CHAPTER IV

RESULTS AND CALCULATIONS

The figures showed in this chapter except those of the Onsager plot, are linear. They all are the least square lines.

4.1 The Onsager Plot

The Onsager plots, Λ vs. $\sqrt{C}$ of tetramethyl and tetraethylammonium picrates at 25°, 30°, 35° and 40°C exhibited nonlinearity. They are shown in Tables 4.1.1 and 4.1.2, Figures 4.1.1 and 4.1.2.

Table 4.1.1

The Onsager plot of tetramethylammonium picrate at 25°, 30°, 35° and 40°C

$\sqrt{C}^* \times 10^3$ (equi/l)	Λ 25° ($cm^2.ohm^{-1}.equi^{-1}$)	Λ 30° ($cm^2.ohm^{-1}.equi^{-1}$)	Λ 35° ($cm^2.ohm^{-1}.equi^{-1}$)	Λ 40° ($cm^2.ohm^{-1}.equi^{-1}$)
4.44972	35.56655	37.82412	41.70555	48.51785
7.04273	32.22205	-	37.51861	42.60963
8.91627	30.65805	33.07479	35.24492	39.50627
10.45466	29.68937	31.31805	34.10188	38.06237
11.79406	28.74110	30.58463	32.99758	36.84250

C^* = concentration of tetramethylammonium picrate in 80% dioxane-water

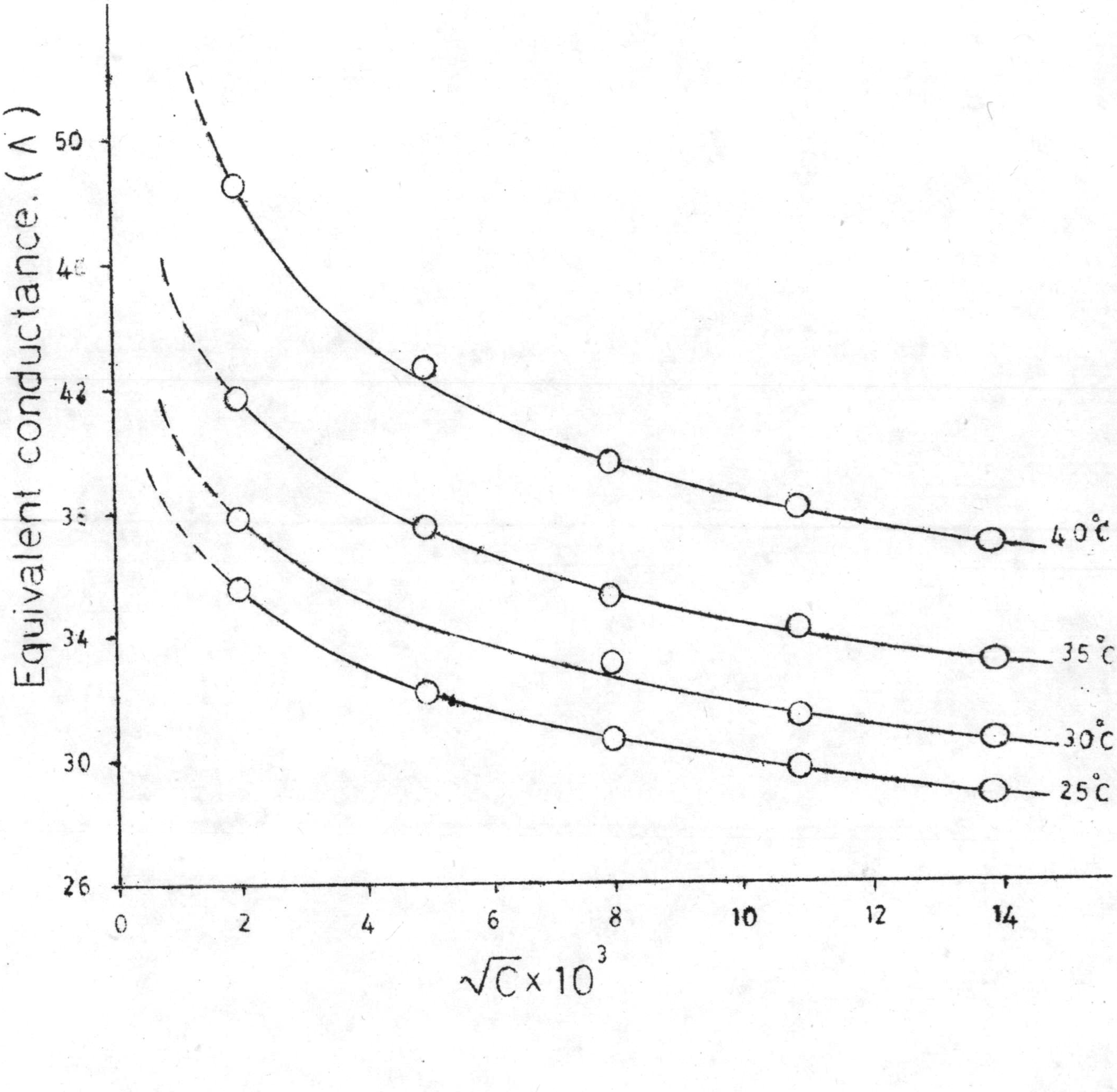

Fig. 4.1.1 The Onsager plot of $(CH_3)_4NPi$ in 80% dioxane-water.

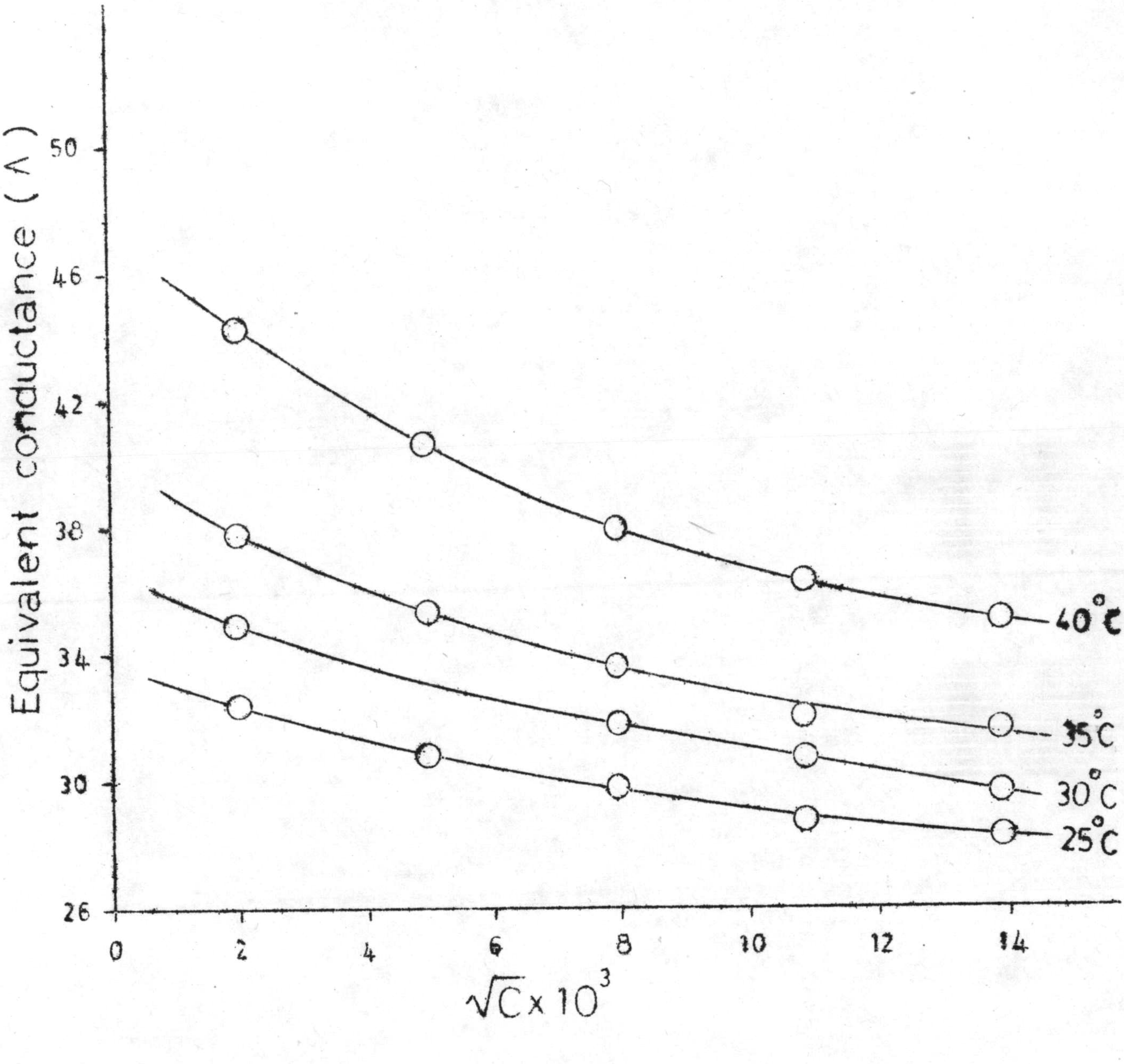

Fig. 4.1.2 The Onsager plot of $(C_2H_5)_4NPi$ in 80% dioxane-water.

Table 4.1.2

The Onsager plot of tetraethylammonium picrate

at 25°, 30°, 35° and 40°C

$\sqrt{C^*} \times 10^3$ (equi/l)	Λ 25° ($cm^2 . ohm^{-1} . equi^{-1}$)	Λ 30° ($cm^2 . ohm^{-1} . equi^{-1}$)	Λ 35° ($cm^2 . ohm^{-1} . equi^{-1}$)	Λ 40° ($cm^2 . ohm^{-1} . equi^{-1}$)
4.44972	32.43765	34.93285	37.82412	44.35918
7.04273	30.83070	-	35.33674	40.17235
8.91628	29.87877	31.86650	33.58773	37.97731
10.45466	28.69924	30.72254	31.96378	36.23280
11.79406	28.16041	29.65568	31.50358	35.01024

C^* = concentration of tetraethylammonium picrate in 80% dioxane-water

4.2 Determination of limiting equivalent conductance, Λ^0 using Walden's rule

Equivalent conductances of tetramethyl and tetraethylammonium picrates in various organic solvents including 80% dioxane-water mixture were obtained from conductance measurements. The limiting equivalent conductances were calculated and are shown together with the appropriate viscosities in Tables 4.2.1, 4.2.2, 4.2.3 and 4.2.4 at 25°, 30°, 35° and 40°C.

Table 4.2.1

Limiting equivalent conductance, Λ^o of $^*(CH_3)_4$ NPi at 25°C

solvent	$\eta \times 10^2$ (poise)	$\frac{1}{R}_{corr} \times 10^6$ (ohm^{-1})	Λ $(cm^2.ohm^{-1}.equi^{-1})$	$\Lambda^o\eta$
cyclohexanone	1.91967	1.420	33.6304	0.645592
ethanol	1.17575	2.300	54.4719	0.640455
water	0.89370	3.045	72.1161	0.644501
methanol	0.56265	4.850	114.8647	0.646292
acetone	0.30415	9.000	213.1512	0.648307
			average	0.6450294
80% dioxane-water	1.75550	-	Λ^o = 36.7424	

$^*(CH_3)_4$ NPi - tetramethylammonium picrate

Table 4.2.2

Limiting equivalent conductance, Λ^o of $^*(C_2H_5)_4$ NPi at 25°C

solvent	$\eta \times 10^2$ (poise)	$\frac{1}{R}_{corr} \times 10^6$ (ohm^{-1})	Λ $(cm^2.ohm^{-1}.equi^{-1})$	$\Lambda^o\eta$
cyclohexanone	1.91967	1.30	30.7885	0.591037
ethanol	1.17575	2.10	49.7352	0.584763
water	0.89370	2.77	65.6031	0.586290
methanol	0.56265	4.47	105.8650	0.595655
acetone	0.30415	8.19	193.9675	0.589960
			average	0.58954
80% dioxane-water	1.75550	-	Λ^o = 33.58168	

$^*(C_2H_5)_4$NPi - tetraethylammonium picrate

Table 4.2.3

Limiting equivalent conductance, Λ^o of $(CH_3)_4NPi$ at 30^o, 35^o and 40^o C

solvent	$\eta \times 10^2$ (poise)	$\frac{1}{R_{corr}} \times 10^6$ (ohm^{-1})	Λ ($cm^2.ohm^{-1}.equi^{-1}$)	$\Lambda^o\eta$
ethanol	1.03079	2.65	62.7611	0.646935
water	0.80070	3.29	77.9186	0.623894
methanol	0.54593	4.90	116.0489	0.633548
acetone	0.28029	9.54	225.9402	0.633287
			average	0.634412
80% dioxane-water	1.66645^{30^o}	-	$\Lambda^o_{30^o}$ = 38.06953	
	1.4559^{35^o}	-	$\Lambda^o_{35^o}$ = 43.57475	
	1.2643^{40^o}	-	$\Lambda^o_{40^o}$ = 50.17765	

Table 4.2.4

Limiting equivalent conductance, Λ^{o} of $(C_2H_5)_4NPi$ at 30^{o}, 35^{o} and $40^{o}C$

solvent	$\eta \times 10^2$ (poise)	$\frac{1}{R}_{corr} \times 10^6$ (ohm^{-1})	Λ $(cm^2.ohm^{-1}.equi^{-1})$	$\Lambda^{o}\eta$
ethanol	1.03079	2.45	58.0244	0.598109
water	0.80070	3.10	73.4187	0.587863
methanol	0.54593	4.50	106.5755	0.581830
acetone	0.28029	8.88	210.3091	0.589474
			average	0.589319
80% dioxane-water	$1.66645^{30^{o}}$	-	$\Lambda^{o}_{30^{o}}$ = 35.36359	
	$1.4559^{35^{o}}$	-	$\Lambda^{o}_{35^{o}}$ = 40.47751	
	$1.2643^{40^{o}}$	-	$\Lambda^{o}_{40^{o}}$ = 46.61108	

4.3 Calculation for dissociation constant, K and the activity coefficient, $f_{\pm}$

For non aqueous media, especially those of low D, the proportion of undissociated molecules may be quite large even at small concentration. The Onsager equation for incomplete dissociation can be written as follows[17]

$$\Lambda' = \Lambda^{o} - (A + B\Lambda^{o})\sqrt{\alpha C} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4.1)$$

and the degree of dissociation is

$$\alpha = \frac{\Lambda}{\Lambda'} = \frac{\Lambda}{\Lambda^{o} - (A+B\Lambda^{o})\sqrt{\alpha C}} \quad \text{...........} \quad (4.2)$$

In the limit, equation (4.2) reduces to $\alpha = \Lambda/\Lambda^{o}$. By the simple expedient of successive substitution of equation (4.2) back into its own correction term, $1-(A+B\Lambda^{o})\sqrt{\alpha C}/\Lambda^{o}$, the latter may be replaced by the continued function

$$F(Z) = 1-Z\left\{1-Z\left[1-Z(\text{etc.})^{-1/2}\right]^{-1/2}\right\}^{-1/2} \quad \text{.........} \quad (4.3)$$

$$\text{in which} \quad Z = (A+B\Lambda^{o})\sqrt{C\Lambda}/\Lambda^{o\,3/2} \quad \text{................} \quad (4.4)$$

$$\text{where} \quad (A+B\Lambda^{o}) = \frac{82.4}{\eta(DT)^{1/2}} + \frac{8.2 \times 10^{5}\Lambda^{o}}{(DT)^{3/2}} = \gamma$$

Fuoss[17] tabulated numerical values of F(Z), for $0 \leq Z \leq 0.209$, so that α can be calculated by

$$\alpha = \frac{\Lambda}{\Lambda^{o} F(Z)} \quad \text{..................} \quad (4.5)$$

By the thermodynamic ionization constant

$$K = \frac{\alpha^{2} C f_{\pm}^{2}}{1-\alpha} \quad \text{................} \quad (4.6)$$

then the obtained expression is

$$\frac{F(Z)}{\Lambda} = \frac{1}{K\Lambda^{o2}} \cdot \frac{\Lambda C f_{\pm}^{2}}{F(Z)} + \frac{1}{\Lambda^{o}} \quad \text{.......} \quad (4.7)$$

$$\text{where} \quad -\log f_{\pm}^{2} = 2\beta\sqrt{C\alpha},$$

$$\beta = 0.4343 \frac{\varepsilon^{2}}{2DkT}\left[\frac{8\pi N\varepsilon^{2}}{1000DkT}\right]^{1/2}$$

and Λ^{o} was obtained from Walden's Rule.

The value of the function $F(Z)/\Lambda$ and $\Lambda C f_{\pm}^{2}/F(Z)$ were plotted as ordinate and abscissa respectively. The intercept of each plot on the axis of ordinates yields the value of Λ^{o} and the slope yields value of the dissociation constant K of the ion-ion pair equilibrium. Results are shown in Tables 4.3.1, 4.3.2, 4.3.3 and 4.3.4, Figures 4.3.1, 4.3.2, 4.3.3 and 4.3.4.

Table 4.3.1

Dissociation constant of $(CH_3)_4NPi$ and $(C_2H_5)_4NPi$

in 80% dioxane-water at 25°C

electrolyte	$c \times 10^5$ (equi/l)	Λ ($cm^2 ohm^{-1} equi^{-1}$)	F (Z)	F (Z)/Λ	$f_\pm^2$	$\Lambda c f_\pm^2 / F(Z) \times 10^5$
$(CH_3)_4NPi$	1.98	35.56655	0.96978	0.0272666	0.81359	59.0798
	4.96	32.22205	0.95425	0.0296148	0.73148	122.51100
	7.95	30.65805	0.94264	0.0307469	0.67811	175.33391
	10.93	29.68937	0.93397	0.0314580	0.63754	221.51386
	13.91	28.74110	0.92645	0.0322343	0.60548	261.28129
$(C_2H_5)_4NPi$	1.98	32.43765	0.96891	0.0298699	0.81396	53.95531
	4.96	30.83070	0.95163	0.0308663	0.72596	116.65667
	7.95	29.87877	0.93933	0.0314380	0.66911	169.20343
	10.93	28.69924	0.92989	0.0324012	0.62878	212.10831
	13.91	28.16041	0.92123	0.0327136	0.55641	236.58812
			$^*\Lambda^o = 38.1679$		$K^* = 2.831 \times 10^{-4}$	
			$^{**}\Lambda^o = 34.4827$		$K^{**} = 5.466 \times 10^{-4}$	

$^*\Lambda^o$, K^* = limiting conductance and dissociation constant of $(CH_3)_4NPi$

$^{**}\Lambda^o$, K^{**} = limiting conductance and dissociation constant of $(C_2H_5)_4$ NPi

Table 4.3.2

Dissociation constant of $(CH_3)_4NPi$ and $(C_2H_5)_4NPi$

in 80% dioxane-water at 30°C

electrolyte	$c \times 10^5$ (equi/l)	Λ ($cm^2 . ohm^{-1} . equi^{-1}$)	F (Z)	F (Z)/Λ	$f_{\pm}^2$	$\Lambda c f_{\pm}^2 / F(Z) \times 10^5$
$(CH_3)_4NPi$	1.98	37.82412	0.96891	0.0256161	0.80929	62.55395
	4.96	-	-	-	-	-
	7.95	33.07479	0.94094	0.0284488	0.66880	186.89537
	10.93	31.31805	0.93225	0.0297671	0.63066	121.56757
	13.91	30.58463	0.92417	0.0302168	0.59676	274.71234
$(C_2H_5)_4NPi$	1.98	34.93285	0.96819	0.0277157	0.80984	57.85459
	4.96	-	-	-	-	-
	7.95	31.48665	0.93858	0.0298088	0.66513	177.38986
	10.93	30.72254	0.92849	0.0302217	0.62202	224.95952
	13.91	29.66568	0.92035	0.0310240	0.58939	264.25983
			$^*\Lambda^o$ = 41.3223		K^* = 2.509 X 10^{-4}	
			$^{**}\Lambda^o$ = 57.2714		K^{**} = 4.607 X 10^{-4}	

Table 4.3.3

Dissociation constant of $(CH_3)_4NPi$ and $(C_2H_5)_4NPi$ in 80% dioxane-water at 35°C

electrolyte	$c \times 10^5$ (equi/l)	Λ ($cm^2.ohm^{-1}.equi^{-1}$)	F (Z)	F (Z)/Λ	$f_{\pm}^2$	$\Lambda c f_{\pm}^2/F(Z) \times 10^5$
$(CH_3)_4NPi$	1.98	41.70555	0.86922	0.0242395	0.81021	67.02943
	4.96	37.51861	0.95331	0.0254089	0.72712	141.93854
	7.95	35.24492	0.94243	0.0267394	0.67484	200.63899
	10.93	34.10188	0.93322	0.0273656	0.63387	253.17138
	13.91	32.99758	0.92558	0.0280499	0.60172	298.39373
$(C_2H_5)_4NPi$	1.98	37.82412	0.96881	0.0256135	0.81207	62.77531
	4.96	35.33674	0.95141	0.0269241	0.72529	133.61404
	7.95	33.58773	0.94008	0.0279887	0.67111	190.62359
	10.93	31.96378	0.93118	0.0291323	0.63228	237.22151
	13.91	31.50358	0.92253	0.0292833	0.59704	283.60243

$^{*}\Lambda^{o} = 45.1467$	$K^{*} = 2.289 \times 10^{-4}$
$^{**}\Lambda^{o} = 40.6504$	$K^{**} = 3.444 \times 10^{-4}$

Table 4.3.4

Dissociation constant of $(CH_3)_4NPi$ and $(C_2H_5)NPi$

in 80% dioxane-water at $40^{\circ}C$

electrolyte	$c \times 10^5$ (equi/l)	Λ ($cm^2 \cdot ohm^{-1} \cdot equi^{-1}$)	F (Z)	F (Z)/Λ	$f_{\pm}^2$	$\Lambda c f_{\pm}^2/F(Z) \times 10^5$
$(CH_3)_4NPi$	1.98	48.51785	0.96871	0.0199660	0.80668	79.99710
	4.96	41.81910	0.95352	0.0223681	0.72310	160.34274
	7.95	39.50627	0.94253	0.0238574	0.67437	224.71713
	10.93	38.06237	0.93354	0.0245265	0.63416	282.60633
	13.91	36.84250	0.92590	0.0251313	0.60199	333.19724
$(C_2H_5)_4NPi$	1.98	44.35918	0.96809	0.0218238	0.80798	73.30499
	4.96	40.71235	0.95120	0.0233639	0.72177	153.22683
	7.95	37.97731	0.93998	0.0247510	0.66957	215.06448
	10.93	36.23280	0.93085	0.0256908	0.63023	268.12753
	13.91	35.01024	0.92308	0.0263660	0.59800	315.48887
			${}^{*}\Lambda^{o} = 53.1349$		$K^{*} = 1.747 \times 10^{-4}$	
			${}^{**}\Lambda^{o} = 49.0196$		$K^{**} = 2.164 \times 10^{-4}$	

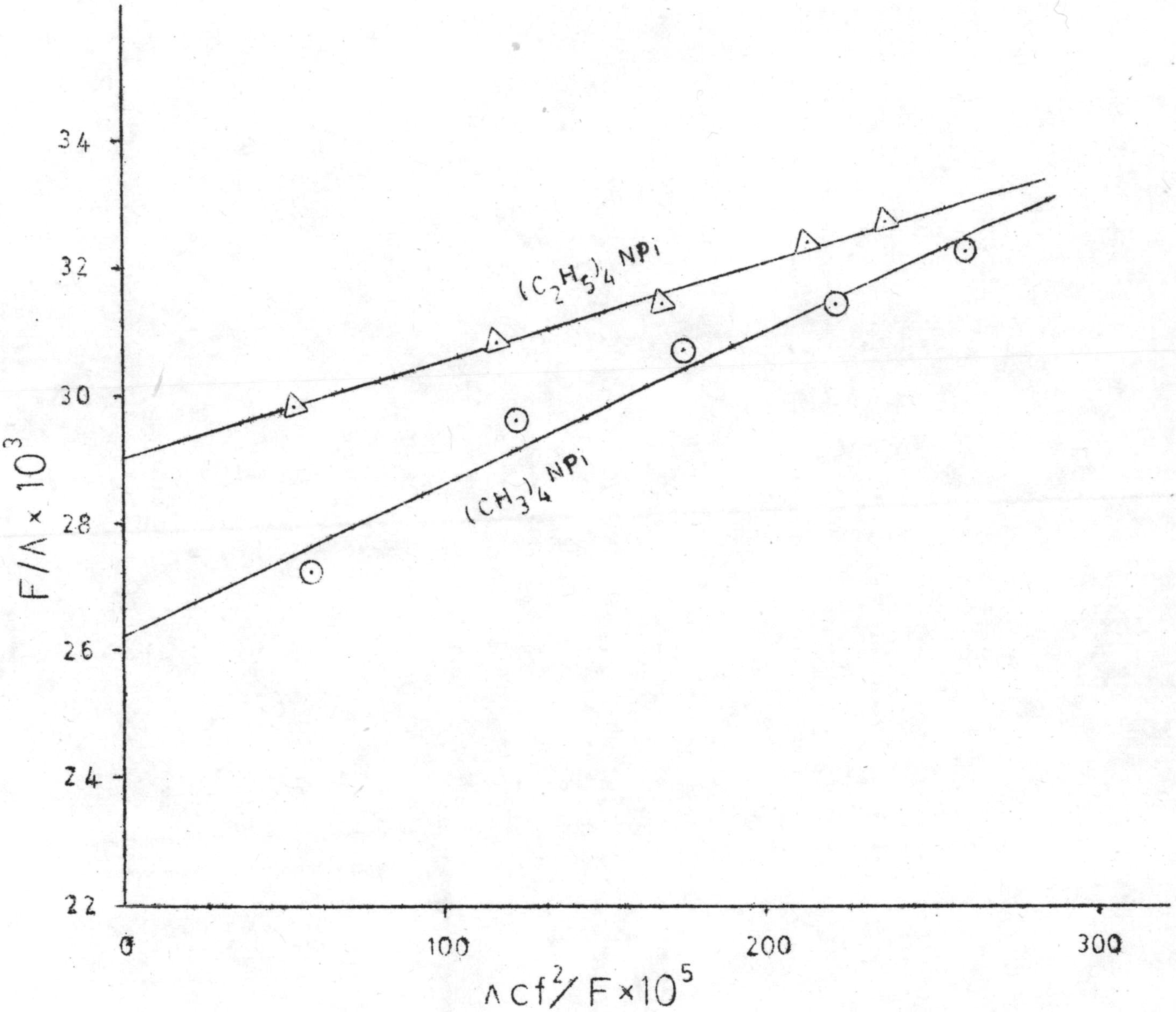

Fig. 4.3.1 Evaluation of K by equation (4.7), $(CH_3)_4$ NPi and $(C_2H_5)_4$ NPi in 80% dioxane--water at 25 °C

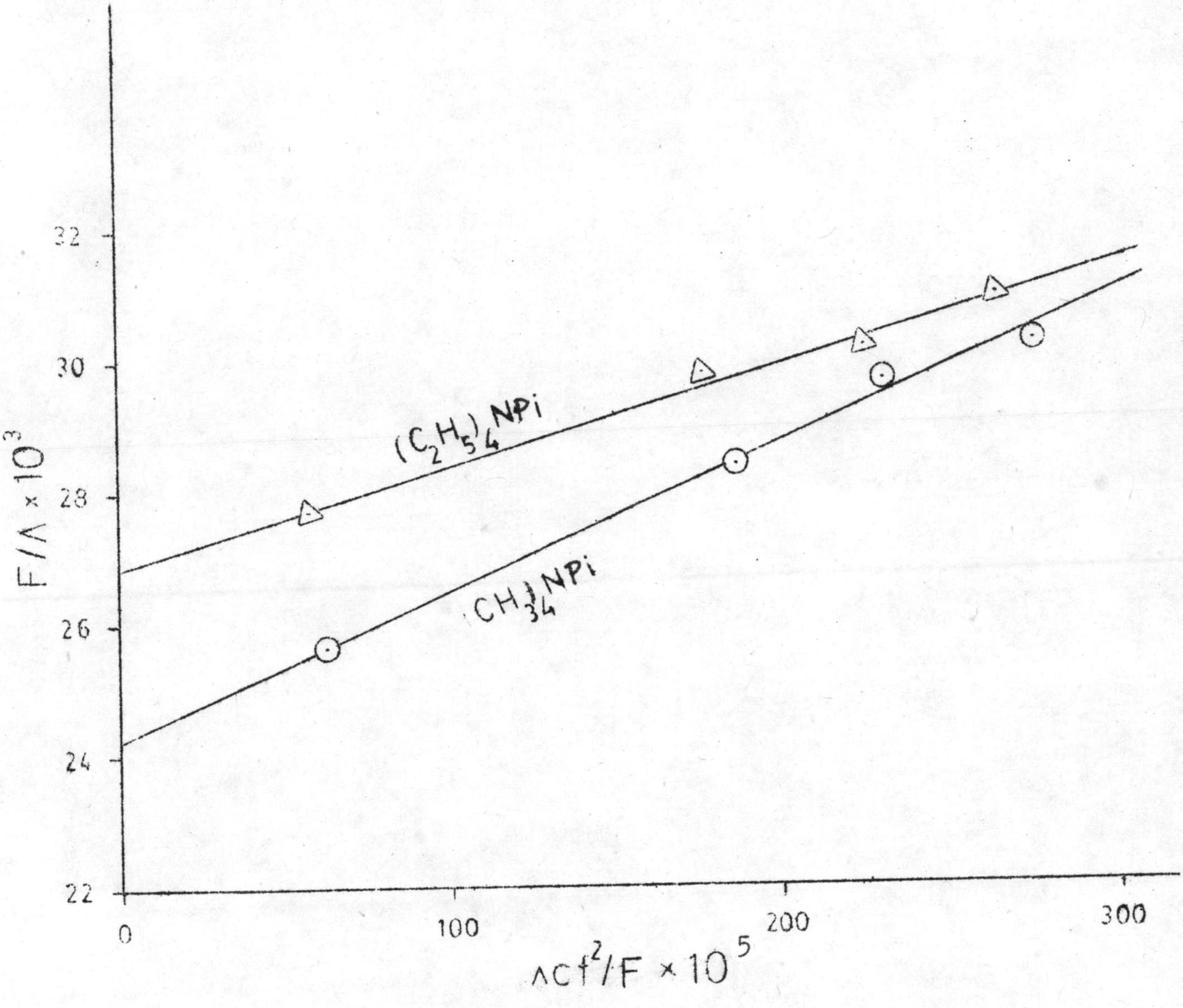

Fig. 4.3.2 Evaluation of K by equation (4.7), $(CH_3)_4NPi$ and $(C_2H_5)_4NPi$ in 80% dioxane–water at 30°C.

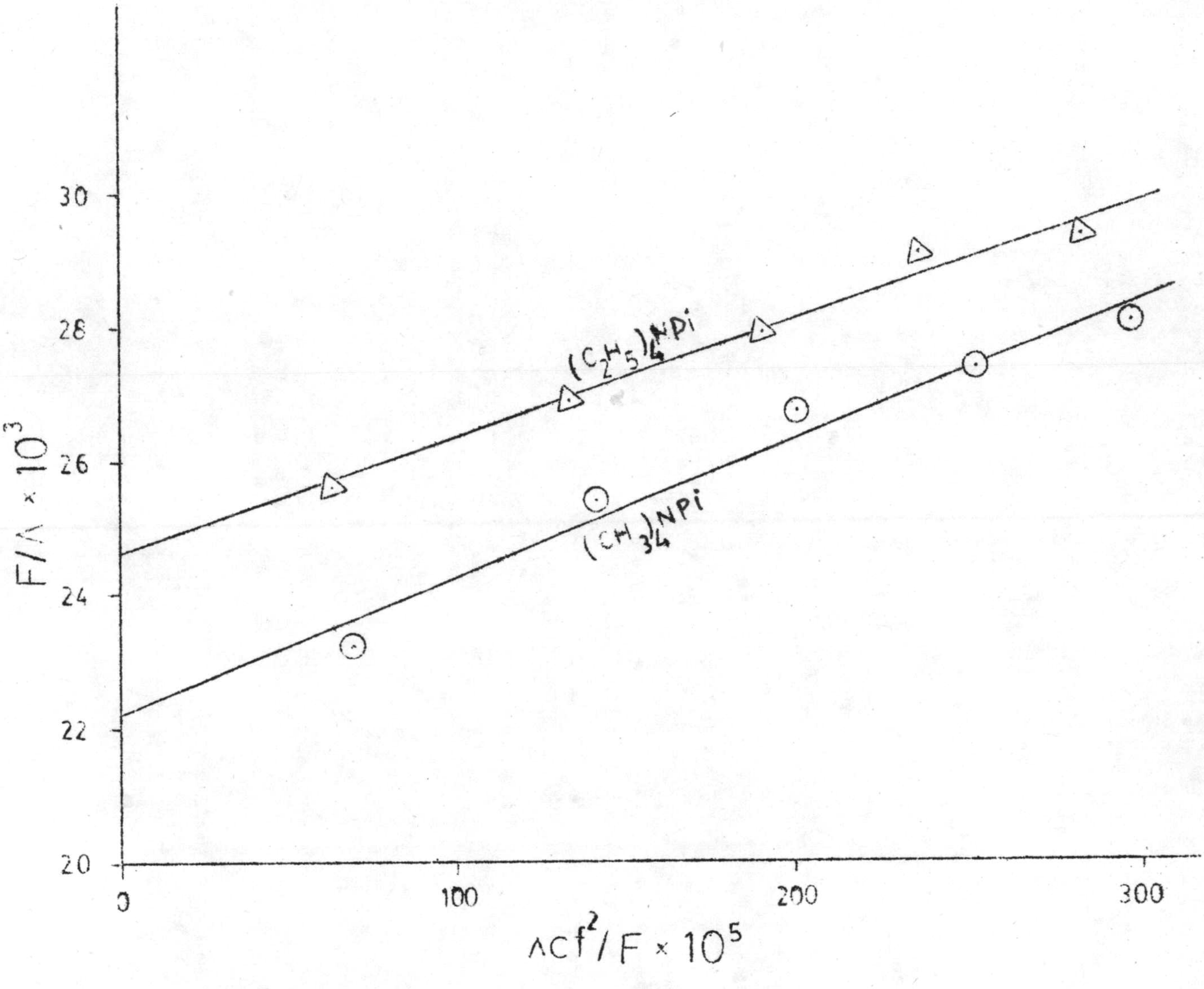

Fig.4.3.3 Evaluation of K by equation (4.7), $(CH_3)_4NPi$ and $(C_2H_5)_4NPi$ in 80% dioxane-water at 35°C.

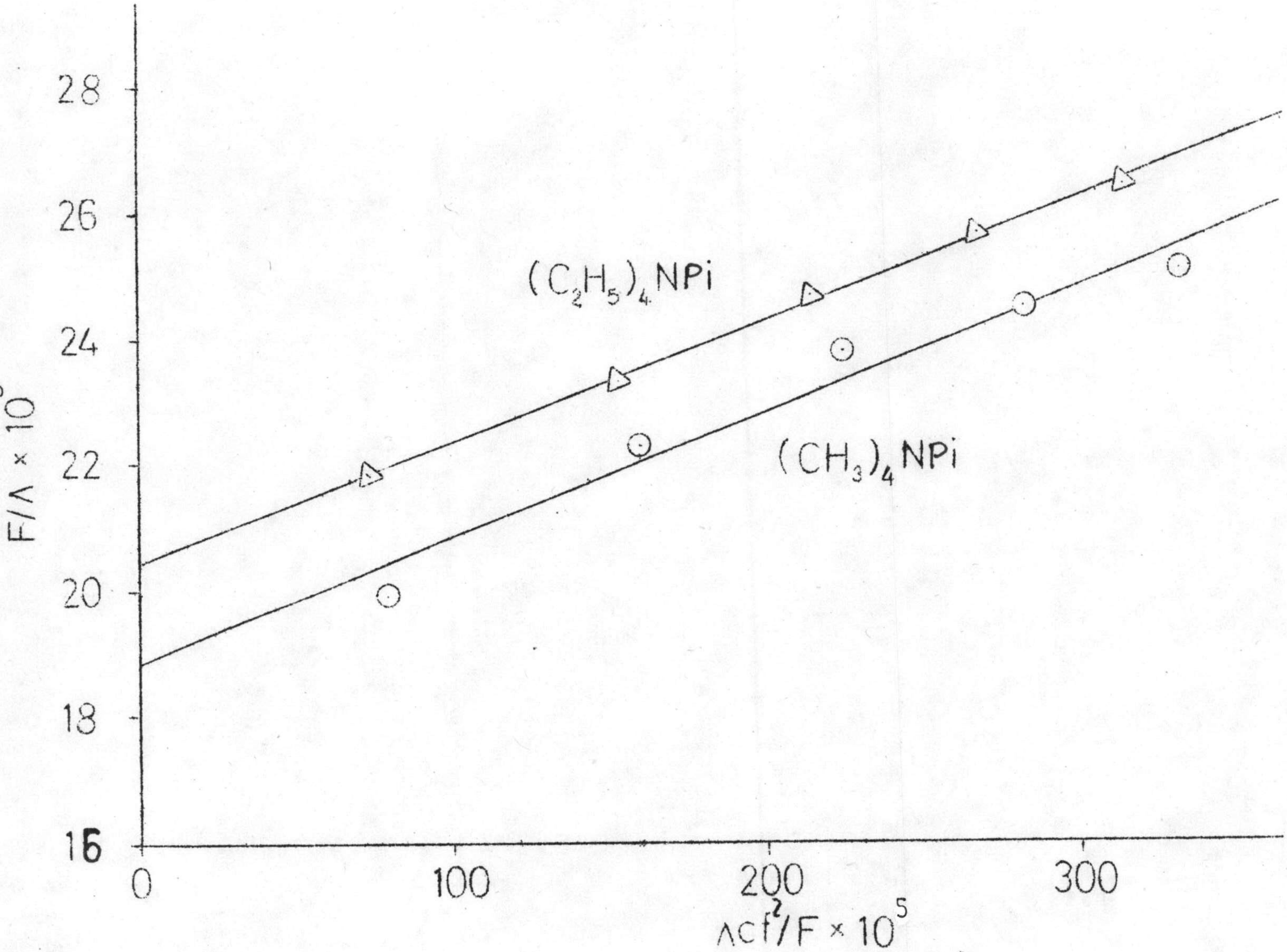

Fig. 4·3·4 Evaluation of K by equation(4. 7), $(CH_3)_4NPi$ and $(C_2H_5)_4NPi$ in 80 % dioxane-water at 40°C.

4.4 Calculation of the distance of closest approach "a"

The values of "a" were calculated from Bjerrum's equation

$$\frac{1}{K} = \frac{4\pi N}{1000}\left[\frac{|Z_1Z_2|\epsilon^2}{DkT}\right]^3 Q(b) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.8)$$

where

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

$$x = -\frac{Z_1Z_2\epsilon^2}{DkTr}$$

$$2 \equiv \frac{|Z_1Z_2|\epsilon^2}{DkTq}$$

$$b \equiv \frac{|Z_1Z_2|\epsilon^2}{DkTa} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.9)$$

Inserting numerical values into (4.8) and (4.9) the following expression was resulted

$$\frac{1}{K} = \frac{4X3.1416X6.023X10^{23}}{1000}\left[\frac{(1X1)\ X\ (4.8X10^{-10})^2}{1.38054\ X\ 10^{-16}DT}\right]^3 Q(b)$$

and K was obtained from section 4.3

Typical calculation

Tetramethylammonium picrate in 80% dioxane-water at 25°C

$$\frac{1}{K} = 75.68743\ X\ 10^{20}\left[\frac{23.04X10^{-20}}{1.38054X10^{-16}X10.708X298}\right]^3 Q(b)$$

$$= 1082.8051\ Q(b) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.10)$$

since $K = 2.831\ X\ 10^{-4}$, equation (4.10) becomes

$$\frac{1}{2.831X10^{-4}} = 1082.8051\ Q(b)$$

Hence, $Q(b) = 3.262194$

values of Q(b) and log Q(b) as a function of "b" are tabulated and presented in Appendix III. For Q(b) = 3.262194, b = 9.185833

Next "b" was substituted into the equation(4.9) which enabled "a" to be directly obtained and it was 5.6936 X 10^{-8} cm. Table 4.4.1 shows the constancy of "a" at various temperature for tetramethylammonium picrate while Table 4.4.2 shows slight fluctuation of "a" with temperature of tetraethylammonium picrate.

Table 4.4.1

The "a" value of $(CH_3)_4NPi$ in 80% dioxane-water at 25°, 30°, 35° and 40°C

temperature °C	D	K X 10^4	Q(b)	b	a X 10^8 (cm)
25	10.708	2.831	3.26219	9.1858	5.69
30	10.435	2.509	3.58080	9.37559	5.63
35	10.169	2.289	3.18519	9.3150	5.60
40	9.9083	1.747	4.85304	10.02540	5.36

Table 4.4.2

The "a" value of $(C_2H_5)_4NPi$ in 80% dioxane-water at 25°, 30°, 35° and 40°C

temperature°C	D	K X 10^4	Q(b)	b	a X 10^8 (cm)
25	10.708	5.466	1.68958	7.46379	7.007
30	10.435	4.607	1.950126	7.91379	6.670
35	10.169	3.444	2.53571	8.56389	6.22
40	9.9083	2.164	3.91786	9.57611	5.62

4.5 Specific rate of self association reaction

The specific rate of the reactions were obtained from the slopes of the rectilinear plot $\frac{1}{a_o - x} - \frac{1}{a_o}$ vs. time. Data used for the above plots and the resulted graphs are shown in Tables and Figures 4.5.1, 4.5.2, 4.5.3, 4.5.4, 4.5.5, 4.5.6, 4.5.7 and 4.5.8.

The increase in the conductance with time at the beginning of the observations are due to the dissociation reactions and was neglected in the subsequent treatment of the data. Only the portion that showed the association phenomenon was considered here.

Table 4.5.1

The specific rate constant of the association reaction of $(CH_3)_4NPi$ in 80% dioxane-water at 25°C from conductivity measurement

time (min)	$1/R_{corr} X 10^6$ (ohm^{-1})	$(a_o-x)10^5$ (mole $litre^{-1}$)	$1/a_o-x$ (litre $mole^{-1}$)	$1/a_o-x - 1/a_o$ (litre $mole^{-1}$)
5	34.46	not considered	—	—
10	34.975			
15	35.020			
20	35.025			
25	35.035			
30	35.060			
35	35.080			
40	35.090			
45	35.095	9.23525	10828.07	0
47	35.090	9.23383	10829.73	1.66
50	35.080	9.23100	10833.06	4.99
52	35.075	9.22958	10834.72	6.65
55	35.060	9.22533	10839.71	11.64
57	35.050	9.22250	10843.04	14.97
60	35.040	9.21967	10846.37	18.30
62	35.030	9.21683	10849.71	21.64
65	35.025	9.21542	10851.37	23.30
67	35.025	9.21400	10853.04	24.97
				$k = 2 X 10^{-2}$ (litre $mole^{-1} sec^{-1}$)

Table 4.5.2

The specific rate constant of the association reaction of $(CH_3)_4NPi$ in 80% dioxane-water at 30°C from conductivity measurement

time (min)	$1/R_{corr} \times 10^6$ (ohm^{-1})	$(a_o-x)\ 10^5$ (mole litre^{-1})	$1/a_o-x$ (litre mole^{-1})	$1/a_o-x - 1/a_o$ (litre mole^{-1})
5	37.340	not considered	—	—
10	38.260			
15	38.340			
20	38.360			
25	38.365	9.56400	10455.87	0
27	38.355	9.56133	10458.79	2.92
30	38.345	9.55866	10461.71	5.84
32	38.340	9.55733	10463.17	7.30
35	38.335	9.55600	10464.62	8.75
40	38.330	9.55466	10466.09	10.22
42	38.325	9.55333	10467.55	11.68
45	38.320	9.55200	10469.01	13.14
				$k = 1.333 \times 10^{-2}$ (litre mole^{-1}sec^{-1})

Table 4.5.3

The specific rate constant of the association reaction of $(CH_3)_4NPi$ in 80% dioxane-water at 35°C from conductivity measurement

time (min)	$1/R_{corr} \times 10^6$ (ohm^{-1})	$(a_o-x)\ 10^5$ (mole $litre^{-1}$)	$1/a_o-x$ (litre $mole^{-1}$)	$1/a_o-x - 1/a_o$ (litre $mole^{-1}$)
5	40.820			
10	42.140	not considered	——	——
15	42.240			
20	42.245			
25	42.245	9.63286	10381.12	0
27	42.240	9.63164	10382.45	1.33
33	42.230	9.62918	10385.09	3.97
38	42.225	6.62795	10386.42	5.3
40	42.220	9.62673	10387.74	6.62
47	42.215	9.62550	10389.07	7.95
50	42.210	9.62427	10390.39	9.27
57	42.200	9.62182	10393.04	11.92
60	42.195	9.62059	10394.37	13.25
65	42.190	9.61936	10395.69	14.57
				$k = 6.44 \times 10^{-3}$ (litre.$mole^{-1}sec^{-1}$)

Table 4.5.4

The specific rate constant of the association reaction of $(CH_3)_4NPi$ in 80% dioxane-water at 40°C from conductivity measurement

time (min)	$1/R_{corr} \times 10^6$ (ohm^{-1})	$(a_o-x)10^5$ (mole $litre^{-1}$)	$1/a_o-x$ (litre $mole^{-1}$)	$1/a_o-x - 1/a_o$ (litre $mole^{-1}$)
5	45.630			
10	46.835			
15	46.940	not considered	—	—
20	46.975			
25	46.995			
30	47.005	9.66635	10345.66	0
33	47.000	9.66522	10346.37	1.21
42	46.990	9.66296	10348.79	3.63
50	46.985	9.66183	10350.01	4.85
52	46.980	9.66069	10351.22	6.06
				$k = 4.615 \times 10^{-3}$ (litre $mole^{-1} sec^{-1}$)

Table 4.5.5

The specific rate constant of the association reaction of $(C_2H_5)_4NPi$ in 80% dioxane-water at 25°C from conductivity measurement

time (min)	$1/R_{corr} \times 10^6$ (ohm^{-1})	$(a_o-x)10^5$ (mole $litre^{-1}$)	$1/a_o-x$ (litre $mole^{-1}$)	$1/a_o-x - 1/a_o$ (litre $mole^{-1}$)
5	33.640	not considered	—	—
10	34.085			
15	34.135			
20	34.150			
25	34.150	9.13737	10944.07	0
27	34.140	9.13453	10947.47	3.40
30	34.130	9.13168	10950.88	6.81
31	34.125	9.13026	10952.58	8.51
33	34.120	9.12884	10954.29	10.22
34	34.115	9.12742	10955.99	11.92
				$k = 2.133 \times 10^{-2}$ (litre $mole^{-1} sec^{-1}$)

Table 4.5.6

The specific rate constant of the association reaction of $(C_2H_5)_4NPi$ in 80% dioxane-water at 30^oC from conductivity measurement

time (min)	$1/R_{corr} \times 10^6$ (ohm^{-1})	$(a_o-x)\,10^5$ (mole $litre^{-1}$)	$1/a_o-x$ (litre $mole^{-1}$)	$1/a_o-x - 1/a_o$ (litre $mole^{-1}$)
5	35.710			
10	36.775			
15	36.865	not considered	——	——
20	36.890			
25	36.895			
26	36.900	9.49050	10536.85	0
27	36.895	9.48915	10538.35	1.5
28	36.890	9.48780	10539.85	3
30	36.885	9.48645	10541.35	4.5
35	36.875	9.48375	10544.35	7.5
35	36.870	9.48240	10545.85	9

$k = 1.538 \times 10^{-2}$ (litre $mole^{-1}$ sec^{-1})

Table 4.5.7

The specific rate constant of the association reaction of $(C_2H_5)_4NPi$ in 80% dioxane-water at 35^oC from conductivity measurement

time (min)	$1/R_{corr} \times 10^6$ (ohm^{-1})	$(a_o-x)10^5$ (mole $litre^{-1}$)	$1/a_o-x$ (litre $mole^{-1}$)	$1/a_o-x - 1/a_o$ (litre $mole^{-1}$)
5	40.420			
10	41.440			
15	41.520			
20	41.540	not considered	—	—
25	41.575			
30	41.595			
35	41.605			
40	41.605	10.10723	9893.90	0
43	41.600	10.10594	9895.16	1.26
47	41.595	10.104659	9896.42	2.52
50	41.590	10.10337	9897.68	3.78
55	41.585	10.10209	9898.94	5.04
				$k = 6.00 \times 10^{-3}$ (litre $mole^{-1} sec^{-1}$)

Table 4.5.8

The specific rate constant of the association reaction of $(C_2H_5)_4NPi$ in 80% dioxane-water at 40^oC from conductivity measurement

time (min)	$1/R_{corr} \times 10^6$ (ohm^{-1})	$(a_o-x)10^5$ (mole $litre^{-1}$)	$1/a_o-x$ (litre $mole^{-1}$)	$1/a_o-x - 1/a_o$ (litre $mole^{-1}$)
5	44.430	not considered	—	—
10	45.415			
15	45.500			
20	45.540			
25	45.565	9.82706	10175.98	0
26	45.560	9.82588	10177.20	1.22
28	45.555	9.82470	10178.42	2.44
29	45.550	9.82353	10179.64	3.66
31	45.545	9.82235	10180.86	4.88
32	45.540	9.82117	10182.07	6.09
33	45.535	9.82000	10183.29	4.31
35	45.530	9.81882	10184.51	8.53
36	45.525	9.81765	10185.74	9.76
37	45.520	9.81647	10186.96	10.98
39	45.515	9.81529	10188.18	12.20
40	45.510	9.81412	10189.40	13.42

$k = 1.48 \times 10^{-2}$ (litre $mole^{-1} sec^{-1}$)

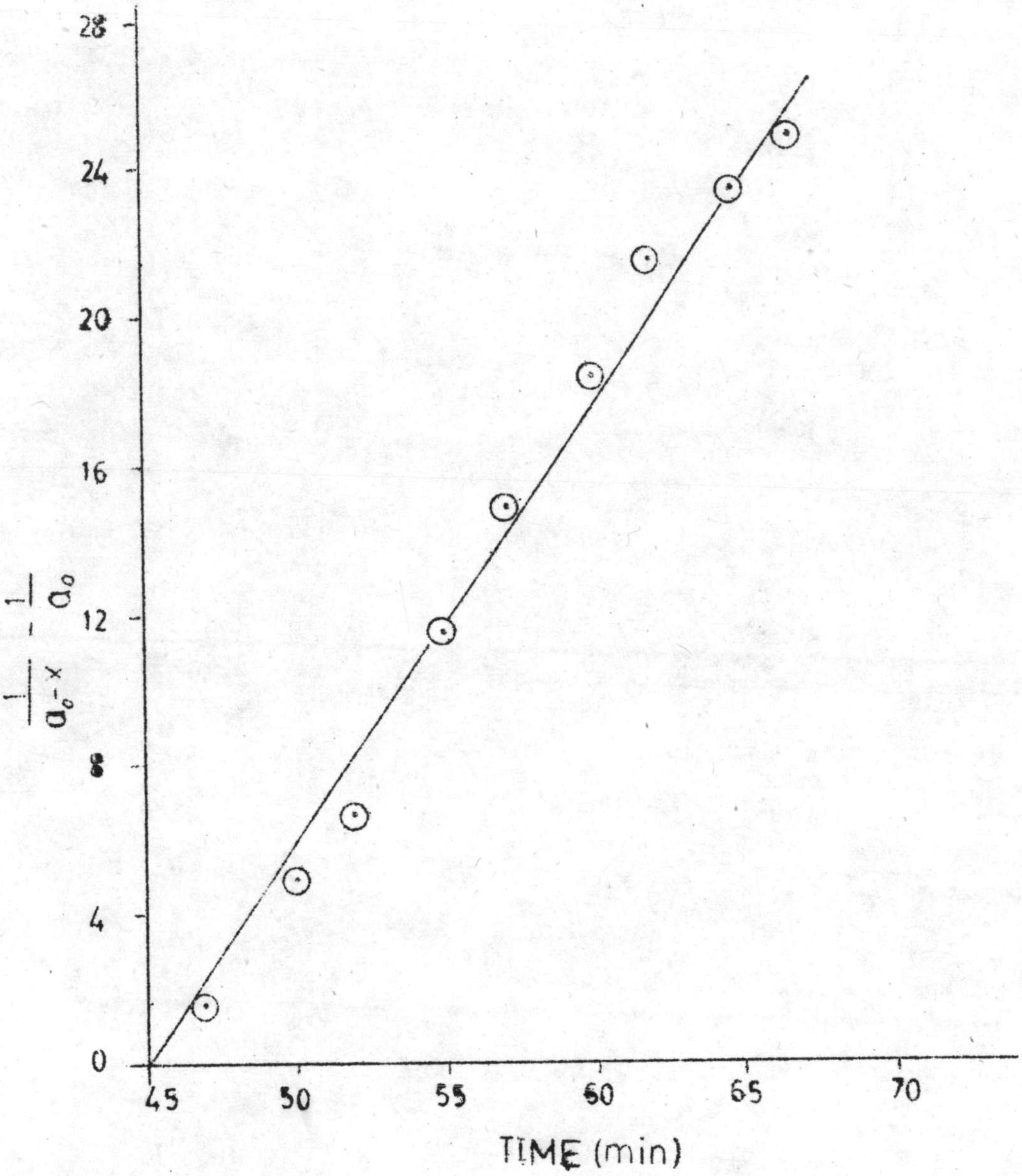

Fig.4.5.1 The second order plot of association reaction of $(CH_3)_4NPi$ in 80% dioxane-water at 25°C

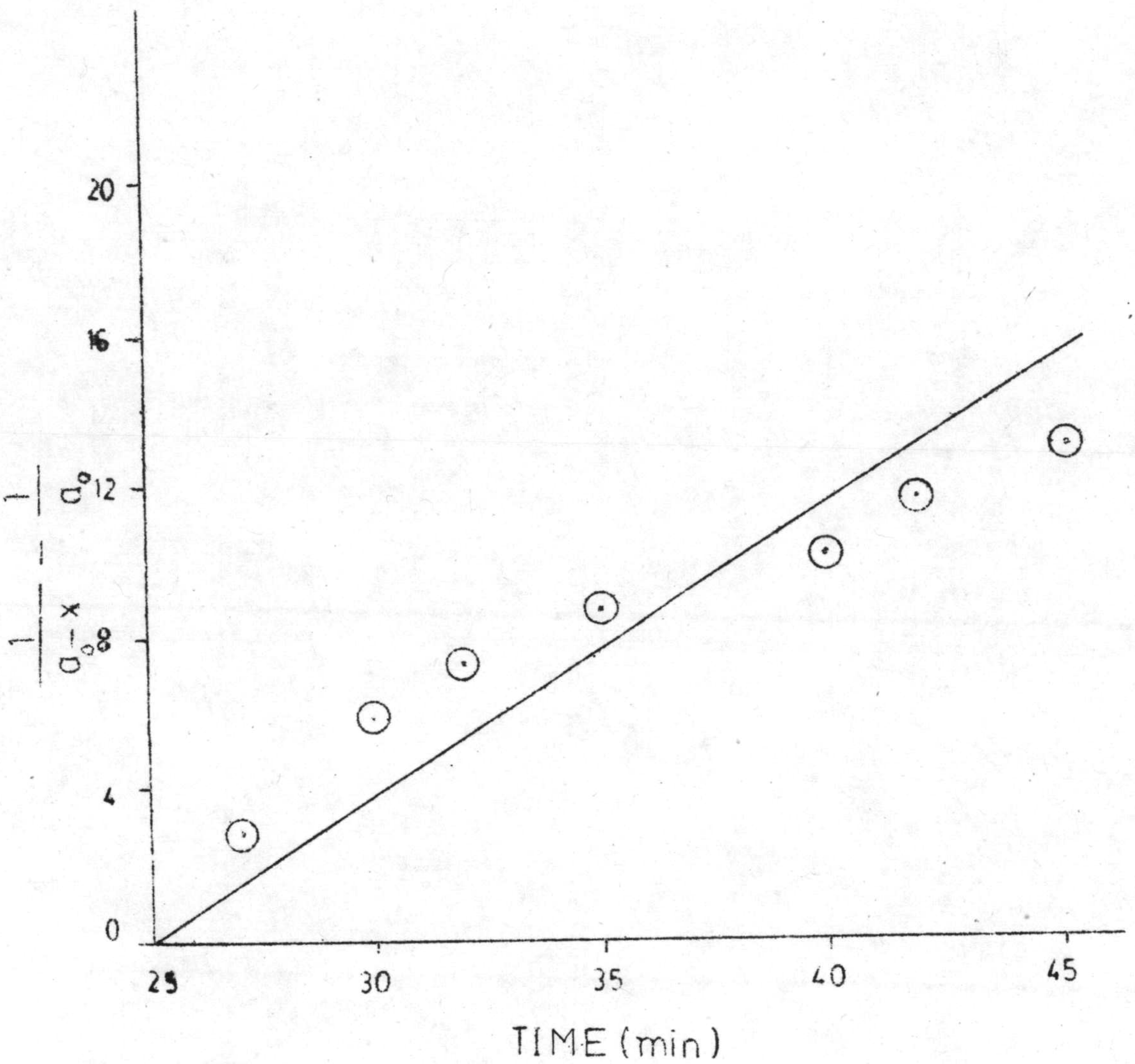

Fig. 4.5.2 The second order plot of association reaction of $(CH_3)_4NPi$ in 80% dioxane-water at 30°C

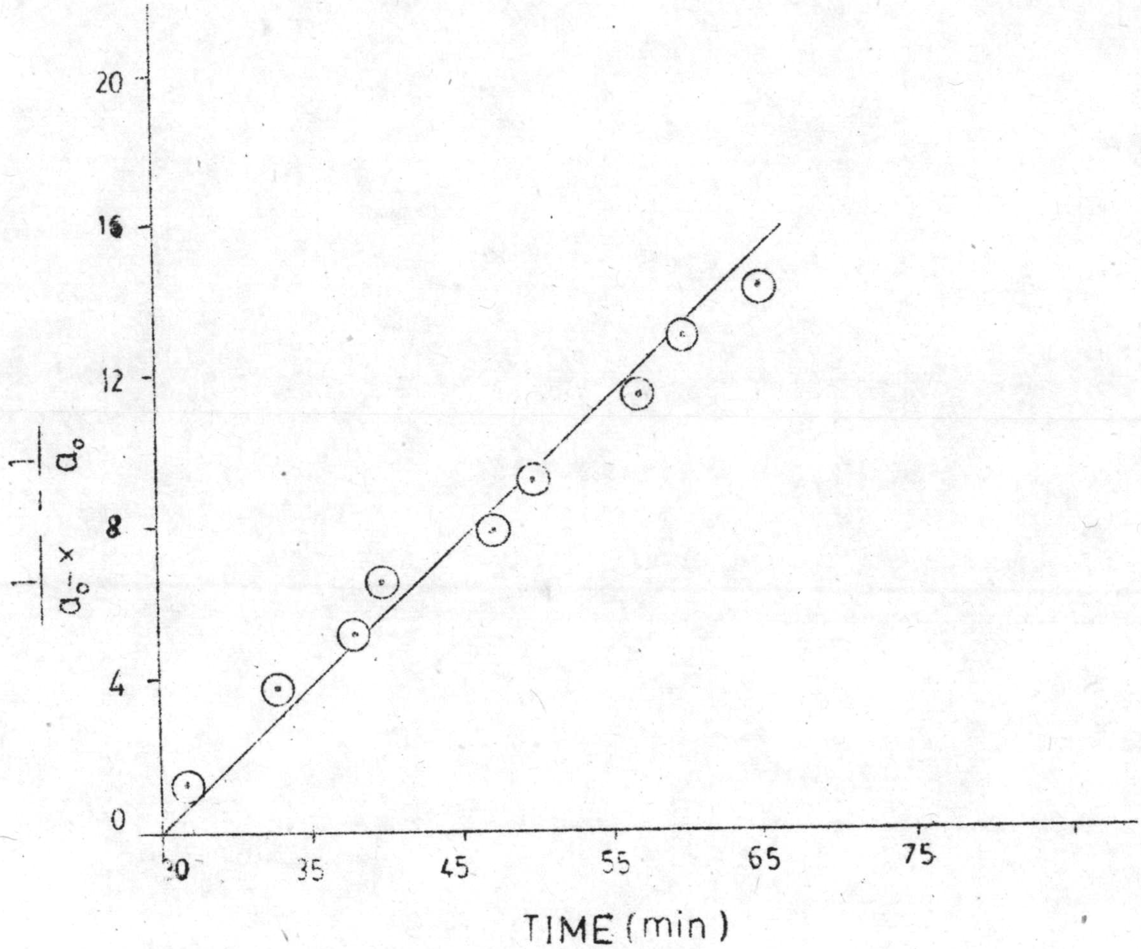

Fig. 4.5.3 The second order plot of association reaction of $(CH_3)_4NPi$ in 80% dioxane-water at 35°C

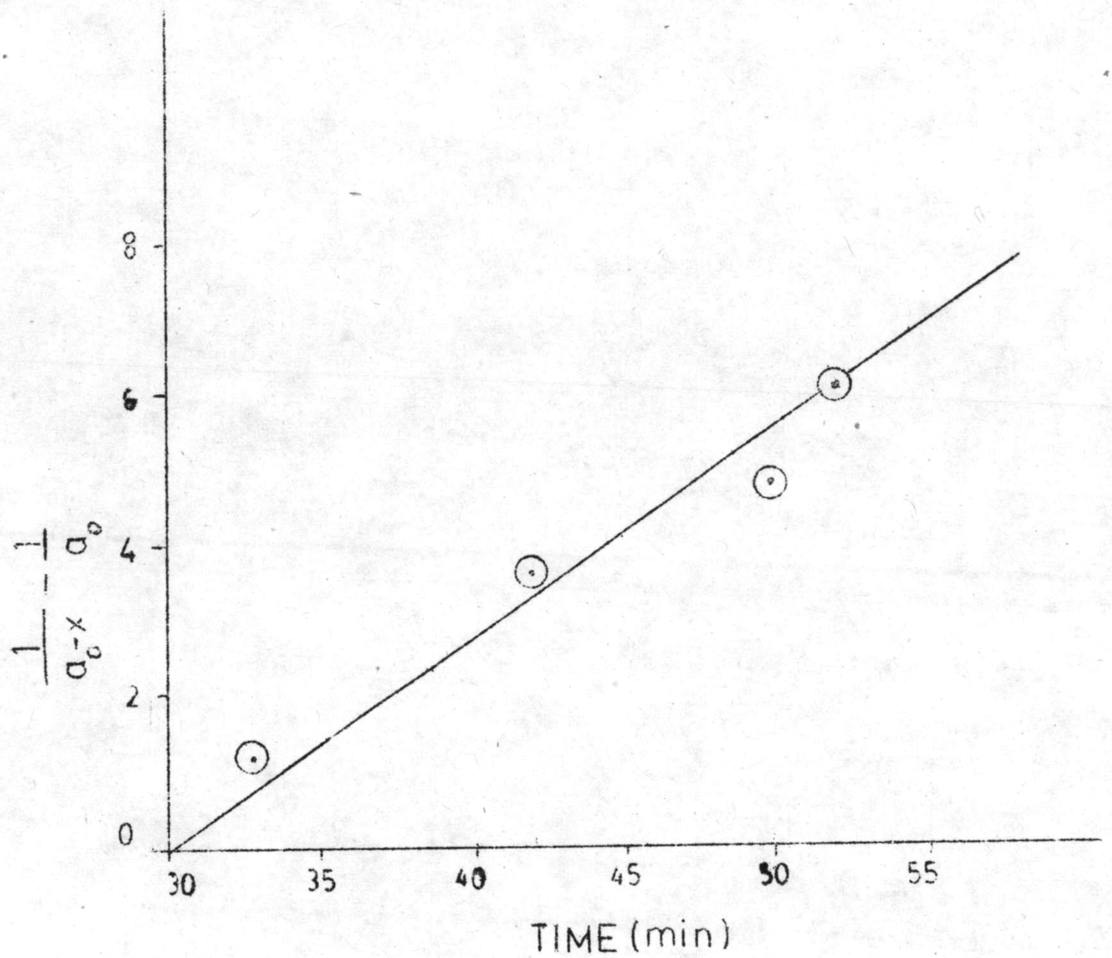

Fig. 4.5.4 The second order plot of association reaction of $(CH_3)_4NPi$ in 80% dioxane-water at 40°C

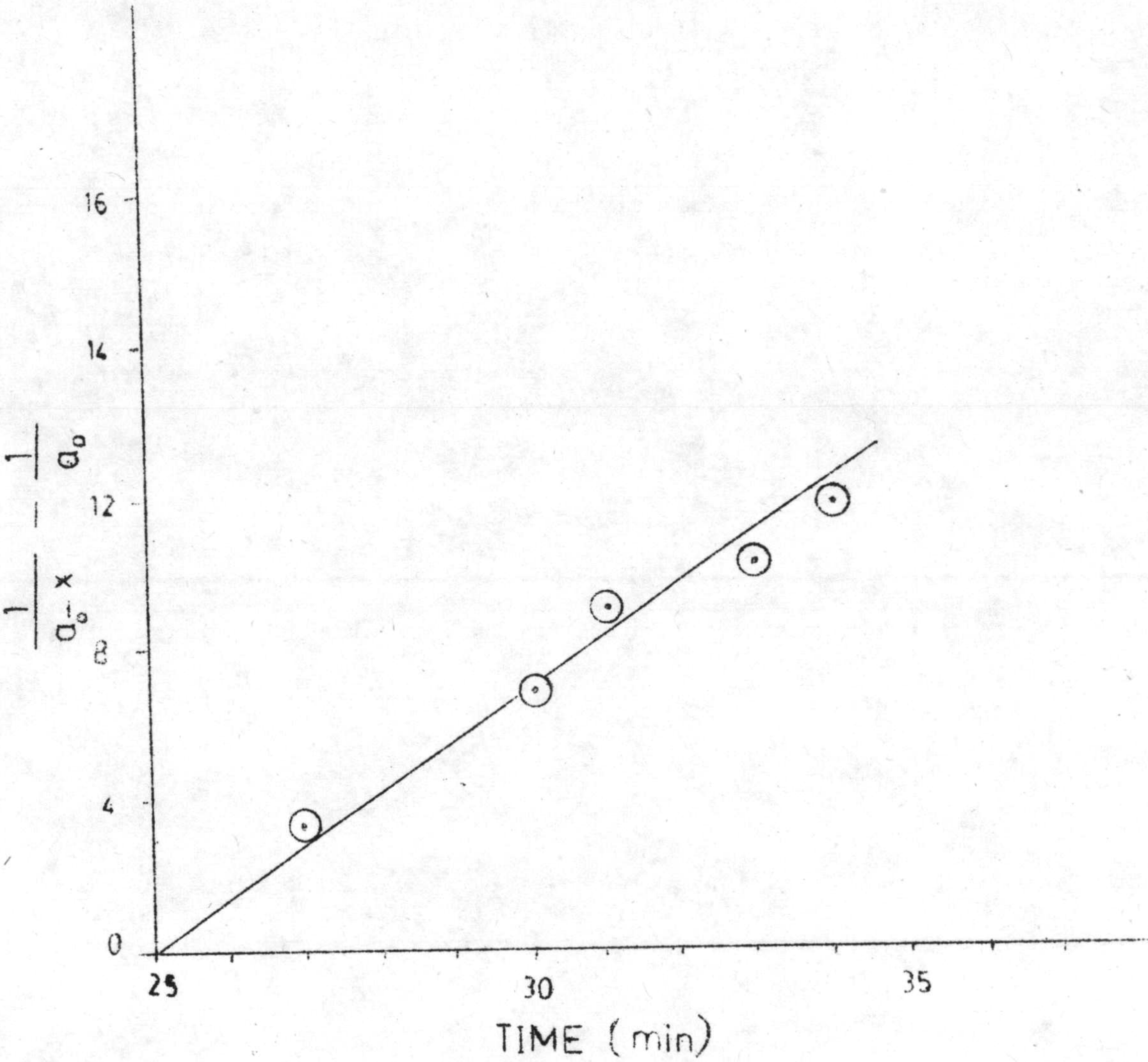

Fig. 4.5.5 The second order plot of association reaction of $(C_2H_5)_4NPi$ in 80% dioxane-water at 25°C

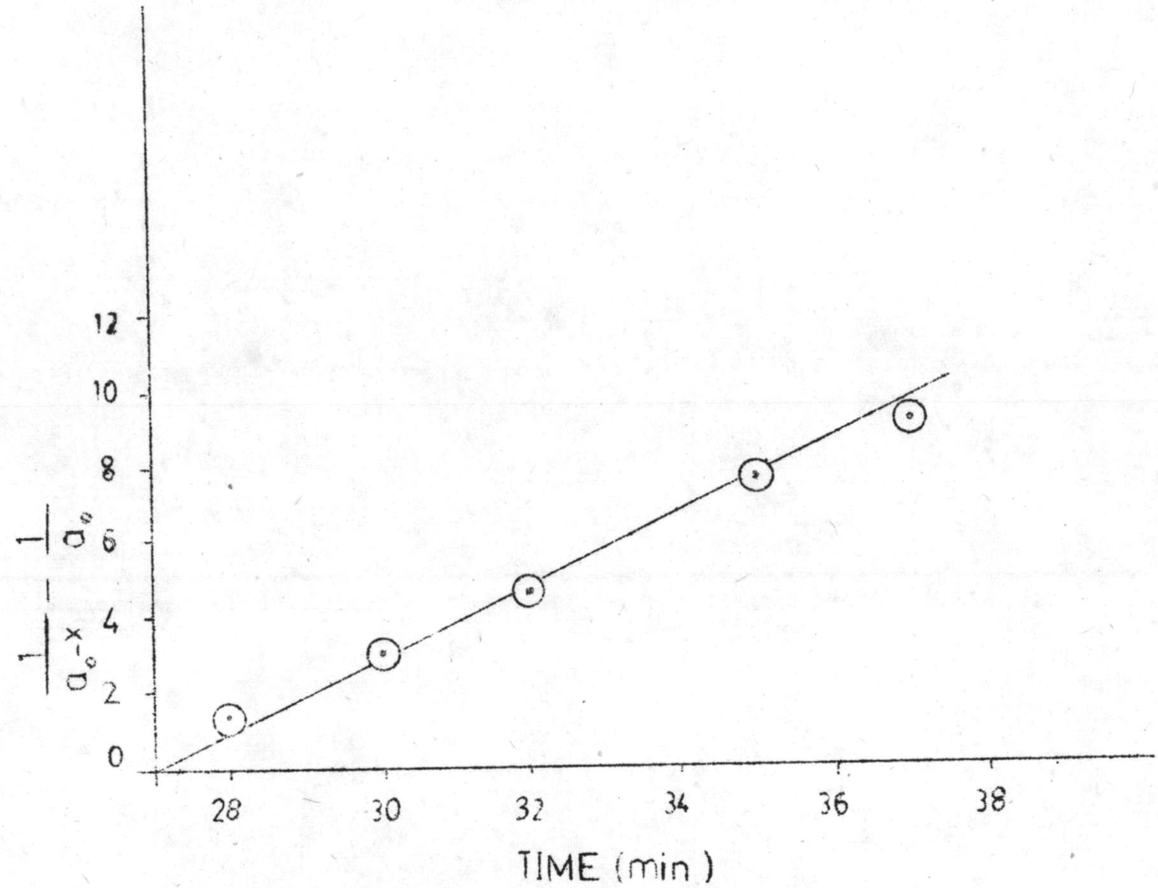

Fig. 4.5.6 The second order plot of association reaction of $(C_2H_5)_4NPi$ in 80% dioxane-water at $30^\circ C$

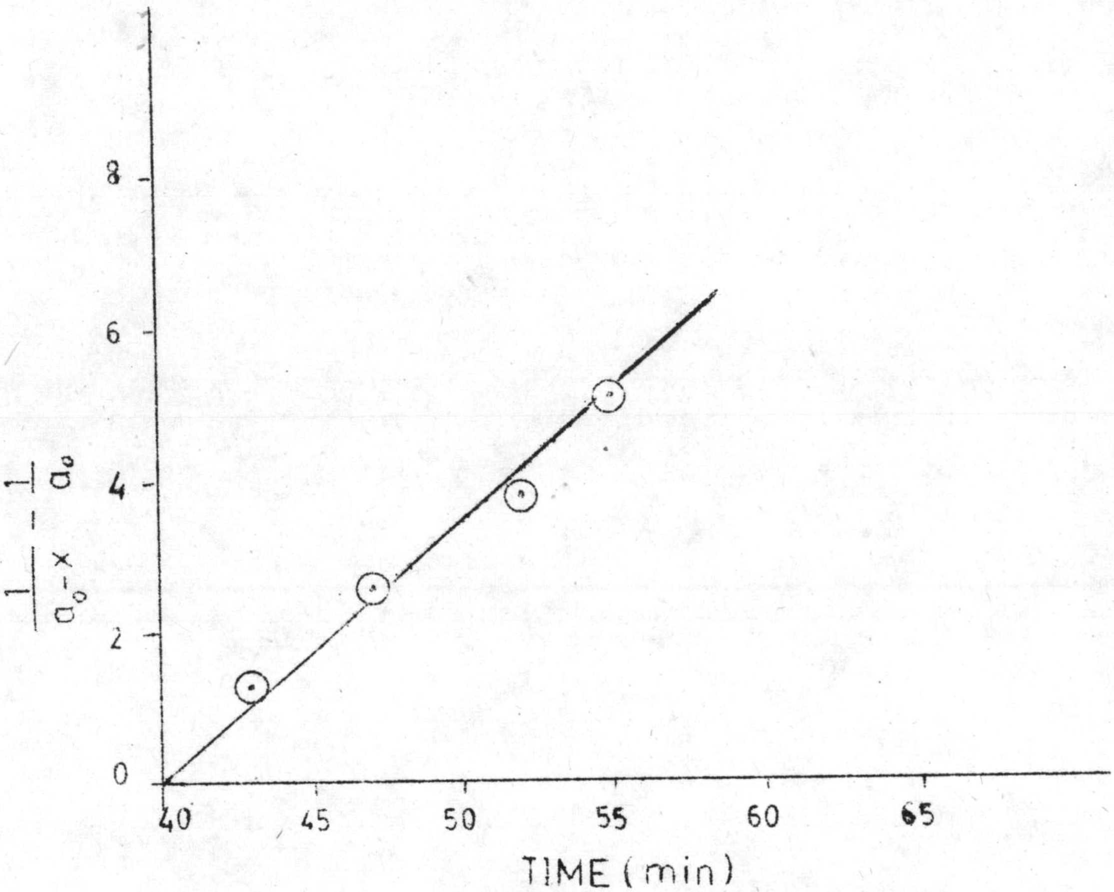

Fig. 4.5.7 The second order plot of association reaction of $(C_2H_5)_4NPi$ in 80% dioxane-water at 35°C

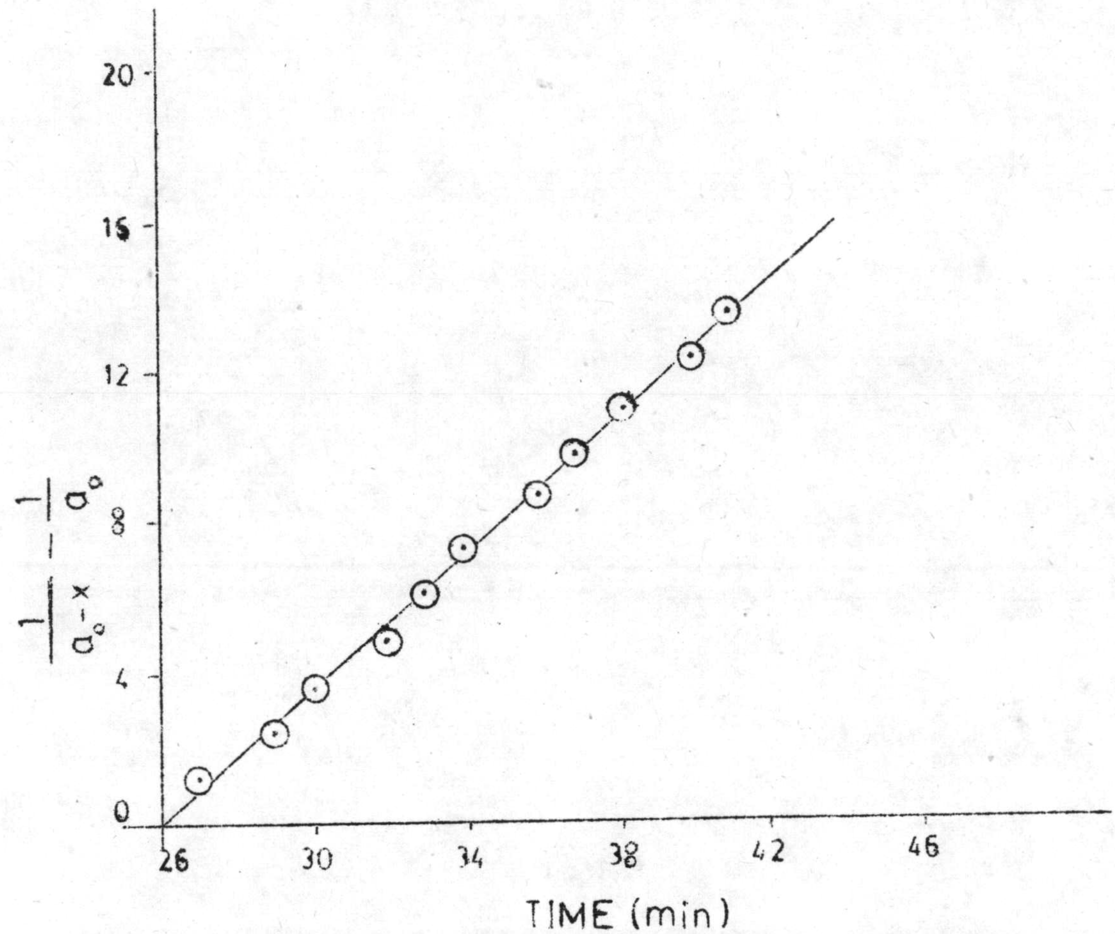

Fig. 4.5.8 The second order plot of association reaction of $(C_2H_5)_4NPi$ in 80% dioxane-water at 40°C