# Hydration of the Complex of 4-Methylquinoline *N*-Oxide with Chloroacetic Acid in Benzene

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Vapour pressure osmometry (v.p.o.) and $^1$H n.m.r. measurements of the 4-methylquinoline *N*-oxide complex (B) with chloroacetic acid (HA) in benzene containing different amounts of water provide evidence for an interaction interpreted in terms of the overall equilibrium $(BHA)_2 + H_2O \xrightleftharpoons{K_3} BHA + BHA.H_2O$, equivalent to a system of two competing equilibria $2(BHA) \xrightleftharpoons{K_1} (BHA)_2$ and $BHA + H_2O \xrightleftharpoons{K_2} BHA.H_2O$. Quantitative treatment of the v.p.o. and n.m.r. data gave $K_1$ 1.78 ± 0.47 molal$^{-1}$, $K_2$ 24.35 ± 7.57 molal$^{-1}$, and $K_3$ 13.68 ± 4.89. The previously reported anomalously high value for the difference between the chemical shift of dimer ($\delta_d$) and monomer ($\delta_m$) was an effect of residual moisture. Instead, $\delta_d - \delta_m = 0.95$ p.p.m.

MOLECULAR complexes of water in organic solvents have been investigated using a variety of classical and spectral techniques.[1] Water in organic solvents may be present as monomeric and/or polymeric species, such as dimer, trimer, and so on. In spite of some reports to the contrary,[2] it is generally believed that water dissolves in the aliphatic and aromatic hydrocarbons primarily as the monomer.[3]

There have been numerous studies on the interaction of polar solutes with water in nonpolar solvents.[1] Several specific complexes of water with monocarboxylic acids[4-8] and various bases have been reported.[9-13] The interaction between polar solutes and water in nonpolar solvents can be strong and specific. The behaviour of acids and bases are always strongly affected by water, even when the latter is present in trace amounts.

In view of the general importance of the hydration of acid or base molecules, it is of interest to investigate the hydration of acid–base complexes. Measurements of vapour pressure osmometry (v.p.o.) and $^1$H n.m.r. of benzene solutions containing small amounts of water and various concentrations of 4-methylquinoline *N*-oxide (B) complex with chloroacetic acid (HA) are here reported. This complex was recently investigated for toluene solution,[14] however, the effect of traces of water was neglected.

## EXPERIMENTAL

The complex of 4-methylquinoline *N*-oxide with chloroacetic acid was prepared in a manner described previously.[14] Benzene washed successively with sulphuric acid, sodium hydroxide, and water was finally distilled. The method of

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[1] S. D. Christian, A. A. Taha, and B. W. Gash, *Quart. Rev.*, 1970, **24**, 20.

[2] M. Gordon, C. S. Hope, L. D. Laon, and K-J. Roe, *Proc. Roy. Soc.*, 1960, **A258**, 215.

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[10] J. R. Johnson, P. J. Kilpatrick, S. D. Christian, and H. E. Affsprung, *J. Phys. Chem.*, 1968, **72**, 3223.

[11] D. N. Glew and N. S. Rath, *Canad. J. Chem.*, 1971, **49**, 837.

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Christian *et al.*[15] was used for equilibrating benzene. Benzil was recrystallized from ethanol and benzene. All solutions were prepared by weighing. The concentration of water in benzene was determined by the Karl Fischer method on a Radiometer titration assembly, type TTA1/KF, with a dead-stop end-point.

Molecular weights were measured with a Knauer vapour pressure osmometer, calibrated with benzil in benzene containing two different amounts of water at 27 °C. The resistance required to balance the solvent and solution thermistors was recorded as a function of time; the observed changes became linear within 1—3 min. All measurements were carried out for 15 min. The linear portion of the curve was extrapolated back to zero time. In this manner the time zero extrapolated resistance was measured for five drops and five separate and fresh prepared solutions.

N.m.r. spectra were measured at 80 MHz on a Tesla BS 487 A spectrometer in benzene at 27 ± 1 °C relative to the resonance of solvent and then converted to $\delta$ values. For a sample of benzene with 2% tetramethylsilane, the benzene peak is at 576 Hz ($\delta$ 7.20) from tetramethylsilane at 27 °C, and this value changes by less than ±1 Hz if complex is added. The chemical shifts quoted are average of at least three determinations, usually on three separate and freshly prepared solutions. The reproducibility of the chemical shift of hydrogen bonded protons was ±5 Hz.

## RESULTS AND DISCUSSION

Figure 1 shows a plot of molecular weight ($M$) against concentration ($x$) in benzene containing two different amounts of water. It is clear that (i) there are aggregates (dimers) present since $M > M_1$ and that (ii) water interacts with complex and lowers $M$.

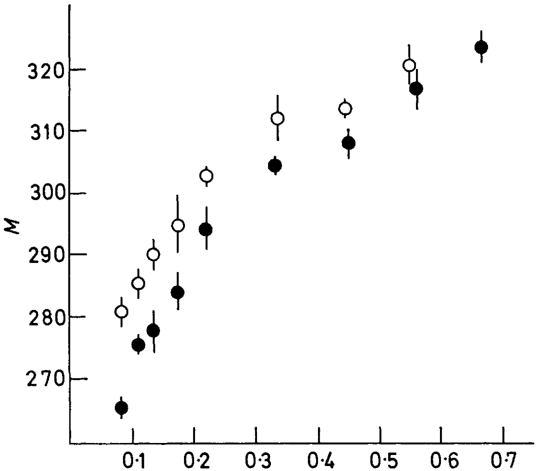

FIGURE 1 Plot of molecular weight ($M$) determined from v.p.o. measurements, against the stoicheiometric molality of the complex of 4-methylquinoline *N*-oxide with chloroacetic acid ($M_1$ 253.68) in benzene containing water: ○, 0.0033%; ●, 0.040%

The chemical shift of the hydrogen bonded protons plotted against concentration in benzene containing different amounts of water are shown in Figure 2. Figure 3 shows a plot of chemical shift *versus* water concentration. It is quite obvious that water strongly interacts with the complex to give variations of this magnitude.

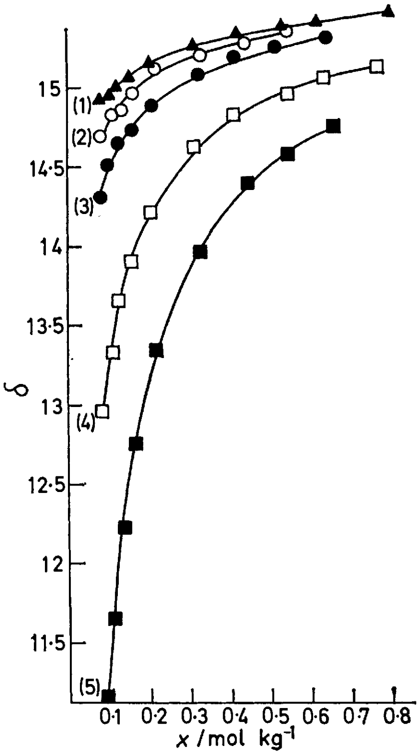

FIGURE 2 Hydrogen bonded shift in 4-methylquinoline *N*-oxide; $HO_2CCH_2Cl$ as a function of concentration in benzene containing water: (1) 0.0017%, (2) 0.0033%, (3) 0.0069%, (4) 0.020%, (5) 0.040%

The equilibria (1)—(6) for the interaction of water with complex were considered. Equation (5) is rejected since

$$2(\mathrm{BHA}) \xrightleftharpoons{K_1} (\mathrm{BHA})_2 \qquad (1)$$

$$\mathrm{BHA} + \mathrm{H_2O} \xrightleftharpoons{K_2} \mathrm{BHA,H_2O} \qquad (2)$$

$$(\mathrm{BHA})_2 + \mathrm{H_2O} \xrightleftharpoons{K_3} \mathrm{BHA} + \mathrm{BHA,H_2O} \qquad (3)$$

$$(\mathrm{BHA})_2 + 2\mathrm{H_2O} \xrightleftharpoons{K_4} 2(\mathrm{BHA,H_2O}) \qquad (4)$$

$$(\mathrm{BHA})_2 + \mathrm{H_2O} \xrightleftharpoons{K_5} (\mathrm{BHA})_2\mathrm{,H_2O} \qquad (5)$$

$$\mathrm{BHA} + 2\mathrm{H_2O} \xrightleftharpoons{K_6} \mathrm{B,H_2O} + \mathrm{HA,H_2O} \qquad (6)$$

$M$ decreases when the concentration of water increases (Figure 1). In the case of equilibrium (6) there are also objections. (i) Enthalpies of formation of acid–base complexes are much higher than those of complexes between water and bases or acids.[8,12,16] Hydration constants of acids in benzene are *ca.* 35 times lower in comparison with dimerization constants. (ii) In our experiments the concentration of complex ($x$) is always greater than that of water ($y$) ($y : x = 1 : 3.8$—$660$). We suppose that the existence of equilibrium (6) requires

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[15] S. D. Christian, H. E. Affsprung, J. R. Johnson, and J. D. Worley, *J. Chem. Educ.*, 1963, **40**, 419.

[16] (*a*) D. Hadži and J. Rajnvajn, *J.C.S. Faraday I*, 1973, **151**; (*b*) D. Hadži and R. Smerkolj, *ibid.*, 1976, **72**, 1188.

a comparable concentration of $y$ with $x$ or larger. (iii) According to equation (6) $M$ would decrease much more than we have observed. We have therefore rejected equation (6). Equation (4) can be expressed through equations (1) and (2) ($K_4 = K_2^2/K_1$) or (1) and (3) ($K_4 = K_3^2K_1$). We thus consider equation (3) to represent the simplest reasonable equilibrium consistent with both v.p.o. and n.m.r. measurements. It is equivalent to a system of two competing equilibria (1) and (2).

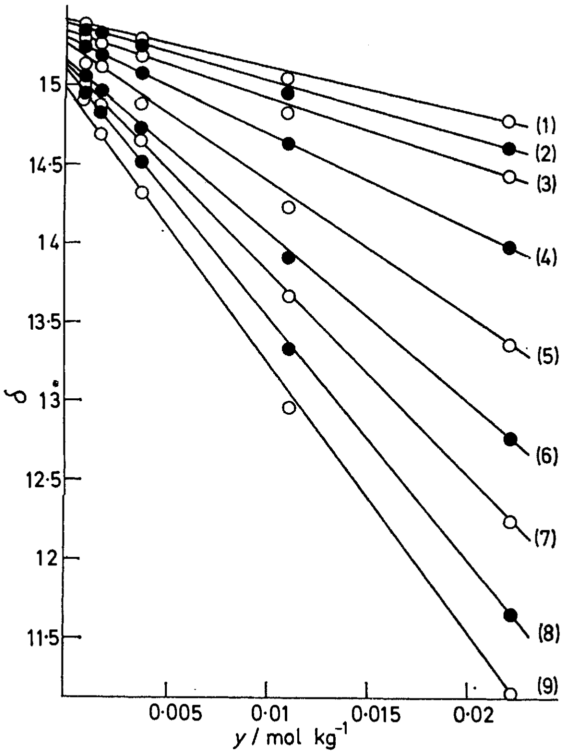

FIGURE 3 Hydrogen bonded shift in 4-methylquinoline $N$-oxide; $HO_2CCH_2Cl$ in benzene as a function of water concentration: (1) $x$ 0.67; (2) $x$ 0.55; (3) $x$ 0.45; (4) $x$ 0.33; (5) $x$ 0.22; (6) $x$ 0.16; (7) $x$ 0.13; (8) $x$ 0.11; (9) $x$ 0.085 molal

The overall equilibrium constant $K_3$ is expressed by equation (7) where $m$, $d$, $h$, and $w$ are the equilibrium

$$K_3 = \frac{mh}{dw} = \frac{(x - m - 2K_1m^2)}{K_1m(y - x) + m + 2K_1m^2} \qquad (7)$$

concentrations of monomer (BHA), dimer [$(BHA)_2$], hydrate ($BHA,H_2O$), and non-bonded water, respectively, and $K_1 = d/m^2$.

The exchange-average hydrogen-bond shift is given by equation (8). Here $\delta_m$, $\delta_d$, $\delta_h$, and $\delta_w$ are the characteristic

$$\delta = \frac{m\delta_m + 2d\delta_d + 3h\delta_h + 2w\delta_w}{x + 2y} = \frac{m\delta_m + 2K_1m^2\delta_d + 3(y - w)\delta_h + 2w\delta_w}{x + 2y} \qquad (8)$$

chemical shifts of monomer, dimer, hydrate, and water, while the concentration of water is given by equation (9). The monomer concentration is given by (10).

$$w = y/(K_1K_3m + 1) \qquad (9)$$

$$(2K_1^2K_3)m^3 + (K_1K_3 + 2K_1)m^2 + [K_1K_3(y - x) + 1]m - x = 0 \qquad (10)$$

The estimation of the $\delta_{calc.}$ values from equation (8) requires six variables, $K_1$, $K_3$, $\delta_m$, $\delta_d$, $\delta_h$, and $\delta_w$.

In the majority of our experiments, however, $x \gg y$ and water is probably bonded. It seems reasonable to assume that $w$ is small in comparison with $y$ when $x > 20y$. Equation (11) follows. The monomer concentration is given by (12). Equation (11) contains only four unknowns, $K_1$, $\delta_m$, $\delta_d$, and $\delta_h$.

$$\delta = (m\delta_m + 2K_1m^2\delta_d + 3y\delta_h)/(x + 2y) \qquad (11)$$

$$2K_1m^2 + m + y - x = 0 \qquad (12)$$

The $K_1$ value was calculated from v.p.o. data. It can be easily shown that equation (13) applies and this

$$m = \frac{x(2M_1 - M)}{M} - (y - w)\frac{M - 2M_{H_2O}}{M} \qquad (13)$$

was solved with the assumption that $w = 0$ for $x > 20y$. This yields $K_1 = 1.78 \pm 0.47$ molal$^{-1}$.

The $\delta_m$, $\delta_d$, and $\delta_h$ values were obtained by a least-squares method so as to give the best fit between the calculated [by equation (11)] and experimental data. The validity of the $\delta_m$ and $\delta_d$ values was checked against the data in anhydrous benzene obtained by extrapolation (Figure 3). Table 1 lists the values of chemical shifts obtained. The influence of $K_1$ on $\delta_m$, $\delta_d$, and $\delta_h$ is small.

TABLE 1

Parameters obtained experimentally or by calculation for complex of 4-methylquinoline $N$-oxide with chloroacetic acid in benzene with trace of water

| $K_1$ | $\delta_m$ | $\delta_d$ | $\delta_h$ | $R^2$ [d] |
|---|---|---|---|---|
| 1.31 | 14.981 [a] | 15.896 [a] | 8.260 [a] | $2.2 \times 10^{-2}$ |
| | 14.964 [b] | 15.924 [b] | 8.260 [b] | $1.3 \times 10^{-2}$ |
| | 14.935 [c] | 15.981 [c] | | $2.6 \times 10^{-3}$ |
| 1.78 | 14.947 [a] | 15.835 [a] | 8.257 [a] | $2.3 \times 10^{-2}$ |
| | 14.927 [b] | 15.862 [b] | 8.260 [b] | $1.3 \times 10^{-2}$ |
| | 14.897 [c] | 15.910 [c] | | $2.7 \times 10^{-3}$ |
| 2.25 | 14.918 [a] | 15.797 [a] | 8.254 [a] | $2.4 \times 10^{-2}$ |
| | 14.894 [b] | 15.824 [b] | 8.255 [b] | $1.4 \times 10^{-2}$ |
| | 14.864 [c] | 15.866 [c] | | $2.9 \times 10^{-3}$ |
| | 14.925 [e] | 15.877 [e] | 8.258 [e] | |
| | ±0.037 | ±0.057 | ±0.003 | |

[a] Results for 38 data points with the assumption that $y = h$ for $x > 20y$. [b] Results for 32 data points with the assumption that $y = h$ for $x > 30y$. [c] Results for 10 data points evaluated by extrapolation (Figure 3): $\delta = [\delta_d - m(\delta_d - \delta_m)]/x$ and $m = (-1 \pm \sqrt{1 + K_1x})/2K_1$. [d] $R^2 = \Sigma(\delta_{exp.} - \delta_{calc.})^2$. [e] Average value.

TABLE 2

Equilibrium calculation for 4-methylquinoline $N$-oxide,$HO_2CCH_2Cl$–water interaction in benzene

| | | | | $K_3$ | | |
|---|---|---|---|---|---|---|
| $\delta_m$ | $\delta_d$ | $\delta_h$ | $\delta_w$ | $K_1$ 1.31 | $K_1$ 1.78 | $K_1$ 2.25 |
| 14.925 | 15.877 | 8.258 | 0.542 | 18.569 | 12.817 | 9.648 |

$K_3 = 13.68 \pm 4.52$

The calculated values of chemical shifts from equation (11) and average parameters from Table 1 agree well with experimental data only for the range $x > 15y$ (Figure 4). The observed deviation for the range $x < 15y$ is caused by non-bonded water. These experimental values and a least-squares method were used to obtained the best set of $K_3$ from equation (8). The value of $\delta_w$ of 0.54 was directly determined by n.m.r. measurement of water in benzene.[3b] The values of $K_3$ obtained are listed in Table 2. The equilibrium constant $K_2$ for complex formation (2) is then 24.35 ± 7.57 molal$^{-1}$.

Figures 4 and 5 show a plot of the experimental chemical shifts against the calculated values from equation (8) and the parameters in Table 2. Good agreement is obtained for the entire range investigated.

It is quite evident then, that water in organic solvents interacts with acid–base complexes and should be taken into consideration when interpreting experimental results, in particular n.m.r. and colligative measurements. Neglecting this interaction gave quite different results.[17,18] The anomalously high value of $\delta_d - \delta_m$, reported earlier is now corrected and seems to have been the result of moisture.

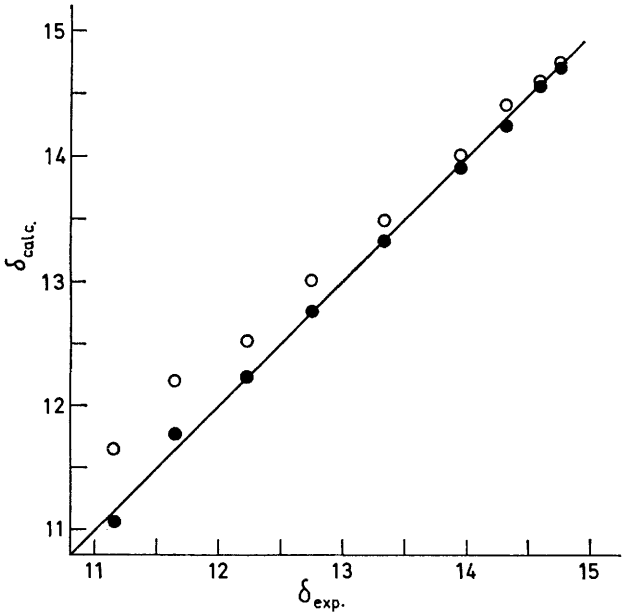

FIGURE 4 Plot of $\delta_{exp.}$ against $\delta_{calc.}$: ○ calculated from equation (11); ●, calculated from equation (8); $y$ 0.0222 molal

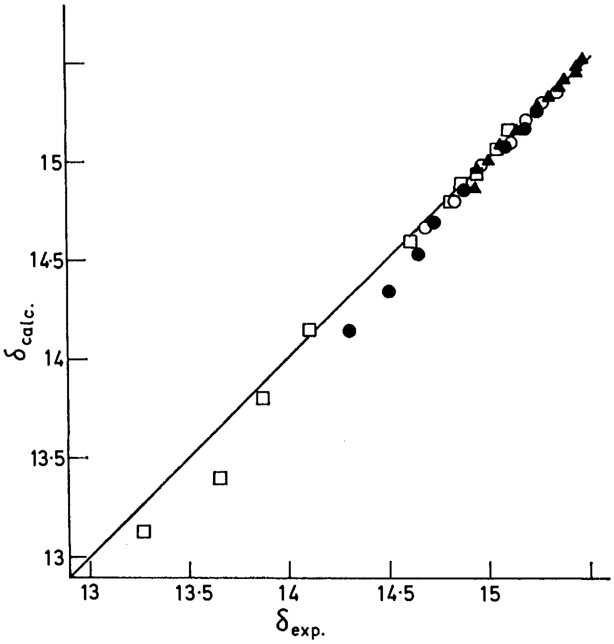

FIGURE 5 Plot of $\delta_{exp.}$ against $\delta_{calc.}$ from equation (8): ▲, $y$ 0.000 95; ○, $y$ 0.0018; ●, $y$ 0.0038; □, $y$ 0.0111 molal

It is expected *a priori* that interactions in solution are strongly dependent on the ratio water : solute. This ratio is a function of concentration since the amount of water in the solvent during the experiment is usually constant.

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