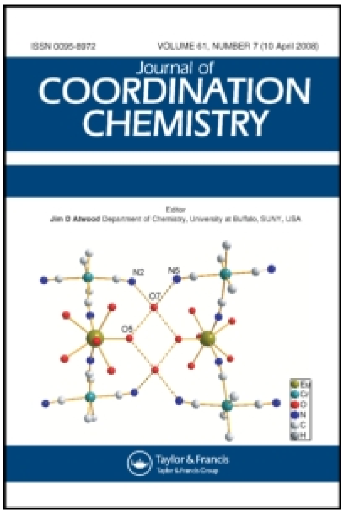

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

FORMATION CONSTANTS OF OUTER SPHERE COMPLEXES AT HIGH IONIC STRENGTH. A RE-EVALUATION OF KINETIC RESULTS

Berta Perlmutter-hayman[a]; Eliana Tapuhi[a]
[a] Department of Physical Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel

To cite this Article Perlmutter-hayman, Berta and Tapuhi, Eliana(1978) 'FORMATION CONSTANTS OF OUTER SPHERE COMPLEXES AT HIGH IONIC STRENGTH. A RE-EVALUATION OF KINETIC RESULTS', Journal of Coordination Chemistry, 8: 2, 75 — 79

To link to this Article: DOI: 10.1080/00958977808073074

URL: http://dx.doi.org/10.1080/00958977808073074

J. Coord. Chem.
1978, Vol. 8, pp. 75–79

FORMATION CONSTANTS OF OUTER SPHERE COMPLEXES AT HIGH IONIC STRENGTH. A RE-EVALUATION OF KINETIC RESULTS

BERTA PERLMUTTER-HAYMAN and ELIANA TAPUHI

Department of Physical Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel

(Received June 27, 1977; in final form November 9, 1977)

The formation constants of the inner sphere complexes of Fe(III) with Cl^- and $CHCl_2COO^-$ ions are determined kinetically, at 25°C and an ionic strength of 1 M. The formation constants of the ion pairs or outer sphere complexes are obtained from these results, together with previous data about the sum of the two constants. The values obtained are compatible with measurements concerning other complexes, but are lower than those calculated from the Fuoss equation. The results are discussed on the basis of the Eigen mechanism.

INTRODUCTION

The kinetics of the formation of labile complexes frequently follow the Eigen mechanism.[1] According to this mechanism, the rate determining step, taking place with a rate constant k^*, is the exchange between a water molecule in the inner coordination sphere and the entering ligand. This step is preceded by a fast pre-equilibrium in which an ion pair between metal ion and ligand is formed, with an equilibrium constant K_{out}. The simplest possible reaction can then be written

$$M + A \overset{K_{\text{out}}}{\rightleftharpoons} M,A \underset{k_d}{\overset{k^*}{\rightleftharpoons}} MA \tag{I}$$

where water molecules, and charges, have been omitted for the sake of simplicity.

Such reactions are conveniently studied by relaxation methods. The reciprocal relaxation time is given by

$$1/\tau = k_f \frac{[M] + [A]}{1 + K_{\text{out}}([M] + [A])} + k_d \tag{1}$$

where

$$k_f = K_{\text{out}} k^* \tag{2}$$

and all concentrations have their equilibrium values.

Provided $K_{\text{out}}([M] + [A])$ is small in comparison with unity – a condition which is often fulfilled – a plot of $1/\tau$ against $[M] + [A]$ is a straight line. From its slope and intercept k_f and k_d are obtained. Their ratio equals

$$k_f/k_d = [MA]/[M][A] = K_{\text{in}} \tag{3}$$

This defines K_{in} as the formation constant of the inner sphere complex *from the reactants.*[2]

When K_{in} can be assumed to be known, it is often convenient to rewrite equation (1) in the form[3,4] (again assuming K_{out} $([M] + [A])$ to be small in comparison with unity)

$$1/\tau = k_f([M] + [A] + 1/K_{\text{in}}) \tag{4}$$

Although this seems to be an equation for k_f, the result depends on the value adopted for K_{in}. This is especially true when the complex is weak and $1/K_{\text{in}}$ is the leading term in the parenthesis.[5,6]

Now, how do we obtain K_{in}? A spectrophotometric determination of the formation constant of the complex can easily be shown to yield an *overall* constant

$$K = K_{\text{out}} + K_{\text{in}} = ([MA] + [M,A])/[M][A] \tag{5}$$

no matter whether the complex M,A has a characteristic molar absorptivity or whether its spectroscopic properties resemble those of MA or those of the reactants. For lack of information about K_{in}, this quantity is often replaced in equation (4) by K. This gives values of k_f which are too high by a factor of $1 + K_{\text{out}}/K_{\text{in}}\,[K([M] + [A]) + 1]$. When the inner sphere complex is strong then, at least at the ionic strengths employed in T-jump experiments,

$K_{out} \ll K_{in}$, and this factor differs insignificantly from unity. When the complex is weak, this may no longer be the case. On the other hand, it is just for weak complexes, where, at all reasonable concentrations, $k_f([M] + [A])$ is much smaller than k_d, that k_f and, therefore, k_f/k_d, become unreliable.

In this paper we have tried to find experimental conditions which nevertheless permit a reasonably accurate kinetic estimate of K_{in} for weak complexes. This enables us to re-evaluate some previous mechanistic conclusions[3,4,6] which had been based on equation (4) or an analogous expression, with K replacing K_{in}, in the study of the reactions between Fe(III) and bromide,[4] chloride,[4] di- and trichloroacetate[6] and sulphate[3] ions.

EXPERIMENTAL

All experiments were carried out by the temperature-jump method as described before.[6] The ionic strength was again[6] 1 M, and the temperature was 25°C.

For the Fe(III)-Cl^- system, solutions were prepared from $Fe(ClO_4)_3$, HCl, and $HClO_4$, so that the stoichiometric concentration of Fe(III) ranged from 1.1×10^{-2} to 9.0×10^{-2} M and was always in excess of over that of the chloride ion which ranged from 5×10^{-3} to 8×10^{-2} M. With $[FeCl_2^+]/[FeCl^{2+}][Cl^-]$ equal[2] to $1.3\ M^{-1}$ we calculate that under our conditions $FeCl_2^+$ constitutes at most 4% of the total complexed Fe(III) and can therefore be neglected. The total hydrogen ion concentration was 0.5 M.

For the systems Fe(III)-substituted acetic acids the total hydrogen ion concentration was 0.1 M, again regulated by the addition of perchloric acid. The stoichiometric concentration of the metal ion lay between 2×10^{-3} and 5×10^{-3} M, and that of the ligand between 5×10^{-3} to 9×10^{-2} M. For these ligands there is no evidence for higher complexes.[6]

RESULTS

Our systems are more complicated than reaction I because FeA^{2+} can be formed by several parallel paths involving Fe^{3+}, $FeOH^{2+}$, A^- and, in the case of the weaker acids, also HA. Therefore, k_f and k_d in equation (1) are now composite quantities which depend on $[H^+]$.[6] This need not concern us here since, in each of the systems investigated, $[H^+]$ was kept constant. Furthermore, in the case of the weaker acids which are only partly dissociated and for which the hydrogen ion concentration was such that $[FeOH^{2+}]$, though small, is not completely negligible in comparison with $[Fe^{3+}]$, we have to replace $[M] + [A]$ in equation (1) by[3,6]

$$[Fe^{3+}]\frac{K_{HA}}{K_{HA} + [H^+]} + [A^-]\frac{[H^+]}{K_{OH} + [H^+]} \qquad (6)$$

where, again,[6] K_{HA} is the acid dissociation constant of HA, and K_{OH} the hydrolysis constant of Fe(III); we used[6] $K_{OH} = 1.6 \times 10^{-3}$.

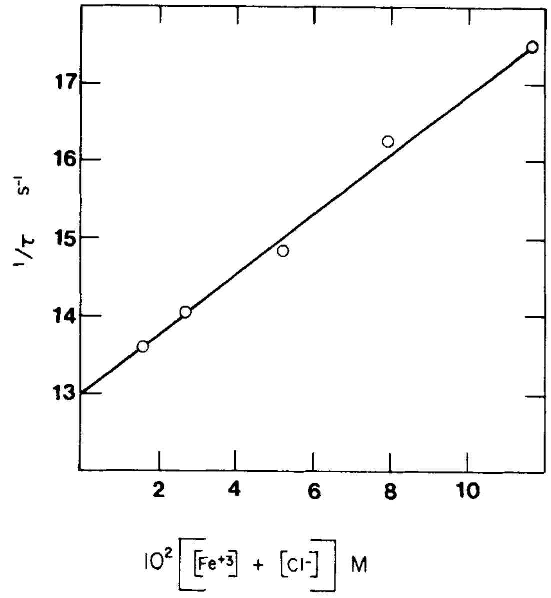

FIGURE 1 The dependence of $1/\tau$ on $[Fe^{3+}] + [Cl^-]$.

Figure 1 shows the dependence of $1/\tau$ on $[Fe^{3+}] + [Cl^-]$. A straight line is seen to be obtained. From its slope and intercept we obtain

$$k_f = 38.4 \pm 1.8\ M^{-1}s^{-1};\ k_d = 13.00 \pm 0.12\ s^{-1}$$

which yields

$$K_{in} = 2.95 \pm 0.14\ M^{-1}$$

In the case of di- and trichloro acetic acids our experimental conditions were chosen as the result of a compromise: for given values of the stoichiometric concentrations of the reactants, expression (6) is larger the smaller the hydrogen ion concentration; this increases the chances of getting a significant value for k_f. On the other hand, at low hydrogen ion concentration, $FeOH^{2+}$ is formed which has a tendency to dimerise.[7] This was avoided by taking the ligand in excess which has the additional advantage that high reactant concentrations can be achieved without overstepping the ionic strength of 1 M.

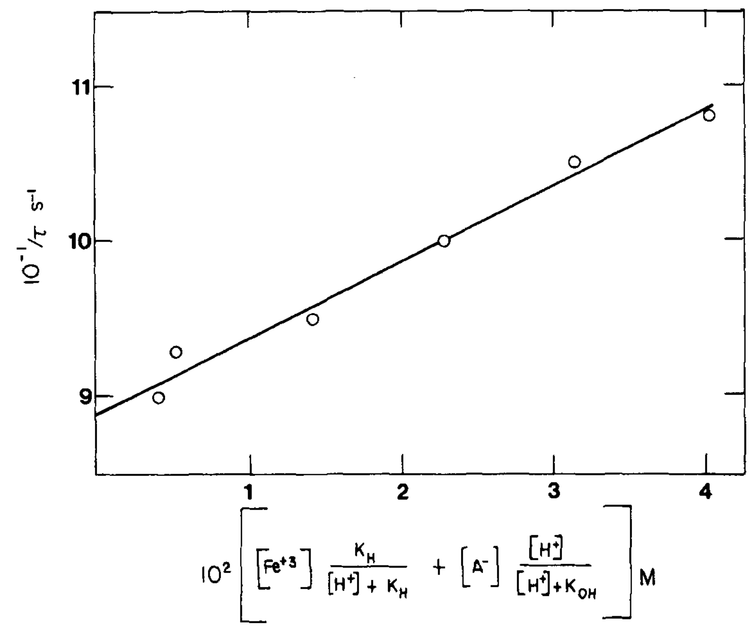

FIGURE 2 The dependence of $1/\tau$ on expression (6), with A^- meaning $CHCl_2COO^-$.

Nevertheless, with trichloracetic acid the complex is so weak that trend of $1/\tau$ with reactant concentration could be detected. For dichloroacetic acid, the dependence of $1/\tau$ on expression (6), with[8] $K_{HA} = 8 \times 10^{-2}$ M, is presented in Figure 2. From the slope and intercept we obtain

$$k_f = (4.8 \pm 0.3) \times 10^2 \text{ M}^{-1}\text{s}^{-1};\ k_d = 89.0 \pm 0.8 \text{ s}^{-1}$$

and

$$K_{in} = 5.4 \pm 0.4 \text{ M}^{-1}$$

DISCUSSION

Evaluation of K_{out}. Values of K as defined in equation (5) for $FeCl^{2+}$ at an ionic strength of 1 M are summarized by Rowley and Sutin;[2] they vary between 2.9 and 5.2 M^{-1}. When we combine this with our value for K_{in} we find

$$K_{out} \leqslant 2.2 \text{ M}^{-1}$$

For the dichloroacetate complex, comparison with our spectrophotometric value[6] of K, namely 6.8 ± 0.5 M^{-1}, gives

$$K_{out} \sim 1.4 \text{ M}^{-1}.$$

Comparison with Experimental Values.

While this work was in progress, a recent paper by Schwarz and Dodson[9] has come to our notice. These authors measured K_{in} from the change of absorbance when $FeCl^{2+}$, formed as a primary product in the oxidation of Fe^{2+} in the presence of chloride ion, decays to its equilibrium concentration. Their result, at $I = 1$ M, is 2.9 M^{-1}; this agrees with our result rather better than can reasonably be expected. Similarly, there is surprisingly close agreement between our value of K_{out}, and Wendt and Strehlow's[10] 2 ± 1 M^{-1}, obtained by an entirely different method. On the other hand, Rowley and Sutin,[2] from an analogy with $CrBr^{2+}$, assume a considerably lower value for K_{out}.

For the dichloroacetate-Fe^{3+} complex, no experimental data seem to be available. We therefore scan the literature for values of K_{out} for other ter- or divalent cations and monovalent ligands, at our, or similar, ionic strengths. We find that spectrophotometric results are available for a number of substitution-inert cations.[11-13] The measurement of K_{out} from kinetic experiments becomes possible when the plot of $1/\tau$ as a function of [M] + [A] is significantly curved (see below),[13-16] or when the inner sphere complex is even weaker than those considered here, and the difference between k_f/k_d and the spectrophotometrically determined value of K becomes very marked.[17] With few exceptions[14, 18] the experimental values lie between ~0.2 and ~1 M^{-1}, and definite specific effects are discernible. Thus, K_{out} for $[Co(NH_3)_5H_2O, NCS]^{2+}$ was found[13] to be 0.4 M^{-1} whereas the analogous chloride complex, measured by the same authors by the same method, had the unusually high value of 3.2. Similarly,[15] K_{out} for $[Cr(NH_3)_5H_2O, NCS]^{2+}$ was 0.68 M^{-1}, whereas for the analogous $CCl_3CO_2^-$, $CF_3CO_2^-$, and Cl^- compounds it was so small that it could not be detected by kinetic methods.

Comparison with Theoretical Values

Since the original suggestion by Bjerrum,[19] a number of approaches to the question of ion pairs have been suggested[20-23] (see also reference 24 for some recent advances). However, in conjunction with the Eigen mechanism it is the Fuoss equation[25] which is almost universally used to calculate values of K_{out}. Its appeal lies in its simplicity, and possibly also in the fact that it can be obtained from both electrostatic[25] and kinetic[26] considerations. An early warning that the results can be expected to be correct only within a factor of two or three[27] has never been refuted but is often disregarded. According to the Fuoss equation,

$$K_{out} = (4\pi Na^3/3000)\exp(u/kT) \qquad (7)$$

where u is the electrostatic interaction energy; the only adjustable parameter in this equation is a, the largest distance between two ions which still allows them to be classified as a pair. It is usually taken as 5 Å.[28] For non-zero ionic strength u contains a correction term which is in fact $2\,kT \times 2.3 \log \gamma_\pm$; it is usually taken from the Debye-Hückel theory, a theory which is not expected to hold at ionic strengths above 0.1 M. For higher ionic strength, u is sometimes[29] assumed equal to that at $I = 0.1$ M. We have preferred (see, for example, reference 6) to use the Davies equation[21] for the calculation of $\gamma_\pm$. The two approaches give very similar results, whereas Wilkins[28] estimates that at an ionic strength of 0.5 M the value of K_{out} should be considerably below that at $I = 0.1$ M. For a charge product of (−3), using the Davies equation, we obtained that at an ionic strength of 1 M, the value of K_{out} equals 3 to 5 M^{-1} according to whether we use $b = 0.2$ or 0.3 in the Davies equation. Comparison with experimental results – both ours and those of other authors – shows clearly that this estimate is too high. For some very weak complexes[4, 6, 17] it is higher even than the spectrophotometrically determined value of K, a fact which has sometimes been overlooked.

Mechanistic Implications

Inspection of Figures 1 and 2 provides a further reason why K_{out} cannot be as high as 3 to 5 M^{-1}. Within the limit of the experimental error these graphs are straight lines. We estimate that with $K_{out} \sim 1$ M^{-1} the downward curvature predicted by equation (1) is still so slight as to escape our notice, but already with our upper limit of 2.2 M^{-1} for $[Fe,Cl]^{2+}$ we should have been able to detect a curvature.[30]

If 1 M^{-1} or less is indeed a typical value for K_{out}, then, even in the case of the rather weak complexes with which we are concerned in this paper, the difference between K_{in} and K is small, and the values of k_f, calculated previously[3-6] on the basis of equation (4) are not very much in error (except, possibly, in the case of trichloroacetate[6]).

However, these are not the only kinetic implications. If we want to test the applicability of the Eigen mechanism[1] we calculate k^* and compare it with the rate of water exchange between the inner hydration sphere and bulk water (after applying an appropriate statistical correction factor[31]). But k^* is calculated from equation (2). If this calculation is carried out with too high a value of K_{out} then the resulting k^* is too low by the same factor.

The kinetic results for Fe^{3+} which we summarized in Table III of our previous paper[6] refer, with one exception, to experiments carried out at ionic strengths of 0.4 or above; the values of K_{out} we employed for the calculation of k^* for Fe^{3+} were all around 3 M^{-1}. We can now assume that these k^*-values should be higher than reported by a factor of at least three. This brings the results for the strong acids nearer to those calculated from NMR-measurements. For the anions of the weaker acids $HC_2O_4^-$ CH_2ClOO^-, SO_4^{2-} and, possibly, NCS^-, the enhancement of the rate, ascribed to internal hydrolysis,[6, 32] becomes even more evident.

It would be interesting to obtain K_{in} from kinetic data also at lower values of ionic strength. However, if the complex is sufficiently weak for the difference between K and K_{in} to be statistically meaningful then k_f is small and can be obtained only when the reactant concentrations are rather high. Furthermore, it is especially for tervalent metal ions that the deviations from the Debye-Hückel or Davies equations are most pronounced and which are therefore of special interest in this context. A tervalent ion automatically makes for high ionic strength. In addition, many of these ions undergo hydrolysis and dimerisation, and acid has to be added to the reaction mixture.

REFERENCES

1. M. Eigen and R. Wilkins, *Adv. Chem. Ser.*, No. **49**, 55 (1965).
2. J. K. Rowley and N. Sutin, *J. Phys. Chem.*, **74**, 2043 (1970).
3. F. P. Cavasino, *J. Phys. Chem.*, **72**, 1378 (1968).
4. T. Yasunaga and S. Harada, *Bull. Chem. Soc. Japan*, **42**, 2165 (1969).
5. R. Koren and B. Perlmutter-Hayman, *Inorg. Chem.*, **11**, 3055 (1972).
6. B. Perlmutter-Hayman and E. Tapuhi, *J. Coord. Chem.*, **6**, 31 (1976).
7. R. M. Milburn and W. C. Vosburgh, *J. Am. Chem. Soc.*, 77, 1352 (1955).
8. B. Perlmutter-Hayman and E. Tapuhi, *J. Chem. Eng. Data.*, **22**, 22 (1977).
9. H. A. Schwarz and R. W. Dodson, *J. Phys. Chem.*, **80**, 2801 (1976).
10. H. Wendt and H. Strehlow, *Z. Elektrochem.*, **66**, 228 (1962).
11. E. L. King, J. H. Espenson and R. E. Visco, *J. Phys. Chem.*, **63**, 755 (1959).
12. T. W. Swaddle and G. Guastalla, *Inorg. Chem.*, **8**, 1604 (1969).
13. C. H. Langford and W. R. Muir, *J. Am. Chem. Soc.*, **89**, 3141 (1967).
14. G. G. Hammes, *Inorg. Chem.*, **5**, 1286 (1966).
15. T. Ramasami and A. G. Sykes, *Inorg. Chem.*, **15**, 2885 (1976).
16. O. Nor and A. G. Sykes, *J. Chem. Soc. Dalton Trans.*, 1232 (1973).
17. J. H. Espenson, *Inorg. Chem.*, **8**, 575 (1969).
18. F. L. Baker and W. MacF. Smith, *Can. J. Chem.*, **48**, 3100 (1970).
19. N. Bjerrum, *Kgl. Danske Videnskab. Selskab. Mat. Fys. Medd.*, 9, 7 (1926).
20. J. E. Prue, *J. Chem. Educ.*, **46**, 12 (1969).
21. C. W. Davies, *Ion Association*, Butterworths, London, 1962.
22. M. T. Beck, *Coord. Chem. Rev.*, **3**, 91 (1968).
23. M. G. Burnett, *J. Chem. Soc.*, **A**, 2480 (1970).
24. D. R. Rosseinsky, *Annu. Rep. Prog. Chem., Sect. A*, **68**, 92 (1971).
25. R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).
26. M. Eigen, *Z. Elektrochem.*, **64**, 115 (1960).
27. G. G. Hammes and J. I. Steinfeld, *J. Am. Chem. Soc.*, **84**, 4639 (1962).
28. R. G. Wilkins, *Acc. Chem. Res.*, **3**, 408 (1970).
29. S. Gouger and J. Stuehr, *Inorg. Chem.*, **13**, 379 (1974).
30. In our calculation of $[Fe^{3+}] + [Cl^-]$ we therefore did not use the recent value ${}^2K = 5.2\ M^{-1}$, but rather the older (E. Rabinowitch and W. H. Stockmayer, *J. Am. Chem. Soc.*, **64**, 335 (1942)) $K = 4.2\ M^{-1}$. The result is very little affected by this choice.
31. J. Neely and R. Connick, *J. Am. Chem. Soc.*, **92**, 3476 (1970).
32. M. Eigen, in *Advances in the Chemistry of Coordination Compounds*, S. Kirschner, Ed., Macmillan, New York, N.Y., p. 371, 1961.