AN ELECTRON PARAMAGNETIC RESONANCE STUDY OF THE ASSOCIATION OF MANGANESE(II) WITH SULPHATE IONS

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The association of manganese(II) sulphate in aqueous solutions was studied as a two-step equilibrium process. The first step corresponds to the path $Mn(II)_{aq} + SO_{4aq}^{-2} \underset{K_1}{=} Mn(H_2O)SO_{4aq}$ and the second one to the path $Mn(H_2O)SO_{4aq} \underset{K_1}{=} MnSO_{4aq}$. The values of both constants were determined, $K_1 = 57 \cdot 2 \pm 1 \cdot 61 \, mol^{-1}$ and $K_2 = 3 \cdot 5 \pm 0 \cdot 1$, at a temperature of approx. 25°C, using EPR spectrometry, from the dependence of the signal intensity of Mn(II) ions on the concentration of sulphate·ions.

The spectrum of Mn(II) ions in dilute aqueous solution consists of six lines, corresponding to the interaction of the electron spin with the nuclear spin Mn^{55} ($I = 5/2$). Myers and coworkers[1,2] studied the influence of halide and sulphate ions on the EPR line width of manganese. They used the fourth line (on the low field side) which has the minimum width. Analysis by the mentioned authors showed that this line, corresponding to $m_I = +1/2$ ($m_I = -I, -I + 1, ..., + +I$), is not split at the wave lengths of the X-band and is most favorable for the study of the magnetic relaxation of Mn(II) ions. Further it was shown that sulphate ions lead to Mn(II) ion line broadening at any temperature while Cl^- behaves similarly only at high temperatures (above 80°C). Study of the association of Mn(II) ions in aqueous solutions employing EPR spectrometry was carried out by Burlamacchi and coworkers[3,4]. In the papers[3,4], these authors observed line broadening and a decrease of the signal intensity with increasing concentration of $S_2O_4^{2-}$ ions at room and higher temperatures. The cited authors interpreted the decrease of the signal intensity as the formation of a inner-sphere complex and the broadening of the line as the formation of an outer-sphere complex. In the paper[5], the authors studied the ionic equilibria involving Mn(II) ions and Cl^-, ClO_4^- and NO_3^- ions on the basis of the mentioned effects.

The influence of sulphate ions on the signal intensity of Mn(II) ions, presented in this work, has not yet been described in the literature.

EXPERIMENTAL

EPR spectra of the aqueous solutions of Mn(II) ions were measured with the spectrometer ER-9, Zeiss, Jena, (working frequency $\nu = 9.37$ GHz) with 100 kHz field modulation. Aqueous solutions of Mn(II) ions were placed in a special silica cell used for samples with large dielectric losses. The solutions were prepared from r.g. $MnCl_2.4\,H_2O$ and Na_2SO_4 (Lachema, Brno)

and re-distilled water. All measurements were carried out at room temperature; the inner temperature of the sample cavity was approx. 25°C. The line width, ΔH, as the difference between points of maximum slope, was measured from the distance between the peaks of the fourth line of the first derivative of the curve. The line shape of the hyperfine components in effect corresponds to the Lorentzian line shape. The signal intensity is expressed as $(\Delta H)^2 h$, where h is the peak-to-peak amplitude of the derivative spectrum.

RESULTS

Mn(II) ions in aqueous solution yield an EPR spectrum as shown on Fig. 1. The signal intensity of the fourth line decreases non-linearly with increasing concentration of sodium sulphate, and the line width increases (Figs 2 and 3). The decrease of signal intensity and broadening of the line was observed in the concentration range $0-2\text{M}$ sodium sulphate at manganese(II) chloride concentrations of 10^{-2}, $5 \cdot 10^{-3}$ and 10^{-3}M. The decrease of signal intensity at low Na_2SO_4 concentration is relatively large and gradually becomes smaller; at a concentration of Na_2SO_4 of 2M, it approaches a limiting value corresponding to $22 \cdot 2\%$ of the original signal intensity. The decrease of the signal intensity does not occur when the 2M solution of sodium sulphate is replaced by a 2 to 4M solution of sodium perchlorate.

DISCUSSION

The previous papers[1-5] pointed to a stepwise equilibrium process between the solvated free ions, Mn_{aq}^{2+}, and ionic ligands:

$$Mn_{aq}^{2+} + SO_{4aq}^{2-} \xrightleftharpoons{K_1} Mn(H_2O)SO_{4aq} \xrightleftharpoons{K_2} MnSO_{4aq},$$
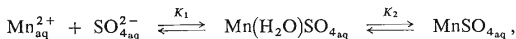
where K_1 is the equilibrium constant of the ion pair and K_2 is the equilibrium con-

Fig. 2

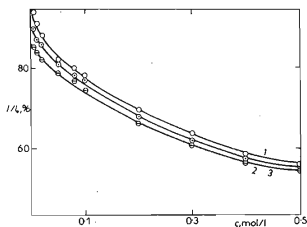Dependence of the Signal Intensity of Mn(II) Ions on Na_2SO_4 Concentration

1 10^{-2}M-$MnCl_2$ ($I_1 = 22.7\%$), *2* 5.10^{-3} M-$MnCl_2$ ($I_1 = 22.2\%$), *3* 10^{-3} M-$MnCl_2$ ($I_1 = 21.8\%$).
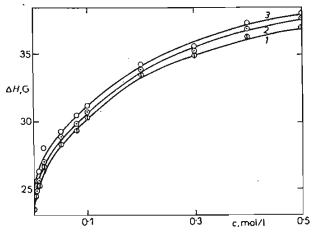

Fig. 3

Dependence of the Line Width (fourth line of the EPR spectrum of Mn(II) ions) on Na_2SO_4 Concentration

1 10^{-2}M-$MnCl_2$ ($\Delta H_1 = 40.76$ G), *2* $5 . 10^{-3}$M-$MnCl_2$ ($\Delta H_1 = 40.93$ G), *3* 10^{-3}M-$MnCl_2$ ($\Delta H_1 = 41.10$ G),

stant expressing the ratio of the equilibrium concentrations of inner- and outer-sphere complexes (ion pairs). Broadening of the line width and decrease of the signal intensity for Mn(II) is caused by substitution of one or more water molecules by sulphate ion in the coordination sphere resulting in relaxation of the electron spin. Quantitative treatment of the general dependence of the line width on the concentration of sulphate ions is difficult (due to the fact that the broadening of the line is influenced by ion pairs and complexes); the signal can, however, be attributed solely to ion pairs at high concentrations of sulphate ions where the signal intensity reaches the limiting value I_1 and where the equilibrium is shifted to the right hand side. Under these conditions the expression $(I_0 - I_1)/I_1$ gives the ratio of the equilibrium concentration of the inner-sphere complex and the equilibrium concentration of the ion pair, and is thus the value of the equilibrium constant, $K_2 = 3.5 \pm 0.1$. Because the product $K_1 K_2$ represents the value of the total equilibrium constant, $K = 200$ l . . mol^{-1}, determined conductometrically for the temperature[6] 25°C, it was possible to determine also the value of the association constant of the ion pair $K_1 = 57.2 \pm 1.6$ l mol^{-1}. This value agrees with the value $K_1 = 52.5$ l mol^{-1} as determined by Atkinson and Kor by means of sonic absorption[7]. The value of the constant $K_2 = 3.5 \pm 0.1$ determined in this work agrees plausibly with the value $K_2 = 3.44$ as determined by the mentioned authors[8] using the ultrasonic absorption method.

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Translated by M. Štuliková.