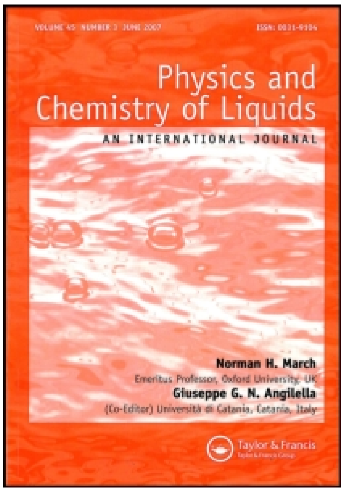

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# Excess permittivity and excess conductivity of binary fluid mixture isobutyric acid - water along the coexistence curve

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# Excess permittivity and excess conductivity of binary fluid mixture isobutyric acid – water along the coexistence curve

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Excess permittivity and excess conductivity of the binary fluid mixture isobutyric acid–water (I–W) have been computed at three temperatures and along the coexistence curve, on the basis of refractive index and electrical conductivity data of the mixture. The other related properties, molar volume, molar refraction and polarisablities have also been reported. The temperature dependence of the molar refraction was also examined. The results have been interpreted in terms of the nature of specific intermolecular interactions between the components.

**Keywords:** permittivity; polarisability; molar refraction; Lorentz–Lorenz relation; electrical conductivity

## 1. Introduction

Studies of the physical properties of liquid mixtures are important for understanding the thermophysics of such systems and for their use in chemical engineering industry. Among physico-chemical properties, the refractive index, electrical conductivity of liquid mixtures has received attention both for its significance and relative simplicity in performing the measurements. Actually, the refractive index correlates to density, by serval theorical and empirical expressions [1–6]. In fact, linear, optical properties of liquid and liquid mixtures have been widely studied to obtain information on their physical, chemical and molecular properties. Also, studies on the transport properties of liquid mixtures are of great importance to obtain information as to the salvation and association behaviour of ions in solutions.

Earlier, we have reported data on heat capacity and excess molar heat capacities [7], excess molar volume and excess viscosity [8] for the binary mixture (I–W), in order to investigate the molecular interactions in the solution. Subsequently, we measured the electrical conductivity and the refractive indices in the homogeneous phase at three temperatures $T = 302.15\,\mathrm{K}$; $T = 305.15\,\mathrm{K}$ and $T = 308.15\,\mathrm{K}$ over the entire concentration range of the binary system (I–W). The permittivity $\varepsilon$ was also calculated from refractive indices values. The experimental data has been used to calculate excess properties and the

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results are used to understand molecular behaviour and nature of solute–solvent interactions.

## 2. Experimental details

### 2.1. *Simple preparation*

The isobutyric acid (IBA) was purchased from Reidel de Haën (Germany). The purity was stated to be 99.99 mol %, the main impurities is probably water. The water was obtained from deionised operation, and has a specific conductivity of about $10^{-6}\,\Omega^{-1}\,\text{cm}^{-1}$.

These gave a critical separation temperature, which is a good indication of purity of $T_c = 26.945°\text{C}$ that compared favourably with 26.945°C for data of [9–11]. All electrolytes were prepared from weight was obtained with a resolution of 0.1 mg. Same care were taken to avoid moisture and dust in the final simple, namely, baking the syringes and the cells overnight under vacuum and preparing the mixtures in a dust-free area. The isobutyric acid and water were mixed together with salt in a high-precision parallelepipedic cell. The critical masse fraction of acid (IBA) was 0.389, which corresponds to $x_c = 0.113$ critical masse fraction.

### 2.2. *Refractive index measurement*

Refractive indices were measured with the help of a thermostated Abbe refractometer. Calibration of the instrument was done by measuring the refractive indices of doubly distilled water at known temperatures [12]. The sample mixtures were directly injected into the prism assembly of the instrument by means of an airtight hydrodynamic syringe. When the liquid mixtures attained constant temperature, the refractive index measurements were made. The error in refractive index measurements was less than ±0.0001 units. The temperature of the solutions was maintained constant in an electronically controlled thermostatic water bath attached with the refractometer.

### 2.3. *Electrical conductivity measurement*

The electrical conductivity data we present have been measured using a commercial conductometer of Phywe. We have employed a special designed measurement cell suitable for low-conductivity measurement (with a cell constant of $C = 0.875\,\text{cm}^{-1}$). The temperature was measured using a quartz thermometer (HP 2804A) giving a resolution of 0.1 mK. The measurement procedure has been designed to obtain the maximum resolution and to avoid contamination of the samples. Before any measurement session the conductometer is calibrated with a certified 0.001 M de KCl solution, thus the resolution of the apparatus is 1% (or $1\,\text{nS}\,\text{cm}^{-1}$ depending on the measured $\sigma$ value). After calibration, the cell containing the solution was immersed in a thermally stabilised bath with good thermal regulation. The long-term stability of the cell was better than 3 mK. When the temperature of the simple is stable, we performed the measurement as soon as possible (a few seconds) to neglect no desired effects that would modify the measured values (as self-heating of the samples, ionization in the electrodes…) [13], and proceed to change the temperature for the next measurement. The measurement where reproducible over several weeks, showing that the glass electrode are not reacting with acid.

## 3. Results

### 3.1. *Excess optical properties*

The permittivity $\varepsilon$, of non-polar solvents can be determined by both the properties the isolated molecules and the effects of the molecular interactions. At different densities, the variations of permittivity with temperature are calculated from theories that take account only of pair interactions. The Classic calculation of the average field at a molecule due to identically polarized neighbours in a structure of cubic symmetry lead to the Clausius–Mossotti equation, which related a microscopic property $\varepsilon$ [14,15]:

$$\left[\frac{(\varepsilon-1)}{(\varepsilon+2)}\right]=\frac{4\pi}{3}\alpha\rho, \tag{1}$$

where $\rho$ is the density, $M$ the molecular weight and $\alpha$ the total polarisability of the isolated molecule, assumed to be independent of interactions with neighbours.

However, it is known from Maxwell's theory for electromagnetic materials the permittivity is related to the refractive index as follows [16–19]:

$$\varepsilon=n^2. \tag{2}$$

Using the values of measured refractive index and according to the Maxwell's theory ($\varepsilon=n^2$) for transparent non-magnetic materials (permiability $\approx$1), we are able to calculate the optical permittivity ($\varepsilon$) along the coexistence curve and mentioned temperatures. The dependence of permittivity with acid composition at given temperatures are presented in Figure 1.

From the values of density, the binary mixture was treated as a pure solvent and molar volume ($V$) was calculated using the relation:

$$V=\frac{(x_1M_1+x_2M_2)}{\rho}, \tag{3}$$

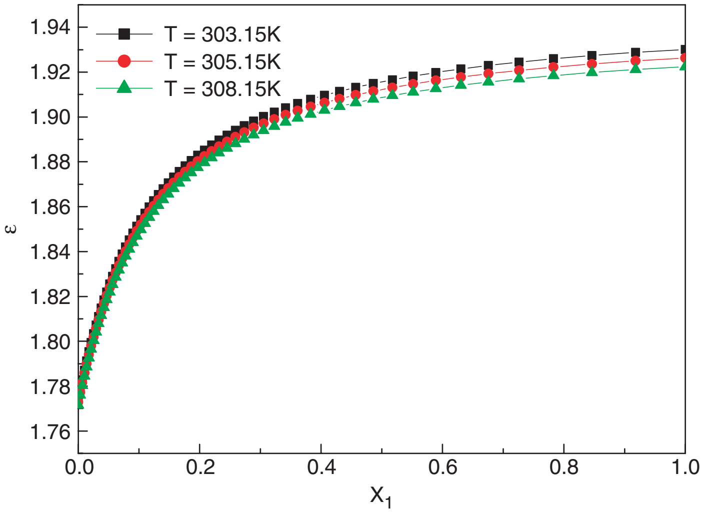

Figure 1. Variations of the optical permittivity $\varepsilon$ of (I–W) mixture, as function of isobutyric acid composition ($x_1$) and for three temperatures $T=302.15$ K; 305.15 K and 308.15 *K*.

Table 1. Molar volume $V$ ($\mathrm{cm^3\,mol^{-1}}$) and permittivity $\varepsilon$ of (I–W) mixture at three temperatures $T = 302.15$ K; $T = 305.15$ K and $T = 308.15$ K.

| | $T = 302.15$ K | | $T = 305.15$K | | $T = 308.15$ K | |
|---|---|---|---|---|---|---|
| $x_1$ | $V$ | $\varepsilon$ | $V$ | $\varepsilon$ | $V$ | $\varepsilon$ |
| 0 | 17.0759 | 1.77401 | 17.0927 | 1.7729 | 17.1096 | 0 |
| 0.010 | 17.7737 | 1.7994 | 17.7930 | 1.7858 | 17.8121 | 0.0102 |
| 0.021 | 18.5478 | 1.8110 | 18.5701 | 1.7980 | 18.5930 | 0.0214 |
| 0033 | 19.4132 | 1.8147 | 19.4385 | 1.8095 | 19.4650 | 0.0336 |
| 0.047 | 20.3831 | 1.8220 | 20.4128 | 1.8203 | 20.4437 | 0.0470 |
| 0.056 | 21.0848 | 1.8289 | 21.1165 | 1.8272 | 21.1494 | 0.0566 |
| 0.062 | 21.4629 | 1.8323 | 21.4967 | 1.8305 | 21.5318 | 0.0617 |
| 0.072 | 22.2482 | 1.8389 | 22.2838 | 1.8370 | 22.3213 | 0.07255 |
| 0.083 | 23.0906 | 1.8452 | 23.1285 | 1.8432 | 23.1684 | 0.0840 |
| 0.090 | 23.5503 | 1.8482 | 23.5906 | 1.8462 | 23.5008 | 0.0901 |
| 0.103 | 25.0119 | 1.8570 | 25.0559 | 1.8549 | 25.1018 | 0.1098 |
| 0.124 | 26.0727 | 1.8599 | 26.1209 | 1.8604 | 26.1720 | 0.1243 |
| 0.132 | – | 1.8653 | 26.6967 | 1.8630 | 26.7481 | 0.1320 |
| 0.140 | 27.2662 | 1.8680 | 27.3165 | 1.8656 | 27.3700 | 0.1400 |
| 0.166 | 29.2262 | 1.8757 | 29.2850 | 1.8732 | 29.3470 | 0.1664 |
| 0.208 | 32.2944 | 1.8852 | 32.3654 | 1.8825 | 32.4410 | 0.2079 |
| 0.232 | 34.1259 | 1.8897 | 34.2053 | 1.8869 | 34.2900 | 0.2320 |
| 0.323 | 40.9611 | 1.9021 | 41.0646 | 1.8990 | 41.1755 | 0.3229 |
| 0.457 | 51.1219 | 1.9132 | 51.2621 | 1.9098 | 51.4133 | 0.4572 |
| 0.486 | 53.3889 | 1.9149 | 53.5386 | 1.9114 | 53.6992 | 0.4861 |
| 0.630 | 64.4834 | 1.9214 | 64.6709 | 1.9178 | 64.8724 | 0.6303 |
| 0.782 | 76.4901 | 1.9259 | 76.7219 | 1.9222 | 76.9714 | 0.7827 |
| 1 | 93.7879 | 1.9302 | 94.0884 | 1.9263 | 94.4140 | 1 |

where $x_1$, $M_1$ and $x_2$, $M_2$ are the mole fraction and the molecular weight of the Isobutyric acid (I) and Water (W), respectively, and $\rho$ is the density of the mixture (I–W) that was reported in [8]. The values of determined permittivity and those of the molar volume $V$ are presented in Table 1.

From the values of determined permittivity, molar refractions $R_m$, were calculated using the relation proposed by Lorentz–Lorenz:

$$R_m = \frac{[(\varepsilon - 1)/(\varepsilon + 2)]}{V}. \tag{4}$$

The values of $R_m$ were uncertain with ±0.3%.

As the excess heat capacity measurements have great importance, this property being mainly related to specific interactions. In the same way, the molar refraction gives an account of the dispersion forces, which represent only a part of energetic contribution of the heat of mixing and are usually masked by other effects. Since the molar refraction depend on the composition of the solution and (slightly) on the temperature [20], the information about intermolecular forces existing in the pure liquids and liquid mixtures can be obtained from the dependence of $R_m$ on composition and temperature.

In order to gain further information about specific intermolecular interactions of any kind, the electronic polarisability of the system is computed. The values of $R_m$ are listed in Table 2 along with the value of $\alpha$.

Table 2. Polarisability $\alpha$ ($\mathrm{cm^3\,g^{-1}}$) and molar refraction $R_m$ ($\mathrm{cm^3\,mol^{-1}}$) of (I–W) mixture at $T = 302.15$ K; 305.15 K and 308.15 K.

| | $T = 302.15$ K | | $T = 305.15$ K | | $T = 308.15$ K | |
|---|---|---|---|---|---|---|
| $x_1$ | $\alpha$ | $R_m$ | $\alpha$ | $R_m$ | $\alpha$ | $R_m$ |
| 0 | 0.0491 | 3.502 | 0.04915 | 3.5014 | 0.0491 | 3.5002 |
| 0.010 | 0.0497 | 3.6939 | 0.04972 | 3.6932 | 0.049 | 3.6922 |
| 0.021 | 0.050 3 | 3.9025 | 0.05028 | 3.9018 | 0.0502 | 3.9009 |
| 0033 | 0.0508 | 4.1313 | 0.05084 | 4.1306 | 0.0508 | 4.1297 |
| 0.047 | 0.0514 | 4.3837 | 0.05143 | 4.3832 | 0.0514 | 4.3823 |
| 0.056 | 0.0518 | 4.5647 | 0.0518 | 4.5640 | 0.0518 | 4.5630 |
| 0.062 | 0.0520 | 4.6614 | 0.0520 | 4.6609 | 0.0520 | 4.6599 |
| 0.072 | 0.0524 | 4.8617 | 0.0524 | 4.8609 | 0.0523 | 4.8599 |
| 0.083 | 0.0527 | 5.0753 | 0.0527 | 5.0743 | 0.0527 | 5.0733 |
| 0.090 | 0.0529 | 5.1910 | 0.0529 | 5.1901 | 0.0526 | 5.1600 |
| 0.103 | 0.0535 | 5.5577 | 0.0534 | 5.5565 | 0.0534 | 5.5549 |
| 0.124 | 0.0538 | 5.8228 | 0.0538 | 5.8216 | 0.0537 | 5.8203 |
| 0.132 | – | – | 0.0539 | 5.9643 | 0.0539 | 5.9625 |
| 0.140 | 0.0542 | 6.1188 | 0.0541 | 6.1171 | 0.0541 | 6.1153 |
| 0.166 | 0.0546 | 6.6035 | 0.0546 | 6.6020 | 0.0546 | 6.6004 |
| 0.208 | 0.0552 | 7.3581 | 0.0552 | 7.3568 | 0.0552 | 7.3557 |
| 0.232 | 0.0556 | 7.8058 | 0.0556 | 7.8049 | 0.0556 | 7.8043 |
| 0.323 | 0.0565 | 9.4700 | 0.0565 | 9.4688 | 0.0565 | 9.4684 |
| 0.457 | 0.0575 | 11.9299 | 0.0575 | 11.9286 | 0.0575 | 11.9290 |
| 0.486 | 0.0577 | 12.4768 | 0.0577 | 12.4758 | 0.0577 | 12.4765 |
| 0.630 | 0.0585 | 15.1515 | 0.0585 | 15.1950 | 0.0585 | 15.1510 |
| 0.782 | 0.0593 | 18.0405 | 0.0592 | 18.0392 | 0.0593 | 18.0415 |
| 1 | 0.0601 | 22.1970 | 0.0601 | 22.1980 | 0.0601 | 22.2023 |

The Lorentz–Lorenz relation can be derived in a number of ways with correction terms which depend on the assumptions and techniques [21]. In the limit where the mean polarisability approximated the average over all possible orientations of the molecule, the theories collapse to the Lorentz–Lorenz relation [22] stated here for a single component. When two or more components are present, than the Lorentz–Lorenz relation becomes [22–24]:

$$\left[\frac{(\varepsilon - 1)}{(\varepsilon + 2)}\right] = \frac{4\pi}{3}\sum_i \frac{m_i \alpha_i}{V}, \tag{5}$$

where the sum is over all the mass $m_i$ and polarisability $\alpha_i$. This can be rewritten from the case of two components using the refraction as:

$$R_m = \frac{4\pi}{3}(M_1 x_1 + M_2 x_2), \tag{6}$$

where $x_1$ and $M_1$ the molar fraction and the molecular weight of isobutyric acid and water, respectively.

As $R_m$ is affect values by the presence of isobutyric acid in the mixture, its provide information about intermolecular forces acting in the liquid mixture. The different methods of calculating the excess refractive properties $n^E$ found in the literature [25] make

Table 3. Excess permittivity $\varepsilon^E$ and excess refraction $R_m^E$ of studied mixture at $T = 302.15$ K; 305.15 K and 308.15 K.

| | $T = 302.15$ K | | $T = 305.15$ K | | $T = 308.15$ K | |
|---|---|---|---|---|---|---|
| $X_1$ | $\varepsilon^E$ | $R_m^E$ | $\varepsilon^E$ | $R_m^E$ | $\varepsilon^E$ | $R_m^E$ |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.0102 | 0.0115 | 6.2E-4 | 0.0113 | 4.8E-4 | 0.0113 | 6.4E-4 |
| 0.0213 | 0.0221 | 7.2E-4 | 0.0218 | 6.0E-4 | 0.0217 | 7.9E-4 |
| 0.0335 | 0.0318 | 0.0016 | 0.0314 | 0.0014 | 0.0312 | 0.0015 |
| 0.0469 | 0.0406 | 0.0037 | 0.0402 | 0.0036 | 0.0398 | 0.0038 |
| 0.0566 | 0.0461 | 0.0037 | 0.0456 | 0.0035 | 0.0451 | 0.0034 |
| 0.0617 | 0.0487 | 0.0051 | 0.0481 | 0.0051 | 0.0477 | 0.0051 |
| 0.0724 | 0.0536 | 0.0049 | 0.0530 | 0.0046 | 0.0524 | 0.0044 |
| 0.0839 | 0.0581 | 0.0032 | 0.0574 | 0.0027 | 0.0568 | 0.0022 |
| 0.0900 | 0.0602 | 0.0051 | 0.0595 | 0.0047 | 0.0588 | −0.0246 |
| 0.1029 | 0.0659 | 0.0034 | 0.0651 | 0.0026 | 0.0644 | 0.0016 |
| 0.1242 | 0.0692 | −0.0027 | 0.0684 | −0.0035 | 0.0676 | −0.0044 |
| 0.1320 | 0.0707 | – | 0.0699 | −0.0051 | 0.0691 | −0.006 |
| 0.1400 | 0.0722 | −0.0015 | 0.0713 | −0.0028 | 0.0704 | −0.0042 |
| 0.1664 | 0.0757 | −0.0102 | 0.0747 | −0.0113 | 0.0738 | −0.0126 |
| 0.2079 | 0.0788 | −0.0311 | 0.0777 | −0.0321 | 0.0767 | −0.0332 |
| 0.2320 | 0.0795 | −0.0338 | 0.0784 | −0.0345 | 0.0774 | −0.0352 |
| 0.3229 | 0.0778 | −0.0685 | 0.0766 | −0.0696 | 0.0756 | −0.0706 |
| 0.4572 | 0.0678 | −0.1194 | 0.0668 | −0.1208 | 0.0658 | −0.1217 |
| 0.4860 | 0.0650 | −0.1125 | 0.0640 | −0.1136 | 0.0631 | −0.1144 |
| 0.6303 | 0.0490 | −0.1343 | 0.0482 | −0.1362 | 0.0475 | −0.1375 |
| 0.7827 | 0.0298 | −0.0951 | 0.0292 | −0.0970 | 0.0288 | −0.0979 |
| 1 | 0 | 0 | 0 | 0 | 0 | 0 |

use of the volume and the mole fraction in the expression of the ideal mixing rule. These can be used to analyse the excess permittivity using:

$$\varepsilon^E = \varepsilon - (x_1\varepsilon_1 + x_2\varepsilon_2), \tag{7}$$

Where $\varepsilon$, $\varepsilon_1$, $\varepsilon_2$ are the optical permittivity of solution, isobutyric acid and water, respectively.

The $R_m$ values for the mixtures along the coexistence curve at three studied temperatures have been used to calculate excess molar refraction $R_m^E$ using:

$$R_m^E = R_m - (x_1 R_m^1 + x_2 R_m^2), \tag{8}$$

On the basis of the additive properties rule when the composition is expressed in mole fraction [26,27]. $R_m^1$ and $R_m^2$ are molar refraction of isobutyric acid and water. The values of $\varepsilon^E$ and $R_m^E$ are listed in Table 3.

### 3.2. *Excess electrical conductivity*

Electrical conductivity of the binary fluid mixture (I–W) are measured along the coexistence curve at three temperatures $T = 302.15$ K; 305.15 K and 308.15 K. Figure 6, display the experimental variations of the electrical conductivity of the pure

Table 4. Electrical conductivity $\sigma$ ($\mathrm{mS\,cm^{-1}}$) and excess conductivity $\sigma^E$ ($\mathrm{mS\,cm^{-1}}$) of studied mixture at $T = 302.15\,\mathrm{K}$; 305.15 K and 308.15 K.

| | $T = 302.15\,\mathrm{K}$ | | $T = 305.15\,\mathrm{K}$ | | $T = 308.15\,\mathrm{K}$ | |
|---|---|---|---|---|---|---|
| $X_1$ | $\sigma$ | $\sigma^E$ | $\sigma$ | $\sigma^E$ | $\sigma$ | $\sigma^E$ |
| 0 | 1.7062 | 0 | 1.7565 | 0 | 1.8234 | 0 |
| 0.0102 | 1.5117 | −0.1770 | 1.5630 | −0.1755 | 1.6209 | −0.1838 |
| 0.0214 | 1.3172 | −0.3525 | 1.3695 | −0.3494 | 1.4185 | −0.3660 |
| 0.0336 | 1.1227 | −0.5262 | 1.1760 | −0.5215 | 1.2161 | −0.5462 |
| 0.0470 | 0.9360 | −0.6900 | 0.9895 | −0.6845 | 1.0213 | −0.7166 |
| 0.0567 | 0.8263 | −0.7833 | 0.8782 | −0.7788 | 0.9059 | −0.8144 |
| 0.0617 | 0.775 | −0.8254 | 0.8263 | −0.8218 | 0.8522 | −0.8588 |
| 0.0725 | 0.6813 | −0.9012 | 0.7292 | −0.9000 | 0.7523 | −0.9392 |
| 0.0840 | 0.5964 | −0.9665 | 0.6407 | −0.9683 | 0.6615 | −1.0090 |
| 0.0901 | 0.5571 | −0.9954 | 0.5996 | −0.9987 | 0.6193 | −1.0401 |
| 0.1029 | 0.4506 | −1.0683 | 0.4868 | −1.0768 | 0.5042 | −1.1193 |
| 0.1243 | 0.3883 | −1.1059 | 0.4201 | −1.1180 | 0.4363 | −1.1609 |
| 0.1320 | 0.3594 | −1.1216 | 0.3891 | −1.1356 | 0.4046 | −1.1785 |
| 0.1400 | 0.3320 | −1.1352 | 0.3595 | −1.1510 | 0.3745 | −1.1939 |
| 0.1664 | 0.2577 | −1.1645 | 0.2789 | −1.1853 | 0.2923 | −1.2280 |
| 0.2079 | 0.1750 | −1.1765 | 0.1884 | −1.2030 | 0.1998 | −1.2451 |
| 0.2320 | 0.1395 | −1.1708 | 0.1494 | −1.1996 | 0.1598 | −1.2413 |
| 0.3229 | 0.0527 | −1.1026 | 0.0540 | −1.1354 | 0.0604 | −1.1753 |
| 0.4572 | 7.9E-4 | −0.9254 | 8.1E-4 | −0.9528 | 0.0080 | −0.9832 |
| 0.4861 | 7E-4 | −0.8762 | 7.2E-4 | −0.9022 | 0.0076 | −0.9311 |
| 0.6303 | 5E-4 | −0.6303 | 4E-4 | −0.6492 | 0.006 | −0.6701 |
| 0.7828 | 3.5E-4 | −0.3705 | 5.5E-4 | −0.3813 | 0.0047 | −0.3940 |
| 1 | 2E-4 | 0 | 4E-4 | 0 | 0.0033 | 0 |

(I–W), as function of isobutyric acid composition and the three mentioned temperatures in the homogeneous phase.

On the base of the experimentally determined electrical conductivity data, we have calculated the excess electrical conductivity using the relation:

$$\sigma^E = \sigma - (x_1\sigma_1 + x_2\sigma_2), \tag{9}$$

where $\sigma$, $\sigma_1$, $\sigma_2$ are the electrical conductivity of mixture (I–W), isobutyric acid and water, respectively. The values of $\sigma^E$ are summarised in Table 4 and the change in excess conductivity of the mixture by change of acid composition and temperature are shown in Figure 7.

## 4. Discussion

Increased interest in the optical properties of liquid and liquid mixtures led us to determine the optical permittivity, which was used to calculate the molar refraction from Lorentz–Lorenz equation. As evident from Figure 2, $R_m$ is proportional to the dispersive forces, the increasing magnitude of $R_m$ of (I–W) mixture for all temperature, shows strong interactions between the isobutyric acid and water molecules. In general, the polarisability consists of two contributions, the one measuring the ease with which the molecules are

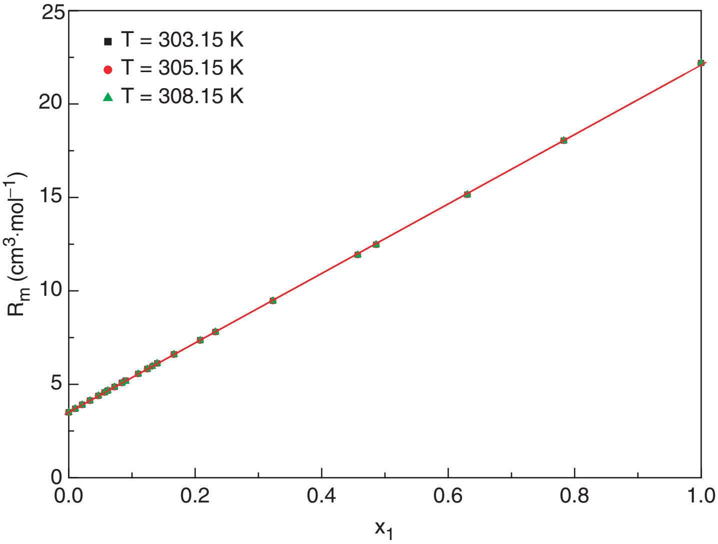

Figure 2. Molar refraction $R_m$ of (I–W) mixture at $T = 302.15$ K; 305.15 K and 308.15 K.

deformed by an electric field and the other due to the orientation of the molecular dipoles under the action of this field. The second effect depends on 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. Since we measured the refractive indexes in the optical region, the polarisability should not include orientational effects. Therefore, the molar refraction should not depend on $T$ over a small temperature range, as can be seen in Figure 2. This shows that $R$ values can, in fact, be associated with electronic polarisabilities.

An inspection of Figure 3 show that the polarisability of the study mixture increases monotonously with acid composition. This trend is slightly influenced by temperature and obvious decrease with temperature indicates the presence of intermolecular and intermolecular interactions between the isobutyric acid and water molecules. From Figure 3, the polarisability of isobutyric acid and water at the three studied temperature were determined to be $\alpha_1 = 0.059\,\text{cm}^3\,\text{g}^{-1}$ and $\alpha_2 = 0.0488\,\text{cm}^3\,\text{g}^{-1}$, respectively, which are in agreement with the values obtained by Jacobs [28] and those in [29].

Figure 4, shows that for all studied temperatures $\varepsilon^E$ are positive over the entire concentration range. Thus, dispersion forces in the solutions are higher than in the mixed solvent. Moreover, the $\varepsilon^E$ data decreases as temperature increases. It can be seen from Figure 5 that the shapes of $R_m^E$ curves changes with acid composition and their changes can be interpreted qualitatively by the consideration of the molecular interactions in solution, $R_m^E$ values are negatives over a large part of the concentration range for the systems of (I–W). $R_m^E$ appears to be positive at the water-rich region and have a maximum at $x_c = 0.11$ (critical composition), which is the effect of strong correlations on $R_m^E$ between water and isobutyric acid molecules which began at $x_c$. In the other composition range $x > 0.2$, $R_m^E$ are negative with the largest magnitude of negative values obtained in the zone of [0.5–0.7] acid mole fraction. This result is not surprising, because of the molecular correlations between water and isobutyric acid are feeble in this region. Moreover, the

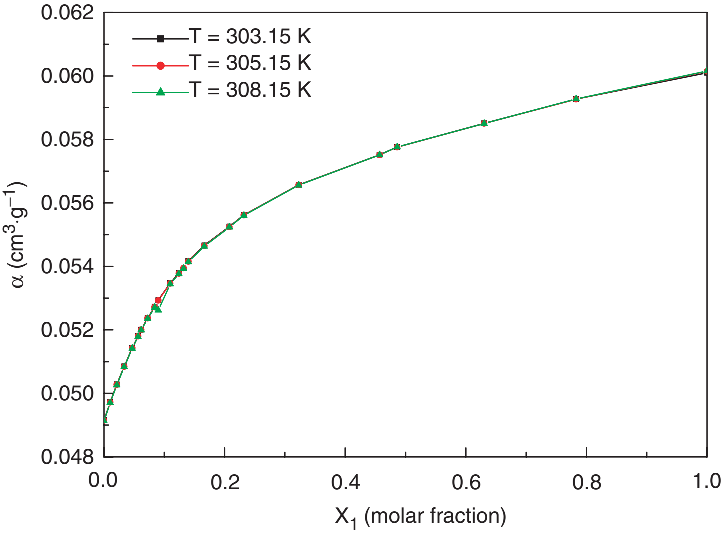

Figure 3. Polarisability $\alpha$ of (I–W) mixture at $T = 302.15$ K; 305.15 K and 308.15 K.

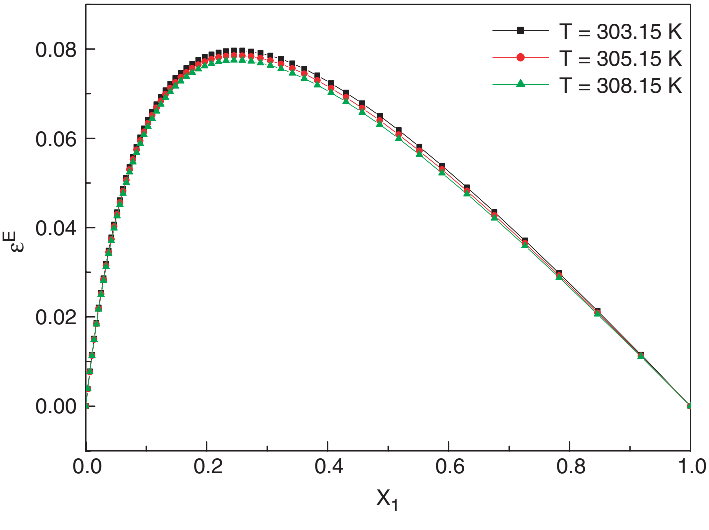

Figure 4. Variation of excess permittivity $\varepsilon^E$ of (I–W) mixture as function acid composition at $T = 302.15$ K; 305.15 K and 308.15 K.

$R_m^E$ data decreases as the temperature increases; this is attributed to the predominance of the contributions to $R_m^E$ arising from the dipolar induction and dispersion forces.

It is clear from Figure 6 that the electrical conductivity $\sigma$ *versus* the Isobutyric acid composition have similar character for studied temperatures. We note that electrical conductivity exhibits a slight decrease with increase isobutyric acid concentration. The relative conductivity changes are significantly larger for compositions larger than the

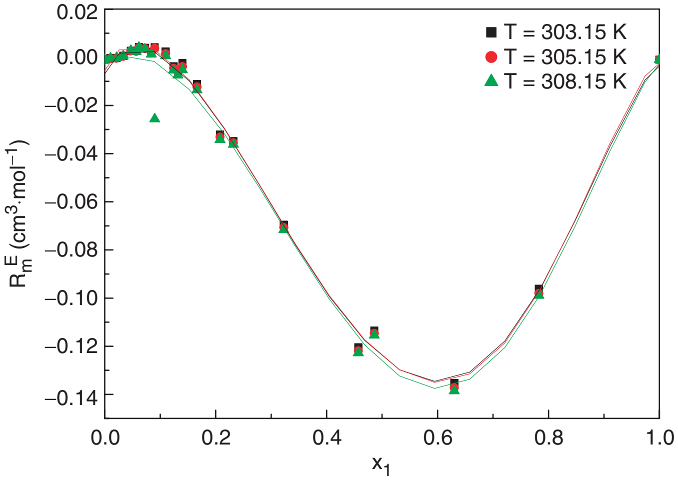

Figure 5. Excess molar refraction $R_m^E$ along the coexistence curve at studied temperatures.

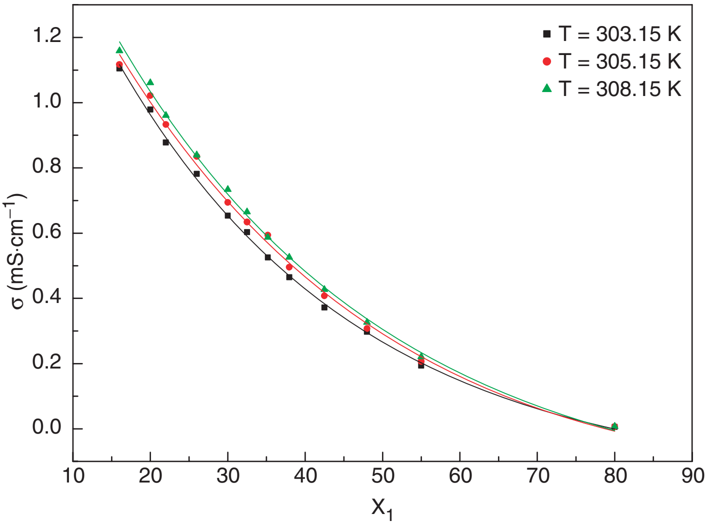

Figure 6. Variations of the electrical conductivity $\sigma$ of (I–W) mixture, as function of isobutyric acid composition ($x_1$) and for three temperatures $T = 302.15$ K; 305.15 K and 308.15 K.

critical composition. Our results might be attributed to the decrease in the ion mobility with increasing concentration of isobutyric acid observed in [30].

The excess conductivity, shown in Figure 7, is a concave parabola, this indicates that the conductivity of the mixture is smaller than the sum of the linear contribution of the pure components at the corresponding concentrations.The negative deviation results from the increase of the ionic interacting forces in the mixture relative to those present in the pure components. The ionic mobility is thereby decreased. Hence the conductivity of the mixture is reduced. It can also be seen from Figure 7, that the maximum of $\sigma^E$ is obtained

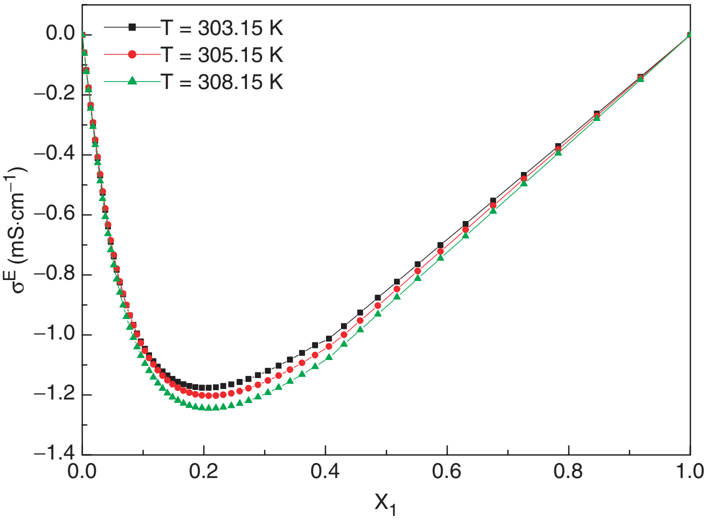

Figure 7. Excess conductivity along the coexistence curve at the three mentioned temperatures.

in the region of [0.11–0.3] mole fraction, which represent the critical region around $x_c = 0.113$. This result is not surprising because of the strong molecular correlations between water and isobutyric acid in the vicinity of $x_c$, which is characterised by a correlation length according to the scaling law:

$$\xi = \xi_0 \left(\frac{T - T_C}{T_C}\right)^{-\nu} \left[1 + a_\xi \left(\frac{T - T_C}{T_C}\right) + \cdots\right], \tag{10}$$

where $\xi_0$ is the critical amplitude of (I–W) mixtures and $\nu$ is the universal critical exponent ($\nu = 0.63$). The correlation length $\xi$ diverges at $T = T_C$ and all molecules of isobutyric acid were correlated with water molecules. This phenomenon is well-known for the critical mixture. In the rich region of the water, the $\sigma^E$ increase when $T$ tends to $T_c$ and $x_1$ tends to $x_c$ and in acid rich region, $\sigma^E$ decreases when $x_1$ increases.

## 5. Conclusion

In summary, new and accurate experimental results on permittivity, and electrical conductivity at 302.15 K, 305.15 K and 308.15 K for the binary mixture of isobutyric acid and water are presented. From these data, polarizability, excess refraction, excess permittivity, excess electrical, conductivity molar refractivity have been computed. These results are discussed in terms of molecular interactions between the mixing components. Such data are useful to understanding the solvation process in binary mixtures.

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