

CHAPTER 4.
CALCULATION

In this chapter, all of the linear curves shown were drawn by applying the least square method.

4.1 Determination of the chemical shift of hydrogen ions

Results shown in Table 3.3 were modified by eqs (A5.1) and (A6.3) of Appendices 5. and 6. respectively, then Table 4.1 and Fig 4.1 were obtained.

Table 4.1 Fraction of proton of hydronium ions and the difference of proton shifts of aqueous hydrochloric acid and water.

| Concentration of hydrochloric acid (mf)* | Fraction of proton of hydronium ions f(1) | $\delta(\text{HCl})$ | $\delta(\text{HCl}) - \delta(\text{H}_2\text{O})^{**}$ |
|--|---|----------------------|--|
| 2.450×10^{-4} | 3.675×10^{-4} | 4.75 | 0.05 |
| 1.216×10^{-3} | 1.825×10^{-3} | 4.92 | 0.22 |
| 2.350×10^{-3} | 3.529×10^{-3} | 5.15 | 0.45 |
| 4.756×10^{-3} | 7.151×10^{-3} | 5.63 | 0.93 |
| 8.850×10^{-3} | 1.292×10^{-2} | 6.43 | 1.73 |

* (mf) signifies the mole fraction.

** $\delta(\text{H}_2\text{O}) = 4.70$ ppm (see page 21)

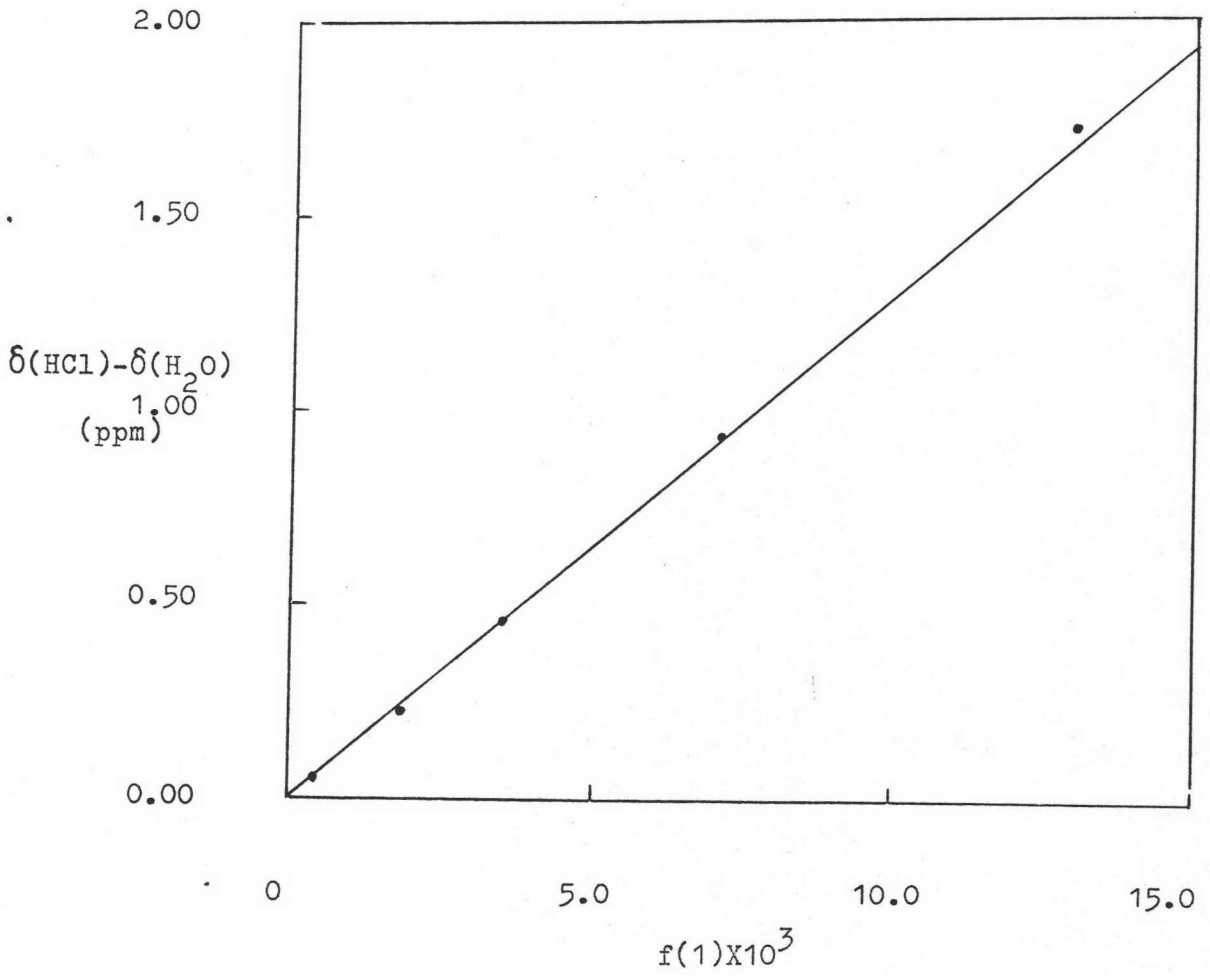


Figure 4.1 Plot of $\delta(\text{HCl}) - \delta(\text{H}_2\text{O})$ against $f(1)$.

The slope of the least square line shown in Fig 4.5 is equal to 134.44 ppm, it is then obvious from eq (2.4) i.e.

$$\delta(\text{HCl}) - \delta(\text{H}_2\text{O}) = \delta(\text{H}_3\text{O}^+) - \delta(\text{H}_2\text{O}) \quad \text{f(1) that}$$

$$\delta(\text{H}_3\text{O}^+) - \delta(\text{H}_2\text{O}) = 134.44 \text{ ppm}$$

$\delta(\text{H}_3\text{O}^+)$ is readily evaluated from the above equation, and is equal to 139.14 ppm. Finally, $\delta(\text{H}^+)$ can be calculated from $\delta(\text{H}^+) = 3\delta(\text{H}_3\text{O}^+) - 2\delta(\text{H}_2\text{O})$ (eq (2.5) page 8) and is equal to 408.02 ppm.

4.2 Determination of the limiting molar conductance of acetic acid

The resistances and the concentrations of aqueous hydrochloric acid, sodium chloride and sodium acetate shown in Tables 3.4, 3.5 and 3.6 were used to calculate the molar conductances of these electrolyte solutions using eqs (A7.11), (A7.2) and (A7.3) of Appendix 7. The resulting molar conductances are shown in Tables 4.2, 4.3 and 4.4 for hydrochloric acid, sodium chloride and sodium acetate respectively. The appropriate Onsager plots are shown in Figs 4.2, 4.3 and 4.4.

Table 4.2 Molar conductances of hydrochloric acid at various concentrations.

| $(c_{\text{HCl}})^{1/2}$ (M ^{1/2}) | $K_{\text{HCl}} \times 10^5$ (ohm ⁻¹ cm ⁻¹) | Λ_{HCl} (ohm ⁻¹ cm ² mole ⁻¹) |
|---|---|---|
| 0.0156 | 8.4690 | 348.80 |
| 0.0110 | 4.7001 | 387.16 |
| 0.0055 | 1.3163 | 432.99 |

Table 4.3 Molar conductances of sodium chloride at various concentrations.

| $(c_{\text{NaCl}})^{1/2}$ (M ^{1/2}) | $K_{\text{NaCl}} \times 10^6$ (ohm ⁻¹ cm ⁻¹) | Λ_{NaCl} (ohm ⁻¹ cm ² mole ⁻¹) |
|--|--|--|
| 0.0316 | 107.4952 | 107.50 |
| 0.0224 | 60.2508 | 120.50 |
| 0.0158 | 31.1714 | 124.68 |
| 0.0112 | 16.6946 | 133.56 |
| 0.0079 | 8.7526 | 140.04 |
| 0.0056 | 4.4759 | 143.46 |

Table 4.4 Molar conductances of sodium acetate at various concentrations.

| $(C_{\text{NaOAc}})^{1/2}$ ($M^{1/2}$) | $K_{\text{NaOAc}} \times 10^5$ ($\text{ohm}^{-1} \text{cm}^{-1}$) | Λ_{NaOAc} ($\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$) |
|---|--|--|
| 0.0704 | 49.3663 | 99.54 |
| 0.0498 | 25.0667 | 101.09 |
| 0.0352 | 12.6502 | 102.03 |
| 0.0316 | 10.2257 | 102.22 |
| 0.0224 | 5.1282 | 102.52 |
| 0.0158 | 2.5737 | 102.91 |

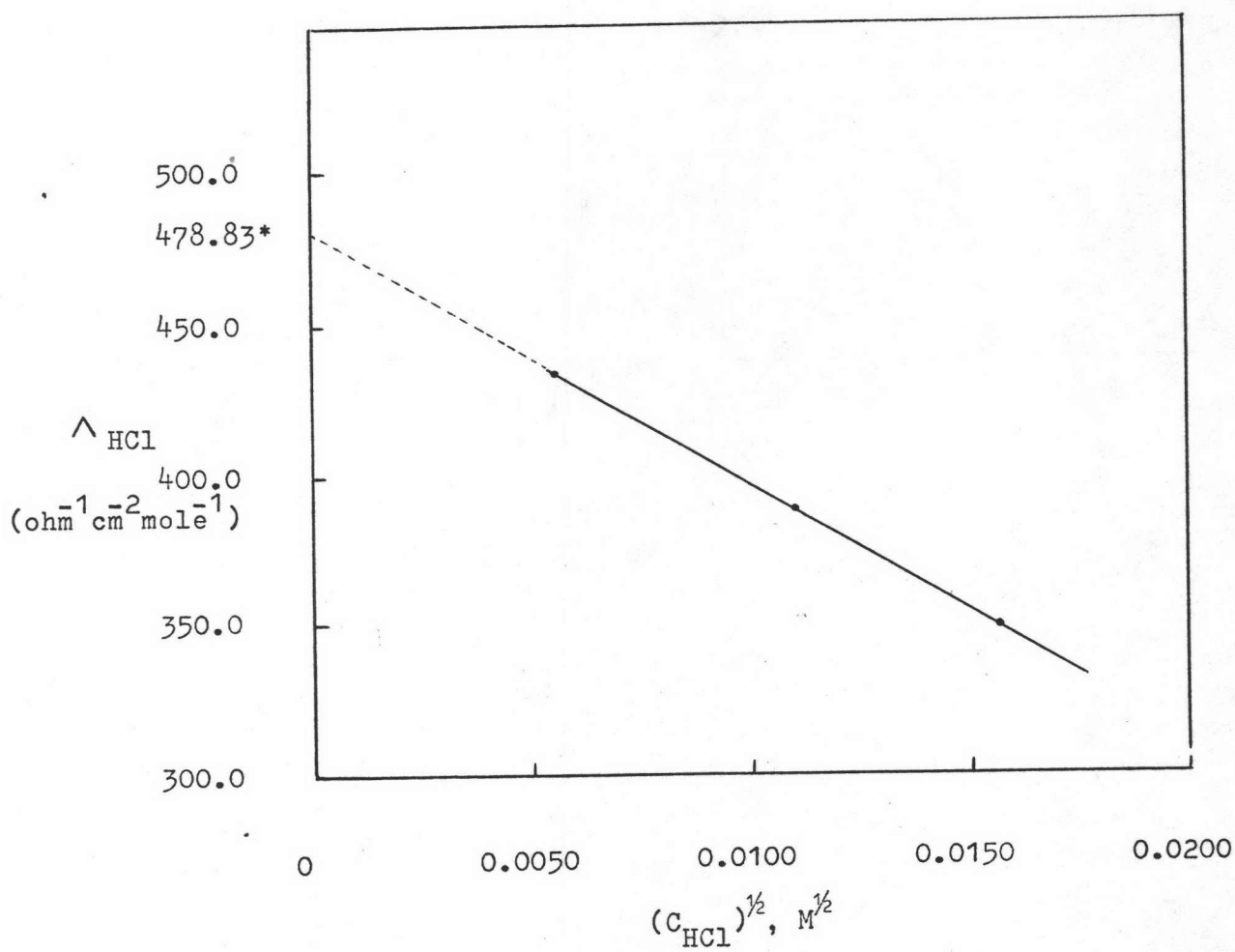


Figure 4.2 The Onsager plot of hydrochloric acid.

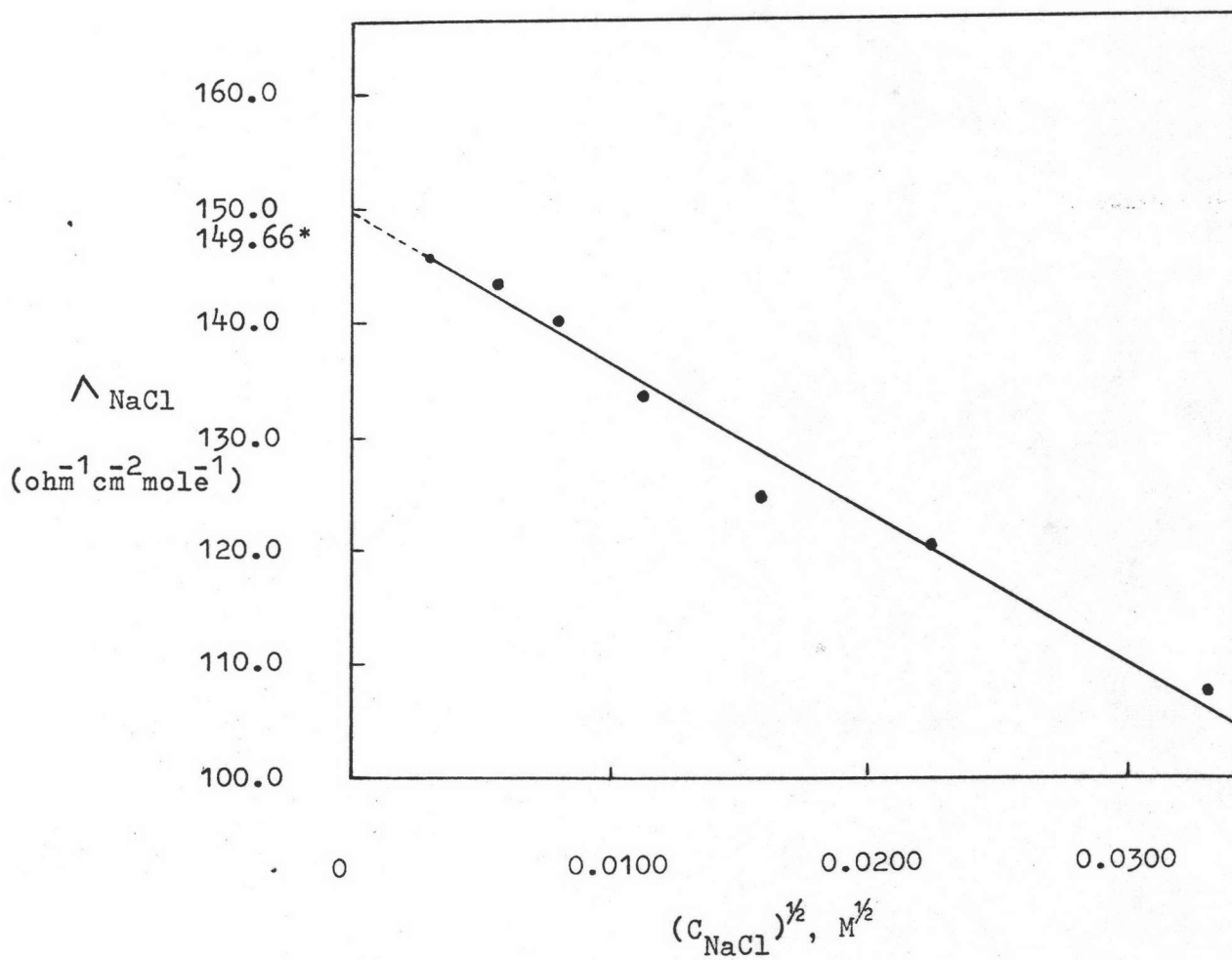


Figure 4.3 The Onsager plot of sodium chloride.

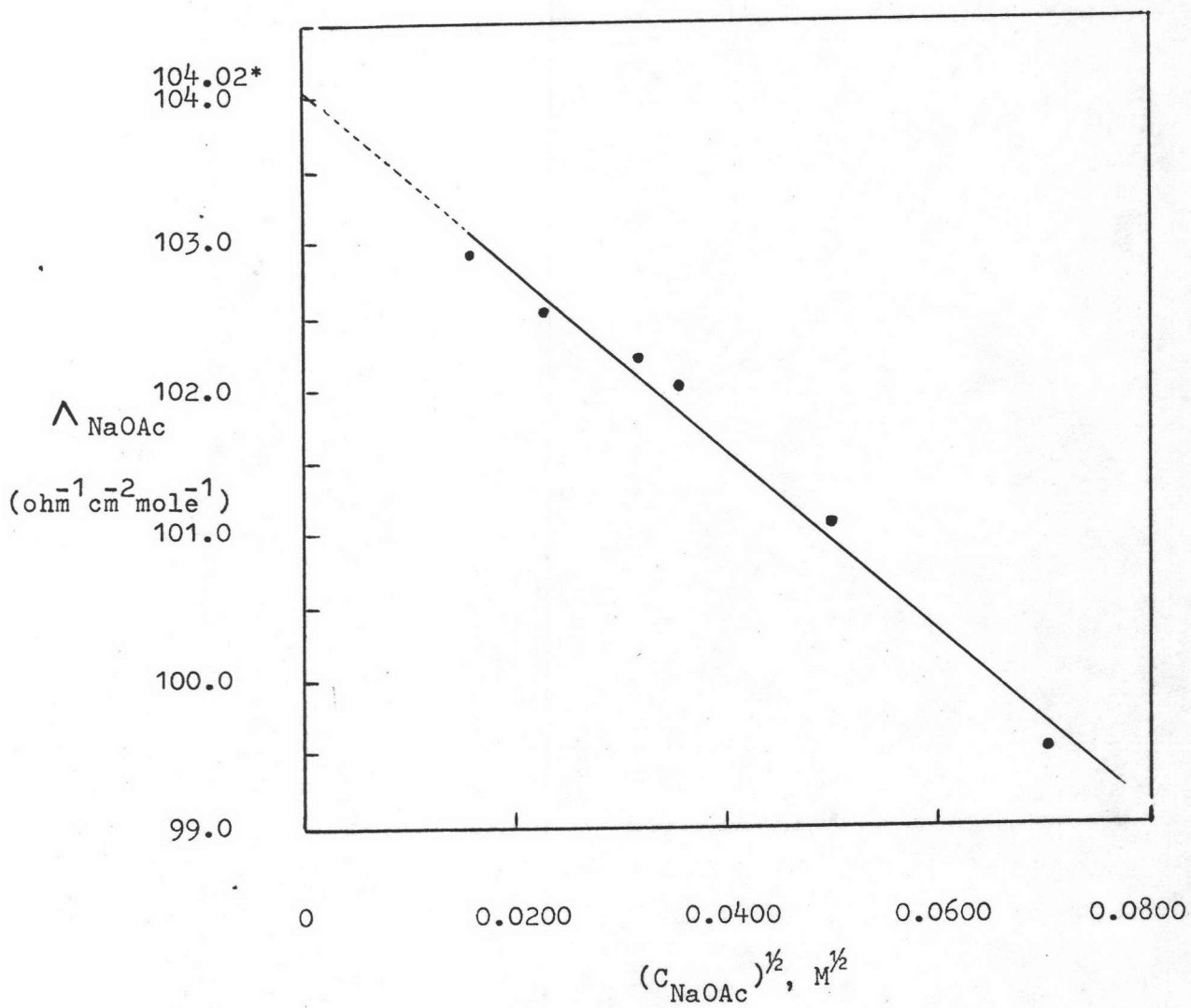


Figure 4.4 The Onsager plot of sodium acetate.

The limiting molar conductance of the electrolytes in question are obtained by the extrapolation of the straight line in each figure to the ordinate. The intercept on the ordinate was read and taken as Λ° (according to the Onsager equation $\Lambda = \Lambda^{\circ} + b\sqrt{c}$). Then

$$\text{From Fig 4.2 } \Lambda_{\text{HCl}}^{\circ} = 478.83 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$$

$$\text{From Fig 4.3 } \Lambda_{\text{NaCl}}^{\circ} = 149.66 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$$

$$\text{From Fig 4.4 } \Lambda_{\text{NaOAc}}^{\circ} = 104.02 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$$

The limiting molar conductance of acetic acid, $\Lambda_{\text{HOAc}}^{\circ}$ a weak electrolyte can be calculated from Kohlrausch's equation (eq(A7.8) of Appendix 7). The calculation gave

$$\Lambda_{\text{HOAc}}^{\circ} \text{ (at } 32^{\circ}\text{C)} = 433.19 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$$

4.3 Calculation involving data for the computer program

Data in Tables 3.7 and 3.8 were used in conjunction with eq(A5.8) of Appendix 5 to calculate the molar concentration of acetic acid. They were also fed into eqs(A7.1), (A7.2) and (A7.3) of Appendix 7 in order to calculate the molar conductance of acetic acid. Results are tabulated in Tables 4.5 and 4.6.

Table 4.5 Molar concentrations and molar conductances of acetic acid.

| Concentration of acetic acid (M) | $K_{\text{HOAc}} \times 10^4$ ($\text{ohm}^{-1} \text{cm}^{-1}$) | Λ_{HOAc} ($\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$) |
|----------------------------------|---|---|
| 14.1032 | 1.0637 | 7.5422 |
| 13.2442 | 2.0217 | 15.2648 |
| 12.8622 | 2.4582 | 19.1118 |
| 12.3121 | 3.2013 | 26.0012 |
| 11.7688 | 4.0285 | 34.2303 |
| 11.4121 | 4.6163 | 40.4509 |
| 11.0546 | 5.2536 | 47.5241 |
| 10.6946 | 5.9184 | 55.3401 |
| 10.5328 | 6.2431 | 59.2729 |
| 8.7127 | 10.1221 | 116.1764 |

Table 4.6 Molar concentrations and molar conductances of acetic acid.

| Concentration of acetic acid (M) | K_{HOAc} ($\text{ohm}^{-1}\text{cm}^{-1}$) | Λ_{HOAc} ($\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$) |
|----------------------------------|--|---|
| 16.8726 | - | - |
| 16.1334 | 8.7626×10^7 | 5.4313×10^5 |
| 15.3622 | 1.1560×10^5 | 7.5248×10^4 |
| 14.6290 | 4.5751×10^5 | 3.1274×10^3 |
| 6.9262 | 1.2453×10^3 | 1.7979×10^1 |
| 5.1482 | 1.5785×10^3 | 3.0662×10^1 |
| 3.3952 | 1.7816×10^3 | 5.2475×10^1 |
| 1.6776 | 1.6587×10^3 | 9.8873×10^1 |
| 0.8338 | 1.3249×10^3 | 1.5890 |
| 0.3322 | 8.9523×10^4 | 2.6948 |
| 0.1658 | 6.3112×10^4 | 3.8065 |
| 0.0331 | 3.2973×10^4 | 9.9236 |
| 0.006628 | 1.4504×10^4 | 21.7864 |
| 0.001326 | 5.3823×10^5 | 40.4385 |
| 0.000265 | 2.3896×10^5 | 90.1260 |
| 0.000053 | 8.7869×10^6 | 165.6968 |

The mole fraction of acetic acid, X_{AS} was converted from the weight percent using eq (A5.2) of Appendix 5. The degree of dissociation of acetic acid, α_A was evaluated from the limiting molar conductance of acetic acid (from page 42) and the molar conductance of acetic acid (from Tables 4.5 and 4.6) using eq (A7.4) of Appendix 7.

The mole fraction of hydrogen ions (simple type, X_{HS}^\ddagger determined from α_A using eq (A7.6) of Appendix 7 was converted to the fraction of proton of hydrogen ions, $f(H^+)$ by eq (A6.3) of Appendix 6. Both are shown together with X_{AS} , α_A in Tables 4.7 and 4.8.

Table 4.7 Fraction of protons of hydrogen ions at various concentrations.

| X_{AS} | $\alpha_A \times 10^5$ | $X_{HS}^\ddagger \times 10^6$ | $f(H^+) \times 10^6$ |
|----------|------------------------|-------------------------------|----------------------|
| 0.5468 | 1.7411 | 9.5203 | 6.5513 |
| 0.4761 | 3.5238 | 16.7768 | 11.0104 |
| 0.4489 | 4.4119 | 19.8050 | 12.7685 |
| 0.4116 | 6.0023 | 24.7055 | 15.5519 |
| 0.3783 | 7.9019 | 29.8929 | 19.4352 |
| 0.3576 | 9.3379 | 33,3923 | 20.3319 |
| 0.3379 | 10.9707 | 37.0700 | 22.3045 |
| 0.3192 | 12.7750 | 40.7778 | 24,2601 |
| 0.3110 | 13.6829 | 42.5538 | 25.2004 |
| 0.2300 | 26.8188 | 61.6832 | 34.8548 |

Table 4.8 Fraction of protons of hydrogen ions at various concentrations.

| X_{AS} | α_A | X_{HS} | $f(H^+)$ |
|-------------------------|-------------------------|-------------------------|-------------------------|
| 1.0000 | 0 | 0 | 0 |
| 0.8506 | 1.2538×10^{-7} | 1.0665×10^{-7} | 9.2788×10^{-8} |
| 0.7296 | 1.7371×10^{-6} | 1.2674×10^{-6} | 9.9764×10^{-7} |
| 0.6294 | 7.2195×10^{-6} | 4.5440×10^{-6} | 3.3153×10^{-6} |
| 0.1666 | 4.1504×10^{-4} | 6.9146×10^{-5} | 3.7715×10^{-5} |
| 0.1138 | 7.0782×10^{-4} | 8.0550×10^{-5} | 4.2705×10^{-5} |
| 0.0697 | 1.2114×10^{-3} | 8.4434×10^{-5} | 4.3741×10^{-5} |
| 0.0322 | 2.2824×10^{-3} | 7.3493×10^{-5} | 3.7348×10^{-5} |
| 1.5531×10^{-2} | 3.6681×10^{-3} | 5.6865×10^{-5} | 2.8654×10^{-5} |
| 6.0802×10^{-3} | 6.2208×10^{-3} | 3.7947×10^{-5} | 1.9032×10^{-5} |
| 3.0186×10^{-3} | 8.7871×10^{-3} | 2.6361×10^{-5} | 1.3200×10^{-5} |
| 6.0034×10^{-4} | 2.2908×10^{-2} | 1.3752×10^{-5} | 6.8781×10^{-6} |
| 1.1993×10^{-4} | 5.0293×10^{-2} | 6.0316×10^{-6} | 3.0160×10^{-6} |
| 2.3981×10^{-5} | 9.3350×10^{-2} | 2.2386×10^{-6} | 1.1193×10^{-6} |
| 4.7960×10^{-6} | 2.0805×10^{-1} | 9.9781×10^{-7} | 4.4891×10^{-7} |
| 9.5920×10^{-7} | 3.8250×10^{-1} | 3.6689×10^{-7} | 1.8344×10^{-7} |

The α_A (from Table 4.8) and C_A (from Table 4.5) were used to calculate the molar conductance of hydrogen ions, C_{H^+} . The density of aqueous acetic acid (from Tables 3.7 and 3.8), C_A and C_{H^+} were used to calculate β in eq (A4.2) of Appendix 4. The ratio of the C_{H^+}/β are contained in Tables 4.9 and 4.10. Data in Table 4.9 was used in the computer program I (see Appendix 8) whereas those in Table 4.10 was used in the computer program II (also Appendix 8).

Table 4.9 The ratio of C_{H^+}/β for using in the computer program I.

| Concentration of hydrogen ions, C_{H^+} $\times 10^4$, (M) | β (M) | C_{H^+}/β $\times 10^5$ |
|---|----------------|----------------------------------|
| 2.4555 | 11.6895 | 2.1006 |
| 4.6670 | 14.5724 | 3.2026 |
| 5.6747 | 15.7914 | 3.5935 |
| 7.3901 | 17.6047 | 4.1978 |
| 9.2996 | 19.3398 | 4.8085 |
| 10.6565 | 20.5023 | 5.1977 |
| 12.1277 | 21.6619 | 5.5786 |
| 13.6623 | 22.8132 | 5.9888 |
| 14.4119 | 23.3310 | 6.1772 |
| 23.3664 | 29.0715 | 8.0376 |

Table 4.10 The ratio of C_{H^+}/β for using in the computer program II.

| Concentration of hydrogen ions, C_{H^+} (M) | β (M) | C_{H^+}/β |
|---|-------------------------|----------------------|
| 0 | 2.0556×10^{-5} | 0 |
| 2.0228×10^{-6} | 2.8327 | 7.1408×10^7 |
| 2.6686×10^{-5} | 5.6945 | 4.6863×10^6 |
| 1.0561×10^{-4} | 8.6129 | 1.2262×10^5 |
| 2.8747×10^{-3} | 34.6658 | 8.2927×10^5 |
| 3.6440×10^{-3} | 40.0823 | 9.0913×10^5 |
| 4.1129×10^{-3} | 45.3148 | 9.0763×10^5 |
| 3.8290×10^{-3} | 50.3777 | 7.6006×10^5 |
| 3.0590×10^{-3} | 52.8578 | 5.7872×10^5 |
| 2.0665×10^{-3} | 54.3070 | 3.8052×10^5 |
| 1.4569×10^{-3} | 54.7776 | 2.6597×10^5 |
| 7.5825×10^{-4} | 55.1744 | 1.3743×10^5 |
| 3.3334×10^{-4} | 55.2619 | 6.0320×10^6 |
| 1.2378×10^{-4} | 55.2792 | 2.2392×10^6 |
| 5.5133×10^{-5} | 55.2826 | 9.9729×10^7 |
| 2.0272×10^{-5} | 55.3832 | 3.6669×10^7 |

The fraction of protons of water, $f(\text{H}_2\text{O})$ was tabulated in Tables 4.11 and 4.12. These values were resulted from the calculation using eq (A6.2) of Appendix 6 and mole fraction of acetic acid. These two Tables are also containing other necessary quantities for the computer programs I and II which have been shown in previous Tables.

Table 4.11 The collection of necessary data for using in the computer program I.

| $\delta^{\text{obsd}}^{\text{a}}$ (ppm) | X_{AS}^{b} | $C_{\text{H}^+}/\beta^{\text{c}}$ $\times 10^7$ | $f(\text{H}_2\text{O})$ | $f(\text{H}^+)^{\text{b}}$ $\times 10^6$ |
|--|----------------------------|--|---|---|
| 6.87 | 0.5468 | 4.5444 | 0.6236 | 6.5513 |
| 6.48 | 0.4761 | 8.5890 | 0.6875 | 11.0104 |
| 6.34 | 0.4489 | 10.4297 | 0.7106 | 12.7685 |
| 6.20 | 0.4116 | 13.5423 | 0.7409 | 15.5519 |
| 5.96 | 0.3783 | 17.0092 | 0.7667 | 18.4352 |
| 5.92 | 0.3576 | 19.4585 | 0.7823 | 20.3319 |
| 5.80 | 0.3379 | 22.1102 | 0.7967 | 22.3045 |
| 5.72 | 0.3192 | 24.8761 | 0.8101 | 24.2601 |
| 5.68 | 0.3110 | 26.2258 | 0.8158 | 25.2004 |
| 5.42 | 0.2300 | 42.3096 | 0.8696 | 34.8548 |
| a from Table 3.1 | | | $\delta(\text{H}_2\text{O})^{\text{a}}$ | $\delta(\text{H}^+)^{\text{d}}$ |
| b from Table 4.7 | | | (ppm) | (ppm) |
| c from Table 4.9 | | | | |
| d from page 36 | | | 4.70 | 408.02 |

Table 4.12 The collection of necessary data for using in the computer program II.

| X_{AS}^e | C_{H^+}/β^f | $f(H_2O)$ | $f(H^+)^e$ |
|----------------------|----------------------|-----------|----------------------|
| 1.0000 | 0 | 0 | 0 |
| 0.8506 | 7.1408×10^7 | 0.2600 | 9.2788×10^8 |
| 0.7296 | 4.6863×10^6 | 0.4257 | 9.9764×10^7 |
| 0.6294 | 1.2262×10^5 | 0.5408 | 3.3153×10^6 |
| 0.1666 | 8.2927×10^5 | 0.9091 | 3.7715×10^5 |
| 0.1138 | 9.0913×10^5 | 0.9397 | 4.2705×10^5 |
| 0.0697 | 9.0763×10^5 | 0.9639 | 4.3741×10^5 |
| 0.0322 | 7.6006×10^5 | 0.9838 | 3.7348×10^5 |
| 1.5531×10^2 | 5.7872×10^5 | 0.9922 | 2.8654×10^5 |
| 6.0802×10^3 | 3.8052×10^5 | 0.9969 | 1.9032×10^5 |
| 3.0186×10^3 | 2.6597×10^5 | 0.9985 | 1.3200×10^5 |
| 6.0034×10^4 | 1.3743×10^5 | 0.999699 | 6.8781×10^6 |
| 1.1993×10^4 | 6.0320×10^6 | 0.999940 | 3.0160×10^6 |
| 2.3981×10^5 | 2.2392×10^6 | 0.999988 | 1.1193×10^6 |
| 4.7960×10^6 | 9.9729×10^7 | 0.999997 | 4.4891×10^7 |
| 9.5920×10^7 | 3.6669×10^7 | 0.999999 | 1.8344×10^7 |

e from Table 4.8

f from Table 4.10

4.4 Calculation of the equilibrium constants by the computer

In the computer program I (shown in Appendix 8) used was made of the data from Table 4.11, however six variables namely the set of equilibrium constants (K , K_1 , K_c) and the set of chemical shifts ($\delta(E)$, $\delta(I)$, $\delta(C)$) were still unknown. The solution of the set of equilibrium constants must be treated simultaneously with the set of chemical shifts by the iteration method as described stepwisely below.

Step I This step was devised in such a way that the "best approximate value" of the equilibrium constant set was obtained through the pre-assigned value set of the chemical shifts which was fed into the computer program I simultaneously with the assigned value of the equilibrium constant set. As a start, the assigned chemical shift set* i.e. $\delta(E) = 6.63$ ppm, $\delta(I) = 9.72$ ppm and $\delta(C) = 11.08$ ppm was obtained from reference 13 whereas the assigned equilibrium constant set was obtained by the "trial and error" process. The "best approximate value" means the set with the minimum standard deviation (σ) and this set was used in step II.

Step II The "best approximate value" of a set of chemical shifts was achieved in this step. Repetition of step I was made. This time the best set of equilibrium constants from step I was fed to the computer program I simultaneously with a set of chemical shifts which was then obtained by the trial and error process. The program was so written that a set of

* down field shift from methyl proton of TMS (at 31°C)

chemical shifts with a minimum standard deviation was obtainable.

Step III The identical procedure as (I) was performed. The only difference was to use the "best approximate value" of a set of chemical shifts from (II) instead of taking from the reference. It is quite obvious that this step should yield a more accurate value of an equilibrium constant set.

Step IV The processes in step II and III were alternately treated until the values of the equilibrium constants and the chemical shifts were constant (under the minimum condition of the standard deviation). Those values are as given below.

$$\begin{aligned}
 \delta(E) &= 5.02 \text{ ppm} \\
 \delta(I) &= 7.17 \text{ ppm} \\
 \delta(C) &= 14.77 \text{ ppm} \\
 K &= 54.4 \text{ mf}^{-1} \\
 K_1 &= 141.7 \text{ mf}^{-1} \\
 K_c &= 262.5 \text{ mf}^{-1} \\
 \sigma &= \pm 0.02287
 \end{aligned}$$

4.5 Calculation of the mole fraction and other results

The values of the equilibrium constants, the chemical shifts (both from page 52) and the data from Table 4.1 were processed in the computer program II. The calculated chemical shifts (δ) obtained from the computer programs I and II are tabulated in Tables 4.13 and 4.14 respectively. The mole fraction (X) and the mole percent (%X) of the hydrogen-bonded species are shown in Tables 4.15 and 4.16 respectively. The results of the fraction of protons of species group (f) are given in Table 4.17.

Table 4.13 The chemical shifts (observed and calculated) at various concentrations of acetic acid (from the computer program I)

| Concentration of acetic acid | | δ_{obsd} | δ_{calcd} | $\Delta\delta$ |
|------------------------------|--------|------------------------|-------------------------|----------------|
| (%w/w) | (mf) | (ppm) | (ppm) | (%) |
| 80.1 | 0.5468 | 6.87 | 6.87 ₃ | -0.044 |
| 75.2 | 0.4761 | 6.48 | 6.48 ₅ | -0.077 |
| 73.1 | 0.4489 | 6.34 | 6.34 ₂ | -0.032 |
| 70.0 | 0.4116 | 6.20 | 6.15 ₂ | +0.758 |
| 67.0 | 0.3783 | 5.96 | 5.99 ₁ | -0.520 |
| 65.0 | 0.3576 | 5.90 | 5.89 ₆ | +0.068 |
| 63.0 | 0.3379 | 5.80 | 5.80 ₉ | -0.155 |
| 61.0 | 0.3192 | 5.72 | 5.72 ₉ | -0.157 |
| 60.1 | 0.3110 | 5.68 | 5.69 ₅ | -0.264 |
| 50.0 | 0.2300 | 5.42 | 5.38 ₈ | +0.572 |

Standard deviation = 0.02287

Table 4.14 The chemical shifts (observed and calculated) at various concentrations of acetic acid (from the computer program II)

| Concentration of acetic acid | | δ^{obsd} | δ^{calcd} | $\Delta\delta$ |
|------------------------------|-----------|------------------------|-------------------------|----------------|
| (%w/w) | (mf) | (ppm) | (ppm) | (%) |
| 100.0 | 1.0000 | 11.06 | 7.13 ₁ | +35.524 |
| 95.0 | 0.8506 | - | 7.89 ₁ | - |
| 90.0 | 0.7296 | 8.02 | 7.74 ₉ | +3.379 |
| 85.0 | 0.6294 | 7.40 | 7.31 ₉ | +1.094 |
| 40.0 | 0.1666 | 5.20 | 5.18 ₄ | +0.308 |
| 30.0 | 0.1138 | 5.02 | 5.03 ₀ | -0.199 |
| 20.0 | 0.0697 | 4.89 | 4.90 ₇ | -0.378 |
| 10.0 | 0.0322 | 4.80 | 4.80 ₀ | -0.000 |
| 5.0 | 0.0155 | - | 4.75 ₀ | - |
| 1.0 | 0.0061 | - | 4.72 ₀ | - |
| 2.0×10^{-1} | 0.0030186 | - | 4.71 ₁ | - |
| 4.0×10^{-2} | 0.0006003 | - | 4.70 ₃ | - |
| 8.0×10^{-3} | 0.0001199 | - | 4.70 ₁ | - |
| 1.6×10^{-3} | 0.0000239 | - | 4.70 | - |
| 3.2×10^{-4} | 0.0000048 | - | 4.70 | - |
| 6.4×10^{-5} | 0.0000009 | - | 4.70 | - |

Table 4.15 The mole fraction of the hydrogen-bonded species at various concentrations of acetic acid.

| Concentration of acetic acid (%w/w) | The mole fraction of species | | | | |
|---|------------------------------|--------|--------|---------|---------|
| | X_c | X_1 | X_2 | X_3 | X_4 |
| 85.0 | 0.0593 | 0.0150 | 0.0320 | 0.0262 | 0.0214 |
| 80.1 | 0.0554 | 0.0145 | 0.0299 | 0.0236 | 0.0187 |
| 75.2 | 0.0518 | 0.0140 | 0.0280 | 0.0214 | 0.0164 |
| 73.1 | 0.0504 | 0.0138 | 0.0272 | 0.0205 | 0.0154 |
| 70.0 | 0.0482 | 0.0136 | 0.0260 | 0.0192 | 0.0142 |
| 67.0 | 0.0462 | 0.0133 | 0.0250 | 0.0180 | 0.0130 |
| 65.0 | 0.0449 | 0.0131 | 0.0242 | 0.0172 | 0.0123 |
| 63.0 | 0.0436 | 0.0129 | 0.0235 | 0.0165 | 0.0116 |
| 61.0 | 0.0422 | 0.0127 | 0.0228 | 0.0157 | 0.0109 |
| 60.1 | 0.0417 | 0.0126 | 0.0225 | 0.0154 | 0.0106 |
| 50.0 | 0.0350 | 0.0116 | 0.0189 | 0.0119 | 0.0075 |
| 40.0 | 0.0285 | 0.0104 | 0.0154 | 0.0087 | 0.0049 |
| 30.0 | 0.0217 | 0.0091 | 0.0117 | 0.0058 | 0.0029 |
| 20.0 | 0.0146 | 0.0075 | 0.0079 | 0.0032 | 0.0013 |
| 10.0 | 0.0072 | 0.0052 | 0.0039 | 0.0011 | 0.0003 |
| 5.0 | 0.0034 | 0.0036 | 0.0018 | 0.0004 | 0.00007 |
| 1.0 | 0.0012 | 0.0021 | 0.0006 | 0.00007 | 0.00001 |

Table 4.16 The mole percent of the hydrogen-bonded species at various concentrations of acetic acid.

| Concentration of acetic acid (%w/w) | %X _c | %X ₁ | %X ₂ | %X ₃ | %X ₄ | %X ₅ | %X ₆ | %X ₇ | *%X _{GT4} | %X _{A-} |
|-------------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|--------------------|------------------|
| 85.0 | 23.72 | 6.01 | 12.80 | 10.47 | 8.56 | 7.00 | 5.73 | 4.68 | 38.43 | 0.000 |
| 80.1 | 26.05 | 6.83 | 14.06 | 11.12 | 8.79 | 6.94 | 5.49 | 4.34 | 33.15 | 0.009 |
| 75.2 | 28.06 | 7.61 | 15.15 | 11.58 | 8.85 | 6.77 | 5.17 | 3.95 | 28.73 | 0.015 |
| 73.1 | 28.85 | 7.94 | 15.58 | 11.74 | 8.84 | 6.66 | 5.02 | 3.78 | 27.03 | 0.018 |
| 70.0 | 29.96 | 8.42 | 16.17 | 11.93 | 8.80 | 6.49 | 4.78 | 3.53 | 24.70 | 0.024 |
| 67.0 | 30.98 | 8.89 | 16.72 | 12.07 | 8.71 | 6.29 | 4.54 | 3.28 | 22.60 | 0.029 |
| 65.0 | 31.62 | 9.21 | 17.07 | 12.14 | 8.64 | 6.14 | 4.37 | 3.11 | 21.28 | 0.034 |
| 63.0 | 32.29 | 9.54 | 17.41 | 12.20 | 8.55 | 5.99 | 4.20 | 2.94 | 20.02 | 0.038 |
| 61.0 | 32.85 | 9.86 | 17.73 | 12.24 | 8.45 | 5.83 | 4.02 | 2.78 | 18.82 | 0.043 |
| 60.1 | 33.12 | 10.02 | 17.88 | 12.25 | 8.40 | 5.76 | 3.94 | 2.70 | 18.29 | 0.046 |
| 50.0 | 35.91 | 11.84 | 19.38 | 12.18 | 7.66 | 4.81 | 3.02 | 1.90 | 12.95 | 0.078 |
| 40.0 | 38.25 | 13.98 | 20.65 | 11.70 | 6.63 | 3.76 | 2.13 | 1.21 | 8.68 | 0.11 |
| 30.0 | 40.14 | 16.83 | 21.67 | 10.71 | 5.30 | 2.62 | 1.29 | 0.64 | 5.18 | 0.16 |
| 20.0 | 41.23 | 21.07 | 22.26 | 9.03 | 3.66 | 1.48 | 0.60 | 0.24 | 2.50 | 0.25 |
| 10.0 | 40.12 | 29.21 | 21.65 | 6.16 | 1.75 | 0.50 | 0.14 | 0.04 | 0.70 | 0.42 |
| 5.0 | 36.42 | 38.52 | 19.66 | 3.85 | 0.75 | 0.15 | 0.03 | 0.006 | 0.18 | 0.62 |
| 1.0 | 29.16 | 52.10 | 15.74 | 1.83 | 0.21 | 0.02 | 0.02 | 0.000 | 0.03 | 0.93 |
| 2.0×10^{-1} | 22.76 | 62.74 | 12.29 | 0.92 | 0.06 | 0.000 | 0.000 | 0.000 | 0.005 | 1.21 |
| 4.0×10^{-2} | 9.41 | 82.76 | 5.08 | 0.11 | 0.002 | 0.000 | 0.000 | 0.000 | 0.000 | 2.63 |
| 8.0×10^{-3} | 2.50 | 90.91 | 1.35 | 0.007 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 5.22 |
| 1.6×10^{-3} | 0.50 | 89.81 | 0.27 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 9.41 |
| 3.2×10^{-4} | 0.08 | 79.06 | 0.04 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 20.82 |
| 6.4×10^{-5} | 0.01 | 61.75 | 0.005 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 38.23 |

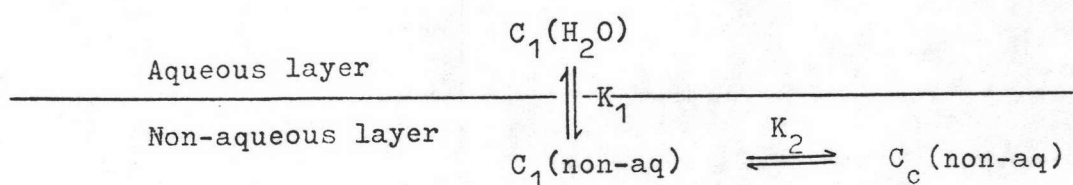
* %X_{GT4} = %X₅ + %X₆ + ... + %X_∞

Table 4.17 Fraction of protons of the species groups at various concentrations of acetic acid.

| Concentration of acetic acid (%w/w) | Fraction of protons of the species groups | | |
|---|---|--------|--------|
| | f(E) | f(I) | f(C) |
| 100.0 | 0.0464 | 0.9455 | 0.0081 |
| 95.0 | 0.0945 | 0.7852 | 0.0382 |
| 90.0 | 0.1008 | 0.6220 | 0.0530 |
| 85.0 | 0.0947 | 0.4786 | 0.0589 |
| 80.1 | 0.0848 | 0.3672 | 0.0597 |
| 75.2 | 0.0743 | 0.2819 | 0.0580 |
| 73.1 | 0.0700 | 0.2521 | 0.0568 |
| 70.0 | 0.0639 | 0.2141 | 0.0547 |
| 67.0 | 0.0584 | 0.1830 | 0.0525 |
| 65.0 | 0.0550 | 0.1650 | 0.0509 |
| 63.0 | 0.0518 | 0.1488 | 0.0493 |
| 61.0 | 0.0488 | 0.1342 | 0.0477 |
| 60.1 | 0.0474 | 0.1281 | 0.0470 |
| 50.0 | 0.0345 | 0.0757 | 0.0387 |
| 40.0 | 0.0248 | 0.0443 | 0.0308 |
| 30.0 | 0.0170 | 0.0242 | 0.0229 |
| 20.0 | 0.0107 | 0.0115 | 0.0151 |
| 10.0 | 0.0054 | 0.0039 | 0.0073 |
| 5.0 | 0.0030 | 0.0014 | 0.0034 |
| 1.0 | 0.0014 | 0.0004 | 0.0012 |

4.6 Calculation of the heat of solvent transfer

It has been well established that in the water-benzene system, acetic acid presents in the form of monomer in a water layer whereas cyclic dimer is believed to constitute a major constituent in a benzene layer. This simple model was adopted in this part of the work in which carbon tetrachloride was introduced in place of benzene and results were compared.



Where $C_1(\text{H}_2\text{O})$ and $C_1(\text{non-aq})$ are the molar concentration of monomers in aqueous and non-aqueous layer respectively. $C_c(\text{non-aq})$ is the molar concentration of cyclic dimers in non-aqueous layer. K_1 and K_2 are the equilibrium constants of distribution between monomeric species in aqueous and non-aqueous layer, and cyclic dimers and monomers in non-aqueous layer. The mathematical relation can be written as

$$C_1(\text{non-aq}) = C_1(\text{H}_2\text{O})/K_1 \quad (4.1)$$

$$C_c(\text{non-aq}) = K_2 [C_1(\text{non-aq})]^2 \quad (4.2)$$

or

$$C_c(\text{non-aq}) = \frac{K_2}{K_1} C_1(\text{H}_2\text{O}) \quad (4.3)$$

The molar concentration of acetic acid in non-aqueous layer, $C_A(\text{non-aq})$ is equal to the sum of $C_1(\text{non-aq})$ and $2 C_c(\text{non-aq})$. Thus

$$C_A(\text{non-aq}) = \frac{C_1(\text{H}_2\text{O})}{K_1} + \frac{2K_2 [C_1(\text{H}_2\text{O})]^2}{K_1^2} \quad (4.4)$$

Equation (4.4) can be rearranged.

$$\frac{C_A(\text{non-aq})}{C_1(\text{H}_2\text{O})} = \frac{1}{K_1} + \frac{2K_2}{K_1^2} C_1(\text{H}_2\text{O}) \quad (4.5)$$

A plot of $C_A(\text{non-aq})/C_1(\text{H}_2\text{O})$ against $C_1(\text{H}_2\text{O})$ is obviously a straight line and its slope and intercept are equal to $2K_2/K_1^2$ and $1/K_1$ respectively. The heat of solvent transfer or the enthalpy (ΔH) can be obtained from the equilibrium constant at various temperatures by the Van't Hoff equation viz

$$\frac{d \ln K}{d(1/T)} = - \frac{\Delta H}{R} \quad (4.6)$$

Hence at the narrow range of temperature a straight line should be obtained when $\ln K$ is plotted against $1/T$ with $-\Delta H/R$ is its slope. This was illustrated graphically in Figs 4.5, 4.7-4.9 from which K_1 and K_2 were derived and shown in Table 4.20. The anomaly was occurred in the $\text{HOAc-H}_2\text{O-CCl}_4$ system which can be seen from Fig 4.6 indicating the inadequacy of the simple model employed in such a case.

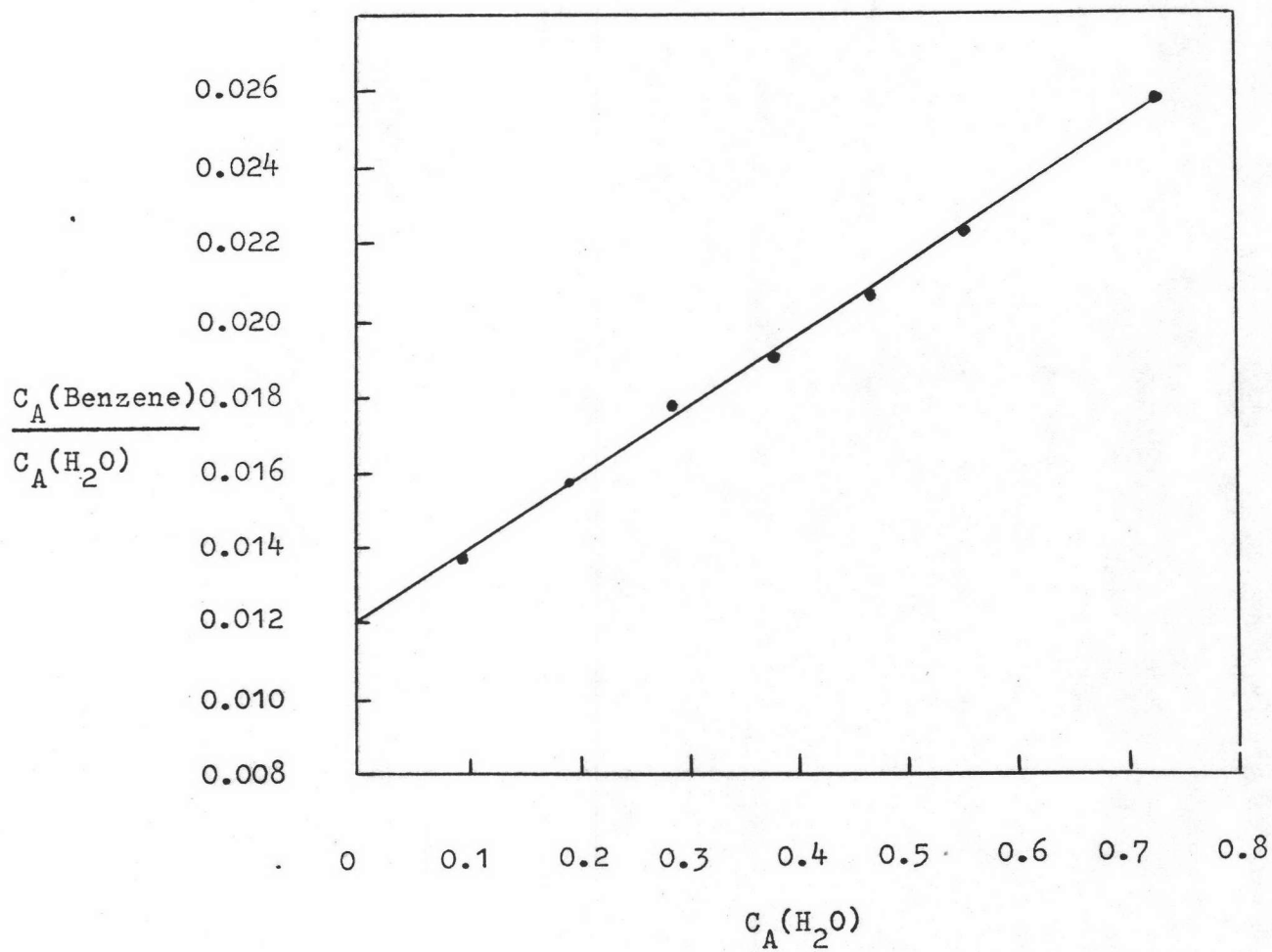


Figure 4.5 Plot of $C_A(\text{benzene})/C_A(\text{H}_2\text{O})$ against $C_A(\text{H}_2\text{O})$ at 32°C .

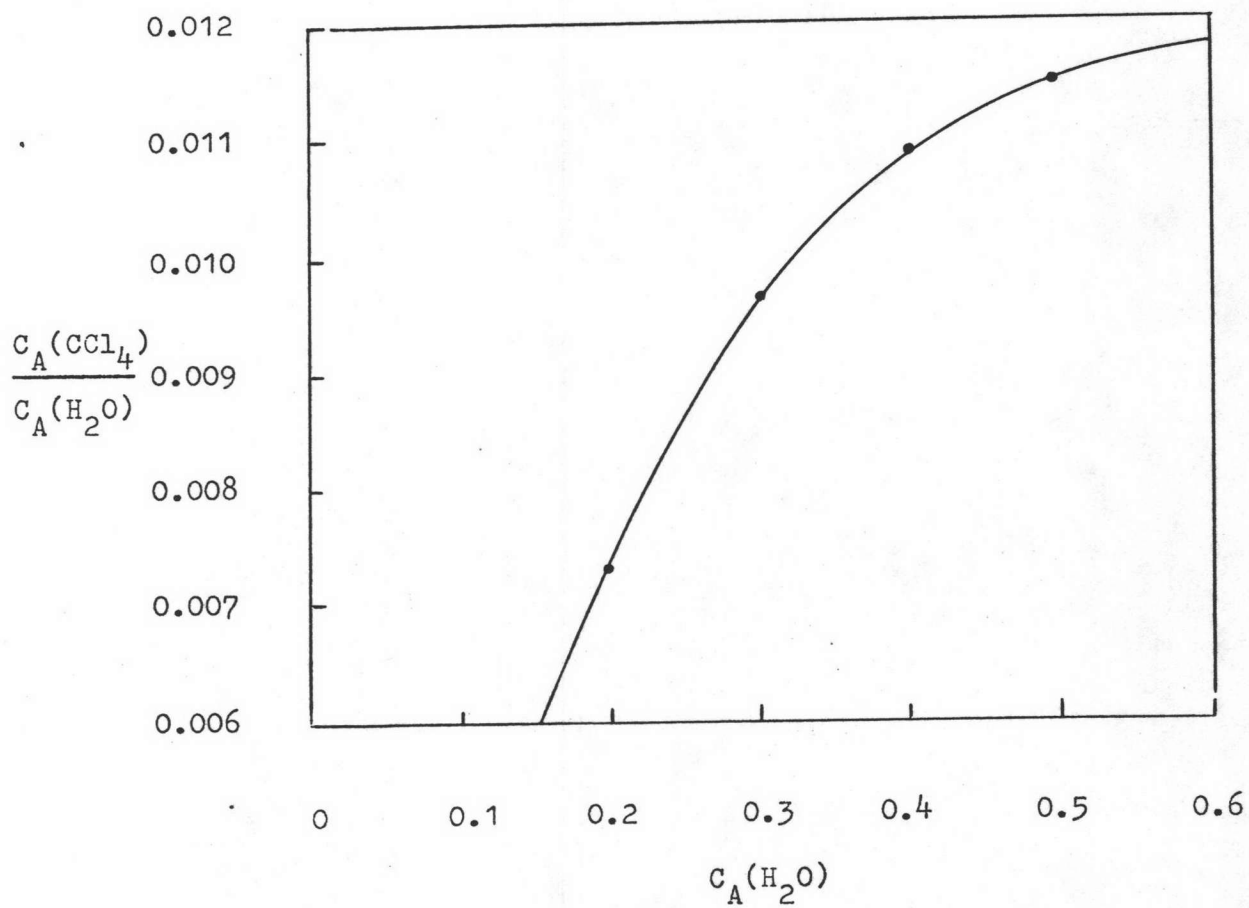


Figure 4.6 Non-linear relationship between $C_A(\text{CCl}_4)/C_A(\text{H}_2\text{O})$ and $C_A(\text{H}_2\text{O})$.

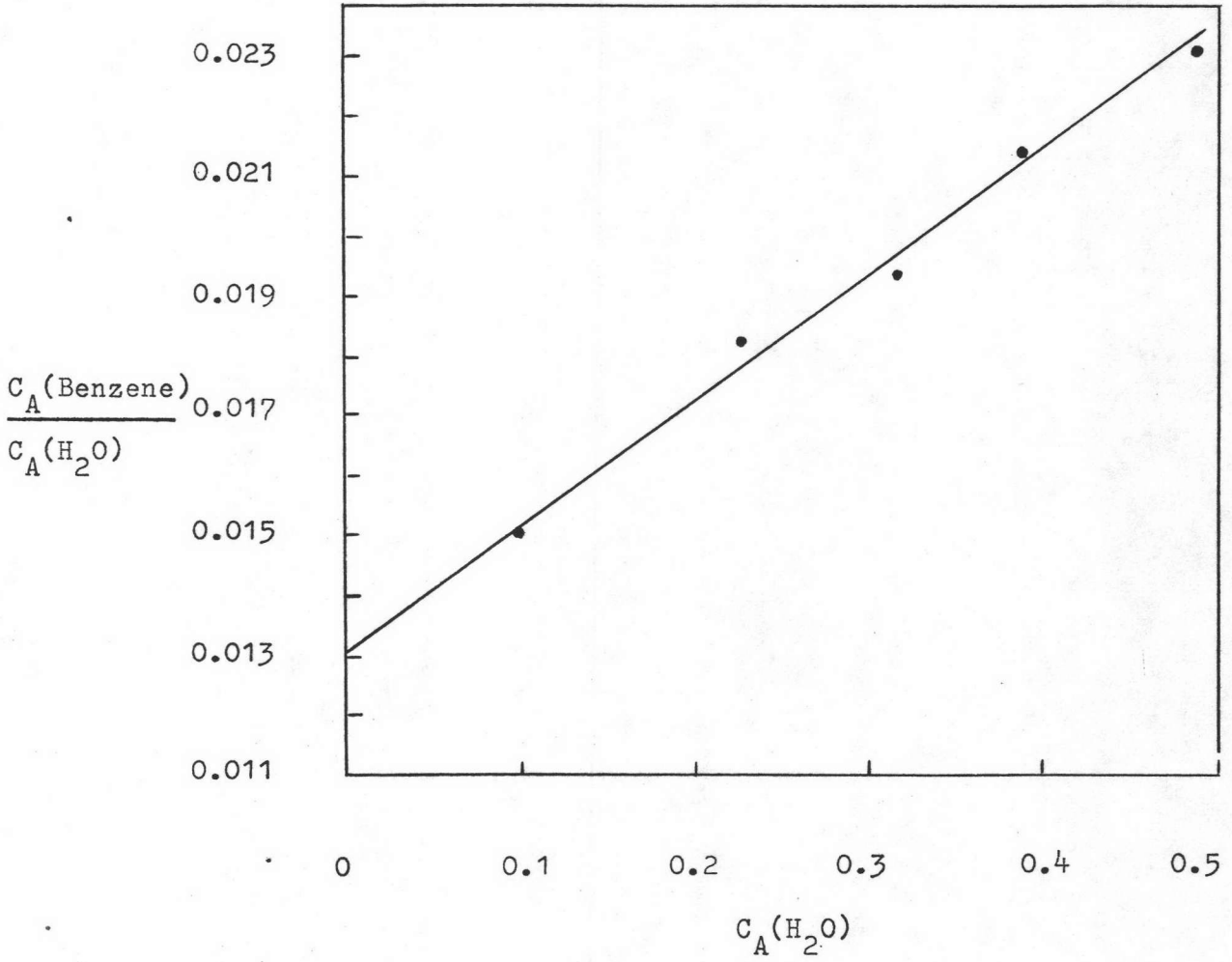


Figure 4.7 Plot of $C_A(\text{benzene})/C_A(\text{H}_2\text{O})$ against $C_A(\text{H}_2\text{O})$ at 35°C.

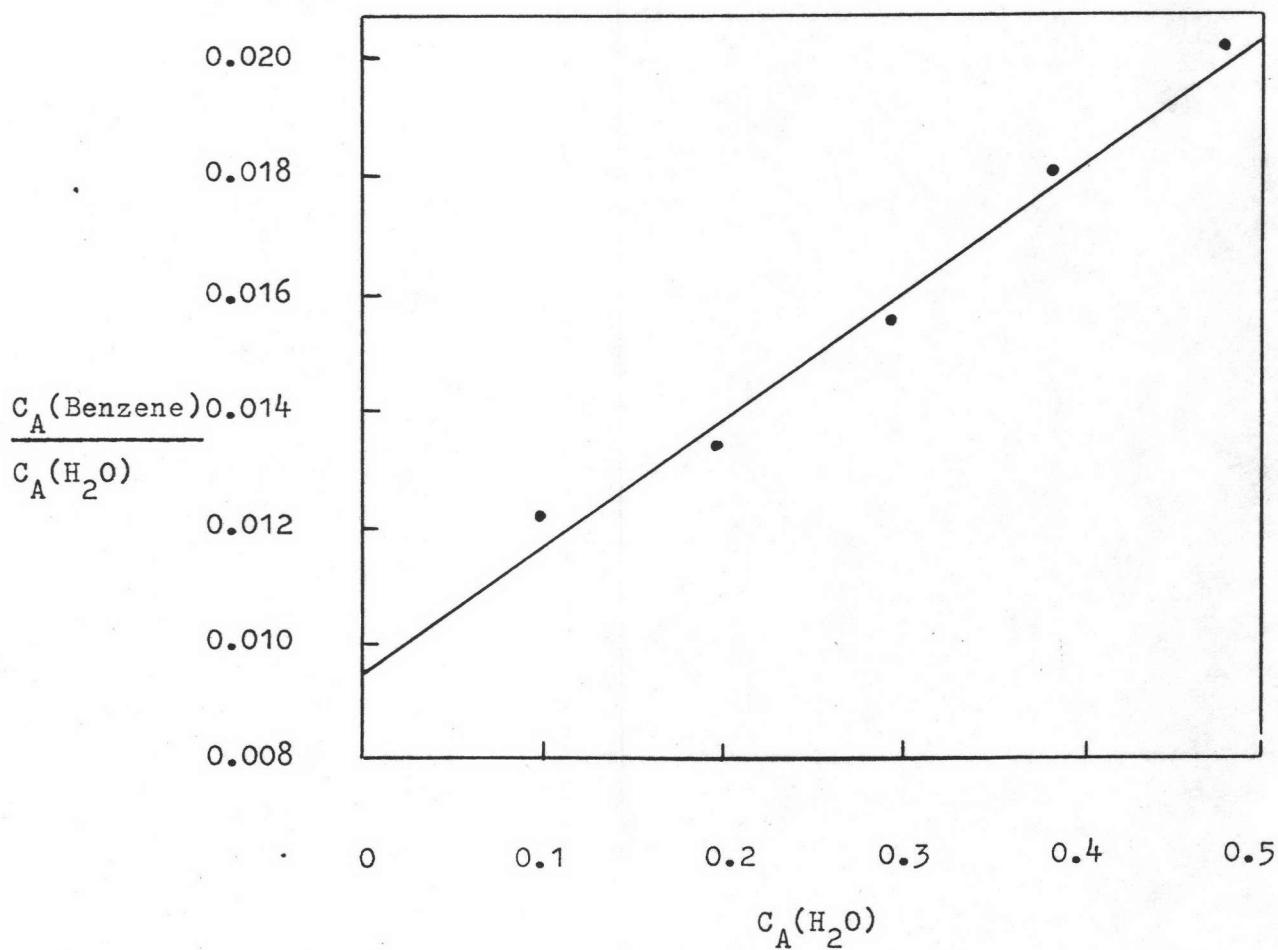


Figure 4.8 Plot of $C_A(\text{benzene})/C_A(\text{H}_2\text{O})$ against $C_A(\text{H}_2\text{O})$ at 25°C .

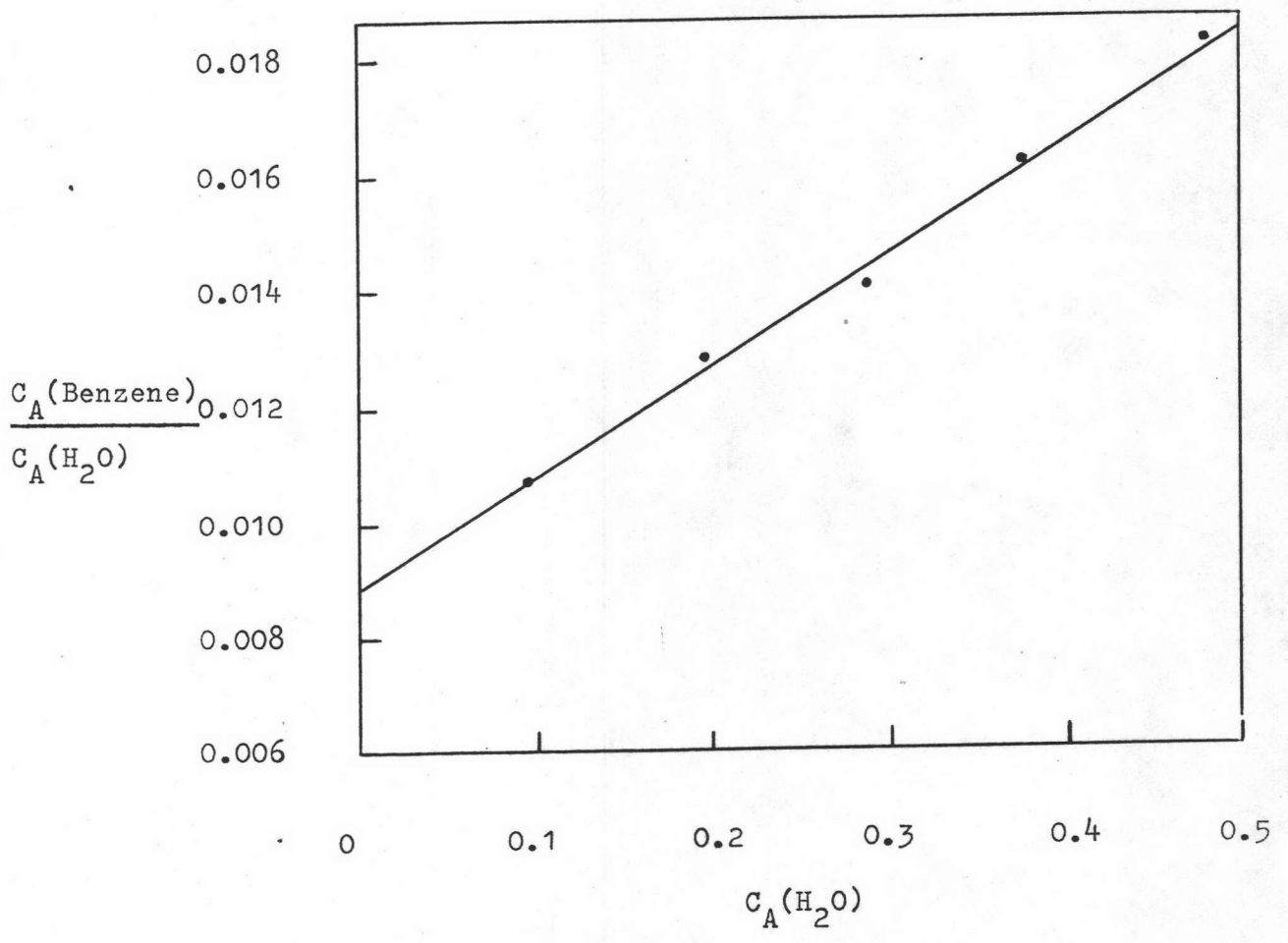


Figure 4.9 Plot of $C_A(\text{benzene})/C_A(\text{H}_2\text{O})$ against $C_A(\text{H}_2\text{O})$ at 20°C .

Table 4.18 Equilibrium constants K_1 and K_2 at various temperature

| Temperature (°C), (°K) | $1/T \times 10^3$ (\bar{K}^{-1}) | K_1 | $\ln K_1$ | K_2 | $\ln K_2$ |
|---------------------------|---|-------|-----------|-------|-----------|
| 20 , 293 | 3.4130 | 113.2 | 4.7291 | 125.2 | 4.8299 |
| 25 , 298 | 3.3557 | 104.7 | 4.6511 | 119.4 | 4.8299 |
| 32 , 305 | 3.2787 | 82.6 | 4.4140 | 63.2 | 4.1463 |
| 35 , 308 | 3.2468 | 75.8 | 4.3281 | 59.2 | 4.0809 |

Heat of solvent transfer of acetic acid in H_2O -benzene system, $\Delta H_{\text{benzene}-H_2O}$ and heat of dimerization of acetic acid in benzene, ΔH_{dimer} can be determined from the slope of the plot $\ln K_1$ against $1/T$ and $\ln K_2$ against $1/T$ (show in Figs 4.10 and 4.11) respectively. The results are obtained below.

$$\begin{aligned} \Delta H_{\text{benzene}-H_2O} &= -22.46 \text{ KJ mole}^{-1} \\ \Delta H_{\text{dimer}} &= -4.95 \text{ KJ mole}^{-1} \end{aligned}$$

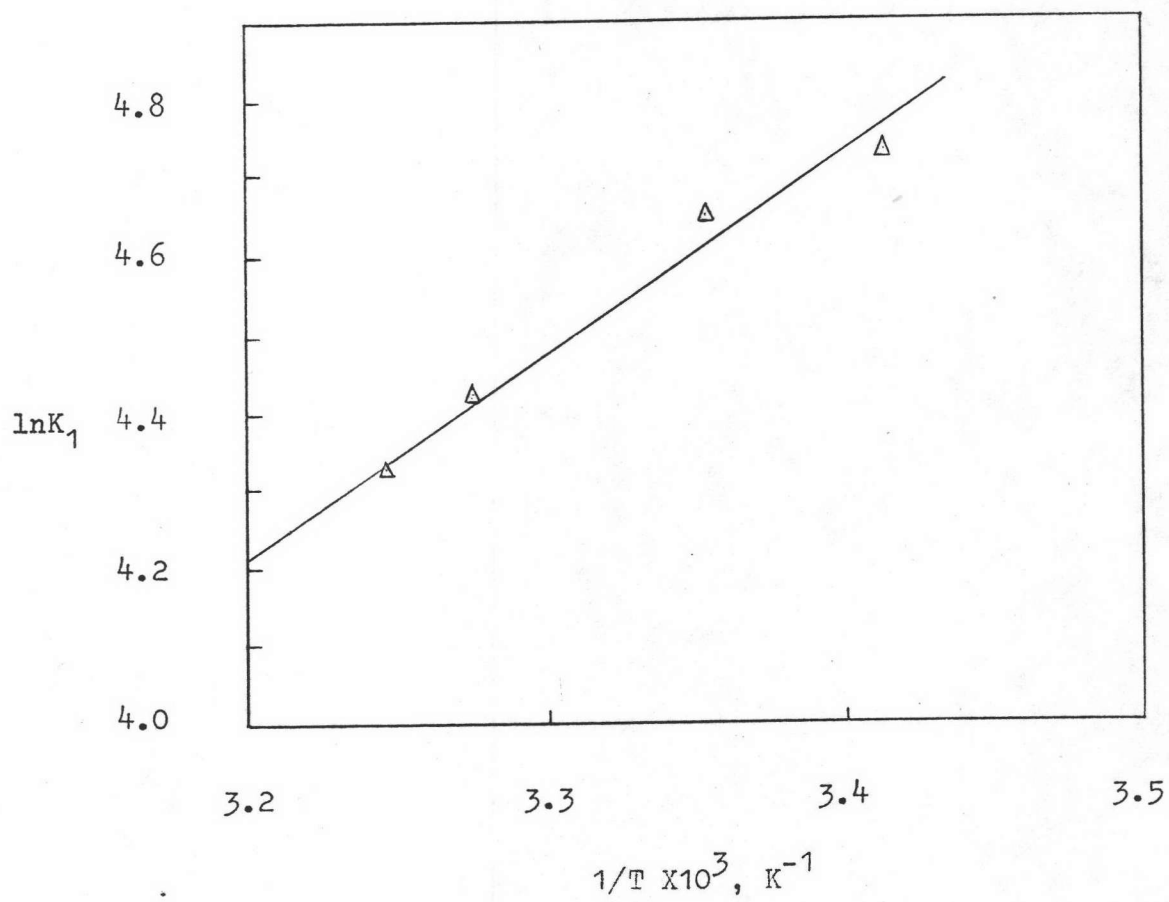


Figure 4.10 Plot of $\ln K_1$ against $1/T$

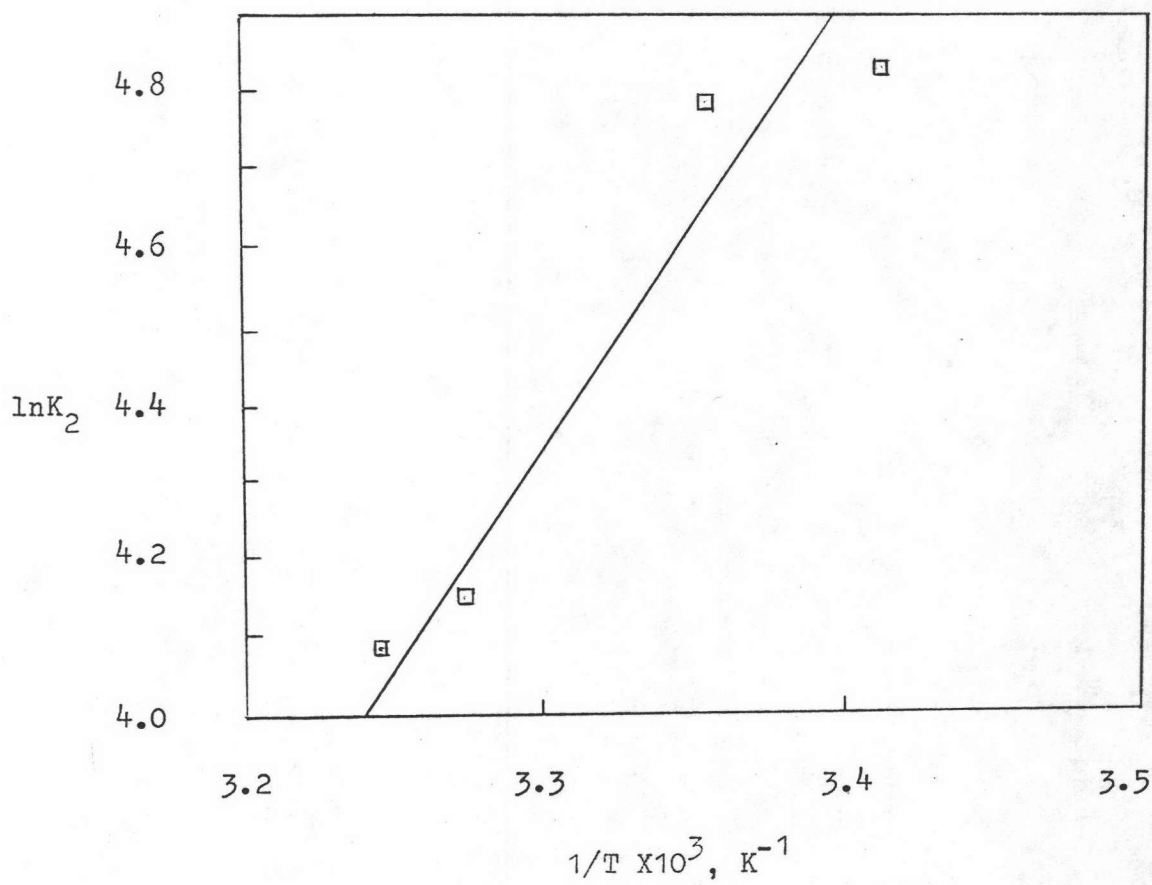


Figure 4.11 Plot of $\ln K_2$ against $1/T$