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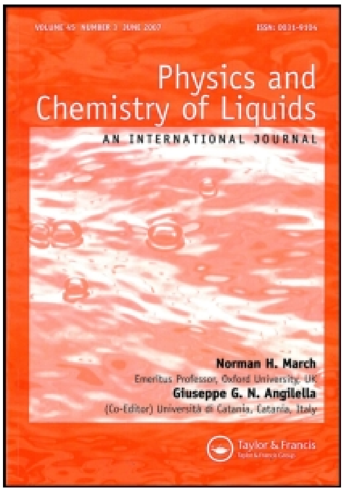

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Density, viscosity and electrical conductivity of isobutyric acid-water with added ions in the critical regions

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Density, viscosity and electrical conductivity of isobutyric acid–water with added ions in the critical regions

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Density, viscosity and electrical conductivity of the six concentrated binary ionic mixtures of isobutyric acid–water with X M [KCl] at the critical concentrations were measured as functions of temperature ($\Delta T = T - T_c \leq 2\,K$) and at various compositions, X, in the critical regions. The molar volumes have been calculated from their densities. The molar volume data dependence of viscosity and conductivity has been fitted to an equation similar to the Vogel–Tammann–Fulcher (VTF) based on the free volume model. The concentration of ions (K^+, Cl^-), dependence of the Vogel temperature, the intrinsic volume and the transport properties are primarily governed by the existence of intermolecular interactions.

Keywords: liquid–liquid critical mixture; phase transition; electrical conductivity; viscosity

1. Introduction

This work continues our previous systematic study of the thermodynamic and physical properties of binary liquid mixtures of isobutyric acid–water (IBAW) with X M [KCl].

We have been investigating and reporting data for this mixture for many years. The electrical conductivity of (IBAW) mixtures has been also studied [1]. The resistivity–viscosity relation for IBAW critical mixtures with added K^+ and Cl^- ions have been performed in the Arrhenius temperature domain of the electrolyte [2].

In [3] we have extensively studied the coexistence curves of electrical conductivity in the one-and-two regions of three different solutions: IBAW, IBAW $+ 5 \times 10^{-4}$ M [KCl], and IBAW $+ 5 \times 10^{-3}$ M [KCl].

The coexistence curve of the electrolyte mixture takes a new shape and is characterised by a new effective critical exponent $\beta^* = (0.264–0.296)$. The value obtained for β^* is outside of the field of the Fisher-renormalised value. Besides, we have proved that the long-range coulombic interaction in such mixtures is significant and is caused by the potential of the ionic atmosphere. The electrical conductivity of the same electrolytic solution has been also studied, and it shows that the temperature parameter is dependent of the ions. The addition of the ions (K^+, Cl^-) has an important effect on the increase of the electrical conductivity.

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In previous work [4] we extensively studied both the experimental measurements of the electrical conductivity and the shear viscosity *versus* temperature of the six concentrated binary ionic mixtures of (IBAW) with X M [KCl] at critical concentrations. The temperature effect in the Vogel–Fulcher–Tammann region $\Delta T = T - T_c \leq 2\,\mathrm{K}$, where T_c is the critical temperature, and the degree of dissociation α_{diss} [5] of the salt for the critical mixture, from the value of the Walden product [6] computed at the critical temperature, characterise the critical mixture of (IBAW) with X M [KCl] and limit the one phase stability.

In the present article, we report density, viscosity, and electrical conductivity of the six concentrated binary ionic mixtures of (IBAW) with X M [KCl] at critical concentration as a function of temperature and composition. It is well known that the thermophysical properties of liquid systems, such as density, viscosity, and electrical conductivity, among others, are strictly related to the molecular interactions present in different binary liquid mixtures. The variation of these properties with composition gives us important data regarding the intermolecular interactions and their structures.

This article is organised as follows: the experimental methods used in this work are discussed in Section 2. The data collection and analysis techniques used are treated in Section 3, and conclusions are given in Section 4.

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2. Experimental details

The isobutyric acid (IBA) was purchased from Riedel de Haen (Germany). The purity was stated to be 99.99 mol%. The main impurity is probably water. The water was obtained from deionisation and triple distillation, and had a specific conductivity of about $10^{-6}\,\Omega^{-1}\,\mathrm{cm}^{-1}$. These gave a critical separation temperature, which is a good indication of purity, of 26.945°C, which compares favourably with 26.948°C in the data of [7]. The guaranteed purity of the KCl salt (Merck, Germany) was better than 99.5%. In this mixture, the salt can be dissolved in totality. All electrolytes were prepared from weighed amounts of the pure components. The weight was obtained with a resolution of 0.1 mg.

2.1. *Electrical conductivity measurements*

The electrical conductivity measurements were carried out using a conductometer (Konductometer 702 and cell type ZU 6985), with a conductivity cell consisting of fixed spacing stainless-steel circular electrodes. The cell had a conductivity constant of $41\,\mathrm{cm}^{-1}$ when filled with 100 mL of the sample. The cell constant changed by no more than 0.1%. The calibration of the cell was conducted using liquids of known electrical conductivity with NaCl solution. The relative measurement of temperature in the cell can verified as the second electrode that detected the numerical value within 0.020°C. The temperature difference between the cell and the bath does not exceed 0.030°C. The temperature of the cell was varied from to $T - T_{\mathrm{PS}} = 0.050$°C in steps of 0.200°C and the overall accuracy of the temperature determination was 0.020°C. T_{PS} is the phase separation temperature along phase diagram of the critical mixture. The critical temperature T_c is the top of T_{PS}. The conductivity measurements are believed to reproducible to 0.01% $10^{-3}\ \Omega^{-1}\mathrm{cm}^{-1}$. 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 using a quartz thermometer (HP 2804 A) giving a resolution of ±1mK, and which was calibrated on an absolute scale within 0.001 K.

2.2. *Density and viscosity measurements*

The shear viscosity η [10^{-2} Poise (P)] of the electrolyte at different temperatures and concentrations of (K^+, Cl^-) ions was determined by measuring the density (ρ) expressed in (g cm^{-3}) and the kinematic viscosity υ [10^{-2} Stokes (St)]. The densities were measured in a digital precision densimeter (PAAR, Graz, Austria), which was modified in our laboratory. The density of a solution was calculated from the electronically measured frequency of a mechanical oscillator filled with the solution. Filling was accomplished by means of a medical syringe. During filling, the absence of air bubbles was ensured. The oscillator was U-shaped glass tubing (volume 0.7 cm^3) placed in a metal block, which was controlled to temperature about $\pm 10^{-3\circ}C$. This apparatus needs to be carefully calibrated with two liquids of different densities; we chose water as the standard, with density data from [10], and methanol, with density data from [9]. The sensitivity of such measurements is high, and to ensure a final ρ accuracy of $10^{-5}\,g\,cm^{-3}$, a thermal regulation of the sample to within 3 mK is needed. This was obtained by circulating water from the thermostat. The temperature was read by a quartz thermometer. The precision of the density measurement was about $\pm 0.01\,mg\,cm^{-3}$.

The kinematic viscosities, ν, were measured using an Ubbelhode-type viscosimeter. The length of the capillary was 20 cm and its constant $k = 0.0399 \times 10^{-2}\,St\,s^{-1}$. The times at which the meniscus passed by two marks of the viscosimeter were recorded automatically to ±0.01 s. The coefficient ν was calculated from the following equation:

$$\nu = k(\tau - \theta), \tag{1}$$

where τ is the flow time between the two marks, k is a constant for a given viscosimeter, and θ is the correction time. The viscosimeter was calibrated with fluids of known density and viscosity.

3. Data collection and analysis

We measured the density, viscosity, and electrical conductivity of six different solutions: IBAW, IBAW + 5×10^{-4} M [KCl], IBAW + 5×10^{-3} M [KCl], IBAW + 10^{-2} M [KCl], IBAW + 5×10^{-2} M [KCl], and IBAW + 10^{-1} M [KCl] with *versus* temperature above the separation temperature, T_t, at each concentration, X, of the isobutyric acid along the coexistence curve. The conductivity data for these solutions cover a good range of temperature above T_t. The lower limit was considered adequate for the main purpose of this study. Data were taken at the higher temperature in order to establish the temperature dependence of these transport properties well away from T_c. The separation temperature for the critical concentration X_c, $T_c = T_t$ ($X = X_c$, X_c is the critical mole fraction of IBAW + KCl):

$$\text{IBAW (pure)}: \quad X_c = 38.00\%; \quad T_c = 300.095\,K,$$

$$\text{IBAW} + 5 \times 10^{-4}\,M[KCl]: \quad X_c = 39.90\%; \quad T_c = 300.235\,K,$$

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$$\mathrm{IBAW} + 5 \times 10^{-3}\,\mathrm{M[KCl]}: \quad X_c = 42.63\%; \quad T_c = 301.638\,\mathrm{K},$$

$$\mathrm{IBAW} + 10^{-2}\,\mathrm{M[KCl]}: \quad X_c = 43.00\%; \quad T_c = 301.902\,\mathrm{K},$$

$$\mathrm{IBAW} + 5 \times 10^{-2}\,\mathrm{M[KCl]}: \quad X_c = 48.00\%; \quad T_c = 307.977\,\mathrm{K},$$

$$\mathrm{IBAW} + 10^{-1}\,\mathrm{M[KCl]}: \quad X_c = 60.00\%; \quad T_c = 316.500\,\mathrm{K}.$$

The critical temperature T_c and the critical composition X_c increased linearly with the increase of the salt concentration. The effect of KCl salt on the shift of the critical point of this mixture (IBAW) was extensively studied in a previous work [10].

The measured densities (ρ) of IBAW with X M [KCl] are presented in Table 1 and are found to be a linear function of temperature (Table 2) at a fixed composition.

The molar volumes, V (Table 1), of IBAW with X M [KCl], are calculated from their densities.

3.1. *The temperature dependence of the transport properties*

The measured values of conductivity (σ) and viscosity (η) of the systems under study are presented in Table 1. The temperature dependence of conductivity and viscosity is a non-Arrhenius deviation [4]. Such a temperature dependence of transport properties is common in concentrated electrolyte and ionic systems. The conductivity and viscosity values were, therefore, least-squares fitted to the Vogel–Tammann–Fulcher (VTF) equation of the form considering the insignificant contribution of the preexponential temperature term [4]:

$$Y = Y_{0,\mathrm{VFT}} \exp[B_{tY}/(T - T_{0Y})]. \tag{2}$$

Here, Y refers to either conductivity (σ) or viscosity (η). $Y_{0,\mathrm{VFT}}$ and B_{tY} are constant, and T_{0Y} is the intrinsic temperature. The B_{tY} parameter is negative for the electrical conductivity. The computed values of the parameters in Equation (2) are presented in [4]. Variation of T_{0Y} with the salt concentration [KCl] is illustrated in Figure 1(a). T_{0Y} decreases non-linearly with the concentration [KCl].

The relative temperature changes T_{0Y} are significantly larger for compositions larger than the critical composition. Our results might be attributed to the decrease in the ion mobility with increasing concentration of isobutyric acid, as observed in [11].

As evident in Figure 1(a), the intrinsic temperature T_{0Y} is proportional to kinetic energy, which, according to kinetic theory, is due to the velocity of translation in a frame of reference attached to liquid particles. Intermolecular forces restrict the mean free path of liquid molecules so that kinetic energy may be partly due to rotation or vibration rather than translation only. According to kinetic theory, the driving force for thermal diffusion is a gradient of kinetic energy. We assign the dimensions of energy per unit mass to temperature so that the gradient of temperature multiplied by density represents force per unit volume. However, only a portion of the temperature gradient is effective in transporting mass.

In general, the transport properties consist of two contributions: the first is measuring the ease with which the molecules are deformed by an electric field and is due to the orientation of the molecular dipoles under the action of this field; the second depends on

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Table 1. Densities, molar volumes, electrical conductivity and viscosities in the critical region for the electrolyte IBAW + KCl salt at different concentrations.

T (K)	ρ (g cm^{-3})	V (cm^3 mol^{-1})	$10^3\ \sigma$ (Ω^{-1} cm^{-1})	η (10^{-2} P)	T (K)	ρ (g cm^{-3})	V (cm^3 mol^{-1})	$10^3\ \sigma$ (Ω^{-1} cm^{-1})	η (10^{-2} P)
IBAW Critical region: $T - T_c < 0.155$ K					IBAW + 5×10^{-4} M [KCl] Critical region: $T - T_c < 0.778$ K				
300.113	0.99292	26.0101	0.375	2.4569	300.325	0.99286	26.4489	0.555	2.4470
300.115	0.99292	26.0101	0.375	2.4565	300.326	0.99285	26.4489	0.555	2.4468
300.118	0.99292	26.0102	0.375	2.4560	300.337	0.99285	26.4491	0.555	2.4452
300.121	0.99291	26.0102	0.376	2.4554	300.352	0.99284	26.4494	0.556	2.4430
300.123	0.99291	26.0103	0.376	2.4550	300.367	0.99283	26.4496	0.557	2.4408
300.126	0.99291	26.0103	0.376	2.4544	300.380	0.99282	26.4499	0.557	2.4388
300.128	0.99291	26.0104	0.377	2.4540	300.394	0.99281	26.4501	0.558	2.4368
300.131	0.99291	26.0104	0.377	2.4533	300.409	0.99280	26.4503	0.558	2.4345
300.133	0.99291	26.0104	0.377	2.4530	300.421	0.99279	26.4505	0.558	2.4328
300.136	0.99291	26.0105	0.378	2.4525	300.436	0.99279	26.4508	0.559	2.4306
300.139	0.99290	26.0105	0.378	2.4518	300.451	0.99278	26.4510	0.559	2.4284
300.143	0.99290	26.0106	0.378	2.4512	300.460	0.99277	26.4512	0.559	2.4271
300.146	0.99290	26.0106	0.378	2.4506	300.475	0.99276	26.4514	0.561	2.4249
300.149	0.99290	26.0107	0.379	2.4501	300.484	0.99275	26.4516	0.560	2.4236
300.152	0.99290	26.0107	0.379	2.4494	300.499	0.99275	26.4519	0.560	2.4214
300.155	0.99289	26.0108	0.379	2.4489	300.511	0.99274	26.4521	0.560	2.4197
300.159	0.99289	26.0109	0.379	2.4481	300.538	0.99272	26.4525	0.561	2.4158
300.164	0.99289	26.0109	0.382	2.4472	300.559	0.99271	26.4529	0.561	2.4128
300.168	0.99289	26.0110	0.380	2.4464	300.574	0.99270	26.4531	0.561	2.4106
300.173	0.99288	26.0111	0.381	2.4454	300.619	0.99267	26.4539	0.562	2.4042
300.176	0.99288	26.0111	0.380	2.4447	300.715	0.99261	26.4555	0.563	2.3907
300.179	0.99288	26.0112	0.381	2.4443					
300.186	0.99287	26.0113	0.381	2.4431					
IBAW + 5×10^{-3} M [KCl] Critical region: $T - T_c < 0.480$ K					IBAW + 10^{-2} M [KCl] Critical region: $T - T_c < 0.844$ K				
301.648	0.99204	27.4887	0.862	2.5543	302.031	0.99212	28.0530	1.233	2.3296
301.649	0.99204	27.4887	0.862	2.5540	302.065	0.99210	28.0536	1.235	2.3257
301.654	0.99202	27.4888	0.863	2.5535	302.092	0.99208	28.0541	1.236	2.3224
301.657	0.99204	27.4889	0.863	2.5530	302.122	0.99206	28.0546	1.237	2.3189
301.664	0.99203	27.4890	0.864	2.5522	302.152	0.99205	28.0551	1.239	2.3153

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301.670	0.99196	27.4891	0.865	2.5514	302.194	0.99202	28.0559	1.241	2.3103
301.674	0.99202	27.4892	0.865	2.5508	302.231	0.99200	28.0565	1.242	2.3061
301.680	0.99198	27.4893	0.866	2.5501	302.282	0.99196	28.0574	1.244	2.3001
301.683	0.99204	27.4893	0.866	2.5496	302.318	0.99194	28.0580	1.246	2.2959
301.689	0.99200	27.4894	0.867	2.5489	302.342	0.99193	28.0585	1.248	2.2931
301.695	0.99202	27.4895	0.867	2.5482	302.372	0.99191	28.0590	1.248	2.2896
301.701	0.99203	27.4896	0.868	2.5474	302.415	0.99188	28.0597	1.252	2.2848
301.707	0.99199	27.4898	0.869	2.5465	302.472	0.99185	28.0607	1.252	2.2782
301.713	0.99201	27.4899	0.869	2.5458	302.475	0.99185	28.0608	1.252	2.2779
301.715	0.99202	27.4899	0.869	2.5454	302.505	0.99183	28.0613	1.254	2.2745
301.719	0.99201	27.4900	0.870	2.5450	302.508	0.99182	28.0614	1.253	2.2741
301.725	0.99210	27.4901	0.870	2.5443	302.569	0.99179	28.0624	1.255	2.2673
301.731	0.99199	27.4902	0.871	2.5435	302.626	0.99175	28.0634	1.257	2.2609
301.736	0.99200	27.4903	0.871	2.5427	302.680	0.99172	28.0644	1.258	2.2548
301.743	0.99197	27.4904	0.872	2.5420	302.717	0.99170	28.0650	1.259	2.2508
301.749	0.99199	27.4905	0.872	2.5411					
301.758	0.99204	27.4906	0.873	2.5400					
301.762	0.99198	27.4907	0.873	2.5395					
301.768	0.99200	27.4908	0.874	2.5388					
301.774	0.99197	27.4909	0.874	2.5379					
301.784	0.99196	27.4911	0.875	2.5367					
IBAW + 5 × 10^{-2} M [KCl] Critical region: $T - T_c < 1.110$ K					IBAW + 10^{-1} M [KCl] Critical region: $T - T_c < 0.174$ K				
308.001	0.99340	33.3722	2.804	1.9598	316.503	0.99275	41.1806	3.706	1.5394
308.013	0.99339	33.3721	2.815	1.9588	316.509	0.99275	41.1807	3.717	1.5390
308.045	0.99337	33.3732	2.827	1.9562	316.517	0.99274	41.1809	3.728	1.5386
308.076	0.99331	33.3739	2.841	1.9537	316.521	0.99274	41.1810	3.735	1.5383
308.105	0.99333	33.3745	2.854	1.9514	316.529	0.99274	41.1811	3.742	1.5379
308.142	0.99335	33.3753	2.866	1.9485	316.537	0.99273	41.1813	3.751	1.5375
308.180	0.99328	33.3762	2.882	1.9454	316.547	0.99273	41.1815	3.759	1.5369
308.236	0.99325	33.3774	2.901	1.9410	316.554	0.99272	41.1816	3.766	1.5365
308.280	0.99322	33.3783	2.911	1.9376	316.564	0.99272	41.1819	3.773	1.5359
308.346	0.99317	33.3798	2.927	1.9324	316.575	0.99271	41.1821	3.782	1.5353

(*continued*)

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Table 1. Continued.

T (K)	ρ (g cm^{-3})	V (cm^3 mol^{-1})	10^3 σ (Ω^{-1} cm^{-1})	η (10^{-2} P)	T (K)	ρ (g cm^{-3})	V (cm^3 mol^{-1})	10^3 σ (Ω^{-1} cm^{-1})	η (10^{-2} P)
308.377	0.99315	33.3805	2.943	1.9312	316.582	0.99271	41.1822	3.787	1.5349
308.438	0.99311	33.3818	2.957	1.9252	316.591	0.99270	41.1824	3.793	1.5344
308.469	0.99309	33.3825	2.971	1.9228	316.601	0.99270	41.1826	3.799	1.5339
308.528	0.99306	33.3838	2.981	1.9182	316.613	0.99269	41.1829	3.805	1.5332
308.592	0.99301	33.3852	2.995	1.9133	316.623	0.99269	41.1831	3.811	1.5326
308.663	0.99297	33.3867	3.011	1.9079	316.631	0.99268	41.1832	3.814	1.5322
308.685	0.99295	33.3872	3.018	1.9062	316.639	0.99268	41.1834	3.819	1.5317
308.771	0.99290	33.3891	3.027	1.8996	316.654	0.99267	41.1837	3.827	1.5309
308.808	0.99287	33.3899	3.034	1.8968	316.664	0.99267	41.1839	3.831	1.5303
308.870	0.99283	33.3912	3.042	1.8922	316.674	0.99266	41.1841	3.835	1.5298
308.924	0.99280	33.3924	3.051	1.8881	316.691	0.99265	41.1845	3.839	1.5288
308.977	0.99276	33.3936	3.058	1.8841	316.705	0.99265	41.1848	3.844	1.5280
309.054	0.99271	33.3953	3.068	1.8784					
309.122	0.99267	33.3967	3.076	1.8734					
309.223	0.99261	33.3989	3.081	1.8660					

Table 2. Least-squares fitted values of the density equation, $\rho = \rho_0 - a(T)$, for IBAW + KCl for different values of KCl salt concentrations.

Systems	ρ_0 $(\mathrm{g\,cm^{-3}})$	$10^4 a$ $(\mathrm{g\,cm^{-3}\,K^{-1}})$
IBAW	1.18152	6.3
IBAW + 5×10^{-4} M [KCl]	1.18141	6.3
IBAW + 5×10^{-3} M [KCl]	1.17981	6.2
IBAW + 10^{-2} M [KCl]	1.17793	6.2
IBAW + 5×10^{-2} M [KCl]	1.19362	6.5
IBAW + 10^{-1} M [KCl]	1.15632	5.2

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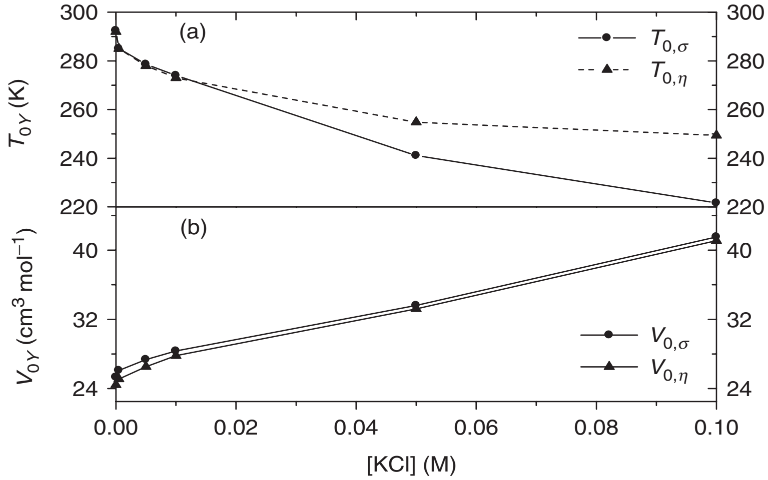

Figure 1. Variation of (a) intrinsic temperature T_{0Y} (K), and (b) intrinsic volume, V_{0Y} (cm^3 mol^{-1}), with the molar concentration [KCl] ions.

the temperature, whereas the first is practically temperature independent. The higher the permanent electric dipole moment of molecules, the more important are the orientational effects.

3.2. *The molar volume dependence of the transport properties*

The molar volume dependence of conductivity and viscosity are shown in Figures 2 and 3, respectively. It is noted that the conductivity increases non-linearly with molar volume (V), whereas viscosity decreases with an increase in V. At this moment we are not able to explain why conductivity and viscosity vary in such a fashion.

The electrical conductivities and viscosities of the present systems also vary non-linearly with the molar volume, and both properties have been explained by using the following equation, similar to Equation (2), and derived on the basis of the free volume model:

$$Y = A_Y \exp[B_Y/(V - V_{0Y})], \tag{3}$$

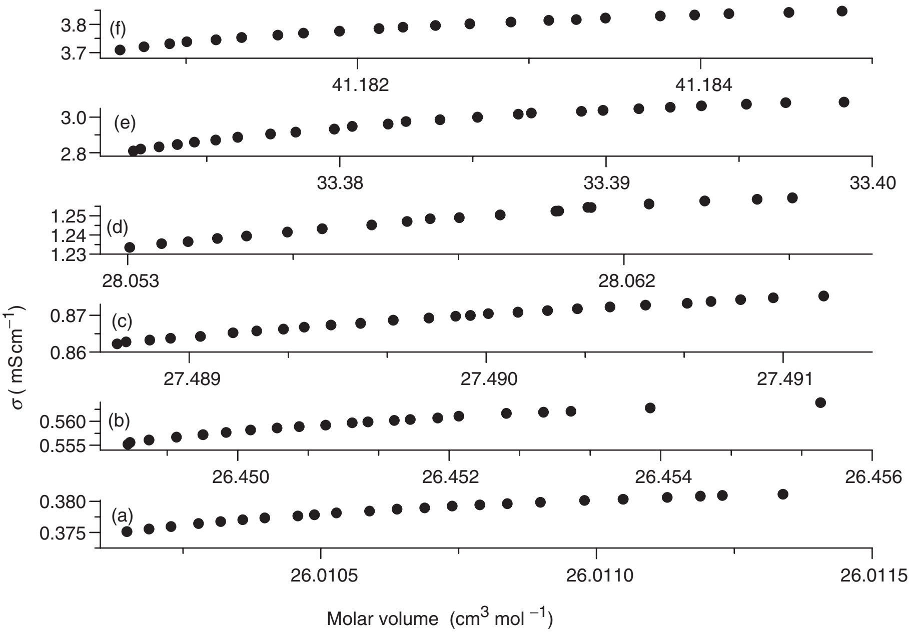

Figure 2. Molar volume (V) dependence on the electrical conductivity (σ) of IBAW + KCl for different values of KCl salt concentrations: (a) 0 M, (b) 5×10^{-4} M, (c) 5×10^{-3} M, (d) 10^{-2} M, (e) 5×10^{-2} M, (f) 10^{-1} M; M is moles of [KCl] per kilogram of liquid–liquid critical mixture.

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where Y refers either to the conductivity or viscosity. A_Y and B_Y are constants, and V_{0Y} is the intrinsic volume. The least-squares fitted values of A_Y, B_Y and V_{0Y} are presented in Table 3. For conductivity, B_Y is negative.

The intrinsic volumes, V_{0Y}, obtained from the conductivity and viscosity increase non-linearly (Figure 1(b)) as the IBAW mixtures are progressively added to by the KCl salt. However, the dependence of the ionic concentration of (K^+, Cl^-) on the intrinsic volumes V_{0Y} can be seen clearly in Figure 1(b).

This result is expected, since the molecular correlations between IBAW and the KCl salt are strong. The parameters B_Y can be interpreted into three terms, namely physical, chemical and structural effects. The physical effects involve dispersion forces and non-specific interactions in the mixture, adding positive contributions to B_η. The specific chemical interactions are the result of the increase in the concentration [KCl] of the ions, which include the charge transfer forces, and other complex forces form which interact between the two species. Therefore, these chemical effects contribute negative values of B_σ. The structural effects that arise from the geometrical fitting of one component into the other are due to the different molar volumes and free volumes of pure components and positive contributions to A_Y.

3.3. *The concentration of ions (K^+, Cl^-) dependence of the transport properties*

Figure 4(a) and (b) show the influence of the KCl salt on the parameters $\sigma_{0,\mathrm{VFT}}$ and A_σ that give the best fit in the Equations (1) and (2), respectively, for the conductivity σ, which increases with the concentration of ions (K^+, Cl^-).

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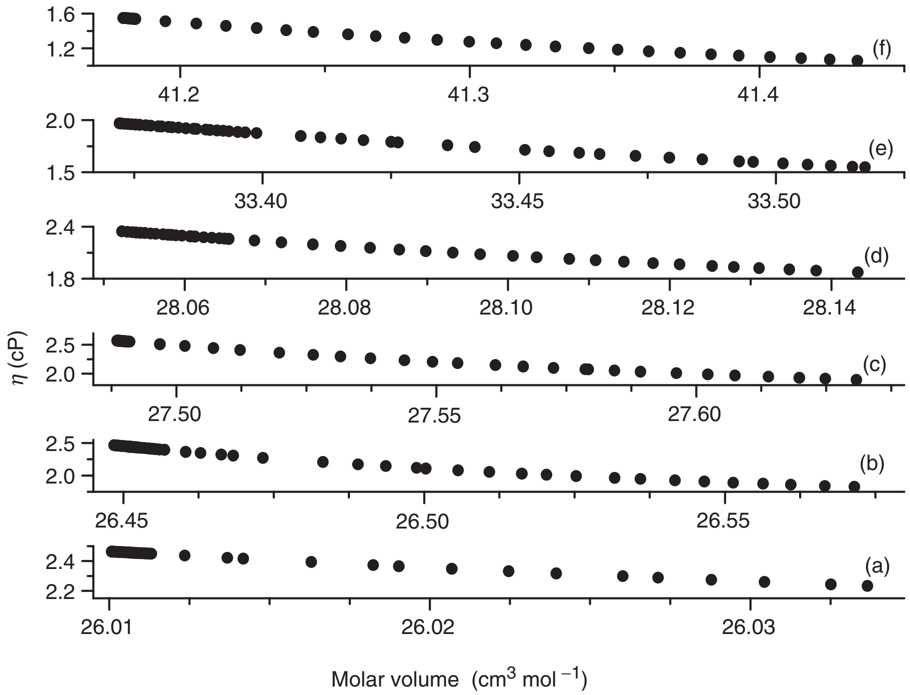

Figure 3. Molar volume (V) dependence on the viscosity (η) of IBAW + KCl for different values of KCl salt concentrations: (a) 0 M, (b) 5×10^{-4} M, (c) 5×10^{-3} M, (d) 10^{-2} M, (e) 5×10^{-2} M, (f) 10^{-1} M; M is moles of [KCl] per kilogram of liquid–liquid critical mixture.

Table 3. Least-squares fitted values of the parameters of Equation (3) for IBAW + KCl systems as functions of different values of KCl salt concentrations.

Systems	A_σ (mS cm^{-1}) A_η (cP)	B_Y (cm^3 mol^{-1})	V_{0Y} (cm^3 mol^{-1})
IBAW	1.293 (8.4521)	−0.7101 (0.3893)	25.3251 (24.4322)
IBAW + 5×10^{-4} M [KCl]	1.984 (4.7241)	−1.7081 (0.2411)	26.1013 (25.1011)
IBAW + 5×10^{-3} M [KCl]	2.455 (3.9152)	−1.1070 (0.0733)	27.3573 (26.5262)
IBAW + 10^{-2} M [KCl]	2.797 (2.2571)	−0.0942 (0.0384)	28.3422 (27.7991)
IBAW + 5×10^{-2} M [KCl]	4.299 (1.8173)	−0.0681 (0.0232)	33.6060 (33.2212)
IBAW + 10^{-1} M [KCl]	4.799 (1.4820)	−0.0202 (0.0091)	41.5271 (41.0993)

Note: Values for the viscosity are given in parentheses.

The curves in Figure 4(c) and (d) show that the parameters $\eta_{0,\mathrm{VFT}}$ and A_η that give the best fit in the Equation (1) and (2), respectively, of the viscosity η *versus* the concentration of ions (K^+, Cl^-) have the same character. They show a monotonic drop in the values of $\eta_{0,\mathrm{VFT}}$ and A_η, with a decrease in the ion content within the whole range of mixture compositions.

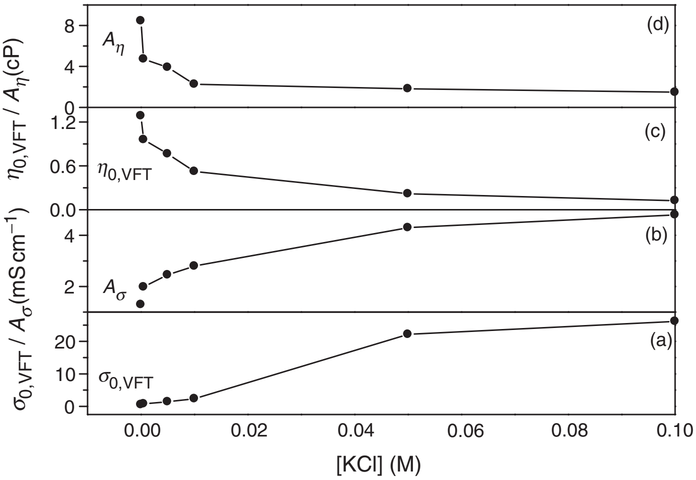

Figure 4. Parameters $\sigma_{0,\mathrm{VFT}}$, A_σ, $\eta_{0,\mathrm{VFT}}$, and A_η as a function of the molar concentrations [KCl] of ions. $\sigma_{0,\mathrm{VFT}}$ and $\eta_{0,\mathrm{VFT}}$ are obtained from a fit of Equation (1). A_σ and A_η are obtained from a fit of Equation (2).

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On the other hand, water is amphiteric and it is both a proton donor and a proton acceptor in terms of hydrogen bonding. Isobutyric acid is also amphiteric: it has an acidic hydrogen and two lone electron pairs on each oxygen. Isobutyric acid is capable of functioning as a base. Therefore, the deviation of the parameters $\sigma_{0,\mathrm{VFT}}$, A_σ, $\eta_{0,\mathrm{VFT}}$, and A_η are an indication of strong heteromolecular interaction in the liquid mixtures, which can be attributed to specific interactions: hydrogen bonding, molecular association, charge transfer, dipole–dipole and dipole-induced dipole interactions [12]. In the acid–water–KCl systems, the following interactions may be occurring:

- Ion-charged group interactions between the K^+ and the COO^- group of acids and between Cl^- and H^+ of the acids and water.
- Ion-non-polar group interactions between K^+, Cl^- and the non-polar groups of the isobutyric acid.

According to the co-sphere overlap model [13], the ion-charged group interactions would lead to positive parameters of $\sigma_{0,\mathrm{VFT}}$, A_σ, $\eta_{0,\mathrm{VFT}}$ and A_η, whereas ion-non-polar group interactions will result in negative parameters of $\sigma_{0,\mathrm{VFT}}$, A_σ, $\eta_{0,\mathrm{VFT}}$ and A_η. The overall $\sigma_{0,\mathrm{VFT}}$, A_σ, $\eta_{0,\mathrm{VFT}}$ and A_η parameter values obtained experimentally consist of these two opposite contributions. Since positive $\sigma_{0,\mathrm{VFT}}$, A_σ, $\eta_{0,\mathrm{VFT}}$ and A_η parameter values were observed for all the liquid mixtures studied, we concluded that the contribution of ion-charged group interactions to parameters of $\sigma_{0,\mathrm{VFT}}$, A_σ, $\eta_{0,\mathrm{VFT}}$ and A_η dominates that of the ion-non-polar group interactions.

A final remark concerns the vicinity of critical temperature; one can clearly see from close observation of Figure 4 that $\sigma_{0,\mathrm{VFT}}$, A_σ, $\eta_{0,\mathrm{VFT}}$ and A_η have not been affected by the correlation of the concentration fluctuations. Indeed, we did not detect any anomaly. Consequently, there will be a significant degree of hydrogen bonding, leading to strong correlation between molecules.

4. Conclusions

The main conclusions of this work could be summarised as follows:

1. New and accurate experimental results on density, viscosity, and electrical conductivity for six concentrated binary ionic mixtures of isobutyric acid–water with X M [KCl] are presented.
2. The electrical conductivities and viscosities of the present systems vary non-linearly with the molar volume.
3. The molar volume data dependence of viscosity and conductivity have been fitted to an equation similar to VTF based on the free volume model.
4. The intrinsic volumes V_{0Y} obtained from the conductivity and viscosity increase non-linearly with increasing concentrations of the KCl salt.
5. It is well known that the thermophysical properties of liquid systems, such as density, viscosity, and electrical conductivity among others, are strictly related to the molecular interactions present in different binary liquid mixtures. The variation of these properties with composition gives us important data about intermolecular interactions and the structures.

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