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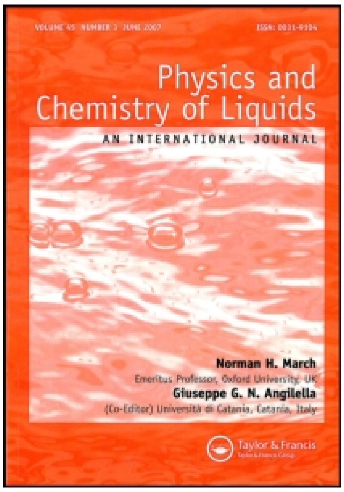

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Muhammad A. Saleh[a]; Shamim Akhtar[a]; Ashiqur Rahman Khan[a]
[a] Department of Chemistry, University of Chittagong, Chittagong, Bangladesh

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EXCESS MOLAR VOLUMES OF AQUEOUS SOLUTIONS OF BUTYLAMINE ISOMERS

MUHAMMAD A. SALEH*, SHAMIM AKHTAR
and ASHIQUR RAHMAN KHAN

*Department of Chemistry, University of Chittagong,
Chittagong - 4331, Bangladesh*

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Excess molar volumes (V^E) and average thermal expansivities (α) of the systems, water (W) + *n*-butylamine (NBA), W + *sec*-butylamine (SBA), and W + *tert*-butylamine (TBA), have been calculated from the density data at temperatures ranging from 298.15 - 323.15 K. The V^E and α values have been plotted as functions of mole fraction of amines. The systems show large negative excess volumes, magnitude of which varies in the order, W + TBA > W + SBA > W + NBA. The curves are found to be symmetrical along the composition axis, with minima occurring at 0.5 mole fraction of butylamines. The negative excess volumes have been interpreted primarily by two effects: (i) strong chemical interaction leading to the formation of 1 : 1 complexes through H-bonding and (ii) hydrophobic hydration causing significant contraction of volume.

Keywords: Density; excess molar volume; isomeric butylamines; hydrophobic hydration

1. INTRODUCTION

This is a part of our continuing studies on volumetric and viscometric properties of aqueous and non-aqueous mixtures. Because of virtually unrestricted solubility amongst liquids, number of non-aqueous systems is almost unlimited. On the other hand, restriction on the solubility of organic substances in water limits the number of aqueous organic systems. A large portion of these systems involves different alcohols, because of their complete solubility in water. Literature

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*Corresponding author.

survey shows that the studies on volumetric properties of aqueous alcohol systems are quite extensive. It has been found that the interaction between organic solutes and water arises mainly from two effects. In aqueous solutions the hydrocarbon or non-polar part of the organic molecules promotes the water structure around it, called the structure-making effect. On the other hand, polar parts, such as, $-OH$, $>CO$, $-NH_2$, *etc.* of the same molecules form H-bond with water, breaking the normal water structure. Consequently, physico-chemical properties of these systems are largely governed by these two effects.

The studies so far available on volumetric behaviour of aqueous amine systems are rather scarce and scattered. The only systematic study of considerable importance in connection with our work is that on volumetric and viscometric properties of aqueous *tert*-butylamine by Kipkemboi *et al.* [1]. In the present paper we report the volumetric properties of aqueous solutions of three butylamine isomers, *n*-butylamine, *sec*-butylamine and *tert*-butylamine – all being soluble in water in the full range of composition. This study provides us way to examine the effect of branching of hydrocarbon parts of the amines on the volumetric properties of these systems.

2. EXPERIMENTAL

The chemicals used for experiment were procured from Aldrich. The quoted purities of these chemicals are: *n*-butylamine (99%), *sec*-butylamine (99%) and *tert*-butylamine (98%). The amines were used without further treatment, except that these were allowed to stand over molecular sieves (4A) for 2–3 weeks prior to their use. A specific gravity bottle of 25 ml capacity was used for measurement of density which was previously calibrated with redistilled water. Weighing was made by an analytical balance with a sensitivity of ± 0.1 mg. A thermostated water bath was used for measurements, the temperature of which was controlled to ±0.05 K. The average uncertainty in measurement of density is estimated as $0.14\,\mathrm{kg\,m^{-3}}$.

The excess molar volume, V^E, was calculated by the following equation,

$$V^E = \frac{X_1M_1 + X_2M_2}{d} - \left(X_1\frac{M_1}{d_1} + X_2\frac{M_2}{d_2}\right)\cdots \qquad (1)$$

where, d is the density of the mixture, M_1, M_2, X_1, X_2, d_1 and d_2 are the molecular weights, mole fractions and densities of the components, the subscripts 1 and 2 denoting the values for water and amines, respectively. Each set of results covering the whole range of composition was fitted to a Redlich-Kister equation of the type,

$$V^E = X_1X_2\sum_{i=0}^{n} A_i(2X_1 - 1)^i \cdots \tag{2}$$

Using $n = 3$ at each temperature, four different A_i values and a standard deviation, σ, were obtained through least squares method.

The average isobaric thermal expansivities (α) have been calculated by the equation, $\alpha = -(d\ln d/dT)_P$. The slope of the plots of $\ln d$ *versus* temperature T yields α.

3. RESULTS AND DISCUSSION

Densities of the systems, water (W) + *n*-butylamine (NBA), W + *sec*-butylamine (SBA) and W + *tert*-butylamine (TBA), have been measured at different temperatures over the whole range of composition. As the boiling point of TBA is very low (319.15 K), the temperature limit for the system W + TBA is set from 298.15 to 313.15 K, while for the other two systems, W + NBA and W + SBA, the temperature ranges are 303.15–323.15 K and 298.15–323.15 K, respectively. The measured densities of pure butylamines are shown in Table I at different temperatures, which correspond well with literature values. At a particular temperature, densities of the amines are found to be in the order, NBA > SBA > TBA.

The excess molar volumes, V^E, of the systems W + NBA, W + SBA and W + TBA, have been calculated from the density data using Eq. (1). The V^E values are shown in Table II. The values are fitted by a polynomial equation [Eq. (2)]. Coefficients of the equation and the standard deviation, σ, are shown in Table III. Figures 1–3 show the smoothed curves of V^E *vs*. mole fraction of amines. For comparison, excess volumes of the three systems at 303.15 K are shown in Figure 4. The V^E data of W + TBA of Kipkemboi *et al.* [1] at 303.15 K are shown in this figure for comparison, showing excellent agreement with our values.

TABLE I Density $d(\mathrm{kg\,m^{-3}})$ of pure butylamines

T/K	*d(NBA)*		*d(SBA)*		*d(TBA)*	
	Expt.	*Lit.*	*Expt.*	*Lit.*	*Expt.*	*Lit.*
298.15			718.0	–	686.4	686.64[a]
303.15	727.3	726.6[b] 728.5[c] 731.5[d]	713.1	–	681.5	681.73[a]
308.15	722.6	722.8[b] 723.7[c]	708.1	–	676.0	675.80[a]
313.15	717.6	719.2[c]	703.1	–	670.6	–
318.15	712.7	–	698.2	–		
323.15	707.8	–	693.2	–		

[a] Ref. [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;
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Generally, it is believed that the amines are self-associated through H-bond. The strength of the bond, however, depends upon the steric effect. With the minimum steric hindrance, NBA is supposed to form the strongest H-bond. Since the steric hindrance in TBA is the maximum, it therefore forms the weakest H-bond. Obviously, the strength of the H-bond in SBA falls in between these two amines. The densities of the amines should depend upon the relative strength and extent of H-bond, and consequently, the order of the densities is expected to be, NBA > SBA > TBA, which is in agreement with the experiment.

The temperature coefficient of densities of the pure amines over the range of temperature studied has been found to be in the order, NBA ($-0.9780\,\mathrm{kg\,m^{-3}K^{-1}}$) > SBA ($-0.9908\,\mathrm{kg^{-3}\,K^{-1}}$) > TBA ($-1.058\,\mathrm{kg\,m^{-3}\,K^{-1}}$). This order can easily be understood in terms of the strength of H-bond formed.

The expansivities of the systems as function of composition are shown in Figure 5. The values increase with the mole fraction of the butylamines, initially at a faster rate, followed by a slower rate at higher concentration of amines. The expansivities have been found to follow the order, W + TBA > W + SBA > W + NBA. The expansivities are thought to be influenced by the relative ease of breaking of H-bonds, presumably formed between water and amines. In terms of steric hindrance the thermal stability of H-bonds formed is in the order, (W...NBA) > (W...SBA) > (W...TBA), where the dotted lines in the

TABLE II Experimental densities $d(\mathrm{kg\,m^{-3}})$ and excess molar volumes $V^E(\mathrm{m^3\,mol^{-1}})$ of Water (X_1) + Butylamine (X_2) systems for different molar ratios at different temperatures

T/K	298.15		303.15		308.15		313.15		318.15		323.15	
X_2	d	$V^E \times 10^6$	d	$V^E \times 10^6$	d	$V^E \times 10^6$	d	$V^E \times 10^6$	d	$V^E \times 10^6$	d	$V^E \times 10^6$
					Water (X_1) + *n*-Butylamine (X_2)							
0.0000	997.1	0.0000	995.7	0.0000	994.1	0.0000	992.2	0.0000	990.3	0.0000	988.1	0.0000
0.1000			918.2	−0.7167	914.9	−0.7158	911.4	−0.7189	908.0	−0.7238	904.4	−0.7280
0.1998			869.3	−1.1835	865.4	−1.1811	861.3	−1.1900	857.2	−1.1967	853.1	−1.2084
0.2999			837.3	−1.5665	833.0	−1.5700	828.7	−1.5906	824.3	−1.6026	819.9	−1.6192
0.3999			812.8	−1.7877	808.4	−1.7985	803.9	−1.8240	799.2	−1.8321	794.5	−1.8440
0.5000			793.4	−1.8830	788.8	−1.8896	784.1	−1.9133	779.5	−1.9381	774.8	−1.9589
0.5997			777.1	−1.8280	772.4	−1.8320	767.6	−1.8554	763.0	−1.8884	758.2	−1.9069
0.7000			762.3	−1.5706	757.6	−1.5766	752.8	−1.6043	747.9	−1.6126	742.9	−1.6127
0.7999			750.2	−1.2710	745.5	−1.2781	740.6	−1.2980	736.0	−1.3413	731.0	−1.3405
0.9001			738.4	−0.7310	733.5	−0.7108	728.8	−0.7545	723.9	−0.7606	719.1	−0.7804
1.0000			727.3	0.0000	722.6	0.0000	717.6	0.0000	712.7	0.0000	707.8	0.0000
					Water (X_1) + *sec*-Butylamine (X_2)							
0.1000	925.2	−1.0179	921.6	−1.0129	918.0	−1.0100	914.3	−1.0335	910.5	−1.0080	906.7	−1.0117
0.1999	874.3	−1.6105	870.3	−1.6210	866.0	−1.6205	861.7	−1.6278	857.6	−1.6406	853.1	−1.6454
0.3000	839.9	−2.0688	835.6	−2.0892	831.2	−2.1023	826.5	−2.1119	822.0	−2.1265	817.6	−2.1553
0.3998	814.6	−2.4007	810.0	−2.4223	805.2	−2.4288	800.4	−2.4450	795.7	−2.4622	791.0	−2.4895
0.4994	792.2	−2.4261	787.5	−2.4524	782.8	−2.4778	778.0	−2.4995	773.3	−2.5258	768.3	−2.5392
0.5999	774.1	−2.3468	769.2	−2.3657	764.3	−2.3797	759.4	−2.3963	754.4	−2.4101	749.4	−2.4239
0.6998	757.8	−2.0316	752.9	−2.0581	748.1	−2.0764	743.0	−2.0817	738.0	−2.0869	732.9	−2.0944
0.7997	743.1	−1.5149	738.1	−1.5251	733.1	−1.5248	728.1	−1.5375	723.0	−1.5267	717.8	−1.5169
0.8999	729.8	−0.8200	724.7	−0.8133	719.7	−0.8068	714.6	−0.8006	709.5	−0.7809	704.3	−0.7612
1.0000	718.0	0.0000	713.0	0.0000	708.1	0.0000	703.1	0.0000	698.2	0.0000	693.2	0.0000

TABLE II (Continued)

T/K	298.15		303.15		308.15		313.15		318.15		323.15	
X_2	d	$V^E \times 10^6$	d	$V^E \times 10^6$	d	$V^E \times 10^6$	d	$V^E \times 10^6$	d	$V^E \times 10^6$	d	$V^E \times 10^6$
Water (X_1) + *tert*-Butylamine (X_2)												
0.1001	921.1	−1.3767	917.2	−1.3676	913.4	−1.3745	909.4	−1.7083				
0.2002	865.0	−2.1984	860.8	−2.2082	856.5	−2.2369	852.1	−2.2639				
0.2998	826.0	−2.7791	821.4	−2.7925	816.9	−2.8431	812.3	−2.8891				
0.3996	796.3	−3.1418	791.5	−3.1584	786.7	−3.2161	781.9	−3.2726				
0.5000	772.0	−3.2740	767.1	−3.2927	762.1	−3.3541	757.1	−3.4121				
0.5999	751.1	−3.1394	746.2	−3.1626	741.0	−3.2176	735.9	−3.2763				
0.6984	732.9	−2.7577	727.7	−2.7496	722.5	−2.8093	717.3	−2.8611				
0.7998	715.9	−2.1454	711.0	−2.1114	705.7	−2.1596	700.3	−2.1847				
0.9000	701.8	−1.3442	696.4	−1.2891	691.1	−1.3332	685.8	−1.3646				
1.0000	686.4	0.0000	681.5	0.0000	676.0	0.0000	670.6	0.0000				

TABLE III Coefficients A_l of Redlich–Kister equation (2) and standard deviations σ in $m^3 mol^{-1}$ for Water + Butylamine systems at different temperatures

System	*T/K*	A_0	A_1	A_2	A_3	σ
W + NBA	303.15	−7.4728	−0.2497	−0.6263	0.0184	0.02688
	308.15	−7.5125	−0.3001	−0.4757	0.2087	0.02755
	313.15	−7.6028	−0.2363	−0.6130	−0.2688	0.02670
	318.15	−7.6843	−0.3605	−0.6583	−0.1790	0.03614
	323.15	−7.7436	−0.2529	−0.6616	−0.4307	0.03940
W + SBA	298.15	−9.7761	0.0003	−0.2884	1.8779	0.03344
	303.15	−9.8863	0.0207	−0.1129	1.9269	0.03037
	308.15	−9.9648	−0.0794	0.0825	2.0696	0.02743
	313.15	−10.0293	−0.1459	0.0891	2.3958	0.03166
	318.15	−10.1297	−0.0419	0.4898	2.2602	0.02349
	323.15	−10.2214	0.0618	0.7416	2.2983	0.02681
W + TBA	298.15	−12.9358	0.1427	−2.4264	0.2044	0.05209
	303.15	−13.0379	0.1643	−1.8281	0.7153	0.04685
	308.15	−13.2790	0.2000	−1.8722	0.2774	0.04747
	313.15	−13.3727	−0.6033	−3.3992	4.0674	0.12735

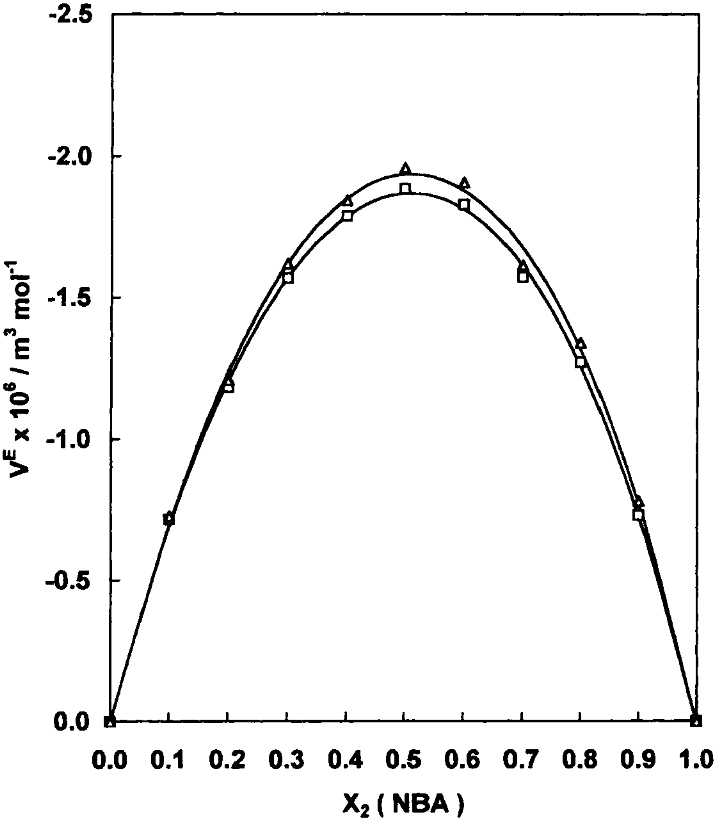


FIGURE 1 Excess molar volumes for W + NBA system as a function of mole fraction of NBA. □ – 303.15 K, Δ – 323.15 K.

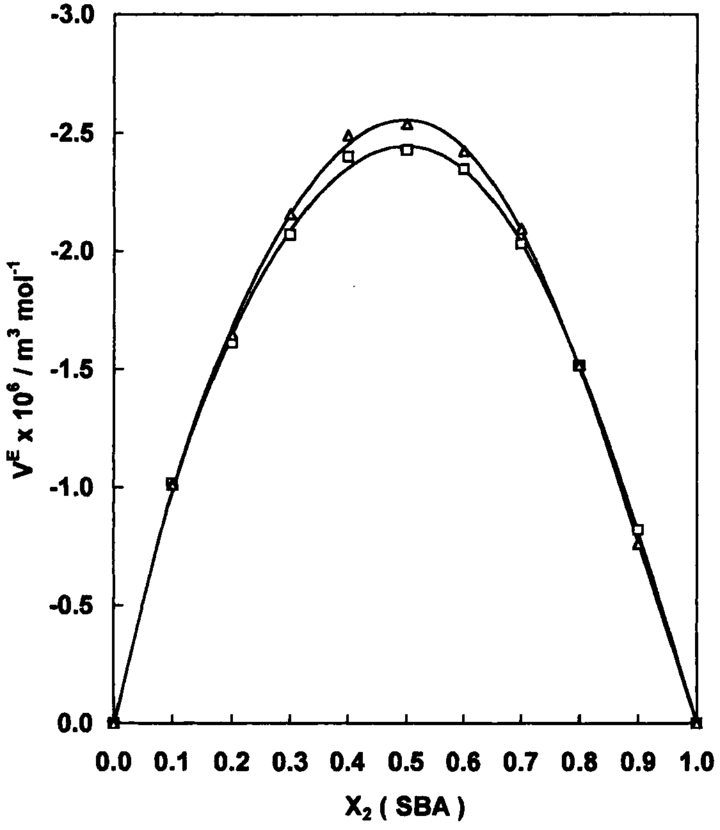


FIGURE 2 Excess molar volumes for W + SBA system as a function of mole fraction of SBA. □ −298.15 K, Δ − 323.15 K.

parentheses denote H-bonds between water and amines. Therefore, the observed order of expansivities which is in the reverse order of the thermal stability of H-bonds appears to be quite consistent.

Examination of the excess molar volumes in Figures 1 – 3 shows the following characteristics:

(a) Mixtures of each of the isomers of butylamines and water exhibit large contraction of volume.

(b) The temperature effect on V^E is not significant either in water-rich or in amine-rich regions, but it is quite apparent in the central region of composition. The dV^E/dT estimated at 0.5 mole frac-

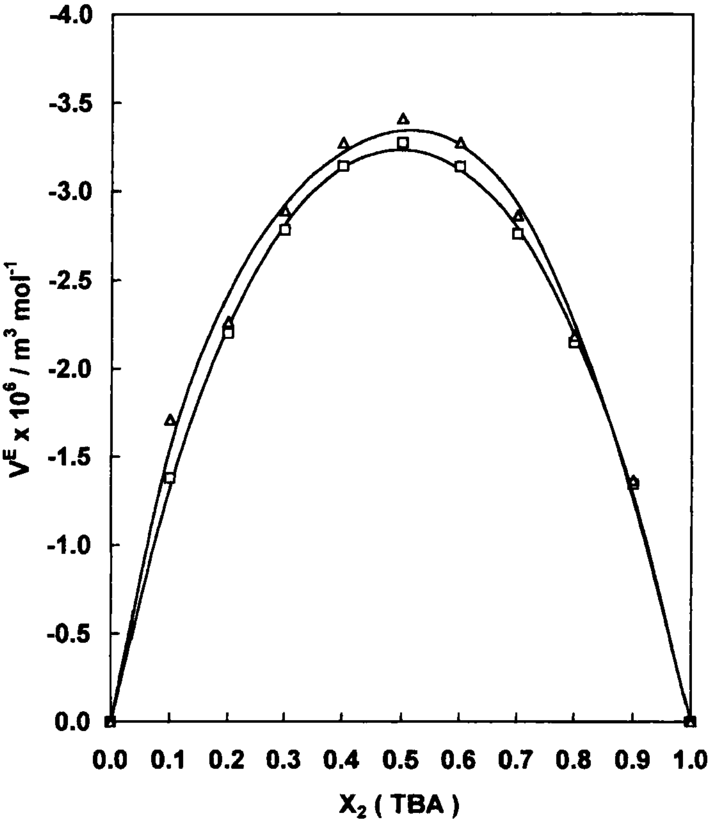


FIGURE 3 Excess molar volumes for W + TBA system as a function of mole fraction of TBA. □ – 298.15 K, Δ – 318.15 K.

tion of amines is negative for all systems and the values are: W+TBA ($-9.21 \times 10^{-3} m^3 mol^{-1} K^{-1}$), W+SBA ($-4.52 \times 10^{-3} m^3 mol^{-1} K^{-1}$) and W+NBA ($-3.80 \times 10^{-3} m^3 mol^{-1} K^{-1}$) over the range of temperature studied.

(c) Clearly defined minima were observed at 1 : 1 composition for all the systems.

(d) The excess volume curves are all symmetrical.

The factors that are generally thought to be important for the contraction of volume are: (a) Chemical interaction between component

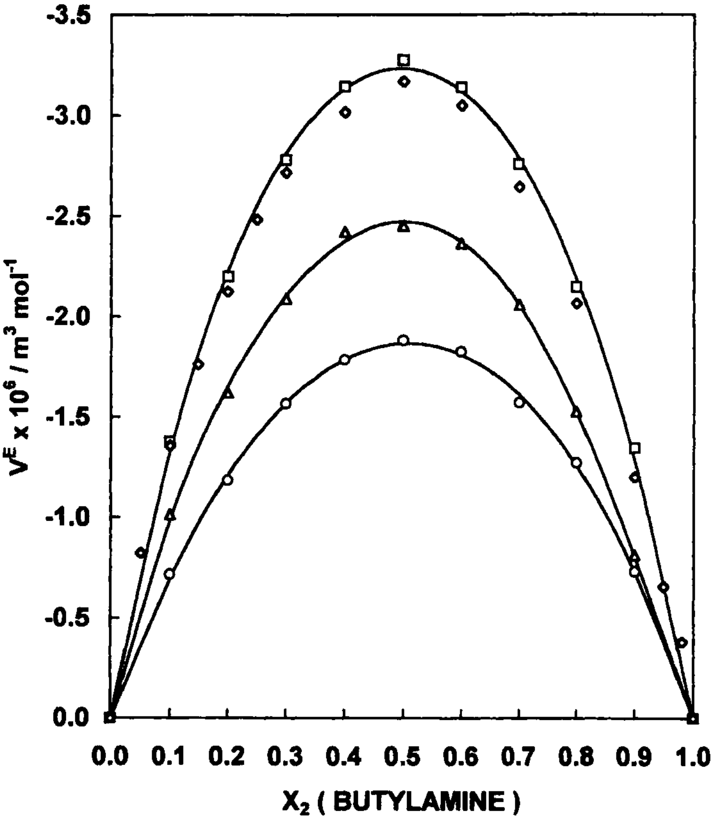


FIGURE 4 Comparison of excess molar volumes of Water + Butylamines at 303.15 K. O – W + NBA, Δ – W + SBA, □ – W + TBA. ◇ – estimated from density data of Ref. [1].

TABLE IV Average isobaric thermal expansivities, $\alpha(K^{-1})$ of Water (X_1) + Butylamine (X_2) systems for different molar ratios

Water + n-Butylamine		*Water + sec-Butylamine*		*Water + tert-Butylamine*	
303.15*K*–323.15*K*		298.15*K*–323.15*K*		298.15*K*–313.15*K*	
X_2	$\alpha \times 10^4$	X^2	$\alpha \times 10^4$	X_2	$\alpha \times 10^4$
		0.0000	3.6322		
0.1000	7.5745	0.1000	8.0790	0.1001	8.5005
0.1998	9.4287	0.1999	9.8178	0.2002	10.0169
0.2999	10.4998	0.3000	10.8256	0.2998	11.1337
0.3999	11.3980	0.3998	11.7949	0.3996	12.1661
0.5000	11.8611	0.4994	12.2233	0.5000	13.0014
0.5997	12.2976	0.5999	12.9633	0.5999	13.6653
0.7000	12.8887	0.6998	13.3633	0.6984	14.3434
0.7999	12.9356	0.7997	13.8316	0.7998	14.7154
0.9001	13.2290	0.8999	14.2019	0.9000	15.3654
1.0000	13.6300	1.0000	14.0439	1.0000	15.5933

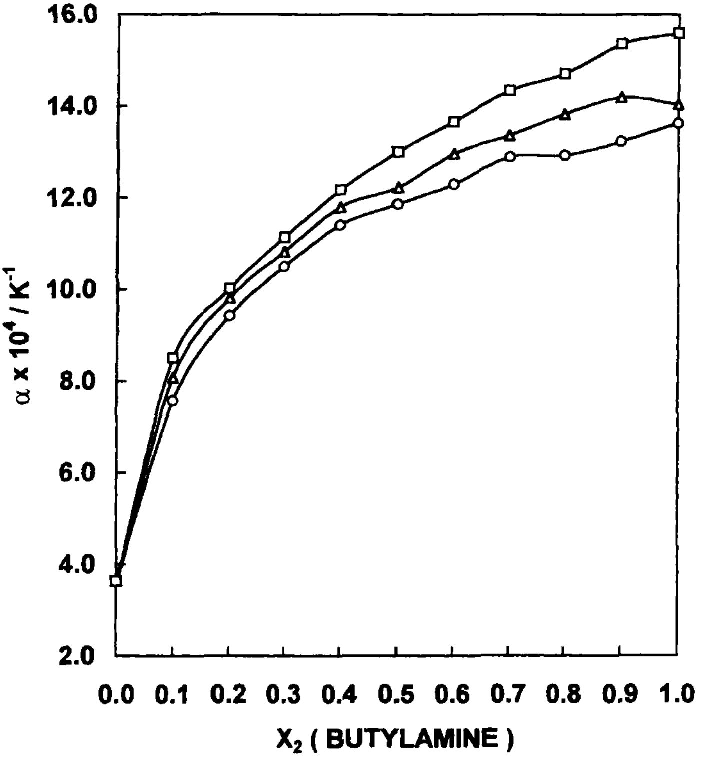


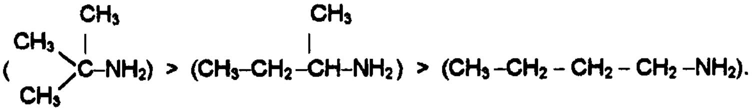
FIGURE 5 Thermal expansivities as a function of mole fraction of Butylamines. O – W + NBA, Δ – W + SBA, □ – W + TBA.

molecules. (b) Physical forces, such as, dipole – dipole, dipole-induced dipole, or van der Waals forces that exist between component molecules. (c) Interstitial accommodation of molecules of one component into the structural network of the other component. (d) Favourable geometrical fitting. (e) Size differences of molecules. (f) Hydrophobic hydration, which is particularly important for these systems.

The factors responsible for volume expansion are: (a) The dispersive forces – by which associated component of a system, formed either by chemical or physical interaction, is dissociated by a non-polar or less polar component. (b) Unfavourable geometrical fitting of molecules. (c) Steric effect-which opposes the molecules from coming to close proximity.

The negative excess volume of the systems indicates that the factors leading to contraction on mixing of components dominate over the factors responsible for volume expansion. Considering the structural features and related properties of water and amines we can easily visualize that, strong chemical interaction takes place between water and amines presumably forming 1 : 1 complex through H-bond, as suggested by the occurrence of minima at 0.5 mole fraction of amines for all water-amine systems. Other factors, such as, dipolar interaction, large size difference between water and amine molecules and hydrophobic hydration which assumes that the amine molecules are encaged by highly structured water molecules – all are important causes for volume contraction. Hence, factors causing volume expansion, as mentioned above, are understandably not strong enough to counterbalance the factors responsible for volume contraction.

In view of unusually high negative excess volumes of these systems we wish to emphasize that, hydrophobic hydration plays the most important role in bringing about contraction of volume. In recent studies on volumetric properties of the aqueous solutions [2–4] it was suggested that hydrophobic hydration was by far the most important factor for volume contraction. This phenomenon was also shown to be primarily responsible for unusually high viscosities of alcohols [5], acetone [3] and alkoxyethanols [6] in water-rich regions. From their recent study on hydrophobic interaction in aqueous solutions of alkane-1,2-diols, Andini *et al.* [7] empirically have established that, hydrophobic capacity of hydrocarbon groups varies in the order, $CH_3 > CH_2 > CH$. Assuming that hydrophobic hydration is the major cause of volume contraction and considering the structural features of the amines used in this investigation, it can be predicted that the magnitude of the negative excess volumes should be in the following order:



$$((CH_3)_3C\text{–}NH_2) > (CH_3\text{–}CH_2\text{–}CH(CH_3)\text{–}NH_2) > (CH_3\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}NH_2).$$

TBA **SBA** **NBA**

This is fully in agreement with the present experiment as shown by the comparative curves in Figure 4 for V^E of aqueous solutions of isomeric butylamines.

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