

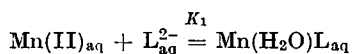
# Electron paramagnetic resonance study of ion pairs of Mn(II) ions with oxalate, malonate, and succinate ions

E. TREINDL and A. OLEXOVÁ

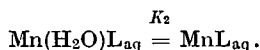
*Department of Physical Chemistry, Faculty of Natural Sciences,  
Komenský University, 801 00 Bratislava*

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The association of manganese(II) ions with oxalate, malonate, and succinate ions was studied as a two-step equilibrium process. The first step corresponds to



and the second one to



In all three cases, values of the equilibrium constants  $K_1$  and  $K_2$  were determined at 25°C using the e.p.r. spectrometry from the dependence of the signal intensity of Mn(II) ions on the concentration of the carboxylate ions.

The found values of the association constants of ion pairs decrease in the series oxalate > malonate > succinate, analogously to a decrease of the hydration entropy of the corresponding inner-sphere complexes.

The study of ion pairs is based predominantly on the conductometry of their solutions, the kinetic investigation of their reactions, the detailed examination of their spectra in various solvents at several temperatures as well as on the relaxation measurements. The e.p.r. spectrometry is perhaps the most efficient tool for investigating the nature of the ion pairs. This was for the first time pointed out by *Weissman* [1, 2] on the example of the splitting of the e.p.r. lines of anion radicals associated with cations possessing a nuclear spin. Valuable information about the location of the cation in an ion pair may follow from the value of the constant of hyperfine splitting while the line width and its shape may provide information on dynamic processes of the ion pairs.

The ion pairs are surrounded in the solution by solvent molecules in various arrangements. A change of one configuration into another one occurs with a frequency which is dependent on the temperature, the nature of the ion pair and the solvent. The ion pairs are inner-sphere, "tight", or outer-sphere, "free", depending on a number of the solvent molecules located between the two ions.

*Weissman* and co-workers [3] pointed out in their pioneer work that the rate of the electron exchange between naphthalenides and naphthalene depends on the structural arrangement of the ionic association of the ion radicals. The electron-exchange rate was determined from the broadening of the e.p.r. line. The Mn(II) ion pairs were studied by an e.p.r. method based on the observation of *Myers* and

co-workers [4, 5] who studied the influence of halide and sulfate ions on the width of the fourth line of Mn(II). *Burlamacchi* and co-workers [6–8] studied the association of Mn(II) ions using line broadening and/or a decrease of the signal intensity with increasing concentration of  $S_2O_4^{2-}$ ,  $Cl^-$ ,  $ClO_4^-$ , or  $NO_3^-$  ions. The interpretation of their results is based on the scheme of the two-step equilibrium process between free ions, outer- and inner-sphere ion pairs. Recently, we described analogously the association of Mn(II) ions with sulfate ions [9] using the dependence of the signal intensity of Mn(II) ions on the concentration of sulfate ions.

In the present work we studied the ion pairs of Mn(II) ions with oxalate, malonate, and succinate ions, in continuity with our previous results.

### Experimental

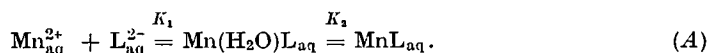
The e.p.r. spectra of aqueous solutions of Mn(II) ions were measured by an ER-9 (Zeiss, Jena) spectrometer with the working frequency 9.37 GHz and the field modulation 100 kHz. Aqueous solutions of Mn(II) ions were placed in a flat quartz cell used for solutions with great dielectric losses. The same results were achieved with a glass capillary cell with 1-mm diameter. The solutions were prepared from  $MnCl_2 \cdot 4H_2O$ , sodium oxalate, sodium malonate, or sodium succinate (all. anal. grade) and redistilled water.

All the measurements were performed at room temperature so that the temperature inside the resonator cavity was *ca.* 25°C. The line width,  $\Delta H$ , as a difference of the maximum slope, was measured from the peak-to-peak distance of the fourth line of the curve of the first derivative. The line shape of the hyperfine components corresponded to the shape of the Lorentz line. The signal intensity was expressed as  $(\Delta H)^2 h$ , where  $h$  is the peak-to-peak amplitude of the first derivative. Dependences of the relative signal intensity  $I/I_0$  being defined as a ratio of the signal intensity at a given concentration of the carboxylate ion and the signal intensity at its zero concentration were used in the work.

### Results and discussion

The signal intensity of the fourth line of the e.p.r. spectrum shows a nonlinear decrease with the increasing concentration of sodium oxalate, malonate, or succinate (Fig. 1). The decrease is relatively sharp at low concentrations of the carboxylate ions, then the slope gradually diminishes and the signal intensity reaches its limiting value at  $10^{-1}$  M concentration of the carboxylate ions. The decrease of the signal intensity is not caused by the increased conductivity of the electrolyte, it does not occur *e.g.* in the presence of 0.1 M sodium perchlorate.

Thus the decrease of the signal intensity of Mn(II) ions is brought about also in the studied cases by a substitution of one or two water molecules in the coordination sphere by oxalate, malonate, or succinate ion. This results in a relaxation of the electron spin. The two-step equilibrium process may be represented, in analogy with other works [6–9], by the scheme



$Mn(H_2O)L_{aq}$  stands for the outer-sphere, "free" ion pair while  $MnL_{aq}$  means the inner-sphere, "tight" ion pair. When the ligand concentration is sufficiently high

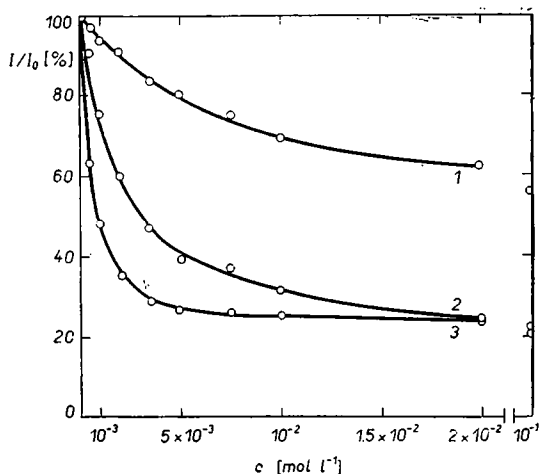


Fig. 1. Dependence of the signal intensity on the concentration of carboxylate ions.  $10^{-3}$  M- $\text{MnCl}_2$ ,  $c$  the concentration of sodium succinate,  $I_1 = 55.9\%$  (1); sodium malonate,  $I_1 = 21.2\%$  (2); sodium oxalate,  $I_1 = 23.8\%$  (3).

( $10^{-1}$  M), the e.p.r. signal intensity reaches its limiting value  $I_1$  which can correspond only to the outer-sphere ion pair. With respect to eqn (A), the equilibrium is then markedly shifted to the right. The expression  $(I_0 - I_1)/I_1$  is therefore equal to the ratio of the equilibrium concentrations of the inner-sphere ion pair (complex) and the outer-sphere ion pair, i.e. the value of the equilibrium constant  $K_2$ .

Since the products  $K_1K_2$  represent the known values of the total complex formation constants [10–12], it was possible to establish also the association constants of the outer-sphere ion pairs of  $\text{Mn}^{2+}$  ions with oxalate, malonate, and succinate ions (Table 1). The values of the association constants  $K_1$  decrease in the series oxalate > ma-

Table 1

Equilibrium constants of the association of  $\text{Mn}(\text{II})$  ions with oxalate, malonate, and succinate ions

System	Equilibrium constants	Ref.
$\text{Mn}^{2+}, \text{C}_2\text{O}_4^{2-}$	$K = K_1K_2 = 9.28 \times 10^3$ $K_1 = 2.9 \times 10^3$ $K_2 = 3.2 \pm 0.1$	[10] This paper This paper
$\text{Mn}^{2+}, \text{C}_3\text{H}_2\text{O}_4^{2-}$	$K = K_1K_2 = 1.93 \times 10^3$ $K_1 = 5.2 \times 10^2$ $K_2 = 3.7 \pm 0.1$	[11] This paper This paper
$\text{Mn}^{2+}, \text{C}_4\text{H}_4\text{O}_4^{2-}$	$K = K_1K_2 = 1.84 \times 10^2$ $K_1 = 2.3 \times 10^2$ $K_2 = 0.79 \pm 0.1$	[12] This paper This paper

lonate > succinate. A similar decrease of the hydration entropy was reported for the corresponding inner-sphere ion pairs (complexes) [13]. The formation of the studied ion pairs (in the first step) is apparently also accompanied by a release of the water molecules according to the mentioned series. This series may also reflect their increasing polarity with decreasing stability.

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