Impedance spectroscopy of binary solutions

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The dielectric properties of three binary mixtures of different molar ratios have been investigated in the frequency range 1 Hz to $10^6$ Hz at 25°C. The variation of ac conductivity with molar ratio of acetone-chloroform is typical of that observed for ideal binary solution. For methanol–water and ethyl ether–water a sudden change has been observed in the conductivity at 30% by mass methanol and 20% by mass ethyl ether, respectively. The same phenomenon has been observed in all other electrical variables. This is attributed to the trend of the partial molar volumes of the different binary mixtures.

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Impedance spectroscopy is an appropriate technique to obtain information about the electrical characteristics and the relaxation phenomena of solid materials and binary solutions. Using this technique the electrical parameters such as permittivity, electric modulus, impedance and admittance can be determined as a function of frequency which can be related with the microstructure of the system. Therefore, to have a better understanding of the microstructure of a liquid mixture sample, it is necessary to find the equivalent electrical response for the sample.

Different techniques were used to study the dielectric behavior of binary solutions. It was reported that in a solution of two liquids which shows a Debye behavior, a single relaxation time can often be experimentally obtained. However, different relaxation functions have been used successfully in the case of a single relaxation band (Debye, Cole-Cole, Cole-Davidson and Havriliak-Negami). The dielectric behavior of different binary solutions was reported in the literature.

In the present work, the electrical behavior of all three types of binary solutions is presented. The binary solutions studies are: acetone-chloroform, methanol–water and ethyl ether–water.

Materials and Methods

The impedance measurements were performed at 25°C in the frequency range 1 Hz to $10^6$ Hz for three binary mixtures of different molar ratios. The binary solutions investigated in the present case are: acetone-chloroform, methanol–water and ethyl ether–water. Binary solutions have been prepared from commercially available, high purity chemicals (Aldrich) without any further purification. The ac measurements were performed using a Solartron-1260 Impedance/gain Phase Analyzer, at zero dc bias in order to eliminate any effect due to electrode polarization, using a conductive cell with fixed electrode dimensions. The cell is standardly calibrated by the manufacturer, and its calibration had been checked using distilled and de-ionized water. The cell was connected to the apparatus through a four point connection. The apparatus was controlled by software packages which maximized the performance and data handling of the system. Using this technique the modulus and the phase angle of the ac impedance were measured. From these measurements the electrical parameters were determined.

Results and Discussion

Generally four electrical complex quantities were reported in terms of real and imaginary components as follows:

- Complex impedance $Z' = R_s - j \omega C_s = Z' - j Z''$
- Complex admittance $Y' = 1/Z' = R_s + j \omega C_p$
- Complex permittivity $\varepsilon' = \varepsilon' + j \varepsilon''$
- Complex modulus $M' = M' + j M''$

where the subscripts p and s refer to the equivalent parallel and series circuits respectively, $\omega$ is the angular frequency, $R$ and $C$ are the equivalent resistance and capacitance, respectively. The measured values of impedance and admittance depend...
on the dimension of the samples, a conductive cell with fixed electrodes dimension were used in our measurements, hence, the measured impedance can be used in analysis of the electrical behavior of binary solutions.

The real ($\varepsilon'$) and imaginary component ($\varepsilon''$) of dielectric relative permittivity are related with the real ($Z'$) and imaginary ($Z''$) of the complex impedance as follows:

\[
\varepsilon' = -\frac{Z'}{(Z'^2 + Z''^2)} \omega C_0
\]

\[
\varepsilon'' = -\frac{Z''}{(Z'^2 + Z''^2)} \omega C_0
\]

where $C_0$ is the vacuum capacitance of the cell.

The complex permittivity is a compliance as in the case of the mechanical compliance, and can be written to give an electric modulus $M' = 1 / \varepsilon'$, therefore the real ($M'$) and the imaginary ($M''$) components of electric modulus can be determined from the following relations

\[
M' = \varepsilon' / (\varepsilon'^2 + \varepsilon''^2)
\]

\[
M'' = \varepsilon'' / (\varepsilon'^2 + \varepsilon''^2)
\]

Here, it is obvious, that the complex permittivity and complex electric modulus contain the same information. For $M''$ relation the real component of permittivity appears in the denominator to the second order, its tendency to overwhelm the loss function is minimized.

Figures 1a, b and c show the real component of impedance ($Z'$) as a function of frequency for acetone-chloroform (AC), methanol-water (MW) and ethyl ether-water (EW), respectively. The variation of $Z'$ shows a resistive type behavior at low and high frequency regions where it is nearly constant with frequency. However, at intermediate frequency ($Z'$) three binary solutions show a high frequency fall-off as inverse of frequency which is mainly due to capacitive effects within the system. This high drop in $Z'$ is associated with well defined relaxation peaks as shown in Figs 2 a, b and c for AC, MW and EW, respectively. The general feature of $Z''$ variation with frequency indicates that the dependence of the sample and the cell equivalent to R-C network in parallel. Therefore, it is expected for such systems that the complex plane plots of $Z'$ vs. $Z''$ and $M'$ vs. $M''$ should yield semi-circles, the angular frequency of the peak maximum and centers of semi-circles coincide and given by the reciprocal of the conductivity $\sigma$ and the relaxation time $\tau$, where

Fig. 1(a, b, c)—Real component of impedance ($Z'$) vs. Frequency for acetone – chloroform, methanol – water, and ethyl ether – water, respectively.
\[ \omega_{\text{max}} = 2\pi f_{\text{max}} = 1/\tau = \sigma / \varepsilon_0 \varepsilon' \]

where, \( \varepsilon_0 \) and \( \varepsilon' \) are the permittivity of free space and relative permittivity respectively.

Nearly perfect semi-circles were constructed for the three binary solutions. The diameter of the semi-circle represents the bulk resistance of the sample. It is clear that the diameter of the semi-circles in the case of AC binary solution decreases with increase in the mass per cent of acetone which reflects again the behavior of an ideal solution. In the case of MW and EW a sudden change was observed at mass percent of 30\% and 20\%, respectively. This phenomenon is associated with a decrease in the intensity of the relaxation peak and a shift to a higher frequency. This may indicate that the relaxation of the binary solution is due to some onset of motions of the polar group. This motion is a rotational motion. The sudden change in the bulk resistance in the case of MW and EW, which has a deviation from the behavior of ideal solution, is due to the strong hydrogen bonding interaction between methanol and water and between ethyl ether and water.

The real component of impedance decreases, which consequently means an increase in the conductivity with increase in the mass ratio of acetone in the AC system. This represents the behavior of ideal mixtures. However, this behavior deviates in the other two binary systems; MW and EW, where it is observed that the impedance increases with increasing the mass ratio of methanol in the mixture up to \(~30\%\), then suddenly drops for mass ratio of 40\%. The same phenomenon was observed in EW system, where the sudden drop was observed at 20\% mass ratio of ethyl ether. This phenomenon was clearly observed in the plot of \( Z'' \) vs. \( Z' \) and in the plot of \( Z'' \) vs. \( f \). The bulk electrical conductivity can be determined from the complex impedance plots using the relation

\[ \sigma = (1/R)(L/A) \]

where, \( L \) is the distance between conductive cell electrodes and \( A \) is the area of the electrode deposited in the solution.

Figure 3 shows the plot of log \( \sigma \) vs. mass ratio for the three binary solutions. The variation of conductivity with mass ratio of AC is typical to that observed for ideal binary solution. However, for MW and EW a sudden change was observed in the conductivity at methanol mass ratio of 30\% for MW system and at ethyl ether mass ratio 20\% for EW.
Fig. 3—Log conductivity vs. Mass ratio for acetone – chloroform, methanol – water, and ethyl ether – water, respectively.

Fig. 4(a, b, c)—Real component of electric modulus ($M'$) vs. Frequency for acetone – chloroform, methanol – water, and ethyl ether – water, respectively.

system. Figures 4 and 5 show the frequency dependence of the real and imaginary parts of the complex electric modulus. The values of the real and imaginary parts of $M$ approaches zero at low frequency show that the electrode effect can be neglected in the modulus representation. The imaginary part of $M$ as a function of frequency in the semi log plot shows a symmetric peak for the three binary solutions indicating that a single relaxation mode is dominant in these systems (Debye relaxation type). On the other hand, a slight increase in the intensity of the relaxation peak was observed for AC binary solution, with a clear shift to higher frequency with increase in the acetone content. However, for MW at methanol mass ratio of 30% the peak of the relaxation occurs at the highest frequency and then shifts to a lower frequency with increase in the mass ratio of methanol. The same trend is observed for EW mixture at 20% mass ratio of ethyl ether.

The behavior of methanol–water can be explained by the behavior of the partial molar volume of the mixture. The partial molar volume of a substance $A$ in a mixture is the change in the total volume upon the addition of one mole of $A$ to a large excess of the mixture. This is defined formally as follows:

$$V_A = (\delta V/\delta n_A)_{\text{P.T.}}$$

where $V_A$ is the partial molar volume of substance $A$, $V$ is the total volume of the mixture, $n_A$ is the number of moles of $A$. This is a property of the mixture and does not show any effect of the solvent on the relaxation process.
of moles of $A$, $P$ and $T$ are the pressure and temperature of the system, respectively. The subscript $n$ signifies that the amounts of all other substances present in the mixture are constant.

The volume occupied by a given number of $A$ molecules depends on the identity of molecules that surround them. For a binary solution of methanol–water, the packing of the molecules, and hence the partial molar volume, depends on the mole fraction of each substance present in the solution. Experimental observations\textsuperscript{50} show that the partial molar volume of methanol in water, across the full composition range at 25 °C, has a “dip” near a mole fraction of 0.2 for methanol (this corresponds to ~ 30% by mass methanol). At this composition the solution is closely packed and the mixture has maximum density. A rigid molecular chain of methanol and water, due to strong hydrogen bonding, restricts the rotational motion of molecules in the binary mixture. This explains the lower impedance (high conductivity) and why it violates the general trend observed for solutions at other compositions. The same argument is applied for ethyl ether–water system, for which a minimum of impedance occurs at 20% by mass of ethyl ether in the mixture.

References


Fig. 5(a, b, c)—Imaginary component of electric modulus (M") vs. Frequency for acetone – chloroform; methanol – water, and ethyl ether – water, respectively.