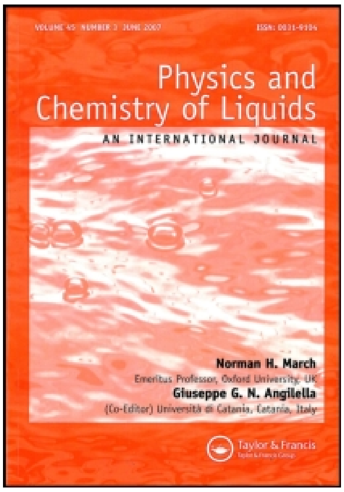

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Excess conductivities of isobutyric acid + water binary mixtures near and far away from the critical temperature

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Excess conductivities of isobutyric acid + water binary mixtures near and far away from the critical temperature

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The excess conductivities, σ^E and excess energy of activation $(\Delta E_\sigma)^E$ of electrical conductivity have been investigated by using electrical conductivities measurements for isobutyric acid + water (IBAW) mixtures over the entire range of mole fractions at six different temperatures, both near and close to the critical temperature $(0.055 < (T - T_c)/\mathrm{K} < 13.055)$. The results were also fitted with the Redlich–Kister equation. This system exhibited very large negative values of σ^E and very large positive values of $(\Delta E_\sigma)^E$ due to increased hydrogen bonding interactions and correlation length between unlike molecules in the critical region, and to very large differences between the molar volumes of the pure components at low temperatures. The activation parameters ΔH_σ and $\Delta S\sigma$ have also been calculated, and show that the critical region has an important effect on the electrical conductivity properties.

Keywords: liquid–liquid critical mixture; phase transition; electrical conductivity; activation energy; interactions; excess electrical conductivities; excess energy of activation

1. Introduction

This article represents another contribution to the study of the critical binary mixture of isobutyric acid + water (IBAW) [1]. We have been investigating and reporting data for this mixture for many years: transport phenomena [2], ionic structure [3], solvation phenomenon in a binary fluid [4], the effect of ions on the mixture IBAW [5] and the phase equilibrium properties occurring in the presence of added ions [6]. The electrical conductivity of IBAW mixtures has also been studied [7–9]. The variables in the present investigation are the temperature and the mole fractions. Here, we determine the temperature effect in the Arrhenius region $(T - T_c) > 2\,\mathrm{K}$ on the conductivities σ $(\Omega^{-1}\,\mathrm{cm}^{-1})$, where T_c is the critical temperature $\{T_c\ (\mathrm{IBAW}) = 300.095\,\mathrm{K}\}$. From our study, we can deduce the thermodynamic properties of IBAW far away from the critical point. The excess electrical conductivies are determined along the coexistence curve for phase separation, which characterise the critical mixture of IBAW and limit the one phase stability to the two phase regions (thermodynamic instability).

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2. Experimental details

2.1. *Materials*

The isobutyric acid (IBA) was purchased from Reidel de Haen. The purity of this IBA was checked and found to be 0.9999 mole fraction, with the main impurity probably being water. The water used in this study was obtained by deionisation and triple distillation, and has a specific conductivity of about $10^{-4}\,S^{-1}\,m^{-1}$. Using these chemicals gave a critical separation temperature of $T_c = 26.945°C$, which compares favourably with 26.948°C reported in reference [10], and which is a good indication of purity. All mixtures of IBAW were prepared from weighed amounts of the pure components (IBA) and water (W). The mass was obtained with a resolution of 10^{-7} kg. The critical mass fraction of the acid (IBA) was 0.38 which corresponds to a critical mole fraction $x_c = 0.1114$. We choose the binary fluid of IBAW for the following reasons: (a) their component densities are very close to each other, and thus this mixture does not have density gradients induced by gravity; and (b) the critical temperature T_c of IBAW is low.

2.2. *Electrical conductivity measurements*

The electrical conductivity measurements were carried out using a (Konductometer 702 and cell-type ZU 6985) conductometer, with a conductivity cell consisting of fixed spacing stainless-steel circular electrodes. The cell had a conductivity constant of $41\,cm^{-1}$ when filled with 100 mL of the sample. The cell constant changed by no more than 0.1%. The calibration of the cell was made by using liquids of known electrical conductivity with NaCl solution. Differential measurement of the cell temperature were checked with the help of a second electrode which measured temperature within a numerical accuracy of 0.02°C. The temperature difference between the cell and the bath never exceeded more than 0.03°C. The temperature of the cell was varied from to $T - T_{PS} = 0.05°C$ in steps of 0.30°C and the overall accuracy of the temperature determination was 0.02°C. T_{PS} is the phase separation temperature along phase diagram of the critical mixture. The critical temperature T_C is the top value of T_{PS}. The conductivity measurements are believed to be reproducible to 0.01% $10^{-3}\Omega^{-1}cm^{-1}$. The cell containing the solution was immersed in a thermally stabilised water bath with good thermal regulation. The long-term stability of the cell was better than 20 mK. The temperature was measured with a resolution of ± 0.1 mK using a quartz thermometer (HP 2804 A) which was calibrated on an absolute scale within 0.01 K.

Excess electrical conductivities σ^E were calculated from electrical conductivity measurements in the single phase region ($T > T_c$). Experimental physical properties of pure components are shown in Table 1.

Table 1. Experimental electrical conductivities σ ($\Omega^{-1}\,cm^{-1}$) for pure components at different temperatures from $T = 300.15$ to 313.15 K.

T (K)	300.15	302.15	305.15	308.15	311.15	313.15
$10^3\ \sigma$ (water) ($\Omega^{-1}\,cm^{-1}$)	1.2124	1.0603	1.0042	0.9346	0.8503	0.7852
$10^3\ \sigma$ (isobutyric acid) ($\Omega^{-1}\,cm^{-1}$)	0.8435	0.7521	0.6987	0.6421	0.5722	0.5214

3. Data collection and analysis

3.1. *Excess electrical conductivities*

Values of the excess conductivities σ^E were calculated from the electrical conductivity measurement according to the following equation:

$$\sigma^E = \sigma_m - X_1\sigma_1 - X_2\sigma_2, \tag{1}$$

where σ_m is the electrical conductivity of the mixture, σ_1 and σ_2 are the electrical conductivities of the respective pure components, where 1 denotes IBA and 2 denotes water (W), respectively.The electrical conductivity and excess electrical conductivities of the IBAW mixtures are given in Table 2 at six different temperatures near and far away from critical temperature: $T - T_c = 0.055$ K, $T - T_c = 2.055$ K, $T - T_c = 5.055$ K, $T - T_c = 8.055$ K, $T - T_c = 11.055$ K and $T - T_c = 13.055$ K.

The conductivities of IBAW mixtures have a minimum (Table 2) at $X_1 = 0.4499$ at 300.15 K ($T - T_c = 2.055$ K). In this temperature region the fluctuation correlations of concentration are also important. It is generally observed that the electrical conductivity depends on both the temperature and mole fraction. We detect an anomaly near the critical composition $X_c = 0.1999$ mole fraction of IBA.

Figure 1 shows the variation of σ^E of binary mixtures of IBAW with the mole fraction of IBA, at the six investigated temperatures. Figure 1 deserves some comments:

(a) The excess electrical conductivities are negative for all temperatures of the mixture IBAW.
(b) The largest magnitude of the negative values of σ^E are obtained in the region of 0.1–0.45 mole fraction of IBA with a critical region centred around $X_c = 0.1999$ mole fraction of IBA. This result is not surprising because the molecular correlations between water and IBA are strong.
(c) Because of the critical behaviour of the IBAW mixtures, the temperature has no significant effect on σ^E.

On the other hand, Figure 1 shows that the magnitude of the negative values of σ^E marginally decreases with an increase of the molecular correlation that is characterised by a correlation length according to the scaling law, Equation (2),

$$\xi = \xi_0\left(\frac{T - T_c}{T_c}\right)^{-\nu}\left[1 + a_\xi\left(\frac{T - T_c}{T_c}\right) + \cdots\right], \tag{2}$$

where ξ_0 is the critical amplitude of the IBAW mixtures and ν is the universal critical exponent ($\nu = 0.63$). The correlation length ξ diverges at $T = T_c$ and all molecules of IBA are correlated with water molecules. This critical phenomenon has been known for a long time in mixtures. On the other hand, the IBA molecule has a proton donor site and the water molecule has a proton acceptor site. Therefore, the negative excess volume is an indication of strong heteromolecular interaction in the liquid mixtures and, according to Fort and Moore [11], this can be attributed to specific interactions (hydrogen bonding) and non-specific interactions (dipole–dipole, dipole–induced-dipole, dispersion interactions) that depends on temperature [11,12]. Hence, there will be a significant degree of H-bonding, leading to strong correlations between the molecules. The difference in the size of the molecules also can play a role in this phenomena [13].

Table 2. Electrical conductivity, σ and excess electrical conductivities, σ^E for the mixtures of IBAW at the different temperatures from $T = 300.15$ to 313.15 K.

	$T_c = 300.095$ K		$T_c = 302.15$ K		$T_c = 305.15$ K		$T_c = 308.15$ K		$T_c = 311.15$ K		$T_c = 313.15$ K	
X_1	$10^3\ \sigma/$ $\Omega^{-1}\,cm^{-1}$	$10^3\ \sigma^E/$ $\Omega^{-1}\,cm^{-1}$	$10^3\ \sigma/$ $\Omega^{-1}\,cm^{-1}$	$10^3\ \sigma^E/$ $\Omega^{-1}\,cm^{-1}$	$10^3\ \sigma/$ $\Omega^{-1}\,cm^{-1}$	$10^3\ \sigma^E/$ $\Omega^{-1}\,cm^{-1}$	$10^3\ \sigma/$ $\Omega^{-1}\,cm^{-1}$	$10^3\ \sigma^E/$ $\Omega^{-1}\,cm^{-1}$	$10^3\ \sigma/$ $\Omega^{-1}\,cm^{-1}$	$10^3\ \sigma^E/$ $\Omega^{-1}\,cm^{-1}$	$10^3\ \sigma/$ $\Omega^{-1}\,cm^{-1}$	$10^3\ \sigma^E/$ $\Omega^{-1}\,cm^{-1}$
0	1.2124	0	1.0603	0	1.0042	0	0.9346	0	0.8503	0	0.7852	0
0.0106	1.0496	−0.1589	0.9169	−0.1400	0.8693	−0.1316	0.8196	−0.1118	0.7540	−0.0933	0.7005	−0.0818
0.0222	0.9295	−0.2747	0.8099	−0.2435	0.7699	−0.2275	0.7258	−0.2022	0.6687	−0.1754	0.6217	−0.1576
0.0348	0.8226	−0.3769	0.7135	−0.3360	0.6813	−0.3121	0.6409	−0.2834	0.5901	−0.2504	0.5489	−0.2271
0.0486	0.7220	−0.4724	0.6220	−0.4232	0.5980	−0.3912	0.5631	−0.3572	0.5192	−0.3175	0.4836	−0.2887
0.0545	0.6842	−0.5081	0.5877	−0.4557	0.5667	−0.4208	0.5340	−0.3846	0.4930	−0.3421	0.4602	−0.3106
0.0638	0.6311	−0.5577	0.5396	−0.5010	0.5227	−0.4619	0.4940	−0.4219	0.4571	−0.3754	0.4276	−0.3407
0.0737	0.5830	−0.6021	0.4962	−0.5413	0.4829	−0.4987	0.4580	−0.4550	0.4251	−0.4047	0.3981	−0.3677
0.0806	0.5541	−0.6285	0.4700	−0.5654	0.4589	−0.5205	0.4363	−0.4747	0.4056	−0.4222	0.3804	−0.3836
0.0915	0.5153	−0.6633	0.4319	−0.6001	0.4268	−0.5493	0.4072	−0.5006	0.3797	−0.4451	0.3568	−0.4042
0.1114	0.4651	−0.7061	0.3901	−0.6358	0.3853	−0.5848	0.3680	−0.5340	0.3443	−0.4749	0.3239	−0.4319
0.1200	0.4500	−0.7181	0.3778	−0.6454	0.3727	−0.5947	0.3580	−0.5415	0.3340	−0.4829	0.3140	−0.4395
0.1290	0.4379	−0.7268	0.3677	−0.6528	0.3627	−0.6020	0.3489	−0.5479	0.3253	−0.4891	0.3054	−0.4457
0.1433	0.4252	−0.7342	0.3563	−0.6598	0.3522	−0.6081	0.3378	−0.5548	0.3148	−0.4956	0.2949	−0.4525
0.1698	0.4082	−0.7415	0.3455	−0.6624	0.3381	−0.6141	0.3237	−0.5612	0.3017	−0.5014	0.2833	−0.4571
0.1999	0.3963	−0.7423	0.3362	−0.6624	0.3283	−0.6148	0.3136	−0.5625	0.2922	−0.5025	0.2741	−0.4584
0.2347	0.3882	−0.7376	0.3303	−0.6576	0.3215	−0.6109	0.3063	−0.5596	0.2852	−0.4997	0.2672	−0.4560
0.3230	0.3826	−0.7106	0.3280	−0.6327	0.3169	−0.5886	0.3001	−0.54	0.2785	−0.4819	0.2601	−0.4399
0.4499	0.3996	−0.6468	0.3463	−0.5753	0.3309	−0.5357	0.3118	−0.4912	0.2872	−0.4379	0.2674	−0.3991
0.4996	0.4131	−0.6149	0.3593	−0.5470	0.3422	−0.5093	0.3218	−0.4666	0.2956	−0.4157	0.2750	−0.3784
0.6404	0.4732	−0.5029	0.4127	−0.4502	0.3919	−0.4165	0.3660	−0.3813	0.3342	−0.3380	0.3095	−0.3068
0.7953	0.5805	−0.3385	0.5124	−0.3027	0.4808	−0.2804	0.4470	−0.255	0.4042	−0.2249	0.3726	−0.2027
0.9529	0.7636	−0.0972	0.6798	−0.0867	0.6325	−0.0805	0.5821	−0.0738	0.5211	−0.0642	0.4764	−0.0574
1	0.8435	0	0.7521	0	0.6987	0	0.6421	0	0.5722	0	0.5214	0

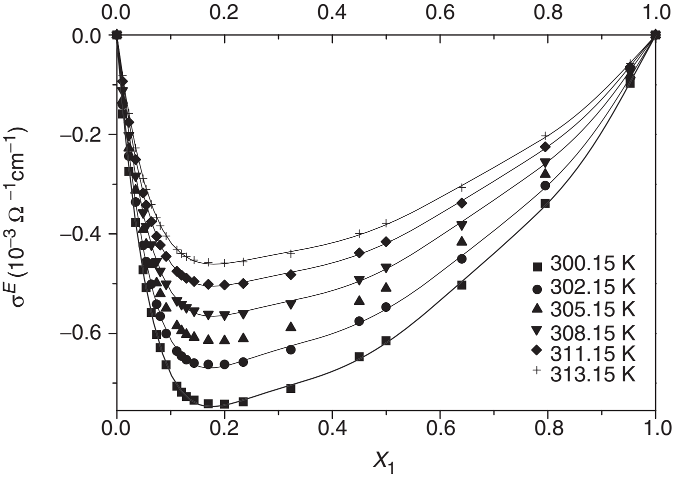

Figure 1. Excess electrical conductivities σ^E for IBAW mixtures *vs*. mole fraction X_1 of IBA at the different temperatures.

3.2. *Excess energies of activation of electrical conductivity*

On the basis of the theory of absolute reaction rates [13–15], the excess energies $(\Delta E_\sigma)^{\mathrm{E}}$ of activation of electrical conductivity were calculated using the following equation:

$$(\Delta E_\sigma)^{\mathrm{E}} = -RT\left[\ln\left(\frac{\sigma_{\mathrm{m}}}{\sigma_2}\right) - \ln\left(\frac{\sigma_1}{\sigma_2}\right)\right], \tag{3}$$

where σ_{m}, σ_1 and σ_2 are the electrical conductivities of the binary critical mixture and the pure components, R is the gas constant and T the absolute temperature. $(\Delta E_\sigma)^{\mathrm{E}}$ values are reported in Table 3 for various temperatures as a function of the mole fraction X_1 of the IBA, and are plotted in Figure 2.

The observed $(\Delta E_\sigma)^{\mathrm{E}}$ values are positive for the entire mole fraction range of IBA. From these large positive values, we can deduce that the importance of $(\Delta E_\sigma)^{\mathrm{E}}$ increases in the critical region $0.10 < X_1 < 0.45$. It is clear that molecular correlations have an effect on $(\Delta E_\sigma)^{\mathrm{E}}$ from small thermal variations. Outside of this domain, $(\Delta E_\sigma)^{\mathrm{E}}$ depends only on X_1 without having a significant dependence on the temperature.

To analyse our electrical conductivity σ_{m} of the mixture one can use an exponential formula due to equivalent Arrhenius law [16,17]:

$$\sigma_{\mathrm{m}} = \sigma_0 \exp\left[\frac{-\Delta E_\sigma}{RT}\right], \tag{4}$$

where σ_0, ΔE_σ, R and T are the Arrhenius constant, the activation energy, the gas constant and the absolute temperature, respectively. Calculated values of ΔE_σ are reported in Table 3 for various temperatures, and are plotted against the mole fraction of IBA in Figure 3.

In the water-rich region and near the critical composition (from $X_1 = 0$ to $X_{\mathrm{c}} \approx 0.1114$), the ΔE_σ values exponentially increase with X_1, which is an effect on ΔE_σ resulting from the strong correlation between the water and IBA molecules in the vicinity of X_{c}.

Table 3. Excess energies of activation, $(\Delta E_\sigma)^E$ and energies of activation, ΔE_σ for the mixtures of IBAW at the different temperatures from $T = 300.15$ to 313.15 K.

	$T_c = 300.095$ K		$T_c = 302.15$ K		$T_c = 305.15$ K		$T_c = 308.15$ K		$T_c = 311.15$ K		$T_c = 313.15$ K			
	$(\Delta E_\sigma)^E$/ kJ mol^{-1}	ΔE_σ/ kJ mol^{-1}	$(\Delta E_\sigma)^E$/ kJ mol^{-1}	ΔE_σ/ kJ mol^{-1}	$(\Delta E_\sigma)^E$/ kJ mol^{-1}	ΔE_σ/ kJ mol^{-1}	$(\Delta E_\sigma)^E$/ kJ mol^{-1}	ΔE_σ/ kJ mol^{-1}	$(\Delta E_\sigma)^E$/ kJ mol^{-1}	ΔE_σ/ kJ mol^{-1}	$(\Delta E_\sigma)^E$/ kJ mol^{-1}	ΔE_σ/ kJ mol^{-1}	ΔS_σ/ kJ mol^{-1} K^{-1}	ΔH_σ/ kJ mol^{-1}
0	0	−23.80	0	−23.63	0	−23.72	0	−23.77	0	−23.76	0	−23.80	57.71	−6.48
0.0106	0.35	−23.02	0.35	−22.83	0.35	−22.92	0.32	−23.00	0.29	−23.00	0.28	−23.02	58.94	−5.32
0.0222	0.64	−22.28	0.65	−22.08	0.65	−22.17	0.62	−22.24	0.59	−22.24	0.58	−22.28	59.59	−4.39
0.0348	0.93	−21.54	0.96	−21.33	0.95	−21.42	0.93	−21.48	0.90	−21.47	0.89	−21.54	59.98	−3.54
0.0486	1.24	−20.80	1.29	−20.56	1.27	−20.66	1.25	−20.71	1.22	−20.70	1.21	−20.80	61.03	−2.48
0.0545	1.37	−20.50	1.43	−20.25	1.40	−20.36	1.38	−20.41	1.35	−20.40	1.33	−20.50	62.35	−1.78
0.0638	1.57	−20.06	1.64	−19.80	1.59	−19.91	1.57	−19.96	1.54	−19.96	1.51	−20.06	63.12	−1.11
0.0737	1.76	−19.63	1.84	−19.35	1.78	−19.48	1.75	−19.53	1.71	−19.53	1.69	−19.63	65.87	1.38
0.0806	1.88	−19.36	1.97	−19.07	1.91	−19.20	1.87	−19.26	1.83	−19.26	1.80	−19.36	68.74	1.27
0.0915	2.052	−18.97	2.17	−18.66	2.08	−18.81	2.04	−18.88	1.99	−18.88	1.95	−18.97	70.32	2.12
0.1114	2.289	−18.43	2.41	−18.11	2.32	−18.26	2.28	−18.32	2.22	−18.33	2.18	−18.43	72.97	3.46
0.1200	2.36	−18.26	2.48	−17.94	2.40	−18.09	2.34	−18.16	2.29	−18.16	2.25	−18.26	73.70	3.85
0.1290	2.42	−18.12	2.54	−17.80	2.46	−17.94	2.40	−18.02	2.35	−18.02	2.32	−18.12	74.22	4.15
0.1433	2.48	−18.39	2.61	−18.07	2.52	−18.22	2.46	−18.29	2.42	−18.29	2.39	−18.39	73.97	3.80
0.1698	2.56	−18.59	2.67	−18.30	2.60	−18.42	2.55	−18.49	2.50	−18.49	2.47	−18.59	70.47	2.55
0.1999	2.60	−18.85	2.71	−18.56	2.65	−18.68	2.60	−18.75	2.55	−18.75	2.52	−18.85	68.37	1.66
0.2347	2.62	−19.17	2.72	−18.89	2.67	−19.01	2.63	−19.07	2.58	−19.07	2.55	−19.17	66.49	7.85
0.3230	2.58	−20.04	2.66	−19.78	2.62	−19.89	2.59	−19.95	2.55	−19.95	2.53	−20.04	63.87	−8.69
0.4499	2.36	−21.33	2.42	−21.12	2.40	−21.21	2.37	−21.27	2.34	−21.26	2.32	−21.33	59.36	−3.52
0.4996	2.23	−21.85	2.28	−21.64	2.27	−21.74	2.25	−21.79	2.22	−21.78	2.19	−21.85	58.01	−4.44
0.6404	1.76	−23.31	1.81	−23.12	1.79	−23.22	1.78	−23.27	1.75	−23.26	1.74	−23.31	57.57	−6.03
0.7953	1.11	−24.87	1.14	−24.72	1.13	−24.81	1.12	−24.86	1.10	−24.84	1.09	−24.87	56.70	−7.85
0.9529	0.29	−26.43	0.29	−26.32	0.29	−26.39	0.29	−26.44	0.29	−26.41	0.28	−26.43	56.11	−9.59
1	0.004	−26.90	0.001	−26.80	0.002	−26.87	0.002	−26.92	0.003	−26.89	0.007	−26.90	55.27	−10.31

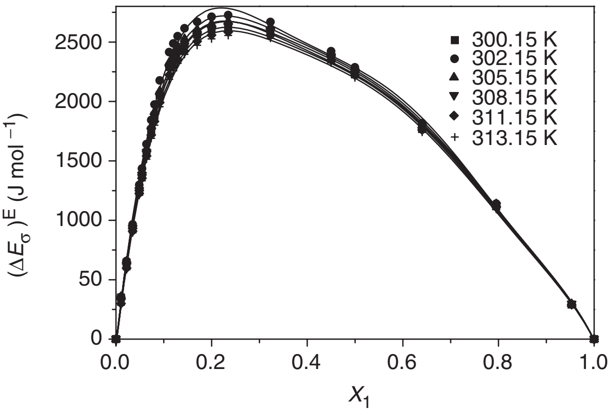

Figure 2. Excess energies of activation $(\Delta E_\sigma)^E$ for IBAW mixtures *vs*. the mole fraction X_1 of IBA at the different temperatures.

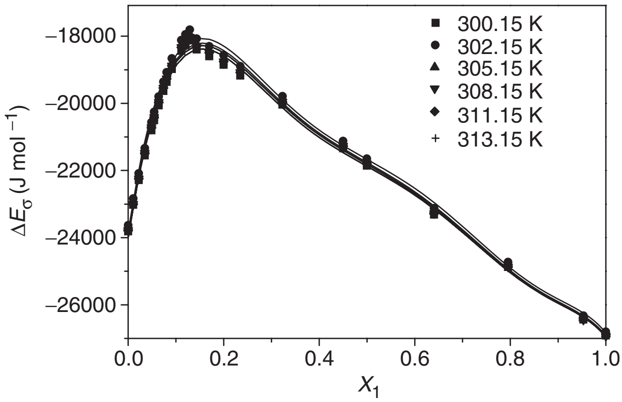

Figure 3. Energies of activation ΔE_σ for IBAW mixtures *vs*. the mole fraction X_1 of IBA at the different temperatures.

For a fixed temperature and away from X_c, the mole fraction has no significant influence on the ΔE_σ values.

3.3. *The activation parameters* ΔH_σ *and* ΔS_σ

We can use Equation (5) to determinate the activation parameters ΔH_σ and ΔS_σ,

$$\Delta E_\sigma = \Delta H_\sigma - T\Delta S_\sigma \tag{5}$$

By assuming that the activation parameters ΔH_σ and ΔS_σ are independent of temperature [16,17] (i.e. far away from the critical temperature), we can obtain these parameters for each mixture composition (X_1, X_2) by plotting $\ln(\sigma_m/\sigma_0)$ against $1/T$. Using both graphical and least-squares fitting methods, the slope of the straight line is equal to $\Delta H_\sigma/R$, and the intercept is equal to $-\Delta S_\sigma/R$. The obtained activation parameters ΔH_σ and ΔS_σ for the binary mixture are presented in Table 3 and are shown in Figure 4.

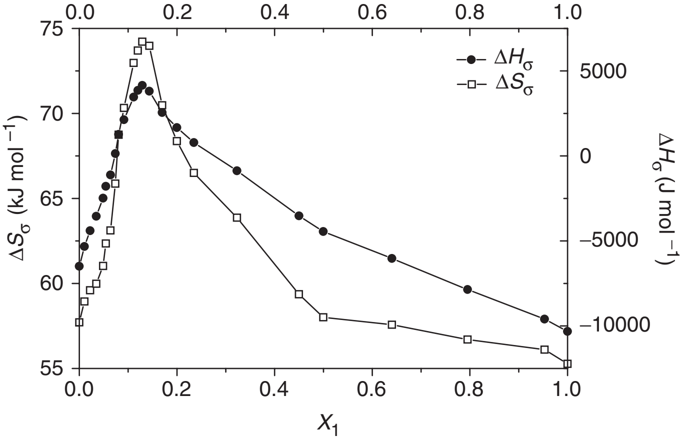

Figure 4. The enthalpy (ΔH_σ) and entropy (ΔS_σ) of activation of electrical conductivity for IBAW mixtures *vs*. molar fraction X_1 of IBA.

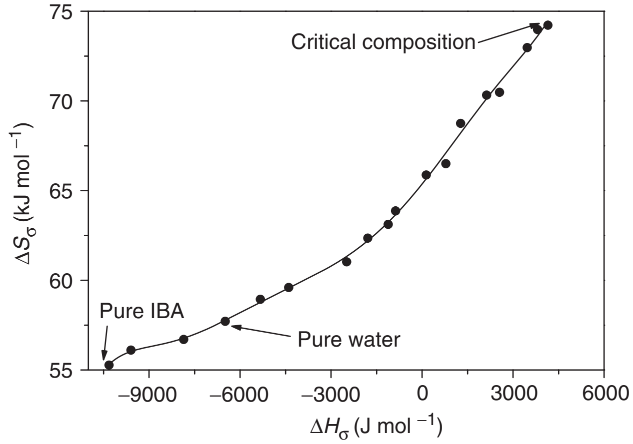

Figure 5. Correlation between the entropy (ΔS_σ) and enthalpy (ΔH_σ) of activation of electrical conductivity for IBAW mixtures *vs*. the mole fraction X_1 of IBA.

The activation parameter values ΔH_σ and ΔS_σ both exponentially increase with the mole fraction X_1 of IBA at the critical composition X_c and then decrease smoothly to the $\Delta H_{\sigma 1}$ and $\Delta S_{\sigma 1}$ of the pure IBA. An anomaly is observed in the very water-rich region (before the critical composition X_c), where ΔH_σ and ΔS_σ increase and rise to a localised maximum. In fact, in the highly dilute region, the IBA is weakly dissociated by water, and the positive values of ΔS_σ suggest that structural order is not destroyed much by the activation process, inasmuch as bonds are not broken between the associated molecules to form smaller units.

These distinct behaviours are clearly shown when the correlation between disorder and order is plotted in Figure 5. If we neglect the observed anomaly from IBA dissociation occurring in water at high dilution solution ($X_1 < 0.02$), we can conclude that there are two association type structures limited by the critical composition $X_c \cong 0.1114$ (corresponding to one IBA molecule + eight water molecules approximately).

Table 4. Coefficient A_i from Equation (6) for excess conductivities σ^{E} and the excess energies of activation of electrical conductivity $(\Delta E_\sigma)^{\mathrm{E}}$ of IBAW at the different temperatures.

	A_i	300.15 (K)	302.15 (K)	305.15 (K)	308.15 (K)	311.15 (K)	313.15 (K)
$10^3\ \sigma^{\mathrm{E}}\ (\Omega^{-1}\,\mathrm{cm}^{-1})$	A_0	−0.0129	−0.008	−0.010	−0.005	−0.002	−0.001
	A_1	−13.47	−12.180	−11.161	−10.261	−9.166	−8.332
	A_2	96.98	87.541	80.326	73.890	65.619	59.323
	A_3	−356.17	−319.683	−295.430	−292.306	−240.619	−216.672
	A_4	738.417	655.877	611.529	564.673	497.068	446.382
	A_5	−859.125	−756.618	−711.467	−657.662	−577.179	−517.266
	A_6	524.097	458.096	433.942	401.284	351.328	314.363
	A_7	−130.097	−113.026	−107.729	−99.613	−87.048	−77.798
$(\Delta \mathrm{E}_\sigma)^{\mathrm{E}}\ (\mathrm{Kj\,mol}^{-1})$	A_0	−0.003	−0.04	−0.03	−0.04	−0.05	−0.05
	A_1	34.49	36.25	35.07	34.77	34.16	33.59
	A_2	−160.88	−165.06	−163.56	−166.24	−163.31	−159.74
	A_3	336.70	312.02	342.33	372.31	367.49	358.19
	A_4	−289.22	−159.56	−294.04	−391.90	−392.39	−381.35
	A_5	−49.14	−279.34	−49.96	97.40	107.91	103.59
	A_6	224.76	405.86	228.51	122.47	111.06	109.22
	A_7	−96.70	−150.12	−98.31	−68.78	−64.900	−63.46

3.4. *The Redlich–Kister function*

For the IBAW mixtures, the excess molar properties were correlated by the Redlich–Kister equation (R–K) [18], Equation (6), and fitted to a polynomial Q_j,

$$Q_j = x_1(1 - x_1)\sum_{i=o}^{i=n-1} A_{ij}(2x_i - 1)^i, \tag{6}$$

where Q_j $(j = 1, 2)$ denotes the excess conductivities σ^{E}, and the excess energies $(\Delta E_\sigma)^{\mathrm{E}}$ of activation of electrical conductivity, respectively. The concordance with experimental data requires more parameters (n in Equation (6)), especially for σ^{E} and $(\Delta E_\sigma)^{\mathrm{E}}$. The values of the coefficients A_i are summarised in Table 4. Therefore, it is observed that the R–K 'model' does not reproduce the main features of the experimental data even by using a high number fitted parameters adjusted to describe σ^{E} and $(\Delta E_\sigma)^{\mathrm{E}}$ for the IBAW mixtures. For these mixtures that show a critical behaviour, the correlation fails. This is not surprising, considering that the R–K model does not consider all the possible interactions occurring in the studied mixtures, such as the critical behaviour around $x_\mathrm{c} \cong 0.1114$ mole fraction and the dissociation of IBA by water in the very dilute region.

The reduced excess quantities $f_j(x_1)$, Equation (7), are plotted in Figures 6 and 7 *versus* the mole fraction X_1 of IBA.

$$f_j(x_1) = \frac{Q_j}{x_i(1 - x_1)} = \sum_{i-0}^{i=n-1} A_{ij}(1x_1 - 1)^i, \tag{7}$$

where $j = 1$, 2 and 3 denote σ^{E} and $(\Delta E_\sigma)^{\mathrm{E}}$, respectively.

However, noteworthy changes in curvature were found for the three studied excess properties $f_j(x_1)$ for dilute solutions of IBA. It is not difficult to find an explanation for these anomalies: (a) In the very dilute region, the slope changes can be associated with the

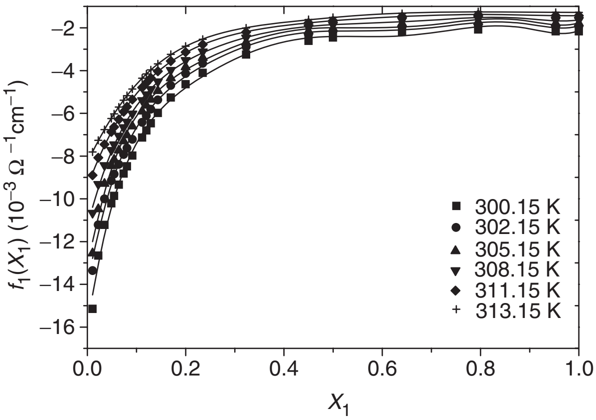

Figure 6. The Redlich–Kister function $f_1(X_1)$ for the ratio $\sigma^E/(X_1(1 - X_1))$ of the excess conductivities for IBAW mixtures *vs*. the mole fraction x_1 of IBA at the different temperatures.

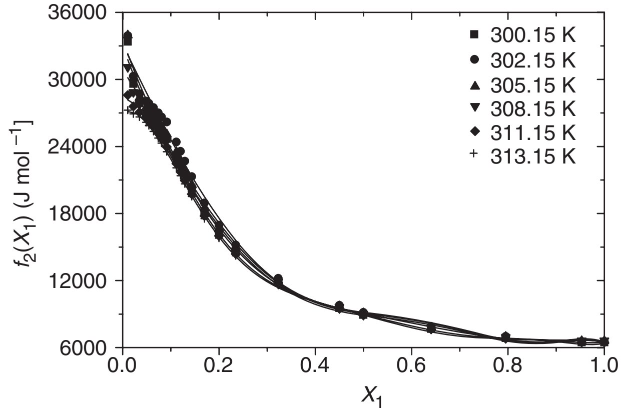

Figure 7. The Redlich–Kister function $f_2(X_1)$ for the ratio $(\Delta E_\sigma)^E/(X_1(1 - X_1))$ of the excess energies of activation of electrical conductivity for IBAW mixtures *vs*. the mole fraction X_1 of IBA at the different temperatures.

thermodynamic dissociation equilibrium, Equation (8). In fact, in the highly dilute region ($0 < x_1 < 0.02$ and molar concentration $c_1 < 1\,\mathrm{mol\,L^{-1}}$), we must take into account the ionisation of IBA and the fractional dissociation α (Equation (9)) that is not negligible ($0.05 < \alpha < 1$),

$$(\mathrm{CH_3})_2\mathrm{CHOOH} \rightleftarrows (\mathrm{CH_3})_2\mathrm{CHOO^-} + \mathrm{H^+}, \tag{8}$$

$$\alpha = [(\mathrm{CH_3})_2\mathrm{CHOO^-}]/c_1 \cong 10^{-\mathrm{pH}}/c_1, \tag{9}$$

where the IBA molarity is $c_1 < 0.15\,\mathrm{mol\,L^{-1}}$, which corresponding to molar fraction $x_1 < 0.003$. (b) The Redlich–Kister theory correlation does not consider all possible interactions that occur in the studied mixtures, especially the critical (correlation) behaviour. In fact, around the critical region, the interaction between (IBA) and (W) molecules are characterised by a divergence of the correlation length (Equation (2)).

The reduced excess electrical conductivity, $f_1(X_1) = \sigma^E/(X_1(1 - X_1))$, exponentially increases at lower concentrations of IBA as shown in Figure 6, and then varies smoothly for compositions greater than the critical mole fraction X_c. We conclude that at higher temperatures, there will be a competition between molecular interactions and thermal agitation. Thermal agitation is dominant at temperatures higher than 313.15 K, and *vice versa* at temperatures lower than ≈300.15 K. The $f_1(X_1)$ curves in Figure 6 exhibit a sharp increase when IBA is added to water, the maximum occurs at the critical composition ($x_c \cong 0.1114$) for all of the studied temperatures. The behaviour was observed at all studied temperatures.

As shown in Figure 7, the reduced excess energy of activation $(\Delta E_\sigma)^E$, $f_2(X_1) = (\Delta E_\sigma)^E/(X_1(1 - X_1))$, exponentially decreases with X_1 around the critical fraction X_c, then it decreases slowly and becomes independent of temperature in the IBA-rich region.

4. Conclusions

We conclude that all reduced excess functions $f_j(X_1)$ monotonically decrease with temperature, as expected. Also, a peculiar change in curvature was found for these functions in dilute solutions of IBA. Distinguishing behaviours are observed, especially near the critical temperature, limited by the critical composition. The Redlich–Kister correlation equations, even for eight or more parameters, are not sufficient to represent the IBAW systems as binary liquid mixtures. From an analysis of the results, it is clear that the complexity of the critical mixtures and the acid dissociation of IBA are reflected in the reduced excess functions. It is obvious that the structure of water is very much effected by IBA and this phenomenon is more pronounced at the critical composition in a larger temperature range, even far away from the critical temperature.

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