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Ministry of Higher Education
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University of Karbala,
College of Science
Department of Chemistry

Ion-pair Formation of Tetraalkylammonium Bromide in Hydroxy Propyl methyl Cellulose-Water Mixtures at Different Temperatures

A Thesis

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By

Hameed Ridha Abed
B.Sc. in Chemistry 2003 Al-Mustansiriya University

Supervised by

Prof. Dr.Hamieda Edan Salman

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بسم الله الرحمن الرحيم

نرفع درجات من نشاء
وفوق كل ذي علم عليم

صدق الله العلي العظيم

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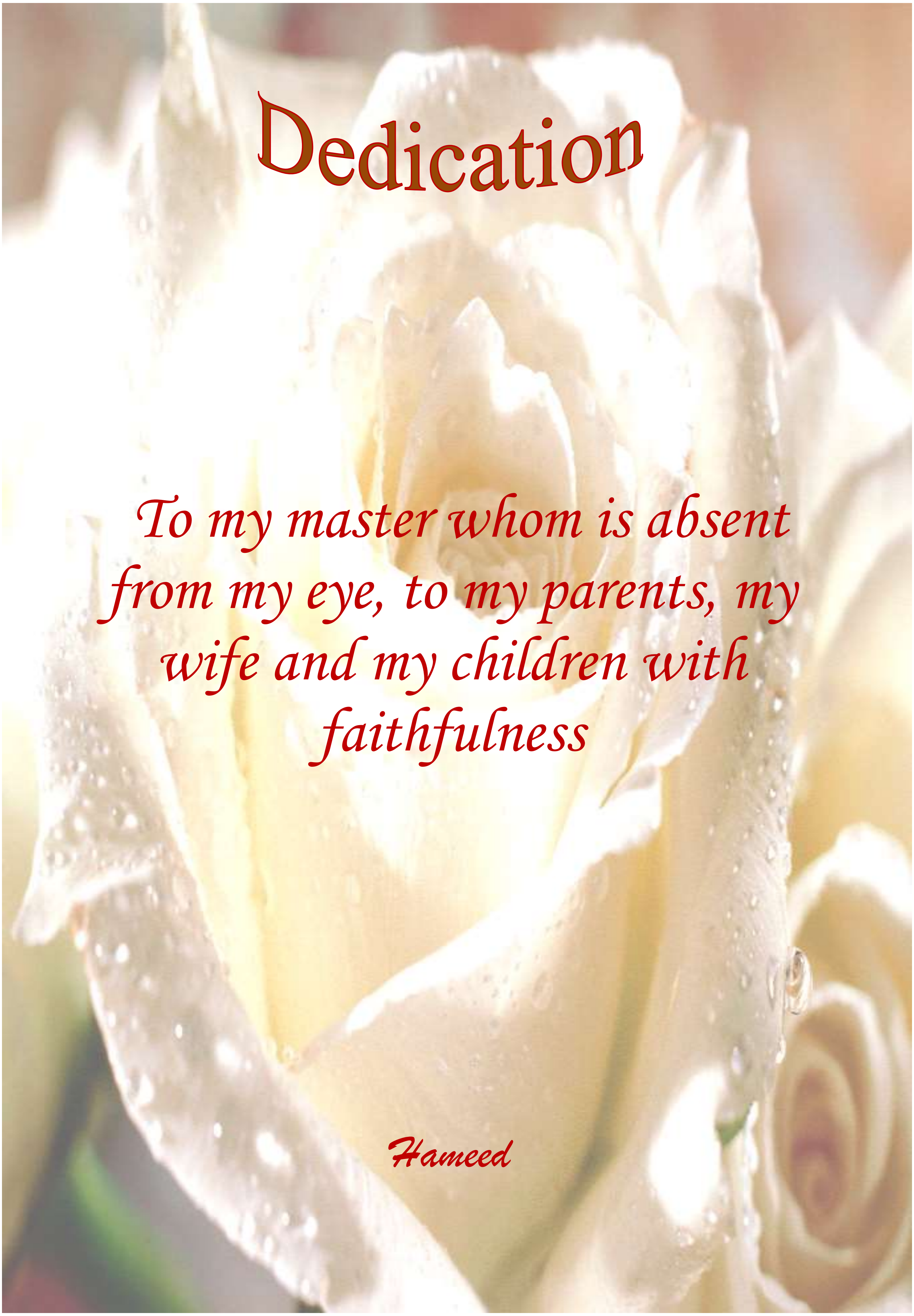
Hameed



Dedication

To my master whom is absent from my eye, to my parents, my wife and my children with faithfulness

Hameed

Abstract:

This thesis involved the study of ion-pair formation of Tetralkylammonium Bromide in three weight percentages of Hydroxypropylmethyl cellulose (HPMC)-water mixtures (0.1%, 0.2% and 0.3%) at six temperatures i.e. (293.15, 298.15, 303.15, 308.15, 313.15, 318.15) K by using deionized water with specific conductance $5x10^{-7}$ *S*cm^{-1} at 298.15K which:

The physical properties of mixed solvents were studying which covered the measurements of densities (d), viscosities (η), dielectric constants (ε) and specific conductances (σ) for the solvent mixtures at specific temperatures from this data. The deviation of solvent mixtures from an ideal behavior was studies by the excess molar volume (V_m^E), excess dielectric constant (ε^E) and temperature dependence of viscosity which can estimated that activation energy for ion flow (Ɛ) and explained the interaction between solvent systems. The physical properties of Tetramethylammonium Bromide (TMAB) and Tetraethylammonium Bromide (TEAB) were studying for nine concentrations for each three wt% of HPMC-water mixture at six experimental temperatures covered densities (d), viscosities (η) and molar conductances (Λ) and it were compared between the two salts. Jones-Dole equation was applied to determine A and B there coefficients, where A values indicate that there is a weak solute-solute interaction in the systems and B-coefficient indicates a good solvation of solute-solvent interaction. Association constant (K_A) was calculated by using Bjerrum equation according to estimate the ion-size parameter (å). The association constant (K_A) and limiting molar conductance (Λ_o) was calculated from a set of equations of Shedlovsky method by using an appropriate computation program. The obtained results give a good agreement between the values of K_A

which have been derived from Bjerrum equation and those obtained by Shedlovsky method. These data used to study the relation between limiting molar conductance (Λ_o) and temperatures to estimate the activation energy of free ions(E), the effective radius (r_i), limiting ionic conductance (λ^o+) and obtain values of the Walden product (W) which reflect the weak ionic interaction and higher conductivity consolidate the higher mobility of free ions. It was calculate the thermodynamics quantities ΔG°, ΔS° and ΔH° for these processes from (K_A) values which were used to known that non-feasibility of the ion pair formation process in these electrolytic solutions.

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ABBREVIATIONS & SYMBOLS

Symbol	**Definition**
å	Ion size parameter
cP	Centi poise
d	Density
E	Activation energy of viscose flow
E	Activation energy of ionic conductance
HPMC	Hydroxypropylmethyl cellulose
IP	Ion pair
K	Kelvin
k	Boltzmann constant
K_A	Association constant
η	Viscosity
N_A	Avogadro number
η_r	Relative dynamic viscosity
q	Ionic distance
$R_4N^+ Br^-$	Tetralkylammonium bromide
r_i	Effective radius
T	Absolute temperature

ABBREVIATIONS & SYMBOLS

TEAB	Tetraethylammonium bromide
TMAB	Tetramethylammonium bromide
Wt%	Weight percentage
X	Mole fraction
ε	Dielectric constant
ε^E	Excess dielectric constant
Λ	Molar conductance
Λ_o	Limiting molar conductance
λ_o^+	Limiting ionic conductance
σ	Specific conductance
V_m^E	Excess molar volume
$\Delta\eta$	Relative change in viscosity

Chapter One 1

INTRODUCTION

1.1 General Introduction

The ion pair formation in aqueous solution refers to the association of cations and anions are present in the electrolytic solution. Ion pair formation process is a kind of very important chemical reaction which theoretical and experimental studies are significant to the revealing of the dynamics of gas phase, liquid-phase reactions and the upper-space atmospheric reactions(1).

The ions of pair together formed an ionic dipole on which the net charge is zero. Ionic association of electrolyte in solution depends upon the mode of salvation of its ions, which in its turn depends on the nature of the solvent or solvent mixtures. The solvent properties such as viscosity and the relative permittivity have been taken into consideration as these properties help in determining the extent of ion association and the solvent–solvent interactions(2).

The measurements of conductivity were used to evaluate the hydration free energy of some electrolytic solutions and to study the nature of the solute-solvent interaction. Provides an insight into the molecular interactions prevailing in solution and helps in the better understanding of the behaviour of the salt with the solvent(3). The viscosity and the concentration of salt have been employed as a function of studying ion–ion and ion–solvent interactions (4). This is useful for the interpretation of the nature of interactions that occur between the salts and mixed solvent systems (5). Ion solvation is one of the most important factors determining the rate and mechanism of various physico-chemical processes occurring in solutions with ionic species as intermediates. Also conductance study of electrolytes over a range of temperature in pure and mixed solvent media provides valuable information about their thermodynamic behaviour (6). The thermodynamic effect of ion – pair formation will be those of removing a certain number of ions from the solution and replacing them by half the number of dipolar entities (7).

1.2 Ion Pair Association

The Debye-Hückel theory assumed that the ion in an electrolyte solution is always in random thermally motion and thus in random positions. The slight deviation from randomness was described as giving rise to an ionic cloud around a given ion, e.g. a positive ion of charge (Z_+) being surrounded by a cloud of excess negative charge (Z_-). However, it was considered that some ions of a given charge in the cloud would get sufficiently close to the central ion of the opposite charge (7). The origin of this effect is that ions of sign opposite to the central ion are more likely to be found close the central ion. The net effect of the diffuse ionic cloud is screening the central ion from the rest of the solution (8). By using general concepts of electrolytic dissociation based on the

Debye-Hückel theory for equivalent ionic conductance. Bjerrum (1926) showed that it is due to partly the variation of equilibrium of a liquid, this variation changes the ion population and conductivity and hence the ionic mobility. The same Bjerrum's basic model its further developments because their validity for electrolytic solutions is still debated. Exact formalisms of the electrostatic effect would require knowledge the shapes of the ions or the molecules, charge distribution, hydrogen bonds, and any other interactions (9).

Bjerrum suggested that a pair of oppositely charged ion may get trapped each other's in columbic field and an ion – pair may thus be formed (7). Whereby free ions associate with ions of opposite charge to make electrically neutral ion pairs that do not contribute to the conductivity within the ionic cloud(10). The locations of such ion pairs are completely random, since being uncharged they are not acted upon the coulombic field of the central ion. Furthermore, the electrostatic forces in the immediate vicinity of the central ion, an excess of ions of the opposite sign is found, which gives rise to a certain space charge compensating for the charge of the central ion(11). This space charge surrounding the central ion is called an (ionic atmosphere or ionic cloud) (12), as shown in Fig. (1.1)

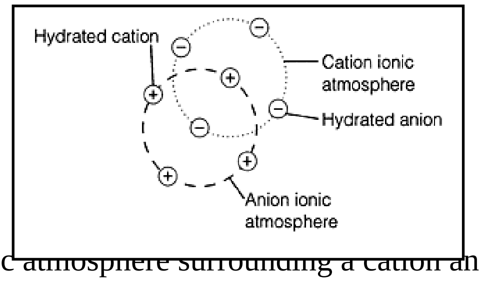


Fig. (1.1) The ionic atmosphere surrounding a cation and an anion in solution.

For two oppositely charged ions to stick together to form an ion-pair, it is necessary that they should be close enough for the coulombic attraction energy to overcome the thermal energy which scatters them apart (the coulombic interaction between the centre of interest and a remote unipole or dipole by direct action through space rather than through bonds)(13). Let this close enough distance be (q), then can saying that an ion-pair will form when the distance between a positive and negative ion becomes less than (q), thus the ion-pair formation is given at (å) smaller than the closest distance of approach of ions called (ion size parameter). Where (q) is calculate as (14):

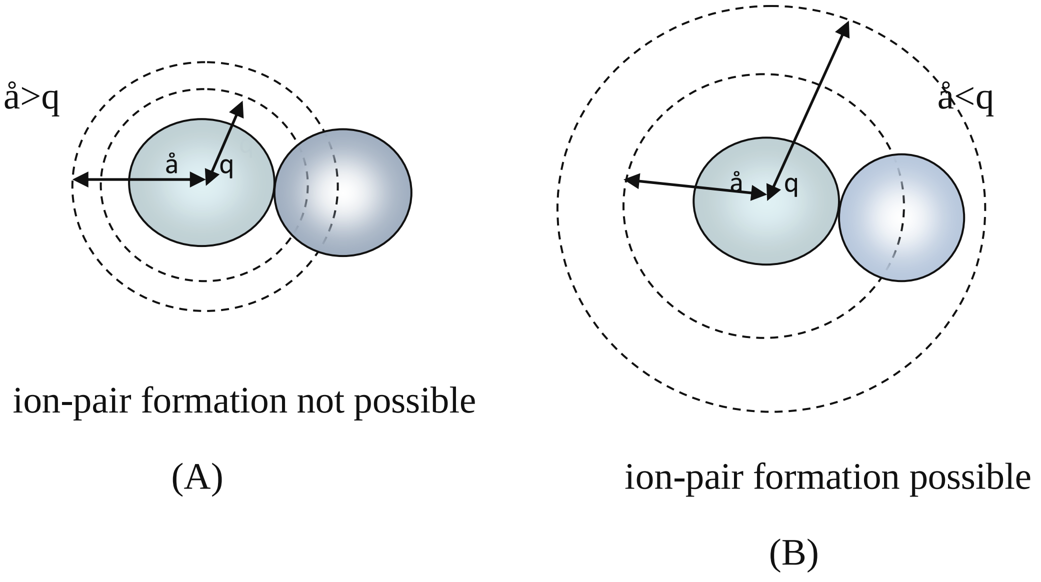
$$\boxed{q = \frac{Z_+ Z_- e^2}{2 \varepsilon k T}} \quad \text{--------} \ (1.1)$$

Where Z_+ and Z_- are respectively the number of charges, e is the electronic charge, ε is the dielectric constant of the medium, *k* is the Boltzmann constant and *T* is the absolute temperature in Kelvin.

Bjerrum concluded that ion-pair formation occurs when an ion of one type of charge, e.g. a negative ion, enters a sphere of radius (q) drawn around a reference ion of the opposite charge, e.g. a positive ion. The ion-size parameter defines the closest distance of approach of a pair of ions. The Bjerrum hypothesis can therefore be stated as follows in Fig. (1.2)(15):

If å<q, then ion-pair formation can occur.

If å>q, the ions remain free.



ion-pair formation not possible

(A)

ion-pair formation possible

(B)

Fig.(1.2): (A) Ion-pair formation does not occurs if å>q. (B) Ion-pair formation occurs if å<q.

Bjerrum theory has some defects the most of them:

Bjerum assumed that å <q. In this case the association of pairs of ions should not be enough condition to be ion-pair occurs. Fuoss has attempted to avoid this defect by defining the ion-pair which was any appositely charges closed to each other by enough distance even when q = å where they together formed an ionic dipole electrically neutral (16).

$$\boxed{b = \frac{\lambda}{å} = \frac{Z_+ Z_- e^2}{\varepsilon å kT} = \frac{2q}{å}} \quad \text{-------------}(1.2)$$

where λ equal to 2q and for uses electrolyte type 1:1, b =2 when the ion-size parameter (å) to be equal to the corresponding Bjerrum critical distance (q), (b) known twice Bjerrum distance (17).

1.3 Ion Association Constant (K_A):

The association constant for ion-pair formation can be defined by considering an equilibrium between free ions (the positive M^+ ions and a negative X^- ions) and the associated ion-pairs (symbolized IP)(18).

$$\underset{}{M^+ + X^-} \rightleftharpoons \underset{(IP)}{M^+....X^-} \rightleftharpoons \underset{(Salt)}{MX}$$

$$\boxed{K_A = \frac{\alpha_{IP}}{\alpha_{m+} + \alpha_{X^-}}} \quad \text{----------}(1.3)$$

In this equation, α refers to activity of ions in the solution and K_A is the reciprocal of dissociation constant of ion-pairs for dilute and moderately concentrated solution.

According to Bjerrum's concept for electrolyte solution ions, the degree of association of an electrolyte may be computed if the ion-size parameter (å) and the dielectric constant (ε) are known.

Bjerrum's theory was tested in solutions with dielectric constant such eqn.(1.1) at b=2 under this condition, the ion association constant (K_A) of Bjerrum (16):

$$\boxed{K_A = \frac{4\,\pi\, N_A\, \hat{a}^3}{1000}\ \left(\frac{e^b}{b}\right)} \text{ - - - - - - - - - } (1.4)$$

where N_A is the Avogadro number.

The values of the association constant (K_A) provides an indication of whether ion-pair formation is occur.

1-When the higher value of (K_A) there is more chance for the ion-pair formation (19).

2-The factor which may increase (K_A) is: the low dielectric constant (ε) (20) of the medium in which the electrolyte is dissolved, however, an increasing fraction of ions becomes associated to form ion-pairs (21). These ideas which are based on Bjerrum's concept of ion-pair formation have received considerable experimental supported.

Values of (K_A) which are calculated by Bjerrum way considered as approximate as the equation does not contain any experimentally measurable data other than the dielectric constant (ε) of the medium which is used in the calculation of the parameter(14).

1.4 Ion Association Constant by Conductivity:

The electric conductivity is one of the most important properties of electrolyte solution(22), electrical conductance theories have been highly developed for examining the states of electrolytes at lower concentrations in solution, Onsager equation indicates that the molar conductivity (Λ) of a 1:1-type of weak electrolytes decrease remarkably with increasing concentration of the electrolytes because of the formation of the ion pair.(23).

Onsager assumed that the electric field causes the charge cloud to be distorted away from spherical symmetry. After taking this into account, together with the specific requirements of moving ions, such as viscosity and electrophoretic effects, Onsager was able to derive a theoretical expression to account for the empirical relation known as Kohlrausch´s law:

$$\boxed{\Lambda=\Lambda_0 - K\sqrt{c}} \quad \text{- - - - - - -(1.5)}$$

Λ is the molar conductivity, Λ_0 is known as the limiting molar conductivity, K is an empirical constant and c is the electrolyte concentration limiting here means "at the limit of the infinite dilution"(24).

Onsager's expression is:

$$\boxed{\Lambda=\Lambda_o -(A+B\ \Lambda_o)\ \sqrt{c}} \text{ - - - - - -(1.6)}$$

where A and B are constants that depend only on known quantities such as temperature, the charges of the ions, the dielectric constant and viscosity of the solvent.

The measurement of electrical conductivity of dilute solutions of salts or complexes is considered one of important methods for studying the ion-pair or multiple-ion association not only in aqueous solutions but also in non-aqueous or mixed ones. Thus the conductance measurement of electrolyte solutions is one of the important methods to identify the possibility of the formation of ion pairs (25). The values of the ion-pair association constants (K_A) have usually been determined by conductance method (26-29).

The more acceptable values of (K_A) which are more dependents on the nature of the ions that are present in the electrolytic solution may be estimate from conductivity measurements. Shedlovsky presented a new method to estimate (K_A) and the limiting molar conductance (Λ_o) by a treatment with a suitable computer program using Shedlovsky method which involved the solution of the following set of equations (30,31):

$$\boxed{\frac{1}{S\Lambda} = \frac{1}{\Lambda_o} + \frac{C\,\Lambda\,S\,f_{\pm}^{2}\mathrm{K_A}}{\Lambda_o^2}} \text{ - - - - - - - - - (1.7)}$$

$$\boxed{S = \left[\frac{B\sqrt{c\Lambda}}{2\,(\Lambda_o)^{3/2}} + \sqrt{(1 + \frac{B^2\ C\Lambda}{4(\Lambda_o)^3})}\ \right]^2} \text{ - - - - - - (1.8)}$$

$$\boxed{B = \frac{8.204 \times 10^5\Lambda_0}{(\varepsilon T)^{3/2}} + \frac{8.25}{\eta(\varepsilon T)^{1/2}}} \text{ - - - - - (1.9)}$$

$$\boxed{\alpha = \frac{S\Lambda}{\Lambda_o}} \text{ - - - - - - (1.10)}$$

$$\boxed{-logf\pm = \frac{1.8246\ \times 10^6(c\alpha)^{1/2}/(\varepsilon T)^{3/2}}{1 + 50.29\ \times 10^8 R(c\alpha)^{1/2}/(\varepsilon T)^{1/2}}} \text{ - - - - - - (1.11)}$$

Where ($f\pm$) is the mean activity coefficient and (α) is the degree of dissociation of ion-pairs. Inserting the experimental values of the conductance (Λ), the dielectric constant (ε) of the HPMC-water mixture, the viscosity (η), (c)concentration of solute ,T absolute temperature and R= å.

Where a° is the ion –size parameter:

$$\boxed{\text{å} = \frac{Z_+ Z_- e^2}{2\varepsilon kT}} \text{ - - - - - - -(1.12)}$$

And Z_+ = Z- =1 for a uni-uivalent electrolyte such as $R_4N^+Br^-$, e the electronic charge and *k* the Boltzmann constant.

1.5 Factors Influence (K_A):

Many studies on K_A show the main way to investigate the thermo physical properties of electrolyte solution. The use of mixed solvents with variation of properties such as dielectric constant or viscosity therefore the ion–ion and ion–solvent interactions can be better studied. Furthermore different quantities strongly influenced by solvent properties can be derived from concentration dependence of the electrolyte conductivity (32-36).

1.5.1 Temperature Effect

Temperature variation of (K_A) has been studied to get the thermodynamic parameters as a function of the solvent structure. The heat of association is obtained by studying the association constant (K_A) over a range of temperature by means of Van’t Hoff’s isochore(33), where log K_A values are plot against 1/T giving a straight line with slope $\Delta H^\circ/R$. This thermodynamic function in addition to ΔG° and ΔS° are giving inference whether the ion pair formed or not. There are marked characteristic behaviors in the K_A values generally decrease as the temperature is increased the thermal motion probably destroys the solvent structure (32) hence increasing the mobility of ions and finally the fraction of associated ions decreased.

1.5.2 Solvent's effect

The nature of the solvent mixtures greatly influences the ionic association of electrolytes in solution due to the effect on mode of solvation of its ions (34). Solvent properties such as viscosity and the relative permittivity have been taken into consideration as these properties help in determining the extent of ion association (5). Thus, extensive studies on electrical conductance's in various mixed organic solvents have been performed in recent years to examine the nature and magnitude of ion–ion and ion–solvent interactions(34) and subsequently on (K_A) which is based on the characteristic of physicochemical properties of this solvent. Such important of these properties:

A- Dielectric Constant

The dielectric constant is an important property for solvent and it plays an important role in the characterization of material electrical properties. The study of this type will reveal the nature of molecular interaction between a polar component and a non-polar component (35). The dielectric property of solvent can play a decisive role in a wide variety of helical structure and intermolecular hydrogen bonds for macro molecules and polymers (36). The solvent molecules which have shown that relatively high dielectric constant and hydrogen-bond acidity will be more efficient in promoting the dissociation of ions of salt and improving the transport properties (37). For strong electrolytes at high temperature lower dielectric constant and for weak electrolytes even at ambient temperature, ionic association takes place at very low concentrations (38).

B- Viscosity

An important thermo physical property is the dynamic viscosity, which is the resistance to fluid flow, or the resistance of a fluid to shear stress. Theoretical investigations of the viscosity for electrolyte solutions have focused mainly upon systems containing a single solute in dilute solutions (39). A rise in temperature always leads to an increase in the electrical mobility and the limiting molar conductance this occurs because the viscosity (η) of medium falls off with increasing temperature so that the ions encounter less mechanical resistance to their movement throughout the medium under the action of electric field(40). The limiting molar conductance thus depends essentially on the viscosity of the solvent, with increasing temperature the value of limiting molar conductance of each ion varies in inverse proportion to the variation of the viscosity of solvent so that the product ($\Lambda_o\ \eta$) remains constant with the change of temperature (41). This constant factor is known "Walden product".

1.5.3 Salts effect

One factor that can limit the free ion concentration in an electrolyte solution is the ion pairing. The ion pairing is the competition between the energy of electrostatic attraction of two oppositely charged ions toward each other, which serves to keep the ion pair together, and the thermal energy in the medium, which serves to break the ion pair. So, it is useful to consider some predictions from theory regarding how ion pairing should depend upon type of ions of electrolyte solutions. The most common approach to treating electrostatic interactions in the presence of salt ions,(42) although the ability of electrolyte solutions to conduct electricity hinted strongly at the existence of ions (charged molecules) in solution. Thus, the electrical conductivity of aqueous solutions depended on the nature of the solute and its concentration (43).

1.6 The Literature Survey:

Polymeric materials have been strongly associated with our daily life. The natural biodegradable polymeric systems have gained importance in the last few years, because of the environmental pollution of non-biodegradable synthetic plastics. The valuable part of these polymers can be used for the preparation of new materials with improved physicochemical and mechanical properties (44). The mixtures of polymer solutions are very important in many polymer processing operations such as the preparation of cosmetics, pharmaceuticals, adhesives, and in surface coatings for plastics, glasses, and metals. Polymer solutions usually exhibit complex phase behaviour due to the large differences between the molecular sizes of components as well as specific interactions (45). Thus, it has been considered as an important field of researchers for several decades (44). One of the most favourable polymers is hydroxy propyl methyl cellulose (HPMC) with β-glycosidic linkage(46). Where aqueous solutions of these carbohydrate polymers have revealed gel reversibility with temperature (47).

Researchers have shown particular interest in the HPMC because of the preparation of polymeric materials with desired properties, low basic cost and improved process ability (48). HPMC is the naturally derived cellulose; this non-ionic cellulose ether is widely used in pharmacology for controlled drug release system or Oral drug delivery systems (49-53) and used in ophthalmic treatment (54). Also in vitro bioactivity and biocompatibility of calcium phosphate bone cements using HPMC(55). The Powders of HPMC a biocompatible polymer and could be used in formulating of hydro gel based dosage forms were used to produce a model granular pharmaceutical dosage system dried by microwave heating(53). HPMC is useful in the food industry as stabilizers of emulsions and foams, a replacement of fat, a non-caloric bulking agent in foods, a barrier to oil and in moisture retention as a binder. HPMC little or no flavour to food (54) and as edible films from a food grade additive that is from a natural vegetable and biodegradable origin(56) which can be eaten as a part of the food.

S. C. Joshi (47) investigated the effects of salt additives on HPMC gelation. Various findings regarding gelation with salt ions as well as with the ionic and non-ionic surfactants are presented. The gel formation in physiological salt fluids such as simulated gastric and intestine fluids is also examined with the interest in oral drug delivery systems. Explanations are provided based on the chemical structure and the molecular binding and association of HPMC in a media. The test results at the body or near-body temperature conditions helped in understanding the progress of the gelation process within the human body environment.

In the view of the large number of papers described the physico-chemical properties and ion association of different solutions. It is shown that they Fuoss method, low concentration chemical model and Lee-Wheaton also preferred to analyses their conductance data where the measurements were over a wide range of dielectric constant values which were closely similar to Shedlovsky´s method. They have shown same results of Λ_o and K_A was found.

Roy and co worker studied (34) the electrolytic conductivity of the Tetraalkylammonium Iodides, $R_4N^+I^-$ (R = butyl to heptyl), in (0.25, 0.50 and 0.75) mass fraction of o-toluidine (C_7H_9N) in n-hexanol ($C_6H_{14}O$) at T = 298.15 K. The limiting molar conductance Λ_o, association constants K_A and the co-sphere diameter (R) for ion-pair formation in solvent mixture evaluated using the Fuoss-equation. From the investigations, the solvated salts was followed the sequence below: $Bu_4N^+I^- > Pen_4N^+I^- > Hex_4N^+I^- > Hep_4N^+I^-$.

H. Shekaarilon and A. Kazempour (57) investigated the association constant of 1-hexyl-3-methylimidazolium halide (Cl^- and Br^-) in aqueous d-fructose solutions by using conductance properties. Limiting molar conductivity Λ_o, association constant K_A and distances parameter (R) were calculated using low concentration chemical model (lccm) at temperatures ranges of (293.15-328.15) K. They showed the Λ_o values increase with increasing temperature and decrease during the addition of d-fructose. Walden products Λ_o η were estimated discussed and studied the thermodynamic of association process (ΔG°, ΔS°, ΔH°) of ion pair formation at different temperatures.

B. A. Akrawi(58) has determined the electrical conductivity of cobalt salicylidiene chloroaniline and cupper salicylidiene chloroaniline in water, methanol, ethanol, isopropanol and mixture of water methanol with different composition (100-20%) were measured at 303K. The molar conductivity of the complexes was treated by Lee-Wheaton equation and Kohlrausch equations. Limiting ionic conductivity ($\lambda^o{}_{M}{}^{+2}$) ($\lambda^o{}_{MX}{}^{+}$) the ionic association constant K_A as well as the main distance between cations and anions (R) measured. The association constants of the two complexes were increased with decreasing the dielectric constants and increasing of viscosity.

Radhika et al. (59) used the electrical conductance nicoitnium dichromate measured in mixture of water- N,N-dimethylformamide for different compositions in the temperature range (283-313)K. The limiting molar conductance (Λ_o) and the association constant of the ion-pair K_A were calculated using Shedlovsky equations. The influences of the mixed solvent composition on the solvation of ions were discussed with the help thermodynamic parameters were evaluated and reported.

The present work deals with the conductance measurements of some Tetraalkylammonium Bromid $R_4N^+Br^-$ (R = Methyl or Ethyl) used as salts. These salts are very suitable for research due to the excellent solubility characteristics in aqueous or non-aqueous solvents. It was a broad range of applications that includes trace analysis, environmental analytic chemistry, pharmaceutical and medicinal (60). Solvent mixtures of HPMC-Water were used as solvent which is find wide industrial usage because of its relatively high dielectric constant with sufficiently high conducting media and ability to dissolve the salt at six different temperatures in the range of (293.15-318.15) K.

1.7 The Scope and Aim of This Research:

The present work involved several aspects which may be summarized as:

1- In order to determine the values of certain parameters which were needed in this work, it was necessary to investigate the physical properties of the solvent mixtures. These involved measurements of density, viscosity, dielectric constant and specific conductivity of all mixtures at various compositions at six different temperatures which were (293.15, 298.15, 303.15, 308.15, 313.15, 318.15) K. The data obtained have been analyzed in attempt to understand the behaviour of the solvent mixtures.

2- Determination of the physical properties of Tetralkylammonium bromide solutions specially involve:

-Densities, viscosities and molar conductances for each solutions of Tetramethylammonium bromide (TMAB) and Tetraethylammoinium bromide (TEAB) in HPMC-water mixtures at specific experimental temperatures.

3-Determination of the non-ideal behaviour of specific electrolytic solution through the investigation of such aspects as:

- Excess molar volumes (V_m^E).

- Viscosity dependence on temperature and activation energy of viscose flow (E).

- Excess dielectric constant (ε^E).

- Application of Jones and Dole equation and its coefficients.

- Ion size parameter (å).

- Association constant (K_A).

- Effective radius of the cation (r_i).

- Estimation of limiting molar conductance (Λ_o).

- Molar conductance depends on temperatures and activation energy of ionic conductance (E).

- Estimation of Walden products (W).

4- The experimental data have finally been used to determine the association constants of the TMAB and TEAB in the various weight percentages of mixture solvents also investigation of thermodynamics function of ion association in solution.

Chapter Two

2

EXPERIMENTAL PART

2.1 Measuring Instruments:

Different types of instruments have been used in this research which involved the following:

1- Densitymeter

The measurements of density for solvent and solute where done by using densitymeter type (Densito 30 px) CPT charges from (METTLER TOLEDO) made in Japan. Which consist of constant cell is provided with external pipe which can be full of the cell and disposal of by slid bottom with display digital screen by gm/cm^3. The capacity of cell which was density measured of solution was 5 mL and the accuracy of measurements lead within $\pm 1.0 \times 10^{-4}$ gm/cm^3 of the density value.

2- Viscometer

The Viscosities (η) of the various solutions were measured using Ostwald Viscometer type (D) with flow time of (25 S) for pure water at 298.15 K. The viscometer was calibrated with deionizer water and pure acetone at each of the six experimental temperatures. The viscosity measurement with each solvent mixture or solution at each temperature was repeated (2-3) times. The deviation of the viscosity measurements was ± 0.01S.

3- Dielectrometer

A universal dielectrometer type OH-301 C Raedelkis, made in Hungary, was used to measure the dielectric constant (ε) of the solvent mixtures using various appropriate cells. The instrument was first calibrated with highly pure acetone. The temperature of the cell solution (or solvent mixture) was kept at the desired temperature to within ± 0.01˚C. The reproducibility of the dielectric constant measurements was found to be within ± 0.2 %.

4- Conductivitymeter

The conductance measurements were used (WTW) type (82362 – weilheim) made in Germany, model / inolab multi 720. The conductivity cell was of the dipping type (Tetra con. 925). The cell constant is ($0.475\ \text{cm}^{-1} \mp 1.5\%$). The deviation in the calculated specific conductance (σ) values has been within ± $1\mu S\ \text{cm}^{-1}$. The measurement parameters could be hold in memory and could be recalled to the display and updated through the keyboard with display temperature. This was also checked frequently using control standard ($0.01\ \text{mol L}^{-1}$ of KCl) solution at experimental temperature with all a set of measurements.

5- Water Bath

During all measurements a thermostatically controlled water bath was occurred with adjustable temperatures in (Lab Tech) digital water bath, (CERTIFIED CE) model (LWB 111D) made in Korea. The bath was filling with distilled water and was used to obtain temperatures in the range (293.15-318.15) K. The constant of each experimental temperature was to within ± 0.01˚C.

6- Digital Balance

A sensitive digital balance was used with an isolated box provided with slid gate type (PW214) from (De ADAM) with accuracy ± 0.0001gm has used in weighting of all using materials that will be needed.

2.2 The Chemicals:

1-Materials

The salt (TMAB) was obtained by Himedia Labortories pvt.ltd. with a purity exceeding 98.0% with mol.wt. (154.06) as white crystals while the other salt (TEAB) was obtained by Fluka AG ,chemische fabric-ch 9470 buchs with purity >98% with mol.wt. (210.16) as whiting yellowish crystals. The salts used in this work was further purified by recrystallization by using acetone and carefully dried to get maximum purity (41).

(HPMC) was obtained by Gold Member China Suppliers, model No. MK10000S with purity 99.0% has been caring description -60 BC-E with density of (0.3- 0.4) gm/cm^3 and it has average mol.wt.(10000).

(HPMC) is an odourless and tasteless, white to slightly off-white, fibrous or granular powder that is a synthetic modification of the natural cellulose(54) chemically presented as $C_6H_7O_2(OH)_x(OCH_3)_y(OC_3H_7)_z$ with $x + y + z = 3$. Fig. (2.1) demonstrate the chemical structure of TMAB, TEAB and HPMC respectively.

Double distillation deionized water with a specific conductance of 5×10^{-7} *S* cm^{-1} at 298.15K has been used for the preparation of the HPMC-water mixture and in all experimental uses, by using (Huma pure – Humah) from Human-Germany, symbol D-652D5-wiesbaden, with inaccuracy 0.1µ*S*.

2-Solutions:

Three solvents mixtures have been used in this work and were prepared by mixing HPMC with water the weighting percentages ranged as in follow (0.1%, 0.2% and 0.3%). These solvent mixtures were used to prepare the solutions of salts TMAB and TEAB in a nine concentrations for each component of the salt solutions. The different concentrations of each salt were (0.047, 0.147, 0.247, 0.347, 0.447, 0.547, 0.647, 0.747and 0.847) mol dm^{-3} and prepared by using for each component of solvent mixture at the experimental temperatures which were (293.15, 298.15, 303.15, 308.15, 313.15 and 318.15) K.

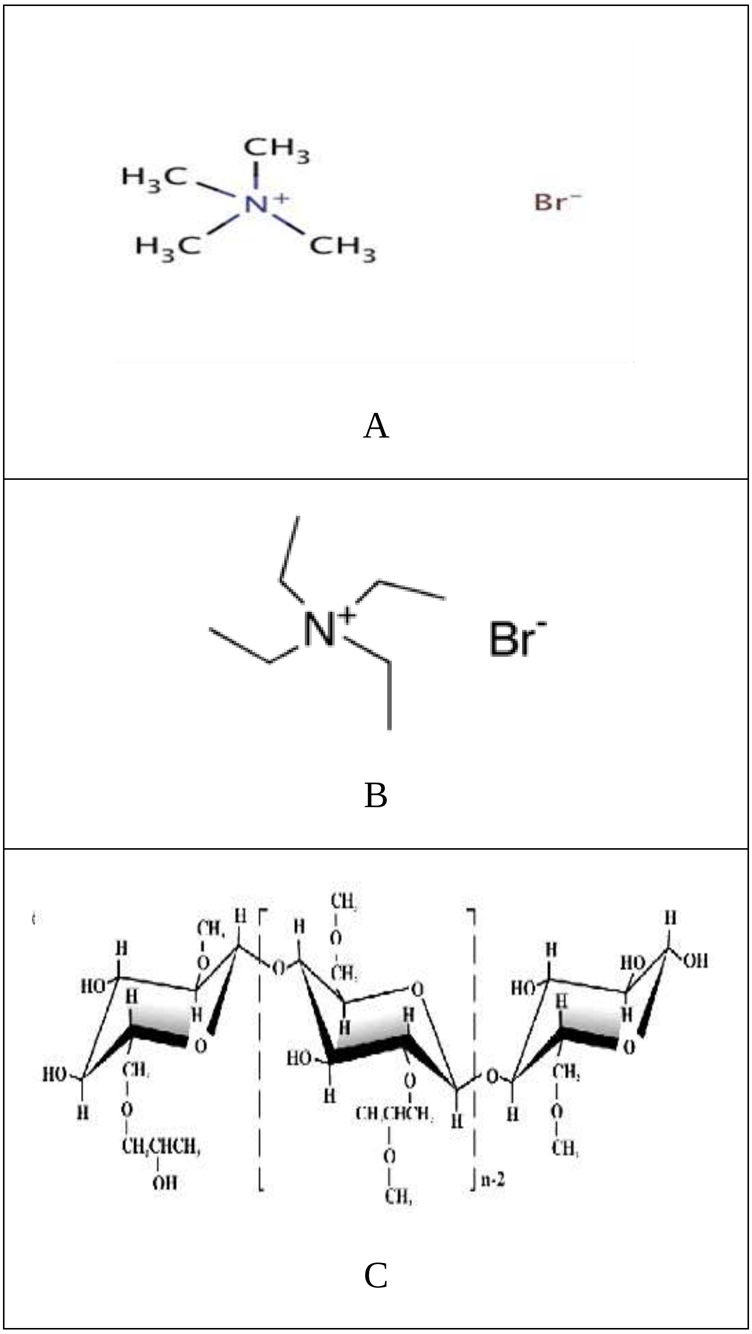


Fig.(2.1) Chemical structure of A-TMAB, B-TEAB and C-HPMC.

Chapter Three

3

RESULTS & DISCUSSION

3.1 Physical Properties of HPMC-Water Mixtures

The solvent mixtures of (HPMC)-water mixture have been used in this investigation, at three weight percentages (0.1, 0.2 and 0.3) % of HPMC. Densities (d), viscosities (ɳ), dielectric constants (ε), and specific conductance (σ) of solvent mixtures have been measured at six temperatures which were: (293.15, 298.15, 303.15, 308.15, 313.15 and 318.15) K.

Density (d) generally increases at a constant temperature with increasing weight percentage of (HPMC) in the mixture. At a constant weight percentage of (HPMC) in mixture, the density decreased with rise of temperature. The results obtained are present in Table (3.1) and Fig. (3.1).

Viscosity (ɳ) increases also with the increasing of wt% of (HPMC) in mixture at constant temperature and decreased with the rise of temperature at constant wt%. The results are obtained present in Table (3.2) and Fig. (3.2).

The dielectric constant (ε) also increased at a constant temperature with increasing wt% of (HPMC) in mixture due to increases the number of dipoles that are present in solution. Dielectric constant (ε) is decreases with the rise of temperature, at a constant weight percentage of (HPMC) in mixture since the dipoles of solvent molecule are weakness with increasing temperature. Farther a rise of temperature is causing the thermal expansion of solvent molecules which will be distortion due to the degree of alignment decreased with increasing temperature(33). The results obtained are present in Table (3.3) and Fig. (3.3).

The specific conductance (σ) values are increased with rise temperatures at constant wt% of HPMC in mixture but increased towards maximum values with increasing wt% of (HPMC) in mixture at constant temperature. These increase due to increases the concentration of solvent molecules and its mobility with rise temperature. The results obtained are presented in Table (3.4) and Fig. (3.4).

Table (3.1): Density (d) g cm^{-3} of HPMC-water mixtures as a function of the weight percentages (wt%) of (HPMC) mixtures at experimental temperatures.

Wt%	(d) g cm^{-3}					
	293.15K	298.15K	303.15K	308.15K	313.15K	318.15K
0.10	0.9965	0.9958	0.9941	0.9925	0.9913	0.9889
0.20	0.9967	0.9959	0.9944	0.9927	0.9916	0.9894
0.30	0.9969	0.9962	0.9946	0.9929	0.9918	0.9898

Table (3.2): Viscosity (ɳ) cP of HPMC-water mixtures as a function of the weight percentages (wt%) of (HPMC) mixtures at experimental temperatures.

Wt%	(ɳ) cP					
	293.15K	298.15K	303.15K	308.15K	313.15K	318.15K
0.10	1.1853	1.0556	0.9277	0.8031	0.7152	0.6479
0.20	1.3357	1.1891	1.0753	0.9364	0.8289	0.7362
0.30	1.5021	1.3556	1.2541	1.1203	0.9646	0.8478

Table (3.3): Dielectric constant (ε) of HPMC-water mixtures as a function of the weight percentages (wt%) of(HPMC) mixtures at experimental temperatures.

wt%	**(ε)**					
	293.15K	298.15K	303.15K	308.15K	313.15K	318.15K
0.10	75.15	74.22	73.18	72.05	71.19	70.89
0.20	75.66	74.75	73.88	72.82	71.62	70.69
0.30	76.24	75.85	75.22	74.64	74.00	73.12

Table (3.4): Specific conductance (σ) µ*S* cm^{-1} of HPMC-water mixtures as a function of the weight percentages(wt%) of(HPMC) mixtures at experimental temperatures.

Wt%	**(σ)** µ *S* cm^{-1}					
	293.15K	298,15K	303.15K	308.15K	313,15K	318.15K
0.10	29.4	33.2	35.4	36.8	38.4	41.1
0.20	41.3	44.6	46.9	48.3	50.1	53.0
0.30	60.6	61.9	63.8	65.5	68.0	70.4

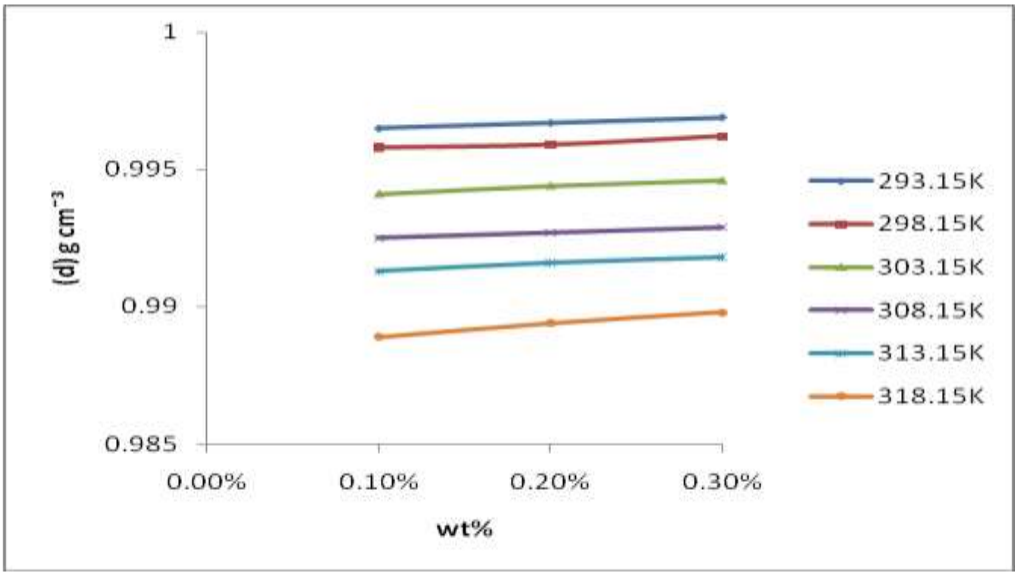


Fig. (3.1): Density (d) of HPMC-water mixtures plotted against the weight percentages (wt %) of HPMC in mixtures at six experimental temperatures.

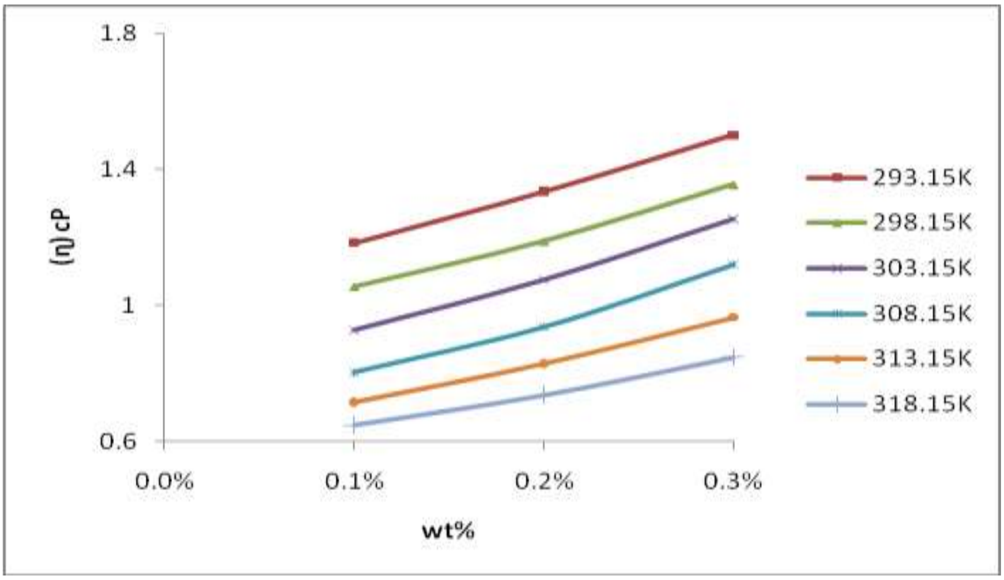


Fig. (3.2): Viscosity (η) of HPMC-water mixtures plotted against the weight percentages (wt %) of HPMC in mixtures at six experimental temperatures.

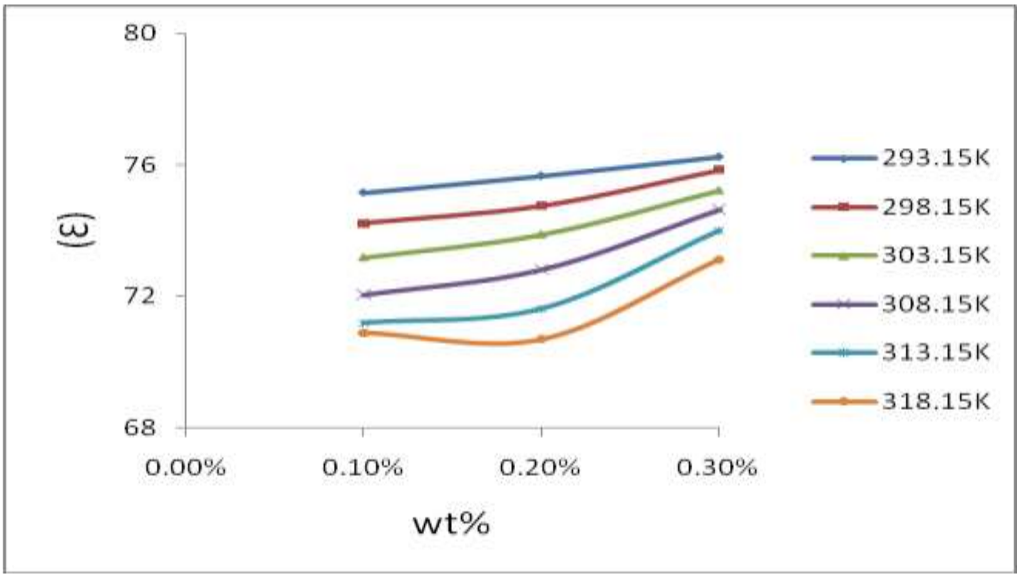


Fig. (3.3): Dielectric constant (ε) of HPMC-water mixtures plotted against the weight percentages (wt %) of HPMC in mixtures at six experimental temperatures.

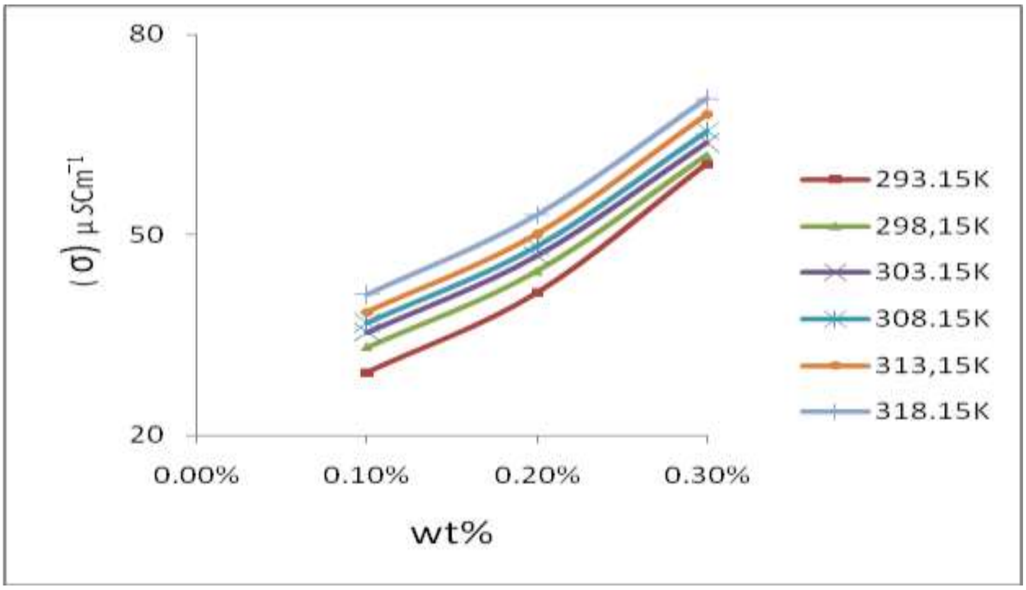


Fig. (3.4): Specific conductance (σ) of HPMC-water mixtures plotted against weight percentages (wt %) of HPMC in mixtures at six experimental temperatures.

3.2 Excess Molar Volumes (V_m^E):

Volume change of mixture or Excess molar volume has been determined by two methods. The first one is directly measured by the change in the volume of mixture using dilatometer. The second is indirect method by measuring the density of pure component of liquid and the binary mixture by densitymeter. In this work the excess molar volumes V_m^E (cm^{3}mol^{-1}) were calculated by the second way as difference between real mixture volume (experimental) and ideal mixture volume (theoretical) (61, 62), as in the following equations:

$$\boxed{V_m^E = V_{exp.} - V_{theo.}} \text{ - - - - - - - (3.1)}$$

$$\boxed{V_m^E = [(M_1\, X_1 + M_2\, X_2) / d_{12}]_{exp.} - [\, (M_1\, X_1 / d_1) + (M_2\, X_2 / d_2)]_{theo.}} \text{ - - - - (3.2)}$$

Where M is the molar mass, X is the mole fraction and d density. The subscripts1, 2 and 12 denoted the property of water, organic component and their mixture respectively. The mole fraction is the ratio of moles of one compound to the total number of moles present in solution. Mole fraction is represented by the symbol X, for a solution containing 2 components (35) where:

$$\boxed{X_1 = n_1 / (n_1+n_2)} \text{ - - - - - - - - - (3.3)}$$

$$\boxed{X_2 = n_2 / (n_1+n_2)} \text{ - - - - - - - - - (3.4)}$$

X_1 and X_2 is the mole fraction of component 1 and 2 respectively, n_1, n_2, the moles of components 1 and 2 respectively.

The sum of the mole fraction for each components in the solution will be equal to 1 where ($X_1 + X_2 = 1$). The obtained results of the excess for the three binary components of HPMC-water mixtures are listed in Table (3.5) and Fig. (3.5) as function to the HPMC mole fraction (X_2) at six experimental temperatures. The negative values of V_m^E for all wt% range at all experimental temperatures and this effect become more visibility with increase mole fraction (X_2) of organic component. These results can be interpreted in term of volume contraction in mixtures, and hence it can be explained the large differences in molar volumes of its components(63). This gives a deeper insight into the intermolecular interactions between such self-associated structures. The result volume contraction is particularly due to the ability of the ether oxygen atom (−O−) with the OH groups in HPMC molecule to form intermolecular H-bonds with water molecules through OH…O linkages. However, another interpretation for the marked change in V_m^E may also be assigned due to accommodation of solute molecules within the lattice/void space of three dimensional networks of water(64).

Table (3.5): Values of mole fractions of HPMC (X_2) and water (X_1), the density of their mixtures (d_{12}), experimental ($V_{exp.}$), theoretical ($V_{theo.}$) molar volumes and excess molar volume of the mixture.

wt%	X2	X1	T(K)	d_{12}	$V_{exp.}$	$V_{theo.}$	V_m^E

				$(g\ cm^{-3})$	(cm^3mol^{-1})	(cm^3mol^{-1})	(cm^3mol^{-1})
0.10%	0.0002	99.9998	293.15	0.9965	1810.132	1810.539	-0.407
			298.15	0.9958	1811.405	1812.640	-1.235
			303.15	0.9941	1814.502	1815.181	-0.679
			308.15	0.9925	1817.427	1818.113	-0.686
			313.15	0.9913	1819.628	1821.438	-1.810
			318.15	0.9889	1824.044	1825.088	-1.044
0.20%	0.0004	99.9996	293.15	0.9967	1811.582	1815.859	-4.277
			298.15	0.9959	1813.037	1817.959	-4.922
			303.15	0.9944	1815.772	1820.501	-4.729
			308.15	0.9927	1818.881	1823.433	-4.552
			313.15	0.9916	1820.899	1826.758	-5.859
			318.15	0.9894	1824.948	1830.408	-5.460
0.30%	0.0005	99.9995	293.15	0.9969	1813.031	1821.178	-8.147
			298.15	0.9962	1814.305	1823.279	-8.974
			303.15	0.9946	1817.223	1825.821	-8.598
			308.15	0.9929	1820.335	1828.752	-8.417
			313.15	0.9918	1822.354	1832.078	-9.724
			318.15	0.9898	1826.036	1835.728	-9.692

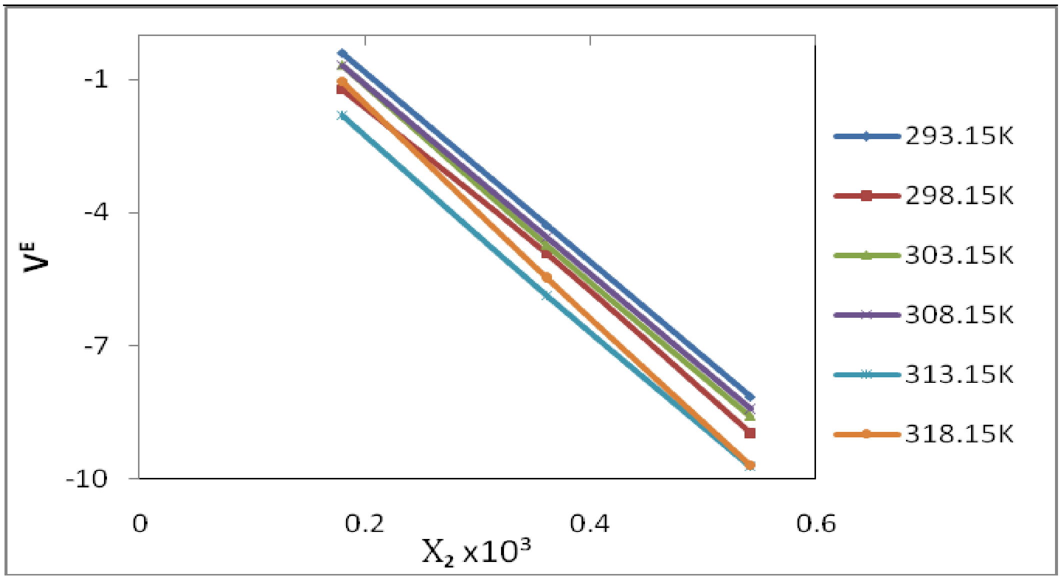


Fig. (3.5): Excess molar volume (V_m^E) as a function of the HPMC mole fraction (X_2) at six experimental temperatures.

3.3 Viscosity Dependence on Temperature:

Knowledge of solution viscosity is needed for the design of numerous industrial processes and provides useful insights into solution structure and interactions (65, 66). The viscosity of HPMC-water mixtures as function to the temperature was described by the empirical equation of Andrade (67):

$$\boxed{\eta = A \exp (B/T)} \text{ - - - - - - - - (3.5)}$$

Where A and B are constants, T temperature by Kelvin and η is the viscosity regarding flow as act resistance process. As compatibility to Arrhenius –Andrade type correlation (68), if E is the activation energy of the viscose flow, the express be:

$$\boxed{\eta = A \exp (E/RT)} \text{ - - - - - - - - - - (3.6)}$$

Where B = E/R. The activation energy for viscose flow in HPMC-water mixtures (E) can be estimated from the slope of a straight line obtained from the plot of log (η) versus 1/T. The experimental viscosity data used as a function to temperature obtained the values of log (η) for three Wt% of HPMC –water mixtures at six experimental temperatures represented in Fig. (3.6). The values of E of HPMC in water mixtures are shown in Table (3.6) are decreased with increasing in wt% of solvent that due to increasing in viscosity of solvent mixture at constant temperature with increasing wt%. Since viscosity means the resistance of one part of the fluid to move relative to another one, therefore, viscosity must be closely correlated with the structural parameters of the fluid particles(67) interpreted a good interaction between solvent partials.

Table (3.6): Activation energy E (KJ mol^{-1}) values for ion flow in HPMC-water mixture as function of the weight percentages (Wt %) of HPMC in mixture.

wt%	E(KJ $mole^{-1}$)
0.10	8.343
0.20	8.078
0.30	7.657

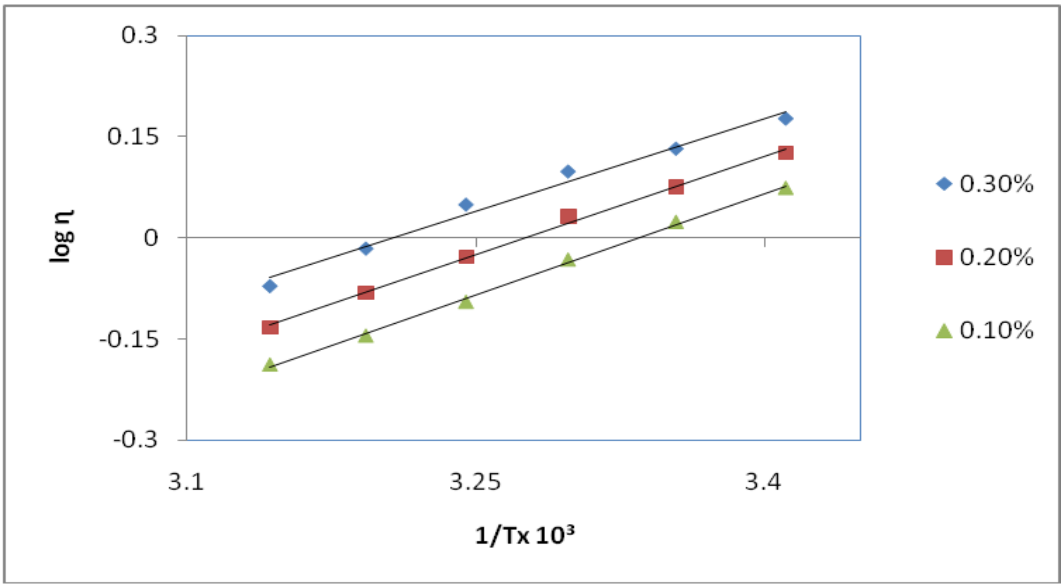


Fig.(3.6): Log (η) for three Wt% of HPMC –water mixtures plotted against to 1/T for six experimental temperatures.

3.4 Excess Dielectric Constant:

The excess dielectric constant plays an important role in the domain of binary dielectrics systems. Knowledge of dielectric properties of binary mixtures is important both in fundamental studies of solvent structure determination and its dynamics as well as in the practical applications. The frequency-dependent dielectric behaviour of solutions mixtures provides information on molecular interactions and mechanism of molecular process which consequently plays an important role in determining the physical properties of these molecules (69). The excess dielectric constant ε^E is defined as:-

$$\boxed{\varepsilon^E = \varepsilon_{o\ \mathrm{observed}} - \varepsilon_{i\ \mathrm{ideal}}} \text{ - - - - - - - - - } (3.7)$$

Where

$$\boxed{\varepsilon^E = \varepsilon_{12} - (\varepsilon_1 X_1 + \varepsilon_2 X_2)} \text{ - - - - - - - - - - } (3.8)$$

Where ε_{12} is dielectric constant of the mixture, ε_1 and ε_2 are the dielectric constants of pure water and pure (HPMC) as an organic component respectively, X_1 and X_2 are the mole fractions of water and pure (HPMC) as an organic component respectively. The results shown in Table (3.7) are presents values of ε^E and mole fractions of solvent components, while the Fig. (3.7) were shown the ε^E plotted against the mole fraction (X_2) of the organic component of the solvent mixtures. The variation of excess dielectric constant ε^E with mole fraction of the organic component of the mixture may be interpreted as the change in the degree of alignment of the dipoles with changing composition of HPMC of the three dimensional hydrogen-bonded water structures. Which interact in such a way that they act with parallel dipolar alignment in the same direction. It is result increase of effective number of aligned dipoles contributing to the mixture dielectric polarization (70). The negative deviation from ideal behaviour (ε^E being negative) is explained qualitatively either due to interstitial solvation or due to breaking of aggregates (71). The excess dielectric constant ε^E is also one such parameter that indicates the strength and nature of intermolecular interactions in binary mixtures. The excess dielectric constant data provide following information in relation to the molecular conformation (72-76):

(i) $\varepsilon^E = 0$ indicates that mixture constituents do not interact and thus have ideal mixing behaviour.

(ii) $\varepsilon^E < 0$ indicates that mixture constituents interact so as to reduce the total number of effective dipoles that contributed to the mixture dielectric polarization.

(iii) $\varepsilon^E > 0$ indicates that the constituents of a mixture interact in such a way that there is an increase in number of effective dipoles contributed in the mixture dielectric polarization.

(iv) The magnitude of ε^E values is the evidence of the strength of unlike molecules H-bond interactions, i.e. higher ε^E values represent the stronger H-bond unlike molecular connectivity's between unlike molecules and vice versa.

Also the dielectric parameter shows systematic change with temperature, therefore the excess dielectric constant values evaluated from mole fraction mixture conclude that these mixtures have intermolecular interactions and the degree of alignment decreased with increasing temperature as abstracted in the Table (3.7) and Fig. (3.7).

Table (3.7): Values of excess dielectric constant ε^E, dielectric constant and mole fractions of components at experimental temperatures.

Wt%	X1	X2	T(K)	ε_{12}	ε_1	ε_2	$X_1\ \varepsilon_1$	$X_2\ \varepsilon_2$	ε^E
0.10	99.99982	0.00018	293.15	75.15	80.36	7.93	8035.9855	0.0014	-7960.8370
			298.15	74.22	78.54	7.85	7853.9859	0.0014	-7779.7673
			303.15	73.18	76.75	7.71	7674.9862	0.0014	-7601.8076
			308.15	72.05	75.00	7.53	7499.9865	0.0014	-7427.9379
			313.15	71.19	73.28	7.39	7327.9868	0.0013	-7257.7981
			318.15	70.89	71.59	7.14	7158.9871	0.0013	-7088.0984
0.20	99.99964	0.00036	293.15	75.66	80.36	7.93	8035.9710	0.0029	-7960.3139
			298.15	74.75	78.54	7.85	7853.9716	0.0028	-7779.2245
			303.15	73.88	76.75	7.71	7674.9723	0.0028	-7601.0951
			308.15	72.82	75.00	7.53	7499.9729	0.0027	-7427.1556
			313.15	71.62	73.28	7.39	7327.9735	0.0027	-7256.3562
			318.15	70.69	71.59	7.14	7158.9742	0.0026	-7088.2867
0.30	99.99946	0.00054	293.15	76.24	80.36	7.93	8035.9564	0.0043	-7959.7207
			298.15	75.85	78.54	7.85	7853.9574	0.0043	-7778.1117
			303.15	75.22	76.75	7.71	7674.9584	0.0042	-7599.7426
			308.15	74.64	75.00	7.53	7499.9594	0.0041	-7425.3234
			313.15	74.00	73.28	7.39	7327.9603	0.0040	-7253.9643
			318.15	73.12	71.59	7.14	7158.9612	0.0039	-7085.8451

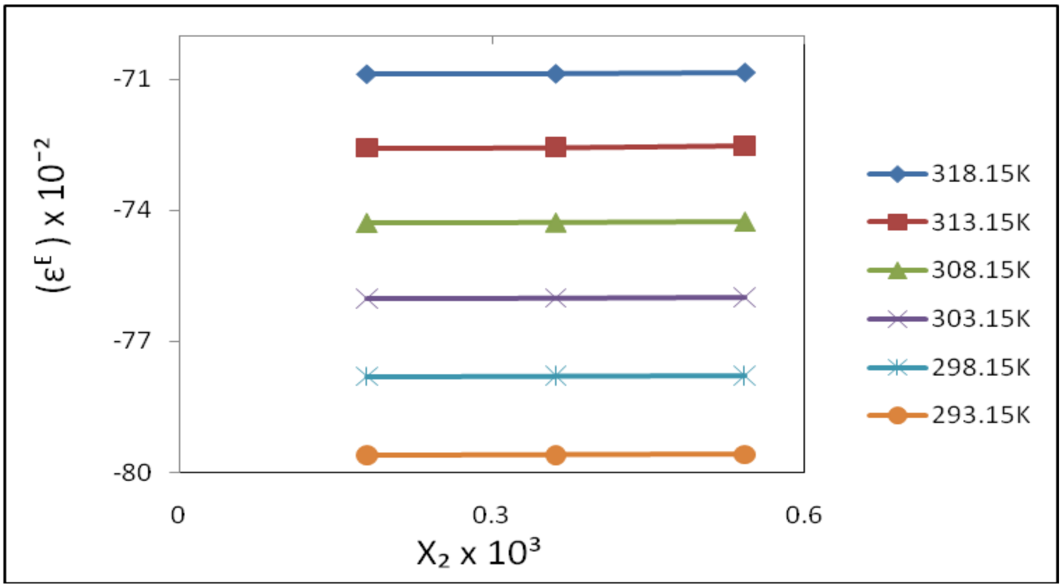


Fig. (3.7): Values of excess dielectric constant plotted against to mole fraction of HPMC in mixture at experimental temperatures.

3.5 Physical Properties of TMAB Solutions

Solutions of Tetramethylammonium Bromide (TMAB) in HPMC-water mixture have been prepared at nine different concentrations which were (0.047, 0.147, 0.247, 0.347, 0.447, 0.547, 0.647, 0.747 and 0.847) mol dm^{-3} in each of the three wt% of HPMC-water mixtures at six different temperatures in range (293.15 -318.15) K as mentioned before. The investigation covered density (d), viscosity (η) and molar conductance (Λ) of each salt solution have been measured at specified temperatures.

Density (d) is generally increased at a constant temperature with increasing of concentration of TMAB in each of three wt% of HPMC-water mixtures. At a constant concentration of TMAB in HPMC-water mixtures (d) decreased with rise of temperature as appears in Tables (3.8 I- II- III) and Figs. (3.8 I- II- III).

Viscosity (ɳ) increased also at constant temperature with increasing of concentrations of TMAB in each of three wt% of HPMC-water mixtures. At constant concentration of TMAB in HPMC-water mixtures (ɳ) decreased with rise of temperature as shown in Tables (3.9 I- II- III) and Figs. (3.9 I- II- III).

Molar conductivity (Λ) is generally decreased at a constant temperature with increasing of concentration of TMAB in each of three wt% of HPMC-water mixtures. At a constant concentration of TMAB in HPMC-water mixtures, (Λ) increased with rise of temperature as shown in Tables (3.10 I- II- III) and Figs. (3.10 I- II- III).

Table (3.8 I): Densities (d) of TMAB in (0.1%) of HPMC-water mixture at six experimental temperatures.

conc. (mol dm^{-3})	(d) g cm^{-3}					
	293.15K	298.15K	303.15K	308.15K	313.15K	318.15K
0.047	0.9981	0.9968	0.9952	0.9936	0.9918	0.9898
0.147	1.0012	1.0000	0.9985	0.9967	0.9947	0.9924
0.247	1.0044	1.0035	1.0022	0.9995	0.9978	0.9959
0.347	1.0079	1.0071	1.0058	1.0032	1.0013	0.9999
0.447	1.0121	1.0111	1.0094	1.0077	1.0055	1.0038
0.547	1.0159	1.0145	1.0137	1.0119	1.0096	1.0078
0.647	1.0203	1.0189	1.0172	1.0159	1.0141	1.0119
0.747	1.0235	1.0221	1.0210	1.0189	1.0175	1.0155
0.847	1.0271	1.0261	1.0241	1.0220	1.0204	1.0189

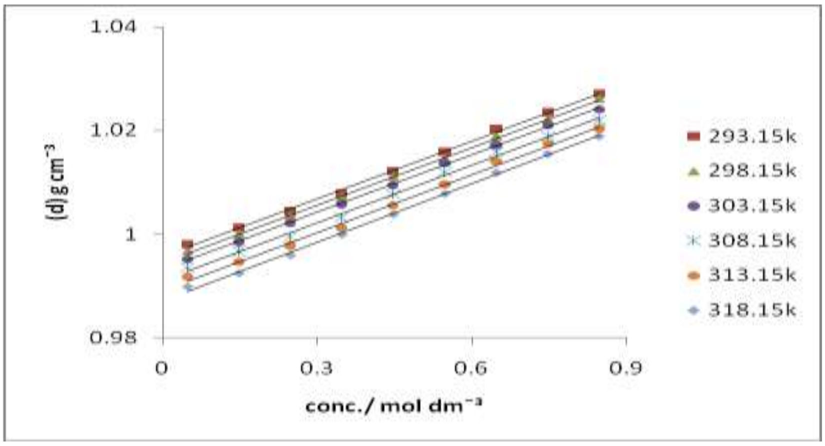
Table (3.8 II): Densities (d) of TMAB in (0.2%) of HPMC-water mixture at six experimental temperatures.

conc. (mol dm^{-3})	(d) g cm^{-3}					
	293.15K	298.15K	303.15K	308.15K	313.15K	318.15K
0.047	0.9988	0.9975	0.9958	0.9941	0.9922	0.9902
0.147	1.0021	1.0011	0.9989	0.9972	0.9951	0.9930
0.247	1.0054	1.0044	1.0026	1.0003	0.9985	0.9968
0.347	1.0093	1.0083	1.0061	1.0044	1.0019	1.0003
0.447	1.0131	1.0123	1.0101	1.0086	1.0061	1.0041
0.547	1.0170	1.0158	1.0141	1.0125	1.0104	1.0087
0.647	1.0212	1.0202	1.0180	1.0167	1.0148	1.0127
0.747	1.0248	1.0235	1.0212	1.0200	1.0181	1.0164
0.847	1.0281	1.0269	1.0247	1.0233	1.0211	1.0193

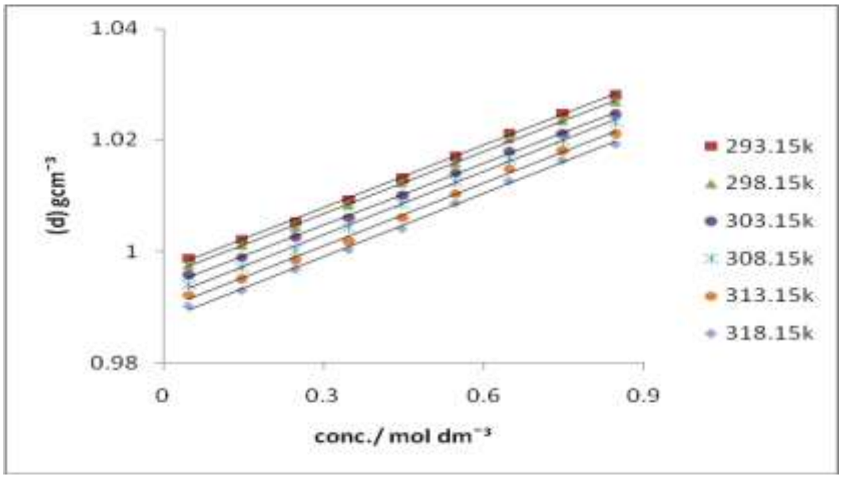
Table (3.8 III): Densities (d) of TMAB in (0.3%) of HPMC-water mixture at six experimental temperatures.

conc. (mol dm^{-3})	(d) g cm^{-3}					
	293.15K	298.15K	303.15K	308.15K	313.15K	318.15K
0.047	0.9995	0.9978	0.9964	0.9946	0.9928	0.9911
0.147	1.0029	1.0015	0.9998	0.9978	0.9958	0.9942
0.247	1.0062	1.0047	1.0031	1.0011	0.9991	0.9973
0.347	1.0104	1.0088	1.0065	1.0051	1.0025	1.0012
0.447	1.0141	1.0128	1.0106	1.0092	1.0070	1.0049
0.547	1.0179	1.0161	1.0147	1.0131	1.0113	1.0091
0.647	1.0222	1.0209	1.0188	1.0175	1.0157	1.0135
0.747	1.0258	1.0245	1.0222	1.0209	1.0188	1.0171
0.847	1.0292	1.0279	1.0259	1.0240	1.0220	1.0201

I



II



III

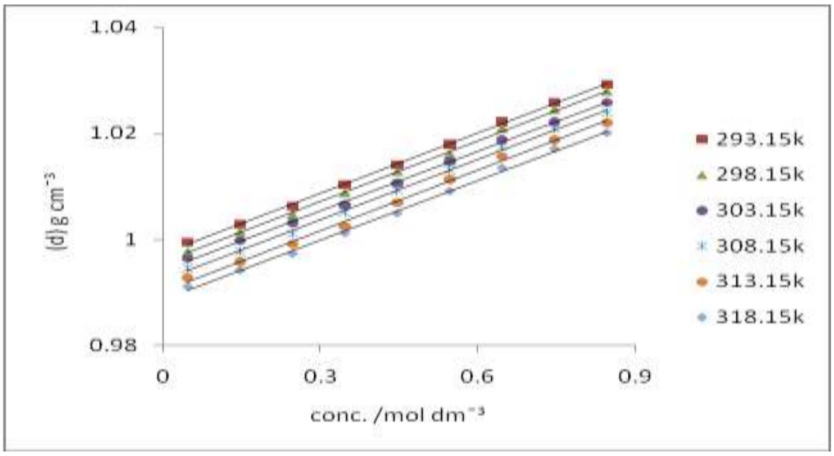


Fig. (3.8 I- II- III): Densities (d) of TMAB plotted against the concentrations of TMAB in (0.1, 0.2, and0.3) % respectively of HPMC-water mixture at six experimental temperatures.

Table (3.9 I): Viscosities (η) of TMAB in (0.1%) of HPMC-water mixture at six experimental temperatures.

Conc. (mol dm^{-3})	(η) cP					
	293.15K	298.15K	303.15K	308.15K	313.15K	318.15K
0.047	1.1107	0.9194	0.8455	0.7709	0.6841	0.5937
0.147	1.1129	0.9206	0.8463	0.7721	0.6854	0.5955
0.247	1.1258	0.9370	0.8560	0.7884	0.6987	0.6071
0.347	1.1339	0.9449	0.8664	0.7951	0.7111	0.6190

0.447	1.1426	0.9553	0.8772	0.8161	0.7253	0.6352
0.547	1.1519	0.9734	0.8982	0.8302	0.7409	0.6502
0.647	1.1681	0.9817	0.9133	0.8429	0.7559	0.6635
0.747	1.1845	0.9973	0.9358	0.8576	0.7711	0.6862
0.847	1.2097	1.0294	0.9546	0.8736	0.7814	0.7030

Table (3.9 II): Viscosities (η) of TMAB in (0.2%) of HPMC-water mixture at six experimental temperatures.

Conc. (mol dm^{-3})	(η) cP					
	293.15K	298.15K	303.15K	308.15K	313.15K	318.15K
0.047	1.1591	1.0201	0.9269	0.8272	0.7344	0.6439
0.147	1.1602	1.0214	0.9280	0.8287	0.7359	0.6451
0.247	1.1570	1.0144	0.9221	0.8297	0.7337	0.6398
0.347	1.1709	1.0231	0.9340	0.8431	0.7478	0.6490
0.447	1.1999	1.0417	0.9472	0.8545	0.7538	0.6528
0.547	1.2206	1.0540	0.9681	0.8690	0.7660	0.6752
0.647	1.2430	1.0796	0.9859	0.8919	0.7754	0.6890
0.747	1.2956	1.0949	1.0284	0.9150	0.8020	0.6993
0.847	1.3214	1.1192	1.0421	0.9272	0.8283	0.7146

Table (3.9 III): Viscosities (η) of TMAB in (0.3%) of HPMC-water mixture at six experimental temperatures.

Conc. (mol dm^{-3})	(η) cP					
	293.15K	298.15K	303.15K	308.15K	313.15K	318.15K
0.047	1.3782	1.2009	1.1100	1.0048	0.8499	0.7411
0.147	1.3837	1.2070	1.1184	1.0188	0.8556	0.7467
0.247	1.3800	1.2061	1.1229	1.0218	0.8520	0.7430
0.347	1.3945	1.2181	1.1327	1.0269	0.8621	0.7553

0.447	1.4034	1.2283	1.1454	1.0457	0.8700	0.7681
0.547	1.4335	1.2486	1.1563	1.0585	0.8866	0.7846
0.647	1.4549	1.2589	1.1770	1.0756	0.9123	0.7961
0.747	1.4689	1.2884	1.1995	1.0957	0.9259	0.8100
0.847	1.5030	1.3178	1.2261	1.1194	0.9390	0.8227

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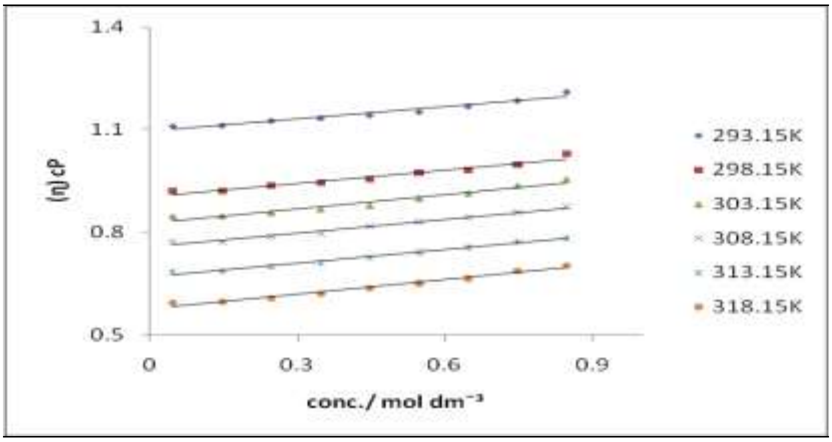

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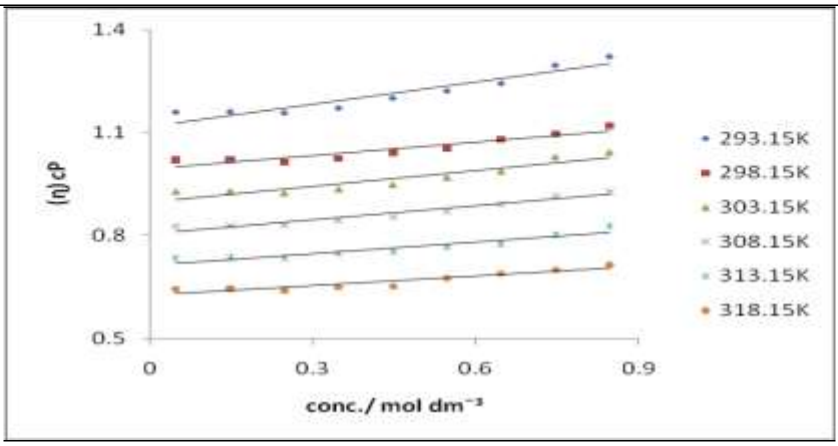

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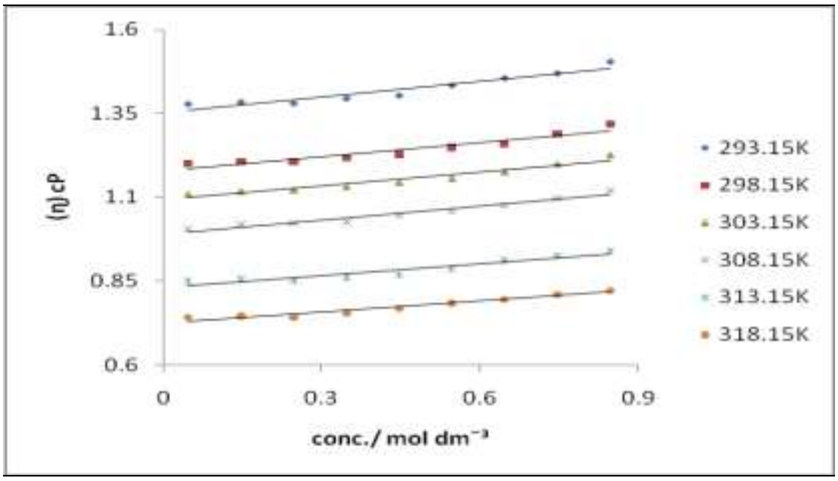

Fig.(3.9 I- II- III): Viscosity (η) of TMAB plotted against the molar concentration of TMAB in (0.1,0.2 and0.3)% respectively of HPMC-water mixture at six experimental temperatures.

Table (3.10 I): Molar conductance (Λ) of TMAB in (0.1%) of HPMC-water mixture at six experimental temperatures.

Conc. (mol dm^{-3})	(Λ)S cm^2 mol^{-1}					
	293.15K	298.15K	303.15K	308.15K	313.15K	318.15K
0.047	106.313	108.121	111.532	113.293	117.046	125.277
0.147	90.773	92.714	95.755	100.116	103.165	110.004
0.247	85.113	89.139	93.26	95.259	97.757	104.003
0.347	80.504	83.098	86.709	90.322	93.354	97.536
0.447	77.497	80.112	82.744	86.576	90.232	93.443
0.547	73.309	77.514	79.89	83.084	85.009	89.379

0.647	71.261	76.043	78.053	80.453	83.694	86.192
0.747	69.155	73.967	75.904	78.447	80.589	83.802
0.847	65.544	70.373	73.2	75.443	77.922	81.11

Table (3.10 II): Molar conductance (Λ) of TMAB in (0.2%) of HPMC-water mixture at six experimental temperatures.

Conc. (mol dm^{-3})	(Λ)*S* cm^2 mol^{-1}					
	293.15K	298.15K	303.15K	308.15K	313.15K	318.15K
0.047	118.149	122.479	127.447	130.247	133.638	137.419
0.147	100.787	104.559	109.401	112.113	114.163	119.687
0.247	92.694	95.69	101.73	104.308	106.133	110.19
0.347	86.224	89.126	92.726	96.473	99.496	104.253
0.447	80.976	83.668	87.221	91.291	95.595	97.394
0.547	75.824	79.265	83.365	84.826	88.472	92.859
0.647	71.879	75.125	79.989	81.884	84.008	88.253
0.747	70.112	72.236	74.315	76.152	79.184	84.203
0.847	66.101	68.466	71.189	73.467	76.749	80.711

Table (3.10 III): Molar conductance (Λ) of TMAB in (0.3 %) of HPMC-water mixture at six experimental temperatures.

Conc. (mol dm^{-3})	(Λ)*S* cm^2 mol^{-1}					
	293.15K	298.15K	303.15K	308.15K	313.15K	318.15K
0.047	127.596	130.617	135.363	142.632	147.277	155.596
0.147	107.401	110.884	116.286	120.728	125.635	133.937
0.247	95.444	99.282	105.51	111.422	115.112	119.478
0.347	89.189	91.167	98.625	102.351	107.542	111.832
0.447	84.742	88.201	93.557	96.611	100.966	104.676
0.547	80.162	83.804	88.162	90.553	95.517	97.422

0.647	74.108	78.516	82.762	84.235	88.325	91.924
0.747	71.491	73.718	79.25	81.794	83.802	86.345
0.847	67.838	70.528	73.994	75.325	77.714	81.102

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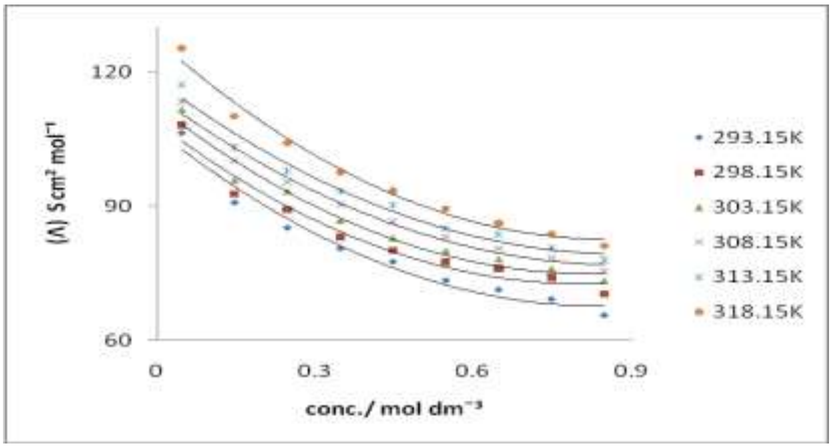

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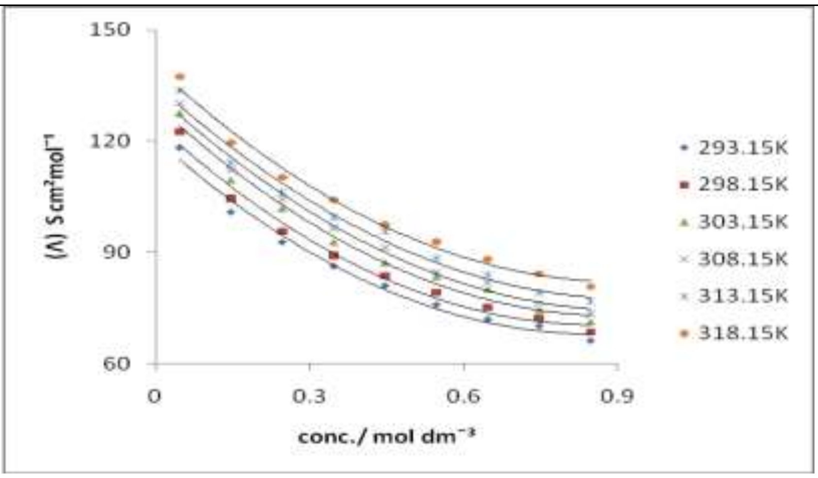

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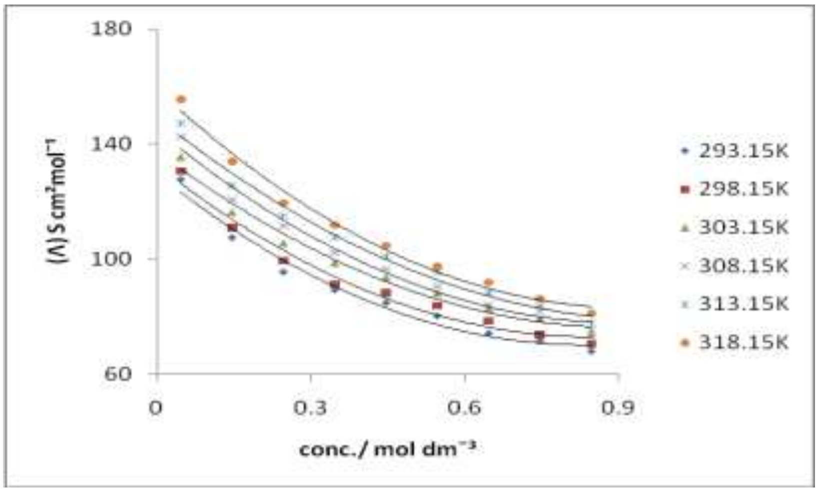

Fig. (3.10 I- II- III): Molar conductance (Λ) of TMAB plotted against the concentration of TMAB in (0.1, 0.2 and 0.3) % respectively of HPMC-water mixture at six experimental temperatures.

3.6 Physical Properties of TEAB Solutions

Solutions of Tetraethylammonium Bromide (TEAB) in HPMC-water mixture also have been prepared at nine different concentrations which were (0.047, 0.147, 0.247, 0.347, 0.447, 0.547, 0.647, 0.747 and 0.847) mol dm^{-3} in each of the three wt% of HPMC-water mixtures at six different temperatures in range (293.15 -318.15) K as mentioned before.

Density (d), viscosity (ɳ) and molar conductance (Λ) of each salt solution have been measured at specified temperatures.

Density (d) is generally increased at a constant temperature with increasing concentration of TEAB in each of three different wt% of HPMC-water mixtures. At a constant concentration of TEAB in HPMC-water mixtures, (d) decreased with rise of temperature as appears in Tables (3.11 I- II- III) and Figs. (3.11 I- II- III).

Viscosity (ɳ) increased also at a constant temperature with increasing of concentrations of TEAB in each of three different wt% of HPMC-water mixtures. At a constant concentration of TEAB in HPMC-water mixtures, (ɳ) decreased with the rise of temperature as appears in Tables (3.12 I- II- III) and Figs. (3.12 I- II- III).

Molar conductivity (Λ) is generally decreased at a constant temperature with increasing of concentration of TEAB in each of three different wt% of HPMC-water mixtures. At a constant concentration of TEAB in HPMC-water mixtures, (Λ) increased with rise of temperature as shown in Tables (3.13 I- II- III) and Figs. (3.13 I- II- III).

Table (3.11 I): Densities (d) of TEAB in (0.1%) of HPMC-water mixture at six experimental temperatures.

conc. (mol dm^{-3})	(d) g cm^{-3}					
	293.15K	298.15K	303.15K	308.15K	313.15K	318.15K

0.047	0.9989	0.9974	0.9959	0.9944	0.9922	0.9903
0.147	1.0021	1.0008	0.9989	0.9975	0.9951	0.9935
0.247	1.0056	1.0043	1.0025	1.0010	0.9987	0.9965
0.347	1.0089	1.0078	1.0058	1.0042	1.0020	1.0004
0.447	1.0132	1.0118	1.0101	1.0083	1.0059	1.0043
0.547	1.0172	1.0161	1.0142	1.0125	1.0103	1.0080
0.647	1.0213	1.0198	1.0179	1.0165	1.0142	1.0122
0.747	1.0245	1.0229	1.0210	1.0197	1.0179	1.0162
0.847	1.0281	1.0266	1.0245	1.0229	1.0212	1.0194

Table (3.11 II): Densities (d) of TEAB in (0.2%) of HPMC-water mixture at six experimental temperatures.

conc. (mol dm^{-3})	(d) g cm^{-3}					
	293.15K	298.15K	303.15K	308.15K	313.15K	318.15K
0.047	0.9996	0.9981	0.9965	0.9948	0.9928	0.9911
0.147	1.0028	1.0017	0.9995	0.9977	0.9958	0.9939
0.247	1.0061	1.0051	1.0032	1.0009	0.9994	0.9974
0.347	1.0100	1.0089	1.0066	1.0049	1.0029	1.0013
0.447	1.0139	1.0128	1.0107	1.0090	1.0069	1.0049
0.547	1.0175	1.0161	1.0148	1.0132	1.0112	1.0092
0.647	1.0218	1.0204	1.0185	1.0173	1.0154	1.0135

0.747	1.0253	1.0242	1.0219	1.0207	1.0189	1.0169
0.847	1.0288	1.0275	1.0251	1.0237	1.0220	1.0202

Table (3.11 III): Densities (d) of TEAB in (0.3%) of HPMC-water mixture at six experimental temperatures.

conc. (mol dm^{-3})	(d) g cm^{-3}					
	293.15K	298.15K	303.15K	308.15K	313.15K	318.15K
0.047	1.0003	0.9987	0.9971	0.9955	0.9935	0.9917
0.147	1.0037	1.0023	1.0001	0.9983	0.9963	0.9949
0.247	1.0069	1.0054	1.0038	1.0018	0.9998	0.9980
0.347	1.0111	1.0096	1.0073	1.0057	1.0035	1.0020
0.447	1.0149	1.0133	1.0113	1.0097	1.0076	1.0056
0.547	1.0186	1.0169	1.0155	1.0139	1.0120	1.0098
0.647	1.0229	1.0215	1.0195	1.0181	1.0162	1.0143
0.747	1.0264	1.0251	1.0229	1.0215	1.0195	1.0177
0.847	1.0298	1.0285	1.0268	1.0247	1.0225	1.0207

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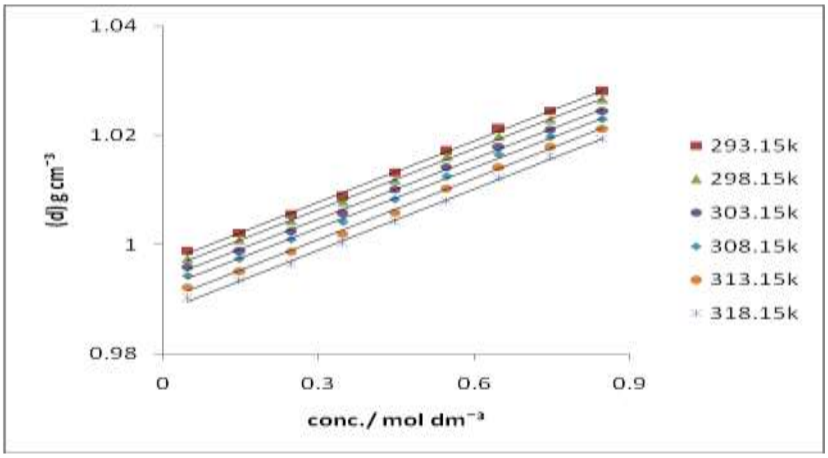

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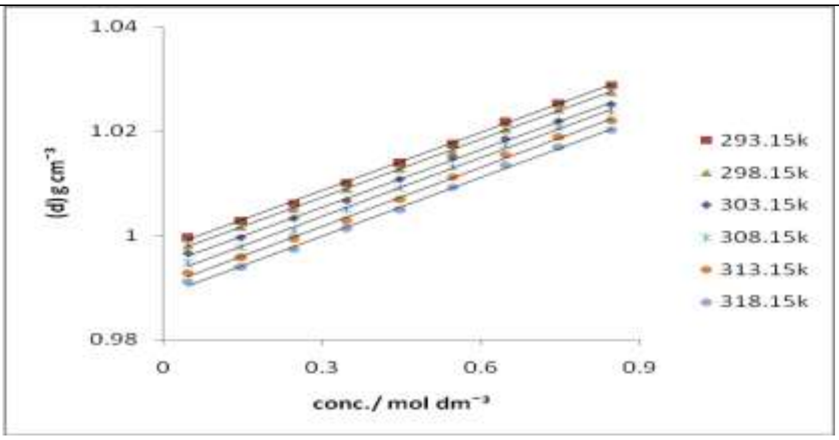

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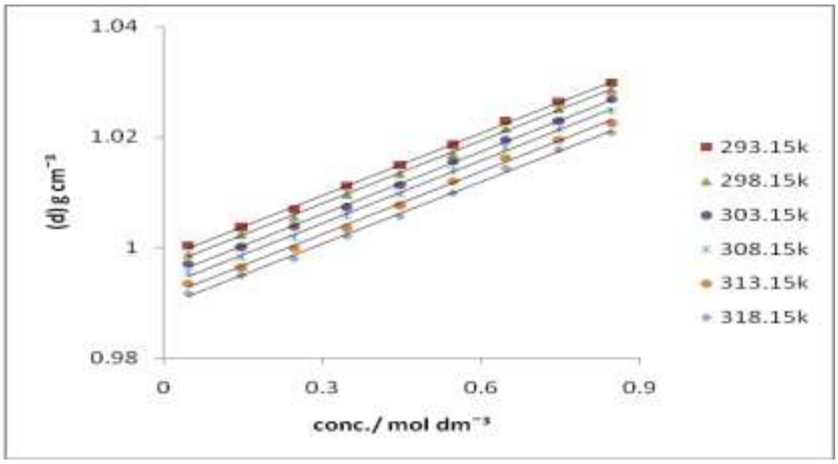

Fig. (3.11 I- II- III): Densities (d) of TEAB plotted against the concentrations of TEAB in (0.1, 0.2 and0.3) % respectively of HPMC-water mixture at six experimental temperatures.

Table (3.12 I): Viscosity (η) of TEAB in (0.1%) of HPMC-water mixture at six experimental temperatures.

Conc. (mol dm^{-3})	(η) cP					
	293.15K	298.15K	303.15K	308.15K	313.15K	318.15K
0.047	1.0855	0.9637	0.8545	0.7409	0.6589	0.5972
0.147	1.0873	0.9654	0.8558	0.7422	0.6600	0.5984
0.247	1.1244	0.9911	0.8800	0.7564	0.6754	0.6144
0.347	1.1978	1.0487	0.9404	0.8210	0.7241	0.6457
0.447	1.2297	1.0703	0.9712	0.8631	0.7577	0.6686
0.547	1.2622	1.1060	0.9922	0.8889	0.7782	0.6909

0.647	1.3137	1.1552	1.0297	0.9353	0.8062	0.7220
0.747	1.3675	1.1970	1.0661	0.9691	0.8440	0.7460
0.847	1.3944	1.2239	1.1064	1.0163	0.8747	0.7627

Table (3.12 II): Viscosity (η) of TEAB in (0.2%) of HPMC-water mixture at six experimental temperatures.

Conc. (mol dm^{-3})	(η) cP					
	293.15K	298.15K	303.15K	308.15K	313.15K	318.15K
0.047	1.2204	1.0899	0.9695	0.8589	0.7571	0.6629
0.147	1.2323	1.0905	0.9704	0.8602	0.7583	0.6641
0.247	1.2728	1.1207	1.0085	0.8951	0.7723	0.6765
0.347	1.3047	1.1390	1.0256	0.9057	0.7931	0.6972
0.447	1.3791	1.2129	1.0908	0.9633	0.8411	0.7409
0.547	1.4165	1.2428	1.1230	1.0016	0.8715	0.7669
0.647	1.4453	1.2691	1.1501	1.0384	0.9083	0.7957
0.747	1.5057	1.3321	1.2092	1.0733	0.9362	0.8178
0.847	1.5799	1.4019	1.2492	1.1156	0.9835	0.8516

Table (3.12 III): Viscosity (η) of TEAB in (0.3%) of HPMC-water mixture at six experimental temperatures.

Conc. (mol dm^{-3})	(η) cP					
	293.15K	298.15K	303.15K	308.15K	313.15K	318.15K
0.047	1.3389	1.2221	1.0865	0.9969	0.8466	0.7387
0.147	1.3474	1.2237	1.0878	0.9983	0.8487	0.7401
0.247	1.4055	1.2579	1.1148	1.0269	0.8763	0.7532
0.347	1.4832	1.2984	1.1624	1.0616	0.9107	0.7809
0.447	1.5568	1.3694	1.2406	1.1125	0.9518	0.8441

0.547	1.6202	1.4335	1.2837	1.1460	0.9862	0.8779
0.647	1.6754	1.4842	1.3396	1.2010	1.0298	0.9092
0.747	1.7581	1.5242	1.3921	1.2402	1.0810	0.9526
0.847	1.8299	1.6119	1.4598	1.3282	1.1390	0.9916

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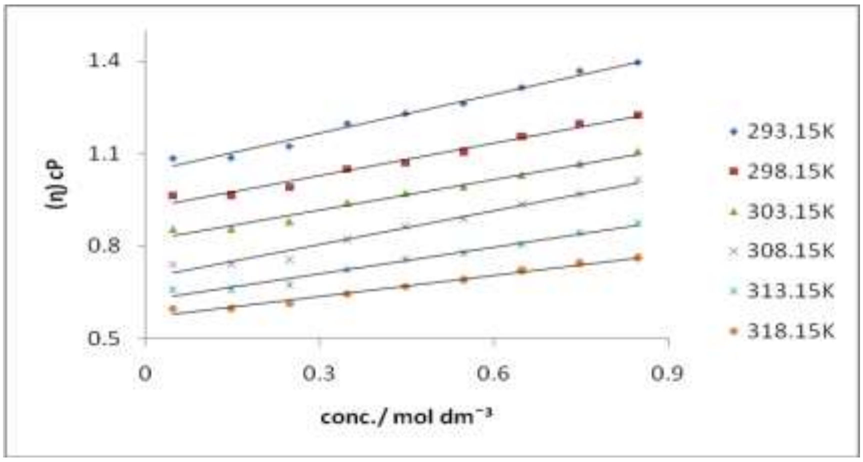

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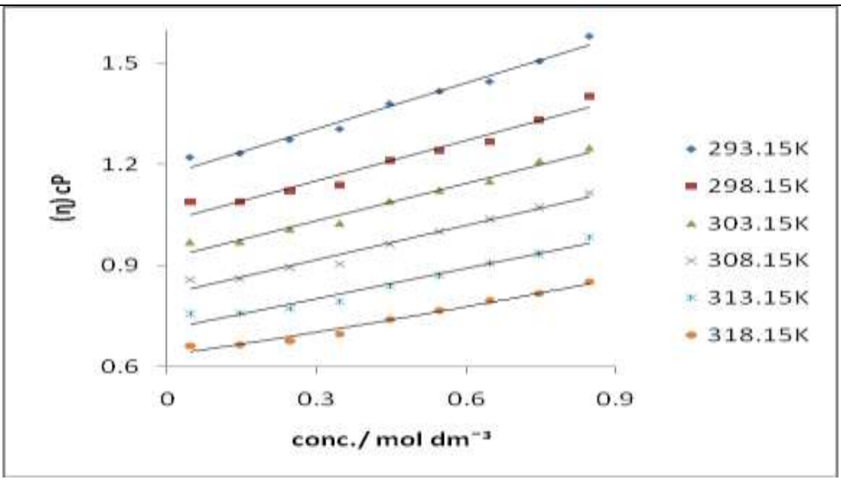

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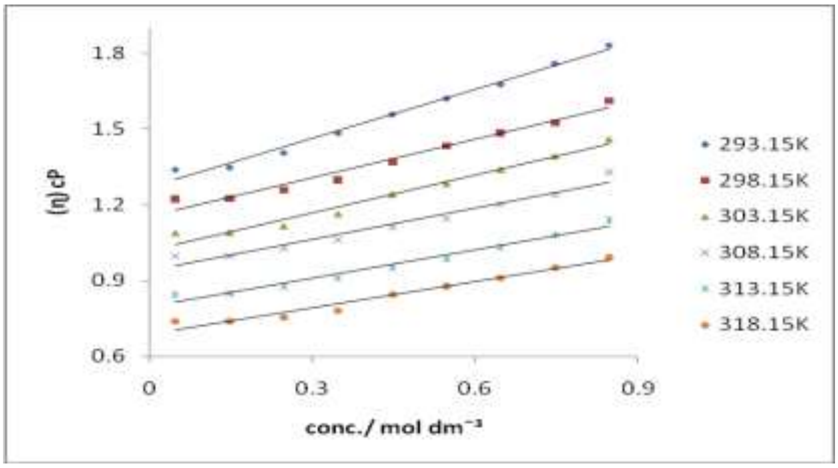

Fig. (3.12 I- II- III): Viscosities (η) of TEAB plotted against the concentrations of TEAB in (0.1, 0.2 and 0.3) % respectively of HPMC-water mixture at six experimental temperatures.

Table (3.13 I): Molar conductance (Λ) of TEAB in (0.1%) of HPMC-water mixture at six experimental temperatures.

Conc. mol dm^{-3}	(Λ)*S* cm^2 mol^{-1}					
	293.15K	298.15K	303.15K	308.15K	313.15K	318.15K
0.047	82.104	85.234	88.787	91.489	95.468	98.447
0.147	69.411	72.503	76.748	79.014	82.871	85.952
0.247	61.703	65.237	68.640	70.019	71.878	74.684
0.347	58.925	61.508	63.997	65.556	67.128	70.109
0.447	54.315	57.077	59.866	61.816	63.535	65.219
0.547	51.371	54.027	56.673	58.318	60.695	62.340

0.647	49.304	51.705	53.787	54.869	56.878	58.733
0.747	46.355	48.862	50.870	52.477	53.083	55.982
0.847	43.746	45.989	48.878	50.059	51.833	53.955

Table (3.13 II): Molar conductance (Λ) of TEAB in (0.2%) of HPMC-water mixture at six experimental temperatures.

Conc. mol dm^{-3}	(Λ)*S* cm^2 mol^{-1}					
	293.15K	298.15K	303.15K	308.15K	313.15K	318.15K
0.047	89.277	93.342	97.243	100.985	107.532	114.298
0.147	76.000	78.255	83.272	86.354	90.775	95.837
0.247	67.743	70.040	73.270	75.304	80.128	85.781
0.347	62.248	64.841	67.487	69.588	72.911	79.657
0.447	59.159	62.640	65.101	67.492	69.128	74.378
0.547	55.941	58.318	61.792	63.803	65.265	69.642
0.647	51.632	55.332	57.496	59.351	62.206	65.278
0.747	49.736	52.477	53.548	56.211	58.894	60.755
0.847	46.517	48.406	49.587	52.886	55.779	57.664

Table (3.13 III): Molar conductance (Λ) of TEAB in (0.3%) of HPMC-water mixture at six experimental temperatures.

Conc. mol dm^{-3}	(Λ)*S* cm^2 mol^{-1}					
	293.15K	298.15K	303.15K	308.15K	313.15K	318,15K
0.047	90.617	95.255	102.021	107.298	114.702	121.581
0.147	76.155	83.231	87.395	92.837	96.599	103.041
0.247	70.04	76.471	78.620	82.328	86.972	92.145
0.347	63.977	69.112	72.605	75.509	80.510	84.593
0.447	60.850	63.535	66.219	69.904	74.036	77.839
0.547	56.124	59.232	62.157	64.351	70.567	73.566

0.647	53.941	56.569	58.733	61.124	64.697	67.379
0.747	50.870	53.012	54.752	59.438	60.432	62.911
0.847	47.226	48.996	51.004	55.445	57.664	59.316

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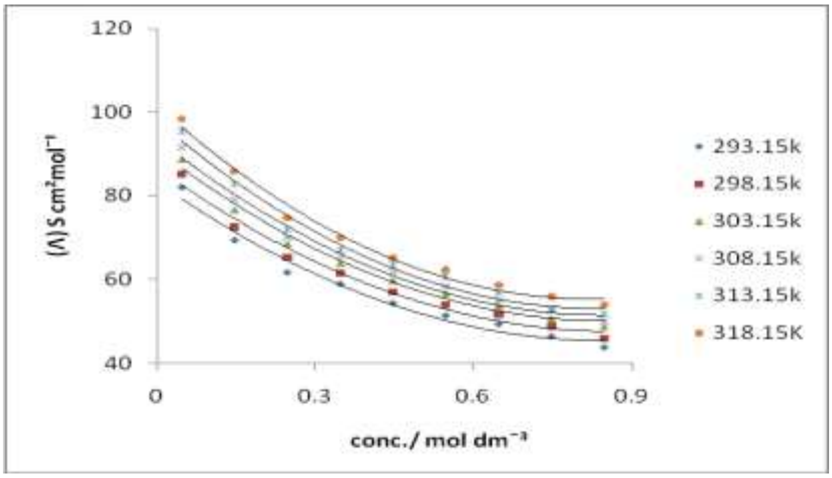

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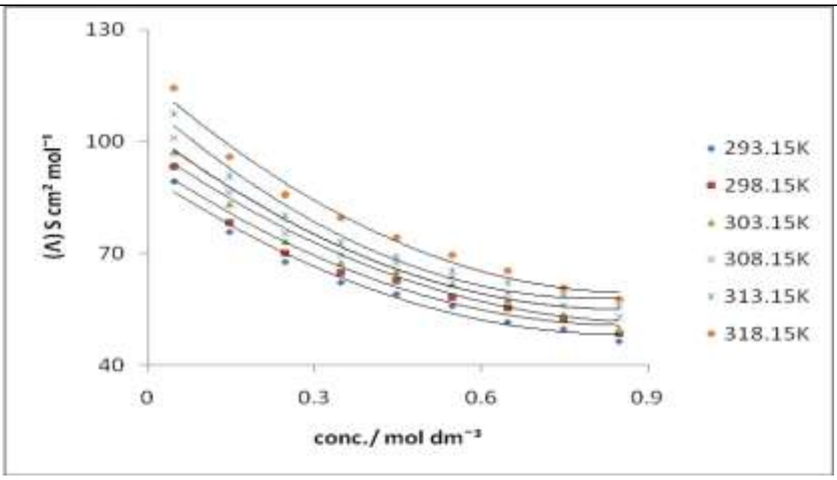

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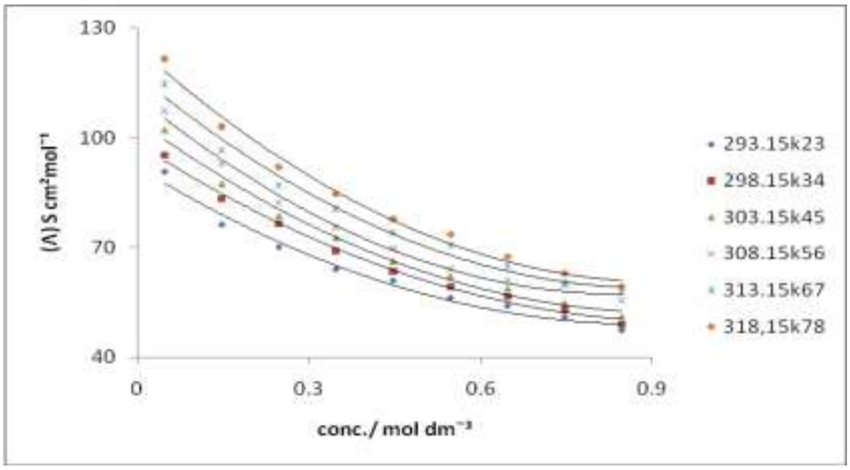


Fig. (3.13 I- II- III): Molar conductance (Λ) of TEAB plotted against the concentration of TEAB in (0.1, 0.2and 0.3) % respectively of HPMC-water mixture at six experimental temperatures.

The increase of density at constant temperature (298.15) K was summarized in the Fig. (3.14 I) showed the little different between the two salts. There is a decrease of the density with rise temperatures at the same concentration shown in fig. (3.14 II).

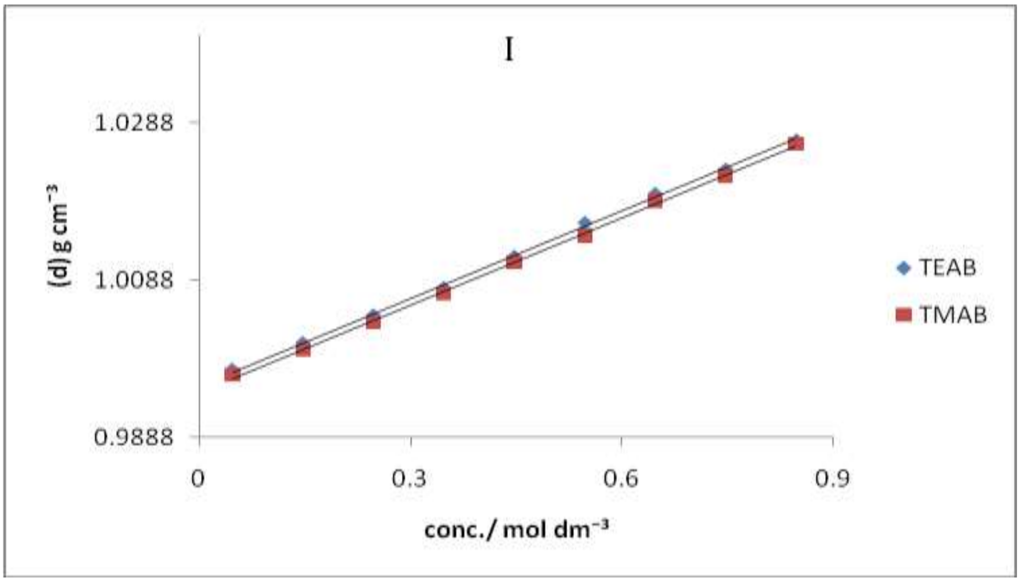


Fig. (3.14 I): Densities (d) of TMAB and TEAB plotted against the concentrations of each salt in (0.1%) of HPMC-water mixture at 298.15K.

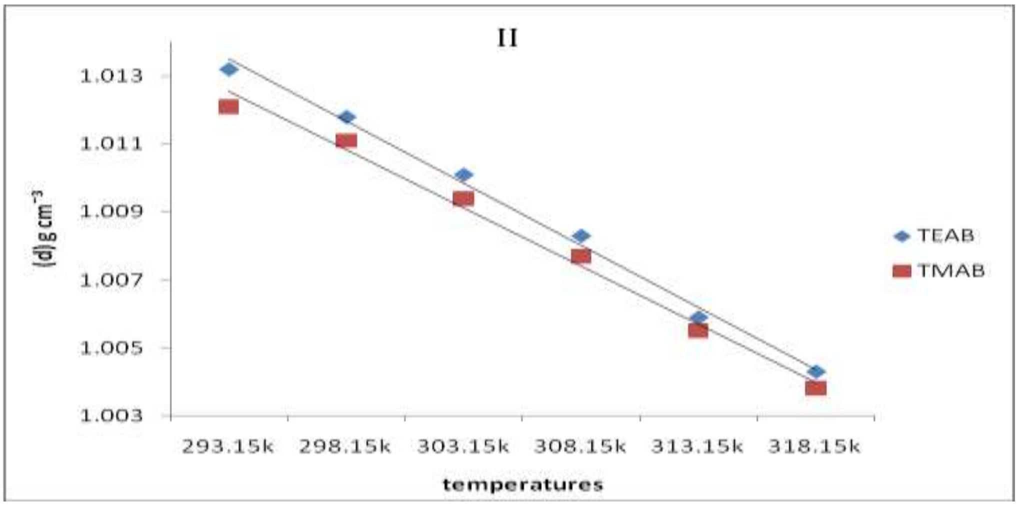


Fig. (3.14 II): Densities (d) of TMAB and TEAB at concentration 0.447 mol dm^{-3} plotted against six experimental temperatures.

The difference in viscosity between TMAB and TEAB at a constant temperature (298.15)K appears clearly in case TEAB the viscosity has been highly than TMAB as shown in Fig.(3.15 I). There is also a decrease in the viscosity with rise temperatures at the same concentration (0.447) mol dm^{-3} summarize in Fig. (3.15 II).

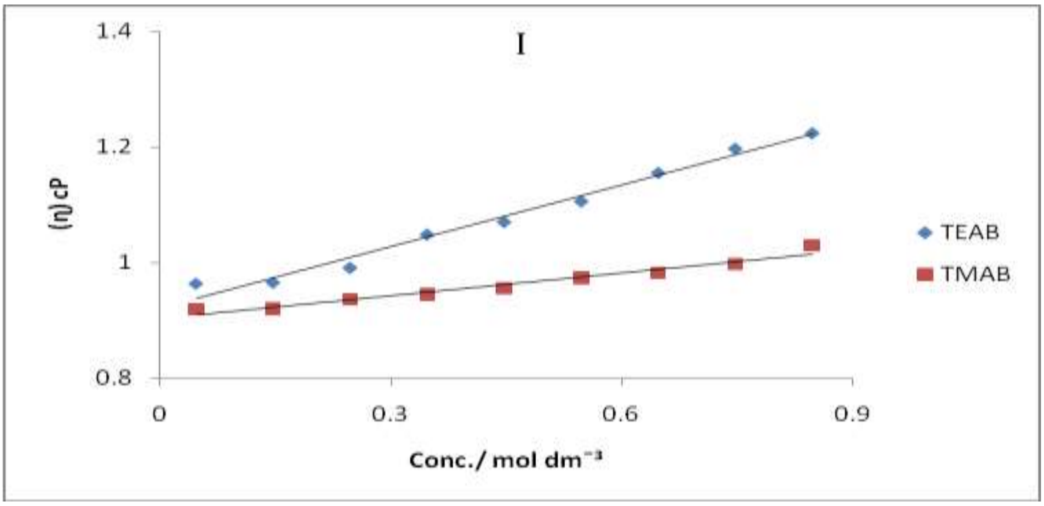


Fig. (3.15 I): Viscosity (ɳ) of TMAB and TEAB plotted against the concentration of each salt in (0.1%) of HPMC-water mixture at 298.15K.

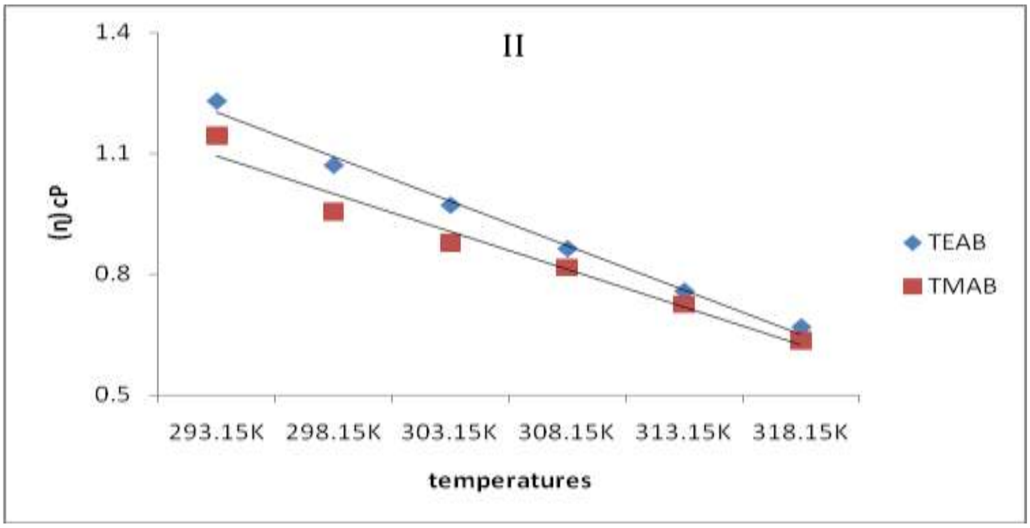


Fig. (3.15 II): Viscosity (ɳ) of TMAB and TEAB at concentration 0.447 mol dm^{-3} plotted against six experimental temperatures.

Molar conductance (Λ) decreasing with increasing of concentrations at constant temperature (298.15) K in same range as compared between TMAB and TEAB as shown in Fig.(3.16 I). There is also an increasing at constant concentration (0.447) mol dm^{-3} with rise experimental temperatures represented in Fig.(3.16 II).

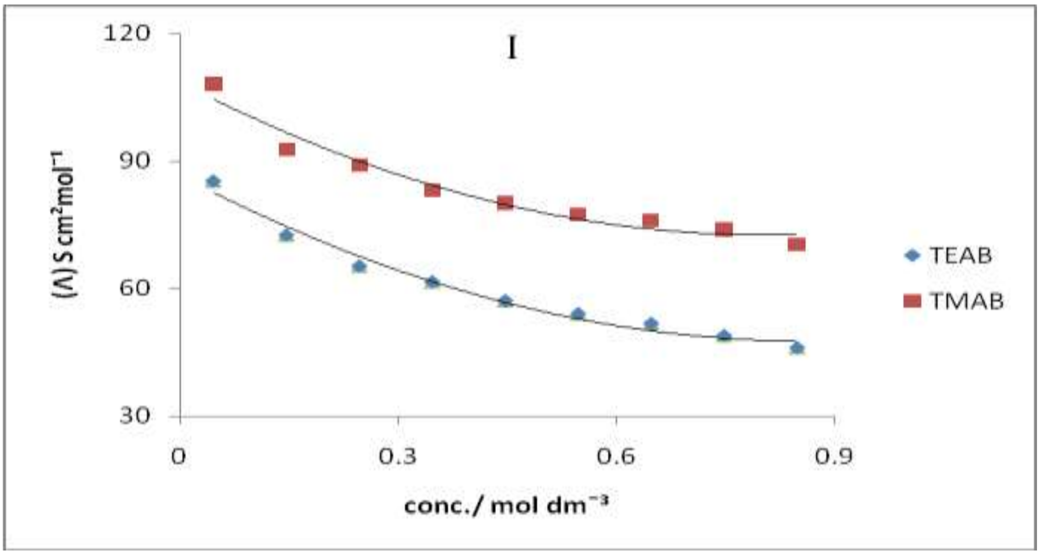


Fig. (3.16 I): Molar conductance (Λ) of TMAB and TEAB plotted against the concentration of each salt in (0.1%) of HPMC-water mixture at 298.15K.

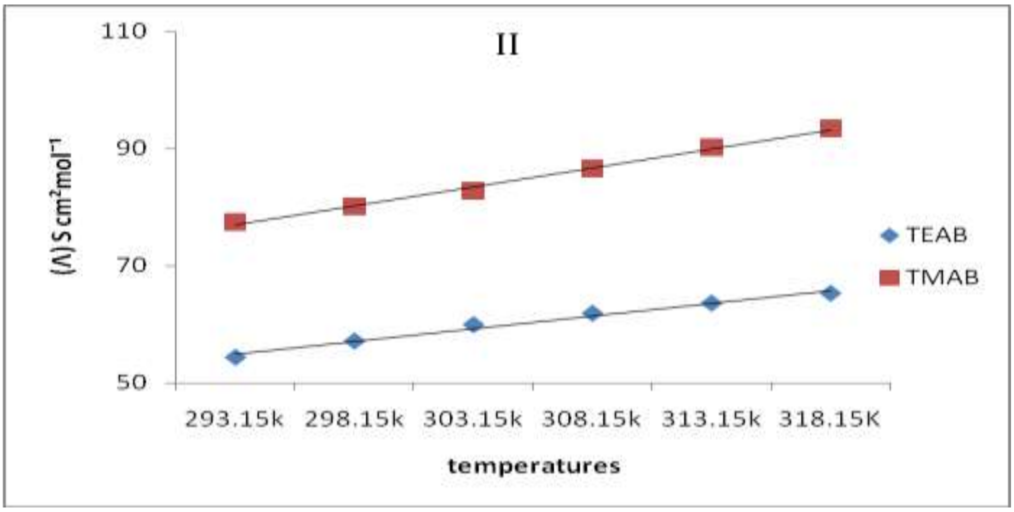


Fig. (3.16 II): Molar conductance (Λ) of TMAB and TEAB at concentration 0.447 mol dm^{-3} plotted against six experimental temperatures.

3.7 Relative Viscosity and Viscosity Coefficients

Electrolytic solutions of moderate concentration generally have relative dynamic viscosities (η_r) which obey the empirical equation has been analyzed using Jones–Dole equation (77):

$$\boxed{\eta_r = \frac{\eta}{\eta_0} = 1 + A\sqrt{C} + BC}$$

- - - - - - - - - (3.9)

Where η is the measured viscosity of the electrolyte solution, η_0 is the viscosity of the pure solvent at the same temperature, A and B are the Jones–Dole (78) coefficients, C is the molar concentration of electrolyte in solution.

The coefficient A in the equation above accounts for electrostatic interactions of the solute particles with one another(79). While the viscosity B-coefficients reflects the cumulative effects the interactions between the solvent and the solute particles(80). It represents coulombic interactions, size, shape effect of solute or Einstein effect, structural effect, and effect of solvation caused by solute–solvent interaction. It is a main contributor to η_r. The relative changes in viscosity represented (specific viscosity) as (81):

$$\boxed{\Delta\eta = \frac{\eta - \eta_0}{\eta_0} = \frac{\eta}{\eta_0} - 1} \quad \text{- - - - - - - - - - - (3.10)}$$

Also Jones–Dole equation may be expressed by:

$$\boxed{\frac{(\eta_r - 1)}{\sqrt{c}} = A + B\sqrt{c}} \quad \text{- - - - - - - - - (3.11)}$$

The results obtained in Tables (3.14 I- II- III) for measurements of TMAB in the three wt% of HPMC-water mixture (0.1, 0.2 and 0.3) %

respectively at six experimental temperatures. Also, Tables (3.15 I- II- III) for measurements of TEAB in the three wt% of HPMC-water mixture at six experimental temperatures. Fig. (3.17 I- II- III) represent the values of $(\frac{(\eta_r-1)}{\sqrt{c}})$ for TMAB in three of wt% of HPMC-water mixture respectively plotted against $\sqrt{c}$ at six experimental temperatures. Fig. (3.18 I- II- III) represent the values of $(\frac{(\eta_r-1)}{\sqrt{c}})$ for TEAB in wt% of HPMC-water mixture plotted against $\sqrt{c}$ at six experimental temperatures. According to the result above the possibility obtained the A and B coefficients values by plotting the left –hand term of equation (3.11) as a function to $\sqrt{c}$. A straight line is obtained of a slope B and an intercept A on the y coordinate. Tables (3.16 I) give the values of A and B viscosity coefficients for TMAB as function to wt% of HPMC-water mixture at six experimental temperatures. While Table (3.16 II) give the values of A and B viscosity coefficients for TEAB as function to wt% of HPMC-water mixture at six experimental temperatures. The values of A obtained are negative in all systems for each salt TMAB and TEAB which were studied. The negative values of A indicate there is a weak solute-solute interaction in the systems. B-coefficient is known as measure of solute-solvent interaction. It means that the structure-breaking effect becomes predominant in these solutions. The values of these properties may be affected by two factors(82). The first is the molar concentration of solute in the mixture. The second factor is the strength of bonds between solvent and solute molecules due to the values of polarity (dipole-dipole interaction and the H-bonds).

Table (3.14 I): Values of ((η_r-1)/$\sqrt{c}$) for TMAB in 0.1% HPMC-water mixture as function of √C at six experimental temperatures.

√C	$(\eta_r\ 1)/\sqrt{c}$					
	293.15K	298.15K	303.15K	308.15K	313.15K	318.15K
0.2168	-0.2901	-0.5950	-0.4087	-0.1850	-0.2006	-0.3861
0.3834	-0.1594	-0.3336	-0.2287	-0.1006	-0.1088	-0.2110
0.4969	-0.1010	-0.2262	-0.1556	-0.0368	-0.0465	-0.1265
0.5891	-0.0737	-0.1781	-0.1122	-0.0169	-0.0097	-0.0757
0.6686	-0.0538	-0.1421	-0.0814	0.0243	0.0211	-0.0293

0.7396	-0.0381	-0.1053	-0.0430	0.0456	0.0485	0.0047
0.8044	-0.0180	-0.0870	-0.0193	0.0615	0.0707	0.0300
0.8643	-0.0008	-0.0639	0.0101	0.0786	0.0904	0.0684
0.9203	0.0224	-0.0269	0.0315	0.0954	0.1006	0.0924

Table (3.14 II): Values of $((\eta_r-1)/\sqrt{c})$ for TMAB in 0.2% HPMC-water mixture as function of √C at six experimental temperatures.

√C	$(\eta_r\ 1)/\sqrt{c}$					
	293.15K	298.15K	303.15K	308.15K	313.15K	318.15K
0.2168	-0.6098	-0.6554	-0.6365	-0.5378	-0.5258	-0.5784
0.3834	-0.3426	-0.3678	-0.3574	-0.2999	-0.2926	-0.3229
0.4969	-0.2693	-0.2956	-0.2868	-0.2293	-0.2311	-0.2637
0.5891	-0.2095	-0.2370	-0.2231	-0.1691	-0.1660	-0.2011
0.6686	-0.1521	-0.1855	-0.1781	-0.1308	-0.1355	-0.1695
0.7396	-0.1165	-0.1536	-0.1348	-0.0973	-0.1026	-0.1119
0.8044	-0.0863	-0.1145	-0.1033	-0.0591	-0.0802	-0.0797
0.8643	-0.0347	-0.0916	-0.0504	-0.0265	-0.0375	-0.0580
0.9203	-0.0116	-0.0639	-0.0336	-0.0106	-0.0008	-0.0320

Table (3.14 III): Values of $((\eta_r-1)/\sqrt{c})$ for TMAB in 0.3% HPMC-water mixture as function of √C at six experimental temperatures.

√C	$(\eta_r\ 1)/\sqrt{c}$					
	293.15K	298.15K	303.15K	308.15K	313.15K	318.15K
0.2168	-0.3805	-0.5263	-0.53	-0.4756	-0.5484	-0.5807
0.3834	-0.2055	-0.2859	-0.2821	-0.2363	-0.2948	-0.3112
0.4969	-0.1637	-0.222	-0.2105	-0.1768	-0.2349	-0.2487
0.5891	-0.1215	-0.1722	-0.1643	-0.1415	-0.1804	-0.1852
0.6686	-0.0983	-0.1404	-0.1297	-0.0996	-0.1467	-0.1406
0.7396	-0.0618	-0.1067	-0.1055	-0.0746	-0.1094	-0.1007

0.8044	-0.039	-0.0886	-0.0764	-0.0496	-0.0674	-0.0758
0.8643	-0.0256	-0.0574	-0.0503	-0.0255	-0.0464	-0.0516
0.9203	0.0007	-0.0303	-0.0242	-0.0009	-0.0288	-0.0322

Table (3.15 I): Values of $((\eta_r-1)/\sqrt{c})$ for TEAB in 0.1% HPMC-water mixture as function of √C at six experimental temperatures.

√C	$(\eta_r\ 1)/\sqrt{c}$					
	293.15K	298.15K	303.15K	308.15K	313.15K	318.15K
0.2168	-0.3884	-0.4018	-0.3639	-0.3570	-0.3630	-0.3612
0.3834	-0.2156	-0.2237	-0.2011	-0.1981	-0.2009	-0.1990
0.4969	-0.1035	-0.1232	-0.1042	-0.1188	-0.1136	-0.1057
0.5891	0.0178	-0.0110	0.0233	0.0379	0.0210	-0.0057
0.6686	0.0561	0.0208	0.0701	0.1117	0.0888	0.0477
0.7396	0.0878	0.0645	0.0940	0.1444	0.1191	0.0898
0.8044	0.1346	0.1174	0.1366	0.2046	0.1581	0.1422
0.8643	0.1778	0.1550	0.1726	0.2392	0.2084	0.1752
0.9203	0.1917	0.1732	0.2093	0.2885	0.2423	0.1925

Table (3.15 II): Values of $((\eta_r-1)/\sqrt{c})$ for TEAB in 0.2% HPMC-water mixture as function of √C at six experimental temperatures.

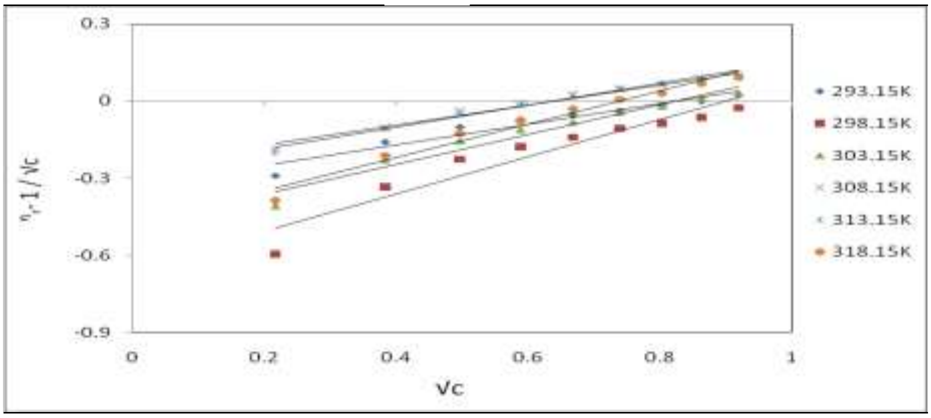
√C	$(\eta_r\ 1)/\sqrt{c}$					
	293.15K	298.15K	303.15K	308.15K	313.15K	318.15K
0.2168	-0.3981	-0.3847	-0.4539	-0.3819	-0.3994	-0.4594
0.3834	-0.2020	-0.2163	-0.2546	-0.2122	-0.2222	-0.2557
0.4969	-0.0947	-0.1158	-0.1250	-0.0887	-0.1374	-0.1632
0.5891	-0.0394	-0.0714	-0.0784	-0.0557	-0.0733	-0.0900
0.6686	0.0488	0.0289	0.0222	0.0432	0.0228	0.0095
0.7396	0.0820	0.0612	0.0606	0.0944	0.0694	0.0558

0.8044	0.1022	0.0839	0.0866	0.1350	0.1188	0.1000
0.8643	0.1470	0.1393	0.1440	0.1686	0.1487	0.1277
0.9203	0.1987	0.1951	0.1757	0.2084	0.2035	0.1704

Table (3.15 III): Values of ($(\eta_r-1)/\sqrt{c}$) for TEAB in 0.3% HPMC-water mixture as function of √C at six experimental temperatures.

√C	$(\eta_r\ 1)/\sqrt{c}$					
	293.15K	298.15K	303.15K	308.15K	313.15K	318.15K
0.2168	-0.5009	-0.4543	-0.6162	-0.5078	-0.5641	-0.5936
0.3834	-0.2686	-0.2538	-0.3459	-0.2840	-0.3136	-0.3312
0.4969	-0.1294	-0.1452	-0.2235	-0.1678	-0.1841	-0.2246
0.5891	-0.0214	-0.0717	-0.1241	-0.0889	-0.0949	-0.1339
0.6686	0.0546	0.0153	-0.0162	-0.0105	-0.0199	-0.0066
0.7396	0.1063	0.0777	0.0319	0.0309	0.0303	0.0480
0.8044	0.1435	0.1180	0.0848	0.0895	0.0840	0.0900
0.8643	0.1972	0.1439	0.1273	0.1238	0.1397	0.1430
0.9203	0.2371	0.2055	0.1782	0.2017	0.1965	0.1843

I



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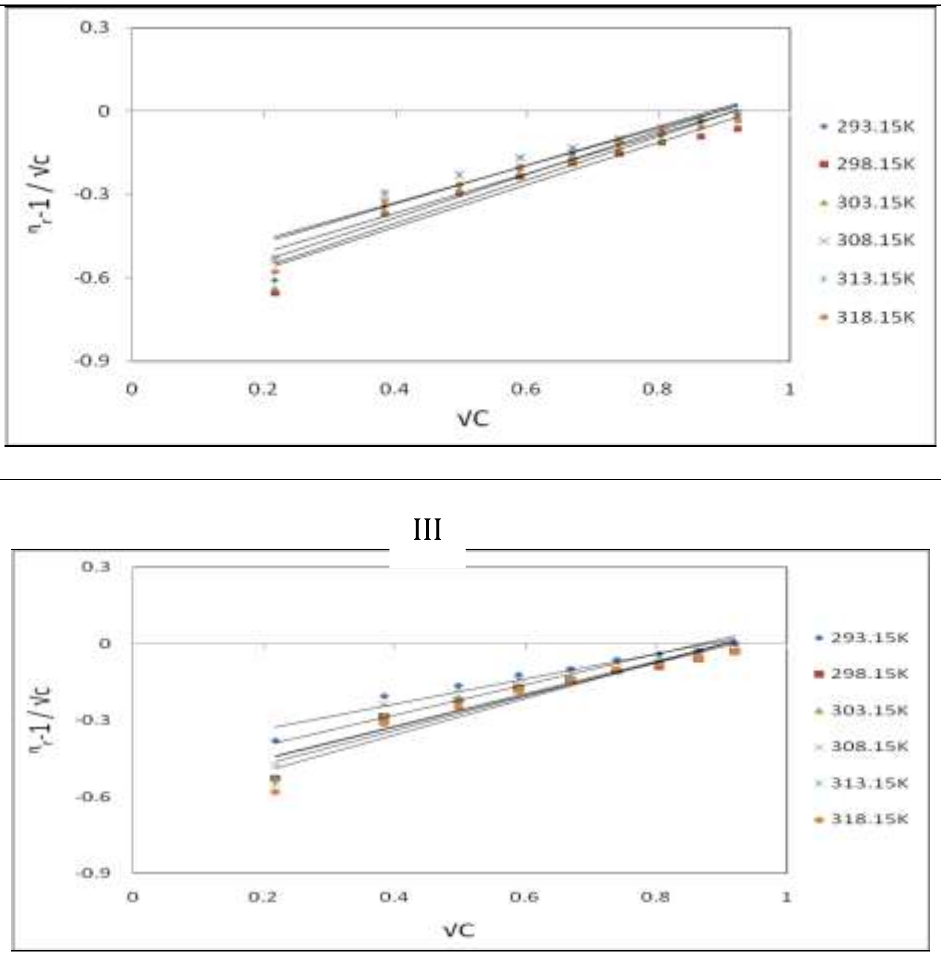

Fig. (3.17 I- II- III): Values of ((η_r-1)/√c) for TMAB in 0.1,0.2 and 0.3% of HPMC-water mixture respectively plotted against √c at six experimental temperatures.

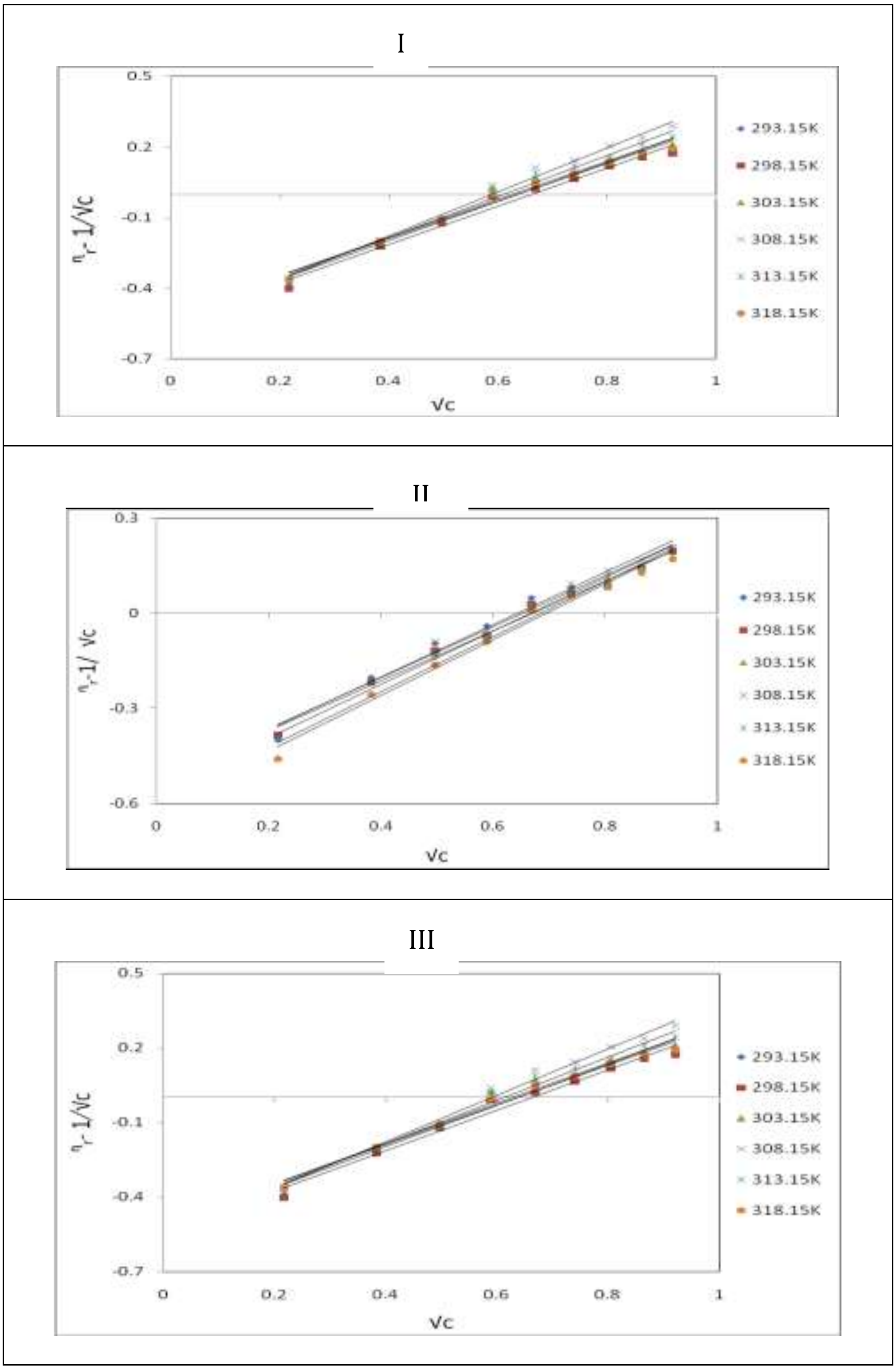

Fig. (3.18) I- II- III values of ((η_r-1)/√c) for TEAB in 0.1,0.2 and 0.3% of HPMC-water mixture respectively plotted against √c at six experimental temperatures.

Table (3.16 I): A and B viscosity coefficients for TMAB as function to wt% of HPMC-water mixture at six experimental temperatures.

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Wt%	T(K)	A	B
0.10%	293.15	-0.3318	0.4000
	298.15	-0.6510	0.7215
	303.15	-0.4791	0.5815
	308.15	-0.2506	0.3909
	313.15	-0.2733	0.4267
	318.15	-0.4776	0.6450
0.20%	293.15	-0.6960	0.7797
	298.15	-0.7204	0.7599
	303.15	-0.7177	0.7838
	308.15	-0.6108	0.6927
	313.15	-0.5964	0.6678
	318.15	-0.6516	0.7121
0.30%	293.15	-0.4318	0.4911
	298.15	-0.5771	0.6271
	303.15	-0.5777	0.6381
	308.15	-0.5193	0.5970
	313.15	-0.6087	0.6723
	318.15	-0.6412	0.7115

Table (3.16 II): A and B viscosity coefficients for TEAB as function to wt% of HPMC-water mixture at six experimental temperatures.

Wt%	T(K)	A	B
0.10%	293.15	-0.5275	0.8280
	298.15	-0.5395	0.8141
	303.15	-0.5064	0.8084
	308.15	-0.5512	0.9348
	313.15	-0.5304	0.8681
	318.15	-0.5062	0.7974
0.20%	293.15	-0.5259	0.8055
	298.15	-0.5298	0.7898
	303.15	-0.5972	0.8713
	308.15	-0.5336	0.8293
	313.15	-0.5605	0.8402
	318.15	-0.6124	0.8810
0.30%	293.15	-0.6682	1.0263
	298.15	-0.6169	0.9128
	303.15	-0.7920	1.0952
	308.15	-0.6689	0.9514
	313.15	-0.7309	1.0296
	318.15	-0.7773	1.0858

Chapter Four

4

APPLICATIONS

4.1 The Ionic Distance Parameter

Equation (1.1) which was discussed in chapter one can be written as:

$$\boxed{q = \frac{Z_+ Z_- e^2}{8\pi\ \varepsilon_0 \varepsilon kT}}$$

Where ε_0 is the permittivity of vacuum, the additional factors on Eq.(1.1) were used to obtain values of the ionic distance parameter(25) q or (R as in some recent literatures(34,57,58)) by scale (nm) and these are resultant for different values of the dielectric constants (ε) and temperatures (T). Where q = å at ion pair is formed the values in Table (4.1) proffered values of ionic distance in the three wt% of HPMC-water mixtures as solvent at six experimental temperatures. The results shown of å are contract with decrease of dielectric constant of the medium of solvent as well as there is a decrease with rise of temperature. In general that two factors influence on å values which were independent on the concentration of solute according to the Bjerrum theory(83). Fig.(4.1) shown the relationship of å values with the corresponding values of inverse T. It can probably be interpreted as a thermal expansion of the solvent sheath (which envelops an ions and moves by ion–solvent interactions, i.e, the expansion of a solvated ion) because of the rise of the activation of solvent molecules that forming the sheath with rise temperature(33). With increase wt% of HPMC the ionic cloud will be more crowding so the ionic distance more contracts.

Table (4.1): Values of ionic distances (å) of the three wt% of HPMC-water mixtures at six experimental temperatures.

wt%	T(K)	ε	å(nm)
0.10%	293.15	75.15	0.3793
	298.15	74.22	0.3776
	303.15	73.18	0.3766
	308.15	72.05	0.3763
	313.15	71.19	0.3748
	318.15	70.89	0.3705
0.20%	293.15	75.66	0.3767
	298.15	74.75	0.3749
	303.15	73.88	0.3731
	308.15	72.82	0.3723
	313.15	71.62	0.3725
	318.15	70.69	0.3715
0.30%	293.15	76.24	0.3738
	298.15	75.85	0.3695
	303.15	75.22	0.3664
	308.15	74.64	0.3632
	313.15	74.00	0.3606
	318.15	73.12	0.3592

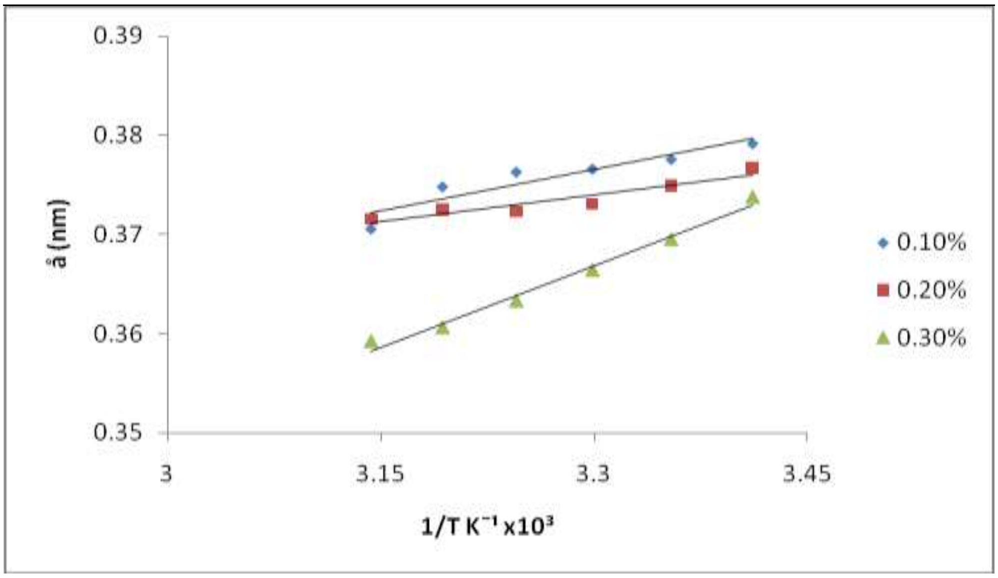


Fig (4.1): Values of å for three wt% of HPMC-water mixture as solvent against to 1/T for six experimental temperatures.

4.2 Ion Association Constant by Bjerrum Method

The possibility to obtain the values of the ion association constant (K_A), when å = q, which is ionic distance was obtained from Table (4.1), by taking b=2 in Eq. (1.4) presented

$$\boxed{K_A = \frac{4\,\pi\,N_A\,å^3}{1000}\;(\frac{e^b}{b})}$$

The values of association constant were presented in Table (4.2) which shown a decrease with the decrease of the values of ionic distance as well as decrease dielectric constant with rise temperature. Suggesting a weak extent of association of the ions into ion-pairs in media with lower dielectric constant as compared with those of higher values of dielectric constant(21). Fig.(4.2) shows the relationship of K_A values with the corresponding values of ε for three wt% of HPMC-water mixture at six temperatures. This is indicating that when the molecular solvent has relatively high dielectric constant, it could form strong intermolecular interaction (37). If it is consider that from a rudimentary standpoint the ion pair is formed with only the action of the Columbic force in the medium (32).

Table (4.2): Values of association constant (K_A), å ionic distances and ε for the three wt% of HPMC-water mixture at six temperatures.

wt%	T(K)	ε	å(nm)	K_A(dm^{3}mol^{-1}) x 10^3
0.10	293.15	75.15	0.3792	1.524
	298.15	74.22	0.3776	1.505
	303.15	73.18	0.3766	1.493
	308.15	72.05	0.3763	1.489
	313.15	71.19	0.3748	1.472
	318.15	70.89	0.3705	1.421
0.20	293.15	75.66	0.3767	1.494
	298.15	74.75	0.3749	1.473
	303.15	73.88	0.3731	1.452
	308.15	72.82	0.3723	1.442
	313.15	71.62	0.3725	1.445
	318.15	70.69	0.3715	1.433
0.30	293.15	76.24	0.3738	1.460
	298.15	75.85	0.3695	1.410
	303.15	75.22	0.3664	1.375
	308.15	74.64	0.3633	1.340
	313.15	74.00	0.3606	1.310
	318.15	73.12	0.3592	1.295

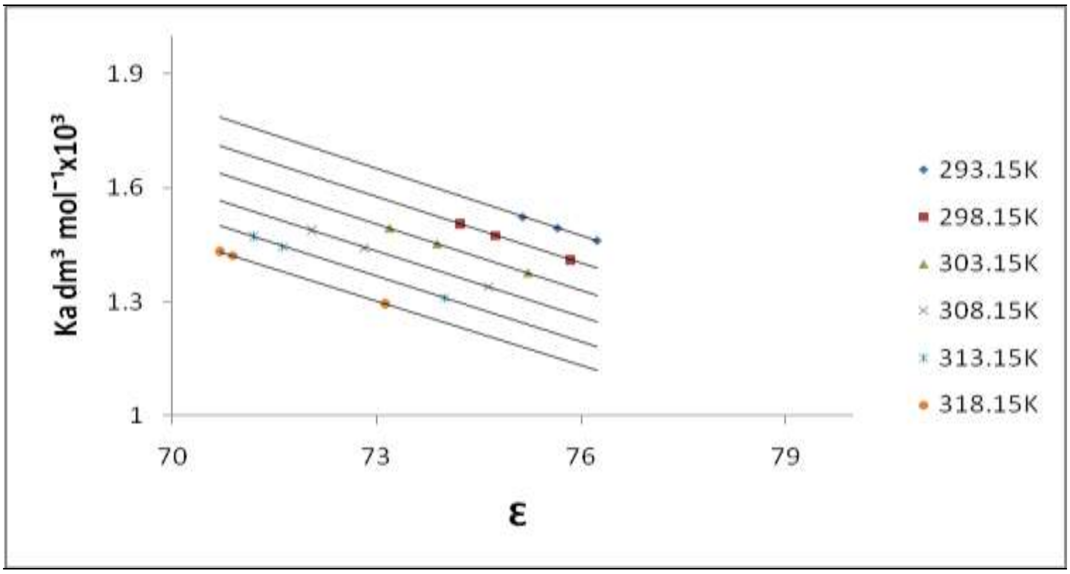


Fig. (4.2): Association constant (K_A) plotted against to ε of HPMC-water mixture at six temperatures.

4.3 Ion Association Constant by Shedlovsky Method

The equations (1.7 -1.12 pages10) which have been presented earlier in chapter one for analysis of conductance data, were used to estimate the values of association constant (K_A) and limiting molar conductance at infant dilution (Λ_o) for each TMAB and TEAB salts in all wt% of HPMC-water mixtures at six experimental temperatures are reported in Table (4.3 I- II). The values were obtained from this method more suitable and more acceptable due to it used all factors in the electrolyte solution such as concentrations of the salt in solution, molar conductance, temperatures and viscosities of solutions data farther more the dielectric constant for solvent mixtures. The results of Table (4.3 I-II) were indicate that a good agreement between the values of K_A which have been calculated from Bjerrum equation and those obtained by Shedlovsky method. This reflects the suitability of both methods for the determination of the association constant as well as for the accuracy the conductance measurements which have been made. Values of K_A generally show an increase at a constant temperature with increasing wt% of HPMC-water mixture as the value of dielectric constant increase, in the agreement with the theoretical expectation according to the electrolyte theories(84). The increase of K_A was more pronounced with TEAB than TMAB because of the TEAB cation larger than the TMAB cation and may be ascribed to the more coulombic type of interaction between the salts ions. This is because the charge density of TMAB cation is greater than the charge density of TEAB cation. The low in surface charge density (34) allow the ions trapped each other and may be the formation of the ion pairs take best chance. The decrease of K_A with the increase of temperature in the one concentration of solvent mixture, and in the higher temperatures return to increase generally interpreted as an expansion of the solvent sheath. These expansion of a solvated ions through the electrolyte taken as a whole(85). Hence the thermal motion probably destroys the solvent structure (33). This extent of ion association in the solutions decreases with increasing temperature and thus ion-solvent interactions decreases. This is interpreted by the occupation of intermolecular cavities of solvent structure by organic chains of these ions. This pattern of ion hydration is called “hydrophobic hydration” or “cage association”. These ions are incapable of donor–acceptor interact with solvent molecules and ion pairs in such solutions can mainly stabilized by intrinsic water structure. The interaction in such way of hydrocarbon portion of ionic liquid is considerable importance to the phenomenon of their ion pair formation in aqueous solutions (86).

Table(4.3 I): Values of K_A by Shedlovsky methods and limiting molar conductance Λ_o for TMAB in HPMC-water mixture at six experimental temperatures.

Wt%	T(K)	ε	$\Lambda_o(Scm^2mol^{-1})$	Bjerrum	Shedlovsky
				K_A $(dm^3mol^{-1})\times10^3$	K_A $(dm^3mol^{-1})\times10^3$
0.10	293.15	75.15	111.96	1.524	0.841
	298.15	74.22	116.75	1.505	1.462
	303.15	73.18	112.08	1.493	0.448
	308.15	72.05	123.59	1.489	1.445
	313.15	71.19	120.01	1.472	0.452
	318.15	70.89	132.78	1.421	0.853
0.20	293.15	75.66	128.78	1.494	1.404
	298.15	74.75	133.40	1.473	1.369
	303.15	73.88	139.73	1.452	1.314
	308.15	72.82	143.22	1.442	1.311
	313.15	71.62	145.77	1.445	1.360
	318.15	70.69	150.08	1.433	1.119
0.30	293.15	76.24	141.62	1.460	1.478
	298.15	75.85	144.40	1.410	1.455
	303.15	75.22	149.66	1.375	1.373
	308.15	74.64	157.66	1.340	1.401
	313.15	74.00	165.56	1.310	1.361
	318.15	73.12	175.46	1.295	1.369

Table(4.3 II): Values of K_A by Shedlovsky methods and limiting molar conductance Λ_o for TEAB in HPMC-water mixture at six experimental temperatures.

Wt%	T(K)	ε	$\Lambda_{o}(Scm^{2}mol^{-1})$	Bjerrum	Shedlovsky
				$K_A(dm^3mol^{-1})\times10^3$	$K_A(dm^3mol^{-1})\times10^3$
0.10%	293.15	75.15	87.19	1.524	1.504
	298.15	74.22	90.14	1.505	1.377
	303.15	73.18	94.08	1.493	1.354
	308.15	72.05	96.45	1.489	1.205
	313.15	71.19	98.36	1.472	1.213
	318.15	70.89	102.48	1.421	1.153
0.20%	293.15	75.66	96.34	1.494	1.477
	298.15	74.75	99.93	1.473	1.451
	303.15	73.88	106.31	1.452	1.389
	308.15	72.82	111.24	1.442	1.353
	313.15	71.62	118.18	1.445	1.477
	318.15	70.69	127.44	1.433	1.569
0.30%	293.15	76.24	100.14	1.460	1.440
	298.15	75.85	108.26	1.410	1.438
	303.15	75.22	115.02	1.375	1.629
	308.15	74.64	120.33	1.340	1.469
	313.15	74.00	127.51	1.310	1.696
	318.15	73.12	136.38	1.295	1.741

4.4 The Activation Energy of Free Ions

The limiting molar conductance (Λ_o) examine the validity the Fuoss-Edelson Eq.(4.1) since the conductance of an ion depends on its mobility. It is reasonable to treat the conductance data similar to that employs for rate processes taking place with change of temperature as:

$$\boxed{\Lambda_0 = Aexp^{\frac{-E}{RT}}} \text{-------(4.1)}$$

$$\boxed{log\Lambda_0 = logA - \frac{E}{RT}} \text{---------(4.2)}$$

Where A is the frequency factor, R is the ideal gas constant and E is the Arrhenius activation energy of transport processes. Thus from the plot of log Λ_o vs. 1/T for each salt solution, the intercept of line was obtained represents A coefficient and the slope of this line represents E/R, as shown in the Fig. (4.3 I -II) for TMAB and TEAB solutions respectively. Hence obtained E values have been evaluated the activation energy for mobility of free ionic conductance(33). The Table (4.4) listed the values of E obtained for each salt solutions at different experimental temperatures, which give the amount of energy require for ions mobility(32). These values enhance the high conductivity of the salt TMAB in the solution than the conductivity of TEAB due to E values of first lower than E values of the last. Also shown that E increases as wt% of solvent increases in the mixture, it reflects the higher energy for ions mobility in the specific solutions with increases the ratio of organic portion of solvent.

Table(4.4): Values of E in solutions of TMAB and TEAB in the three wt% of HPMC-water mixtures.

solution	Wt%	E (KJ mol^{-1})
TMAB	0.1	1.9738
	0.2	2.0378
	0.3	2.9399
TEAB	0.1	2.1085
	0.2	3.7390
	0.3	4.0059

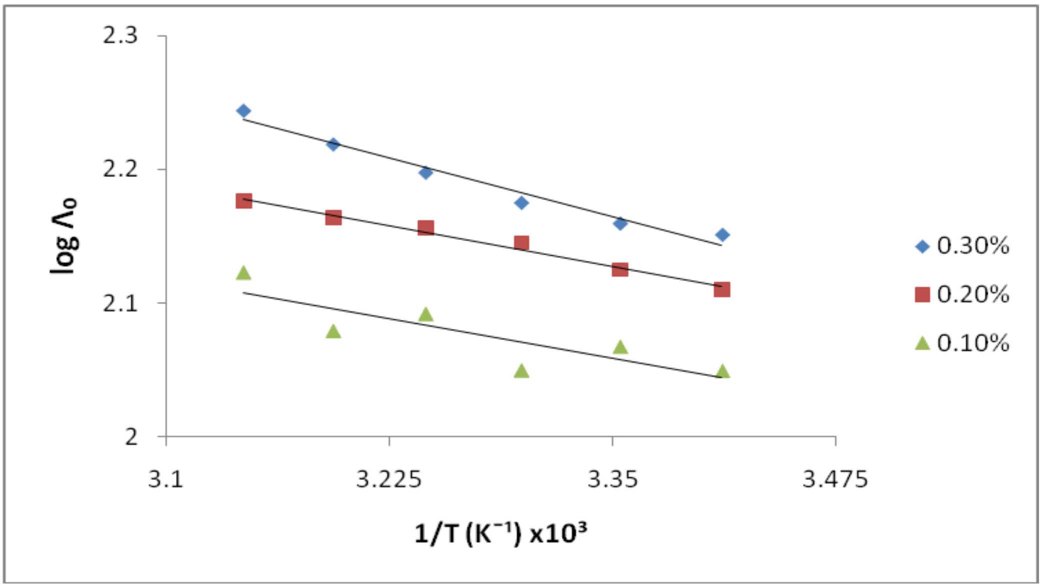


Fig.(4.3 I): Log Λ_o plotted against of 1/T for TMAB in three components of HPMC - water solutions.

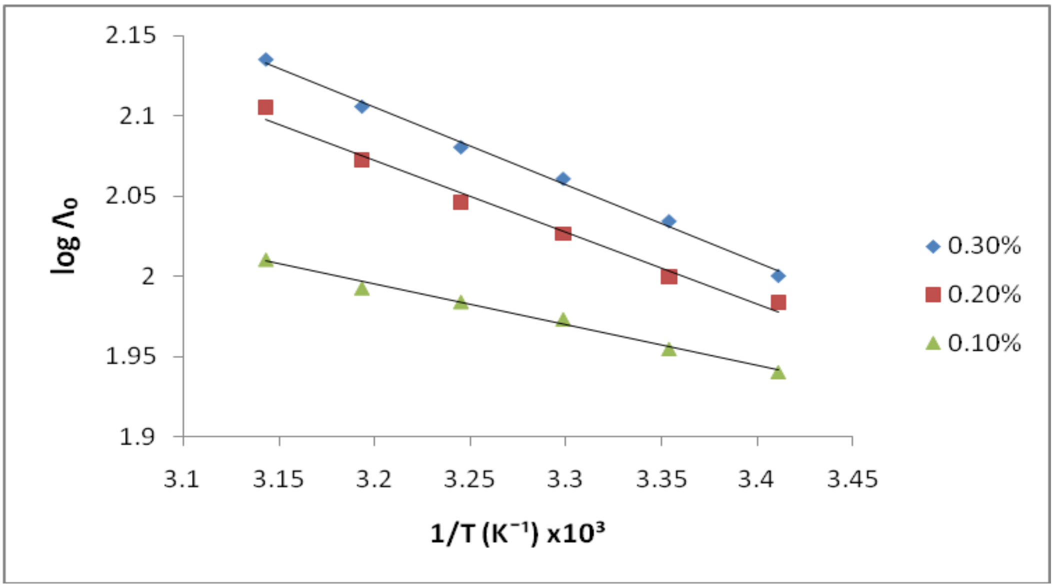


Fig.(4.3 II): Log Λ_o plotted against of 1/T for TEAB in three components of HPMC - water solutions.

4.5 The Effective Radii of Cations

The effective ionic radii (r_i) of the cation in each solvent system used are calculated by using Stoke's radius equation modified by Gill, Eq. (4.3): (59)

$$\boxed{r_i = \frac{|Z|F^2}{6\pi N_A \eta \lambda^\circ_+} + 0.0103\varepsilon + r_\gamma} \text{ - - - - - - - (4.3)}$$

Where F is Faraday constant, N_A is Avogadro's number, η is the viscosity of solvent mixture, ε is the dielectric constant of the solvent mixture and r_γ is a parameter equal to 0.85 Å(59) for a given type of solvent mixture. λ°_+ is the values of the limiting ionic conductance which have been obtained using the relationship(87):

$$\boxed{\lambda^\circ_+ = t^\circ_+ \Lambda_0} \text{ - - - - - - - - - - (4.4)}$$

Where t°_+ is the cationic limiting transference number that can be taken as 0.5, values of Λ_0 have been determined in the present work as will be discussed above.

The resulting values of (r_i) are presented in Table (4.5 I- II) for each TMAB and TEAB salts in the HPMC-water mixtures at six experimental temperatures. The effective radius (r_i) generally decreased with decreasing values of viscosity η as well as dielectric constant ε of the solvent mixtures decreased also with rise temperatures. The Table (4.5 I-II) exhibited the values of limiting ionic conductance λ°_{+} and exposed that the values of λ°_{+} increased with decreased of each η and ε as well as (r_i) decreasing also. Interpreted the ions will given more free in motion and conductivity (88). This can be ascribed to the fact that when the viscosity of the mixtures decreases thereby the mobility of ions increases. Interpreted that the solvated radii of ions become contract through the interactions between ions in solution therefore, the mobility of ions increases so the solvated radii were decreased with temperature increase. Indicating a lower solvation process due to decrease in the electronic clouds around the solvated molecules as a result of an increase in their vibration and rotational motion(89) with rise temperature.

Table (4.5 I): Values of effective ionic radius of cation r_i and limiting ionic conductance (λ^{o}) of TMAB solutions at six experimental temperatures.

Wt%	T(K)	ε	η (cP)	Λ_o(Scm^{2}mol^{-1})	λ^o_+(Scm^{2}mol^{-1})	r_i (nm)
0.10	293.15	75.15	1.1853	111.96	55.98	0.859
	298.15	74.22	1.0556	116.75	58.38	0.849
	303.15	73.18	0.9277	112.08	56.04	0.839
	308.15	72.05	0.8031	123.59	61.79	0.827
	313.15	71.19	0.7152	120.01	60.01	0.815
	318.15	70.89	0.6479	132.78	66.39	0.803
0.20	293.15	75.66	1.3357	128.78	64.39	0.864
	298.15	74.75	1.1891	133.40	66.7	0.855
	303.15	73.88	1.0753	139.73	69.87	0.846
	308.15	72.82	0.9364	143.22	71.61	0.835
	313.15	71.62	0.8289	145.77	72.89	0.823
	318.15	70.69	0.7362	150.08	75.04	0.813
0.30	293.15	76.24	1.5021	141.62	70.81	0.870
	298.15	75.85	1.3556	144.40	72.20	0.866
	303.15	75.22	1.2541	149.66	74.83	0.860
	308.15	74.64	1.1203	157.66	78.83	0.854
	313.15	74.00	0.9646	165.56	82.78	0.847
	318.15	73.12	0.8478	175.46	87.73	0.838

Table (4.5 II): Values of effective ionic radius of cation r_i and limiting ionic conductance (λ^o) of TEAB solutions at six experimental temperatures.

Wt%	T(K)	ε	η(cP)	Λ_o(Scm^{2}mol^{-1})	λ^o_+(Scm^{2}mol^{-1})	r_i (nm)

0.10	293.15	75.15	1.1853	87.19	43.59	0.859
	298.15	74.22	1.0556	90.14	45.07	0.849
	303.15	73.18	0.9277	94.08	47.04	0.839
	308.15	72.05	0.8031	96.45	48.23	0.827
	313.15	71.19	0.7152	98.36	49.18	0.818
	318.15	70.89	0.6479	102.48	51.24	0.815
0.20	293.15	75.66	1.3357	96.34	48.17	0.864
	298.15	74.75	1.1891	99.93	49.97	0.855
	303.15	73.88	1.0753	106.31	53.16	0.846
	308.15	72.82	0.9364	111.24	55.62	0.835
	313.15	71.62	0.8289	118.18	59.09	0.823
	318.15	70.69	0.7362	127.44	63.72	0.813
0.30	293.15	76.24	1.5021	100.14	50.07	0.870
	298.15	75.85	1.3556	108.26	54.13	0.866
	303.15	75.22	1.2541	115.02	57.51	0.860
	308.15	74.64	1.1203	120.33	60.17	0.854
	313.15	74.00	0.9646	127.51	63.76	0.847
	318.15	73.12	0.8478	136.38	68.19	0.838

4.6 Walden Product

The Walden product is informative from in viewpoint of ion-solvent interaction. As simplest theoretical expression, which relates the limiting molar conductance Λ_o with the dynamical viscosity η of solvent mixture is Walden's rule as(90):

$$\boxed{\Lambda_o \eta = W} \text{ - - - - - - - - } (4.5)$$

This parameter should be constant value at a given temperature due to the molar conductance of an ions of solute at infinite dilution depends only upon its speed and the mobility of ions or charge carriers. The conductivity of an electrolyte solution depends on the number and the mobility of the charge carriers. When the conductivity is increased due to the viscosity reduction and hence the solution becomes more conductive. Therefore, the Walden product is expected to be constant for a given electrolyte in which the ion-solvent interactions are uniform at a given temperature. This proves that the radius of the ions remains unchanged, (91) in order to eliminate that effect on viscosity of the ionic mobility. The values of Walden product (W) were calculated and given in Table (4.6 I -II) which in all cases decrease as temperature increases while decrease with viscosity of solvent mixture is decrease also with rise temperature. This enhances the increasing the mobility of ions and hence increasing the conductivity of solution. Also show the values of

(W) for TMAB salt larger than the values of (W) for TEAB which is interpreted as enhancing to the decreasing the Λ_o values with bulking alkyl chain of ionic liquids in the order methyl > ethyl. As a long alkyl chain makes difficult the movement of the cations and so the ionic liquids with longer chains contribute lower to electrical conductivity(92). This large variation in the Walden product values of the electrolytes for the present mixed solvent medium demonstrates changed solute–solvent interactions, possibly due to changing solvodynamic size of the constituting ions (93).

The values of the Walden product (W) in solvent with varying dielectric constant (ɛ) could be summarized in Fig.(4.4) which decrease with dielectric constant decrease. This succession is due to the expected differences in the salvation of ions in the different solutions and the resulting differences in the moving of ions. This moving particle is large dissociation in case TMAB solution since they are probably solvated into certain extent more over TEAB solution. This consolidates increasing the values of Λ_o with decrease values of (ɛ).

Table (4.6 I): Values of Walden product (Λ_o η) for TMAB in three wt% of HPMC-water mixture at six experimental temperatures.

wt%	T(K)	Λ_o(S cm^2 mol^{-1})	η (c P)	W(S cm^2 mol^{-1} c P)
0.10	293.15	111.96	1.1853	132.7062
	298.15	116.75	1.0556	123.2413
	303.15	112.08	0.9277	103.9766
	308.15	123.59	0.8031	99.25513
	313.15	120.01	0.7152	85.83115
	318.15	132.78	0.6479	86.02816
0.20	293.15	128.78	1.3357	172.0114
	298.15	133.40	1.1891	158.6259
	303.15	139.73	1.0753	150.2517
	308.15	143.22	0.9364	134.1112
	313.15	145.77	0.8289	120.8288
	318.15	150.08	0.7362	110.4889
0.30	293.15	141.62	1.5021	212.7274
	298.15	144.40	1.3556	195.7486
	303.15	149.66	1.2541	187.6886
	308.15	157.66	1.1203	176.6265
	313.15	165.56	0.9646	159.6992
	318.15	175.46	0.8478	148.7550

Table (4.6 II): Values of Walden product (Λ_o η) for TEAB in three wt% of HPMC-water mixture at six experimental temperatures.

wt%	T(K)	Λ_o(S cm^2 mol^{-1})	η(c P)	W(*S* cm^2 mol^{-1} c P)
0.10	293.15	87.19	1.1853	103.3463
	298.15	90.14	1.0556	95.15178
	303.15	94.08	0.9277	87.27802
	308.15	96.45	0.8031	77.4590
	313.15	98.36	0.7152	70.34707
	318.15	102.48	0.6479	66.39679
0.20	293.15	96.34	1.3357	128.6813
	298.15	99.93	1.1891	118.8268
	303.15	106.31	1.0753	114.3151
	308.15	111.24	0.9364	104.1651
	313.15	118.18	0.8289	97.9594
	318.15	127.44	0.7362	93.82133
0.30	293.15	100.14	1.5021	150.4203
	298.15	108.26	1.3556	146.7573
	303.15	115.02	1.2541	144.2466
	308.15	120.33	1.1203	134.8057
	313.15	127.51	0.9646	122.9961
	318.15	136.38	0.8478	115.623

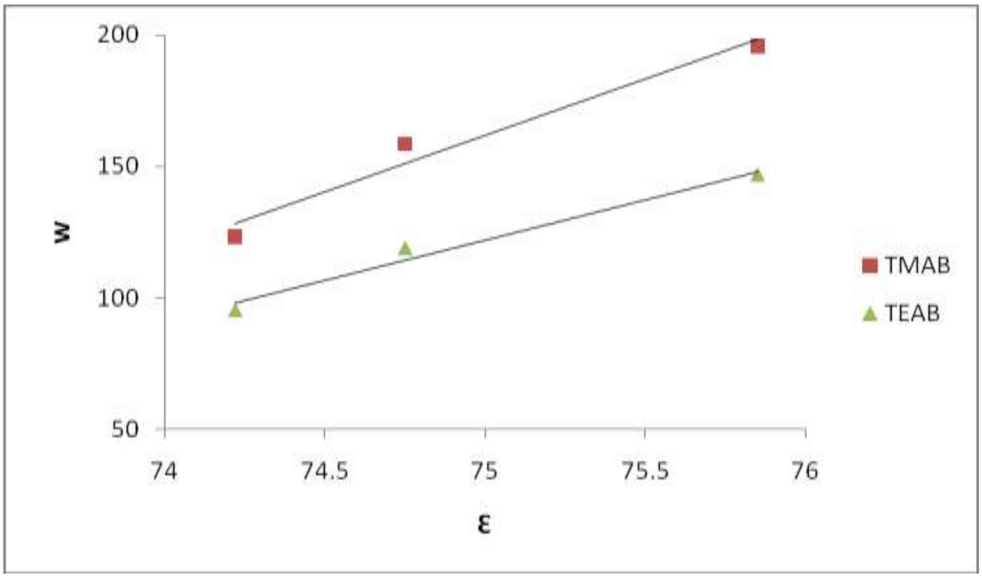


Fig.(4.4): Walden product for each TMAB and TEAB plotted against dielectric constant(ε) of solvent mixtures at 298.15K.

4.7 Thermodynamic Quantities for Association Ions

The association constant (K_A) of the ionic association reaction can serve to study the thermodynamics of this process. Consequently, Gibbs free energy(86) of ion pair formation (ΔG_A°) has been calculated as follows:

$$\boxed{\Delta G\mathring{A}\ (T) = -\, R\, T \ln K_A(T)} \text{ - - - - - - - - - - } (4.6)$$

Temperature-dependent of ΔG° was expressed with the help of a polynomial.

$$\boxed{\Delta G\mathring{A}\ (T) = A_0 + A_1\,(298.15\text{-}T) + A_2\,(298.15 - T)^2} \text{ - - - - } (4.7)$$

Enthalpy and entropy of ion association are obtained as follows:

$$\boxed{\Delta S\mathring{A}(T) = -\left(\frac{\partial \Delta G\mathring{A}(T)}{\partial T}\right)_p = A_1 + 2A_2(298.15 - T)} \text{ - - - - - - } (4.8)$$

$$\boxed{\Delta H\mathring{A}(T) = \Delta G\mathring{A}\ (T) + T\,\Delta S\mathring{A}(T) = A_0 + 298.15\,A_1 + A_2(298.15^2\ \text{-}T^2)} \text{ - - - } (4.9)$$

The values of the coefficients A_0, A_1 and A_2 at the solvent components are given in Table (4.7). The calculated thermodynamic functions are also listed in Table (4.8 I -II) which give the standard thermodynamic quantities ΔG°, ΔS° and ΔH° for ions association of TMAB and TEAB solutions in three wt% of HPMC-water mixtures as solvent. Which depicted by Fig.(4.5 I -II).

The standard thermodynamic quantities for the association ions are resulted from dissociation of salts TMAB and TEAB solutions in the various wt% of the solvent mixtures and temperatures. It is show that the values of ΔG_A° are positive in all temperatures and increase with the rise of temperature and shown that the increase of TEAB solutions more clearly and less in the value than TMAB solutions. Suggesting the positive values of ΔG° indicate the non-feasibility of the ion –pair formation process in these electrolytic solutions(94).

In the majority of cases, the ΔS_A° values are negative and decreased with increased temperature in TMAB solutions while in TEAB solutions the values of ΔS_A° are increased with increasing temperatures. This may be attributing to the increasing number of degrees of freedom due to the release of solvent molecules from solvation shells as the association takes place. In other words, the solvation of the individual ions is more stable as soon as these ion pairs are weakened (57), it means that ion-pair formation is entropy-driven at low temperatures(95).

The main factors (4) which govern the standard entropy ΔS_A° of ion association of electrolytes are:

(i) The size and shape of ions.

(ii) Charge density of ions.

(iii) Electrostriction of the solvent molecules around the ions.

(iv) The penetration of the solvent molecules inside the ionic space.

The values of enthalpy ΔH_A° decreased with increasing temperature at TMAB in (0.1 and 0.2) % of solvent mixtures while at TMAB in 0.3% of solvent mixture and at TEAB in the three wt% of solvent mixtures well be increased and converted from negative to positive sign with rise temperature(96). The values of ΔH_A° are generally exothermic for TMAB solutions but for TEAB the values of ΔH_A° are generally endothermic process. Thus the ion –pairs are slightly unstable in the association from these which are present in free ions forms (97). Also this conversion attributed to the hydrophobic hydration was mentioned before due to probably the thermal motion destroys the structure of solvent(86).

Table (4.7): Values coefficients Eq. (4.7) for TMAB and TEAB solutions in the HPMC-water mixtures.

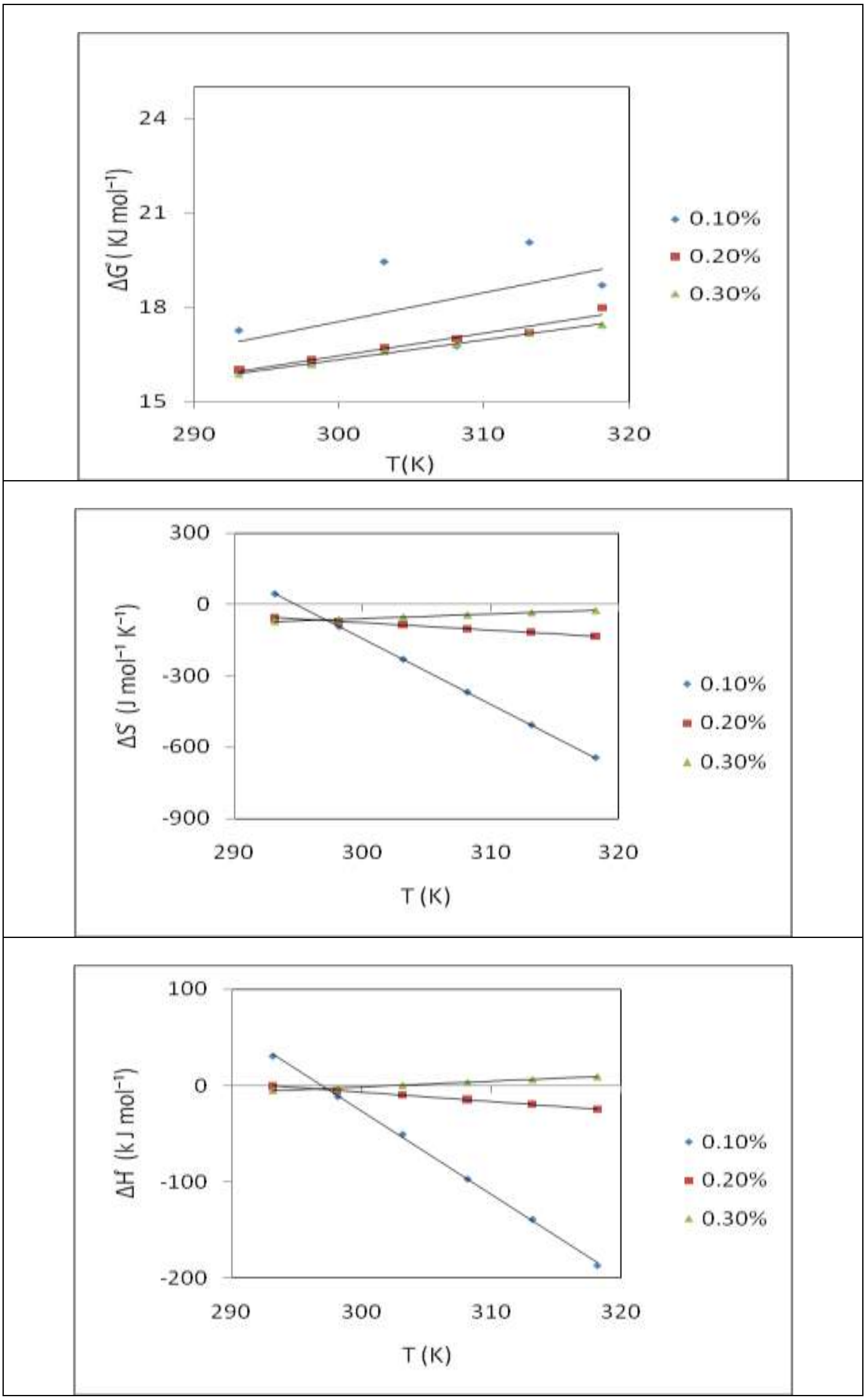
salt	Wt%	Ao	A1	A2
TMAB	0.1	17373	-92.021	13.842
	0.2	16333	-72.159	1.504
	0.3	16221	-62.712	-0.913
TEAB	0.1	16291	-81.707	-1.614
	0.2	16238	-49.269	-4.216
	0.3	16157	-34.178	-1.521

Table (4.8 I): The standard thermodynamic quantities ΔG˚, ΔS˚ and ΔH˚ for ion-pair formation for TMAB solutions in three wt% of HPMC-water mixtures at experimental temperatures.

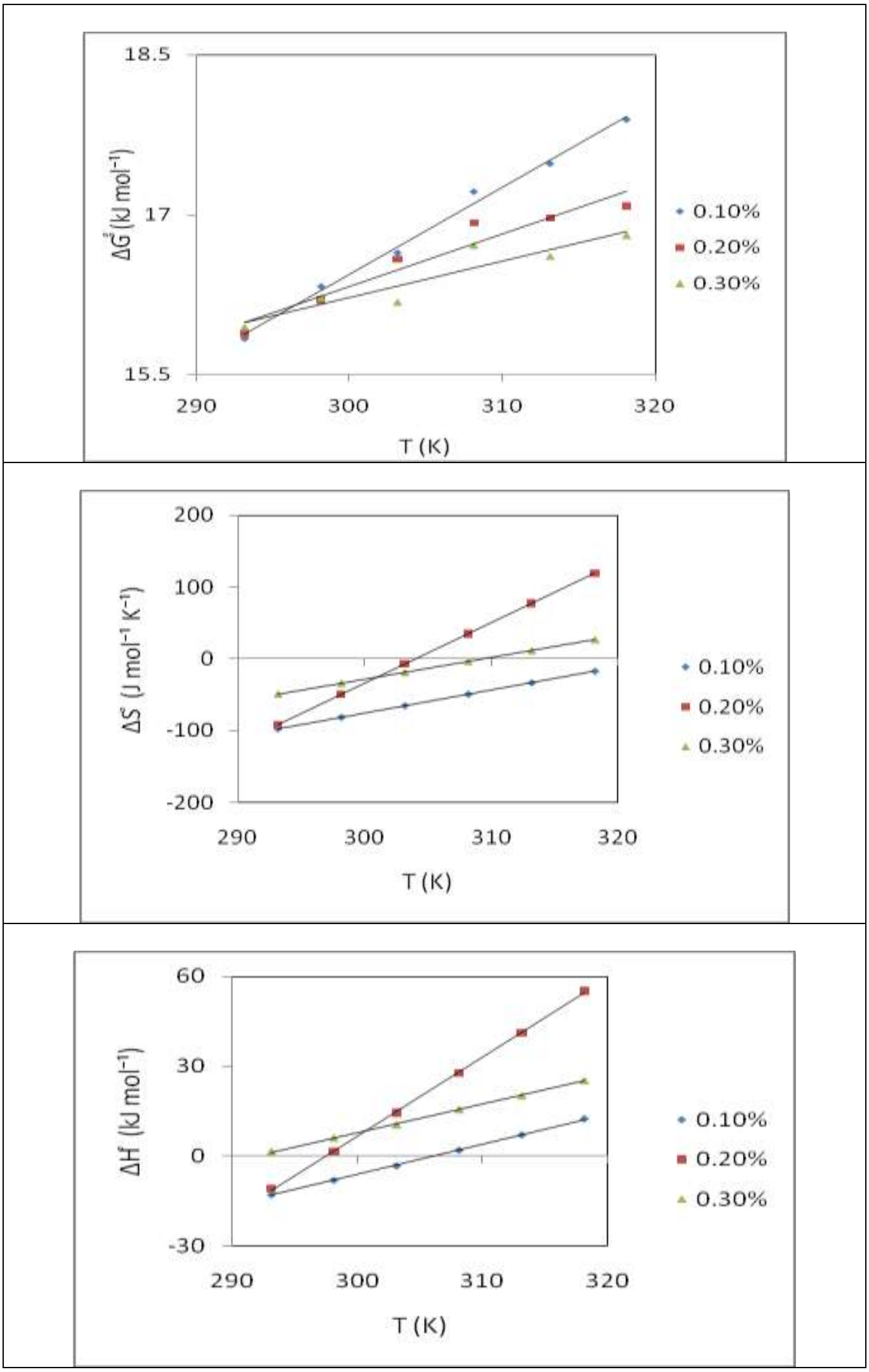
Wt%	T(K)	K_A(dm^{3}mol^{-1})×10^3	ΔG˚ (kJ mol^{-1})	ΔS˚ (J mol^{-1} K^{-1})	ΔH˚ (kJ mol^{-1})
0.10	293.15	0.841	17.258	46.399	30.860
	298.15	1.462	16.182	-92.021	-11.253
	303.15	0.448	19.435	-230.441	-50.423
	308.15	1.445	16.755	-368.861	-96.909
	313.15	0.452	20.053	-507.581	-138.802
	318.15	0.853	18.693	-645.701	-186.736
0.20	293.15	1.404	16.009	-57.119	-0.734
	298.15	1.369	16.345	-72.159	-5.168
	303.15	1.314	16.722	-87.199	-9.711
	308.15	1.311	17.004	-102.239	-14.500
	313.15	1.360	17.184	-117.279	-19.540
	318.15	1.119	17.975	-132.319	-24.121
0.30	293.15	1.478	15.884	-71.842	-5.175
	298.15	1.455	16.194	-62.712	-2.503
	303.15	1.373	16.612	-53.582	0.368
	308.15	1.401	16.834	-44.452	3.136
	313.15	1.361	17.183	-35.322	6.121
	318.15	1.369	17.441	-26.192	9.108

Table (4.8 II): The standard thermodynamic quantities ΔG°, ΔS° and ΔH° for ion-pair formation for TEAB solution in three wt% of HPMC-water mixtures at expermental temperatures.

Wt%	T(K)	K_A(dm^{3}mol^{-1})$\times10^3$	ΔG° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	ΔH° (kJ mol^{-1})
0.10%	293.15	1.504	15.842	-97.897	-12.841
	298.15	1.377	16.331	-81.707	-8.029
	303.15	1.354	16.647	-65.567	-3.229
	308.15	1.205	17.220	-49.427	1.989
	313.15	1.213	17.482	-33.287	7.058
	318.15	1.153	17.896	-17.147	12.440
0.20%	293.15	1.477	15.886	-91.429	-10.916
	298.15	1.451	16.201	-49.269	1.511
	303.15	1.389	16.583	-7.109	14.427
	308.15	1.353	16.923	35.051	27.724
	313.15	1.477	16.970	77.211	41.148
	318.15	1.569	17.081	119.371	55.059
0.30%	293.15	1.440	15.948	-49.388	1.470
	298.15	1.438	16.223	-34.178	6.033
	303.15	1.629	16.181	-18.968	10.431
	308.15	1.469	16.713	-3.758	15.555
	313.15	1.696	16.610	11.452	20.196
	318.15	1.741	16.806	26.662	25.288



Figs.(4.5 I): The standard thermodynamic quantities ΔG°, ΔS° and ΔH° plotted against temperatures for TMAB solution in solvent mixtures.



Figs.(4.5 II): The standard thermodynamic quantities ΔG˚, ΔS˚ and ΔH˚ plotted against temperatures for TEAB solution in solvent mixtures.

4.8 Conclusion

The conclusions from the results and previous discussions of this research may be summarized in the following few points:

1- The values of K_A have been derived from Bjerrum equation and obtained by inserting the experimentally measured by a set of equations using Shedlovsky method. This reflects the suitability of both methods for the determination of the association constant as well as for the accuracy with the conductance measurements has been made. Values of K_A reflect a greater extent of association of the ions into ion-pairs in media with lower dielectric constant as compared with those of higher values of ε.

2- The values of ionic distance (å) of HPMC-water mixtures at six experimental temperatures decreased with the decrease of dielectric constant of the medium of solvent and also decreased with rise of temperature. While the effective radius (r_i) is generally decreased with decreasing values of viscosity ɳ as well as dielectric constant ε of the solvent mixtures decreased. The consequence from general purpose data that ion –pair will be formed at higher concentrations of salt in the solution and at low temperatures.

3- The walden prodct (W) values of TMAB solutions are larger than the values of TEAB solutions which enhance the decreasing in Λ_o values with bulking alkyl chain of ionic liquid reflects the difficult ionic mobility due to increases viscosity.

4- The values of ΔG_A° are positive in all temperatures indicate the non-feasibility of the ion –pair formation process in these electrolytic solutions.

5- The ions are present in solution in form free ion more favorite, due to the fraction of free ions larger than the pair of ions but both types are present in solution due to the molecular of solvent is polymer mixture. In this case it weakens the coulombic interaction between oppositely charge ions and the higher conductivity consolidates the higher mobility of free ions.

Prospective studies

Due to the importance of this type of solutions, and its properties which were investigated in this work, it is recommend to study in details the following:

1. The solvent mixture could be used as alternative to the organic solvents in various electrochemical systems and for pharmaceuticals studies.

2. It can use other Tetralkylammonium Halide such as; Tetrapropylammonium and Tetrabutylammonium Bromide or Chloride.

3. The transfer properties of these electrolytes have a great importance for the studying of its uses in high-energy batteries.

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الخلاصة :

تتضمن هذه الرسالة دراسة تكوين المزدوجات الايونية لاملاح رباعي الكيل امنيوم بروميد في ثلاثة امزجة من الهيدروكسي بروبيل مثيل سيليلوزمع الماء هي (0.1%, 0.2%, 0.3%) عند ستة درجات حرارية مختلفة هي (293.15, 298.15, 303.15, 308.15, 313.15, 318.15) كلفن. باستخدام ماء لأيوني ذو توصيلية ($5\times10^{-7}\ Scm^{-1}$) يستخدم لكل القياسات وهي:

دراسة الخصائص الفيزيائية لامزجة المذيب تتضمن قياسات الكثافة واللزوجة وثابت العزل الكهربائي و التوصيلية النوعية للمكونات الثلاثة للمذيب عند الدرجات الحرارية الستة ومن هذه المعطيات يمكن دراسة انحراف المزيج عن السلوك المثالي من خلال دراسة السلوك الحجمي بدلالة الفيض الحجمي المولاري (V_m^E) وفيض ثابت العزل الكهربائي (ε^E) ودراسة علاقة اللزوجة بدرجة الحرارة ومنها تم حساب طاقة تنشيط انسياب الايون(E) في المذيب مفسرة التداخل الواضح بين مكونات النظام.

دراسة الخصائص الفيزيائية لكل من املاح رباعي مثيل امونيوم بروميد ورباعي أثيل أمونيوم بروميد بتسعة تراكيز لكل من المكونات الثلاثة في الدرجات الحرارية الستة تتضمن قياسات الكثافة واللزوجة و التوصيلية المولارية واجراء المقارنات بين قيم الملحين. وتطبيق معادلة جون- دول وتقدير معاملات جون- دول A وB , حيث قيم A تدل على التداخلات الضعيفة بين اجزاء المذاب في النظام بينما المعامل B يفسرالتمذوب الجيد بين اجزاء المذاب والمذيب.

حساب ثوابت التجمع (K_A) بطريقة بيرم في الدرجات الحرارية التجريبية عن طريق تعيين المسافات الايونية (å). وحساب ثوابت التجمع والتوصيلية المولارية عند التخفيف النهائي (Λ_o) باستخدام مجموعة من المعادلات تعرف بطريقة شدلوفسكي باستخدام برنامج حسابي مناسب وقد وجد ان القيم باستخدام الطريقتين متوافقة, من خلال القيم الحاصلة تم دراسة العلاقة بين

التوصيلية ودرجة الحرارة وحساب طاقة تنشيط الايون الحر (E), وحساب نصف القطر الفعال للايون (r_{i}) , التوصيلية الايونية ($\lambda^{o}+$) وحاصل والدن (W) والتي تعكس ضعف التداخلات الايونية و التوصيل العالي اللذان يدعمان قابلية الحركة الايونية العالية للايونات الحرة. ايضا من قيم (K_{A}) امكننا دراسة القيم الثرموديناميكية (ΔG°, ΔS° and ΔH°) للتجمعات الايونية و التي ساعدنتا على فهم صعوبة تكوين الازواج الايونية لهكذا نوع من المحاليل الاليكتروليتية.

جمهورية العراق
وزارة التعليم العالي والبحث العلمي
جامعة كربلاء/كلية العلوم
قسم الكيمياء

تكوين المزدوجات الايونية لاملاح رباعي الكيل امونيوم بروميد في أمزجة هيدروكسي بروبيل مثيل سيليلوز- ماء في درجات حرارية مختلفة

رسالة إلى
مجلس كلية العلوم - جامعة كربلاء
كجزء من متطلبات نيل درجة الماجستير في علوم الكيمياء

تقدم بها
حميد رضا عبد
بكالوريوس علوم كيمياء (2003) الجامعة المستنصرية

بإشراف

أ.د.حميدة عيدان سلمان

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البحث المقدم بعنوان:

دراسة تكوين مزدوجات ايونية لرباعي مثيل امونيوم بروميد في امزجة هيدروكسي بروبيل مثيل سيليلوز مع الماء من قياسات التوصيلية

مقدم من قبل الباحث حميد رضا عبد و الاستاذ الدكتورة حميدة عيدان سلمان

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