Annual Academic Sessions 2011
ISSN 2012-9912; ©2011 Open University of Sri Lanka

EFFECT OF SOLVENT COMPOSITION AND SOLUTE CONCENTRATION ON CONDUCTIVITY IN MIXED SOLVENT SYSTEMS.

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INTRODUCTION

The studies of the thermodynamic and transport properties of liquid mixtures are essential in various industrial process areas such as fluid flow, mass, and heat transfer and also for the development of theoretical models for the molecular interactions in solutions. The intermolecular forces between the molecules of the liquid govern the magnitude of the energy of the molecule, but the problem of calculating it is immensely difficult and still largely unsolved. The nature of molecular motion can be obtained by studying the motion of ions in solution. The fundamental measurement used to study the motion of ions is that of the electrical conductance of the solution. In the study, the variation of conductivity with solvent composition and solute concentration is interpreted in terms of the intermolecular interactions. Viscosity is measure of the resistance of a fluid to flow. Walden's rule relates viscosity of a solution to the limiting molar conductivity of the electrolyte dissolved in it. This rule is used to derive an empirical equation that relates viscosity of the mixed solvents to that of their composition.

METHODOLOGY

The following ethanol-water mixed solvents were prepared using various ratios of redistilled ethanol and distilled water by volume at room temperature (32^{o}C).

Table 1: The solvent composition in different mixtures

Percentage of Ethanol solution (v/v %)	Added volume of Redistilled Ethanol (ml)	Added volume of Distilled water (ml)
00	00	100
10	10	90
20	20	80
30	30	70
40	40	60
50	50	50
60	60	40
70	70	30
80	80	20
90	90	10
100	100	00

Using each of these mixed solvent systems 0.1 mol dm^{-3}, 0.05 mol dm^{-3}, 0.02 mol dm^{-3}, 0.01 mol dm^{-3}, 0.005 mol dm^{-3}, 0.002 mol dm^{-3}, 0.001 mol dm^{-3} and 0.0005 mol dm^{-3} sodium chloride solutions were prepared by continuous dilution method. The conductivity meter was calibrated using the standard 0.100 mol dm^{-3} potassium chloride solution at room temperature (32^{o}C). Conductance of each sample was measured at room temperature (32^{o}C) using flask type model conductivity cell which was connected to the conductivity meter.

RESULTS AND DISCUSSION

The results obtained, when the conductance of different concentrations of sodium chloride in pure water, in ethanol and in various mixtures of these two solvents at 32^{o}C are given in Table1. The conductivity of pure ethanol, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% solutions of ethanol in pure water were measured. They were too small compared to the conductance of NaCl solutions and therefore neglected.

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Distilled water (%)	100	90	80	70	60	50	40	30	20	10	00
Distilled Ethanol (%)	00	10	20	30	40	50	60	70	80	90	100
Concentrations	Conductance (Siemens) * 10^{-2}										
0.1mol dm^{-3} NaCl(aq)	10.000	9.600	9.600	8.200	8.200	8.400	9.400	8.800	8.400	8.200	8.200
0.05 mol dm^{-3} NaCl(aq)	5.400	5.100	5.300	4.200	4.300	4.500	4.800	4.500	4.300	4.200	4.200
0.02 mol dm^{-3} NaCl(aq)	2.300	2.100	2.200	1.800	1.900	1.900	2.000	1.900	1.800	1.700	1.700
0.01 mol dm^{-3} NaCl(aq)	1.200	1.100	1.100	1.000	0.980	0.980	1.000	0.960	0.930	0.910	0.870
0.005 mol dm^{-3} NaCl(aq)	0.600	0.590	0.580	0.530	0.510	0.510	0.510	0.490	0.470	0.460	0.440
0.002 mol dm^{-3} NaCl(aq)	0.240	0.240	0.240	0.220	0.210	0.210	0.210	0.200	0.190	0.190	0.180
0.001 mol dm^{-3} NaCl(aq)	0.120	0.120	0.120	0.110	0.110	0.110	0.110	0.100	0.097	0.095	0.091
0.0005 mol dm^{-3} NaCl(aq)	0.062	0.062	0.061	0.058	0.056	0.053	0.053	0.051	0.049	0.048	0.047

Table 2: The conductance of NaCl with concentration and solvent composition

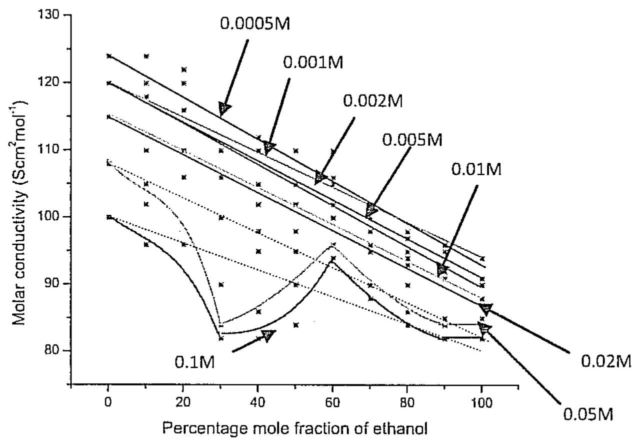

Figure 1: Plot of molar conductivity versus percentage mole fraction of ethanol for NaCl

The plots (Figure 1) of molar conductivity versus composition for sodium chloride at 32 ^{o}C, in dilute solutions (0.0005moldm^{-3}-0.02moldm^{-3}) follow a linear relationship and may be assumed to show the ideal behavior. In dilute solutions the ions are away from each other The long range ion-ion interactions are reduced. And short range solvent-solvent interactions and ion-solvent interactions contribute very little to the molar conductivity. Anomalous behavior is found in the case of concentrated solutions in the intermediate composition range (30-70%).In this composition range the two solvents are present in comparable amounts. The attraction forces between these two types of solvent molecules are approximately the same to consider them to form an ideal two component liquid system according to Raoult's law. However, their molecular sizes are different. Therefore, it is possible that the molecular arrangement in either of the pure solvents is considerably disturbed in this composition range. This will affect the solvation of ions in the mixed solvents in this composition range. This effect will be more pronounced at high concentrations of the ions because there will be a competition for solvent molecules. This may be the reason for the anomalous behavior at high concentrations of the electrolyte in the intermediate composition range of the solvent mixture.

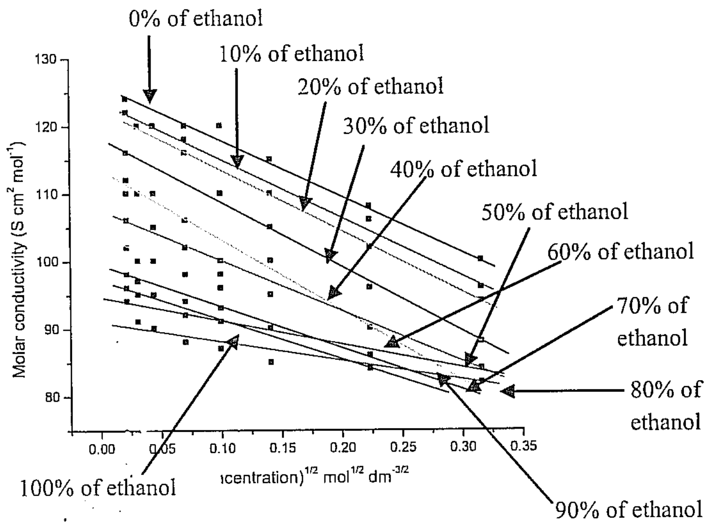

Figure 2: Plot of molar conductivity versus square root of molar concentration for NaCl

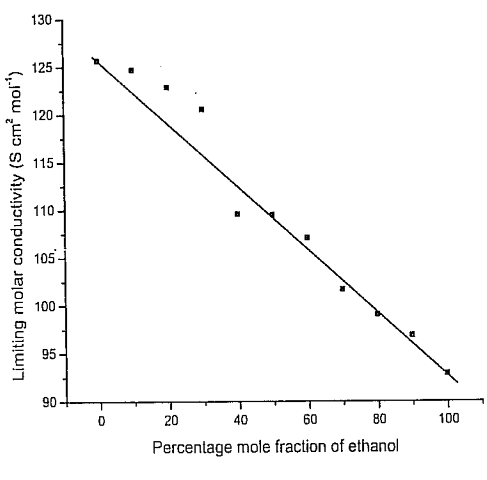

Figure 3: Plot of limiting molar conductivity versus percentage mole fraction of ethanol for NaCl

The limiting molar conductivity (Λ^o) in mixed solvents was calculated by extrapolating the Λ versus (concentration)$^{1/2}$ curves at each composition (Figure 2). Λ^o decreases as the percentage of ethanol increases (Figure 3). This phenomenon may be explained in terms of the dielectric constant. Due to the low dielectric constant of ethanol (ε=24.3) attractive forces between the ions in ethanol rich solutions are strong and this causes a decrease in the limiting molar conductivity compared to the aqueous rich solution. Walden's rule is an empirical observation that the product $\Lambda^o\eta$, where η is a viscosity of the solution, is approximately the same for the same ions in different solvents. This assumes constant ionic radius in different solvents. From the Walden's rule we have derived equations relating viscosity and percentage mole fraction.

For sodium chloride at 32^{o}C the relationship can be written as $\eta = 1.29 * 10^{-5} / (125.6-34.66X)$, $S^{-1}\ cm^{-2}\ C^2\ mol^2$.Where X is the percentage mole fraction of ethanol. This equation is only applicable to water-ethanol mixed solvent systems.

CONCLUSIONS/RECOMMENDATIONS

The molar conductivities of NaCl in the 30-70% composition range of ethanol-water solvent systems exhibit anomalous behavior. This is explained in terms of the disturbed solvent structure at intermediate compositions. The limiting molar conductivity exhibits linear relationship with composition .From this relationship an empirical equation relating the viscosity of mixed solvents with composition has been derived. To clearly explain the anomalous behavior of conductivity at high concentrations of the electrolyte at intermediate composition range and to propose a common equation more experiments with different pairs of solvent systems with different electrolytes should be performed.

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