

## **Ion-Pair Formation of Ammonium Fluoride in Tetramethyl Urea-Water Mixtures from Conductivity Measurements**

دراسة تكوين مزدوجات ايونية لفلوريد الامونيوم في امزجة رباعي مثيل يوريا مع  
الماء من قياسات التوصيلية

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### **Abstract**

The equivalent conductivity ( $\Lambda$ ) at different concentrations of  $\text{NH}_4\text{F}$  solutions in tetramethyl urea (TMU-water) mixtures at  $25^\circ\text{C}$  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 ( $\Lambda_\infty$ ) in the different mixtures by a least square method with an appropriate computer programme using Shedlovsky method. Densities, viscosities and dielectric constants have been measured for all the solvent mixtures at  $25^\circ\text{C}$ . Walden products ( $W$ ) have been calculated for  $\text{NH}_4\text{F}$  from the ( $\Lambda_\infty$ ) and the viscosities ( $\eta_0$ ) of the TMU-water mixtures.

### **الخلاصة :**

امكن تقدير التوصيل المكافئ ( $\Lambda$ ) عند تراكيز مختلفة من محاليل فلوريد الامونيوم المذاب في امزجة من رباعي مثيل اليوريا مع الماء بدرجة 25 مئوية وذلك من قياسات التوصيلية في تلك المحاليل وامكن الحصول على ثابت التجمع ( $K_a$ ) لتكوين الايونات المزدوجة وكذلك على التوصيل المكافئ عند التخفيف النهائي ( $\Lambda_\infty$ ) للالكتروليت في الامزجة المختلفة من معلومات التوصيل المولاري باستخدام معالجة المربع الاصغر من خلال برنامج حسابي مناسب اعتمادا على طريقة شيدلوفسكي وامكن كذلك قياس كثافات ولزوجات وثوابت عزل امزجة رباعي مثيل اليوريا مع الماء عند درجة 25 مئوية. ويربط القيم المستخرجه ل ( $\Lambda_\infty$ ) مع قيم الزوجه ( $\eta_0$ ) للامزجة امكاني ايجاد قيم جداء والذن ( $w$ )

### **Introduction**

The Debye –Huckel theory<sup>1</sup> assumed that ion in an electrolyte solution are in almost random thermal motion and therefore in almost random positions . The slight deviation from randomness was pictured as giving rise to an ionic cloud around a given ion. The possibility was not considered that some ions of a given charge in the cloud would get sufficiently close to the central ion of the opposite charge in the course of their quasi random solution movements . Bjerrum<sup>2</sup> suggested that a pair of oppositely charged ion may get trapped in each other's columbic field . an ion – pair may thus be formed .

The ions of the pair together form an ionic dipole on which the net charge is zero. Within the ionic cloud , the locations of such uncharged ion pairs are completely random , since being uncharged , they are not acted upon the columbic field of the central ion . Further , on the average , certain fraction of the ions in the electrolyte solution will be stuck together in the form of Ion pairs . 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<sup>3,4</sup> . The association of ions in solvents of low dielectric constants<sup>5,6</sup> 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<sup>6,7</sup>.

The present paper deals with conductance measurements . and association constant determinations of a purely uni- univalent . Ionic compound such as ammonium fluoride in tetra methyl – urea +water mixtures of dielectric constants far lower than of water .

### Experimental

The chemicals (ammonium fluoride and tetra methyl urea) were purum grade obtained from fluka , with a purity exceeding 99.9% the symbol TMU was used throughout this paper to represent tetra methyl urea . deionizer water a specific conductance of  $4 \times 10^{-7} \text{ scm}^{-1}$  at  $25\text{C}^\circ$  has been used for the preparation of the TMU-water mixture and of the ammonium fluoride solution . the TMU-water mixtures have been prepared by four composition of the TMU-water mixture have been utilized in this work in which the weight percentages of TMU ranged from 0.0166 to 0.7833 . the solution of ammonium fluoride have been prepared using each of the four TMU-water mixtures . six concentrations of the ammonium fluoride in the mixture have been prepared

The conductance measurements were made using tacusselelectronique digital conductometer , type CD 810 . The Pyrex conductance cell was of the dipping type with bright platinum electrodes .The frequency of the alternating current could be adjusted at the desired value in the range 60 to 4000 Hz . the cell constant could be adjusted at the desired value in the range  $10^3$  to  $30 \text{ cm}^{-1}$  through a programmed checking procedure . the value of the cell constant was always checked by the method of hind , zwolenick and fuoss<sup>(8-9)</sup>.

The selected frequency of all the conductance measurements was 1000 Hz the uncertainty in the calculated molar conductance ( $\Lambda$ ) values was estimated to be within  $\pm 0.1 \text{ scm}^2 \text{ mol}^{-1}$  .

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  $\pm 0.2 \%$  .

The densities of the solvent mixtures have been measured using paar digital density meter , type DMA 60 , in connection with a DMA 602 remote cell the accuracy of the measurements lied within  $\pm 1.5 \times 10^{-5} \text{ gcm}^{-3}$  of the density value .

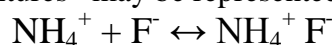
The viscosity ( $\eta$ ) of the various binary TMU-water mixture were measured using an Ostwald viscometer , type D with a flow time of 63Sec for pure water at  $25 \text{ C}^\circ$  the uncertainty of the measurement was  $\pm 0.1 \%$  . The temperature of the solution was controlled to within  $\pm 0.01 \text{ C}^\circ$ . Table 1 gives the results of such measurements .

### Results and discussion :

#### 1- Calculation the association constant (Ka)

The equivalent conductivity ( $\Lambda$ ) of  $\text{NH}_4 \text{ F}$  solution at  $25 \text{ C}^\circ$  TMU-water mixtures containing 0.0166 , 0.2600 , 0.5759 and 0.7833 weight percentage of TMU solvent of II –IV are given in table 2. The corresponding values of  $1/\Lambda$  and  $\Lambda C$  are given also in table 2 ,fig.1 .

The association of  $\text{NH}_4^+$  and  $\text{F}^-$  ions to form ion pairs (IP) in the solvent mixtures may be represented as <sup>10</sup> .



Ion-pair (IP)

The association constant (Ka) and the limiting molar conductance ( $\Lambda_0$ ) of  $\text{NH}_4\text{F}$  in TUM-water mixtures at constant temperature have been calculated from the measured molar conductance ( $\Lambda$ ) data (table 2) by a least-square treatment with an appropriate computer program using shedlovsky method <sup>(11)</sup> which involved the solution of the following set of equations.

$$\frac{1}{S\Lambda} = \frac{1}{\Lambda_0} + \frac{C\Lambda S f_{\pm}^2 K_a}{\Lambda_0^2} \text{-----(1)}$$

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

$$B = \frac{8.204 \times 10^5 \Lambda_0}{(DT)^{3/2}} + \frac{82.5}{(DT)^{1/2}} \text{-----(3)}$$

$$\alpha = \frac{S\Lambda}{\Lambda_0} \text{-----(4)}$$

Where  $f_{\pm}$  is the mean activity coefficient of  $\text{NH}_4\text{F}$  in TMU-water mixture and  $\alpha$  is the degree of dissociation of ion-pairs the mean activity coefficient (FI) in eqn .(1) has mean determined from the modified Debye-Huckel equation <sup>(12)</sup> as :

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

Where  $a^{\circ}$  is the ion –size parameter  $a^{\circ} = \frac{Z_+ Z_- e^2}{2DKT} \text{-----(6)}$

and  $Z_+ = Z_- = 1$  for a uni-ivalent electrolyte such as  $\text{NH}_4\text{F}$  ,  $e$  the electronic charge ,  $K$  the Boltzman constant and  $D$  is the dielectric constant of the TMU-water mixture .

The values of  $K_a$  and  $\Lambda_0$  which have been calculated by shedovsky method are presented in table 3

The influence of the dielectric constant of the association constant ( $K_a$ ) is indicated in fig.2 where  $\log K_a$  values are plotted against the reciprocal of the dielectric constant  $1/D$  , the result suggests an initial linear increase of  $\log K_a$  with  $1/D$  covering the behavior of the electrolyte in the solvent mixtures .

## 2- waldens product

Values of the walden product ( $w$ ) have been calculated using the relation <sup>(13)</sup>

$$W = \Lambda_0 \eta_0 \text{----- (7)}$$

where ( $\eta_0$ ) is the viscosity of the urea-water mixture, the resulting data are given in table ( 3)

values of  $W$  for  $\text{NH}_4\text{F}$  varied at constant temperature with the variation of the dielectric constant of TMU-water mixture as shown in fig (3) that indicate the product of  $\Lambda_0 \eta_0$  decreases as  $D$  decreases that because the values  $\Lambda_0 \eta_0$  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  $\Lambda_0$  are also expected to decrease 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 constants of TMU-water mixtures at 25 C° .

Solvent W%TMU	d (g.ml <sup>-1</sup> )	D	η(cp)	k x 10 <sup>-2</sup> (s cm <sup>-1</sup> )
0.0000	0.9982	78.30	0.890	10 <sup>-4</sup>
0.0166	1.0025	72.11	5.266	1.09
0.2600	1.0136	41.01	4.665	1.33
0.5759	0.9897	28.49	2.462	1.15
0.7833	0.9816	24.18	2.008	0.95
1.0000	0.9683	9.02	1.450	0.85

Table 2. The conductivity data for NH<sub>4</sub>F in TMU-water mixtures at 25C°.

Solvents	C x 10 <sup>4</sup>	√c x 10 <sup>2</sup>	Λ	1/Λ x 10 <sup>3</sup>	Λ. C x 10 <sup>3</sup>
I	24.3137	4.9309	68.33	14.14634	166.1302
	43.5006	6.5955	67.95	14.7167	295.58
	57.6992	7.5960	66.65	15.0037	384.565
	69.2157	8.3196	65.41	15.2881	452.739
	77.9247	8.8275	64.62	15.475	503.549
	85.9792	9.2725	63.79	15.6764	548.461
II	30.3397	5.5081	54.32	18.4094	164.805
	48.9143	6.9938	51.59	19.3836	252.34
	62.8911	7.9303	49.92	20.032	313.952
	73.5946	8.5787	48.67	20.5465	358.18
	86.5139	9.3012	47.50	21.0526	410.94
	94.8556	9.7393	47.26	21.1595	448.28
III	14.7204	3.8367	44.60	22.4215	65.6529
	24.7182	4.9717	42.01	23.8038	103.8411
	30.9731	5.5653	41.02	24.3783	127.05
	35.6797	5.9732	40.37	24.7708	144.0389
	39.5939	6.2923	39.64	25.227	156.95
	43.0025	6.5576	38.94	25.6805	167.451
IV	7.3118	2.7040	25.31	39.51	18.506
	11.4340	3.8142	23.55	42.4628	26.927
	15.0227	3.8759	22.46	44.5235	33.7409
	18.0031	4.2430	21.77	45.9347	39.1927
	20.4262	4.5195	21.26	47.0366	43.4261
	22.3441	4.7269	20.87	47.9156	46.6321

Table 3. Association constants (Ka) and Walden product for (NH<sub>4</sub>F) in different mixtures consisting TMU-water at 25 C° .

Solvent	w%	Λ <sub>o</sub>	Λ <sub>o</sub> η	Log k <sub>a</sub>	1/D
I	0.0166	0.074003	0.3897	-4.67044	0.013868
II	0.2600	0.059421	0.277199	-4.4478	0.024384
III	0.5759	0.04884	0.120244	-4.13673	0.035100
IV	0.7833	0.029144	0.058521	-3.60092	0.041356

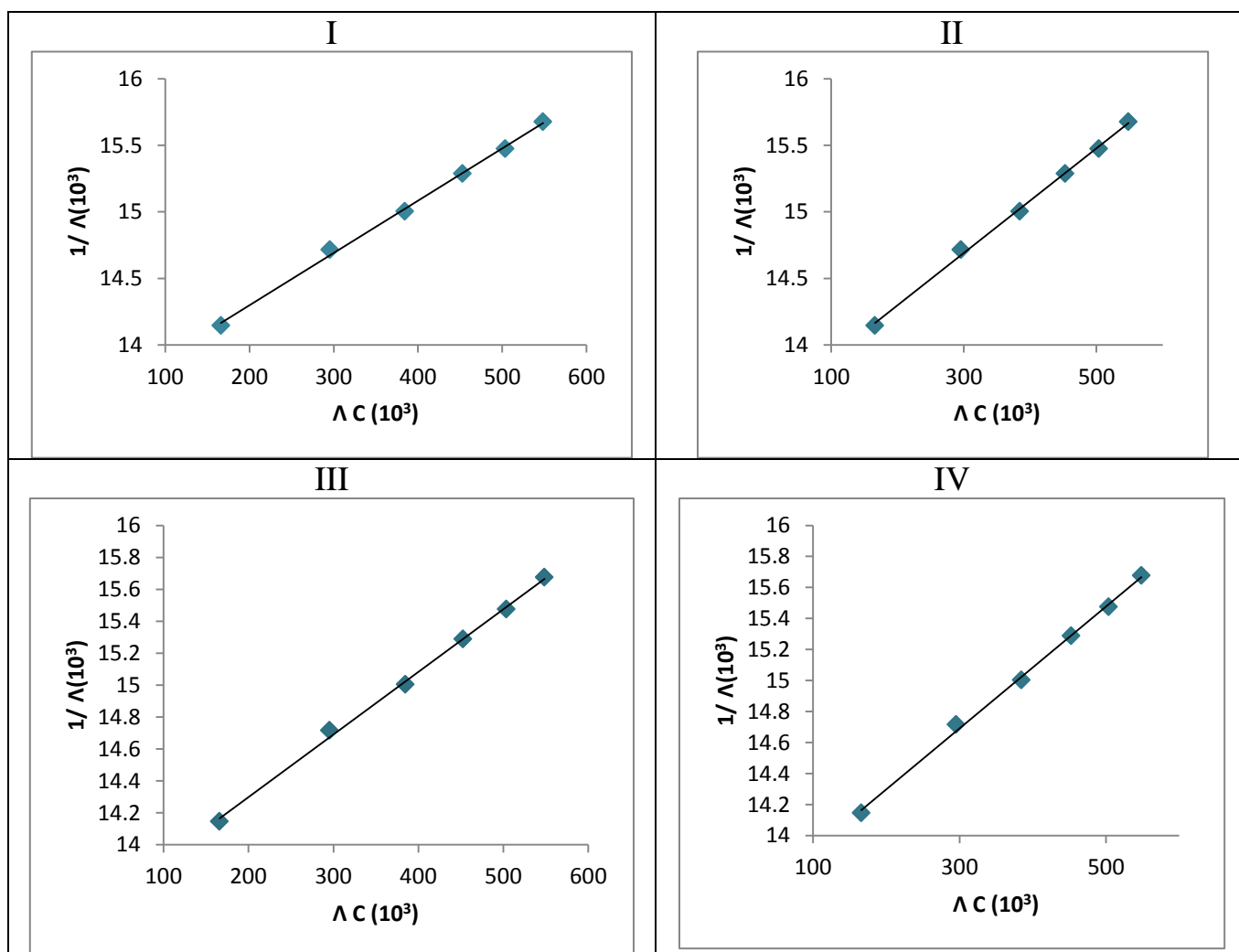


Fig. 1: The reciprocal of the equivalent conductivity ( $1/\Lambda$ ) of  $\text{NH}_4\text{F}$  in TMU-water mixtures (numbered I to IV) at  $25^\circ\text{C}$  plotted against the ( $\Lambda C$ ) of the electrolyte.

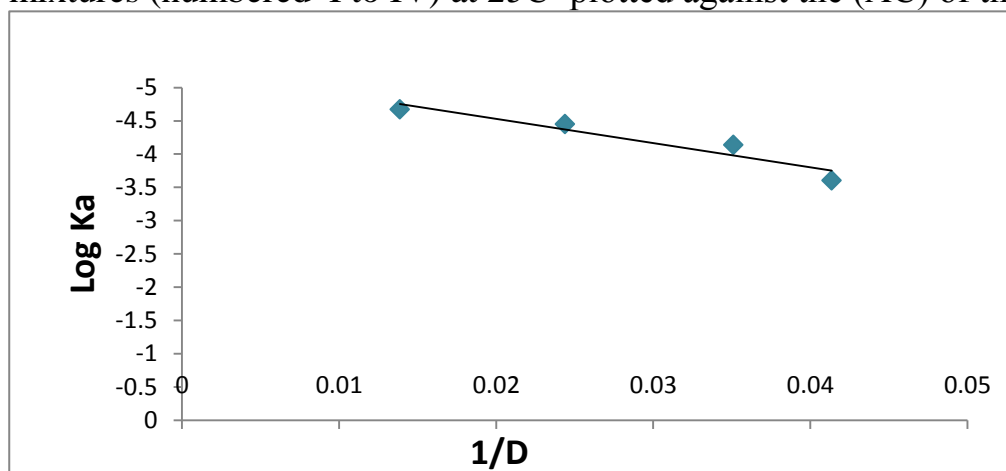


Fig. 2: Logarithm of the association constant ( $\text{log } K_a$ ) for  $\text{NH}_4\text{F}$  ions in four TMU-water mixtures plotted against the reciprocal of the dielectric constant ( $1/D$ ) of the mixtures at  $25^\circ\text{C}$ .

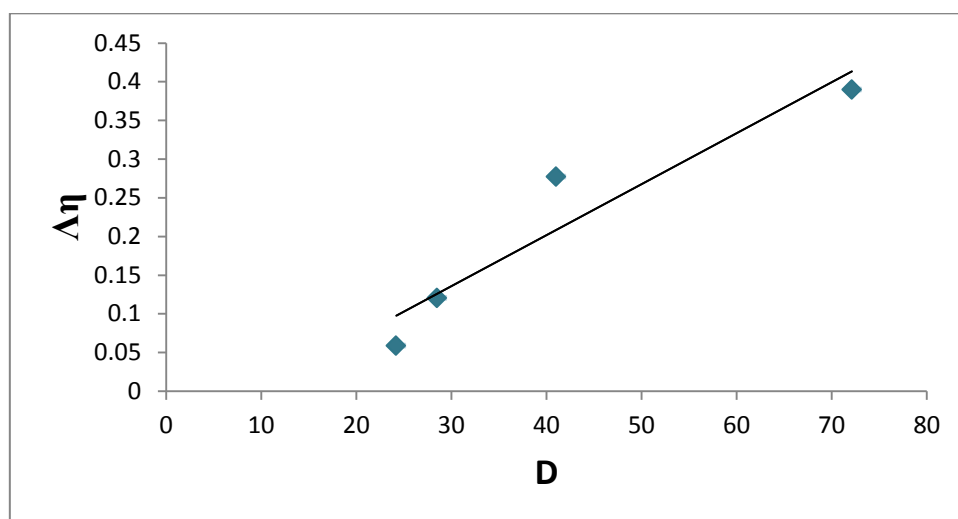


Fig. 3: Walden's product ( $\Delta\eta$ ) for  $\text{NH}_4\text{H}$  in four different TMU-water mixtures at  $25^\circ\text{C}$  versus the dielectric constant (D) of the mixtures.

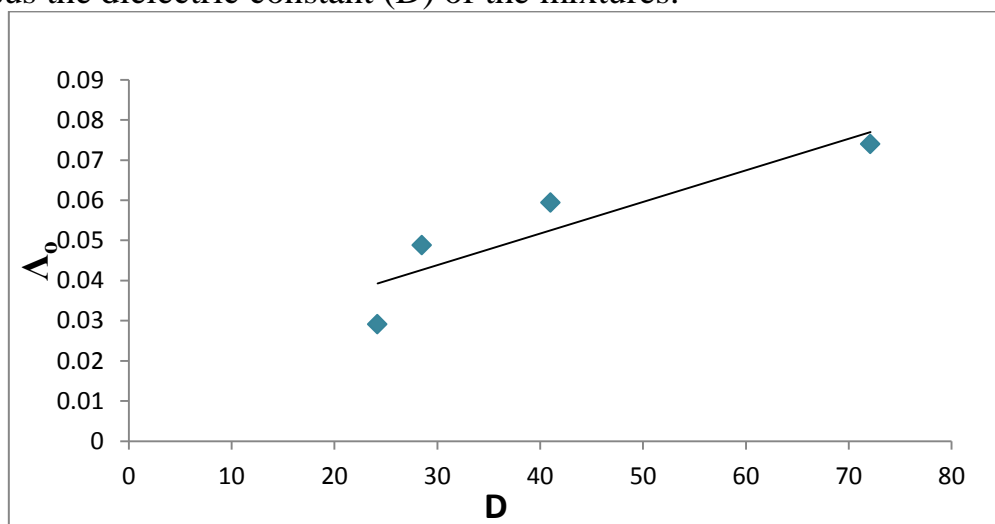


Fig. 4: The plot of the equivalent conductivity at infinite dilution ( $\Lambda_0$ ) for  $\text{NH}_4\text{F}$  in TMU-water mixtures versus (D) of the mixtures at  $25^\circ\text{C}$ .

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