CHAPTER V

DISCUSSION AND CONCLUSIONS

5.1 The Determination of Λ^{o}

The two tetraalkylammonium picrates behave as a weak electrolyte as can be seen that the curve in the plot of Λ vs. $\sqrt{c}$ (Figures 4.1.1 and 4.1.2) does not approach linearity in dilute solutions. Instead, Λ exhibits a very rapid increase with decrease in concentration. Hence it was not practical to determine Λ^{o} by the method of extrapolation from such a plot and an approximation known as Walden's Rule(18) was applied. Previous workers(19) have shown that for the large ions with low surface charge like $N(CH_3)_4^+$, $N(C_2H_5)_4^+$, the product $\Lambda^{o}\eta$ is very nearly constant over a fair range of temperature in several solvents. Λ^{o} obtained from the application of Walden's Rule are reported in Tables 4.2.1 and 4.2.2 and were used for the subsequent calculations for other parameters. It should be noted that the constancy of the product $\Lambda^{o}\eta$ for several organic solvents are quite striking.

5.2 Kinetics of the self association reactions

When tetraalkylammonium picrates are dissolved in a low dielectric constant solvent such as 80% dioxane-water mixture (D = 10.708), ionic association will take place whereby ion-pairs formed are stabilized by their high electrostatic potential. The rate of approaching equilibrium and the equilibrium constant of the reaction of the type

$$B^+ + A^- \rightleftharpoons [B^+A^-]^o \rightleftharpoons BA$$

were studied. Results recorded in Tables 4.5.1 - 4.5.8 showed the variation of the ionic concentration with time at various temperatures. At each temperature, the dissociation reaction occurred first followed by the reverse reaction namely the association reaction in accord with the following equations

$$(CH_3)_4NPi \rightleftharpoons (CH_3)_4N^+ + Pi^-$$
$$(C_2H_5)_4NPi \rightleftharpoons (C_2H_5)_4N^+ + Pi^-$$

where Pi^- represents a picrate ion.

Attempts were made to attach some physical meanings of the not so large increase in conductance to the order of reaction. Uncertainty may be obvious but by assuming, with a reasonable ground, that the simple dissociation and association reactions, as shown above taking place, a graph of $\frac{1}{a_o - x} - \frac{1}{a_o}$ against time should be a straight line. Figures 4.5.1 - 4.5.8 may be regarded, at least, as one piece of evidence that the association reaction obeys the second order rate law. From the graph that was mentioned above, the specific rate constants of the association were obtained, and showed that their values decrease as temperature increases. This can be explained that both ions were stable in an ion-pair formation by the coulombic force but when the temperature was raised the thermal energy kT became greater than the coulombic force and destabilized the ion-pair.

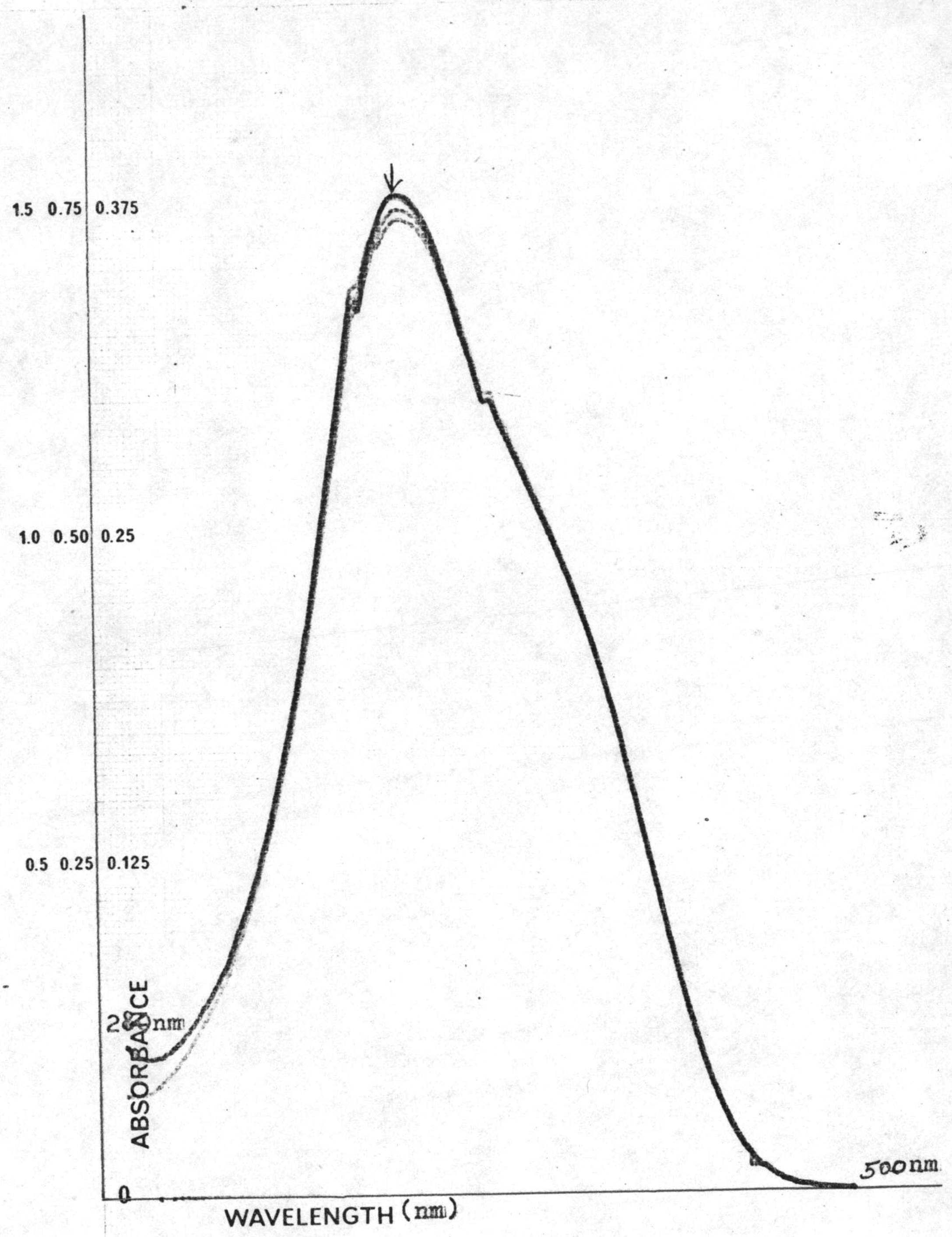

Fig.5.2.1 The variations of absorbance with time of $(CH_3)_4NPi$ in 80% dioxane-water at 30^{o}c , λ_{max} 368 nm.

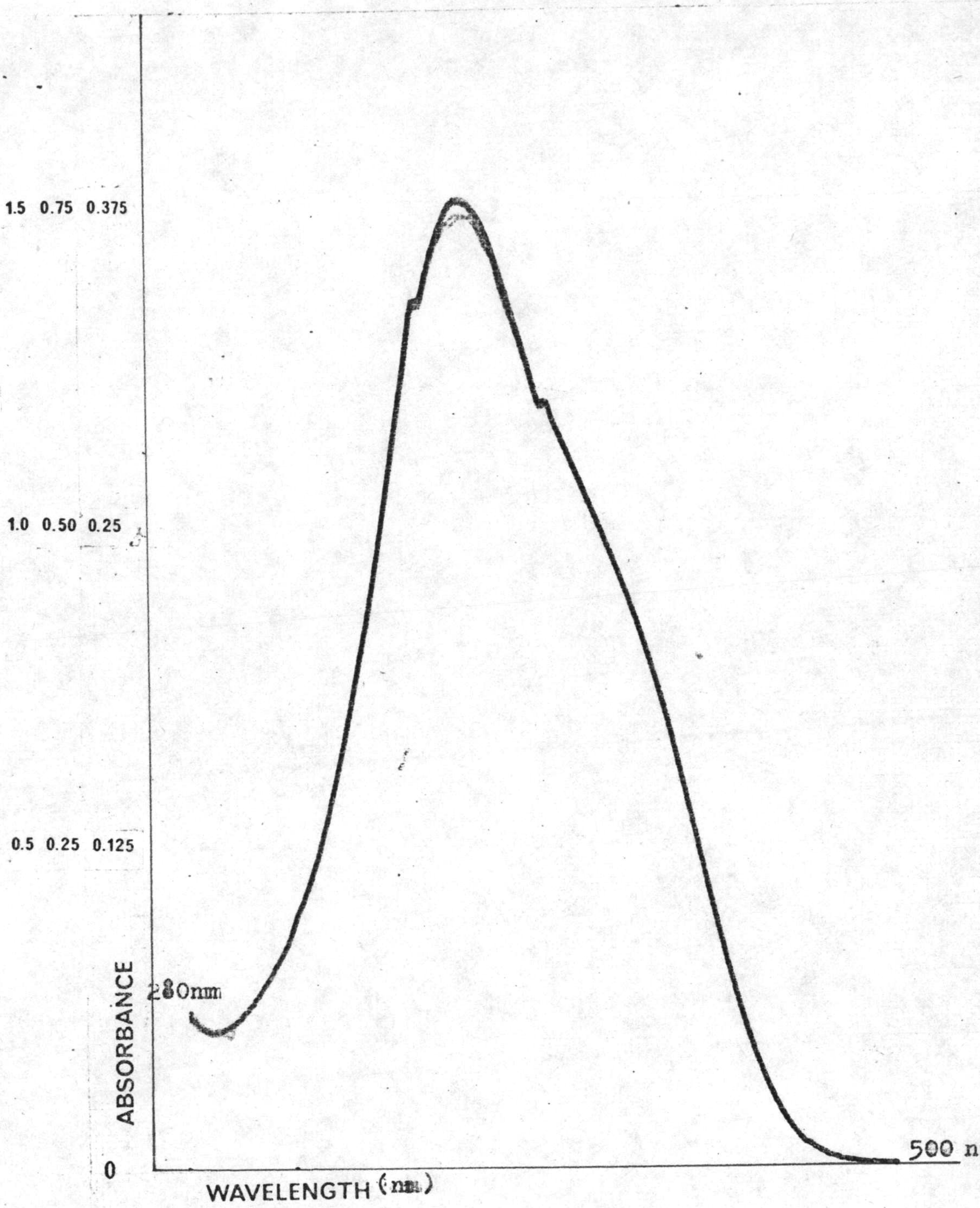

Fig.5.2.2 The variations of absorbance with time of $(C_2H_5)_4NPi$ in 80% dioxane-water at $30^{\circ}c$, λ_{max} 367 nm.

As has been mentioned earlier that changes in concentrations of such reactions can be detected either via those of ionic species or of neutral ones, hence the association reaction was studied by U.V. spectrophotometry. The variation of the absorbance with time was too small to follow quantitatively but qualitatively. Examination of Figures 5.2.1 and 5.2.2 confirms the re-union of the dissociated ions.

5.3 Dissociation Constant

The experimental data have been analyzed graphically according to the method of Fuoss(17) and the dissociation constants were calculated. The nature and the structure of both cation and anion are involved in determining the magnitude of the dissociation constant(7). Although tetramethyl and tetraethylammonium ions are the same spherically symmetrical ions, the conductance falls off with increasing number of carbon atoms in the substituent group. Thus, the tetramethylammonium picrate has a small dissociation constant (2.831×10^{-4} at $25^{\circ}C$) comparing to tetraethylammonium picrate (5.466×10^{-4} at $25^{\circ}C$). The explanation based on the ionic size only, is that, tetramethylammonium ion with low charge sphere is smaller than tetraethylammonium ion, hence it can approach the counter anion much more easily than the larger tetraalkylammonium ion. For these two salts the dissociation constants decrease when temperature increases (Tables 4.3.1-4.3.4) in accord with the Bjerrum equation

$$\frac{1}{K} = \frac{4\ Ne}{1000}\left[\frac{|Z_1Z_2|\,\epsilon^2}{DkT}\right]^3 Q(b)$$

the dissociation constant is related to dielectric constant and absolute temperature through a distance of closest approach "a". Although the value of K depends on product DT, the value of D decreases so much to give the decreasing the values of DT as T increases (see Table 3.1).

The graph of -log K vs. 1/D at 25°C of tetramethyl and tetraethylammonium picrates in some solvents give a linear curve,(19) hence, if dielectric constants are known, the dissociation constants of these two salts can be read off directly. It was thought worthwhile to evaluate the reliability of the values of K obtained from this work by compiling experimental results of other workers(7,8,20-23) and construct a graph of -log K vs. 1/D at 25°C. Thus K was read off for dielectric constant of 80% dioxane-water mixture from Fig. 5.3. The results of this cross check were very satisfactory as can be seen from Tables 5.3.1 and 5.3.2.

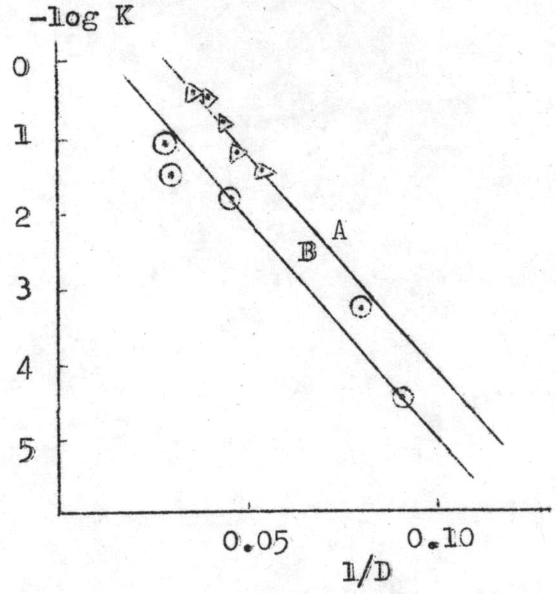

Figure 5.3

Dissociation constant of $(CH_3)_4NPi$ as a function of dielectric constant of solvent

$A = (CH_3)_4NPi$ in dioxane-water

$B = (C_2H_5)_4NPi$ in other solvents

Table 5.3.1

Relation of K and D of $(CH_3)_4NPi$ in other solvents and 80% dioxane-water at 25°C

solvents	D	$K_{lit} \times 10^4$	$K^*_{obs} \times 10^4$	$K^{**}_{cal} \times 10^4$
Ethylenechloride	10.23	0.32		
Nitrobenzene	34.50	400		
Acetone	20.70	112		
Pyridine	12.01	6.7		
Dioxane-water	27.21	3300		
	25.15	2700		
	23.14	980		
	21.12	490		
	19.07	380		
80% dioxane-water	10.708	-	2.8184	2.8310

K^*_{obs} = dissociation constant read from the graph.

K^{**}_{cal} = dissociation constant obtained from Bjerrum equation.

Table 5.3.2

Relation of K and D of $(C_2H_5)_4Npi$ in other solvents and in 80% dioxane-water at 25°C

solvents	D	$K_{lit} \times 10^4$	$K^*_{obs} \times 10^4$	$K^{**}_{cal} \times 10^4$
Ethylene chloride	10.23	1.59		
Nitrobenzene	34.5	1400		
Acetone	20.7	175		
Pyridine	12.01	10.4		
Acetic acid	6.15	0.0163		
Acetronitrile	37.5	1508		
80% dioxane-water	10.708	-	5.0119	5.466

5.4 Distance of closest approach "a"

The values of "a" are practically independent of temperature;it is unambiguous that they depend upon the nature of the solvent as well as the solute. That is, the values of "a" of tetramethylammonium picrate at four temperature were in the range of 536 - 569 pm while the same parameters of tetraethylammonium picrate were 562 - 701 pm. From conductivity measurement it was found that r_+ was 305 pm for tetraethylammonium ion and r_- was 305 pm for picrate ion in a variety of non aqueous solvents,(24) hence results obtained independently in this work are in good agreement with the published work where r is 610 pm. For tetramethylammonium ion, however, only that distance r_+ from Stoke's law was found to be 205 pm(19) and r_- 305 pm for picrate ion as mentioned above, thus r is 510 pm which is not far from the computed "a" value reported here.

The advantage of using the mixed solvent such as dioxane-water mixture is due to the fact that a continuous increase of the dielectric constant of the medium ranging from that of pure dioxane (D = 2.21) to that of water (D = 78.6) can be achieved by regulating the percentage of water in the mixture. It is accepted that the lower the dielectric constant the better is a chance of the association reaction to take place. However, the problem that faces electrochemists is the lack of the sensitive technique suitable to follow the association reaction occurring in a very low dielectric constant medium. The moderately low dielectric constant solvents are therefore favourable but pure solvent either have too high or too low dielectric constant to be useful for such a purpose. Mixed solvent seems to be the solution of such a problem. Nevertheless the use of mixed solvent introduces other problems which can be illustrated by an inspection of Figure 5.3 Although the dielectric constants are the same, the values of log K of the same solute are different, in other words A and B having the same slope but different intercepts. This is the well known effect of the addition of the second solvent which unavoidably will assume the role in both short range and long range interactions namely solvent-solvent interaction and solvent-ion interaction in the system under study. It is suspected that new entity which is not possible to identify might be formed in such a solvent

In addition, as far as the choice of dielectric constant of solvent is concerned one should be aware that if the dielectric constant is too low it is not only the formation of ion-pair, but also ion triples(25) may be involved. The presence of the triple ion (e.g.$B^+A^-B^+$) is explained by taking into account of the change in energy of the species in the system. Here, the energy of a negatively charged sphere in contact with two positively charged spheres is larger than the energy of two oppositely charged spheres. A complex ion of the type (+-+) or (-+-) can be seen as being formed from an already existing neutral ion pair which is really dipole. The complex aggregate may be stable in the solvent of sufficiently low dielectric constant. This is the reason why the author has spent the first few months in investigating the most suitable percentage of water in dioxane, the work of which is not reported here.

5.5 Concluding remarks

Only few kinetic studies on the self association reactions appeared in the literatures(26,27), none have been reported for the system of tetramethyl and tetraethylammonium picrates in dioxane water mixture. However, as this is a self association reaction, therefore changes in concentration were so small that even with quite a sensitive method employed namely the conductance method, the uncertainty was still fairly large. It was hoped at the beginning of this work that concentration changes should be detected concurrently for both ionic and neutral species of the system. Unfortunately, U.V. spectrophotometry has proved unsuccessful. Future work should be concentrated in improving of the technique, some modification of the instrument may be necessary for a better result to be expected.

Some comments should be made on "a" values which were calculated using Bjerrum model. Results seem to be acceptable. However, it must be borne in mind that when ions move they carry solvent with them, and some of this is undoubtedly included in the effective ionic size "a". Not only may different measurements yield different results but the same measurements may yield different radii depending on the method of calculation. This is particularly true of ion pair contact distances, where differences of several Angstrom units (picometer) are not unusual.

Since the variation of "a" with T becomes noticeable for $(C_2H_5)_4N^+$, it is interesting to explore the temperature dependence of "a" for a larger tetraalkylammonium ions and the logical explanation may be arrived at.

Appendix I

The preparation of ethyl iodide, tetraethylammonium iodide and tetraethyammonium hydroxide:

Ethyl iodide 125 g. of pulverized iodine was added gradually to 150 cm^3 95% ethanol in a 1000 cm^3 round-bottom flask, having red phosphorus as catalyst. During the addition of iodine, the flask was shaken frequently and the mixture was kept cool. The reaction mixture was allowed to stand at least 4 hours at room temperature. In order to complete reaction, the mixture was refluxed very gently for 2 hours on a steam bath. Then the mixture was distilled into 500 cm^3 of cold water. The distillate was transferred to a separatory funnel and the lower layer of the ethyl iodide was run off. Brown colour of ethyl iodide is due to the presence of free iodine, hence it must be washed with about 250 cm^3 of water and with a few drops of 10% sodium hydroxide solution. The heavy, almost colorless oil was separated and allowed to dry for about 4 hours with 5 - 6 g. of anhydrous calcium chloride, in a bottle.

Through a funnel containing a small plug of glass wool, the dried product was decanted into a small distilling flask which was set for distillation. 50 cm^3 (19 g.) of ethyl iodide was collected at 71 - 72°C. It usually becomes violet and brown on standing, therefore it was collected on a globule of mercury in a dark bottle.

<u>Tetraethylammonium iodide</u> Equimolar quantities of ethyl iodide, 16.4 cm^3 was mixed with 28 cm^3 triethylamine (laboratory grade). The mixture was allowed to stand overnight. The crude product was filtered off and dried by washing with petroleum ether, and then it was dissolved in 100 cm^3 of boiling 95% ethanol and treated with alcoholic potassium hydroxide until it turned pink to phenolphthalein. The mixture was then cooled in an ice bath and the solid was filtered off. It was recrystallized twice from 95% ethanol. The pure product, 15 g. (m.p. 299 - 301°C) was finally dried in a vacuum desiccator.

<u>Tetraethylammonium hydroxide</u> 100 cm^3 of 5% aqueous tetraethylammonium iodide solution was mixed with 5 g. silver oxide until the solution is alkaline. Silver iodide was precipitated and about 30 cm^3 of tetraethylammonium hydroxide remained in solution.

Appendix II

The measurement of conductance of non-aqueous solution is quite straight forward, the main requirements being careful attention to the purity of materials and the exclusion of atmospheric moisture. It is however, much more difficult to obtain from the experimental values of the limiting conductance (Λ^o). First, the low dielectric constant of most non aqueous solvents results in a much more pronounced decrease in the equivalent conductance with concentration than is the case for aqueous solutions, and the theory required in extrapolating the conductance to zero concentration is complicated by the effects of ion pair formation. In this case, it has generally been necessary to employ an approximation known as "Walden's Rule".(a) This rule, as originally proposed, was empirical, but it can be shown to be a direct consequence of the application of Stokes law(a) to the motion of ions. If the motion of any ion obeys Stoke's law then for any given salt the product of Λ^o and viscosity (η) of the solvent should be constant, independent of solvent and temperature(b)

$$\Lambda^o\eta = \text{constant}$$

This rule appears to be most closely obeyed by ions of the type NR_4^+, where R is a relatively large radical. Ions of small size, or unsymmetrical shape or distribution of charge, would be expected to show most serious departure from Walden's Rule, especially compared with solvent of widely differing polarizability and molecular volume.

From Robinson, R.A. and Stokes, R.H., Electrolyte Solutions, Butterworths (1959). and Harned, S. and Owen, B. The Physical Chemistry of Electrolytic Solutions, Reinhold Book Corp., New York (1957).

[a] Gonick, E., J. Phys. Chem., 50, 291 (1946)

[b] Walden, P., and Ulich, H., Z. Physik. Chem., 107, 219 (1923).

Appendix III

Values of the definite integral Q(b)

in equation: $Q(b) = \int_2^b x^{-4} e^x dx$

b	Q(b)	b	Q(b)	b	log Q(b)
2.0	0	5	0.771	15	1.97
2.1	0.044	6	1.041	17	2.59
2.2	0.084	7	1.42	20	3.59
2.4	0.156	8	2.00	25	5.35
2.6	0.218	9	2.95	30	7.19
2.8	0.274	10	4.63	40	11.01
3.0	0.326	12	13.41	50	14.96
3.5	0.442	14	47.0	60	18.98
4.0	0.550	15	93.0	70	23.05

Reference: Fuoss, R.M., and Kraus, C.A., J. Amer. Chem. Soc., 55, 1019 (1933).