Nuclear Magnetic Resonance Determination of the Stability of the Silver Ion+Benzene Complex

BY M. I. FOREMAN * J. GORTON * AND R. FOSTER †

Received 12th March, 1970

The association of Ag^+ with benzene in aqueous solution has been estimated from measurements of the chemical shift of the benzene resonance in the presence of varying excess concentrations of silver nitrate. The results are consistent with the formation of a 1 : 1 complex and a 2 : 1 complex between Ag^+ and benzene. The numerical values of the equilibrium quotients agree well with earlier values obtained from solubility measurements.

A method for the determination of equilibrium constants by n.m.r. spectroscopy has been outlined in the literature,^{1, 2} and numerous values derived have been reported.^{3, 4} It has been remarked that such values frequently do not agree with those from optical measurements on the same systems.^{3, 5} Recently a number of instances have been reported which suggest that results from the n.m.r. method may be misleading, e.g., two different values for the equilibrium constant have been determined by measuring the ¹⁹F and proton absorption of 2,4,6-trinitro-benzotrifluoride in both carbon tetrachloride and cyclohexane with hexamethylbenzene as donor.⁶ Certain possibilities exist which would explain this behaviour, e.g., if a 2:1, as well as a 1:1, complex of donor to acceptor were formed.^{4, 7} In the systems so far studied, one component, usually the donor, is in large excess, which effectively rules out the possibility of 1:2 complexes of donor to acceptor ; where the acceptor is in large excess the converse is true.

Suppose the system consists of two components D and A, and two equilibrium constants are defined on a molal concentration scale :

$$A+D \rightleftharpoons AD(1:1 \text{ complex}), \quad K_1 = [AD]/[A][D],$$

 $AD+D \rightleftharpoons AD_2(2:1 \text{ complex}), \quad K_2 = [AD_2]/[AD][D].$

If we designate the stoichiometric (i.e., free and complexed) concentrations of components by the subscript 0, and if $[D] \ge [A]$, then

$$K_{1} = [AD]/[A][D]_{0} = [AD]/\{([A]_{0} - [AD] - [AD_{2}])[D]_{0}\},$$
(1)

$$K_{2} = [AD_{2}]/[AD][D]_{0}$$

For the n.m.r. experiment, fast exchange may be assumed to be taking place in solution so that

$$\Delta = P_{1:1}\Delta_1 + P_{2:1}\Delta_2,\tag{3}$$

where Δ is the observed, exchange-averaged, chemical shift of some particular nucleus in the low concentration component; Δ_1 is the chemical shift of the same nucleus in the pure 1 : 1 complex; Δ_2 likewise for the 2 : 1 complex (neither of which is directly measurable). The chemical shifts are referred to the absorption of the pure uncomplexed species. $P_{1:1}$ and $P_{2:1}$ are the relative populations of the two complexes.

* Dept. of Pure and Applied Chemistry, University of Strathclyde, Glasgow, C.1.

† Dept of Chemistry, University of Dundee, Dundee DD1 4HN.

2120

Therefore,

$$\Delta = [AD]\Delta_1/[A]_0 + [AD_2]\Delta_2/[A]_0.$$
(4)

From eqn (1) and (2),

$$K_1 = [AD] / \{ ([A]_0 - [AD] - K_2 [AD] [D]_0) [D]_0 \}.$$
(5)

From eqn (4) and (5),

$$\Delta[\mathbf{A}]_0 = [\mathbf{A}\mathbf{D}](\Delta_1 + K_2\Delta_2[\mathbf{D}]_0).$$
(6)

From eqn (5),

$$[AD] = K_1[A]_0[D]_0/(1+K_1[D]_0+K_2[D]_0^2).$$
(7)

Substitution for [AD] in (7) gives

$$\Delta = \frac{K_1 \Delta_1 [D]_0 + K_1 K_2 \Delta_2 [D]_0^2}{1 + K_1 [D]_0 + K_2 [D]_0^2},$$

or

$$\Delta = \frac{A_1[D]_0 + A_2[D]_0^2}{1 + A_3[D]_0 + A_4[D]_0^2},$$
(8)

where $A_1 = K_1 \Delta_1$; $A_2 = K_1 K_2 \Delta_2$; $A_3 = K_1$; $A_4 = K_1 K_2$. Eqn (8) may be written as

$$\Delta / [D]_0 = A_1 + A_2 [D]_0 - A_3 \Delta - A_4 [D]_0 \Delta, \qquad (9)$$

which reduces to the equation for the 1:1 case only if $K_2 = 0$. The normal n.m.r. procedure ² is to plot $\Delta/[D]_0$ against Δ , which gives a linear plot of gradient, $-K_1$. From eqn (9), the gradient, for the case $K_2 \neq 0$, is given by

$$d(\Delta/[D]_0)/d\Delta = (A_2 - A_4\Delta)d[D]_0/d\Delta - A_3 - A_4[D]_0.$$

The term $(A_2 - A_4\Delta)d[D]_0/d\Delta$ is a function of the particular nucleus measured, since the values of Δ depend on the relevant Δ_1 and Δ_2 values by eqn (3). The values Δ_1, Δ_2 are a property of the particular nucleus measured. If, therefore, contributions from 2 : 1 complexing are significant, the slope of a plot of $\Delta/[D]_0$ against Δ will be dependent on the nucleus measured. This may account for the differing values obtained from the 2,4,6-trinitrobenzotrifluoride system mentioned above. It also emphasizes the desirability of making measurements on more than one nuclear resonance.

To test this analysis, the system of benzene and silver nitrate in water ^{8, 9} has been re-examined by n.m.r. spectroscopy. The results so obtained have been analyzed using eqn (8). Preliminary measurements at an operating frequency of 60 MHz indicated that the methyl resonance of t-butyl alcohol is a satisfactory internal reference for this system. The change in the chemical shift of the benzene absorption on complexation with silver ion was, however, not sufficiently large to allow measurements to be made with the necessry accuracy. This problem was overcome using a spectrometer operating at 100 MHz. In order to allow a check to be made on the results obtained, conditions similar to those of Andrews and Keefer ⁸ were used throughout. A computer programme was devised to curve-fit by a least-squares criterion. The theoretical and experimental curves so obtained are shown in fig. 1. The values quoted for K_1 and K_2 (table 1) have an estimated error of ± 5 and ± 10 % respectively, and are believed to be sufficiently close to Andrews and Keefer's ⁸ results to justify the analysis outlined above. The values of Δ_1 and Δ_2 are in approximately the ratio 2 : 1, which accords with the notion that two silver ions in a complex will perturb the benzene resonance twice as much as one.



FIG. 1.—Plot of change of chemical shift of benzene resonance against concentration of silver ion, computed curve and experimental points measured at 100 MHz at 33.5°.

TABLE 1

Molal equilibrium constants for the Ag⁺: benzene 1:1 complex (K_1) and for the 2:1 complex (K_2) and the corresponding chemical shifts of the benzene resonance in the two complexes $(\Delta_1 \text{ and } \Delta_2 \text{ respectively})$ relative to the line position in free benzene. All are measured in aqueous solution of unit ionic strength at 33.5°. For comparison previous values on a molar scale *a* obtained from solubility data obtained at 25° are also given.

| | K ₁ | K_2 | Δ_1^b/Hz | Δ_2^b/Hz |
|---------------------------------|---------------------------|---------------------------|-----------------|-----------------|
| present n.m.r. results | 2.30 kg mol ⁻¹ | 0.48 kg mol ⁻¹ | 26 | 51 |
| from solubility data (ref. (8)) | 2.41 l mol ⁻¹ | 0.21 l mol ⁻¹ | | |

^a The small difference between the two concentration scales used is insignificant, particularly in view of the difference in temperatures of the two determinations.

^b Measured at 100 MHz, the benzene resonance shifts to lower fields on complexing.

EXPERIMENTAL

Measurements were made on a series of aqueous solutions of various concentrations of silver nitrate having ionic strength of unity with potassium nitrate as backing electrolyte, and 0.02 M w.r.t. benzene, 0.02 M t-butanol, 0.05 M methanol. The separation of the methyl resonances of methanol and t-butanol were independent of the silver ion concentration, t-butanol was therefore adopted as internal reference. The position of the benzene resonance was measured in a series of such solutions (omitting the methanol) with reference to an audio-frequency sideband generated on the t-butanol methyl resonance using a Perkin-Elmer R 14 spectrometer operating at 100.004 MHz. Measurements were considered to be accurate to ± 0.2 Hz.

The data so obtained was fitted to eqn (8) by a computer search programme using a

least-squares criterion. Only one minimum was observed corresponding to the parameters given above.

The authors are grateful to Dr. P. Blaydon, Strathclyde University for the provision of n.m.r. facilities and for his advice.

- ¹ M. W. Hanna and A. L. Ashbaugh, J. Phys. Chem., 1964, 68, 811.
- ² R. Foster and C. A. Fyfe, *Trans. Faraday Soc.*, 1965, 61, 1626.
- ³ e.g. R. Foster and C. A. Fyfe, *Prog. Nuclear Magnetic Resonance Spectroscopy*, ed. J. Emsley,
- J. Freeney and L. Sutcliffe, (Pergamon, Oxford and New York, 1969), vol. 4, p. 1. ⁴ R. Foster, *Organic Charge-Transfer-Complexes* (Academic Press, London, and New York,
- 1969), chap. 7.
- ⁵ P. H. Emslie, R. Foster, C. A. Fyfe and I. Horman, *Tetrahedron*, 1965, **21**, 2843.
- ⁶ M. I. Foreman, R. Foster and D. R. Twiselton, Chem. Comm., 1969, 1318.
- ⁷ D. A. Deranleau, J. Amer. Chem. Soc., 1969, 91, 4050.
- ⁸ L. J. Andrews and R. M. Kcefer J. Amer. Chem. Soc., 1949, **71**, 3644. ⁹ J. C. Schug and R. J. Martin, J. Phys. Chem., 1962, **66**, 1554.