Conductometric Studies of Aqueous Solution of Thymine and Adenosine At Different Temperatures

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Abstract

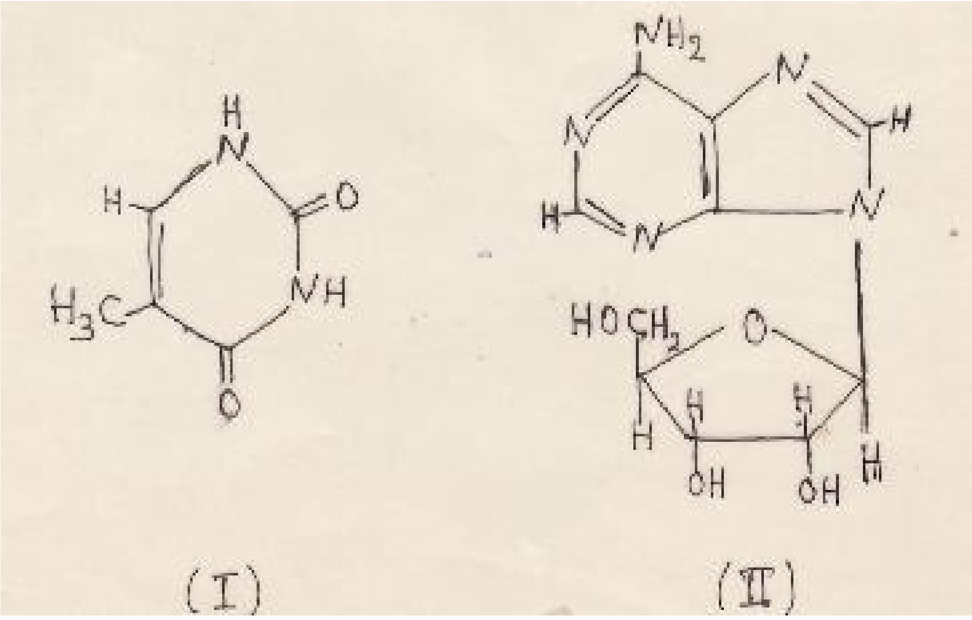
Molar conductivity of different concentrations of thymine and adenosine in water , sodium acetate and ammonium chloride solution at different temperatures , 283. 15-323.15 K has been determined from direct conductivity measurements , examination of aqueous mixture of thymine and adenosine with Onsager equation reveal deviation from linearity at high concentration .This deviation was explained in term of molecular interaction . Ostwald dilution law also examined with the above mixtures lead to calculation of limiting molar conductivities and dissociation constants of both nucleic acid in water , sodium acetate and ammonium chloride. The agreement between the values obtained for Onsager equation and Ostwald law was reasonable . Calculation of activation energies of flow using modified Arrhenius equation gives a result showed that the molecular interaction of both acids in all different mixtures were the same .

Introduction

Measuremens of the conductivity of solute in solution-provide us with important information concering the nature and dissolvation phenomenone of solute-solvent interaction [1]. Therefore , this work was chosen to study the behaviour of nucleic acids in aqueous solution . Information concerning such behaviour is considered to be of a fundamental importance in understanding the factors that determine the stability of bioacids [2,3].

In recent years , in biochemical studies , aqueous solvent or mixture of water and organic solvent have been used more and more frequently as media in which to carry out these studies , because the rate of the reaction is much effected in this solvent system [4].

Thymine (I) and Adenosine (II) are stable nucleic weak acids , PKa at 25^{o}C are 9.94 and 10.2 respectively.



Both of those acids are widely used in biochemical research [5].In spite of these interesting physical and biochemical properties., little work has been done on the properties of aqueous solution an acid-water interaction . Since those acids have many interaction sites with water , the solute-water interaction with this system might provide us with some interesting results

The present investigation was undertaken to discover the molecular interaction between those acids and water in presence of acids and basic salts.

Materials

Thymine and adenosine (BHD) , were purified by tewic recrystallization from water , thymine decomposes at 335-337^{O}C lit. , 335^{O}C ,adenosine m.p. 234-2335^{O} C lit. , 234^{O} C.

Sodium acetate and ammonium Choloride , Aldrich chemical were with purity not less than 99.99 % .

Conductivity water had a conductivity of 0.3×10^{-6} $S.Cm^{-1}$ at 25 ^{O} C.

Conductivity measurements were performed with a Pye –Unicam conductivity bridge model E 7566/4 , and Mullard conductivity cell type /E 7597/A .

The platinum electrodes of the conductivity cell were plated with platinum black by the electrolysis of 100 ml of solution contanies 3 gm of chloroplatinic acid and 0.02 gm of lead acetate, the current was adjusted so as to produce a moderate flow of hydrogen . The precicion of the conductivity measurements was withine ± 0.04 % .The cell constant was determined using KCl solution prior to each of conductivity measurements

The temperature precision of the thermostate , Hewlettpaclacard quartz thermometer , used was ± 0.1^{o}C .

The solution were prepared by weighting out (0.32070 gm) of adenosine and (0.15134 gm) of thymine in volumetric flask (100 ml) to give stock solution of 0.012M . from these stock solutions different concentrations were prepared for 0.0001 to 0.00075 M.

The concentration were prepared in Sodium acetate 0.05 M solution and ion ammonium chloride 0.05 M solutions.

For in compiated electrolytes such as thymine and adenosine the following Onsager equation can be used [6,8] :

$$\Lambda = \alpha \ \Lambda^{o} - \alpha (A+B \ \Lambda^{o})(\alpha C)^{1/2} \ldots\ldots\ldots\ldots\ldots..(1).$$

Where (Λ),(Λ^{o}) are the molar and limiting conductivities , respectivety ,(C) is the molar concentration and (A,B) are constants .
Equation (1) can be written
As:

$\Lambda = \alpha\ \Lambda^{-} = \alpha [\ \Lambda^{o} -(A+B\ \Lambda^{o})] (\alpha\ C)^{1/2}$

$= \alpha [\ \Lambda^{o} -(A+B\ \Lambda^{o})](\Lambda / \Lambda^{-} C)^{1/2}$

$\alpha\ \Lambda^{-} = \alpha\ [\Lambda^{o} -K(\Lambda C/\Lambda^{-})^{1/2}]$

$\Lambda^{-} = \Lambda^{o} -K(\Lambda C/ \Lambda^{-})^{1/2}$

Where(Λ^{-}) is the molar condctivity of one mole of ions at any concentration and
$K=A+B\Lambda^{o}$.

Poltting (Λ) against ($C^{1/2}$) gives (Λ^{o}) by extraplating to zero concentration . In order to obtain a batter value of(Λ^{-}) it was introduced in term ($C\ \Lambda / \Lambda^{-})^{1/2}$ as (Λ^{-} - □ Λ^{o}) by using the values of (Λ) and (C) . Then ,the corrected values of (Λ^{-}) were plotted against (α C) $^{1/2}$ to obtain the correct value of (Λ^{o}) [9,10].

The coductivities of solution of thmine and adenosine with different concentrations in water , sodium acetate and ammonium chloride at different temperatures , 283.15 to 323.15 K are listed in Table 1,2,3 and 4 respectively.

Onsager equation was plotted in Figure (1) for thymine and adenosine , respectively in water at 298.15 K ,the , the limiting molar conductivity of thymine is 900 S. Cm^{2} $mole^{-1}$ and adenosine 1110 S. Cm^{2} $mole^{-1}$ .The hihg value of Λ^{o} of adenosine could be due to presence of more then one active sites compared with that of thymine molecule (see structural formula above) .

The deviation from linearity with both nucleic acid at high concentration reflects that solvent effect become weaker and weaker when concentration increases until no solvent effect is shown in a concentration above 0.006 mole L^{-1}.

The conductivity of weak electrolyte like weak Bronsted acids such as thmine and adenosine depends on the number of ions in the solution , and therefore on the degree of dissociation (α) of those electrolyte . The degree of dissociation (α)
for the acid (HA) at molar concentration (C) at equilibrium :

$HA \Leftrightarrow H^{+} + A^{-}$

$$Ka = \frac{[H^{+}][A^{-}]}{[HA]} = \frac{(\alpha C)(\alpha C)}{C - \alpha C}$$

$$Ka = \frac{\alpha C^{2}}{1-\alpha} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

When concentration of ions in solution is low , we can approximate equation (1) to the following :

$$\alpha = \frac{\Lambda}{\Lambda_{o}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

By substitute the value of equation (3) in eqution(2) , we obtain Ostwald dilution law [11].

$$\frac{1}{\Lambda} = \frac{1}{\Lambda^{O}} + \frac{Ka}{\Lambda^{O2}} \Lambda C \text{ ....(4)}$$

The estimation of (Λ^{o}) and (Ka) values is done by plotting of Ostwald dilution law for both nucleic acids in water . The agreement between the values of calculated using Onsager and Ostwald equation can not take the number of active sites in consideration and it is applied only to mono-mono valent acids

The value of (K_a) for thymine and adenosine obtained from the plot of Ostwald equation gives values $1.1x10^{-13}$ and $1x10^{-14}$ respectively , which is reasonable comparing with that given in literature[12]

Conductivities of thymine and adenosine were also measured in solutions of 0.05 mole sodium acetate and 0.05 mole ammonium chloride as well as in water. Figures (2,3) show the plotting of (Λ C) against (1/ Λ) of those solutions . The values of (Λ^{o}) ,(K_a) are presented in Table (4) . As expected the values are high in ammonium chloride and low in sodium acetate . The acid and basic character of those solvent play an important rule in dissolution of thymine and adenosine nucleic acids .

Conductivity of electrolyte solution can be related to the activation energy of flow through Arrhenius equation

$$\Lambda = A\, e^{-E_a/RT} \text{ ....(5).}$$

Where A pre-exponential factor , E_a activation energy of flow , R gas constant and T the absolute temperature . Arrhenius equation can be written in the following form [13]

$$\ln \Lambda = \ln A - E_a / RT \text{ ....(6)}$$

Table 3 listed the data for the molar conductivies at different temperatures 283.15-323.15 K for thymine and adenosine in water , sodium acetate and ammonium chloride solution . By plotting logarithmic conductivity (ln Λ) vereus (1/T) , Figures (4,5) show a straight line obtained for thymine and adenosine in each solvent , the slope equals E_a/R , form which E_a. was calculated (see Table4).

It was founed that values are the some approximately with both system and increase from water to ammonium chloride through sodium acetate solution . This result indicates that both thymine and adenosine molecular interactions in theses solution are weak.

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Table (1) The conductivity data for thymine in water , sodium acetate and ammonium chloride at 298.15 K.

Water					Sodium acetate			Ammonium chloride		
C mole/L	^ $S.Cm^2/mole$	$C^{1/2}$	^ C	1/^	^ $S.Cm^2/mole$	^ C	1/^	^ $S.Cm^2/mole$	^ C	1/^
0.01200	22.92	0.109	0.275	4.363	7.50	0.900	1.333	14.58	0.175	6.859
0.00600	43.33	0.077	0.259	2.307	13.67	0.820	0732	27.50	0.165	3.638
0.00300	76.67	0.055	0.230	1.304	25.00	0.790	0.400	53.33	0.160	1.875
0.00150	144.00	0.038	0.216	0.694	48.08	0.750	0.208	103.41	0.155	0.967
0.00075	266.67	0.027	0.200	0.313	90.09	0.675	0.111	244.49	0.153	0.409
0.00038	489.47	0.019	0.186	0.204	144.90	0.550	0.069	359.71	0.137	0.278
0.00019	857.87	0.014	0.163	0.165	212.76	0.399	0.047	552.79	0.105	0.181
0.00010	950.00	0.010	0.095	0.105	303.03	0.300	0.033	650.19	0.060	0.154

Water					Sodium acetate			Ammonium chloride		
C mole/L	^ $S.Cm^2/mole$	$C^{1/2}$	^ C	1/^	^ $S.Cm^2/mole$	^ C	1/^	^ $S.Cm^2/mole$	^ C	1/^
0.01200	29.67	0.109	0.356	3.370	10.42	2.149	1.044	19.58	0.234	5.107
0.00600	54.33	0.077	0.326	1.841	20.00	2.099	0.546	36.67	0.220	2.727
0.00300	103.67	0.055	0.311	0.965	38.33	2.055	0.273	70.00	0.210	1.428
0.00150	200.67	0.038	0.301	0.500	73.33	1.200	0.149	116.67	0.209	0.857
0.00075	381.33	0.27	0.286	0.262	133.33	1.143	0.053	186.67	0.200	0.375
0.00038	542.11	0.019	0.206	0.185	250.00	0.843	0.043	342.10	0.144	0.209
0.00019	652.63	0.014	0.124	0.153	388.95	0.699	0.027	578.95	0.110	0.173
0.00010	700.00	0.010	0.070	0.143	465.55	0.400	0.025	680.00	0.068	0.147

Table (2) The conducticity datya for adenosine in water , sodium acetate and ammonium chloride at 298.15 K.

Table (3) molar conductivity of 0.0015 M aqueous solution of thymine and adenosine at different temperature.

	Thymine			Adenosine		
	Water	Sodium acetate	Ammonium chloride	Water	Sodium acetate	Ammonium chloride
$1/T \times 10^{-3}$	ln Λ	ln Λ	ln Λ	ln Λ	ln Λ	ln Λ
3.531	3.200	1.902	2.293	2.905	1.386	2.303
3.470	3.243	2.079	2.425	3.078	1.541	2.539
3.411	3.356	2.325	2.610	3.178	1.673	2.773
3.354	3.551	2.485	2.928	3.284	2.080	3.016
3.298	3.696	2.588	3.030	3.379	2.485	3.205
3.245	3.738	2.688	3.058	3.515	2.773	3.283
3.193	3.952	2.815	3.227	3.576	2.960	3.401
3.143	4.001	2.929	3.330	3.695	3.114	3.507
3.095	4.072	3.122	3.619	3.829	3.258	3.753

Table (4): Limitting molar conductivties , dissocation constants and activation eneries of viscous flow of thymine and adenosine in water , sodium acetate and ammonium chloride at 298.15 K.

Thymine								
Water			Sodium acetate			Ammonium chloride		
Λ^o	K_a	E_a / KJ	Λ^o	K_a	E_a / KJ	Λ^o	K_a	E_a / KJ
1215	$9.95 X\, 10^{-13}$	18.48	1341	$1.49 X\, 10^{-10}$	20.32	3472	$5.76 X\, 10^{-12}$	23.92
Adenosine								
Water			Sodium acetate			Ammonium chloride		
Λ^o	K_a	E_a / KJ	Λ^o	K_a	E_a / KJ	Λ^o	K_a	E_a / KJ
335	$11.35 X\, 10^{-12}$	17.30	1205	$8.3 X\, 10^{-14}$	20.47	1651	$0.636 X\, 10^{-11}$	25.98

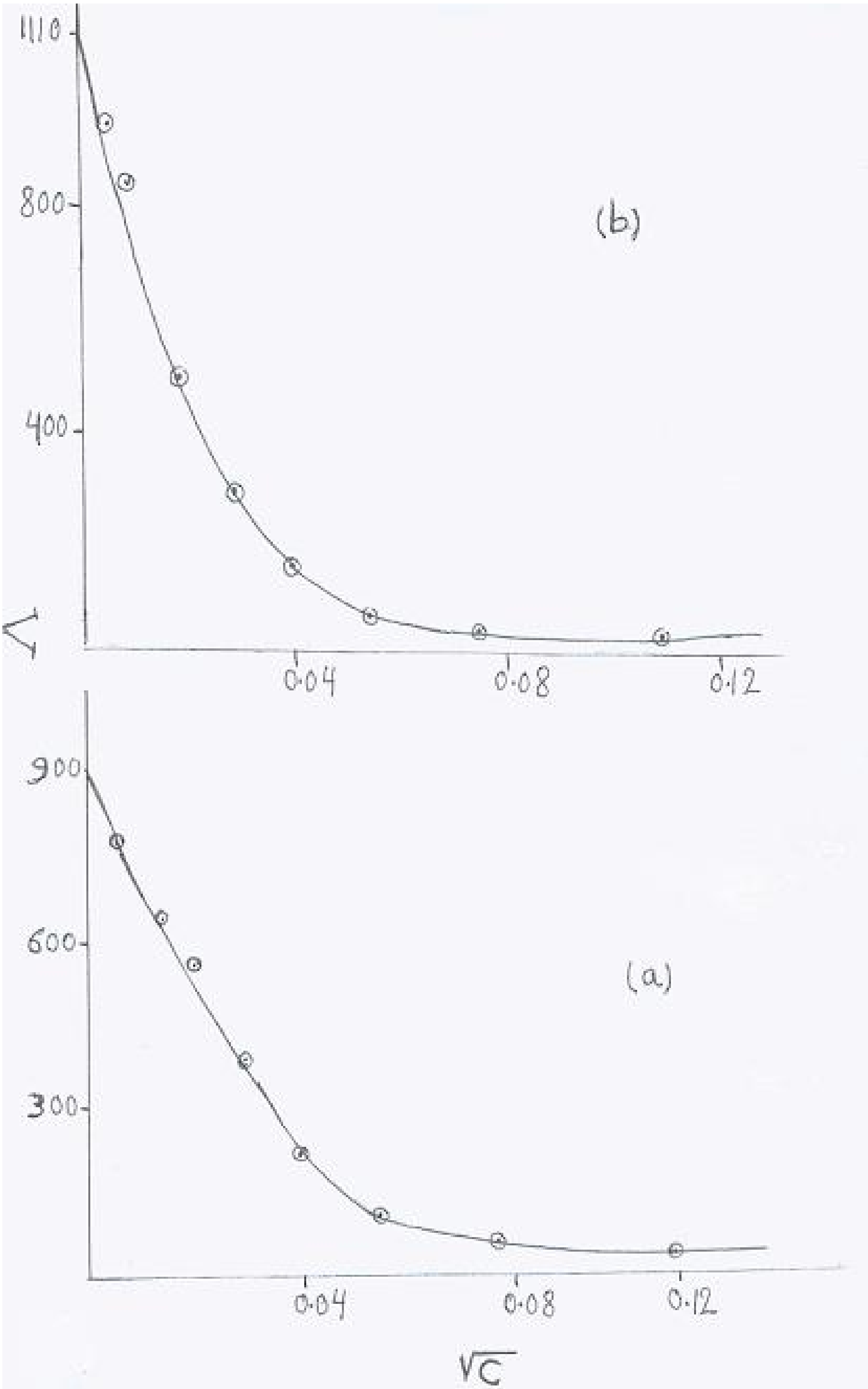
1110
800
400
(b)
Λ
0.04
0.08
0.12
900
600
300
(a)
0.04
0.08
0.12
√C

Fig. (1): Molar conductivity as function of C $^{1/2}$ for (a) thymine and (b) adenosine in water at 298.15 k°

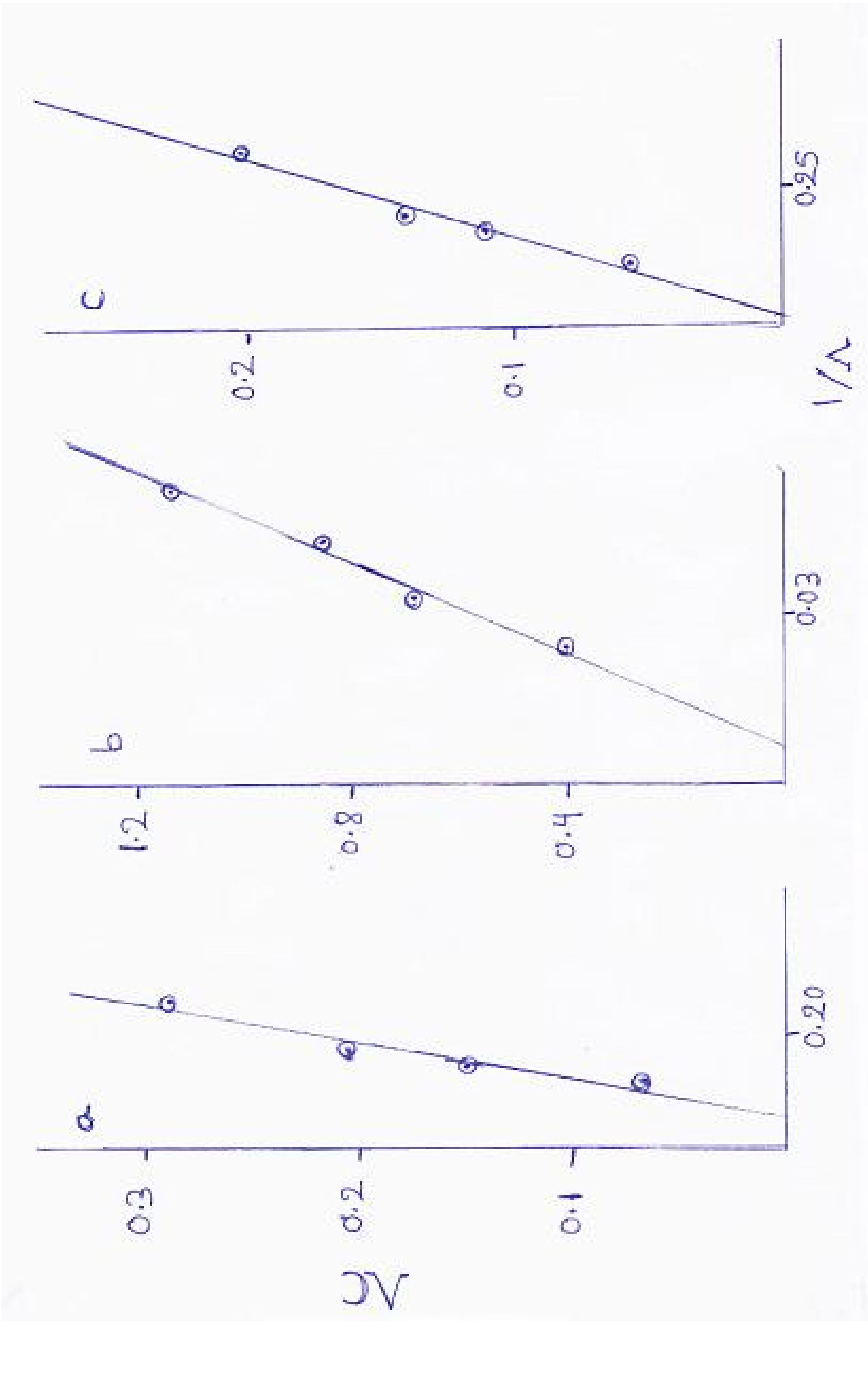

Fig.(2): Plotting between ΛC aginst 1/Λ for thymine in (a) water , (b) sodium acetate solution , (C) ammonium chloride solution at 298.15 K°

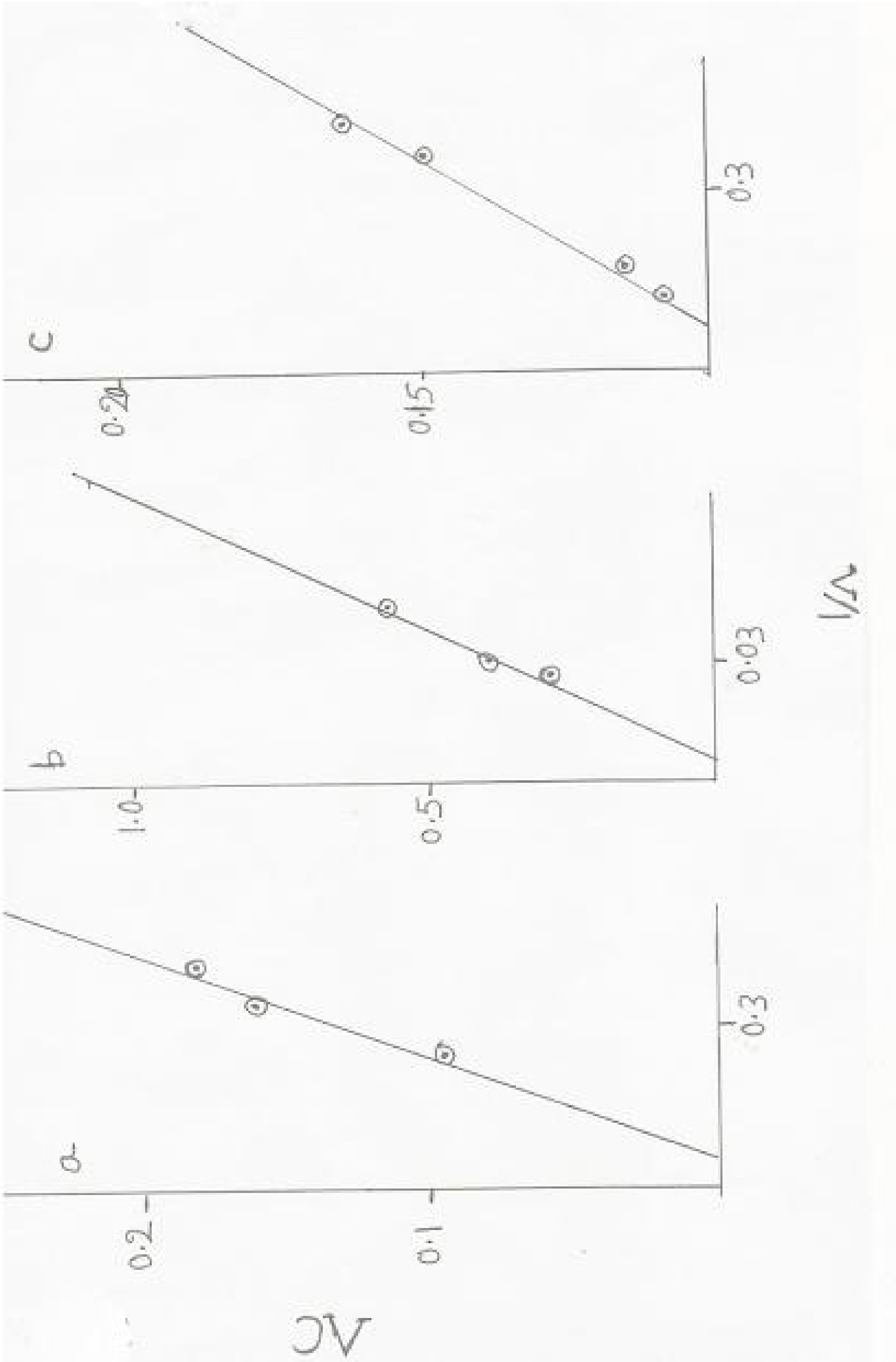

Fig. (3): Plotting between ΛC aginst 1/Λ for adenosine in (a) water , (b) sodium acetate solution , (C) ammonium chloride solution at 298.15 K^{o}

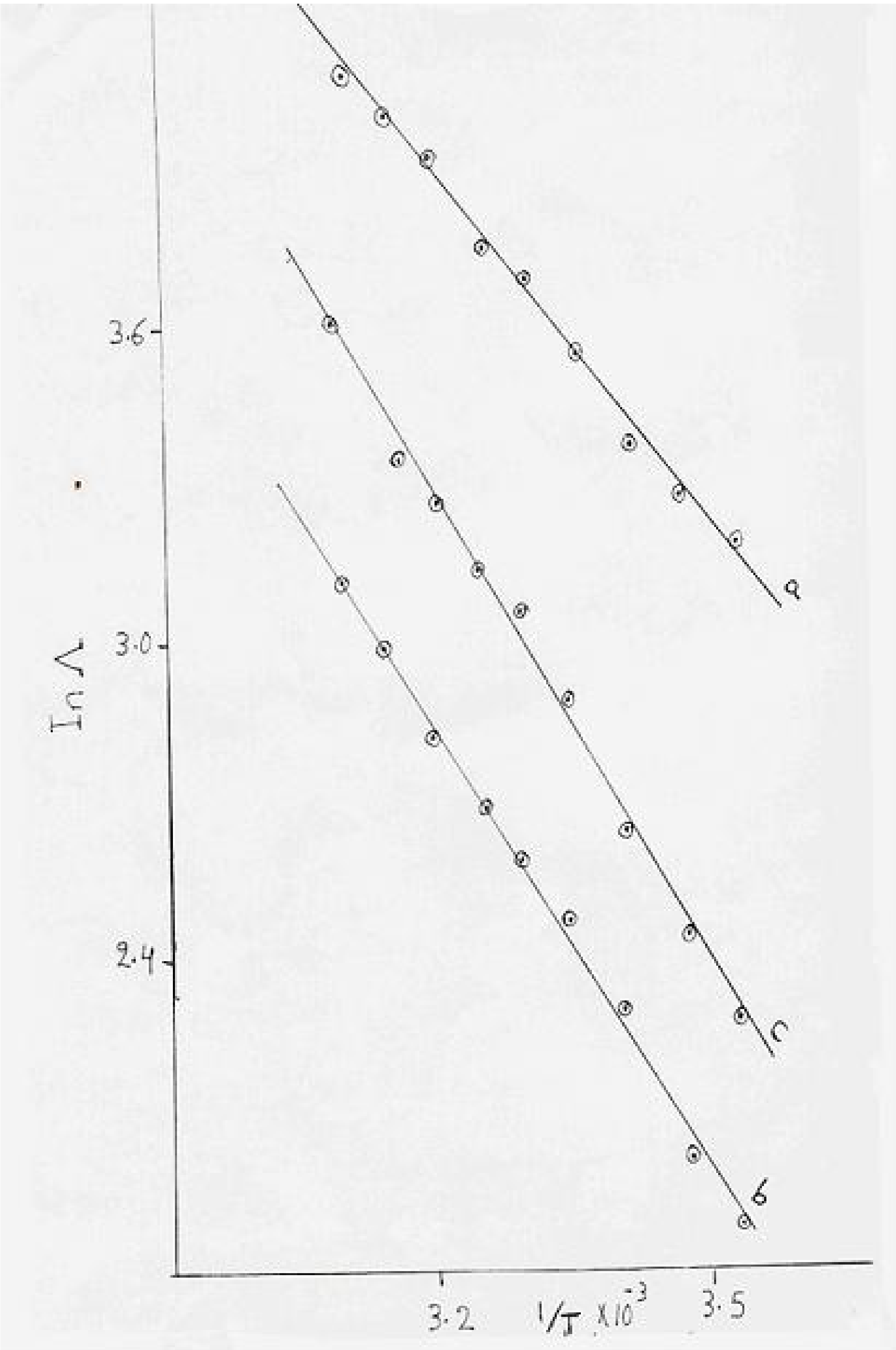

Fig. (4) :Plotting between ln Λ aginst 1/T for thymine in(a) water , (b) sodium acetate solution , (c) ammonium chloride solution in 0.0015 M.

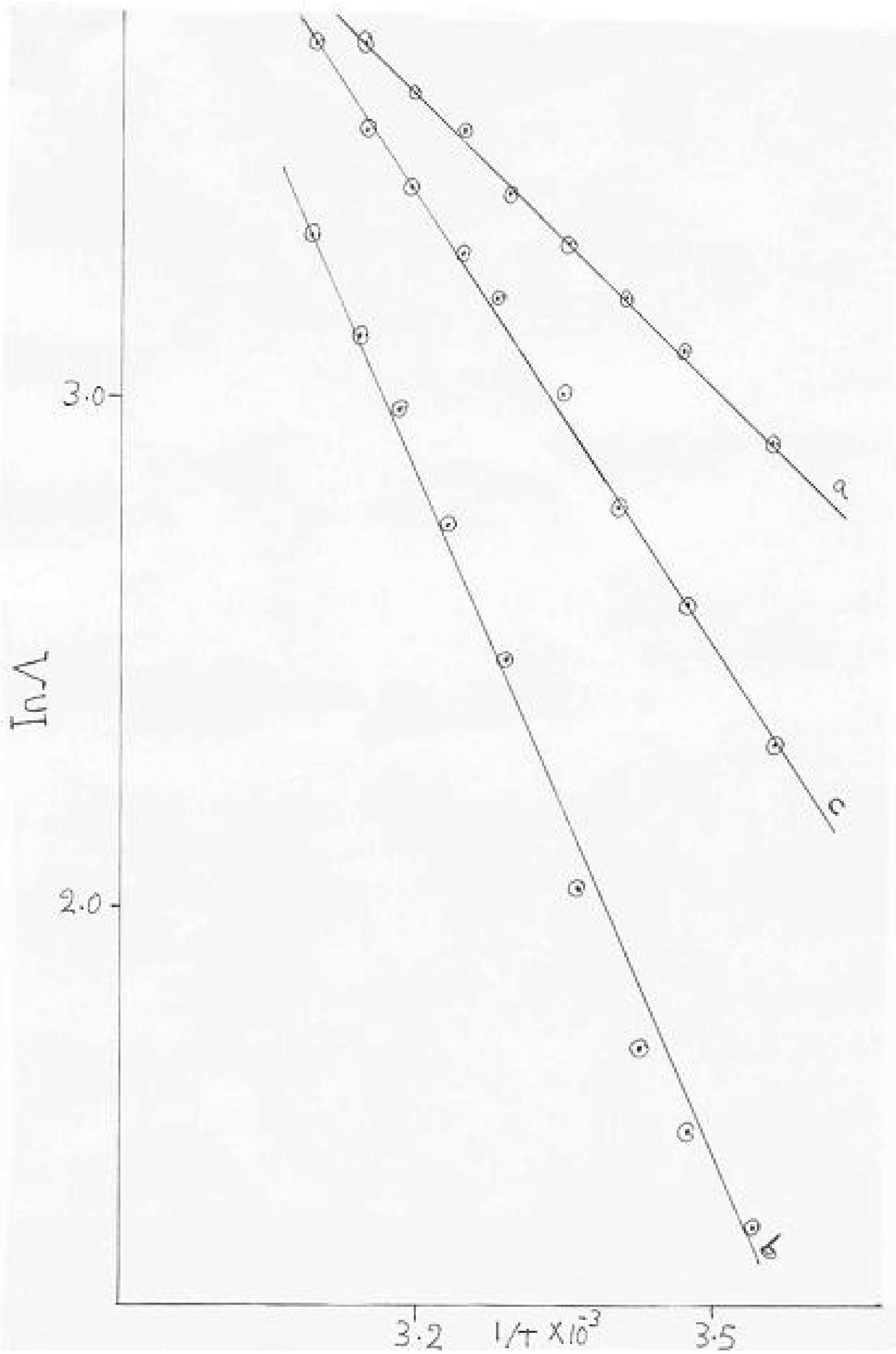

Fig. (5): Plotting between ln Λ aginst 1/T for adenosine in(a) water , (b) sodium acetate solution , (c) ammonium chloride solution in 0.0015 M.

مجلة ابن الهيثم للعلوم الصرفة والتطبيقية المجلد24 (2) 2011

دراسة توصيلية للمحاليل المائية للثايمين والادنوسين في درجات حرارة مختلفة

ساهرة صادق العاني
قسم الكيمياء ،كلية التربية – ابن الهيثم ، جامعة بغداد

استلم البحث في : 22 كانون الأول 1996

قبل البحث في : 30 حزيران 1997

الخلاصة

تم قياس التوصيلة المولارية لمخاليط الثايمين والادنوسين في الماء ،خلات الصوديوم ،وكلوريد الامونيوم بتراكيز مختلفة وبدرجات حرارة تتراوح بين 15و283 ، 15و323 كلفن .
ولقد تم استخدام معادلة اونساكر للمحاليل الالكترونية المخففة ووجد ان هذه المخاليط في محاليلها المائية تشذ عن الخطية بالتراكيز العالية ولقد اعزي هذا التصرف الى التاثيرات المتبادلة بين الالكتروليتات والمذيبات .
استخدمت معادلة اوستولد لحساب التوصيلة المولارية المحددة لهذه المحاليل مع حساب ثوابت التفكك لها .تطابقت النتائج المستحصلة من معادلة اوستولد مع معادلة اونساكر . كما تم قياس التوصيلية المولارية للمخاليط بدرجات حرارة مختلفة واستخدمت معادلة أرهينوس لحساب طاقة التنشيط لهذه المخاليط ووجد انها متساوية تقريبا مما يؤيد ان عملية الاستذواب متشابهة من حيث استهلاك الطاقة .