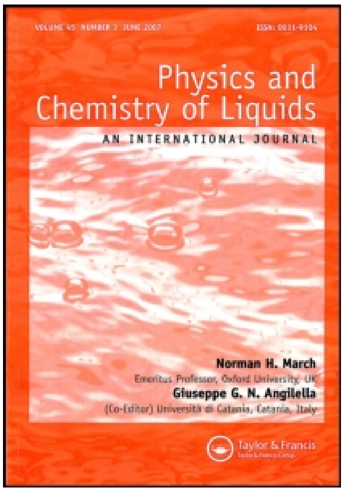

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Thermodynamic activation parameters for viscous flow of aqueous solutions of butylamines

Muhammad A. Saleh[a]; Shamim Akhtar[a]; M. Shamsuddin Ahmed[a]; Muhammad A. R. Khan[a]
[a] Department of Chemistry, University of Chittagong, Chittagong - 4331, Bangladesh

To cite this Article Saleh, Muhammad A. , Akhtar, Shamim , Ahmed, M. Shamsuddin and Khan, Muhammad A. R.(2006) 'Thermodynamic activation parameters for viscous flow of aqueous solutions of butylamines', Physics and Chemistry of Liquids, 44: 5, 501 — 512

To link to this Article: DOI: 10.1080/00319100600647691

URL: http://dx.doi.org/10.1080/00319100600647691

Physics and Chemistry of Liquids
Vol. 44, No. 5, October 2006, 501–512

Taylor & Francis
Taylor & Francis Group

Thermodynamic activation parameters for viscous flow of aqueous solutions of butylamines

MUHAMMAD A. SALEH*, SHAMIM AKHTAR,
M. SHAMSUDDIN AHMED and MUHAMMAD A. R. KHAN

Department of Chemistry, University of Chittagong, Chittagong – 4331, Bangladesh

(*Received 4 February 2006; in final form 6 April 2006*)

The thermodynamic activation parameters, enthalpies, $\Delta H^{\neq}$, free energies, $\Delta G^{\neq}$, and entropies, $\Delta S^{\neq}$, for viscous flow of the systems, water (W) + *n*-butylamine (NBA), W + *sec*-butylamine (SBA) and W + *tert*-butylamine (TBA), have been determined by using the density and the viscosity data. These properties and their excess values have been represented graphically against their composition. With respect to the composition, $\Delta G^{\neq}$ show a typical behaviour for all the systems – a fast rise in the water-rich region with a maximum followed by the values that decline up to the pure state of amines. The $\Delta H^{\neq}$ and $\Delta S^{\neq}$ *versus* composition curves follow the similar trend. For all systems the excess properties, $\Delta G^{\neq E}$, $\Delta H^{\neq E}$ and $\Delta S^{\neq E}$ are characterized by sharp maxima in the water-rich region, which are thought to be mainly due to the hydrophobic hydration and the hydrophilic effect.

Keywords: Aqueous solutions of butylamines; Thermodynamic activation parameters for viscous flow; Hydrophobic hydration

1. Introduction

It is a part of our ongoing project on the physical properties and the molecular interactions in binary liquid mixtures. Under this project, we have been studying the volumetric and the viscometric properties of binary liquid mixtures with particular reference to aqueous solutions of hydrophobic solutes. Although quite a significant amount of work on the viscometric properties of the aqueous solutions of hydrophobic solutes, such as, amines [1,2], diamines [3–6], alcohols [7–12], amides [13,14] and diols [15–19] has been published, only a very little attention has been paid to the thermodynamic studies of the viscous flow of these solutions. This prompted us to study systematically the thermodynamic properties of these solutions. Very recently, we reported the thermodynamic activation parameters for the viscous flow of the aqueous solutions of five different alcohols, 1-propanol, 2-propanol, *tert*-butanol, allyl alcohol and propargyl alcohol [20]. Here, we report on the thermodynamic activation parameters for the viscous flow of the aqueous solutions of butylamines. The choice of these amines would provide us an opportunity to study the effect of branching as well as

*Corresponding author. Fax: 880-31-726310. Email: masaleh786@yahoo.com

Physics and Chemistry of Liquids
ISSN 0031-9104 print/ISSN 1029-0451 online © 2006 Taylor & Francis
DOI: 10.1080/00319100600647691

position of the $–NH_2$ group on the thermodynamic activation parameters for the viscous flow of the systems.

2. Experimental

The experimental procedure for measuring density and viscosity of the systems has been described in detail elsewhere [1,21]. Since *tert*-butylamine (TBA) boils at 46°C, the experiments were carried out up to a maximum temperature of 40°C. The enthalpies, $\Delta H^{\neq}$, and the entropies, $\Delta S^{\neq}$, of activation for the viscous flow were calculated by using the following form of Eyring equation

$$\ln(\eta V_m/hN) = \Delta H^{\neq}/RT - \Delta S^{\neq}/R \tag{1}$$

where, η, V_m, h, N and R have their usual significance. The variation of $\ln(\eta V_m/hN)$ with $1/T$ shows excellent linearity over the range of temperature studied and $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values were calculated from the slope and the intercept, respectively, obtained by the least-squares method. Free energies of activation for the viscous flow, $\Delta G^{\neq}$, were then obtained from the following equation:

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \tag{2}$$

The thermodynamic activation parameters for the viscous flow are represented by a common polynomial equation of the type,

$$Y = \sum_{i=0}^{n} A_i x_2^i \tag{3}$$

where, A_i is the ith coefficient, Y stands for $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ and x_2 for the mole fraction of amines.

The excess values, Y^E, of the above functions, i.e. $\Delta G^{\neq E}$, $\Delta H^{\neq E}$ and $\Delta S^{\neq E}$ have been calculated by the following general additive equation,

$$Y^E = Y - (x_1 Y_1 + x_2 Y_2) \tag{4}$$

Here, each term has its usual significance and the subscripts 1 and 2 refer to water and amine, respectively.

Each of the excess properties has been fitted to a Redlich–Kister polynomial equation of the form,

$$Y^E = x_1 x_2 \sum_{i=0}^{n} A_i (1 - 2x_1)^i \tag{5}$$

where, A_i is the ith coefficient, Y^E stands for each of $\Delta G^{\neq E}$, $\Delta H^{\neq E}$ and $\Delta S^{\neq E}$ and x_1 and x_2 are the mole fractions of water and amine, respectively.

3. Results and discussion

The thermodynamic parameters have been calculated by using the density and the viscosity data between 303.15 and 323.15 K from our previous works [1,21].

Table 1 lists the $\Delta G^{\neq}$ and the $\Delta G^{\neq E}$ for all the systems at different temperatures. The $\Delta G^{\neq}$ values have been expressed satisfactorily by equation (3), the coefficients of which have been shown in table 2. As the values of r^2 are very close to unity, in all cases, it indicates an excellent fitting of the data by the polynomial equation (3).

In figure 1, $\Delta G^{\neq}$ values of the water (W) + *n*-butylamine (NBA) have been plotted against the mole fraction of NBA in between 303.15 and 323.15 K. As the nature of $\Delta G^{\neq}$ and $\Delta G^{\neq E}$ *versus* x_2 curves for the other two systems is almost similar to that of W + NBA, they are not shown graphically. Figure 2 represents the variation of $\Delta G^{\neq E}$ of the system, W + NBA, against the mole fraction of NBA at temperatures 303.15–323.15 K. Figures 3 and 4 are the comparative diagrams of $\Delta G^{\neq}$ and $\Delta G^{\neq E}$ for W + butylamines at 303.15 K respectively. An examination of figures 1–4 reveals the following:

(a) On addition of amines into water, $\Delta G^{\neq}$ increases sharply in the water-rich region, which passes through a maximum near about $x_2 = 0.25$ and then declines up to the pure state of amines.
(b) The $\Delta G^{\neq E}$ are positive for the whole range of composition and are generally large in magnitude, all the values being fitted well to the Redlich–Kister polynomial equation (5) (table 3).
(c) Sharp maximum for $\Delta G^{\neq E}$ occurs at the same composition, i.e. $x_2 \sim 0.25$ mole fraction of amines.
(d) The system of W + TBA shows much larger values of $\Delta G^{\neq}$ as well as $\Delta G^{\neq E}$ than the other two systems. The values for W + *sec*-butylamine (SBA) are slightly greater than W + NBA in the water-rich region, but the order is reversed in the amine-rich region.
(e) The effect of temperature both on $\Delta G^{\neq}$ and $\Delta G^{\neq E}$ is seen to be significant, particularly in the region at or around the maximum, though the positions of maxima apparently remain unchanged with the variation of temperature.

The large positive $\Delta G^{\neq E}$ values for all the systems imply that all the solutions are highly non-ideal, and that for the flow process to take place, the species formed in the solutions have to surmount a large additional energy barrier. That is to say, the species experience enhanced resistance to flow, which arises primarily from the two effects: (a) hydrophilic effect and (b) hydrophobic hydration.

Table 4 lists the values of $\Delta H^{\neq}$, $\Delta H^{\neq E}$, $\Delta S^{\neq}$ and $\Delta S^{\neq E}$ for different compositions. The $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values are correlated with the mole fraction of amines by equation (3). The coefficients of this equation are listed in table 5 together with the values of r^2. The $\Delta H^{\neq E}$ and $\Delta S^{\neq E}$ values are fitted to the Redlich–Kister polynomial equation (5). The coefficients of the equation and the standard deviations are shown in table 6.

Figure 5 shows the plots of $\Delta H^{\neq}$ against the mole fraction of amines. As $\Delta S^{\neq}$ *versus* x_2 are found to follow similar trend, they are not shown graphically. However, the curves for $\Delta S^{\neq}$ and $\Delta H^{\neq}$ for all the systems i.e. W + NBA, W + SBA and W + TBA, to a large extent are similar in nature showing maxima at ~0.20 mole fraction of amines.

The values of $\Delta H^{\neq E}$ and $\Delta S^{\neq E}$ are all positive. Their variations with respect to x_2 show maxima at $x_2 \sim 0.25$, as represented by figures 6 and 7, respectively.

Table 1. Free energy of activation, $\Delta G^{\neq}$ (kJ mol^{-1}), and excess free energy, of activation $\Delta G^{\neq E}$ (kJ mol^{-1}), for viscous flow of aqueous butylamines.

x_2	$\Delta G^{\neq}$	$\Delta G^{\neq E}$	$\Delta G^{\neq}$	$\Delta G^{\neq E}$	$\Delta G^{\neq}$	$\Delta G^{\neq E}$	$\Delta G^{\neq}$	$\Delta G^{\neq E}$	$\Delta G^{\neq}$	$\Delta G^{\neq E}$	$\Delta G^{\neq}$	$\Delta G^{\neq E}$
W (x_1) + NBA (x_2)												
			303.15 K		308.15 K		313.15 K		318.15 K		323.15 K	
0.0000			9.045	0.000	8.952	0.000	8.858	0.000	8.765	0.000	8.671	0.000
0.1000			12.079	2.753	11.952	2.704	11.825	2.655	11.698	2.607	11.571	2.558
0.1998			13.075	3.469	12.950	3.407	12.826	3.345	12.701	3.284	12.577	3.222
0.2999			13.393	3.506	13.281	3.442	13.169	3.377	13.057	3.314	12.945	3.248
0.3999			13.322	3.155	13.234	3.099	13.146	3.043	13.058	2.987	12.970	2.931
0.5000			13.096	2.648	13.034	2.603	12.972	2.557	12.910	2.512	12.848	2.466
0.5997			12.800	2.073	12.767	2.041	12.734	2.009	12.701	1.978	12.668	1.946
0.7000			12.492	1.483	12.488	1.465	12.483	1.446	12.479	1.427	12.474	1.408
0.7999			12.256	0.967	12.275	0.957	12.294	0.946	12.313	0.935	12.332	0.925
0.9001			12.040	0.470	12.081	0.466	12.123	0.462	12.164	0.459	12.206	0.455
1.0000			11.850	0.000	11.911	0.000	11.971	0.000	12.032	0.000	12.092	0.000
W (x_1) + SBA (x_2)												
	298.15 K		303.15 K		308.15 K		313.15 K		318.15 K		323.15 K	
0.0000	9.163	0.000	9.045	0.000	8.952	0.000	8.858	0.000	8.765	0.000	8.671	0.0000
0.1000	12.318	2.916	12.162	2.861	12.006	2.783	11.850	2.706	11.694	2.628	11.538	2.551
0.1999	13.272	3.632	13.124	3.566	12.975	3.481	12.827	3.397	12.678	3.311	12.530	3.228
0.3000	13.459	3.579	13.330	3.516	13.200	3.434	13.071	3.354	12.941	3.273	12.812	3.193
0.3998	13.335	3.216	13.231	3.161	13.126	3.089	13.022	3.020	12.917	2.949	12.813	2.879
0.4994	13.015	2.658	12.942	2.616	12.870	2.563	12.797	2.646	12.725	2.452	12.652	2.403
0.5999	12.652	2.054	12.616	2.032	12.580	2.000	12.544	1.969	12.508	1.937	12.472	1.906
0.6998	12.283	1.447	12.275	1.435	12.267	1.416	12.259	1.398	12.251	1.380	12.243	1.361
0.7997	11.980	0.905	11.998	0.902	12.015	0.893	12.033	0.886	12.050	0.880	12.068	0.871
0.8999	11.714	0.399	11.755	0.402	11.796	0.403	11.837	0.403	11.878	0.404	11.919	0.405
1.0000	11.555	0.000	11.610	0.000	11.665	0.000	11.720	0.000	11.775	0.000	11.830	0.000

W (x_1) + TBA (x_2)

	298.15 K		303.15 K		308.15 K		313.15 K	
0.0000	9.163	0.000	9.045	0.0000	8.952	0.0000	8.858	0.0000
0.1001	12.720	3.292	12.517	3.192	12.315	3.070	12.112	2.948
0.2002	13.837	4.144	13.641	4.035	13.445	3.907	13.249	3.779
0.2998	14.166	4.209	13.983	4.098	13.800	3.970	13.617	3.843
0.3996	14.039	3.818	13.879	3.715	13.720	3.598	13.560	3.480
0.5000	13.682	3.195	13.557	3.112	13.432	3.016	13.306	2.920
0.5999	13.244	2.492	13.157	2.432	13.070	2.361	12.983	2.291
0.6984	12.807	1.795	12.756	1.755	12.706	1.708	12.655	1.662
0.7998	12.426	1.145	12.406	1.121	12.385	1.090	12.364	1.061
0.9000	12.100	0.554	12.111	0.545	12.122	0.534	12.132	0.523
1.0000	11.811	0.000	11.846	0.000	11.881	0.000	11.915	0.000

Table 2. Coefficients, A_i, of equation (3) expressing free energy of activation for viscous flow, $\Delta G^{\neq}$ (kJ mol^{-1}), and the square of the regression coefficient, r^2, for W + butylamines systems.

Systems	Temperature (K)	A_0	A_1	A_2	A_3	A_4	A_5	A_6	r^2
W + NBA	303.15	9.0474	39.307	−162.22	388.15	−519.28	359.75	−100.16	0.9999
	308.15	8.9572	45.13	−193.57	447.84	−598.22	422.7	−120.93	0.9997
	313.15	8.863	44.562	−190.48	441.02	−589.01	415.94	−118.93	0.9997
	318.15	8.7698	43.962	−187.11	433.16	−577.76	407.24	−116.23	0.9997
	323.15	8.6601	33.836	−124.53	278.67	−357.16	240.95	−65.98	> 0.9999
W + SBA	298.15	9.168	48.573	−217.60	508.20	−674.89	469.84	−131.74	0.9997
	303.15	9.0497	47.864	−213.16	496.97	−658.41	457.21	−127.92	0.9997
	308.15	8.9562	46.722	−206.17	478.67	−631.79	437.30	−122.03	0.9998
	313.15	8.8617	45.569	−198.87	458.81	−602.08	414.69	−115.27	0.9998
	318.15	8.7682	44.428	−191.89	440.52	−575.46	394.79	−109.39	0.9998
	323.15	8.6737	43.273	−184.58	420.65	−545.75	372.18	−102.62	0.9999
W + TBA	298.15	9.1702	53.864	−235.59	551.29	−748.15	536.45	−155.23	0.9996
	303.15	9.0515	52.332	−225.92	523.5	−704.67	502.32	−144.78	0.9996
	308.15	8.9576	50.349	−213.4	487.32	−648.55	458.81	−131.6	0.9997
	313.15	8.8627	48.355	−200.66	450.07	−590.34	413.41	−117.79	0.9998

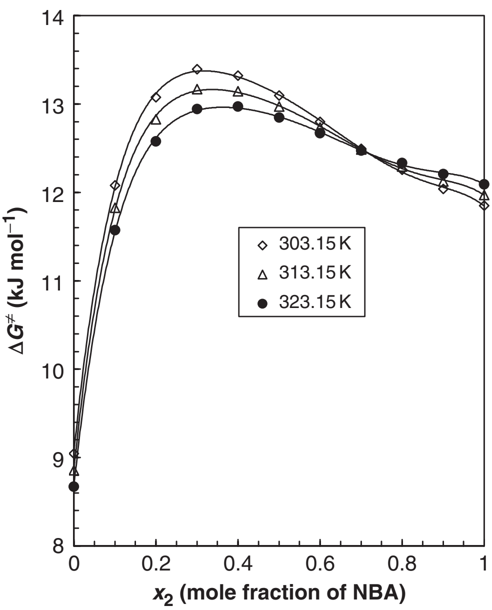

Figure 1. Variation of free energy, $\Delta G^{\neq}$, of W + NBA against the mole fraction of NBA (x_2) at different temperatures.

From careful examination of the figures, the following characteristic features are observed:

(a) Both $\Delta H^{\neq E}$ and $\Delta S^{\neq E}$ values rise sharply on addition of amines and show pronounced maxima in the water-rich regions.
(b) In extremely solute-rich region, $\Delta S^{\neq E}$ values are either small positive or small negative.

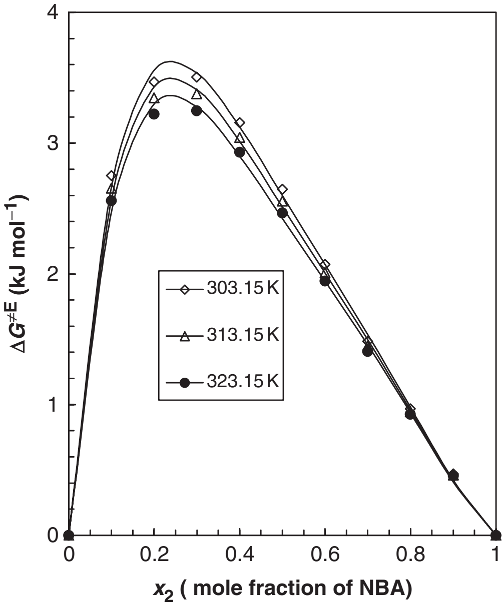

Figure 2. Variation of excess free energy, $\Delta G^{\neq E}$, of W + NBA against the mole fraction of NBA (x_2) at different temperatures.

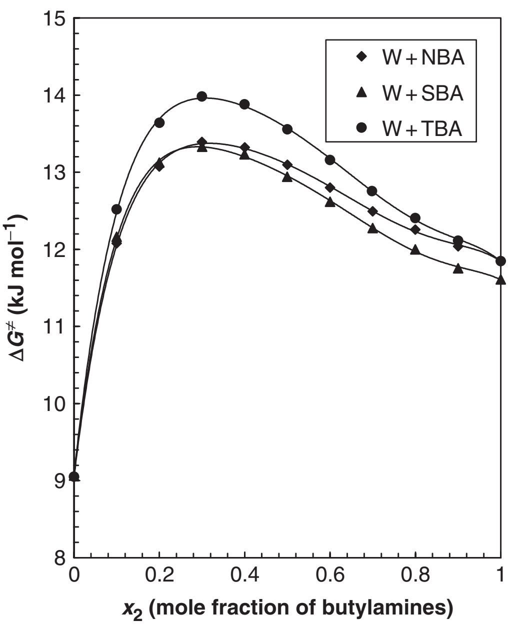

Figure 3. Variation of free energy, $\Delta G^{\neq}$, against mole fraction of amines (x_2) at 303.15 K.

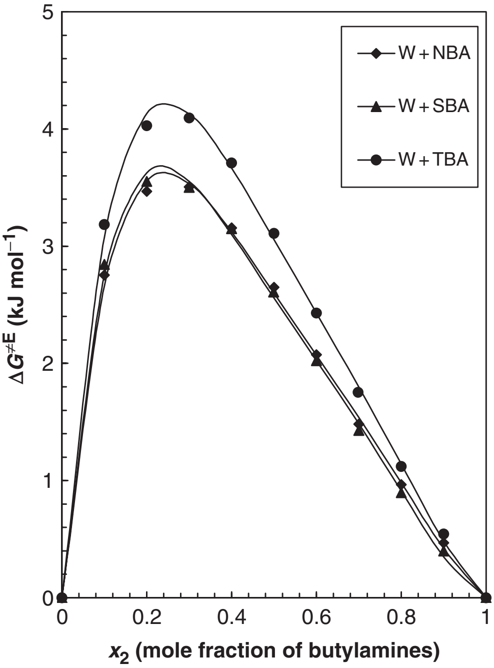

Figure 4. Variation of excess free energy, $\Delta G^{\neq E}$, against mole fraction of amines (x_2) at 303.15 K.

Table 3. Coefficients, A_i, of Redlich–Kister equation, equation (5), expressing excess free energy of activation for viscous flow, $\Delta G^{\neq E}$ (kJ mol^{-1}), and standard deviation, σ, of W + butylamine systems.

Systems	Temperature (K)	A_0	A_1	A_2	A_3	σ
W + NBA	303.15	10.3961	−10.6640	10.5000	−7.6219	0.07202
	308.15	10.2194	−10.6640	10.3444	−7.5346	0.07044
	313.15	10.0427	−10.4157	10.1880	−7.4500	0.06888
	318.15	9.8666	−10.1662	10.0329	−7.3523	0.06721
	323.15	9.6891	−9.9235	9.8772	−7.2767	0.06576
W + SBA	298.15	10.4238	−11.1720	11.2106	−9.3803	0.07585
	303.15	10.2685	−10.8824	11.0346	−9.2260	0.07359
	308.15	10.0666	−10.5509	10.7391	−8.9428	0.06950
	313.15	10.0499	−10.2266	9.9030	−8.6545	0.09420
	318.15	9.8237	−10.8093	8.3749	−3.9326	0.04973
	323.15	9.4714	−9.5715	9.8698	−8.0713	0.05703
W + TBA	298.15	12.5535	−12.8742	12.1766	−8.9313	0.09158
	303.15	12.2350	−12.5130	11.8311	−8.5753	0.08501
	308.15	11.8706	−12.1301	11.3750	−8.0572	0.07664
	313.15	11.5071	−11.7370	10.9276	−7.5514	0.06788

(c) The order of increment of $\Delta H^{\neq E}$ and $\Delta S^{\neq E}$ in the water-rich region is as follows: W + TBA > W + SBA > W + NBA.

On reviewing our previous works on thermodynamic activation parameters for the viscous flow of aqueous solutions of alcohols [20], acetone [21] and also some

Table 4. Enthalpies, $\Delta H^{\neq}$ (kJ mol^{-1}), entropies, $\Delta S^{\neq}$ (J mol^{-1} K^{-1}), excess enthalpies, $\Delta H^{\neq E}$ (kJ mol^{-1}), and excess entropies, $\Delta S^{\neq E}$ (J mol^{-1} K^{-1}), of activation for viscous flow for W+ butylamine systems.

x_2	$\Delta H^{\neq}$	$\Delta H^{\neq E}$	$\Delta S^{\neq}$	$\Delta S^{\neq E}$	x_2	$\Delta H^{\neq}$	$\Delta H^{\neq E}$	$\Delta S^{\neq}$	$\Delta S^{\neq E}$
W (x_1) + NBA (x_2)					W (x_1) + SBA (x_2)				
0.0000	14.714	0.000	18.710	0.000	0.0000	14.714	0.000	18.710	0.000
0.1000	19.779	5.718	25.413	9.785	0.1000	21.620	9.205	31.226	15.485
0.1998	20.623	7.214	24.898	12.346	0.1999	22.127	8.700	29.725	16.958
0.2999	20.183	7.428	22.432	12.964	0.3000	21.181	8.399	25.869	16.077
0.3999	18.658	6.556	17.612	11.227	0.3998	19.566	7.426	20.889	14.064
0.5000	16.855	5.407	12.395	9.095	0.4994	17.338	5.840	14.543	10.679
0.5997	14.801	4.004	6.583	6.353	0.5999	14.798	3.947	7.245	6.369
0.7000	12.765	2.623	0.871	3.734	0.6998	12.760	2.552	1.603	3.697
0.7999	11.104	1.615	−3.843	2.100	0.7997	10.937	1.372	−3.478	1.585
0.9001	9.523	0.689	−8.300	0.731	0.8999	9.269	0.349	−8.227	−0.185
1.0000	8.182	0.000	−12.110	0.000	1.0000	8.275	0.000	−11.018	0.000
W (x_1) + TBA (x_2)									
0.0000	14.714	0.000	18.710	0.000	0.5999	18.429	6.694	17.390	14.054
0.1001	24.799	10.582	40.514	24.369	0.6984	15.812	4.566	10.080	9.269
0.2002	25.510	11.790	39.152	25.573	0.7998	13.656	2.913	4.125	5.912
0.2998	25.071	11.846	36.575	25.548	0.9000	11.470	1.225	−2.114	2.241
0.3996	23.550	10.820	31.900	23.431	1.0000	9.749	0.000	−6.918	0.000
0.5000	21.158	8.927	25.072	19.176					

Table 5. Coefficients, A_i, of equation (3) expressing enthalpy, $\Delta H^{\neq}$ (kJ mol^{-1}), and entropy, $\Delta S^{\neq}$(J mol^{-1} K^{-1}), of activation for viscous flow and the square of the regression coefficients, r^2, for the systems.

Systems	Properties	A_0	A_1	A_2	A_3	A_4	A_5	A_6	r^2
W + NBA	$\Delta H^{\neq}$	14.729	81.142	−392.65	900.82	−1229.8	900.12	−266.18	0.9997
	$\Delta S^{\neq}$	18.743	116.89	−647.6	1481.8	−2081.3	1583.7	−484.42	0.9999
W + SBA	$\Delta H^{\neq}$	14.748	117.43	−646.3	1654	−2366.5	1746.4	−511.48	0.9991
	$\Delta S^{\neq}$	18.806	230.64	−1441.4	3862.2	−5707.7	4306.3	−1280	0.9992
W + TBA	$\Delta H^{\neq}$	14.774	172.84	−991.24	2748.5	−4169	3196.5	−962.66	0.9982
	$\Delta S^{\neq}$	18.89	397.27	2523	7335	−11421	8882	−2696.4	0.9981

Table 6. Coefficients, A_i, of Redlich–Kister equation (5) expressing excess enthalpy, $\Delta H^{\neq E}$ (kJ mol^{-1}), and excess entropy, $\Delta S^{\neq E}$ (J mol^{-1} K^{-1}), of activation for viscous flow and standard deviation, σ, for the W + butylamine systems.

Systems	Property	A_0	A_1	A_2	A_3	σ
W + NBA	$\Delta H^{\neq E}$	21.1139	−25.7618	19.9571	−12.8618	0.17093
	$\Delta S^{\neq E}$	35.3416	−50.1575	31.0666	−16.6544	0.34794
W + SBA	$\Delta H^{\neq E}$	21.6033	−26.4638	36.9468	−47.2602	0.78221
	$\Delta S^{\neq E}$	39.9014	−64.8474	58.1101	−59.3819	0.91135
W + TBA	$\Delta H^{\neq E}$	34.2668	−36.2082	39.2392	−39.2498	0.61603
	$\Delta S^{\neq E}$	72.6531	−78.1322	90.3778	−101.1562	1.75613

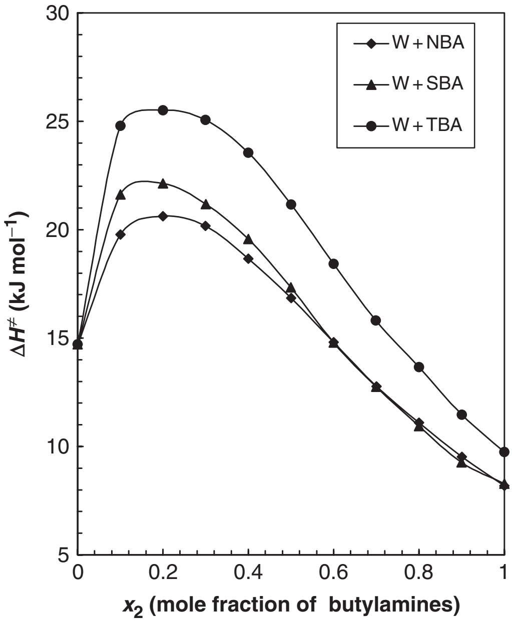

Figure 5. Variation of enthalpy, $\Delta H^{\neq}$, as a function of mole fraction of amines (x_2).

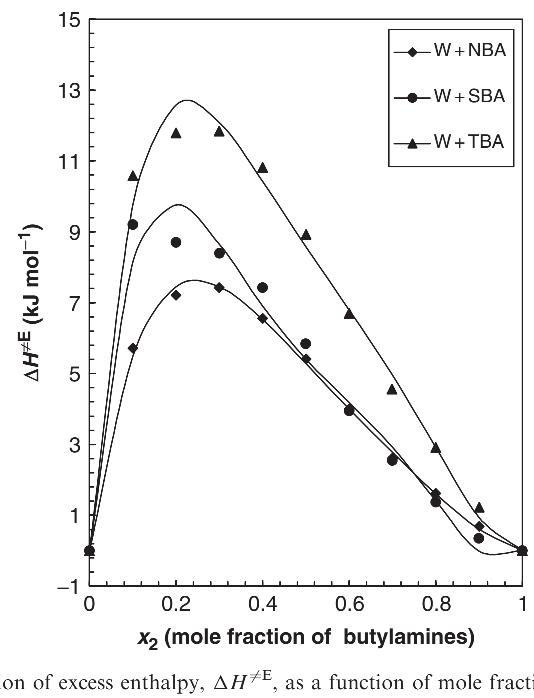

Figure 6. Variation of excess enthalpy, $\Delta H^{\neq E}$, as a function of mole fraction of amines (x_2).

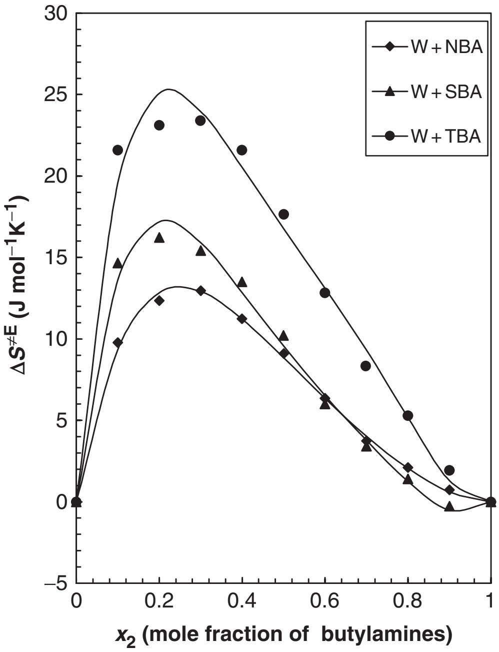

Figure 7. Variation of excess entropy, $\Delta S^{\neq E}$, against mole fraction of amines (x_2).

unpublished works related to aqueous hydrophobic solutes, we observe the above features with remarkable similarity. In order to explain this common behaviour 'hydrophobic hydration' may be considered as the major cause in which it is assumed that in the very dilute solution a hydrophobic solute molecule is encaged by a network of highly structured water molecules – the structure being more labile and thermally less stable than the normal water structure [22,23]. Recent studies on volumetric and viscometric properties by Kipkemboi and Easteal [2], Saleh *et al.* [1,24] and FTIR spectrophotometric studies by Gojło *et al.* [25] on aqueous solutions of these amines unambiguously indicated that the studied amines are hydrophobic in nature. The bulkier species so formed by hydrophobic hydration may be supposed to use large energy for their passage to activated state, causing a substantial loss of structural order, and hence, the large positive $\Delta H^{\neq E}$ and $\Delta S^{\neq E}$ in the water-rich regions. A number of H-bonds formed between water and amine as a result of 'hydrophilic effect' are also disrupted in the activation process, which is supposed to contribute to the positive $\Delta S^{\neq E}$, but to a much lesser extent. All these concepts can equally be applied to explain the positive values of excess thermodynamic functions in the water-rich regions of the present systems.

In the solute-rich region, on the other hand, the cage structures as mentioned above are thought to be destroyed completely, and new structures ensue. These structures could not be understood clearly, but it is thought that some kind of centrosymmetric species is formed in highly amine-rich solutions – a concept used to explain the fall of dielectric constant of aqueous *t*-butanol in highly alcohol-rich solution [26]. These species, possibly because of their spheroidal structure, are thought to face much less resistance to flow, and hence less energy of activation is required in this particular region of composition. The structural rearrangement that takes place in the activation process for the viscous flow in this region is believed to be associated with either loss or gain of some degree of structural order, resulting in a small increase or decrease of entropies, as observed experimentally.

References

[1] M.A. Saleh, S. Akhtar, A.R. Khan. *Phys. Chem. Liq.*, **39**, 85 (2001).
[2] P.K. Kipkemboi, A.J. Easteal. *Can. J. Chem.*, **72**, 1937 (1994).
[3] M.N. Islam, M.A. Ali, M. Islam, M.K. Nahar. *Phys. Chem. Liq.*, **41**, 271 (2003).
[4] M.A. Saleh, M. Shamsuddin Ahmed, M.S. Islam. *Phys. Chem. Liq.*, **40**, 477 (2002).
[5] M.A. Saleh, S. Akhtar, M. Shamsuddin Ahmed. *Phys. Chem. Liq.*, **42**, 103 (2004).
[6] U.R. Kapadi, D.G. Hundiwale, N.B. Patil, M.K. Lande. *Fluid Phase Equilib.*, **205**, 267 (2003).
[7] D. Wolf, A.I. Kudish. *J. Phys. Chem.*, **84**, 921 (1980).
[8] Y. Tanaka, Y. Matsuda, H. Fujiwara, H. Kubota, T. Makita. *Int. J. Thermophys.*, **8**, 147 (1987).
[9] P.C. Senanayake, N. Gee, G.R. Freeman. *Can. J. Chem.*, **65**, 2441 (1987).
[10] H. Kubota, S. Tsuda, M. Murata. *Rev. Phys. Chem., Japan*, **49**, 59 (1979).
[11] Y. Tanaka, T. Yamamoto, Y. Satomi. *Rev. Phys. Chem., Japan*, **47**, 12 (1977).
[12] S. Akhtar, M.M.H. Bhuiyan, M.S. Uddin, B. Sultana, M. Nessa, M.A. Saleh. *Phys. Chem. Liq.*, **37**, 215 (1999).
[13] P. Assarson, F.R. Eirich. *J. Phys. Chem.*, **72**, 2710 (1968).
[14] S. Akhtar, A.N.M.O. Faruk, M.A. Saleh. *Phys. Chem. Liq.*, **39**, 383 (2001).
[15] H. Geyer, P. Ulbig, M. Görnert. *J. Chem. Thermodynamics*, **32**, 1585 (2000).
[16] M.A. Saleh, S. Begum, S.K. Begum, B.A. Begum. *Phys. Chem. Liq.*, **37**, 783 (1999).
[17] U.R. Kapadi, D.G. Hundiwale, N.B. Patil, M.K. Lande, P.R. Patil. *Fluid Phase Equilib.*, **192**, 63 (2001).
[18] J. George, N.V. Sastry. *J. Chem. Eng. Data*, **48**, 1529 (2003).
[19] C. Yang, P. Ma, Q. Zhou. *J. Chem. Eng. Data*, **49**, 582 (2004).
[20] M.A. Saleh, S. Akhtar, M. Shamsuddin Ahmed, M.M.H. Bhuiyan, M.S. Uddin, B. Sultana, M. Nessa. *Phys. Chem. Liq.*, **41**, 475 (2003).
[21] M.A. Saleh, D. Biswas, O. Ahmed, S. Akhtar, M. Habibullah. *Chittagong Univ. Stud. Part II: Sci.*, **17**(2), 127 (1993).
[22] A.K. Covington, P. Jones (Eds). *Hydrogen Bonded Solvent Systems*, p. 221, Taylor & Francis Ltd, London (1968).
[23] F. Franks, *Water*, p. 44, The Royal Society of Chemistry, London (1993).
[24] M.A. Saleh, S. Akhtar, A.R. Khan. *Phys. Chem. Liq.*, **38**, 137 (2000).
[25] E. Gojło, M. Śmiechowski, J. Stangret. *J. Mol. Structure*, **744–747**, 809 (2005).
[26] F. Franks, D.I.G. Ives. *Quart. Rev.*, **20**, 1 (1966).