Determination of the Basicity of Nitric Acid in Concentrated Sulphuric Acid by Raman and Ultraviolet Spectroscopy

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Summary The ionization ratio $[NO_2^+]/[HNO_3]$ of nitric acid, in 80—96% sulphuric acid, has been evaluated by Raman and u.v. methods; the thermodynamic pK_a of the equilibrium involved has been calculated by using the M_C activity coefficient function.

The nature of the molecular and ionic species of nitric acid present in pure sulphuric acid and in water–sulphuric acid mixtures has been extensively studied.[1–4] However, little is known about their concentrations and variation with change of composition of medium.[2–4] An estimation of these species, in the concentration range 80—96% sulphuric acid, would be of particular interest, allowing the calculation of the thermodynamic dissociation constant of equilibrium (1). For this purpose, the concentrations of HNO_3 and NO_2^+ species have been determined at 25 °C by a Raman and a u.v. method.

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^- \qquad (1)$$

The Raman spectroscopy results (Figure 1) were obtained by measuring the areas of the bands due to NO_2^+ and HNO_3 for concentrations of nitric acid in the range 0·1—0·5 M. Within this concentration range we have verified that there is a linear relationship between concentration and area. A small decrease of the NO_2^+ band area with time was observed, especially at the higher acidities. Reproducible data were obtained, with the reagents being mixed immediately before use.

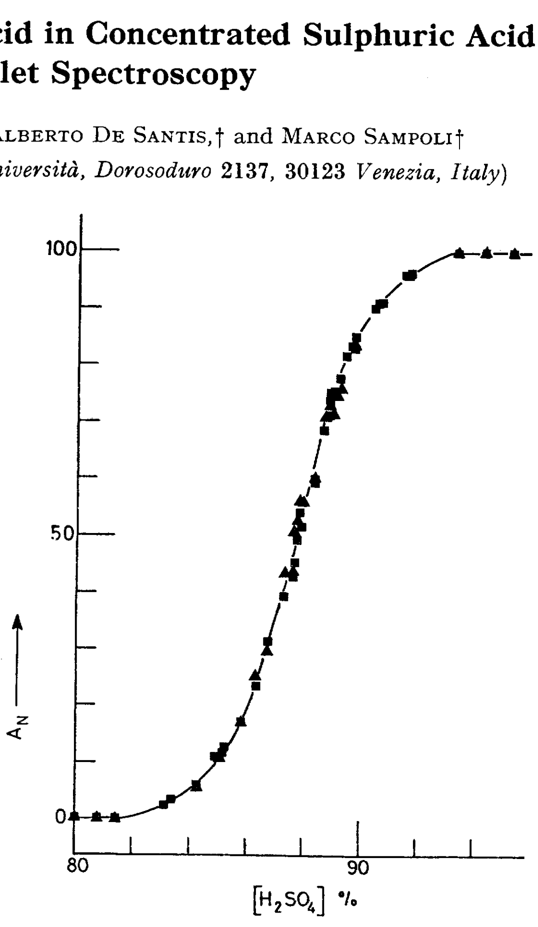

Figure 1. Study of the protonation equilibrium of HNO_3 in 80—96% H_2SO_4 by Raman spectroscopy: ■ normalized areas (A_N) of the NO_2^+ band; ▲ $(1 - A_N)$ [normalized areas (A_N)] of the HNO_3 band.

The thermodynamic pK_a value was calculated from equation (2), since equilibrium (1) can be rewritten in the general form (3). By plotting {log ([NO_2^+]/HNO_3]) − log

$$pK_a = \log\frac{[NO_2^+]}{[HNO_3]} - \log[H^+] + \log a_w - \log\frac{f_{HNO_3}f_{H^+}}{f_{NO_2^+}} \qquad (2)$$

$$R - OH + H^+ \rightleftharpoons R^+ + H_2O \qquad (3)$$

[H^+] + log a_W}[5] against a revised M_C activity coefficient function,[6,7] the value pK_a = − 15·2‡ has been obtained. The important features of the revised M_C function are that a large number of indicators (including tri-arylmethanols[8]) have been used and that its validity has been tested by comparing thermodynamic pK_a values in aqueous sulphuric and perchloric solutions.[7]

Analysis of the u.v. absorption spectra is somewhat more complicated. Unlike the situation in an earlier study,[3] one has to deal here with solutions whose absorbance increases with time over the whole of the acidity range. Linear extrapolation back to the time of mixing of reagents has to be adopted. Difficulties also arose in estimating the value of $\epsilon(BH^+)$, since the absorbance generally decreases at acidities >91% sulphuric acid[3,4] (Figure 2). Therefore the u.v. method is not suitable for determining the precise ratio, [NO_2^+]/[HNO_3]. However, if the experimental uncertainties are reduced as far as possible, the pK_a value estimated by extrapolating the u.v. measurements (pK_a *ca.* −15·3) agrees with that obtained by the Raman method.

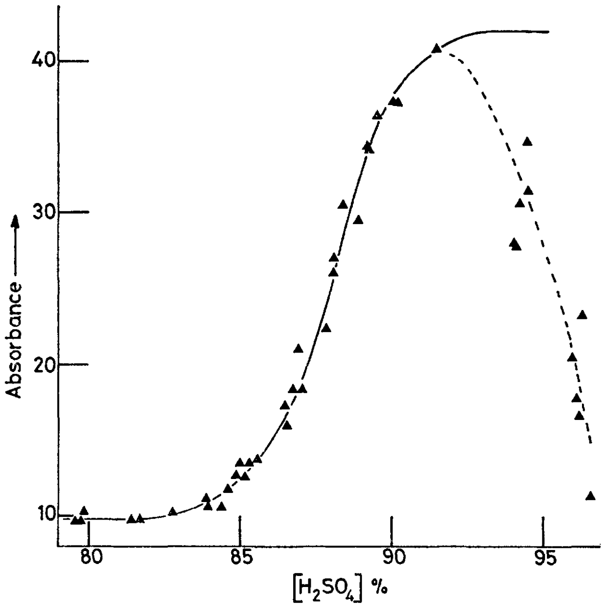

FIGURE 2. Study of the protonation equilibrium of HNO_3 in 80—96% H_2SO_4 by u. v. spectroscopy; plot of absorbance *vs.* [H_2SO_4].

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‡ This pK_a value has been determined within an error range of a few per cent. A more precise estimate will be given in a forthcoming paper.

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