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Viscosity of Binary Mixtures. I. Mono-, Di-, and Tri-*n*-Butyl and -*n*-Octylamine with Cyclohexane

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Viscosities for six binary mixtures of *n*-butylamine, di-*n*-butylamine, tri-*n*-butylamine, *n*-octylamine, di-*n*-octylamine, and tri-*n*-octylamine with cyclohexane have been measured at 303.15 K with an Ubbelohde suspended-level viscometer. Deviations of viscosities from a rectilinear dependence on mole fraction are attributed to H-bonding and to the size of alkylamine compounds. The application of the Eyring's theory of activation energy is examined. The free volume theory of Prigogine–Flory–Patterson (PFP) and the experimental excess enthalpy have been used to estimate excess viscosity $\Delta \ln \eta = (\ln \eta/\eta_1^0 - x_2 \ln \eta_2^0/\eta_1^0)$ and corresponding free volume, enthalpy, and entropy contributions for five binary mixtures of tri-*n*-alkylamine: triethyl, tripropyl, tributyl, trihexyl, and trioctylamine with cyclohexane. A comparison of experimental and theoretical excess viscosities indicates a failure of the PFP theory when two components of the mixture differ considerably in size. The size difference contribution to excess viscosity is related to $(V_2^{*1/2} - V_1^{*1/2})^2$, where V_1^* and V_2^* are hard-core volumes of two components of the mixture.

KEY WORDS: activation energy; alkylamines; binary liquids; cyclohexane; Prigogine–Flory–Patterson theory; viscosity.

1. INTRODUCTION

Amines are important organic bases because of their strong electron donating capability. But the binary mixtures containing an amine are usually difficult to interpret in simple qualitative terms. This is because primary and secondary amines, as well as the usual intermolecular forces associated with polar molecules, can also form H-bonds either in self-

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associated complexes or with the appropriate groups on dissimilar molecular species. Systematic studies on excess volumes and excess enthalpies of binary liquids containing alkyl and arylamines in a number of nonpolar solvents have been reported [1–13], but such systematic work on viscosity does not seem to exist, except for a few studies providing scanty data [14–16]. As part of our studies on the molecular interactions in binary liquid mixtures containing amines as one of the components [16–18], we report here viscosity measurements for six binary mixtures of *n*-butylamine, di-*n*-butylamine, tri-*n*-butylamine, *n*-octylamine, di-*n*-octylamine, and tri-*n*-octylamine compounds with cyclohexane. The present study shows the effect of H-bonding and effects of chain length and size and shape of alkylamine compounds on mixing properties. The experimental results are also analyzed in terms of free volume, enthalpy, entropy, orientation, etc., contributions on the basis of the Prigogine–Flory–Patterson (PFP) theory [19–22] in combination with expressions proposed by Bloomfield and Dewan [23].

2. EXPERIMENTAL

The viscosity measurements were made with a modified Ubbelohde suspended-level viscometer. The efflux time of a definite volume of liquid through the capillary was measured with an accurate stopwatch with a resolution of 0.1 s. In the experiments, the viscometer was suspended vertically for a sufficient time in a constant-temperature bath maintained within 0.02 K. Doubly distilled water and purified benzene were used for the calibration of the viscometer [24, 25]. The densities of pure components

Table I. Density and Refractive Index at 298.15 K of the Pure Liquids Used

	ρ, density (kg · m^{-3})		n_D, refractive index	
Liquid	This work	Literature	This work	Literature
Cyclohexane	773.8	773.89 [24]	1.4242	1.42354 [24]
n-Butylamine	733.2	733.08 [1]	1.3997	1.3987 [24]
Di-*n*-butylamine	755.9	755.7 [1]	1.4159	1.4152 [24]
Tri-*n*-butylamine	773.9	773.78 [1] 774.6 [26, 29]	1.4267	1.4268 [29] 1.4265 [6]
n-Octylamine	779.3	778.9 [27]	1.4271	1.4274 [27]
Di-*n*-octylamine[a]	797.3	796.8 [27]	1.4420	1.4415 [27]
Tri-*n*-octylamine	808.2	807.35 [28] 808.6 [4]	1.4474	1.4478 [6, 29]

[a] ρ and n_D at 299.15 K.

and binary mixtures required for the measurements of viscosity were determined by a glass pycnometer. The details of measurements and procedures of viscosity and density have been described previously [16, 24].

Samples of cyclohexane and all amines were obtained from Fluka AG for the use in this work. The stated label of purity for these samples was better than 99%. Cyclohexane (C_6H_{12}) was dried over molecular sieve 4A and fractionally distilled over sodium. *n*-Butylamine ($ButNH_2$), *n*-octylamine ($OctNH_2$), di-*n*-butylamine (But_2NH), and tri-*n*-butylamine (But_3N) were kept over sodium and fractionally distilled. Di-*n*-octylamine (Oct_2NH) and tri-*n*-octylamine (Oct_3N) were dried over molecular sieve and used. Purity of samples was checked by gas–liquid chromatography and from the measurement of density and refractive index at 298.15 K, which compares well with the accepted literature values [1, 4, 6, 25–29], as shown in Table I.

3. RESULTS AND DISCUSSION

3.1. General

The viscosities η of the pure components and of the binary mixtures $C_6H_{12}+ButNH_2$, $C_6H_{12}+But_2NH$, $C_6H_{12}+But_3N$, $C_6H_{12}+OctNH_2$, $C_6H_{12}+Oct_2NH$, and $C_6H_{12}+Oct_3N$ over the entire range of mole fractions at 303.15 K are listed in Table II. The estimated accuracy of the measured viscosity is about 0.4%. The viscosity values in Table II are represented by

$$\eta=\sum_{i=0}^{5} A_i x_1^i \tag{1}$$

and the parameters obtained from a least-squares fit are given in Table III, together with the standard deviation σ and largest deviations $\delta_{\max}$. Figure 1 shows the viscosities as a function of the mole fractions (x_1) of C_6H_{12} for all six binary mixtures. The $C_6H_{12}+But_2NH$ and $C_6H_{12}+OctN$ mixtures are the only two mixtures that show minima. These occur at about 0.7 and 0.9 mole fractions of C_6H_{12} in dibutyl and octylamine mixtures, respectively.

Figure 1 also indicates that the viscosities show negative deviations from a rectilinear dependence on mole fraction for the four binary mixtures of *n*-butylamine, di-*n*-butylamine, tri-*n*-butylamine, and *n*-octylamine with cyclohexane and show positive deviations in the case of di-*n*-octyl and tri-*n*-octylamines with cyclohexane. A slight positive deviation is also observed for $C_6H_{12}+OctNH_2$ when this mixture is rich in *n*-octylamine.

The negative deviations for $C_6H_{12} + ButNH_2$, $C_6H_{12} + OctNH_2$, $C_6H_{12} + But_2NH$, and $C_6H_{12} + But_3N$, 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 these primary and secondary amines and the destruction of dipolar order in tributylamine [30]. The deviations are large in the case of the butylamine mixtures as compared with the dibutylamine mixtures, because of stronger H-bonding in the primary amines than in the secondary amines. In case of the mixture $C_6H_{12} + Oct_2NH$, the expected small negative deviation, due to the breaking of weak H-bonding in dioctylamine, is not observed, as it has been masked by the deviation due to the large size difference of the two components in the mixture.

Table II. Viscosity of Cyclohexane + Alkylamine at 303.15 K as a Function of the Mole Fraction x_i of Cyclohexane

x_1	η (mPa · s)	x_1	η (mPa · s)	x_1	η (mPa · s)
$C_6H_{12} + ButNH_2$		$C_6H_{12} + But_2NH$		$C_6H_{12} + But_3N$	
0.0000	0.443	0.0000	0.764	0.0000	1.167
0.1009	0.453	0.1011	0.749	0.1133	1.125
0.2007	0.467	0.2001	0.737	0.1972	1.125
0.3012	0.492	0.3025	0.731	0.2987	1.059
0.3987	0.501	0.4034	0.728	0.4020	1.021
0.4982	0.529	0.4997	0.727	0.4990	0.987
0.5729	0.553	0.6050	0.729	0.5952	0.951
0.7003	0.601	0.7025	0.727	0.7042	0.911
0.7863	0.652	0.7989	0.743	0.8018	0.875
0.8993	0.725	0.8971	0.759	0.9005	0.845
1.0000	0.819	1.0000	0.819	1.0000	0.819
$C_6H_{12} + OctNH_2$		$C_6H_{12} + Oct_2NH$		$C_6H_{12} + Oct_3N$	
0.0000	1.169	0.0000	3.665	0.0000	6.950
0.0971	1.138	0.1052	3.382	0.1179	6.488
0.1959	1.096	0.2021	3.137	0.1582	6.333
0.2997	1.036	0.3028	2.950	0.3086	5.344
0.4010	0.970	0.4044	2.591	0.4099	4.830
0.4970	0.952	0.5039	2.306	0.5029	4.330
0.5993	0.913	0.6016	1.976	0.6074	3.468
0.6975	0.863	0.7009	1.653	0.7022	2.757
0.7993	0.820	0.8006	1.364	0.8023	2.054
0.8960	0.810	0.9216	1.055	0.9020	1.416
1.0000	0.819	1.0000	0.819	1.0000	0.819

Table III. Parameters of Eq. (1), Standard Deviation σ and Largest Deviation δ_{max} for the Viscosity of Cyclohexane + Alkylamine Mixtures at 303.15 K

Sr. No.	Mixture	A_0	A_1	A_2	A_3	A_4	A_5	σ	δ_{max}
	C_6H_{12} +								
1	$ButNH_2$ (2)	0.4430	0.1024	−9.0533	0.6668	−0.7814	0.4414	0.002	0.0032
2	But_2NH (2)	0.7640	−0.0333	−0.3038	2.0427	−3.2051	1.6546	0.003	0.0050
3	But_3N (2)	1.1670	−0.3849	0.1549	−0.3114	0.1775	0.0160	0.001	0.0011
4	$OctNH_2$ (2)	1.1690	−0.1469	−2.1411	5.4077	−5.9203	2.4506	0.011	0.0168
5	Oct_2NH (2)	3.6650	−3.3989	8.9318	−28.0514	32.0612	−12.3887	0.024	0.0360
6	Oct_3N (2)	6.9500	−2.9306	−9.3167	13.5541	−12.7802	5.3424	0.082	0.1318

3.2. Activation Energy of Viscous Flow

On the basis of the theory of absolute reaction rates [31] the excess Gibbs energy of activation ΔG^{*E} of viscous flow may be calculated from [32]

$$\Delta G^{*E} = RT\left[\ln \eta V - \sum_i x_i \ln \eta_i^0 V_i^0\right] \tag{2}$$

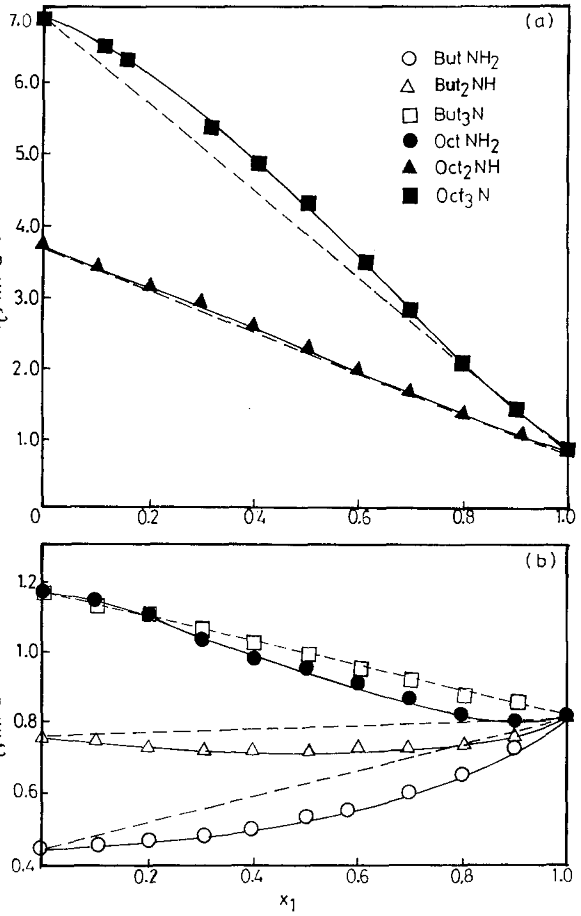

Fig. 1. Composition dependence of the viscosity of cyclohexane (1) + alkylamine (2) at 303.15 K. Alkylamine: (○) $\mathrm{ButNH_2}$; (△) $\mathrm{But_2NH}$; (□) $\mathrm{But_3N}$; (●) $\mathrm{OctNH_2}$; (▲) $\mathrm{Oct_2NH}$; (■) $\mathrm{Oct_3N}$. Solid curves were calculated from Eq. (1), and dashed curves on the basis of mole fraction averaging.

Table IV. Parameters of Eq. (3), Standard Deviation σ, ΔG^{*E}_{max}, and Corresponding Concentration x_1 for Cyclohexane + Alkylamine Mixtures at 303.15 K

Sr. No.	Mixture	A_0	A_1	A_2	A_3	σ	ΔG^{*E}_{max} $(J \cdot mol^{-1})$	x_1
	C_6H_{12} +							
1	$ButNH_2$ (2)	−0.489	0.109	−0.030	0.038	0.0035	−319	0.5729
2	But_2NH (2)	−0.214	0.088	−0.270	0.229	0.0040	−178	0.7025
3	But_3N (2)	0.344	−0.030	−0.009	−0.032	0.0015	216	0.4990
4	$OctNH_2$ (2)	−0.019	0.218	−0.158	0.231	0.0073	−126	0.7993
5	OctNH (2)	1.651	−0.173	−0.100	−1.399	0.0141	1057	0.5039
6	OctN (2)	3.167	−1.312	0.965	−0.641	0.0216	2119	0.6074

where η and V are the viscosity and molar volume of the mixture and η_i^0 and V_i^0 are the viscosity and molar volume of the pure component i, respectively. The values of $\Delta G^{*E}/RT$ were fitted to the polynomial,

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

The parameters A_i and standard deviations σ are listed in Table IV. Table IV also includes $\Delta G^{*E}_{\max}$ and its corresponding mole fraction.

Figure 2 shows the dependence of ΔG^{*E} on the mole fraction x_1 of

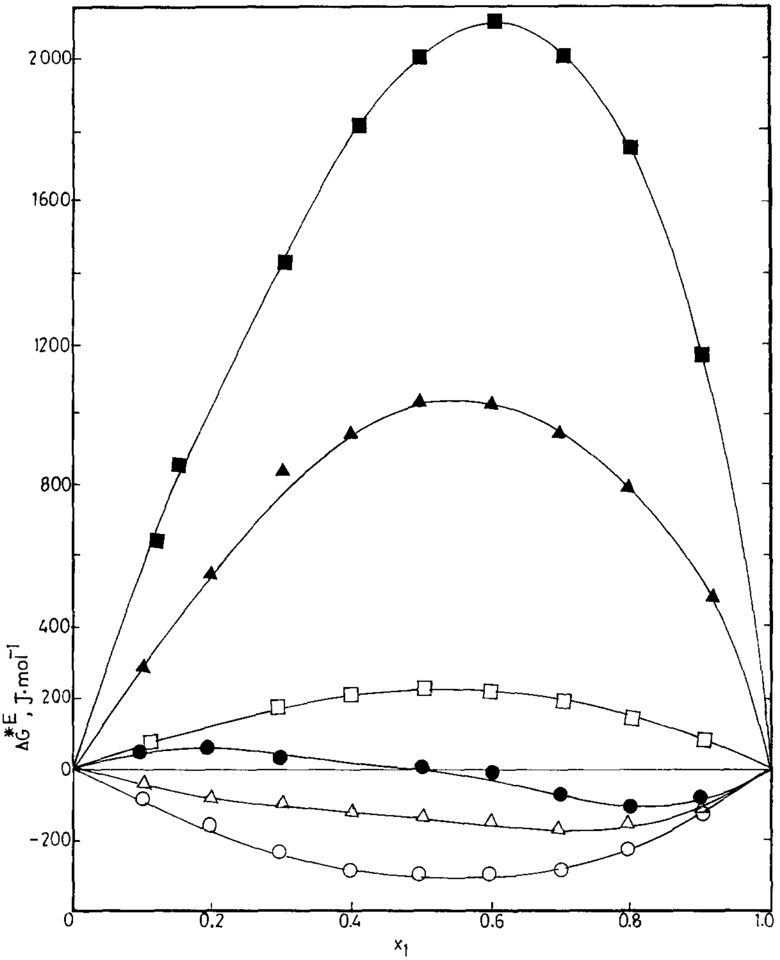

Fig. 2. Variation of ΔG^{*E} with composition for cyclohexane (1) + alkylamine (2) at 303.15 K. Symbols as in the legend to Fig. 1.

cyclohexane for all six binary mixtures at 303.15 K. ΔG^{*E} is estimated to be accurate to $\pm 25\ \mathrm{J \cdot mol^{-1}}$ for the present cyclohexane + alkylamine mixtures investigated. The values of ΔG^{*E} for C_6H_{12} + ButNH$_2$ and C_6H_{12} + But$_2$NH mixtures are large and negative; those for C_6H_{12} + But$_3$N, C_6H_{12} + Oct$_2$NH and C_6H_{12} + Oct$_3$N mixtures are large and positive at all mole fractions. The values of ΔG^{*E} for the C_6H_{12} + OctNH$_2$ mixture is positive at low mole fractions of cyclohecane, up to 0.45, and have opposite sign otherwise.

The order in the values of ΔG^{*E} for the six binary mixtures with cyclohexane is

$$\mathrm{ButNH_2 < But_2NH < OctNH_2 < But_3N < Oct_2NH < Oct_3N}$$

These results indicate the predominant effect of molecular size, shape, and self-association of amine molecules on the values of ΔG^{*E}. The negative values of ΔG^{*E} for C_6H_{12} + ButNH$_2$, and C_6H_{12} + But$_2$NH at all mole fractions and for C_6H_{12} + OctNH$_2$ at higher mole fractions of OctNH$_2$ can be attributed to the destruction of the H-bonded associated structure of the amines by the addition of order breaking cyclohexane molecule [33]. The increasing positive values of ΔG^{*E} from C_6H_{12} + Oct$_2$NH to C_6H_{12} + But$_3$N and to C_6H_{12} + Oct$_3$N are attributed to the large size and cohesive energy difference between the two components. Similar results were observed for the binary mixtures of tetrabutyltin + tetrabutyltin

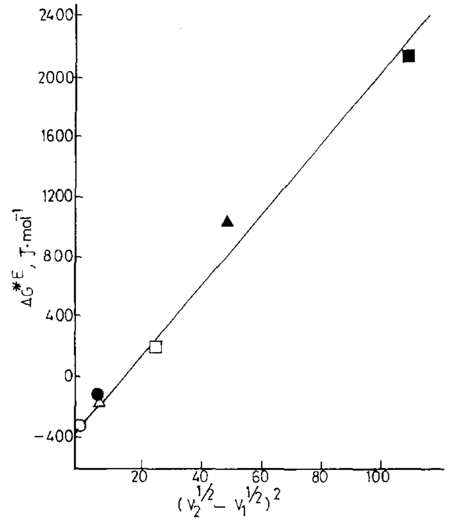

Fig. 3. $\Delta G^{*E}_{\max}$ versus the difference in molar volume of the two components $(V_2^{1/2} - V_1^{1/2})$. Symbols as in the legend to Fig. 1.

(SnR_4; where R = methyl, ethyl, propyl, butyl, octyl, and laryl group) [34], benzene + *n*-alkanes (with C = 6, 8, 10, 12, and 16) [35], and *n*-alkane + *n*-alkane [36–39]. Just to see the effect of size on the values of ΔG^{*E}, an attempt was made in Fig. 3 to plot the values of $\Delta G^{*E}_{\max}$ against the values $(V_2^{1/2} - V_1^{1/2})^2$. $\Delta G^{*E}_{\max}$ is shown to be an increasing function of the size difference.

4. THEORETICAL ANALYSIS OF EXCESS VISCOSITY OF CYCLOHEXANE + TRIALKYLAMINE MIXTURES

The viscosity of a number of binary mixtures has recently been analyzed by Delmas and co-workers [34, 40, 41] in terms of the Prigogine–Flory–Patterson theory [19–22] and expressions developed by Bloomfield and Dewan [23]. For a comprehensive analysis, available excess viscosities for the mixtures $C_6H_{12} + Et_3N$ (triethylamine [16]), $C_6H_{12} + Pr_3N$ (tripropylamine [16]), and $C_6H_{12} + Hex_3N$ (trihexylamine [42]) have also been considered along with the results of the present investigation for the mixtures $C_6H_{12} + But_3N$ and $C_6H_{12} + Oct_3N$.

The details of Prigogine–Flory–Patterson theory have been outlined several times in the literature in the past [7, 21, 43] and are not repeated here. Only the pertinent equation is given here. Following Bloomfield and Dewan [23], the excess viscosity, $\Delta \ln \eta_{th}$,

$$\Delta \ln \eta_{th} = \ln \eta_H + \ln \eta_S + \ln \eta_V \tag{4}$$

where

$$\ln \eta_H = -H^E/RT \tag{5}$$

$$\ln \eta_S = S^E/R \tag{6}$$

$$\ln \eta_V = (\tilde{v} - 1)^{-1} - \sum_i x_i/(\tilde{v}_i - 1) \tag{7}$$

The terms $\ln \eta_H$, $\ln \eta_S$, and $\ln \eta_V$ are the enthalpy, entropy, and free volume contributions, respectively, to $\Delta \ln \eta_{th}$. The excess enthalpy H^E and excess entropy S^E, according to the Prigogine–Flory–Patterson theory [7, 21], are given by

$$\begin{aligned} H^E = \left(\sum_i x_i P_i^* V_i^*\right)\Big\{ &\tilde{C}_P \left[\sum_i \psi_i \tilde{T}_i - \tilde{T}_U\right] \\ &+ X_{12}\theta_2\psi_1 P_1^{*-1}[\tilde{v}^{-1} + \tilde{T}_U \tilde{C}_P]\Big\} \end{aligned} \tag{8}$$

$$S^E = \sum_i 3x_i P_i^* V_i^* T_i^{*-1} \ln[(\tilde{v}_i^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] \tag{9}$$

Here θ_i and ψ_i represent surface fraction and contact-energy fraction, respectively. The quantities $\tilde{v}$, $\tilde{T}$, and $\tilde{C}_P$ represent the reduced volume, temperature, and configurational heat capacity, P_i^*, V_i^*, and T_i^* are the Flory's reduction parameters and X_{12} is the contact interaction parameter. The reduced volume $\tilde{v}_u$ for $\tilde{T}_u$ of the mixture is defined as [7, 21]

$$\tilde{v}_u^{-1} = \sum_i \psi_i \tilde{v}_i^{-1} \tag{10}$$

The values of the reduction parameter of $\tilde{v}$, V^*, and P^* and the molecular surface-to-volume ratio S for the pure components considered are listed in Table V. In the present investigation, we have used the equimolar experimental excess enthalpy data reported by Delmas et al. [7, 8] to estimate the contact interaction parameter X_{12}, which has been used to estimate $\Delta \ln \eta_{th}$ and the three contributions $\ln \eta_H$, $\ln \eta_S$, and $\ln \eta_V$. The results are summarized in Table VI. Table VI also gives the values of the experimental $\Delta \ln \eta_{exp}$ and their difference δ $(= \Delta \ln \eta_{exp} - \Delta \ln \eta_{th})$ with the theoretical values.

A comparison between theoretical and experimental $\Delta \ln \eta$ results at all mole fractions is shown in Fig. 4. The values of $\ln \eta_H$ for all five mixtures are negative, but the values of $\ln \eta_S$ change the sign, being positive for $C_6H_{12} + Et_3N$ and $C_6H_{12} + Pr_3N$, zero for $C_6H_{12} + But_3N$, and negative for $C_6H_{12} + Hex_3N$ and $C_6H_{12} + Oct_3N$. The values of $\ln \eta_V$ are positive for all mixtures except for $C_6H_{12} + Et_3N$. For the first two mixtures, $C_6H_{12} + Et_3N$ and $C_6H_{12} + Pr_3N$, where the free volume difference is relatively small, the enthalpic contribution to the excess viscosity is quite large compared to the entropic and the free volume contribution, resulting in a net negative $\Delta \ln \eta_{th}$. For the mixture $C_6H_{12} + But_3N$ the enthalpic and free volume contributions to the excess viscosity are almost equal but of opposite sign; therefore, the net $\Delta \ln \eta_{th}$ is very small. As the

Table V. Flory's Parameters at 303.15 K

Components	$\tilde{v}$	V^* ($cm^3 \cdot mol^{-1}$)	P^* ($J \cdot cm^{-3}$)	S (A^{-1})
C_6H_{12}	1.2975	84.33	533.3	0.93
Et_3N	1.3126	107.24	469.0	0.85
Pr_3N	1.2665	150.87	441.0	0.90
But_3N	1.2491	192.35	448.6	0.88
Hex_3N	1.2255	277.44	448.0	0.85
Oct_3N	1.2166	361.20	466.5	0.84

Table VI. Excess Enthalpy H^E, Parameter X_{12}, Enthalpic, Entropic, and Free Volume Contributions to Excess Viscosity and Comparison Between Theoretical and Experimental Excess Viscosity for Binary Mixture at Equimolar Composition

Mixture	H^E $(J \cdot mol^{-1})$[a]	X_{12} $(J \cdot cm^{-3})$	$\ln \eta_H$	$\ln \eta_S$	$\ln \eta_V$	$\Delta \ln \eta_{th}$	$\Delta \ln \eta_{exp}$	δ[b]
C_6H_{12} (1) +								
Eth_3N (2)	245.0	9.8	−0.097	0.026	−0.032	−0.103	−0.116	−0.013
PrO_3N (2)	221.2	8.1	−0.088	0.017	0.010	−0.060	−0.112	−0.052
But_3N (2)	150.6	5.5	−0.060	0.000	0.073	0.013	0.009	−0.004
Hex_3N (2)	239.5	8.2	−0.095	−0.016	0.195	0.083	0.263	0.180
Oct_3N (2)	345.5	11.4	−0.137	−0.024	0.297	0.136	0.600	0.464

[a] From Refs. 7 and 8.

[b] $\delta \equiv \Delta \ln \eta_{exp} - \Delta \ln \eta_{th}$.

free volume difference between the two components for the mixtures $C_6H_{12}+Hex_3N$ and $C_6H_{12}+Oct_3N$ increases, the free volume contribution to the excess viscosity dominates over both the enthalpic and the entropic contributions, resulting in large positive theoretical values for the excess viscosity. A comparison of $\Delta \ln \eta_{exp}$ and $\Delta \ln \eta_{th}$ in Table VI and Fig. 4 indicates that the agreement between the theory and the experimental results is reasonably good for the first three mixtures of Et_3N, Pr_3N, and But_3N with C_6H_{12}, whereas large differences are observed for the

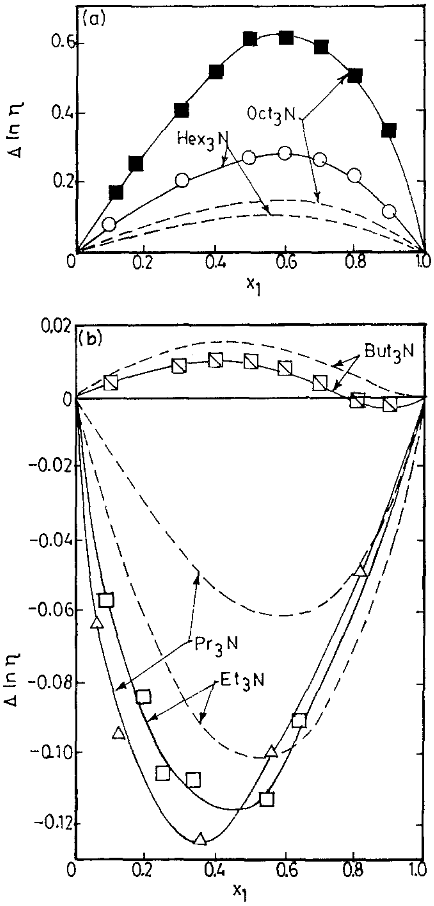

Fig. 4. Composition dependence of excess viscosity $\Delta \ln \eta$: (experimental, ——; PFP theory, -----) of cyclohexane (1) + trialkylamine (2) at 303.15 K. Trialkylamine: (□) Et_3N; (△) Pr_3N; (▨) But_3N; (○) Hex_3N; (■) Oct_3N.

C_6H_{12} + Hex_3N and C_6H_{12} + Oct_3N mixtures. This indicates a failure of the Prigogine–Flory–Patterson theory for the mixtures whose components have large size differences [34]. It is quite likely that, in this case, small molecules of cyclohexane fit well in the cavities left by large molecules, thereby increasing the viscosity of the mixture substantially.

To obtain a more quantitative correlation between the size difference and the deviations, $\delta = \Delta \ln \eta_{\text{exp}} - \Delta \ln \eta_{\text{th}}$ is plotted in Fig. 5 against $(V_2^{*1/2} - V_1^{*1/2})^2$ as suggested by Jambon and Delmas [34], where V_1^* and V_2^* are hard-core volumes. For the five mixtures, of the present study, there is a reasonably linear relationship. Thus, the contributions due to the size difference $\ln \eta_{\Delta V}$ must be added to Eq. (4). It is clear from Fig. 5 that it can be represented as [34]

$$\ln \eta_{\Delta V} = C(V_2^{*1/2} - V_1^{*1/2})^2 \tag{11}$$

The value of C obtained from the curve is 5.3×10^{-3}; it is in excellent agreement with the value of C obtained by Jambon and Delmas [34] for a large number of mixtures with $(V_2^{*1/2} - V_1^{*1/2})^2$ varying from 0 to 200. The condensation effect of volatile Et_3N and Pr_3N molecules may possibly be responsible for the small negative values of δ for C_6H_{12} + Et_3N and C_6H_{12} + Pr_3N mixtures. A similar conclusion was reached by Phuong-Nguyen et al. [8] from the excess heats, heat capacities, and volume of mixtures of trialkylamine compounds with cyclohexane.

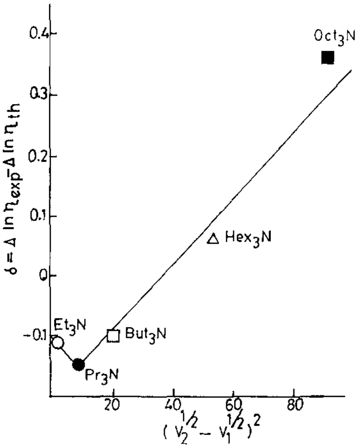

Fig. 5. $\delta = \Delta \ln \eta_{\text{exp}} - \Delta \ln \eta_{\text{th}}$ against the difference in core volume of the two components $(V_2^{*1/2} - V_1^{*1/2})$.

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