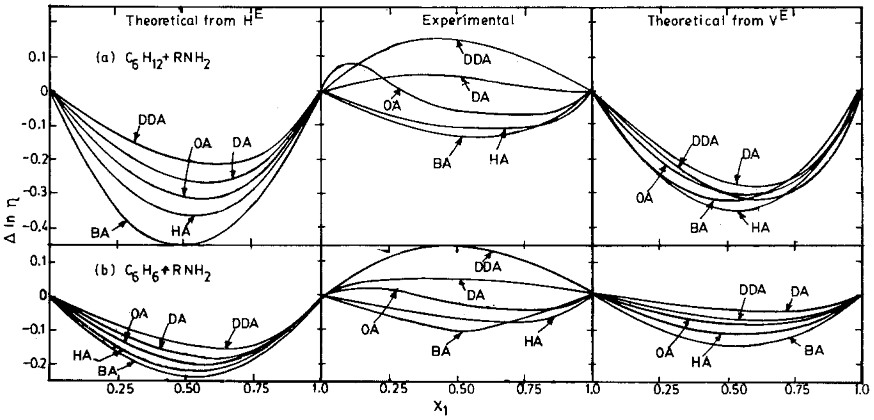

Fig. 4. Comparison of experimental and theoretical values of excess viscosity $\Delta \ln \eta$ at 303.15 K for (a) cyclohexane + alkylamine, and (b) benzene + alkylamine. Butyl, hexyl, octyl, decyl, and dodecyl amine are abbreviated BA, HA, OA, DA, and DDA, respectively. The values of $\Delta \ln \eta$ for C_6H_{12} + BA and C_6H_{12} + OA are from Ref. 1.

PFPBD theory using $X_{12}(V^E)$, with the one exception of C_6H_6 + $C_{12}H_{25}NH_2$ is satisfactory, while the estimated $\Delta \ln \eta_{th}$ using $X_{12}(H^E)$ values differ considerably for all five benzene + alkylamine mixtures. The difference $\delta(\Delta \ln \eta_{exp} - \Delta \ln \eta_{th})$ varies from 0.138 to 0.289.

4.3.2. Cyclohexane + Alkylamine Mixtures

In the case of cyclohexane + alkylamine mixtures, the agreement between $\Delta \ln \eta_{exp}$ and $\Delta \ln \eta_{th}$ obtained either from $X_{12}(V^E)$ or from $X_{12}(H^E)$ is very poor. The estimated $\Delta \ln \eta_{th}$ values are more negative than the $\Delta \ln \eta_{exp}$. The difference δ varies from 0.194 to 0.452 (see Table VII, column 8).

The disagreement between the theoretical and the experimental results may be due partly to the presence of self-association through strong H-bonding in the primary amines, which is disrupted by order-breaking cyclohexane molecules [15].

Study of the δ values in Table VII further indicates that the difference δ is an increasing function of the size difference. Jambon and Delmas [23] have observed a similar discrepancy between $\Delta \ln \eta_{th}$ and $\Delta \ln \eta_{exp}$, while analyzing data for a large number of binary mixtures, containing components differing in size.

This indicates that the failure of PFPBD theory to estimate the correct values of excess viscosity is due partly to association in pure amines and partly to difference in size between the two components of the mixture.

ACKNOWLEDGMENT

The authors wish to thank the staff of the Computer Centre, South Gujarat University, Surat, for their assistance with the computational work.

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