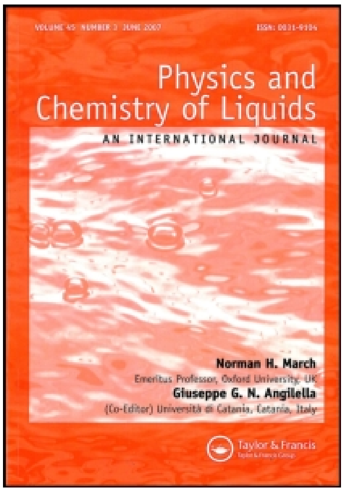

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CORRELATION OF VISCOSITY PARAMETERS AND ENTHALPY OF SOLUTIONS OF ELECTROLYTES IN WATER-ORGANIC SOLVENTS

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Viscosity measurements of $NaClO_4$ solutions in water tetrahydrofuran (THF) mixtures have been performed at 25°C. The salt concentration was $0.05\,mol\,kg^{-1}$ of solvent. A minimum in the relative viscosity corresponding to 5 mol% and a maximum to ca. 70 mol% THF have been observed. The correlation between relative viscosity η_r and the standard enthalpy of solution, ΔH_s^0, has been found to be linear in the system investigated in the water-rich region. The correlation between the B coefficients of the Jones–Dole equation or relative viscosity, η_r, and ΔH_s^0 has been tested for other electrolyte-water-organic solvent systems. For all of them linear correlations have been observed in the water-rich region. Deviations from linearity have been found for solutions containing THF and alcohols (except methanol and ethanol) in the organic solvent-rich region. It has been shown that one of the causes of the observed deviations is the formation of an ion-pair.

KEY WORDS: Mixtures, relative viscosity, enthalpy

In one of our previous papers[1], a linear correlation between the relative viscosity, η_r, or B coefficient of the Jones–Dole equation and the standard enthalpy of solution, ΔH_s^0, was found. It appears in several electrolyte-water-organic solvent systems over a wide region of mixed solvent compositions. All systems investigated up to now[1] exhibit extrema both of the solution enthalpy and of the relative viscosity as a function of mixed solvent composition. In order to test the correlation more stringently, we decided to examine some others. The data of standard enthalpy of solutions of electrolytes and relative viscosities (or B coefficient of the Jones–Dole equation) for electrolyte in water-organic binary solvents measured by us[1–11] and by other authors[12–21] were collected. It was also our aim to test the appearance of the above correlation for the solvent with a low electric permittivity i.e. tetrahydrofuran (THF).

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We have therefore investigated the viscosity of $NaClO_4$ in water-THF mixtures, this system being chosen because the measurements of the solution enthalpy were performed earlier.[4,5]

EXPERIMENTAL

Viscosity measurements were made by means of Ubbelohde-type viscometers with flow times of 200–500 s. for different solutions. The liquids used as standards were water[22] and *n*-butanol.[23] No kinetic energy adjustments were required. The viscometer equipment was similar to that described by Out *et al.*[24] The Ubbelohde-type viscometer was connected by optical fibres with an electronic time counter having a precision of $2 * 10^{-3}$ s. The temperature stability was ca. $5 * 10^{-4}$ K. The accuracy of the relative viscosity data was $+2 * 10^{-4}$. The relative viscosities of $NaClO_4$ solutions were defined as a ratio of the dynamic viscosity of the salt solution to the viscosity of the mixed solvent with the same content of the organic solvent.

The densities of the solutions were determined using a glass pycnometer of the Lipkin type. The maximum error of the density measurements was $1 * 10^{-4}$ g cm^{-3}.

Tetrahydrofuran (Merck, analytical-grade) was purified and dried in the way described previously.[4] $NaClO_4\ xH_2O$ (Merck, puriss-grade) was dried under vacuum to constant weight at 100°C.

All solutions were prepared by weight.

RESULTS AND DISCUSSION

We have measured the viscosities and densities of water-THF mixtures and $NaClO_4$ solutions in this mixed solvent over the whole range of mixed solvent compositions at 25°C. The salt concentration was 0.05 mol per kg of solvent. The data obtained are collected in Tables 1 and 2. The plot of the relative viscosity curve of the sodium perchlorate solutions versus organic solvent content is shown in Figure 1. This curve passes through a minimum corresponding to ca. 5 mol% THF and a maximum in the range of compositions of about 70–80 mol% THF. The minimum is observed in a water-rich region where quasi-clathrates of water with THF are possibly formed.[25,26] It is known that the positions of minima of η_r and of the B coefficient of the Jones–Dole equation are independent of the salt concentration.[1,6–9,27] The wide maximum of the relative viscosity in the THF-rich region may result probably from the changing of properties or structure of the mixed solvent due to formation of aggregates whose composition is unknown.

In Figure 2 the correlation of η_r versus ΔH_s^0 is shown for $NaClO_4$-water-THF system at 25°C. The values of ΔH_s^0 for this system are collected in Table 3 because they were only published earlier[4,5] above 10 mol% THF in a figure. In the organic solvent-rich region i.e. above 70 mol% THF a considerable deviation from linearity can be observed. The ionic association effect in the region of the mixed solvent composition is one of the reasons for the observed deviation.

Table 1 Viscosity, η (cP), and density, ρ (g cm^{-3}), in water-tetrahydrofuran mixtures at 25°C.

x_{THF}(*mol%*)	η	ρ
0.0	0.8903*	0.9907*
2.5	1.172	0.9927
5.0	1.415	0.9890
7.5	1.593	0.9853
10.0	1.704	0.9801
15.0	1.752	0.9705
20.0	1.715	0.9604
25.0	1.597	0.9503
30.0	1.419	0.9436
35.0	1.299	0.9354
40.0	1.160	0.9291
60.0	0.774	0.9078
70.0	0.660	0.9000
80.0	0.567	0.8926
85.0	0.543	0.8897
90.0	0.519	0.8872
95.0	0.497	0.8847
100.0	0.480	0.8819

* Data from Ref. (22).

Table 2 Densities, ρ(g cm^{-3}), and relative viscosities, η_r, for $NaClO_4$ solutions in water-tetrahydrofuran mixtures at a salt concentration of 0.05 mol kg^{-1} of solvent at 25°C.

x_{THF}(*mol%*)	ρ	η_r
0.0	1.0010	1.0019
2.5	0.9965	0.9964
5.0	0.9928	0.9931
7.5	0.9887	0.9946
10.0	0.9828	0.9989
15.0	0.9735	1.0057
20.0	0.9636	1.0121
30.0	0.9464	1.0187
40.0	0.9354	1.0239
60.0	0.9117	1.0290
70.0	0.9039	1.0313
80.0	0.8965	1.0305
85.0	0.8939	1.0289
90.0	0.8910	1.0275
95.0	0.8886	1.0249
100.0	0.8886	1.0234

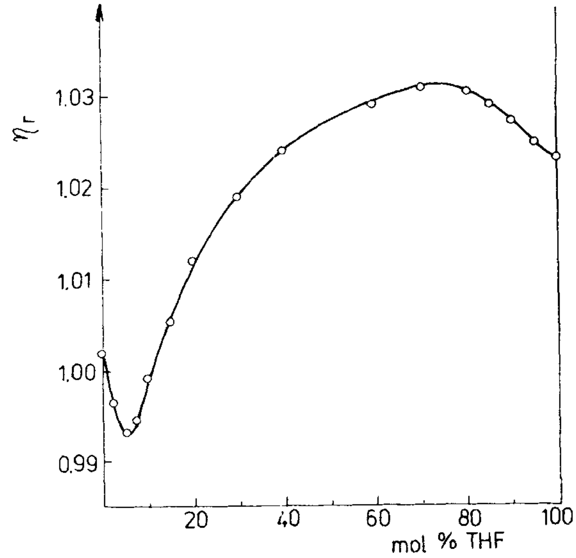

Figure 1 The relative viscosity of $NaClO_4$ in water-THF mixtures at 25°C; salt concentration is 0.05 mol per kg of mixed solvent.

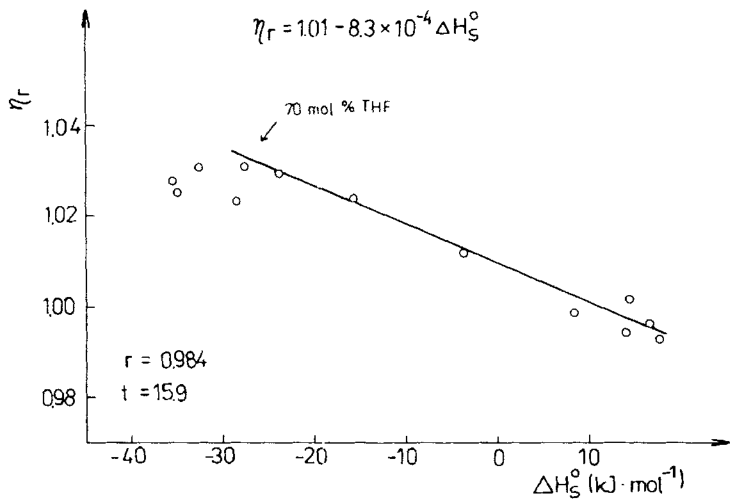

Figure 2 Relative viscosity vs. standard enthalpy of solution for $NaClO_4$-water-THF system at 25°C; η_r—this work, ΔH_s^0 from Ref. (4) and (5), r—correlation coefficient, t—the significance test of the r-coefficient.

Table 3 Standard enthalpies of solution of $NaClO_4$ in water-tetrahydrofuran mixtures at 25°C.

mol% THF	$\Delta H_s^0/kJ\ mol^{-1}$
0	14.57[4]
2.5	16.66[4]
5.0	17.38[4]
7.5	13.82[4]
10.0	8.69[4]
20.0	−3.77
40.0	−15.61
60.0	−23.77
70.0	−27.55*
80.0	−32.52
90.0	−35.76
95.0	−35.04
100.0	−28.39

* Interpolated value.

In order to examine whether the above correlation exists in other systems, data of the standard enthalpy of solutions of electrolytes and of the B coefficients of the Jones–Dole equation or relative viscosities for electrolyte in different water-organic solvent mixtures were collected.

Most data on the solution enthalpy and viscosity were found for electrolyte solutions in water-alcohol systems. In the water-methanol and water-ethanol mixed solvent, the linear correlations can be observed (Table 4) in the whole composition range. In other alcohols there occur evident deviations on the straight lines in the alcohol-rich region (Table 4, Figures 3 and 4). For all these systems, the mixed solvent composition up to which the linear correlation exists is marked in Table 4 and Figures 3 and 4, respectively.

All the electrolyte solutions in the mixtures of water with THF,[1,4,5] acetone[1,14,20,21] and alcohols[1–3,6–9,14–19,27] investigated so far exhibit extrema both of η_r and ΔH_s^0 values in the water-rich regioin with the same compositions of the mixed solvent characteristic for organic solvents. Unlike the above, the systems containing formamide[10,11] and DMSO[12,13] show a monotonic dependence of ΔH_s^0 and η_r vs. mixed solvent compositions functions. Thus, in this region the linear dependence of η_r or B-coefficient as a function of ΔH_s^0 appears in the systems showing extrema of the enthalpy of solution and of the relative viscosity or B-coefficient, as well as in the systems for which these functions do not pass through the extrema. In the organic solvent rich-region linear correlation is observed only for the systems with monotonic character of ΔH_s^0 and η_r (or B coefficient) and other properties as well. The dependencies η_r (or B) $= f(\Delta H_s^0)$ deviate from straight lines in this region for systems showing extrema of many properties i.e. for systems containing a solvent such as alcohols (except methanol and ethanol) and THF. It can be pointed out that the deviation increases along with organic solvent content i.e. with the decrease of

Table 4 The parameters of linearity of the dependence $y = a - b(\Delta H_s^0)$, where $y = \eta_r$ or B coefficient of the Jones–Dole equation for various electrolyte-water-organic solvent system at 25°C.

Organic solvent	*Electrolyte*	*Coefficients of equation*		*r*	*t*	*Range of linearity mol%*
		a	*b*			
Formamide[10,11]	NaI[a]	0.9936	0.0020	0.989	20.4	0–100
DMSO[12,13]	NaI[b]	−0.1763	0.0199	0.989	13.9	0–100
	NaBr[b]	0.0169	0.0324	0.999	62.3	0–100
	KCl[b]	0.7682	0.0446	0.999	57.9	0–100
Methanol[14–16]	LiCl[b]	−1.472	0.0468	0.960	8.39	0–100
	NaCl[b]	0.4010	0.0610	0.982	9.23	0–100
	KCl[b]	1.120	0.0564	0.975	10.7	0–100
	NaI[a]	0.9833	0.0034	0.997	44.7	0–100
Ethanol[1,2]	NaI[a]	0.9700	0.0043	0.987	18.26	0–100
n-Propanol[2,6]	NaI[a]	0.9796	0.0029	0.975	10.8	0– 74
Isopropanol[2,7]	NaI[a]	0.9785	0.0029	0.988	22.6	0– 80
s-Butanol[2,8]	NaI[a]	0.9871	0.0023	0.971	10.7	0– 80
t-Butanol[2,9,17–19]	NaCl[b]	0.1120	0.0081	0.998	26.0	**
	KCl[b]	0.2430	0.0140	0.957	6.61	**
	RbCl[b]	0.1427	0.0105	0.943	6.35	**
	CsCl[b]	0.1676	0.0125	0.964	8.08	**
	KBr[b]	0.2175	0.0134	0.993	18.5	**
	NaI[b]*	−0.1298	0.0193	0.990	18.8	0– 50

[a] $y = \eta_r$, salt concentration was 0.5 mole per 100 moles of mixed solvent.
[b] $y = B$ coefficient of the Jones–Dole equation.
* at 26°C.
** In the whole investigated range i.e. 0–16 mol% *t*-butanol.

electric permittivity. Hence, we anticipate that the occurrence of ionic association may be one of the causes. Unfortunately, it was not possible to take into account the ionic association for the $NaClO_4$-water-THF system in the mixtures containing more than 80 mol% THF, because of experimental difficulties connected with the determination of association constants with sufficient precision.[5,28–30] Accordingly, we sought a system where the influence of ionic association might be included both in B coefficient and ΔH_s^0 values. It proved possible to examine this for the NaI-water-TBA system. The procedures used have been presented elsewhere[9,31] The values of $\Delta H_{s,\mathrm{cor}}^0$ for the necessary content of TBA were calculated by interpolation of the data of Bald *et al.*[31] The results obtained are presented in Figure 5. The above correlation was tested for various numbers of points beginning with number 1, referring for pure water, taking into account the magnitudes of r—correlation coefficient, t—the significance test of the r—coefficient. As is shown in Table 5, all the coefficients have their maximum values for 9 points for correlation $B = f(\Delta H_s^0)$ not including the corrections connected with the ionic association occurrence and for 11 points for the corrected ones $B_{\mathrm{cor}} = f(\Delta H_{s,\mathrm{cor}}^0)$. Thus, the corrections for ionic association in the B coefficients as well as ΔH_s^0 expand the region of linear correlation of the function $B = f(\Delta H_s^0)$ from 50 mol% to about 70 mol% TBA.

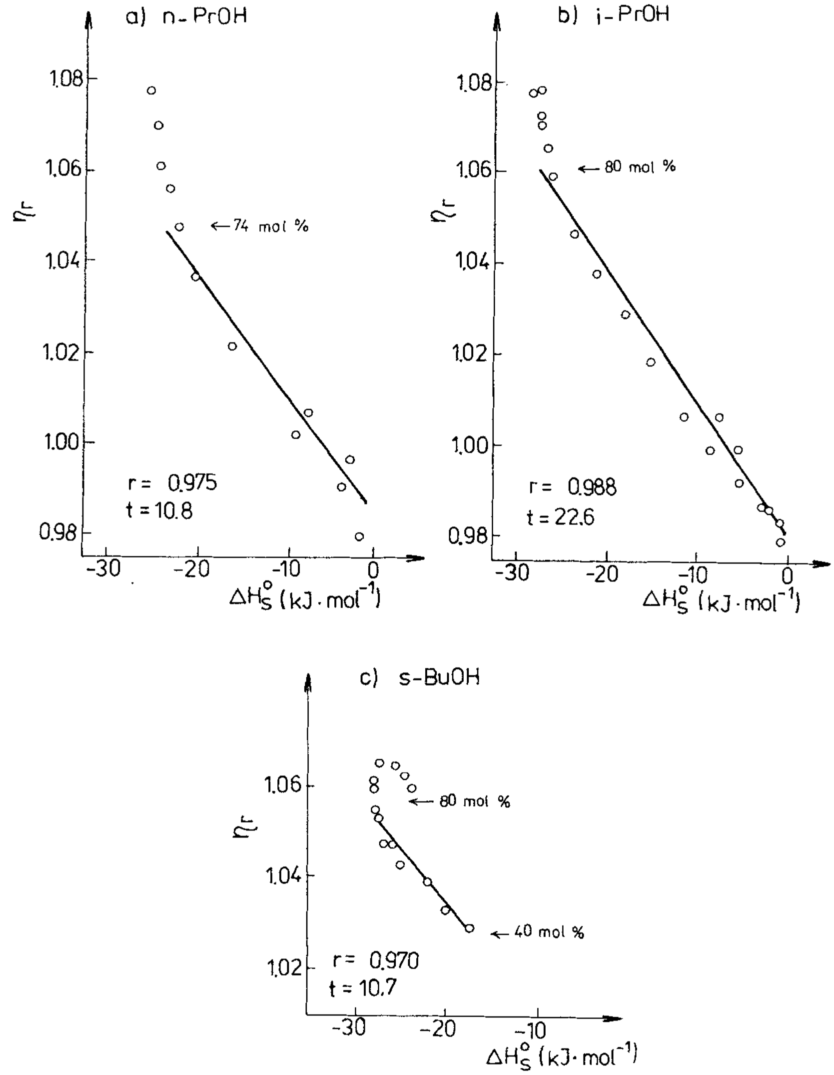

Figure 3 Relative viscosity (at salt concentration 0.5 mole per 100 moles of mixed solvent) vs. standard enthalpy of solution for NaI-water-alcohol systems: (a) *n*-PrOH, (b) *i*-PrOH and (c) *s*-BuOH at 25°C; η_r from Ref. (6–8), ΔH_s^0 from Ref. (2), *r*,*t*—have the same meaning as in Figure 2.

As is known from earlier investigations of the water-TBA system, many properties of this system such as electric permittivity[32–35], dynamic viscosity[8,35], apparent and partial molar volume of water[36], standard enthalpy of electrolytes solution[3] show extrema, connected most probably with structural changes in the mixed solvent. These changes result from various types of solute-solvent and solvent-solvent interactions in this range of solvent composition[3,8,32] The deviation of the dependence

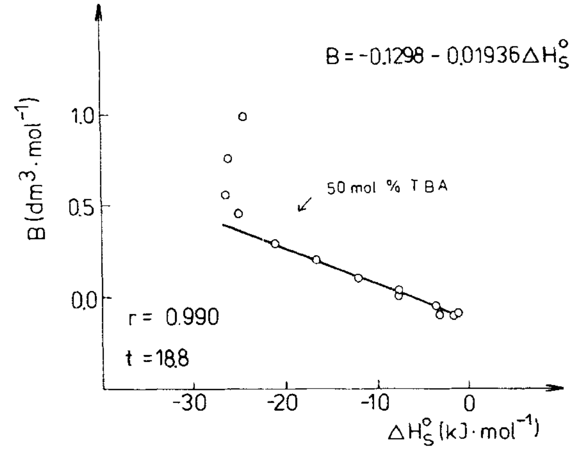

Figure 4 The B coefficient of viscosity vs. standard enthalpy of solution for NaI in water-tert-butanol mixtures at 26°C; B from Ref. (9), ΔH^0_s from Ref. (3), r,t—have the same meaning as in Figure 2.

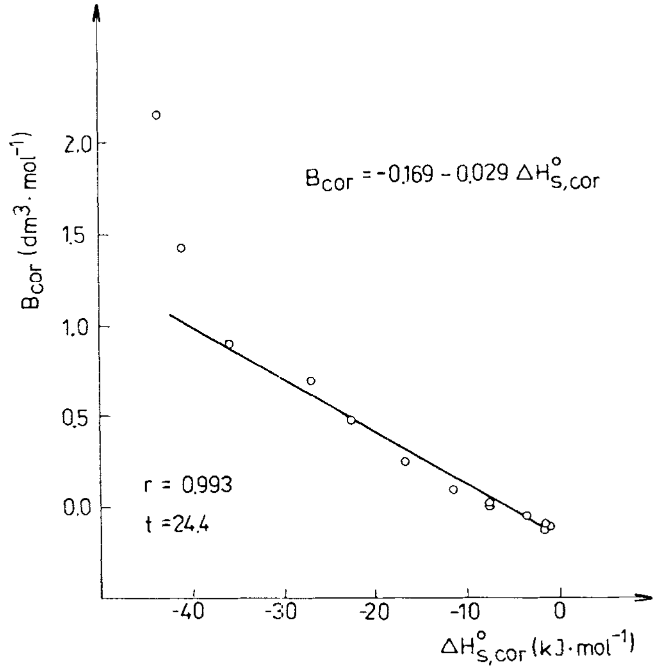

Figure 5 Correlation between the B coefficient of viscosity and standard enthalpy of solution (both corrected for ionic association) for NaI-water-tert-butanol system at 26°C; B from Ref. (9), $\Delta H^0_{s,cor}$ are interpolated from Bald's *et al.* data Ref. (31), r,t—have the same meaning as in Figure 2.

Table 5 The parameters of linearity of the dependence $B = f(\Delta H_s^0)$ for NaI-water-TBA system within various composition ranges of mixed solvent; r—the correlation coefficient, t—the significance test of the r.

Number of points in Figures 4 and 5	*Upper content of TBA mol%*	*Without association*		*With correction for the ionic association*	
		r	*t*	*r*	*t*
6	20	0.937	5.35	0.984	11.2
7	30	0.970	8.96	0.993	18.7
8	40	0.982	12.7	0.985	14.2
9	50	0.990	18.8	0.986	15.4
10	60	0.985	16.2	0.987	17.7
11	70	0.983	16.1	0.993	24.4
12	80			0.977	14.4
13	90			0.943	9.41

$B = f(\Delta H_s^0)$ from the straight line is most probably due to modification of the solvent structure, as already mentioned above.

There are no sufficiently quantitative theories of electrolyte solutions which can aid the discussion of the results of enthalpies of solutions and viscosity of electrolyte solutions in binary solvents. Thus, it is reasonable to apply the expression of Feakins *et al.*[37–39] for the B coefficients of viscosity in order to discuss the parameters in this equation (see below) in terms of the composition of the mixed solvent and compare their behavior with the enthalpy of solution.

The expression of Feakins *et al.*[37–39] for the viscosity B coefficient based on the transition-state theory can be written in the form:

$$B = \frac{vV_{12}^0 - V_3^0}{1000} + \frac{V_{12}^0}{1000}\,\frac{\Delta\mu_3^{0\#} - v\Delta\mu_{12}^{0\#}}{RT} = B_1 + B_2 \tag{1}$$

where V_{12}^0 and V_3^0 are the partial molar volumes of the solvent (subscript 12) and electrolyte (subscript 3), respectively, as $c \Rightarrow O$; $V_{12}^0 = V_{12}$ i.e. the average molar volume of the solvent and $\Delta\mu_{12}^{0\#} = \Delta G_{12}^{\#}$ ($\Delta G_{12}^{\#}$ is a free energy of activation of the pure solvent); $\Delta\mu_3^{0\#}$ is the molar contribution of the solute to the free energies of activation of the solution including any change in the free energy of activation of the solvent molecules caused by the presence of the solute, as well as a contribution from the movement of the solute itself; $v = 1$ for a non-electrolyte, 2 for a (1, 1) electrolyte and so on. So the B coefficient can be divided into two terms:

$$B_1 = \frac{vV_{12} - V_3^0}{1000} = \frac{vM_{12} - M_3}{1000\rho_{12}} + a \tag{2}$$

Table 6 Mean activation quantities for viscous flow of the NaI-water-TBA system at 26°C. The data for calculation were taken from paper (9).

mol% TBA	V_{12} *cm³ mol⁻¹*	$\Delta\mu_{12}^{0\#}$ *kJ mol⁻¹*	a	B_1	B_2	$\Delta\mu_3^{0\#}$ *kJ mol⁻¹*
0	18.1	9.14	0.116	0.001	0.022	21.2
2.5	19.8	10.61	0.119	0.006	−0.051	14.8
5.0	21.5	11.68	0.117	0.005	−0.094	12.5
7.5	23.3	12.46	0.117	0.007	−0.108	13.4
10.0	25.1	13.07	0.117	0.008	−0.107	15.5
20.0	32.6	14.52	0.127	0.025	−0.024	27.2
30.0	40.3	15.25	0.138	0.046	0.048	33.5
40.0	48.0	15.71	0.139	0.057	0.206	42.1
50.0	55.8	16.02	0.144	0.074	0.396	49.7
60.0	63.6	16.24	0.147	0.090	0.628	57.0
70.0	71.5	16.41	0.149	0.105	0.796	60.5
80.0	79.3	16.59	0.154	0.124	1.313	74.3
90.0	87.2	16.79	0.163	0.147	2.013	90.9

and

$$B_2 = \frac{V_{12}}{1000RT}(\Delta\mu_3^{0\#} - v\Delta\mu_{12}^{0\#}) \qquad (3)$$

where a is the parameter of Root's equation.[37]

In order to find the B_1 and B_2 terms we calculated the activation parameters for viscous flow for the NaI-water-TBA system.[9] They are collected in Table 6. For the solutions containing more than 20 mol% TBA we used the B_{cor} values, corrected for ionic association, for calculations.

As may be noted, the magnitude of B_{cor} coefficiennts are mainly determined by B_2 terms and the contributions of B_1 terms in B_{cor} are very small (less than 5% of their value) in the whole composition range of the mixed solvent (Figure 5) and the shapes of B_{cor} and B_2 are very close, contrary to the B_1 contribution. So, the contribution of the B_1 term can be omitted in relation to the B_2. The dependence $B_2 = f(\Delta H^0_{s,\mathrm{cor}})$ is linear in the same composition range of the mixed solvent as $B_{\mathrm{cor}} = f(\Delta H^0_{s,\mathrm{cor}})$.

Seeking the reasons of the above-mentioned deviations and taking into account that the B_2 term depends on the difference between $\Delta\mu_3^{0\#}$ and $v\Delta\mu_1^{0\#}$ we have compared these parameters and $\Delta H^0_{s,\mathrm{cor}}$ in terms of the composition of the mixed solvent in Figure 6. At about 5 mol% TBA $\Delta\mu_3^{0\#}$ displays a slight minimum. This minimum could be a reflection of a property of the binary mixed solvent, namely the enthalpy of mixing, ΔH^E, passes through a minimum at the same composition.[39] As is known, the minimum of ΔH^E is associated with the ordering or stability of the three-dimensional structure of water by alcohol molecules.[32,33,40] Values of $\Delta\mu_3^{0\#}$ remain at or below the value in pure water up to about 15 mol% TBA; this indicates that structural resistance to the co-ordination of ions in the ground-state of the mixed solvents is decreased in the more weakly bounded transition-state of solvent and this

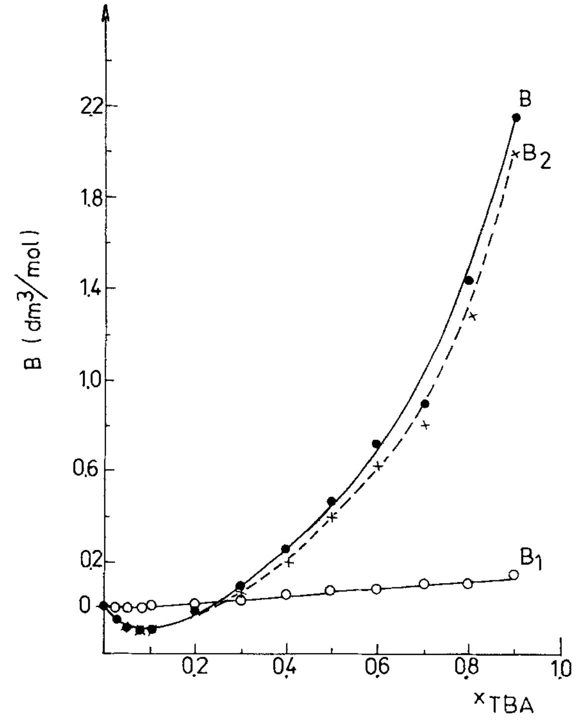

Figure 6 The B, B_1 and B_2, coefficients from the Jones–Dole equation versus mixed solvent composition for NaI in water-TBA mixtures at 26°C.

leads to decrease of $\Delta\mu_3^{0\#}$ by ion-solvent bond-making in the transition-state. The $\Delta\mu_3^{0\#}$ indicates that the relative stabilization of the electrolyte in the transition state should be a maximum.[39]

At 5 mol% TBA the maximum of $\Delta H^0_{s,\mathrm{cor}}$ for NaI is observed. This maximum is associated with the ordering or stability of the structure of water[3] as the maximum of ΔH^E.

The curves of $\Delta H^0_{s,\mathrm{cor}}$ and $\Delta\mu_3^{0\#}$ are almost mirror reflections; their shapes are very similar although they have different slope (not only sign) in the alcohol-rich region. It should be noticed that the shapes of both mentioned above functions are quite different than $(2\Delta\mu_{12}^{0\#})$. So we can expect that $\Delta H^0_{s,\mathrm{cor}}$ and $\Delta\mu_3^{0\#}$ will correlate quite well. This dependence can be described in the whole composition range of the mixed solvent by the equation:

$$\Delta\mu_3^{0\#} = 11.95 - 1.614\ \Delta H^0_{s,\mathrm{cor}}$$

with the correlation coefficient $r = 0.987$. The correlation coefficient is not too high, which may be connected with the fact that $\Delta\mu_3^{0\#}$ values, contrary to $\Delta H^0_{s,\mathrm{cor}}$ contain

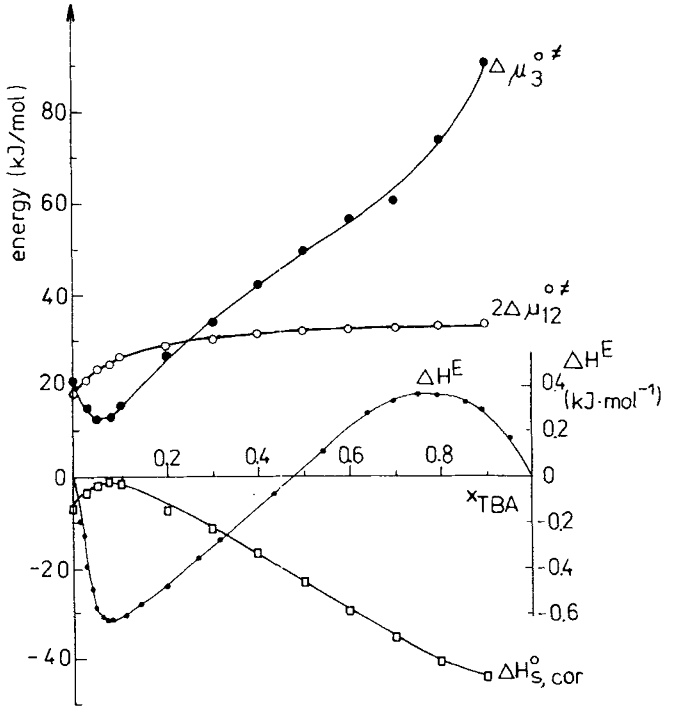

Figure 7 Comparison of the dependences of free energies of activation for viscous flow $\Delta\mu_{12}^{0\#}$ and $\Delta\mu_3^{0\#}$ and enthalpy of solution[31], ΔH_s^0, versus mixed solvent composition for NaI in water-TBA mixtures at 26°C, and ΔH^E for water-TBA mixtures[40] at 25°C.

the additional contributions from the movement of the solute itself which are probably dependent on the mixed solvent composition. As is known, $\Delta\mu_3^{0\#}$ does not contain any contributions from structural changes in solvent-solvent interactions caused by ions and the ion-solvent bond-breaking effect will make an important contribution to $\Delta\mu_3^{0\#}$; and $\Delta\mu_{12}^{0\#}$ reflects the changes in solvent-solvent interactions in the ground and transition states of solvent connected with the mixed solvent composition. The dependence $\Delta\mu_3^{0\#} = f(\Delta H^0_{s,cor})$ turned out to be linear in the whole composition of the mixed solvent. The conclusion is that the difference between solvent-solvent interactions for different compositions of mixed solvent, i.e. the changes of the mixed solvent structure, are probably the main source for all the observed deviations.

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