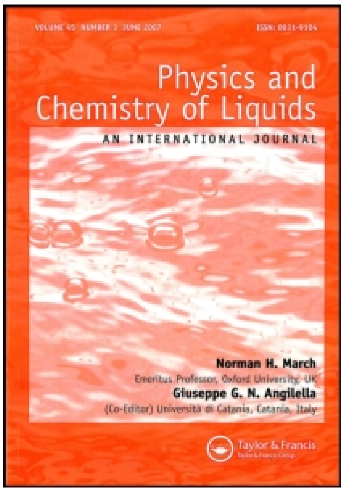

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# Viscosity of Aqueous Solutions of *n*-butylamine, *sec*-butylamine and *tert*-butylamine

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# VISCOSITY OF AQUEOUS SOLUTIONS OF *n*-BUTYLAMINE, *sec*-BUTYLAMINE AND *tert*-BUTYLAMINE

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Viscosities of the systems, water (W) + *n*-butylamine (NBA), W + *sec*-butylamine (SBA) and W + *tert*-butylamine(TBA) have been measured in the temperature range 298.15–323.15 K. The viscosities ($\eta$) and excess viscosities ($\eta^E$) have been plotted against mole fraction of amines ($X_2$). On addition of amines to water, viscosities first increase rapidly, then pass through maxima at 0.2 mole fraction of amines and then decline continuously as the addition of amines is continued. $\eta^E$ show large positive values, with maxima also at 0.2 mole fraction of amines. The maxima of the curves of $\eta$ and $\eta^E$ *vs.* mole fraction of butylamines follow the order, W + TBA > W + SBA > W + NBA. The ascending part of the $\eta$ *vs.* $X_2$ curves in the water-rich region is explained by the hydrophobic hydration caused by the hydrocarbon tails and the hydrophilic effect due to —$NH_2$ group of amines. Following the maxima, amine – amine association is preferred, which accounts for the steady decrease of viscosity up to the pure state of amines.

*Keywords*: Viscosity; *n*-butylamine; *sec*-butylamine; *tert*-butylamine

## 1. INTRODUCTION

This is a part of our program of studying volumetric and viscometric properties of aqueous solutions of organic solutes with particular emphasis on hydrophobic solutes. A large number of aqueous hydrophobic solutes have been studied volumetrically and viscometrically in the recent past. These include a good number of alkanols,

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*Corresponding author.

amides, alkoxyalkanols, glycol ethers *etc.*, which will be mentioned later in the discussion chapter of this paper. However, the work on viscosity of aqueous amine systems is scarcely available. A recent publication on volumetric and viscometric work on *tert*-butyl alcohol and *tert*-butylamine by Kimkemboi and Easteal [1] is none the less significant in relation to our work. In the present paper we report the viscometric properties of aqueous solutions of some butylamines (*n*-butylamine, *sec*-butylamine and *tert*-butylamine) yielding data which are *hitherto* not known. Furthermore, these systems provide us with an opportunity of examining the effect of branching in the butyl group attached to the —$NH_2$ group of the concerned amines.

## 2. EXPERIMENTAL

The amines under investigation were procured from Aldrich, with quoted purity – *n*-butylamine (99%), *sec*-butylamine (99%) and *tert*-butylamine (98%). These were used without further purification except that each of the amines was kept over molecular sieves (4A) for at least

TABLE I Density $d$ (kg $m^{-3}$) and coefficient of viscosity $\eta$ ($10^{-4} \times$ kg $m^{-1}$ $s^{-1}$) of pure Butylamines

| | *NBA* | | *SBA* | | *TBA* | |
|---|---|---|---|---|---|---|
| *T/K* | *d* | $\eta$ | *d* | $\eta$ | *d* | $\eta$ |
| 298.15 | | | 718.0 | 4.176 | 686.4<br>(686.64)[a] | 4.394<br>(4.34)[a] |
| 303.15 | 727.3<br>(727.6)[b]<br>(728.5)[c] | 4.379 | 713.1 | 3.884 | 681.5<br>(681.73)[a] | 4.088<br>(4.03)[a] |
| 308.15 | 722.6<br>(722.8)[b]<br>(723.7)[c] | 4.120 | 708.1 | 3.659 | 676.0<br>(675.80)[a] | 3.803<br>(3.75)[a] |
| 313.15 | 717.6<br>(719.2)[c] | 3.887 | 703.1 | 3.465 | 670.6 | 3.558 |
| 318.15 | 712.7 | 3.676 | 698.2 | 3.274 | | |
| 323.15 | 707.8 | 3.486 | 693.2 | 3.104 | | |

[a] Reference [1].

[b] Acevedo, I. L. and Katz, M. (1990) *J. Solution Chem.*, **19**(10), 1041.

[c] de Schaefer, C. R., Davolio, F. and Katz, M. (1990) *J. Soln. Chem.*, **19**(3), 289.

[d] Ramanjaneyulu, K., Chandrasekhar, A. C. H., Venkateswarlu and Krishnaiah, A. (1987) *Phys. Chem. Liq.*, **16**, 217.

two weeks prior to its use. Thrice distilled water was used in the preparation of all the aqueous amine solutions. The measured density and viscosity of pure liquids corresponded well with literature values (Tab. I).

The density was measured by a 25 ml specific gravity bottle previously calibrated with water. An Ostwald U-tube viscometer of the British Standard Institution with sufficiently long efflux time was used so that no kinetic energy correction was necessary in viscosity measurement. The time of flow was recorded by a timer accurate up to ±0.1 second. An analytical balance of accuracy ±0.0001 g was used in density measurement. For every measurement, a thermostatic water bath controlled up to ±0.05°C was used. In all cases the average uncertainty in the measured viscosity was not more than $3 \times 10^{-7}\,\mathrm{kg\,m^{-1}\,s^{-1}}$.

## 3. RESULTS AND DISCUSSION

The viscosities of the systems, water(W) + *n*-butylamine(NBA), W + *sec*-butylamine(SBA) and W + *tert*-butylamine(TBA) were measured in the temperature range 298.15 to 323.15 K. Because of low boiling point of TBA (319.15 K) the experimental temperature was limited to the range 298.15–313.15 K for the W + TBA system. For the other two systems, W + NBA and W + SBA, temperature ranges were 303.15–323.15 K and 298.15–323.15 K, respectively. The viscosities of the pure components are shown in Table I, showing generally good agreement with the available literature values. The viscosity data of these systems in the whole range of composition are shown in Table II. Figures 1–3 show the plots of viscosities as the function of mole fraction of amines at different temperatures. For comparison, plots of viscosities of these systems at a single temperature are shown in Figure 4.

The excess viscosities were calculated using the following equation,

$$\eta^E = \eta - \exp(X_1 \ln \eta_1 + X_2 \ln \eta_2) \qquad (1)$$

where, $\eta$ is the measured viscosity of the mixtures, $\eta_1$ and $\eta_2$ are the viscosities of water and amines, respectively, and $X_1$ and $X_2$ are the corresponding mole fractions. The excess viscosities were fitted to a

TABLE II Coefficient of viscosity $\eta$ ($10^{-4} \times$ kg m$^{-1}$ s$^{-1}$) and excess viscosity $\eta^E$ ($10^{-4} \times$ kg m$^{-1}$ s$^{-1}$) of aqueous solutions of Butylamines for different molar ratios at different temperatures

| $T/K$ | 298.15 | | 303.15 | | 308.15 | | 313.15 | | 318.15 | | 323.15 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $X_2$ | $\eta$ | $\eta^E$ | $\eta$ | $\eta^E$ | $\eta$ | $\eta^E$ | $\eta$ | $\eta^E$ | $\eta$ | $\eta^E$ | $\eta$ | $\eta^E$ |
| | | | | | Water ($X_1$) + *n*-Butylamine ($X_2$) | | | | | | | |
| 0.0000 | 8.917 | | 8.019 | 0.000 | 7.212 | 0.000 | 6.564 | 0.000 | 6.007 | 0.000 | 5.542 | 0.000 |
| 0.1000 | | | 18.846 | 11.297 | 16.416 | 9.596 | 14.407 | 8.178 | 12.784 | 7.065 | 11.423 | 6.132 |
| 0.1998 | | | 21.493 | 14.386 | 18.610 | 12.121 | 16.251 | 10.339 | 14.327 | 8.881 | 12.706 | 7.654 |
| 0.2999 | | | 19.637 | 12.948 | 17.068 | 10.971 | 14.938 | 9.328 | 13.180 | 7.996 | 11.718 | 6.896 |
| 0.3999 | | | 16.009 | 9.713 | 14.047 | 8.282 | 12.422 | 7.099 | 11.106 | 6.170 | 9.871 | 5.267 |
| 0.5000 | | | 12.590 | 6.664 | 11.177 | 5.726 | 9.974 | 4.922 | 8.979 | 4.279 | 8.131 | 3.735 |
| 0.5997 | | | 9.797 | 4.217 | 8.813 | 3.658 | 7.976 | 3.181 | 7.260 | 2.785 | 6.647 | 2.450 |
| 0.7000 | | | 7.677 | 2.426 | 7.010 | 2.136 | 6.419 | 1.870 | 5.911 | 1.651 | 5.472 | 1.466 |
| 0.7999 | | | 6.277 | 1.334 | 5.795 | 1.186 | 5.366 | 1.049 | 4.994 | 0.938 | 4.656 | 0.831 |
| 0.9001 | | | 5.178 | 0.526 | 4.829 | 0.472 | 4.518 | 0.421 | 4.243 | 0.382 | 3.990 | 0.339 |
| 1.0000 | | | 4.379 | 0.000 | 4.120 | 0.000 | 3.887 | 0.000 | 3.676 | 0.000 | 3.486 | 0.000 |
| | | | | | Water ($X_1$) + *sec*-Butylamine ($X_2$) | | | | | | | |
| 0.1000 | 22.757 | 14.491 | 19.368 | 11.909 | 16.691 | 9.952 | 14.535 | 8.377 | 12.749 | 7.096 | 11.377 | 6.147 |
| 0.1999 | 25.556 | 17.894 | 21.733 | 14.795 | 18.645 | 12.347 | 16.163 | 10.386 | 14.170 | 8.849 | 12.501 | 7.565 |
| 0.3000 | 22.319 | 15.217 | 19.175 | 12.722 | 16.586 | 10.702 | 14.427 | 9.008 | 12.693 | 7.685 | 11.226 | 6.568 |
| 0.3998 | 17.740 | 11.156 | 15.381 | 9.379 | 13.405 | 7.907 | 11.797 | 6.712 | 10.472 | 5.760 | 9.361 | 4.965 |
| 0.4994 | 13.216 | 7.111 | 11.648 | 6.067 | 10.335 | 5.198 | 9.210 | 4.439 | 8.266 | 3.830 | 7.467 | 3.318 |
| 0.5999 | 9.973 | 4.316 | 8.899 | 3.708 | 8.024 | 3.224 | 7.245 | 2.771 | 6.602 | 2.428 | 6.100 | 2.816 |
| 0.6998 | 7.605 | 2.361 | 6.906 | 2.078 | 6.317 | 1.831 | 5.794 | 1.597 | 5.340 | 1.412 | 4.935 | 1.241 |
| 0.7997 | 5.992 | 1.131 | 5.520 | 1.029 | 5.102 | 0.910 | 4.736 | 0.798 | 4.409 | 0.712 | 4.113 | 0.627 |
| 0.8999 | 4.885 | 0.380 | 4.543 | 0.367 | 4.248 | 0.332 | 3.983 | 0.289 | 3.744 | 0.265 | 3.528 | 0.239 |
| 1.0000 | 4.176 | 0.000 | 3.884 | 0.000 | 3.659 | 0.000 | 3.465 | 0.000 | 3.274 | 0.000 | 3.104 | 0.000 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Water ($X_1$) + *tert*-Butylamine ($X_2$) | | | | | | | | |
| 0.1001 | 26.539 | 18.232 | 22.223 | 14.727 | 18.882 | 12.117 | 16.224 | 10.050 |
| 0.2002 | 31.629 | 23.890 | 26.449 | 19.442 | 22.286 | 15.942 | 19.047 | 13.240 |
| 0.2998 | 29.060 | 21.827 | 24.225 | 17.673 | 20.577 | 14.624 | 17.586 | 12.123 |
| 0.3996 | 22.943 | 16.223 | 19.352 | 13.225 | 16.554 | 10.970 | 14.287 | 9.148 |
| 0.5000 | 16.904 | 10.644 | 14.529 | 8.803 | 12.583 | 7.346 | 11.019 | 6.187 |
| 0.5999 | 12.291 | 6.458 | 10.761 | 5.407 | 9.485 | 4.572 | 8.436 | 3.891 |
| 0.6984 | 9.094 | 3.655 | 8.077 | 3.067 | 7.260 | 2.647 | 6.553 | 2.274 |
| 0.7998 | 6.936 | 1.873 | 6.226 | 1.548 | 5.736 | 1.413 | 5.186 | 1.164 |
| 0.9000 | 5.459 | 0.743 | 5.017 | 0.644 | 4.625 | 0.571 | 4.274 | 0.492 |
| 1.0000 | 4.394 | 0.000 | 4.088 | 0.000 | 3.803 | 0.000 | 3.558 | 0.000 |

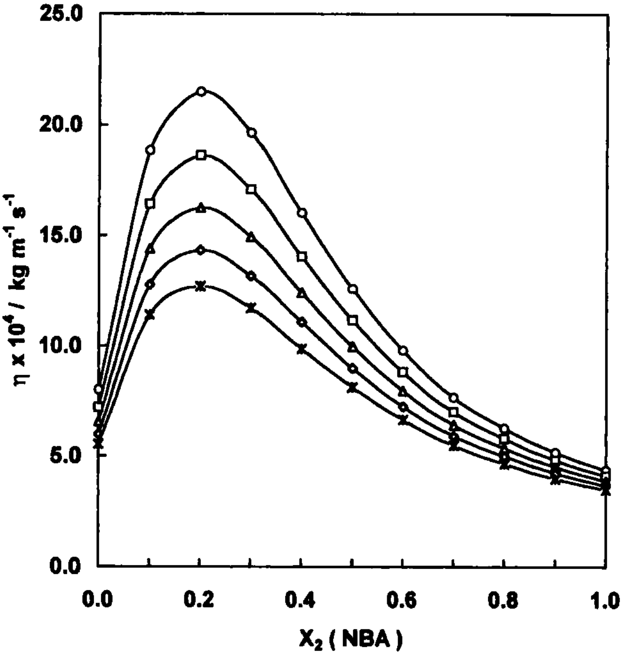


FIGURE 1 Viscosity as a function of mole fraction of *n*-butylamine. ○ - 303.15 K, □ - 308.15 K, Δ - 313.15 K, ◇ - 318.15 K, ✱ - 323.15 K.

polynomial equation of the form,

$$\eta^E = X_1 X_2 \sum_{i=0}^{n} A_i (2X_1 - 1)^i \tag{2}$$

where $A_i$ is the fitting coefficient. Using $n = 3$, at each temperature four $A_i$s and the standard deviation, $\sigma$, were obtained through the least squares method. The coefficients and the standard deviations are shown in Table III. The plots of excess viscosities of the systems as the function of mole fraction of amines are shown in Figures 5–7. Figure 8 shows the comparison curves for the excess viscosities of the systems at 303.15 K.

Examination of the viscosity and excess viscosity *vs.* $X_2$ graphs shows the following characteristics:

(a) The viscosities and excess viscosities increase rapidly on addition of amines to water, which pass through maxima at 0.2 mole fraction of amines and then decline continuously on further addition of amines.

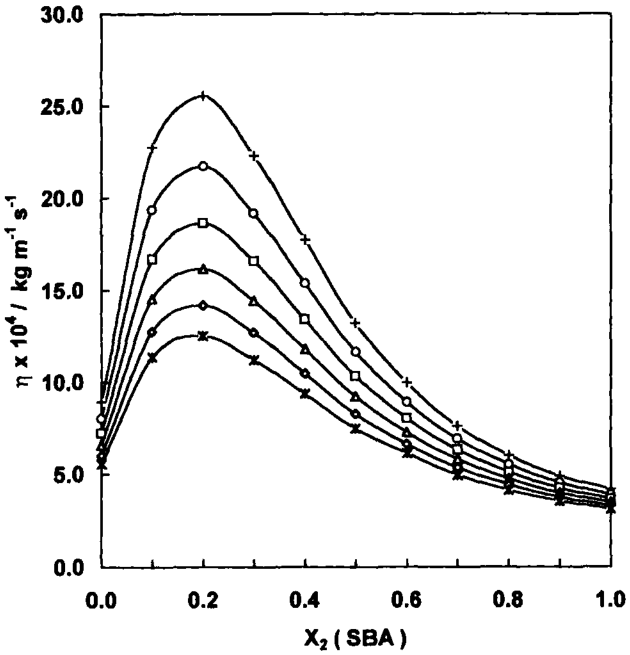


FIGURE 2 Viscosity as a function of mole fraction of *sec*-butylamine. + – 298.15 K. The other symbols are as in Figure 1.

(b) The maxima of both $\eta$ and $\eta^E$ are found to be in the order, W + TBA > W + SBA > W + NBA. In Figures 4 and 8 it is seen that the height of the maximum for W + TBA is much larger than the heights of the maxima for the other two systems. The height of the maximum for the system W + SBA is only slightly larger than that for W + NBA.

(c) Following the maxima, viscosity and excess viscosity curves of W + NBA run slightly higher than that of W + SBA.

(d) The position of the maxima of both $\eta$ and $\eta^E$ remains unchanged with the change of temperature.

(e) The sharpness as well as height of the maxima for $\eta$ and $\eta^E$ decrease with increase in temperature.

The ratios of maximum viscosities, $\eta_{\text{max}}$, to ideal viscosities, $\eta_{\text{id}}$, at the composition of maximum viscosity, *i.e.*, at 0.2 mole fraction of amines, are found to be usually large –3.02, 3.31 and 3.77 at 303.15 K for W + NBA, W + SBA and W + TBA, respectively.

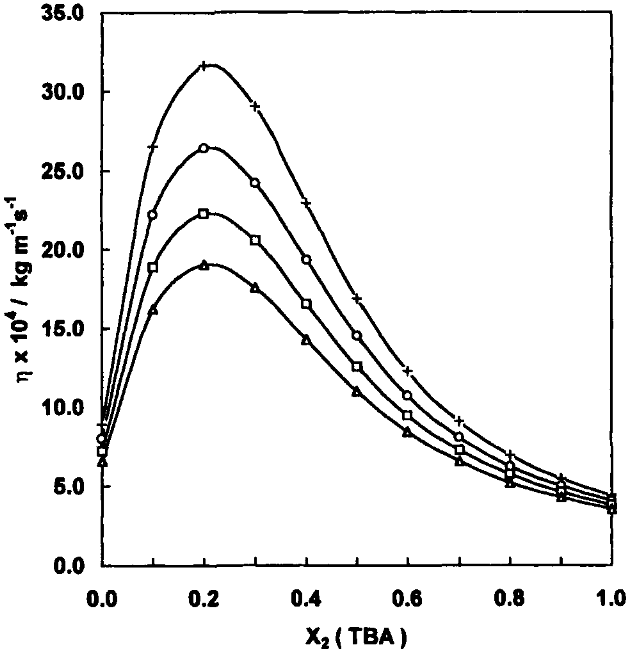


FIGURE 3 Viscosity as a function of mole fraction of *tert*-butylamine. Symbols are as in Figures 1 and 2.

At other compositions the ratios are also quite large, indicating that all the systems are highly non-ideal in behaviour. The observed viscosities and excess viscosities are accounted for mainly by the following factors:

(a) Hydrophobic hydration of the amines.
(b) Strong water–amine interactions.
(c) Amine–amine interactions, *etc.*

The hydrophobic hydration is thought to be the most dominant factor in accounting for the rapidly ascending part of viscosity curves (Figs. 1–4). In water-rich region, it is assumed that water molecules form highly ordered structure through H-bonding around the hydrocarbon moieties of the amines. These are variously known as ice-bergs, clusters or cages. On addition of amines to water, the cages are formed which grow in size or in number until the water molecules necessary to form such cages fall in short. At the same time, the

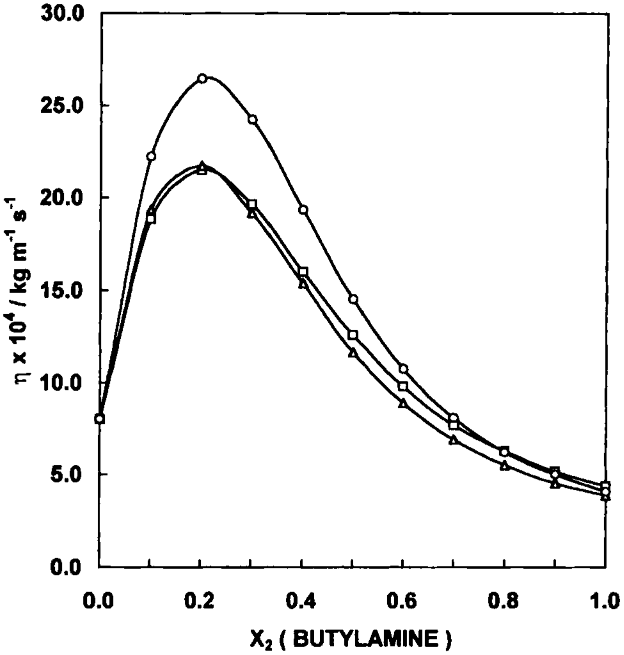


FIGURE 4 Comparison of viscosity of the three systems as the function of mole fraction of the butylamines at 303.15 K: □ – W + NBA, Δ – W + SBA, ○ – W + TBA.

—$NH_2$ group of amines presumably forms H-bonds with water molecules. These two effects together cause the viscosity to rise up rapidly. This behaviour of viscosity is typical of hydrophobic solutes, such as, acetone [2], mono- and di-substituted amides [3, 4], alcohols [5–7], glycol ethers [8], *n*-alkoxyethanols [9], *etc.* As the addition of amines is continued further, both the cages and the amine-water associates are broken down, and instead, amine–amine associates are preferentially formed, which result in the regular decrease in viscosity. The appearance of viscosity maxima is therefore expected as a result of these competing processes.

The hydrophobic effect obviously increases with the branching of hydrocarbon tails of amines, while the hydrophilic effect, by which amine–water association is formed, decreases. Andini *et al.* [10] showed that hydrophobic effect varies in the order, $CH_3 > CH_2 > CH$. Assuming that the major cause of viscosity increase as due to hydrophobic effect and considering in conjunction

TABLE III Fitting coefficients $A_i$ of Redlich–Kister Eq. (2) and the standard deviation $\sigma$ in ($10^{-4}\times \mathrm{kg\,m^{-1}\,s^{-1}}$) for Water + Butylamine systems at different temperatures

| *System* | *T/K* | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $\sigma$ |
|---|---|---|---|---|---|---|
| | 303.15 | 26.6371 | −57.8542 | 61.7841 | −27.1726 | 0.07539 |
| | 308.15 | 22.8514 | −48.3723 | 51.8920 | −23.6811 | 0.04446 |
| Water + NBA | 313.15 | 19.6517 | −40.8362 | 44.0532 | −20.6392 | 0.03242 |
| | 318.15 | 17.0720 | −34.7701 | 37.7543 | −18.2553 | 0.02502 |
| | 323.15 | 4.7778 | −29.3208 | 32.7197 | −17.1887 | 0.03635 |
| | 298.15 | 28.7530 | −69.9218 | 84.8548 | −45.2558 | 0.11125 |
| | 303.15 | 24.3537 | −58.1170 | 68.1170 | −35.4827 | 0.07920 |
| Water + SBA | 308.15 | 20.8163 | −48.2232 | 56.9201 | −29.8642 | 0.05475 |
| | 313.15 | 17.7583 | −40.3123 | 47.5101 | −25.3980 | 0.04476 |
| | 318.15 | 15.3563 | −34.1784 | 40.0301 | −21.3768 | 0.04730 |
| | 323.15 | 13.3315 | −28.6135 | 34.1759 | −19.9027 | 0.05404 |
| | 298.15 | 43.4393 | −103.0244 | 100.7993 | −30.1035 | 0.26109 |
| | 303.15 | 35.7625 | −82.9289 | 80.7245 | −25.0557 | 0.21688 |
| Water + TBA | 308.15 | 29.8887 | −67.7483 | 66.0509 | −20.3885 | 0.17156 |
| | 313.15 | 25.1111 | −55.7342 | 54.1576 | −17.7722 | 0.13636 |

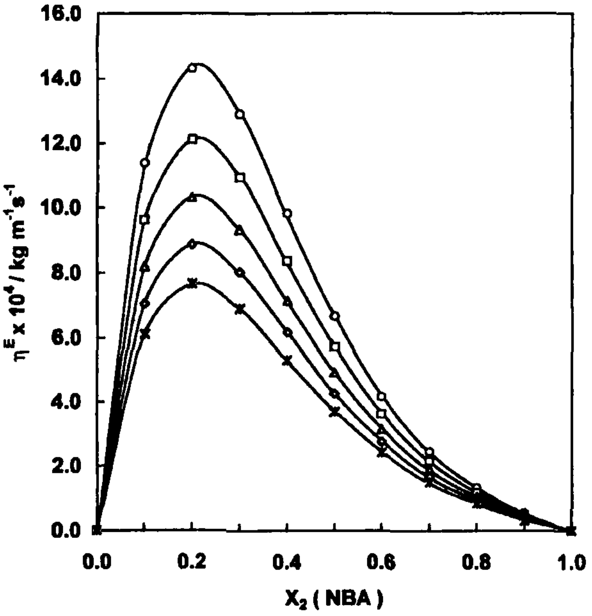


FIGURE 5 Excess viscosity as a function of mole fraction of *n*-butylamine. Symbols are as in Figure 1.

Andini's principle and structural aspects of the amines, it is possible to predict that, viscosity in water-rich region and its maxima (also occurring in water-rich region) should vary in the following order,

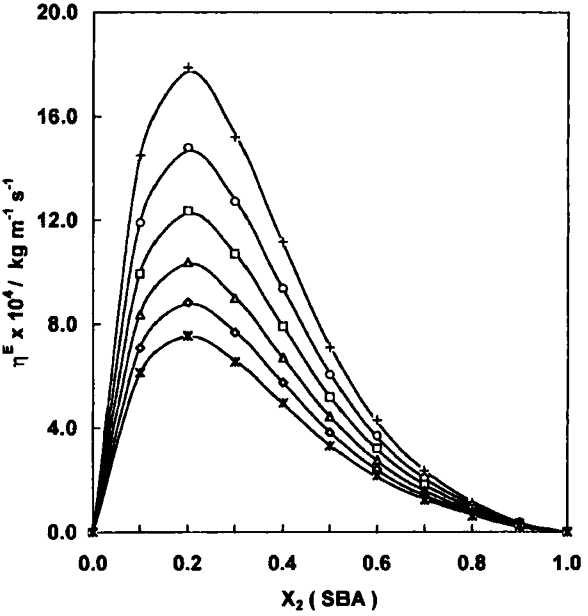


FIGURE 6 Excess viscosity as a function of mole fraction of *sec*-butylamine. + – 298.15 K. Other symbols are as in Figure 1.

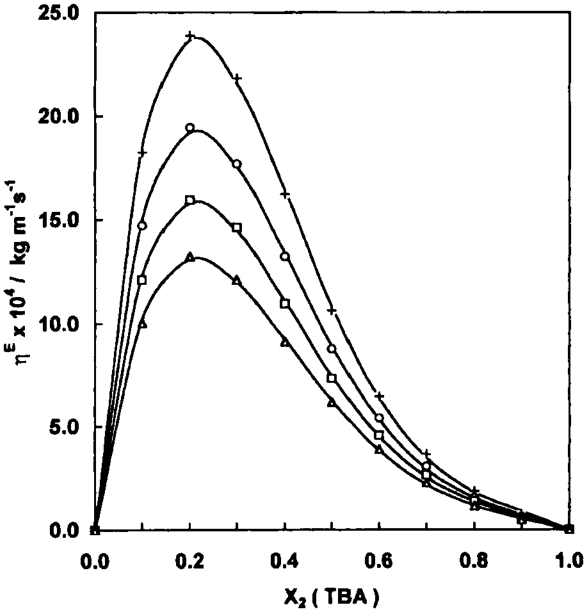


FIGURE 7 Excess viscosity as a function of mole fraction of *tert*-butylamine. Symbols are as in Figures 1 and 2.

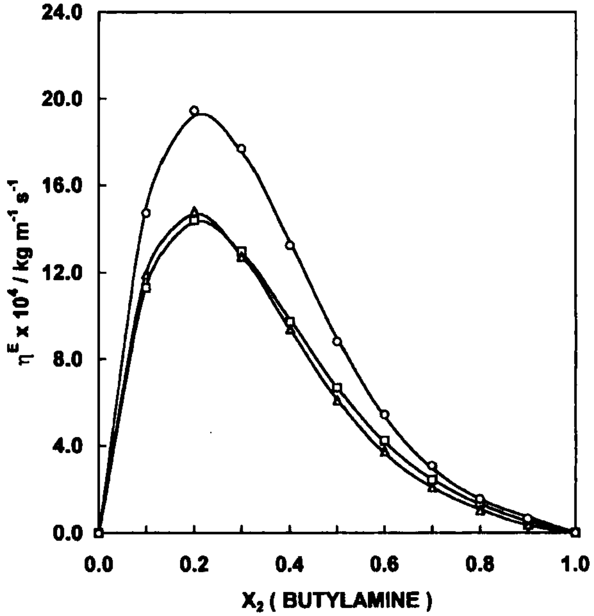
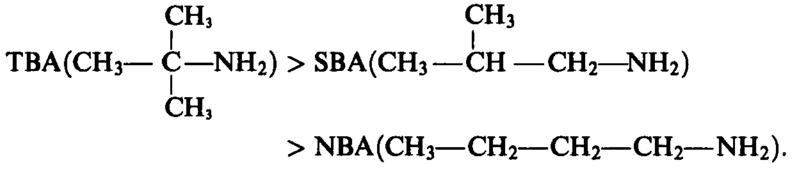


FIGURE 8 Comparison of excess viscosity of the three systems as the function of mole fraction of the butylamines at 303.15 K. Symbols are as in Figure 4.

which is in agreement with the experimental observation.



$$\mathrm{TBA}(\mathrm{CH_3}\text{—}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\text{—}\mathrm{NH_2}) > \mathrm{SBA}(\mathrm{CH_3}\text{—}\overset{\mathrm{CH_3}}{\mathrm{CH}}\text{—}\mathrm{CH_2}\text{—}\mathrm{NH_2})$$

$$> \mathrm{NBA}(\mathrm{CH_3}\text{—}\mathrm{CH_2}\text{—}\mathrm{CH_2}\text{—}\mathrm{CH_2}\text{—}\mathrm{NH_2}).$$

With the rise of temperature the viscosity decreases, *i.e.*, $d\eta/dT$ is negative, and this can conveniently be shown by the suppression of the maxima within a common temperature range. Thus the change of maximum viscosity, $|\Delta\eta_{\max}|$ ($10^{-4} \times \mathrm{kg\,m^{-1}\,s^{-1}}$), within the studied temperature range 303.15–313.15 K is found to be in the order, W + TBA (7.40) > W + SBA (5.57) > W + NBA (5.24). $|\Delta\eta_{\max}|$ thus indicates the extent of destruction of cages formed around hydrocarbon moieties of amines which, in turn, is related to the extent of cage formation, giving indirect support to Andini's principle. The water–water association in cage structures may be considered less stable thermally than water–amine and water–water association in normal water structures as it is presumed in case of other hydrophobic solutes + water systems [11, 12]. These concepts also seem to be quite consistent with the observed $\eta^E$ *vs.* $X_2$ behaviour and its dependence on temperature for the present systems.

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