Ion-Pair Formation of Tetramethylammonium bromid in Hydroxypropylmethylcellulose-WaterMixtures from Conductivity Measurements

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

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Abstract

The equivalent conductivity (Λ) at different concentrations of $(CH_3)_4NBr$ Tetrametylammonium bromide (TMAB) solution in hdroxypropylmethylcellulose(HP MC)-water mixtures at 25˚C has been determined from direct conductance measurements. The association constant (K_a) for ion-pair formation and the equivalent conductivity of the electrolyte at infinite dilution ($Λ_∘$) in the different mixtures component by a least square method with an appropriate computer programme using Shedlovsky method. Density, viscosity and dielectric constant, have been measured for all the solvent mixtures at 25˚C.Walden products (W) have been calculated from the ($Λ_∘$) and the viscosities ($η_∘$) of the HPMC-water mixtures.

الخلاصه :

امكن تقدير التوصيل المكافيء (Λ) عند تراكيز مختلفة من محاليل رباعي مثيل امونيوم بروميد المذاب في امزجة من هيدروكسي بروبيل مثيل سليلوز مع الماء بدرجة 25 مئويه وذلك من قياسات التوصيلية في تلك المحاليل وامكن الحصول على ثابت التجمع (Ka) لتكوين الايونات المزدوجة وكذلك على التوصيل المكافيء عند التخفيف النهائي ($Λ_∘$) للالكتروليت في الامزجة المختلفة من معلومات التوصيل المولاري باستخدام معالجة المربعات الصغرى من خلال برنامج حسابي مناسب اعتمادا على طريقة شدلوفسكي وأمكن كذلك قياس كثافة والزوجة وثابت العزل لثلاثة امزجة من هيدروكسي بروبيل مثيل سليلوز مع الماء عند درجة 25 مئويه .وبربط القيم المستخرجه ل ($Λ_∘$) مع قيم الزوجه ($η_∘$) للامزجة أمكننا إيجادقيم والدن (w) .

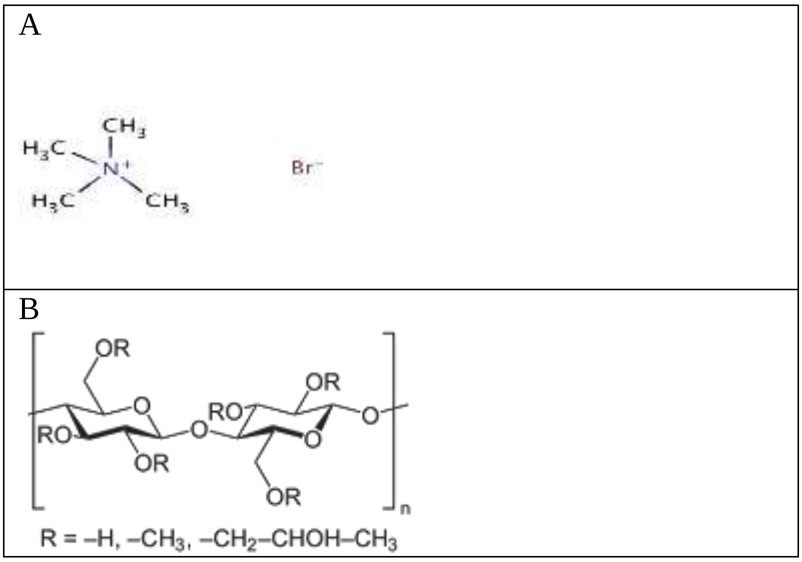
Introduction

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. It is a century old series proposed on the basis of solubility of polymers and stability of sols in electrolyte solution [1]. A number of conductometric methods are well-suited to investigate the ion–solvent and ion–ion interactions in electrolyte solutions [2-6]. Ionic association of electrolytes 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. Such solvent properties as viscosity and the dielectric constant have been taken into consideration as these properties help in determining the extent of ion association[7]. The nature of the solvent mixtures greatly influences the ionic association of electrolytes in solution which is due to the mode of solvation of its ions [8-9].

The association of ions in solvents of low dielectric constants[10] to form ion pairs is considered at present as an accepted fact .conductance measurement of electrolyte solutions is one of the important methods to identify the possibility of the formation of ion pairs[11].The measurement of electrical conductivities of dilute solutions of salts are considered to be one of the important methods for studying the ion-pair or multiple-ion association not only in aqueous solutions but also in non-aqueous, or mixed ones[12-14]. The present paper deals with conductance measurements and association constant determinations of a purely uni- uni valent ionic compound such as TMAB in HPMC-water mixtures of dielectric constants far lower than of water. These results are useful for the interpretation of the nature of interactions that occur between the salts and mixed solvent systems [12]. One of the main objects of this study is to understand the ionic conductivity and the behavior of solvated of $(CH_3)_4N$ Br ions in mixture solvent.

Experimental

The chemicals (TMAB) was obtained from Himedia Labortories pvt.ltd, with a purity exceeding 98.0% as white powder with mol. wt.(154.06) . (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). scheme (1)



Scheme1. Structure of A. (TMAB) and B. (HPMC)

Double distillation deionizer water a specific conductance of 5 x 10^{-7} s cm^{-1} at 25C° has been used for prepare of the HPMC-water mixture and of TMAB. 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 solution of TMAB has been prepared using each of the three of HPMC-water mixtures. Nine concentrations of the TMAB in the mixture have been prepared.

The conductance measurements were made using WTW 82362 digital conductometer ,model inolab multi 720 by Weilheim-Germany . The Pyrex conductance cell was of the dipping type with bright platinum electrodes. The cell constant could be adjusted with the electrode at 1 cm^{-1} through automatically setting. The uncertainty in the calculated specific conductance (σ) values was estimated to be within ± 1 μ s cm^{-1}.

A universal dielectrometer, type OH-301 obtain from radilkis-hungary, was used to measure the dielectric constant (D) of the solvent mixtures. The uncertainty in the D values was found to be within ±0.2 %.

The densities of the solvent mixtures have been measured using Densito 30 px digital density meter, with CPT charges type Mettler Toledo -Japan the accuracy of the measurements lied within ±1.0x10^{-4} gcm^{-3} of the density value.

The viscosity (η) of the various binary HPMC-water mixture were measured using an Ostwald viscometer , type D with a flow time of 25S for pure water at 25 ˚C the uncertainty of the measurement was ± 0.2 % . The temperature of the solution was controlled to within ±0.01 ˚C. Table 1 gives the results of such measurements.

Results and discussion

1- Calculation the association constant (Ka)

The equivalent conductivity (Λ) of TMAB solution at 25 ˚C in each solvent mixtures containing 0.1, 0.2and0.3 weight percentage of HPMC-water are given in Table 2. The corresponding values of 1/ Λ and Λ C are given also in Table 2, Fig.1.

The association of $(CH_3)_4N^+$ and Br^- ions to form ion pairs (IP) in the solvent mixtures may be represented as.

$(CH_3)_4N^+ + Br^- \leftrightarrows (CH_3)_4N^+ Br^-$

Ion-pair (IP)

The association constant (Ka) and the limiting molar conductance (Λ_o) of TMAB in HPMC-water mixtures at constant temperature have been calculated from the measured molar conductance (Λ) data (Table 2) by a least-square treatment with an appropriate computer program using shedlovsky method[15] which involved the solution of the following set of equations.

$$\frac{1}{\Lambda S} = \frac{1}{\Lambda_o} + \frac{C\Lambda S f_{\pm}^{2} K_a}{\Lambda_o^{2}}$$

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

$$B = \frac{8.204 \times 10^5 \Lambda_o}{(DT)^{3/2}} + \frac{82.5}{\eta (DT)^{1/2}} \quad (3)$$

$$\alpha = \frac{S\Lambda}{\Lambda_o} \quad (4)$$

Where $f\pm$ is the mean activity coefficient of TMAB in HPMC-water mixture and α is the degree of dissociation of ion-pairs c is the concentration of salt solution in each mixture, T the absolute temperature by Kelvin and B, S are inert function within the set of equations. The mean activity coefficient ($f\pm$) in Eqn. (1) has been determined from the modified Debye-Huckel equation [16] as:

$$-\log f \pm \frac{1.8246 \times 10^6 (c\alpha)^{\frac{1}{2}}/(DT)^{3/2}}{1 + 50.29 \times 10^8\, \mathring{a}(c\alpha)^{\frac{1}{2}}/(DT)^{1/2}} \quad \text{------ (5)}$$

$$\mathring{a} = \frac{Z_+ Z_- e^2}{2DKT} \quad \text{------ (6)}$$

Where a° is the ion –size parameter and $Z_+ = Z_-$=1 for a uni-uivalent electrolyte such as TMAB , e the electronic charge , K the Boltzmann constant and D is the dielectric constant of the HPMC-water mixture .

The values of Ka and Λ_o which have been calculated by shedovsky method are presented in Table 3. The influence of the dielectric constant of the association constant (Ka) is indicated in Fig.2 where log Ka values are plotted against the reciprocal of the dielectric constant 1/D , the result suggests an initial linear increase of log Ka with 1/D covering the behavior of the electrolyte in the solvent mixtures .

2- Walden’s product

Values of the Walden product (W) have been calculated using the relation [17]

W = $\Lambda_o \eta_o$ -------------------- (7)

where (η_o) is the viscosity of solvent mixture, Λ_o equivalent conductance of solute the resulting data are given in Table 3 values of W for TMAB varied at constant temperature with the variation of the dielectric constant of HPMC-water mixture as shown in Fig. 3 that indicate the product of $\Lambda_o\eta_o$decreases as D decreases that because the values $\Lambda_o\eta_o$will depend to some extent on the fundamental properties of the solvent as well as on the effective size of the ion as a consequence of the enhancement in the structure of the solvation sheath. the values of Λ_o are also expected to decreas with the lowering of D values as shown in Fig 4 due to effect of the enhancing solvation sheath on the contribution of the migrating ions to the values of the equivalent conductivity at infinite dilution.

Table 1. some physical properties of HPMC-water mixtures at 25 ˚C.

Solvent W%	d ($g.ml^{-1}$)	D	η (cp)	k x 10^6 ($s\ cm^{-1}$)
0.00	0.9970	78.54	0.894	0.5
0.10	0.9958	74.22	1.0556	33.2
0.20	0.9959	74.75	1.1891	44.6
0.30	0.9962	75.85	1.3556	61.9

Table 2. the conductivity data for TMAB in HPMC-water mixtures at 25˚C.

Wt%	C x 10 mol dm^{-3}	√cx 10 mol dm^{-3}	Λ s dm^2mol^{-1}	1/Λ x 10^3 mol $s^{-1}dm^{-2}$	Λ. C s dm^{-1}
0.1	0.47	2.17	104.121	9.604	4.893687
	1.47	3.83	93.714	10.671	13.77596
	2.47	4.97	89.139	11.218	22.01733
	3.47	5.89	83.098	12.034	28.83501
	4.47	6.69	80.112	12.483	35.81006
	5.47	7.40	77.514	12.901	42.40016
	6.47	8.04	76.043	13.15	49.19982
	7.47	8.64	73.967	13.52	55.25335
	8.47	9.20	70.373	14.21	59.60593
0.2	0.47	2.17	119.479	8.37	5.615513
	1.47	3.83	106.559	9.384	15.66417
	2.47	4.97	95.69	10.45	23.63543
	3.47	5.89	89.126	11.22	30.92672
	4.47	6.69	83.668	11.952	37.3996

	5.47	7.40	79.265	12.616	43.35796
	6.47	8.04	75.125	13.311	48.60588
	7.47	8.64	72.236	13.844	53.96029
	8.47	9.20	68.466	14.606	57.9907
0.3	0.47	2.17	128.617	7.775	6.044999
	1.47	3.83	113.884	8.7809	16.74095
	2.47	4.97	101.282	9.8734	25.01665
	3.47	5.89	93.167	10.7334	32.32895
	4.47	6.69	88.201	11.3377	39.42585
	5.47	7.40	83.804	11.9326	45.84079
	6.47	8.04	78.516	12.7363	50.79985
	7.47	8.64	73.718	13.5652	55.06735
	8.47	9.20	70.528	14.1788	59.73722

Table 3. association constants (Ka) and Walden product for (TMAB) in different mixtures consisting HPMC-water which symbol (I – III) at 25˚C.

Solvent	w%	Λ_o	W	Log k_a	$1/Dx10^2$
I	0.1	116.75	123.24	-3.0747	1.347
II	0.2	133.40	158.63	-2.9020	1.337
III	0.3	144.40	195.75	-2.8324	1.318

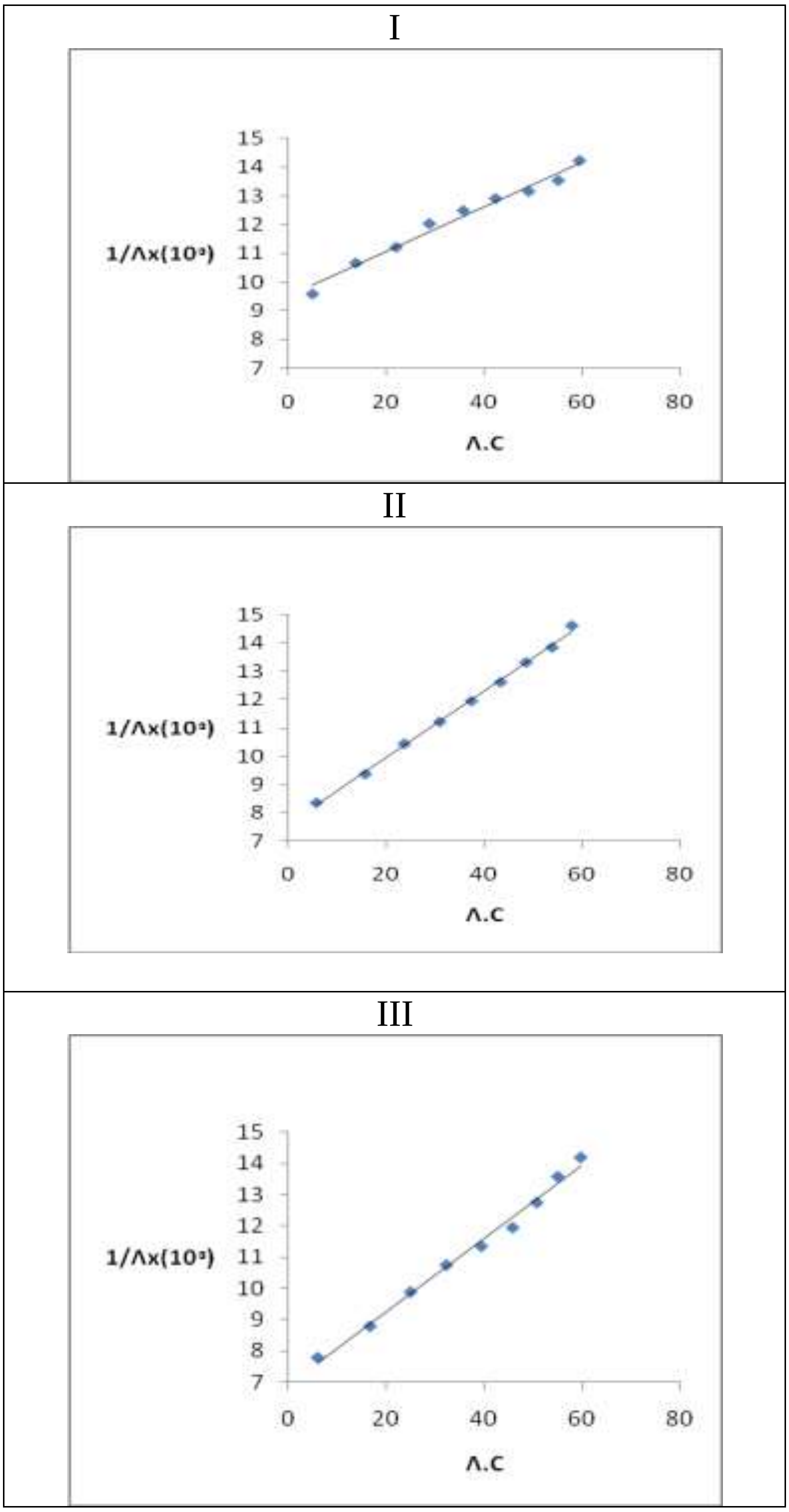


Fig. 1: The reciprocal of the equivalent conductivity (1/Λ) of TMAB in HPMC-water mixtures (numbered Ito III) at 25˚C plotted against the (ΛC) of the electrolyte.

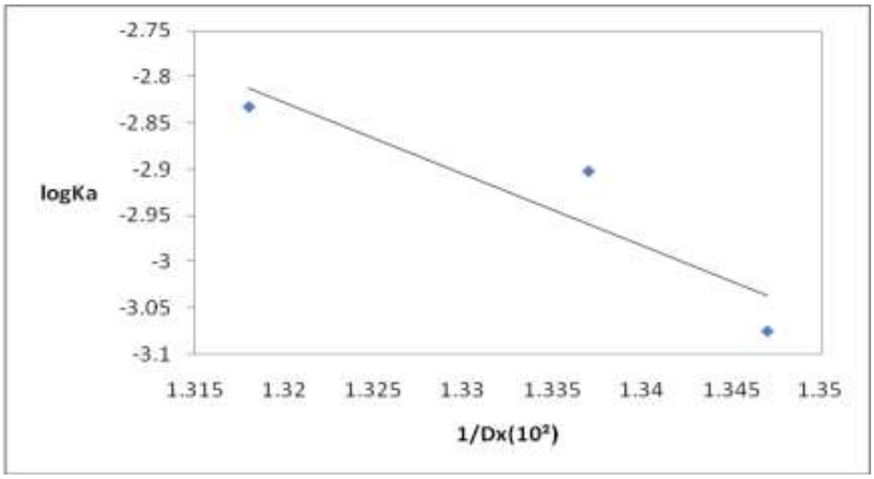


Fig. 2: Logarithm of the association constant (log K_a) for TMAB ions in three HPMC-water mixtures plotted against the reciprocal of the dielectric constant (1/D) of the mixtures at 25˚C.

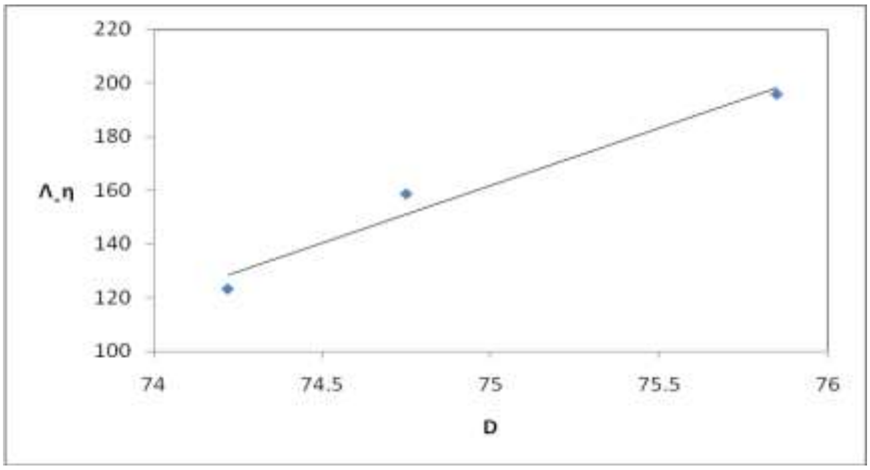


Fig. 3: Walden's product ($\Lambda_o \eta$) for TMAB in three different HPMC-water mixtures at 25˚C versus the dielectric constant (D) of the mixtures.

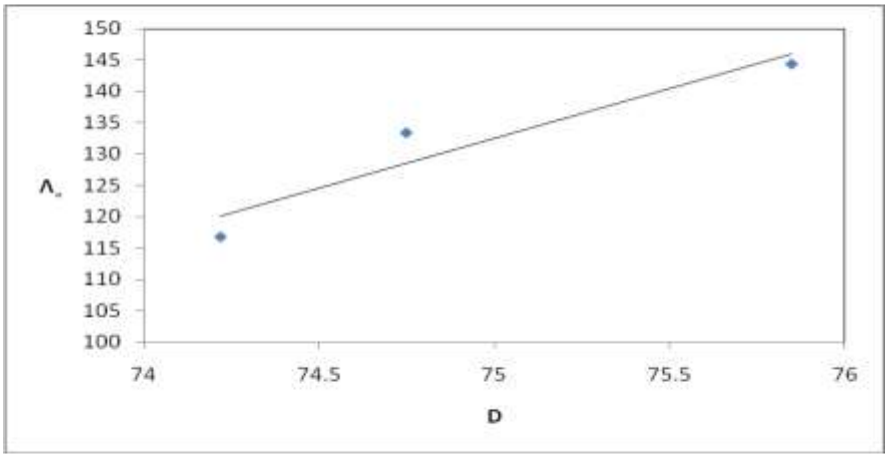


Fig. 4: The plot of the equivalent conductivity at infinite dilution (Λ_o) for TMAB in HPMC-water mixtures versus (D) of the mixtures at 25˚C.

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