Effect of Temperature On The Dissociation Of Cysteine In Aqueous Solutions From Conductivity Measurements

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Abstract

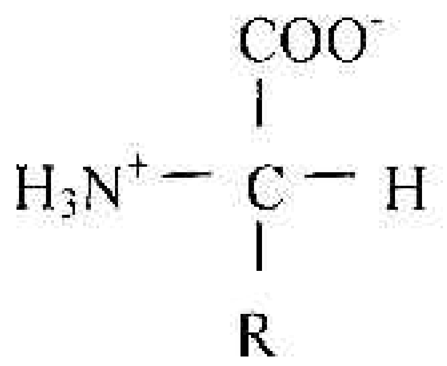
The conductance of solutions of cysteine in water at different concentrations and temperatures has been measured. These solutions obey Onsager equation and give linear relations especially at low concentrations. In more concentrated solutions a deviation from the equation is observed.

The molar conductivity of these solutions decreases with the increase in concentrations at constant temperature.

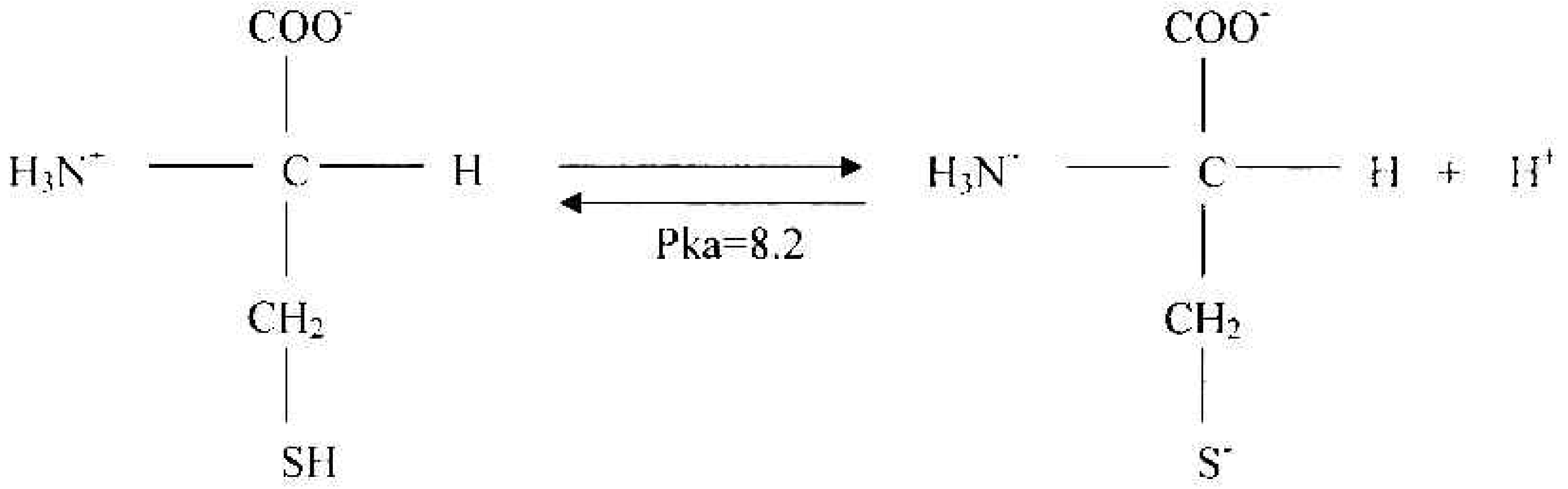
The values of the ionization constants and the conductivity at infinite dilution for each temperature have been calculated.

Introduction

The neutral amino acids, which occur as constituents of proteins, have the same general structure. These molecules contain a central carbon atom (the α-carbon) to which an amino group, a carboxyl group, a hydrogen atom, and R (side chain) group are attached. All amino acids (except glycine where R=H) have a center of symmetry; in cysteine $R=CH_2SH$. Cysteine which readily oxides to form a dimeric amino acid, cystine (1), had been studied thermodynamically and kinetically (2). At a pH of 7 the carboxyl group of an amino acid is in its conjugate base form (COO^-) and the amino group is in its conjugate acid form ($-NH_3^+$). Thus each amino acid can be as either an acid or a base. Neutral molecules that bear an equal number of positive and negative charges simultaneously are called zwitterions, so amino acids are neutral in water. It is the R group, however, that gives an amino acid its unique properties:



Some amino acids contain groups in addition to the protonated carboxyl or amino groups that are capable of dissociating protons. Thus, the sulfhydryl group of cysteine dissociates with a pKa of 8.2 (3):



Although pure water (distilled water in equilibrium with air) is a very poor conductor, ionic species present in aqueous solutions of acids, bases, and other electrolytes significantly improve its conduction. The conductivity of a solution is proportional to the concentration of ions present in a solution, more specifically, the conduction of various ions depends on their charge and mobility.

For substances such as acetic acid and amino acids that do not ionize completely the molar conductance will be lower than that if it were completely ionized (i.e. at infinite dilution) (4-6).

The dissociation of acetic acid (7) and a number of dicarboxylic acids [8] as well as of glycine (9) were investigated by direct conductance in tetramethyl urea + water mixture.

Experimental

Systeine, B.D.H., was purified by crystallization. Conductivity water had a conductivity of $3x10^{-7}S.cm^{-1}$ at $20^{o}C$. The conductivity bridge from Pye-Unicam model E7566/ and mullard conductivity cell type E7597/A (of cell constant = $0.1000cm^{-1}$) were used in measurements. Description of the apparatus is found in the literature (10). The conductance cell was filled with systeine solution of certain concentration $0.05 \leq c \geq 0.0075$ and the resistance R was measured (using the conductivity bridge) immediately after allowing the solution to stand until a thermal equilibrium with a water bath at a given temperature $(353.1 \leq K \geq 303.1)$ was observed.

Results and Discussion

The specific conductance was calculated using the measured resistance for each solution as following:

$$\kappa = \frac{k}{R} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots [1]$$

Where κ in $\Omega^{-1}cm^{-1}$ (Scm^{-1}) is the specific conductance of each solution, k the cell constant ($0.100cm^{-1}$), and R (in ohm Ω) the measured resistance

To obtain the conductance due to the electrolyte the specific conductance of the pure water (distilled water) is subtracted from that of each systeine solution:

$$\kappa_{solute} = \kappa_{solution} - \kappa_{solvent} \quad \ldots\ldots\ldots\ldots [2]$$

Then the equivalent conductance Λ_c $Scm^2equivelant^{-1}$ for each concentration was calculated using the following relation:

$$\Lambda_c = \frac{1000\kappa}{c} \ldots\ldots\ldots\ldots\ldots\ldots[3]$$

Where c is the number of gram equivalents per liter (mole/liter). As a first approximation the experimental values of Λ_c for each concentration of systeine at a given temperature were plotted against the square root of concentration $c^{1/2}$; this was done over a range of temperatures. Each curve was extrapolated to zero concentration to obtain Λ_o at each temperature table (1). It shows that the values of Λ_o increase with the increase in temperature.

For incompletely dissociated electrolytes such as amino acids and acetic acid, the following Onsager equation can be used (4-6, 11):

$$\Lambda = \alpha(\Lambda_o - (a + b\Lambda_o)\sqrt{\alpha c} \ldots\ldots\ldots[4]$$

$$\Lambda = \alpha\overline{\Lambda} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots[5]$$

$$\alpha = \frac{\Lambda}{\overline{\Lambda}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots[6]$$

$$\overline{\Lambda} = \Lambda_o - (a + b\Lambda_o)\sqrt{\alpha c} \ldots\ldots\ldots\ldots[7]$$

or

$$\overline{\Lambda} = \Lambda_o - k\sqrt{\Lambda c / \overline{\Lambda}} \ldots\ldots\ldots\ldots\ldots[8]$$

$\overline{\Lambda}$ is the molar conductivity of 1mole of free ions at the concentration αc mole per liter, at the actual ionic concentration in the solution, where k, representing $(a + b\Lambda_o)$, is constant for a given solute at a definite temperature.

Onsager equation has been applied to cysteine solution at different temperatures; Λ_c–Λ_o was plotted against $c^{1/2}$ where $\overline{\Lambda}$ was replaced by Λ_c in equation 8 to calculate the limiting slope at very low concentrations where $c\rightarrow 0$ and $\Lambda_c \approx \bar{\Lambda}$ this is shown in figure 1. It gives linear relations in dilute solutions over the given range of temperatures. For example, cysteine agrees up to about 0.0016 mole/l over the range of temperatures between 303.1---353.1K. This means that the linearity of cysteine solutions does not depend on temperature. Limiting slopes of cysteine depend on temperature as shown in table 1. As an approximation $\bar{\Lambda}$ in the term $\sqrt{\Lambda c / \Lambda}$ was replaced by Λ_o and equation 8 was solved for $\bar{\Lambda}$ to most systeine solutions at a given temperature at a range of temperatures 303.1---353.1°K. Equation 6 was then solved for the molar conductivities of the solutions of cysteine at given temperatures and the data were plotted against T °K as shown in figure 2, which shows that the molar conductivity increases with the increase in temperature, the least observed temperature dependence of Λ values is to be that for the highest concentration c=0.05mole/l and the greatest dependence appears to be for the lowest concentration c=0.0122.

The dissociation of amino acids obey the following equation:

$\log k_1 = \log Ka - k_2 (\alpha c)^{1/2}$

Where, Ka is the ionization constant,

$$ka = \left(\frac{\alpha^2 . c}{1-\alpha}\right) \text{..................} [9]$$

k_1 is the thermodynamic dissociation constant,

k_2 is constant = slope.

α is the degree of dissociation which was determined by equation 6.

Ka has been calculated for cysteine at each temperature. These values are shown in table 2. For each given temperature, the values of ka at lowest concentration c=0.0015——0.00075mol. /l are approximate to the value reported in the literature where the pk_a value for the dissociation of sulfhydryl group in the systeine = 8.2 (3) as mentioned earlier.

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Table :(1) Limiting slopes and molar conductivities at infinite dilution of cysteine solution at different temperature.

$T(^{O}K)$	Limiting Slope	Λ_O
303.1	-833.3	42
308.1	-857.1	45
313.1	-875.0	50
318.1	-1053.6	58
323.1	-1111.1	62
328.1	-1212.1	65
333.1	-1513.1	79
338.1	-1579.0	84
343.1	-1667.7	89
348.1	-1892.9	96
353.1	-2222.0	110

Table (2): Ionization constants of cysteine at different temperatures and concentrations, ($KaX10^6$):

Concentration (mole/l)	Temperature (K)										
	303.1	308.1	313.1	318.1	323.1	328.1	333.1	338.1	343.1	348.1	353.1
0.05	1.63	4.44	5.17	4.59	4.57	[illegible]	4.31	4.74	4.52	4.14	3.56
0.04	[illegible]	[illegible]	2.0	1.79	2.36	2.48	[illegible]	2.41	2.50	2.37	2.55
0.032	2.57	2.73	3.63	3.35	3.41	3.77	3.41	3.53	4.15	4.22	3.75
0.0256	3.21	3.39	3.46	4.59	3.71	3.63	3.61	3.99	4.34	4.48	3.70
0.0204	9.50	[illegible]	8.91	[illegible]	8.64	[illegible]	6.96	6.15	7.16	5.63	4.66
0.0192	2.16	2.93	3.78	3.43	3.92	4.5	3.52	3.79	4.15	4.08	3.79
0.0154	3.46	3.01	3.38	2.83	3.42	3.76	3.55	3.39	3.97	3.63	3.70
0.0122	—	5.95	6.66	5.98	6.76	7.71	6.38	6.83	6.61	7.19	7.24
0.0061	73.94	78.89	76.51	66.67	68.06	71.64	54.63	54.74	54.84	49.61	39.55
0.003	62.32	63.28	64.22	53.8	56.82	61.57	47.86	56.51	59.73	59.85	52.04
0.0015	120.34	195.99	192.86	151.04	196.18	196.59	153.28	146.47	154.3	140.98	111.67
0.0075	357.16	426.02	463.02	377.45	373.5	457.18	370.34	354.11	340.32	347.74	263.2

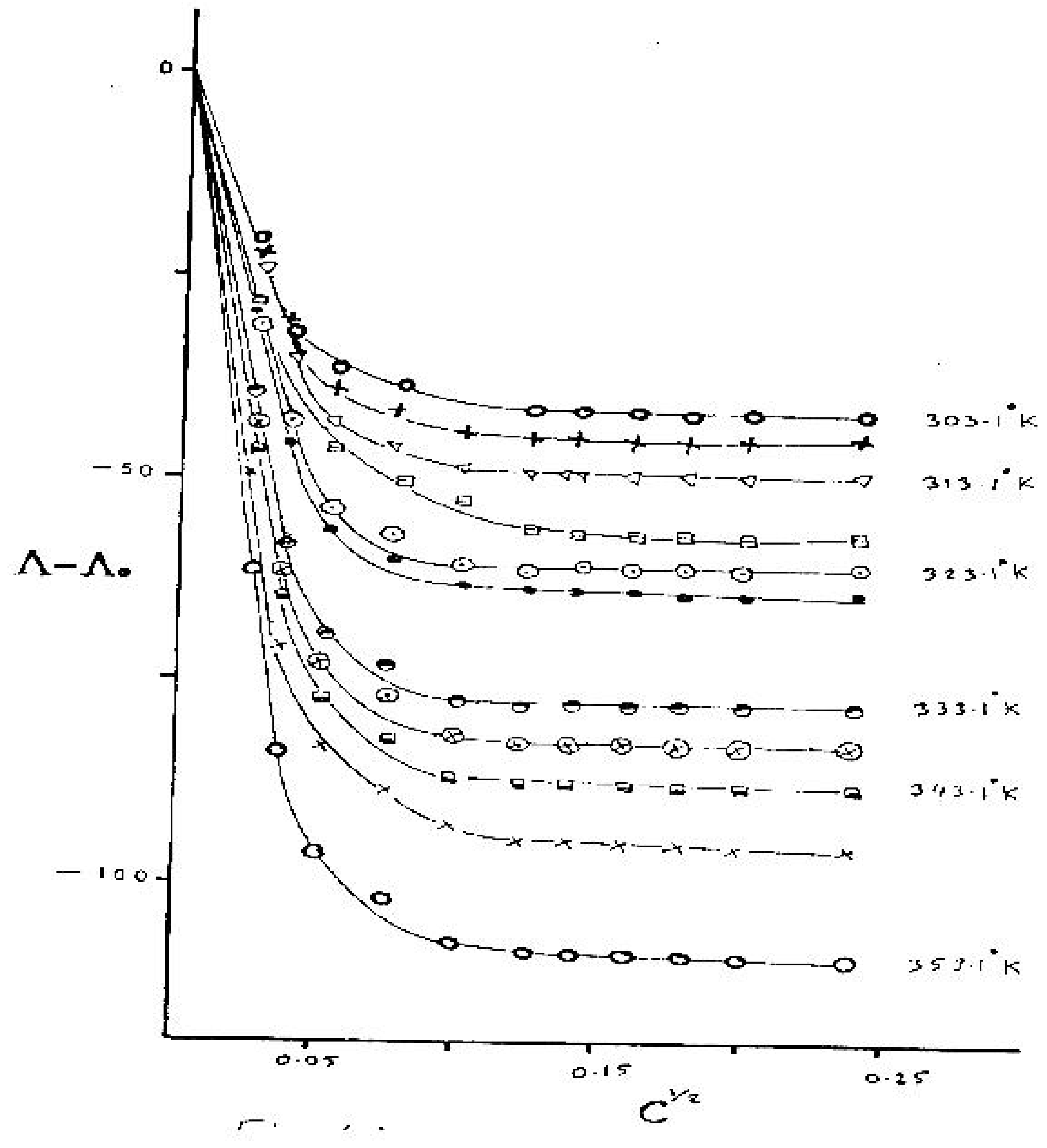

Fig.(1) The difference between molar conductivity Λ_c and molar conductivity at infinite dilution Λ_0 as a function of square root of temperature $C^{1/2}$. Each curve includes the concentrations ($0.05 \leq C \geq 0.0075$) over the temperatures 303.1 – 353.1K as shown.

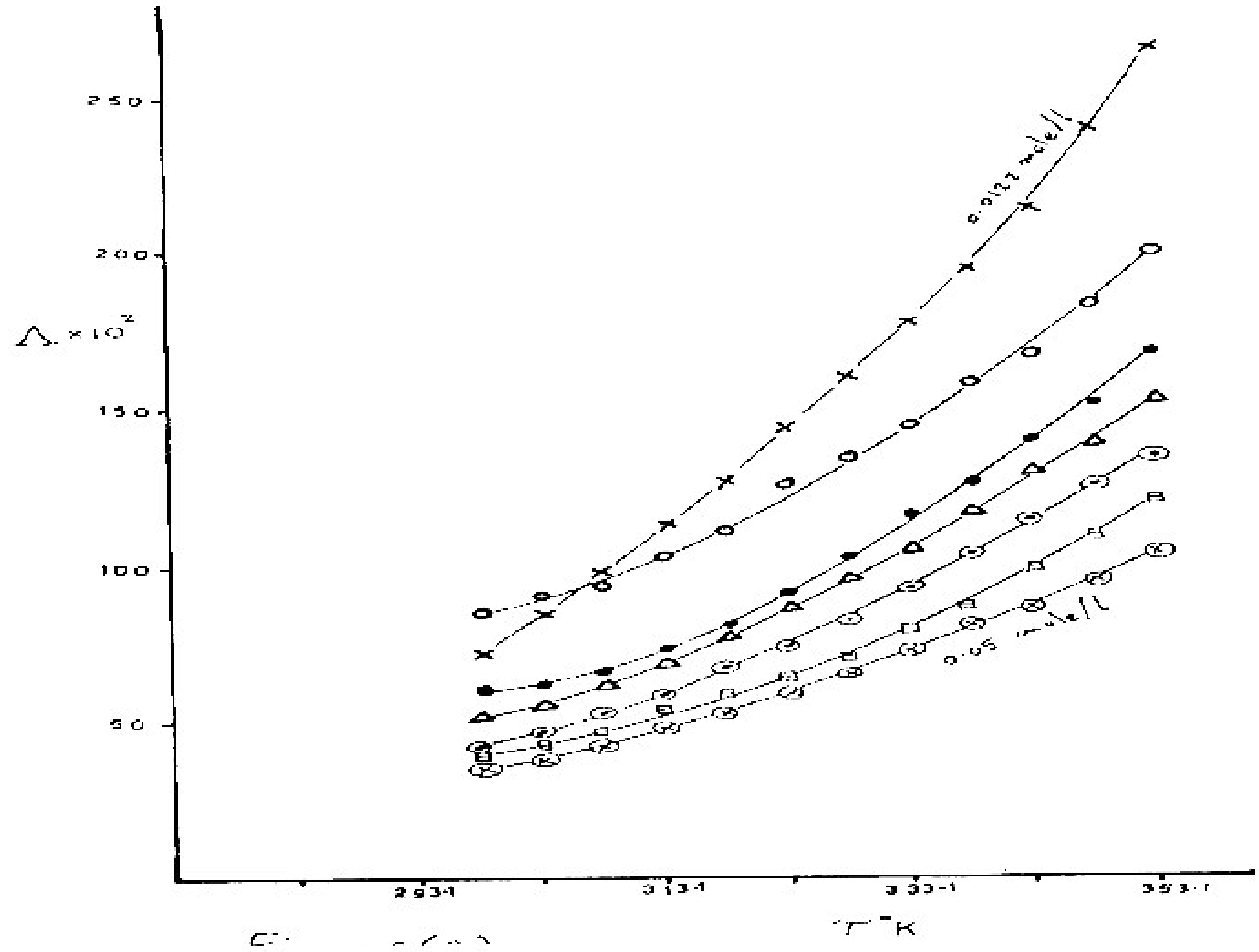

Fig. (2)Molar conductivity ($Smol^{-1}cm^2$)of cysteine solutions as a function of temperature K over a range of concentrations (0.05-0.0122) as shown.

دراسة تأثير درجة الحرارة في تحلل السيستايين في المحاليل المائية من قياسات التوصيلية

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الخلاصة

قيست التوصيلية لمحاليل مختلفة التركيز من السيستايين في الماء في درجات حرارية مختلفة تتراوح بين 1 ، 303 --- 1 ، 353 درجة مطلقة.
وبعد حساب التوصيلية لهذه المحاليل وجد أن التوصيلية المولارية تزداد بارتفاع درجة الحرارة وكذلك تزداد بزيادة التخفيف في درجة حرارية ثابتة.
هذا وأن سلوك المحاليل جميعا جاء خاضعا لمعادلة اونساكر للالكتروليتات الضعيفة وفي جميع درجات الحرارة الواردة أعلاه ولاسيما في المحاليل المخففة جدا بينما ظهر شذوذ عن القاعدة في التراكيز العالية وكما هو متوقع.
وأخيرا فقد حسب ثابت التأين لكل تركيز وفي جميع درجات الحرارة.