# Viscosity of Biniary Mixtures. III. Tri-*n*-Butylamine with Alkanes and Monoalkylamines at 303.15 and 313.15 K

S. L. Oswal[1] and S. G. Patel[1]

Viscosities $\eta$ of seven binary systems of *n*-propylamine, *n*-butylamine, *n*-hexylamine, *n*-octylamine, *n*-hexane, *n*-octane, and isoctane (2,2,4-trimethyl-pentane) with tributylamine have been measured at 303.15 and 313.15 K with an Ubbelohde suspended-level viscometer. Based on Eyring's theory, values of excess Gibbs energy of activation $\Delta G^{*E}$ of viscous flow have been calculated. Deviations of viscosities from linear dependence on the mole fraction and values of $\Delta G^{*E}$ are attributed to the H-bonding and to the size of alkylamine and alkane molecules. The free volume theory of Prigogine–Flory–Patterson in combination with work by 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 the present binary mixtures.

**KEY WORDS:** activation energy; alkylamines; alkanes; binary liquids; propylamine; butylamine; hexylamine; octylamine; *n*-hexane; *n*-octane; iso-octane (2,2,4 trimethyl pentane); tributylamine; Eyring's theory; Prigogine–Flory–Patterson–Bloomfield–Dewan theory; viscosity.

## 1. INTRODUCTION

We have been engaged in a systematic study of the thermodynamic, acoustic, and transport properties of binary liquid mixtures containing alkylamines. In previous papers [1–3], we have reported the viscosities $\eta$ for several binary mixtures of alkylamines with benzene and cyclohexane. It was observed that H-bonding in and the size of alkylamine molecules have considerable effect on the viscosities of binary mixtures. To know how trialkylamines interact with alkanes and primary alkylamines and

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[1] Department of Chemistry, South Gujarat University, Surat 395007, India.

to check further the Prigogine–Flory–Patterson–Bloomfield–Dewan (PFPBD) theory [4–8], in this paper the viscosities $\eta$ of binary mixtures of tributylamine with $n$-propylamine at 303.15 K and $n$-butylamine, $n$-hexylamine, $n$-octylamine, $n$-hexane, $n$-octane, and isooctane (2,2,4-trimethylpentane) at 303.15 and 313.15 K have been reported.

## 2. EXPERIMENTAL

The methods and techniques used to determine the viscosities $\eta$ and the densities $\rho$ have been described in previous papers [1, 2, 9]. The kinematic viscosity $(\eta/\rho)$ measurements were made with a modified Ubbelohde suspended-level viscometer [10, 11]. Four or five sets of readings for the flow time were taken for each pure liquid or liquid mixture at constant temperatures of $303.15 \pm 0.02$ and $313.15 \pm 0.02$ K. The arithmetic mean was taken for the purpose of calculations. The viscometer had been calibrated using doubly distilled water, benzene, cyclohexane, and $n$-hexadecane [12, 13]. The densities $\rho$ at 303.15 and 313.15 K of the pure components and mixtures required for converting kinematic viscosities to absolute viscosities were determined with an Anton–Paar densimeter (Model DMA 60/602). The errors in $\eta$ and $\rho$ are estimated to be 0.002 mPa $\cdot$ s and 0.02 kg $\cdot$ m$^{-3}$, respectively.

Samples of $n$-propylamine ($C_3H_7NH_2$), $n$-butylamine ($C_4H_9NH_2$), $n$-hexylamine ($C_6H_{13}NH_2$), $n$-octylamine ($C_8H_{17}NH_2$), and tributylamine ($C_4H_9)_3N$ were from Fluka AG of stated purity better than 99%; $n$-hexane (n-$C_6H_{14}$), $n$-octane (n-$C_8H_{18}$), and isooctane (2,2,4-trimethylpentane; iso-$C_8H_{18}$) were from Merck, Schuchardt. All amines were kept over sodium and fractionally distilled twice, and alkanes were used after

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

| Liquids | Temp. (K) | $\rho$, density (kg $\cdot$ m$^{-3}$) | | $n_D$, refractive index | |
|---|---|---|---|---|---|
| | | Expt. | Lit. | Expt. | Lit. |
| Tributylamine | 298.15 | 774.23 | 774.3 [13] | 1.4267 | 1.4268 [15] |
| | | | 774.6 [17] | | |
| Propylamine | 298.15 | 712.44 | 712.1 [13] | 1.3853 | 1.3851 [13] |
| Butylamine | 298.15 | 733.23 | 733.1 [14] | 1.3997 | 1.3987 [13] |
| | | | 734.52 [16] | | |
| Hexylamine | 303.15 | 757.60 | 756.5 [17] | 1.4160 | 1.4160 [18] |
| Octylamine | 298.15 | 779.35 | 778.9 [18] | 1.4271 | 1.4279 [18] |
| $n$-Hexane | 298.15 | 654.93 | 654.84 [13] | 1.3720 | 1.3723 [13] |
| $n$-Octane | 298.15 | 698.67 | 698.62 [13] | 1.3950 | 1.3951 [13] |
| Isooctane | 298.15 | 688.08 | 687.81 [13] | 1.3889 | 1.3890 [13] |

further purification and drying over a 4-Å molecular sieve [12, 14]. Details of the purification procedures have been described previously [2, 3, 9].

The purities of the liquids were checked with gas–liquid chromatography and from the measurement of density and refractive index, which compared well with the accepted literature values [13–18] as shown in Table I.

**Table II.** Viscosity of Tributylamine + Alkanes at 303.15 and 313.15 K

| | $\eta$ (mPa · s) | |
|---|---|---|
| $x_1{}^a$ | 303.15 K | 313.15 K |
| $(C_4H_9)_3N + n\text{-}C_6H_{14}$ | | |
| 0.0000 | 0.2759 | 0.2391 |
| 0.0982 | 0.3305 | 0.2890 |
| 0.1945 | 0.3909 | 0.3449 |
| 0.3994 | 0.5434 | 0.4813 |
| 0.4950 | 0.6230 | 0.5536 |
| 0.5384 | 0.6623 | 0.5880 |
| 0.7924 | 0.9230 | 0.8088 |
| 0.9030 | 1.0498 | 0.9100 |
| 1.0000 | 1.1668 | 1.0000 |
| $(C_4H_9)_3N + n\text{-}C_8H_{18}$ | | |
| 0.0000 | 0.4830 | 0.4201 |
| 0.0983 | 0.5320 | 0.4675 |
| 0.1934 | 0.5833 | 0.5129 |
| 0. 950 | 0.7038 | 0.6183 |
| 0.4909 | 0.7674 | 0.6727 |
| 0.5915 | 0.8380 | 0.7340 |
| 0.7854 | 0.9861 | 0.8553 |
| 0.8970 | 1.0788 | 0.9291 |
| 1.0000 | 1.1668 | 1.0000 |
| $(C_4H_9)_3N + \text{iso-}C_6H_{18}$ | | |
| 0.0000 | 0.4474 | 0.4008 |
| 0.1106 | 0.5050 | 0.4465 |
| 0.2474 | 0.5839 | 0.5109 |
| 0.3947 | 0.6783 | 0.5884 |
| 0.4958 | 0.7486 | 0.6462 |
| 0.5982 | 0.8256 | 0.7101 |
| 0.7930 | 0.9844 | 0.8423 |
| 0.8938 | 1.0717 | 0.9171 |
| 1.0000 | 1.1668 | 1.0000 |

$^a$ $x_1$ is the mole fraction of the first component.

**Table III.**  Viscosity of Tributylamine + Alkylamines at
303.15 and 313.15 K

| | $\eta$ (mPa·s) | |
|---|---|---|
| $x_1{}^a$ | 303.15 K | 313.15 K |
| $(C_4H_9)_3N + C_3H_7NH_2$ | | |
| 0.0000 | 0.3479 | |
| 0.2025 | 0.5088 | |
| 0.4055 | 0.6949 | |
| 0.4953 | 0.7795 | |
| 0.6030 | 0.8793 | |
| 0.7931 | 1.0398 | |
| 1.0000 | 1.1668 | |
| $(C_4H_9)_3N + C_4H_9NH_2$ | | |
| 0.0000 | 0.4378 | 0.3891 |
| 0.0993 | 0.5014 | 0.4423 |
| 0.1930 | 0.5660 | 0.4968 |
| 0.3946 | 0.7175 | 0.6233 |
| 0.4948 | 0.7961 | 0.6880 |
| 0.5888 | 0.8701 | 0.7498 |
| 0.7738 | 1.0133 | 0.8682 |
| 0.8887 | 1.0942 | 0.9377 |
| 1.0000 | 1.1668 | 1.0000 |
| $(C_4H_9)_3N + C_6H_{13}NH_2$ | | |
| 0.0000 | 0.7123 | 0.6134 |
| 0.1032 | 0.7562 | 0.6517 |
| 0.1936 | 0.7958 | 0.6853 |
| 0.3936 | 0.8857 | 0.7606 |
| 0.4924 | 0.9301 | 0.7985 |
| 0.6079 | 0.9836 | 0.8436 |
| 0.7820 | 1.0632 | 0.9122 |
| 0.9153 | 1.1255 | 0.9652 |
| 1.0000 | 1.1668 | 1.0000 |
| $(C_4H_9)_3N + C_8H_{17}NH_2$ | | |
| 0.0000 | 1.1646 | 0.9864 |
| 0.1005 | 1.1495 | 0.9719 |
| 0.2020 | 1.1384 | 0.9612 |
| 0.3961 | 1.1265 | 0.9507 |
| 0.5022 | 1.1253 | 0.9506 |
| 0.5949 | 1.1273 | 0.9532 |
| 0.7991 | 1.1404 | 0.9700 |
| 0.8964 | 1.1514 | 0.9821 |
| 1.0000 | 1.1668 | 1.0000 |

$^a$ $x_1$ is the mole fraction of the first component.

## 3. RESULTS

### 3.1. Viscosities

The measured viscosities $\eta$ of the seven binary mixtures $(C_4H_9)_3N + C_3H_7NH_2$, $(C_4H_9)_3N + C_4H_9NH_2$, $(C_4H_9)_3N + C_6H_{13}NH_2$, $(C_4H_9)_3N + C_8H_{17}NH_2$, $(C_4H_9)_3H + n\text{-}C_6H_{14}$, $(C_4H_9)_3N - n\text{-}C_8H_{18}$, and $(C_4H_9)_3N + i\text{-}C_8H_{18}$ over the entire range of mole fractions at 303.15 and 313.15 K are listed in Tables II and III. The viscosity values in Tables II and III are presented 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 IV, together with the standard deviations $\sigma$. Figures 1 and 2 show the viscosities as a function of the mole fractions $x_1$ of tributylamine.

It can be seen from Fig. 1 that viscosities $\eta$ show significant negative deviations from a linear dependence on $x_1$ for all three tributylamine + alkane mixtures at both temperatures. From Fig. 2, it can be observed that large and negative deviations with a minimum around $x_1 = 0.5$ are observed for $(C_4H_9)_3N + C_8H_{17}NH_2$, while for $(C_4H_9)_3N + C_6H_{13}NH_2$, the negative deviations are very small at all mole fractions. In the case of

Table IV. Parameters $A_i$ in Eq. (1) and Standard Deviations $\sigma$ (mPa·s) for the Viscosity of Binary Mixtures at 303.15 and 313.15 K

| Mixture | Temp (K) | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $A_4$ | $\sigma$ |
|---|---|---|---|---|---|---|---|
| $(C_4H_9)_3N + n\text{-}C_6H_{14}$ | 303.15 | 0.2757 | 0.5327 | 0.2832 | 0.1683 | −0.0929 | 0.0009 |
| | 313.15 | 0.2389 | 0.4875 | 0.2644 | 0.1321 | −0.1320 | 0.0004 |
| $(C_4H_9)_3N + n\text{-}C_8H_{18}$ | 303.15 | 0.4829 | 0.4830 | 0.1722 | 0.0680 | −0.0392 | 0.0003 |
| | 313.15 | 0.4206 | 0.4534 | 0.1266 | | | 0.0010 |
| $(C_4H_9)_3N + iso\text{-}C_8H_{18}$ | 303.15 | 0.4473 | 0.5034 | 0.1686 | 0.1254 | −0.0779 | 0.0002 |
| | 313.15 | 0.4007 | 0.3943 | 0.2052 | | | 0.0003 |
| $(C_4H_9)_3N + C_3H_7NH_2$ | 303.15 | 0.3479 | 0.7063 | 0.5009 | −0.2886 | −0.0997 | 0.0002 |
| $(C_4H_9)_3N + C_4H_9NH_2$ | 303.15 | 0.4379 | 0.6079 | 0.3267 | −0.1658 | −0.0399 | 0.0005 |
| | 313.15 | 0.3891 | 0.5112 | 0.2757 | −0.1760 | | 0.0002 |
| $(C_4H_9)_3N + C_6H_{13}NH_2$ | 303.15 | 0.7123 | 0.4146 | 0.1069 | −0.1312 | 0.0639 | 0.0003 |
| | 313.15 | 0.6136 | 0.3657 | 0.0205 | | | 0.0002 |
| $(C_4H_9)_3N + C_8H_{17}NH_2$ | 303.15 | 0.1644 | 0.1632 | 0.1736 | −0.0083 | | 0.0003 |
| | 313.15 | 0.9862 | −0.1569 | 0.1706 | | | 0.0003 |
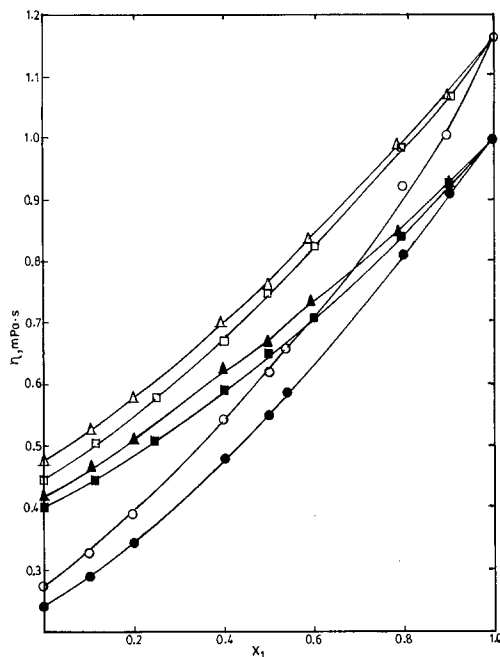
**Fig. 1.** Composition dependence of the viscosity of tributylamine + alkanes. Alkanes: ($\bigcirc$) n-$C_6H_{14}$, ($\triangle$) n-$C_8H_{18}$, ($\square$) and iso-$C_8H_{18}$ at 303.15 K and ($\bullet$) n-$C_6H_{14}$, ($\blacktriangle$) n-$C_8H_{18}$ ($\blacksquare$), and iso-$C_8H_{18}$ at 313.15 K. Solid curves were calculated from Eq. (1).

$(C_4H_9)_3N + C_3H_7NH_2$ and $(C_4H_9)_3N + C_4H_9NH_2$ mixtures, deviations are very small but negative in the low-mole fraction region of tributylamine and very small but positive otherwise.

## 3.2. Activation Energy of Viscous Flow

On the basis of the theory of absolute reaction rates [19], the excess Gibbs energy of activation $\Delta G^{*E}$ of viscous flow may be calculated from [20]

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

where $\eta$ and $V$ are the viscosity and molar volume of the mixture and $\eta_2^0$ and $V_2^0$ are the viscosity and molar volume of the pure component $i$,
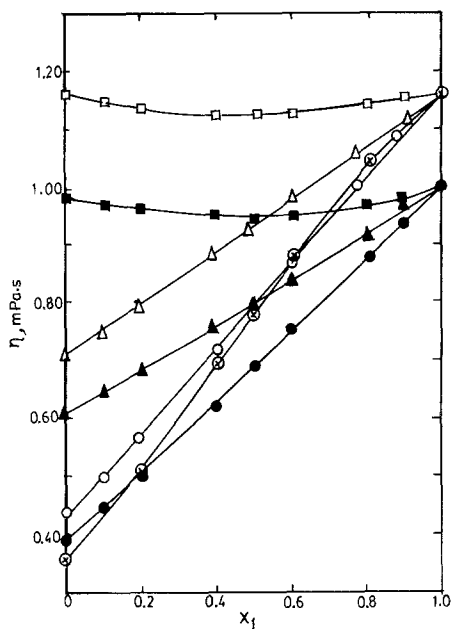
**Fig. 2.** Composition dependence of the viscosity of tributylamine + alkylamines. Alkylamines: ($\otimes$)   $C_3H_7NH_2$,   ($\bigcirc$)   $C_4H_9NH_2$,   ($\triangle$) $C_6H_{13}NH_2$, and ($\square$) $C_8H_{17}NH_2$ at 303.15 K and ($\bullet$) $C_4H_9NH_2$, ($\blacktriangle$) $C_6H_{13}NH_2$, and ($\blacksquare$) $C_8H_{17}NH_2$ at 313.15 K. Solid curves were calculated from Eq. (1).

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 parameters $B_i$ and standard deviations $\sigma$ are listed in Table V. Table V also includes maximum values of excess Gibbs energy of activation $\Delta G^{*E}_{max}$ of flow, along with corresponding mole fractions.

Figures 3 and 4 show the dependence of $\Delta G^{*E}$ on the mole fraction $x_1$ of tributylamine for all the present binary mixtures. The values of $\Delta G^{*E}$ are estimated to be accurate to $\pm 10\, \mathrm{J \cdot mol^{-1}}$ for the investigated binary mixtures.

**Table V.** Parameters $B_i$ in Eq. (3), Standard Deviation $\sigma$, $\Delta G_{max}^{*E}$ (J·mol$^{-1}$), and Corresponding Mole Fraction $x_1$ for Binary Mixtures at 303.15 and 313.15 K

| Mixture | Temp. (K) | $B_0$ | $B_1$ | $B_2$ | $B_3$ | $\sigma$ | $\Delta G_{max}^{*E}$ | $x_1$ | No. in Fig. 5 |
|---|---|---|---|---|---|---|---|---|---|
| $(C_4H_9)_3N +$ | | | | | | | | | |
| n-$C_6H_{14}$ | 303.15 | 0.5662 | 0.0723 | 0.0179 | −0.0250 | 0.0016 | 356.3 | 0.40 | 1 |
| | 313.15 | 0.6818 | 0.0533 | 0.0119 | | 0.0012 | 432.9 | 0.40 | |
| n-$C_8H_{18}$ | 303.15 | 0.1897 | 0.0054 | 0.0039 | −0.0189 | 0.0003 | 120.0 | 0.49 | 2 |
| | 313.15 | 0.2500 | −0.0017 | 0.0363 | 0.0859 | 0.0009 | 162.2 | 0.49 | |
| Iso-$C_8H_{18}$ | 303.15 | 0.2185 | −0.0091 | 0.0127 | | 0.0003 | 136.6 | 0.50 | 3 |
| | 313.15 | 0.1540 | −0.0191 | −0.0062 | | 0.0007 | 100.2 | 0.60 | |
| $C_3H_7NH_2$ | 303.15 | 1.3461 | 0.1881 | 0.0839 | | 0.0001 | 849.1 | 0.50 | 4 |
| $C_4H_9NH_2$ | 303.15 | 0.8355 | 0.0993 | 0.0211 | | 0.0005 | 526.7 | 0.49 | 5 |
| | 313.15 | 0.7950 | 0.1126 | 0.0125 | −0.0226 | 0.0004 | 516.6 | 0.49 | |
| $C_6H_{13}NH_2$ | 303.15 | 0.2741 | 0.0439 | −0.0134 | 0.0072 | 0.0003 | 171.9 | 0.49 | 6 |
| | 313.15 | 0.2692 | 0.0450 | 0.0061 | 0.0134 | 0.0002 | 175.9 | 0.49 | |
| $C_8H_{17}NH_2$ | 303.15 | −0.0728 | 0.0074 | −0.0160 | | 0.0002 | −46.4 | 0.50 | 7 |
| | 313.15 | −0.1068 | 0.0008 | −0.0182 | 0.0181 | 0.0003 | −69.7 | 0.50 | |
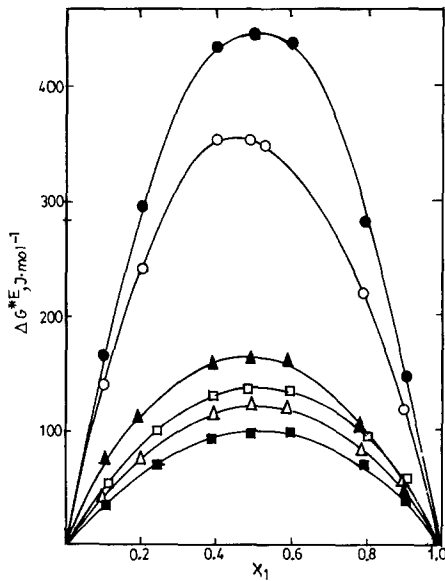


**Fig. 3.** Variation of $\Delta G^{*E}$ with composition for tributylamine + alkanes at 303.15 and 313.15 K. Symbols as in the legend to Fig. 1.
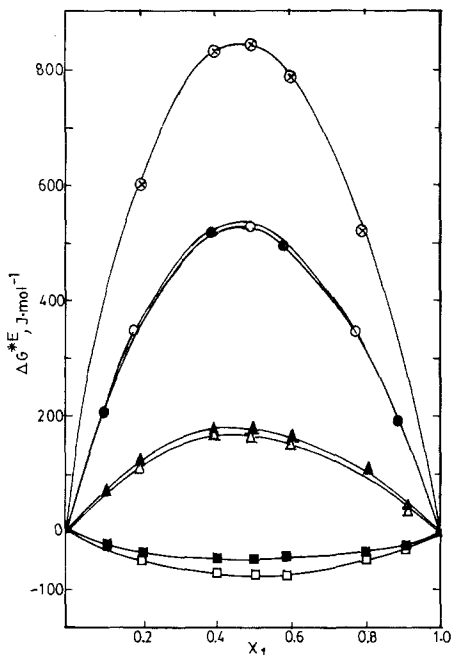
**Fig. 4.** Variation of $\Delta G^{*E}$ with composition for tributylamine + alkylamines at 303.15 and 313.15 K. Symbols as in the legend to Fig. 2.

## 4. DISCUSSION

### 4.1. Tributylamine + Alkanes

Study of Fig. 3 shows that values of $\Delta G^{*E}$ are positive and symmetrical for all three binary mixtures of tributylamine with alkanes at both temperatures of investigation. The values of $\Delta G^{*E}$ at 303.15 K for $(C_4H_9)_3N + n\text{-}C_6H_{14}$ are more than that for $(C_4H_9)_3N + n\text{-}C_8H_{18}$. Thus, the values of $\Delta G^{*E}$ decrease with an increase in carbon atoms in the alkane molecule from six to eight at both temperatures. In the case of mixtures of isomers of octane, there is not much difference in the values of $\Delta G^{*E}$ for $(C_4H_9)_3N + n\text{-}C_8H_{18}$ andc $(C_4H_9)_3N + \text{iso-}C_8H_{18}$ at 303.15 K.

The values of $\Delta G^{*E}$ for $(C_4H_9)_3N + n\text{-}C_6H_{14}$ and $(C_4H_9)_3N + n\text{-}C_8H_{18}$ increase when the temperature is raised from 303.15 to 313.15 K, while the opposite is the trend for $(C_4H_9)_3N + \text{iso-}C_8H_{18}$ mixtures.

## 4.2. Tributylamine + Primary Amines

It is shown in Fig. 4 that values of $\Delta G^{*E}$ are positive for $(C_4H_9)_3N + C_3H_7NH_2$, $(C_4H_9)_3N + C_4H_9NH_2$, and $(C_4H_9)_3N + C_6H_{13}NH_2$ but negative for $(C_4H_9)_3N + C_8H_{17}NH_2$. The maximum in the curve is around 0.5 mole fraction.

The negative values of $\Delta G^{*E}$ for $(C_4H_9)_3N + C_8H_{17}NH_2$ and minima in viscosity versus $x_1$ plot (Fig. 2) clearly identify that the addition of a tributylamine molecule to octylamine results in the breaking of existing H-bonds in the latter.

Like the $(C_4H_9)_3N + C_8H_{17}NH_2$ mixture, one would also expect negative values of $\Delta G^{*E}$ for tributylamine mixtures with other amines, such as propylamine, butylamine, and hexylamine in present study. However, the negative values of these mixtures, which might be associated with the destruction of H-bonding, are masked by the positive values of $\Delta G^{*E}$ resulting from the large size difference between the two components of the



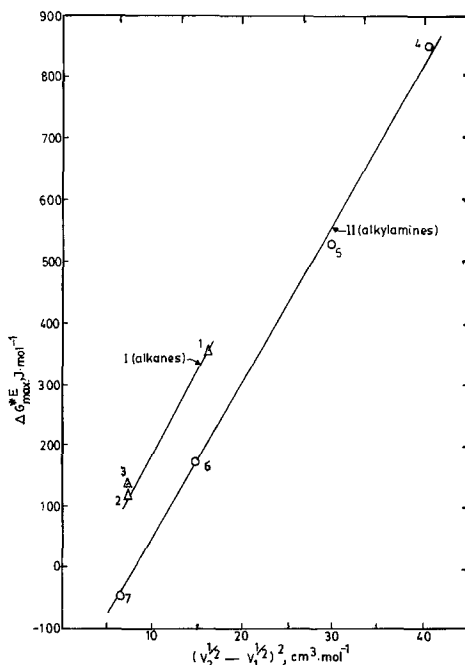**Fig. 5.** $\Delta G^{*E}_{max}$ versus the difference in molar volumes of the two components as $(V_2^{1/2} - V_1^{1/2})^2$ at 303.15 K. (I) Alkanes and (II) Alkylamines. The systems corresponding to the numbers are given in the last column in Table V.

mixtures. As the size difference in tributylamine mixtures increases from octylamine to propylamine through hexylamine and butylamine, the $\Delta G^{*E}$ values, progressively increases.

To see the effect of size on the excess Gibbs energy of activation of flow, the $\Delta G^{*E}_{max}$ values (Table V) are plotted against the $(V_2^{1/2} - V_1^{1/2})^2$ values in Fig. 5, where $V$ is the molar volume. $\Delta G^{*E}$ is shown to be an increasing function of $(V_2^{1/2} - V_1^{1/2})^2$.

# 5. ANALYSIS OF EXCESS VISCOSITY IN TERMS OF PFPBD THEORY

## 5.1. PFPBD Theory

The excess viscosities $\Delta \ln \eta$

$$\Delta \ln \eta = \ln(\eta/\eta_2^0) - x_1 \ln(\eta_1^0/\eta_2^2) \tag{4}$$

of a number of mixtures have recently been analyzed [2, 3, 21, 22] using the PFPBD theory [4–8]. Following Bloomfield and Dewan [7], the theoretical excess viscosity $\Delta \ln \eta_{th}$ is composed of three contributory terms, as

$$\Delta \ln \eta_{th} = \ln \eta_H + \ln \eta_S + \ln \eta_{fv} \tag{5}$$

$$\text{where} \quad \ln \eta_H = -H^E/RT \tag{6}$$

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

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

**Table VI.** Flory's Reduction Parameters of Pure Liquid Components at 303.15 K

| Component | $\tilde{V}$ | $V^*$ $(cm^3 \cdot mol^{-1})$ | $P^*$ $(J \cdot cm^{-3})$ | $S$ $(Å^{-1})$ |
|---|---|---|---|---|
| $(C_4H_9)_3N$ | 1.2491 | 192.35 | 448 | 0.88 |
| $n-C_6H_{14}$ | 1.3282 | 99.76 | 421 | 1.04 |
| $n-C_8H_{18}$ | 1.2840 | 128.08 | 430 | 0.98 |
| Iso-$C_8H_{18}$ | 1.2905 | 129.40 | 379 | 0.81 |
| $C_3H_7NH_2$ | 1.3272 | 62.95 | 581 | 1.23 |
| $C_4H_9NH_2$ | 1.3137 | 76.43 | 582 | 1.14 |
| $C_6H_{13}NH_2$ | 1.2651 | 105.63 | 528 | 1.02 |
| $C_8H_{17}NH_2$ | 1.2443 | 133.92 | 521 | 0.94 |

Table VII. Enthalpic, Entropic, and Free-Volume Contributions to the Excess
Viscosity and Comparison Between Theoretical and Experimental Excess
Viscosity at 303.15 K, Together with the Contact Interaction Parameter
$X_{12}$ (J·cm$^{-3}$) for Binary Mixtures

| Mixture | $X_{12}$ | $\ln \eta_H$ | $\ln \eta_S$ | $\ln \eta_{fv}$ | $\Delta \ln \eta_{th}$ | $\Delta \ln \eta_{exp}$ | $\delta^a$ |
|---|---|---|---|---|---|---|---|
| $(C^4H_9)_3N$ + | | | | | | | |
| n-C$_6$H$_{14}$ | −0.09 | 0.016 | −0.038 | 0.132 | 0.110 | 0.101 | −0.009 |
| n-C$_8$H$_{18}$ | 0.72 | −0.009 | −0.007 | 0.042 | 0.027 | 0.030 | 0.003 |
| Iso-C$_8$H$_{18}$ | −0.76 | 0.019 | −0.016 | 0.069 | 0.072 | 0.040 | −0.032 |
| C$_3$H$_7$NH$_2$ | 14.60 | −0.171 | 0..013 | 0.120 | −0.040 | 0.207 | 0.247 |
| C$_4$H$_9$NH$_2$ | 9.03 | −0.099 | 0.000 | 0.083 | −0.016 | 0.113 | 0.129 |
| C$_6$H$_{13}$NH$_2$ | 8.59 | −0.132 | 0.029 | −0.003 | −0.106 | 0.024 | 0.130 |
| C$_8$H$_{17}$NH$_2$ | 8.18 | −0.138 | 0.032 | −0.031 | −0.137 | −0.035 | 0.102 |

$^a \delta = \Delta \ln \eta_{exp} - \Delta \ln \eta_{th}$.

The terms $\ln \eta_H$, $\ln \eta_S$, and $\ln \eta_{fv}$ in Eq. (5) are the enthalpy, entropy, and free volume contributions, respectively, to $\Delta \ln \eta_{th}$. The values of the Flory reduction parameters $\tilde{V}$, $V^*$, and $P^*$ and the surface-to-volume ratio $S$ for the pure components employed in the present work are listed in Table VI. The terms $\ln \eta_H$, $\ln \eta_S$, and $\ln \eta_{fv}$ in Eq. (5) were evaluated adopting a procedure similar to that described by Delmas and co-workers [8, 22]. For this purpose knowledge of 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 [5, 22–25]. In the present work, equimolar $V_{exp}^E$ [9] has been employed to derive parameter $X_{12}$. Using $X_{12}$ given in Table VII, the theoretical values of excess viscosity $\Delta \ln \eta_{th}$ and the difference $\delta = \Delta \ln \eta_{exp} - \Delta \ln \eta_{th}$ in each case were determined and are reported in columns 7 and 8 in Table VII. In addition, the different contributional terms in Eq. (5), $\ln \eta_H$, $\ln \eta_S$, and $\ln \eta_{fv}$, of equimolar mixtures are also presented in columns 3 to 5 in Table VII. Figures 6 and 7 compare the PFPBD estimates of excess viscosities with experimental ones at all mole fractions.

## 5.2. Different Contributions to Excess Viscosity

It can be seen from Table VII that the values of $\ln \eta_H$ for the binary mixtures of tributylamine with n-octane, propylamine, butylamine, hexylamine, and octulamine are small and negative, while for binary mixtures of tributylamine with n-hexane and isooctane they are small but

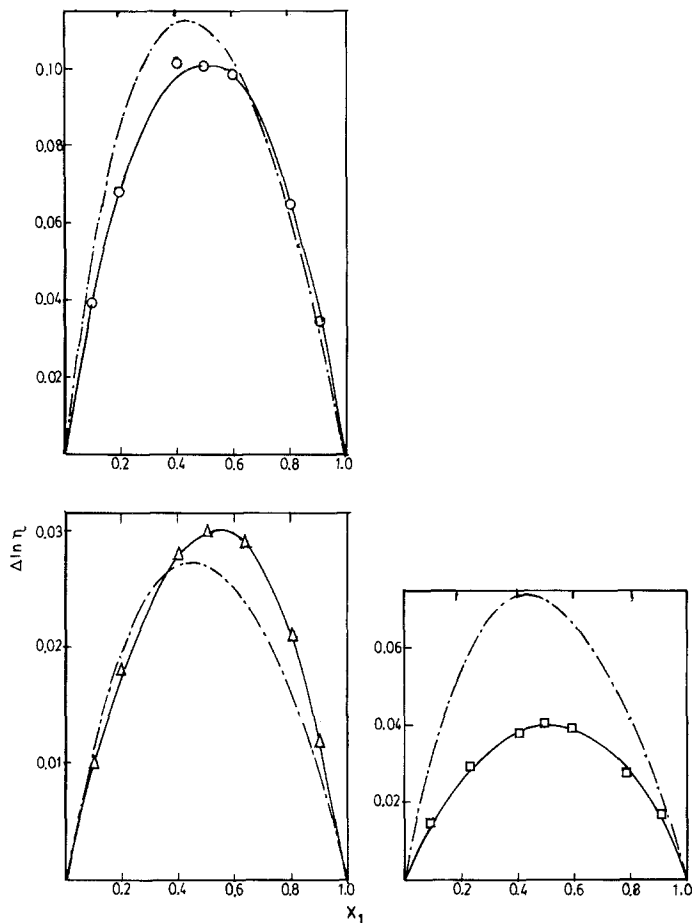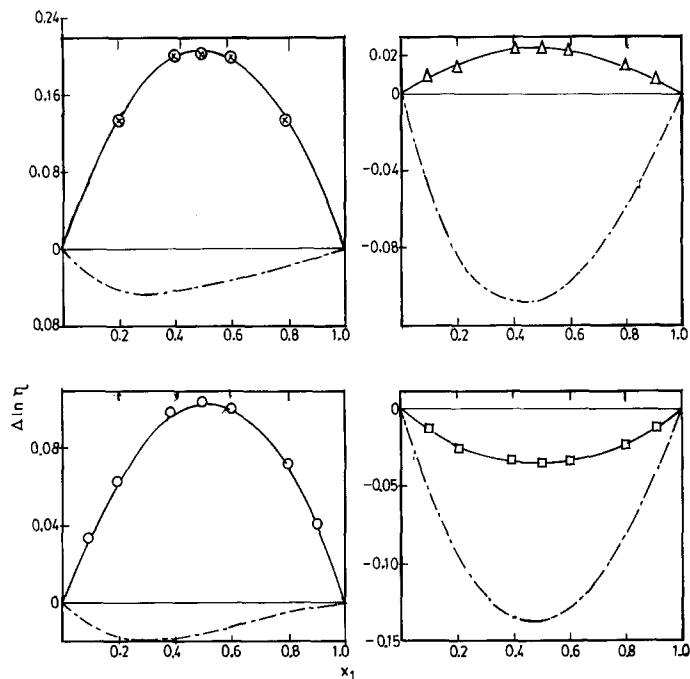**Fig. 6.** Comparison of experimental and theoretical values of excess viscosity $\Delta \ln \eta$ (where $\eta$ is in mPa·s) of tributylamine + alkanes at 303.15 K. Symbols as in the legend to Fig. 1. Solid curves and points, experimental; dashed lines, theoretical.

positive. The negative values of $\ln \eta_H$ suggest a loss of cohesive energy upon mixing the pure liquids; hence, the mixture is less viscous than the ideal value. The inverse holds for the positive values of $\ln \eta_H$.

For the present binary mixtures, the term $\ln \eta_S$ always has the opposite sign and its magnitude is very small compared to the term $\ln \eta_H$.

The term $\ln \eta_{fv}$ is positive for tributylamine + alkane mixtures. In the case of mixtures of primary alkylamines with tributylamine, the values of $\ln \eta_{fv}$ are positive for $(C_4H_9)_3N + C_3H_7NH_2$ and $(C_4H_9)_3N + C_4H_9NH_2$

**Fig. 7.** Comparison of experimental and theoretical values of excess viscosity $\Delta \ln \eta$ (where $\eta$ is in mPa·s) of tributylamine + alkylamines mixtures at 303.15 K. Symbols as in the legend to Fig. 2. Solid curves and points, experimental; dashed lines, theoretical.

and negative for $(C_4H_9)_3N + C_6H_{13}NH_2$ and $(C_4H_9)_3N + C_8H_{17}NH_2$. This gradual variation in the values of $\ln \eta_{fv}$ is attributed to the variation of the free-volume difference between the two components of mixtures.

## 5.3. Excess Viscosity

### 5.3.1. Tributylamine + Alkane Mixtures

From study of Fig. 6 and Table VII, it is observed that the agreement between the experimental and the estimated excess viscosity from the PFPBD theory employing $X_{12}$ is satisfactory. The difference $\delta$ ($\equiv \Delta \ln \eta_{exp} - \Delta \ln \eta_{th}$) varies only from $-0.032$ to $0.003$.

### 5.3.2. Tributylamine + Alkylamine Mixtures

From Fig. 7 and Table VII it is observed that, in the case of tributylamine + alkylamine mixtures, the agreement between $\Delta \ln \eta_{exp}$ and

$\Delta \ln \eta_{th}$ is not as good as for alkane-containing mixtures. The values of the difference $\delta$ ($\equiv \Delta \ln \eta_{exp} - \Delta \ln \eta_{th}$) are in the range from 0.102 to 0.247. The positive values of $\delta$ may be associated with the disruption of H bonds in primary amines. Similarly, failure of the PFPBD theory was observed for alkylamine mixtures with cyclohexane [3].

## ACKNOWLEDGMENTS

## REFERENCES

1. S. L. Oswal and A. V. Rao, *Indian J. Chem.* **24A**:1024 (1985).
2. S. L. Oswal and A. T. Patel, *Int. J. Thermophys.* **12**:821 (1991).
3. S. L. Oswal and A. T. Patel, *Int. J. Thermophys.* **13**:629 (1992).
4. I. Prigogine, *Molecular Theory of Solution* (North-Holland, Amsterdam, 1957).
5. P. J. Flory, *J. Am. Chem. Soc.* **87**:1833 (1965).
6. D. Patterson and G. Delmas, *Disc. Faraday Soc.* **49**:98 (1970).
7. V. A. Bloomfield and R. K. Dewan, *J. Phys. Chem.* **75**:3113 (1971).
8. G. Delmas, P. Purves, and P. de Saint Romain, *J. Phys. Chem.* **79**:1970 (1975).
9. S. G. Patel and S. L. Oswal, *J. Chem. Soc. Faraday Trans.* **88** (1992).
10. L. Ubbelohde, *Ind. Eng. Chem.* **9**:85 (1937).
11. F. A. Goncalves, J. Kestin, and J. V. Sengers, Personal communication.
12. J. H. Dymond and K. J. Young, *Int. J. Thermophys.* **1**:331 (1980).
13. J. R. Riddick, W. B. Bunger, and T. K. Sakono, *Organic Solvents: Physical Properties and Methods of Purification*, 4th ed. (Wiley Interscience, New York, 1986).
14. T. M. Letcher and J. W. Bayles, *J. Chem. Eng. Data* **16**:266 (1971).
15. R. Philipe, G. Delmas, and M. Couchon, *Can. J. Chem.* **56**:370 (1978).
16. A. Krishnaiah and P. R. Naidu, *Acta. Chem. Acad. Sci. Hung.* **104**:295 (1980).
17. J. M. Costello and S. T. Bowden, *Rect. Trav. Chem.* **78**:391 (1970).
18. R. C. Weast, *Hand Book of Chemistry and Physics*, 59th ed. (Chemical Rubber Co., Ohio, 1979).
19. S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw–Hill, New York, 1941).
20. P. K. Katti and M. M. Chaudhri, *J. Chem. Eng. Data* **9**:442 (1952).
21. Cl. Jambon and G. Delmas, *Can. J. Chem.* **55**:1360 (1977).
22. H. Phuong-Nguyen and G. Delmas, *Can. J. Chem.* **64**:681 (1986).
23. G. C. Benson and J. Singh, *J. Phys. Chem.* **72**:1345 (1968).
24. E. Aicart, C. Menduina, R. L. Arenosa, and G. Tardajos, *J. Soln. Chem.* **12**:41, 703 (1983).
25. E. Aicart, C. Menduina, R. L. Arenosa, and G. Tardajos, *J. Soln. Chem.* **11**:559 (1982); **13**:443 (1984).