Ion-pair Formation From of Hydroxyl Propyl Methyl Cellulose (HPMC)-Water in three weight percentages Tetra Ethyl Ammonium Bromide (TEAB) At (293.15 and 303.15)K

دراسة تكوين مزدوجات أيونية لرباعي مثيل امونيوم بروميد في أمزجة هيدرو كسي بروبيل مثيل سيليلوز مع الماء من قياسات التوصيلية فيK(293.15 and 303.15)

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Abstract:

In the present work , investigated some physical properties of polymeric blending for Hydroxyl Propyl methyl cellulose (HPMC)-water mixtures and tetra ethyl ammonium bromide (TEAB) in the water mixtures (0.1%, 0.2% and 0.3%) at (293.15 and 303.15)K, by using deionized water with specific conductance $5x10^{-7}$ Scm^{-1} at 298.15K .

The physical properties of mixed solvents were studying which covered the measurements of densities (d), viscosities (η), dielectric constants (ε) and specific conductance (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). The physical properties of Tetra methyl ammonium Bromide (TMAB) and Tetraethyl ammonium Bromide (TEAB) were studying for nine concentrations for each three wt% of HPMC-water mixture at two experimental temperatures covered densities (d), viscosities (η) and molar conductance (Λ) and it were compared between the two salts. The association constant (K_A) and limiting molar conductance (Λ_0) was calculated from Shedlovsky equations 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 by Shedlovsky method.

Keywords :- Ion pair , Tetra ethyl ammonium bromide , Shedlovsky, dielectric constant .

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، 303.15) كلفن. باستخدام ماء لاأيوني 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_0) باستخدام مجموعة من المعادلات تعرف بطريقة شدلوفسكي

1. 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].

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 blending of polymers can be used for the preparation of new materials with improved physicochemical and mechanical properties. Thus, it has been considered as an important field of research for several decades [3]. A number of conductometric methods are well-suited to investigate the ion–solvent and ion–ion interactions in electrolyte solutions [4-9]. Ionic association of electrolytes in solution depends upon mode of salvation of its ions, which in its turn depends on the nature of the solvent or solvent mixtures.

The electric conductivity is one of the most important properties of electrolyte solution[10], 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 [11].

The theoretical expression to account for the empirical relation known as Kohlrausch´slaw:

$\Lambda=\Lambda_0 - K\sqrt{c}$ .....(1-1)

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"[12].

Onsager's expression is: $\Lambda=\Lambda_0 -(A+B\,\Lambda_0)\sqrt{c}$ .....(1-2)

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 values of the ion-pair association constants (K_A) have usually been determined by conductance method [13-16]. 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_0) by a treatment with a suitable computer program using Shedlovsky method which involved the solution of the following set of equations [17,18]:

$$\frac{1}{S\Lambda} = \frac{1}{\Lambda_o} + \frac{C\,\Lambda\,S\,f_{\pm}^2 K_A}{\Lambda_o^2} \quad ...(1\text{-}3)$$

$$S = \left[\frac{B\sqrt{c\Lambda}}{2\,(\Lambda_0)^{3/2}} + \sqrt{\left(1 + \frac{B^2\,C\Lambda}{4(\Lambda_0)^3}\right)} \right]^2 \quad ...(1\text{-}4)$$

$$B = \frac{8.204\times10^5\Lambda_0}{(\varepsilon T)^{3/2}} + \frac{8.25}{\eta(\varepsilon T)^{1/2}} .....(1\text{-}5)$$

$$\alpha = \frac{S\Lambda}{\Lambda_o} \quad .....(1\text{-}6)$$

$$-log f\pm = \frac{1.8246 \times 10^6 (c\alpha)^{1/2}/(\varepsilon T)^{3/2}}{1+50.29 \times 10^8 R(c\alpha)^{1/2}/(\varepsilon T)^{1/2}} \quad \textbf{.....(1-7)}$$

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: $\text{å} = \frac{Z_+ Z_- e^2}{2\varepsilon kT}$ .....(1-8)

2. Experimental

2.1. Materials and procedure

The salt (TEAB) was obtained by Fluka AG ,chemische fabric-ch 9470 buchs with purity >98% mol,wt.(210,16).the salts has used in this work was puriss grade and was further purified by recrystallization from acetone and carefully dried to ensure maximum purity. (HPMC) was obtained by Gold Member China Suppliers, model No. MK10000S with purity 99.0% has caring description -60 BC-E with density (0.3-0.4)gm/cm^3 and has average mol wt.(10000)Dalton.

Double distillation deionizer water with a specific conductance of 5 x 10^{-7} scm^{-1} at 25C° has been used for the preparation of the HPMC-water mixture and all experimental using.

The HPMC-water mixtures have been prepared by three composition of the HPMC-water mixture have been utilized in this work in which the weight percentages of HPMC ranged (0.1%, 0.2% and 0.3%). The solutions of TEAB have been prepared using each of the three of HPMC-water mixtures with a nine concentrations of the TEAB in the mixture have been prepared (0.047, 0.147, 0.247, 0.347, 0.447, 0.547, 0.647, 0.747and 0.847)

2.2. Apparatus

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

A-The Density Meter:-

The measurements of density for solvent and solute were used density meter type (Densito 30 px) CPT charges from (METTLER TOLEDO) made in Japan. Consist of constant cell 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 measurement of solution was 5 ml and the accuracy of measurements lead within ±1.0 ×10^{-4} gm/cm^3 of the density value.

B- The 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 293.15 and 303.15 K. The viscometer was calibrated with deionizer water and pure methanol at the experimental temperatures 298.15K. The viscosity measurement with each solvent mixture or solution at each temperature was reported twice to three times. The uncertainty of the viscosity measurements was ± 0.01S.

C- The Conductivity Meter:-

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 cm^{-1} ∓1.5%). The deviation in the calculated specific conductance (σ) values has been within ± 1μS 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 mol L^{-1} of KCl) solution at experimental temperature with all a set of measurements.

D-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 mixtures) 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 %.

E- thermostat:-

During all measurements a thermostatically controlled water bath was occurred with adjustable temperatures in (Lab Tech) digital water bath type (CERTIFIED CE) model (LWB 111D) made in Korea. The bath was filled with distilled water and was used to obtain temperatures in the range 298.15K. The constant of each experimental temperature was to within ± 0.01˚c.

F- 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 been used in weighting all using materials that will be needed.

3. Results and discussion:-

3.1. HPMC-water mixtures:-

The solvent mixtures ***Fig. 3.1*** have been used in this investigation, for each of three composites[A,B,C]**,** the important physical properties Densities (d), viscosities (η), dielectric constants (ε), and specific conductance (σ) of solvent mixtures have been measured at (293.15 and 303.15)K. The results obtained are presented in ***table 3.1 and Fig. 3.2 , 3.3 , 3.4 , 3.5 .***

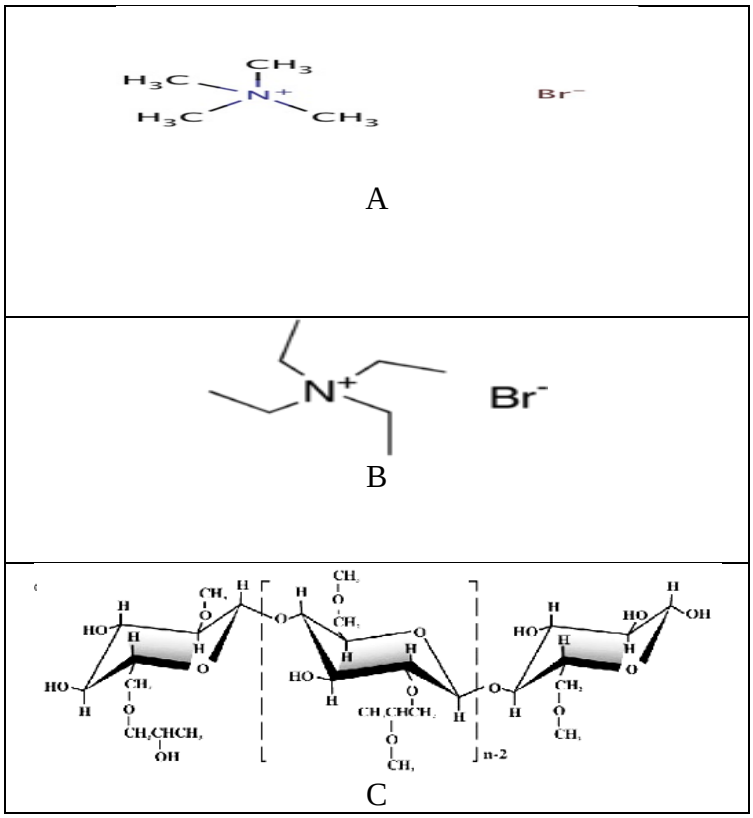

Fig. 3.1 Chemical structure of A-TMAB, B-TEAB and C-HPMC.

Table 3.1 Some physical measurement of HPMC-water mixtures at (293.15 and 303.15)K.

Solvent Wt%	d (g.ml^{-1})		η (cp)		(ε)		σx10^{6} S cm^{-1}	
	293.15 K	303.15 K	293.15 K	303.15 K	293.15 K	303.15 K	293.15 K	303.15 K
0.10	0.9965	0.9941	1.1853	0.9277	75.15	73.18	29.4	35.4
0.20	0.9967	0.9944	1.3357	1.0753	75.66	73.88	41.3	46.9
0.30	0.9969	0.9946	1.5021	1.2541	76.24	75.22	60.6	63.8

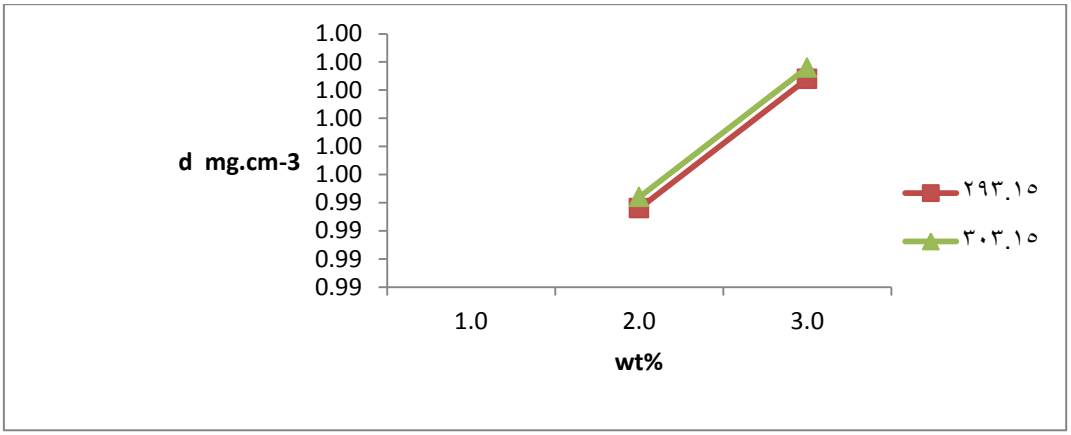

Fig. 3.2 Density (d) of HPMC-water mixtures plotted against the weight percentages (wt %) of HPMC in mixtures at two experimental temperatures.

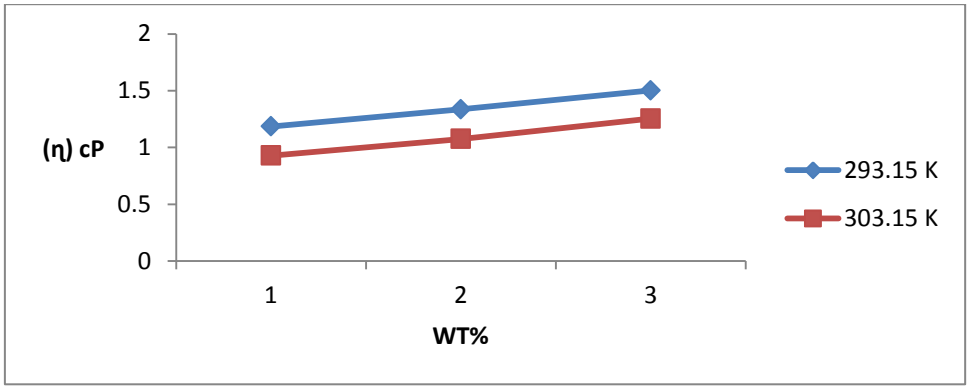

Fig. 3.3 Viscosity (η) cP of HPMC-water mixtures plotted against the weight percentages (wt %) of HPMC in mixtures at two experimental temperatures.

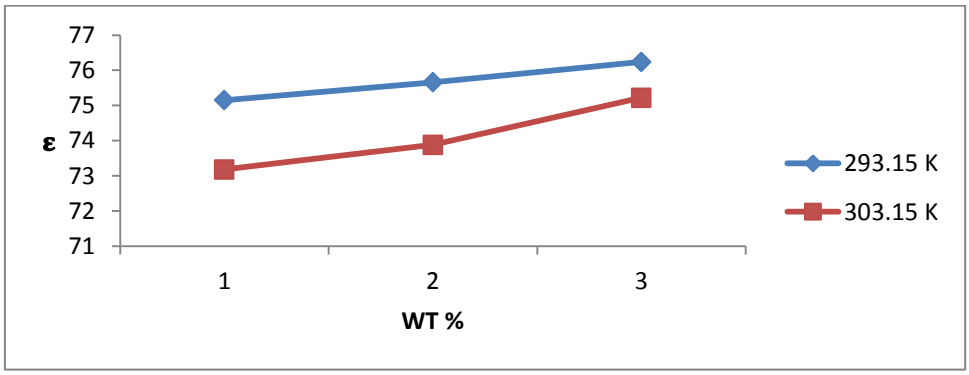

Fig. 3.4 : Dielectric constant (ε) of HPMC-water mixtures plotted against the weight percentages (wt %) of HPMC in mixtures at two experimental temperatures.

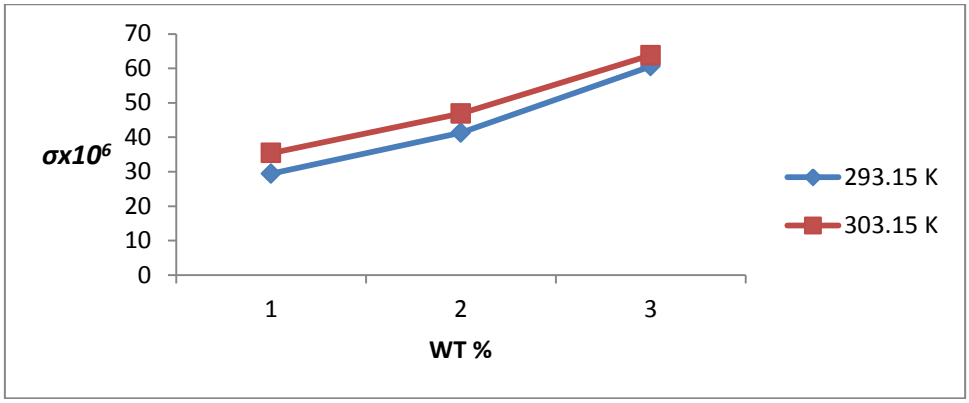

Fig. 3.5 : Specific conductance (σ) of HPMC-water mixtures plotted against weight percentages (wt %) of HPMC in mixtures at two experimental temperatures.

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^3mol^{-1}) were calculated by the second way as difference between real mixture volume (experimental) and ideal mixture volume (theoretical) [19, 20], as in the following equations:

$$V_m^E = V_{exp.} - V_{theo.} \quad \text{.....(3-1)}$$

$$V_m^E = [(M_1 X_1 + M_2 X_2) / d_{12}]_{exp.} - [(M_1 X_1 / d_1) + (M_2 X_2 / d_2)]_{theo} \quad \text{..... (3-2)}$$

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 where:

$X_1 = n_1 / (n_1+n_2)$ - - - - - - - - - (3.3)

$X_2 = n_2 / (n_1+n_2)$ --------(3-4)

Table 3.2 : 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} (g cm^{-3})	$V_{exp.}$ (cm^3mol^{-1})	$V_{theo.}$ (cm^3mol^{-1})	V_m^E (cm^3mol^{-1})
0.10%	0.0002	99.9998	293.15	0.9965	1810.132	1810.539	-0.407
			303.15	0.9941	1814.502	1815.181	-0.679
0.20%	0.0004	99.9996	293.15	0.9967	1811.582	1815.859	-4.277
			303.15	0.9944	1815.772	1820.501	-4.729
0.30%	0.0005	99.9995	293.15	0.9969	1813.031	1821.178	-8.147
			303.15	0.9946	1817.223	1825.821	-8.598

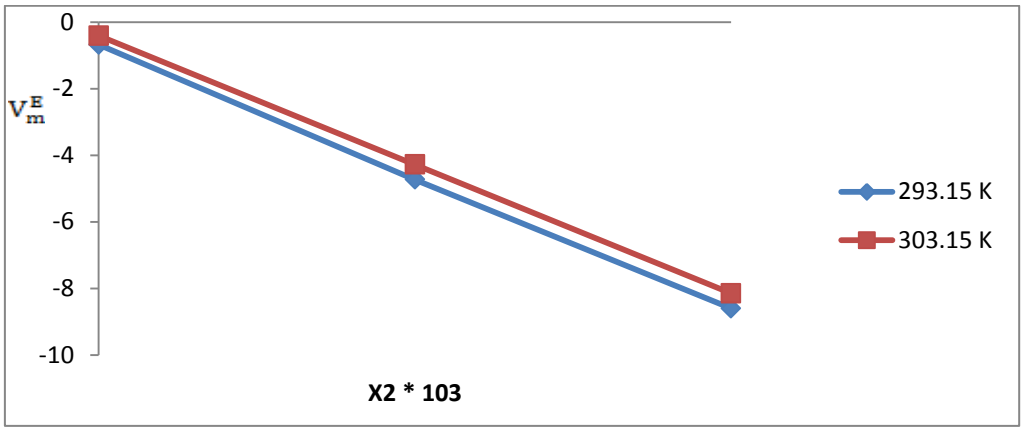

Fig. 3.6 Excess molar volume (V_m^E) as a function of the HPMC mole fraction (X_2) at two experimental temperatures.

3.2. (TMAB) and (TEAB) in HPMC-water mixture:-

Solutions of (TMAB) and (TEAB) in each composition of solvent have been investigation, also the important physical properties Densities (d), viscosities (η) and specific conductance. The results obtained are presented in table***(3.3)and Fig(3.7),(3.8),(3.9).*** .

Table 3.3 Some physical properties of (TMAB) in HPMC-water mixtures containing 0.2% weight percentage of solvent of I – II are given at 293.15 and 303.15K.

I at 293.15 K				II at 303.15K		
C x 10 mol dm^{-3}	(d)g cm^{-3}	(η)cp	*(Λ)S* cm^2 mol^{-1}	(d)g cm^{-3}	(η)cp	(Λ)*S* cm^2 mol^{-1}
0.47	0.9988	1.1591	118.149	0.9958	0.9269	127.447
1.47	1.0021	1.1602	100.787	0.9989	0.9280	109.401
2.47	1.0054	1.1570	92.694	1.0026	0.9221	101.73
3.47	1.0093	1.1709	86.224	1.0061	0.9340	92.726
4.47	1.0131	1.1999	80.976	1.0101	0.9472	87.221
5.47	1.0170	1.2206	75.824	1.0141	0.9681	83.365
6.47	1.0212	1.2430	71.879	1.0180	0.9859	79.989
7.47	1.0248	1.2956	70.112	1.0212	1.0284	74.315
8.47	1.0281	1.3214	66.101	1.0247	1.0421	71.189

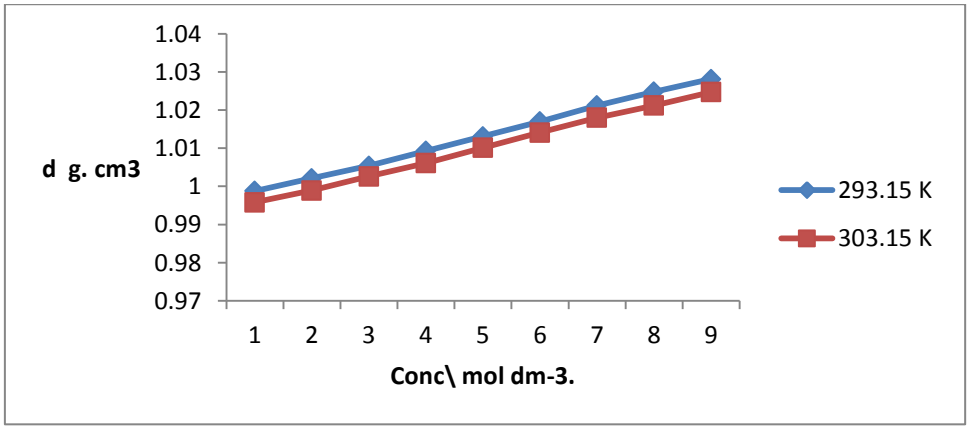

Fig 3.7 : Densities (d) of TMAB plotted against the concentrations of TMAB in (0.2) % respectively of HPMC-water mixture at two experimental temperatures.

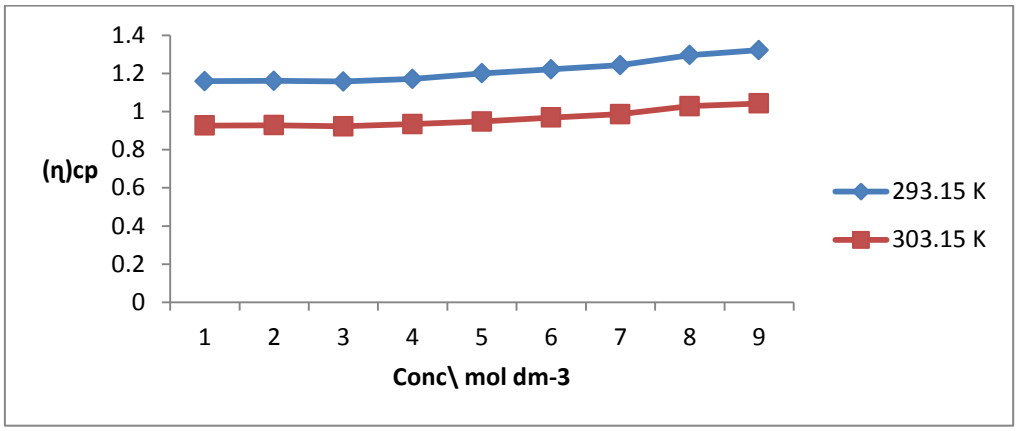

Fig 3.8: Viscosity (η) of TMAB plotted against the concentrations of TMAB in (0.2) % respectively of HPMC-water mixture at two experimental temperatures.

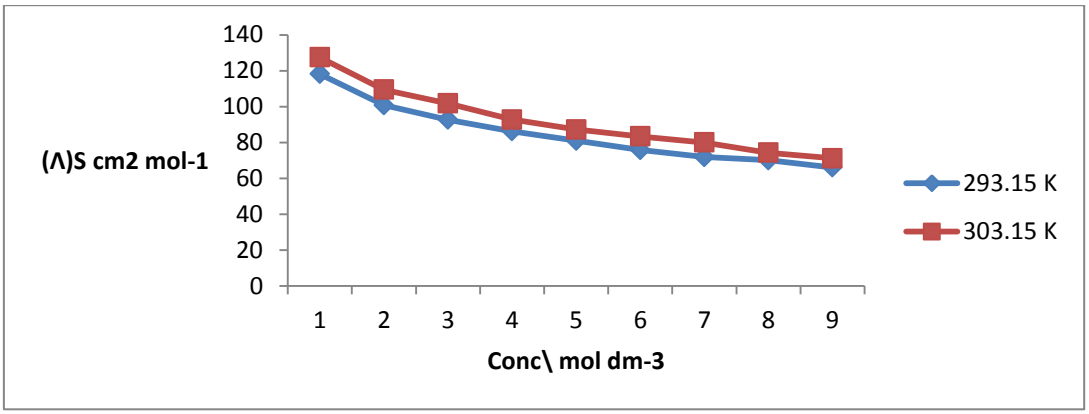

Fig 3.9: Molar conductance (Λ) of TMAB plotted against the concentrations of TMAB in (0.2) % respectively of HPMC-water mixture at two experimental temperatures.

Table 3.4 : Some physical properties of (TEAB) in HPMC-water mixtures containing 0.2% weight percentage of solvent of I – II are given at 293.15 and 303.15K.

I at 293.15 K				II at 303.15K		
C x 10 mol dm^{-3}	(d)g cm^{-3}	(η)cp	*(Λ)S* cm^2 mol^{-1}	(d)g cm^{-3}	(η)cp	(Λ)*S* cm^2 mol^{-1}
0.47	0.9996	1.2304	89.277	0.9965	0.9695	97.243
1.47	1.0028	1.2204	76.000	0.9995	0.9704	83.272
2.47	1.0061	1.2323	67.743	1.0032	1.0085	73.270
3.47	1.0100	1.2728	62.248	1.0066	1.0256	67.487
4.47	1.0139	1.3047	59.159	1.0107	1.0908	65.101
5.47	1.0175	1.3791	55.941	1.0148	1.1230	61.792
6.47	1.0218	1.4165	51.632	1.0185	1.1501	57.496
7.47	1.0253	1.4453	49.736	1.0219	1.2092	53.548
8.47	1.0288	1.5057	46.517	1.0251	1.2492	49.587

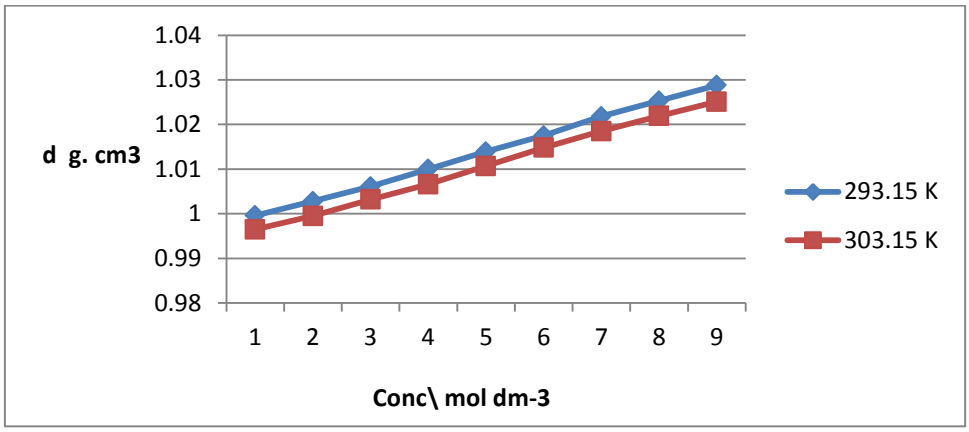

Fig 3.10 : Densities (d) of TEAB plotted against the concentrations of TEAB in (0.2) % respectively of HPMC-water mixture at two experimental temperatures.

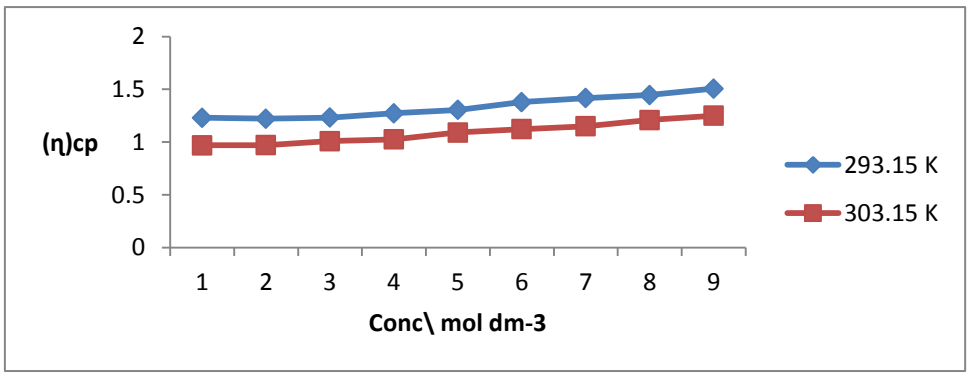

Fig 3.11 Viscosity (η) of TMAB plotted against the concentrations of TMAB in (0.2) % respectively of HPMC-water mixture at two experimental temperatures.

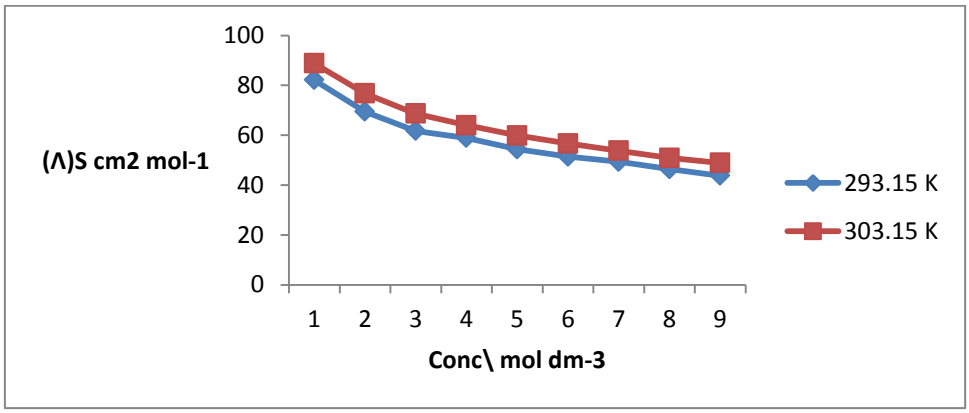

Fig 3.12 Molar conductance (Λ) of TEAB plotted against the concentrations of TEAB in (0.2) % respectively of HPMC-water mixture at two experimental temperatures.

Ion Association Constant by Bjerrum Method

The association of $(CH_3CH_2)_4N^+$ and Br^- ions to form ion pairs (IP) in the solvent mixtures may be represented as

$$(CH_3CH_2)_4N^+ + Br^- \rightleftharpoons (CH_3CH_2)_4N^+ Br^-$$

Ion-pair (IP)

The possibility to obtain the values of the ion association constant (K_A), when å = q, which is ionic distance and taking b=2

$$K_A = \frac{4\pi N_A \text{å}^3}{1000} \left(\frac{e^b}{b}\right)$$

The values of association constant were presented in ***Table (3.5)and Table (3.6)*** 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. ***Fig (3.13)*** shows the relationship of K_A values with the corresponding values of ε for TMAB and TEAB in HPMC-water mixture at two temperatures. This is indicating that when the molecular solvent has relatively high dielectric constant, it could form strong intermolecular interaction [21]. 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 [22]. Also ***Table (3.5), Table (3.6)*** calculated of K_A values by using Shedlovsky method for TMAB and TEAB in HPMC-water mixture

Table 3.5 Values of K_A by Shedlovsky methods and limiting molar conductance Λ_0 for TMAB in HPMC-water mixture at two experimental temperatures.

wt%	T(K)	ε	å(nm)	Λ_o(Scm²mol^{-1})	Bjerrum K_A(dm³mol^{-1}) x 10^3	Shedlovsky K_A(dm³mol^{-1}) x 10^3
0.20%	293.15	75.66	0.3767	128.78	1.494	1.404
	303.15	73.88	0.3731	139.73	1.452	1.314

Table 3.6 : Values of K_A by Shedlovsky methods and limiting molar conductance Λ_0 for TEAB in HPMC-water mixture at two experimental temperatures.

wt%	T(K)	ε	å(nm)	Λ_o(Scm²mol^{-1})	Bjerrum K_A(dm³mol^{-1}) x 10^3	Shedlovsky K_A(dm³mol^{-1}) x 10^3
0.20%	293.15	75.66	0.3767	96.34	1.494	1.477
	303.15	73.88	0.3731	106.31	1.452	1.389

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 [23] allow the ions trapped each other and may be the formation of the ion pairs take best chance.

References

1- M. Singh, N. Lalrosanga and M. Lalhhruaitluanga, "Ion pair formation of hexamine Nickel (II)Chloride and Tris- Ethylene Diamine Nickel(II)Chloride in aqueous medium at different temperatures" , Res. J. Phar. Bio. & Chem. Sci.,3(3),(2012),85-92.

2- M.N.Roy, R.Chanda, P.Chakraborti and A.Das,"Conductativity is acontrivance to explore ion pair and triple ion structure of ethanoates in tetra hydrofuran dimethyl sylfoxide and thierbinaries" , J. Flu. Phs. Equ., 322,(2012),159-166.

3- Sk. E. Haque ,A.Sheela *,"Miscibility of eudragit / chitosan polymer blend in water determined by physical property measurements"*, Int. J. Pharmaceutics, 441, (2013), 648-653.

4- R.I. Kay ,D.F. Evance , *"The effect of solvent structure on the mobility of symmetrical ions in aqueous solution"*, J. Phys. Chem.,70(7), (1966), 2325-2335.

5- R.M. Fouss, *"Parametric analysis of conductance data"*, Proc. Nat. Acad. Sci.U.S.A., 71(11), (1974), 4491-4495.

6- B. Pas ,D.K.Hazra *," Conductometric, Viscometric and Spectroscopic investigations on the salvation phenomena of Alkali-metal ions and ion pairs in 2- methoxy ethanol"*, J. phys. Chem. ,99(1), (1995), 269-273.

7- P.K. Muhuri ,B.Das ,D.K. Hazra, *"Ionic association of some lithium salts in 1,2 dimethoxy ethane, A Raman spectroscopic and conductivity study"*, J. phys. chem.,B101(17), (1997) 3329-3332.

8- P.J.Victor, P.K. Muhuri ,B.Das,D.K. Hazra *,"Thermodynamics of ion association and salvation in 2-methoxy ethanol: Behavior of tetra phenyl arsonium, picrate and tetra phenyl borate ions from conductivity and ultrasonic data "*, J. Phys. chem.,B103(50), (1999), 11227-11232.

9- C.Guha , J.M.Chakraborty, S.Karanjai, B.Das, *" The structure and thermodynamics of ion association and salvation of some thiocyanates and nitrates in 2-methoxy ethanol studied by conductometry and FTIR Spectroscopy"*, J. Phys. Chem.,B107, (2003), 12814-12819.

10- O.N. Kalugiu, V.N. Agieienko and N.A. Otroshko, " Ion association and salvation in solutions of Mg, Ca, Sr, Ba and Ni perchlorates in acetonitrile conducometric study", J. Mol. Liq. ,165, (2012), 78-86.

11- M. Hojo, T. Ueda,H. Hamada, Z. Chen and S. Umetani " Conductometric studies on higher ion aggregation from lithium fluoroalkanoates in propylene carbonate and n,n- dimethyl formamide" , J. Mol. Liq. , 145, (2009), 24-32.

12- C.G. zoski, "Hand book of Electro chemistry" 1st Ed., Elsevier UK, (2007), p. 66.

13- F. I. El. Dossoki, " Conductometric and spectroscopic studies of the ion pair association of sodium and potassium picrate in 2-butanone", J. Mol. liq. , 160, (2011), 119-123.

14- G. Makav and A. Nitazan, "Association of ion pair in clusters of dielectric solvents", J. Phys. Chem. ,96, (1992),2965-2997.

15- . Tomini, R. Tomas, M. Visic, and V. Sokola , "Conductometric Study of Hydrobromic Acid in 2-Propanol + Water Mixtures", Croat. Chem. Acta, 77 (3),(2004), 537-543.

16- S. Richert, A. Rosspeintner, S. Landgraf, G. Grampp, E. Vauthey,and R. Kattnig , " Time-Resolved Magnetic Field Effects Distinguish Loose Ion Pairs from Exciplexes",J.Am.Chem.Soc.,135,(2013),15144−15152.

17- T. Shedlovsky," The electrolytic conductivity of some uni-uni valant electrolytes in water at 25 C°", J.Am.Chem.Soc.,54,(1932),1411-1428.

18- N. Singh, D. Singh, N. Yaiphaba and N. rajmnhon, "Ion pair formation and thermodynamics of glycine bis-1- amidin o,o-mehylurea,Cobalt halides in water+ methanol mixed soloventt at different temperatures" , Asian J. Chem. , 20, (2008), 1750-1760.

19- L. Morávková and J. Linek, "Excess molar volumes of (octane + benzene, or toluene, or 1,3-xylene, or 1,3,5-trimethylbenzene) at temperature between (298.15 and 328.15) K", J. Chem. Therm. , 40, (2008), 671–676.

20- L. Morávková and Z. Sedláková, "Excess Molar Volume of Binary Systems Containing Mesitylene", J. chem. Ind., 62 (5), (2013), 159–170.

21- Q. Yung, K. Yu, H. Xing, B. Su, Z. Bao, Y. Yang and Q. Reu, "The effect of molecular solutions on the viscosity, conductivity and ionicity of mixtures containing Chloride amin based ionic liquid" , J. Inds. & Engn. Chem. , 19, (2013), 1708-1714.

22- V. A. Chialro, M. S. Gruszkiewicz, J. M. Simonson, D. A. Palmer and D. R. Cole, "Ion pair association in extreme aqueous environments, molecular based and electrical conductance approaches", J. Sol. Chem., 38, (2009), 827-841.

23- M. N.Roy, L. Sarkar, R.Dewan, "Ion pair and triple-ion formation of some tetraalkylammonium iodides in n-hexanol and its binary mixtures with o- toluidene" , J. Chem. Therm. , 43, (2011), 371-376.