1018. *Manganese*(II) *Chloride Complexes. Part I. Stability Constants.*

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The existence of the complex species $MnCl^+$, $MnCl_2$, and $MnCl_3^-$ in aqueous solution has been established and their stability constants have been measured by a cation-exchange method. Manganese-54 has been employed as a tracer. The values obtained for the stability constants $\beta_j = [MnCl_j^{(2-j)+}]/[Mn^{2+}][Cl^-]^j$, valid for 20° and ionic strength 0·691M maintained with perchloric acid are: β_1, 3·85 ± 0·15; β_2, 1·80 ± 0·1; β_3, 0·44 ± 0·08.

CHLORIDE complexes of manganese(II) in aqueous solution have been studied previously by anion-exchange,[1] spectrophotometric,[2] refractometric,[3] and conductance[4] methods. Most of this work has provided only qualitative information concerning the stability of the species.

In the present study ^{54}Mn has been used as tracer, together with a cation-exchange resin, to determine stability constants of manganese(II) chloride complexes. The resin, Zeo-Karb 225, has been employed in the H^+-form, and the ionic strength of the solutions has been kept constant (0·691M) by means of perchloric acid. The distribution of the radiomanganese at equilibrium between the ion-exchange resin and the complex solutions has been determined by γ-ray scintillation counting. The conditions employed were similar to those used by us in a study of zinc halide complexes,[5] and the results obtained should be comparable with those for the zinc systems.

The work forms part of a systematic investigation of halide species formed in solution by metals of the first transition series in oxidation state +2. Manganese-54 has a half-life of 291 days. It decays by electron capture with the emission of γ-rays of energy 0·84 Mev.

The method used to derive the individual stability constants, $\beta_j = [MnCl_j^{(2-j)+}]/[Mn^{2+}][Cl^-]^j$ ($j = 1, 2, \ldots n$), has been developed from that due to Fronaeus.[6] It is based on the assumption that no polynuclear manganese complexes are formed either in solution or in the resin phase, which is a reasonable presumption since the total metal concentration was very low ($7{\cdot}6 \times 10^{-6}$M) and the solutions were of quite high acidity (0·691M). Moreover, in a study of the distribution of Mn^{II} between hydrochloric acid and tri-n-butyl phosphate[7] no evidence of the existence of polynuclear complexes was observed with concentrations of manganese in the range $2{\cdot}55 \times 10^{-6}$M to $1{\cdot}024 \times 10^{-4}$M.

The following notation has been used (cf. Carleson and Irving[8]):

C'_{Mn}, C'_{Cl} = total concentrations (moles/l.) of manganese and chloride in solutions before addition of the ion-exchange resin.
C_{Mn}, C_{Cl} = corresponding total concentrations in the solution after equilibration with the resin.
$[M]$ = equilibrium concentration of a species in aqueous solution.
$[M]_R$ = equilibrium concentration of a species in the resin phase (moles/g. of dry resin).

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[1] Kraus and Moore, *J. Amer. Chem. Soc.*, 1953, **75**, 1460; Kraus, Nelson, Clough, and Carlston, *ibid.*, 1955, **77**, 1391; Kraus and Nelson, " Peaceful Uses of Atomic Energy," United Nations, New York, 1956, Vol. VII, p. 113.

[2] Ibers and Davidson, *J. Amer. Chem. Soc.*, 1950, **72**, 4744; Schläfer, *Z. phys. Chem.* (*Frankfurt*), 1956, **6**, 201; Hartmann and Schläfer, *Rec. Trav. chim.*, 1956, **75**, 648.

[3] Deich, *Zhur. neorg. Khim.*, 1958, **3**, 2420.

[4] James, Thesis, London, 1947.

[5] Short and Morris, *J. Inorg. Nuclear Chem.*, 1961, **18**, 192.

[6] Fronaeus, *Acta Chem. Scand.*, 1951, **5**, 859; 1952, **6**, 1200; *Svensk Kem. Tidskr.*, 1953, **65**, 19.

[7] Morris and Short, unpublished work.

[8] Carleson and Irving, *J.*, 1954, 4390.

a' = corrected activity (counts per min. per 2 ml.) of ^{54}Mn in solution before addition of the resin.
a = corresponding activity of ^{54}Mn in the solution after equilibration with the ion-exchanger.
$\phi = (C_{\text{Mn}})_{\text{R}}/C_{\text{Mn}}$.
$X = 1 + \sum_{j=1}^{n} \beta_j[\text{Cl}^-]^j$; $X_j = (X_{j-1} - \beta_{j-1})/[\text{Cl}^-]$; $(X_0 = X;\ \beta_0 = 1)$.
ν = initial volume of the solution.
$\nu\delta$ = volume at equilibrium (where the factor δ is due to the swelling of the dry resin in contact with solution).
m = weight of the dry resin used.

With this notation, it follows that at equilibrium:

$$C_{\text{Mn}} = [\text{Mn}^{2+}] + [\text{MnCl}^+] + [\text{MnCl}_2] + \ldots$$
$$= [\text{Mn}^{2+}](1 + \sum_{j=1}^{n} \beta_j[\text{Cl}^-]^j).$$

Also, if it is assumed that the concentration of complexes with zero or negative charges in the resin is negligible, then

$$(C_{\text{Mn}})_{\text{R}} = [\text{Mn}^{2+}]_{\text{R}} + [\text{MnCl}^+]_{\text{R}} \qquad (1)$$

(Kraus, Michelson, and Nelson [9] have demonstrated strong sorption of some negatively charged chloro-complexes by cation-exchange resins, particularly from solutions of very high ionic strength. However, they have shown that this effect is essentially negligible in the case of Mn$^{\text{II}}$.)

Application of the law of mass action to the exchange equilibria

$$\text{Mn}^{2+} + 2(\text{H}^+)_{\text{R}} \rightleftharpoons 2\text{H}^+ + (\text{Mn}^{2+})_{\text{R}}$$
$$\text{MnCl}^+ + (\text{H}^+)_{\text{R}} \rightleftharpoons \text{H}^+ + (\text{MnCl}^+)_{\text{R}}$$

gives the expressions

$$[\text{Mn}^{2+}]_{\text{R}}/[\text{Mn}^{2+}] = k_0[\text{H}^+]_{\text{R}}^2/[\text{H}^+]^2 = l_0;\ [\text{MnCl}^+]_{\text{R}}/[\text{MnCl}^+] = k_1[\text{H}^+]_{\text{R}}/[\text{H}^+] = l_1 \qquad (2)$$

Here k_0 and k_1 are functions of four activity coefficients. However, if the load $(C_{\text{Mn}})_{\text{R}}$ is kept reasonably constant and $\ll[\text{H}^+]_{\text{R}}$, both $[\text{H}^+]_{\text{R}}$ and the activity coefficients in the resin phase are effectively constant. These conditions were satisfied in the present work and, since $[\text{H}^+]$ was kept constant as was the ionic strength of the aqueous phase, k_0, k_1, and l_0, l_1 could be presumed to be constants. The distribution of manganese between resin and solutions is given by

$$\phi = (C_{\text{Mn}})_{\text{R}}/C_{\text{Mn}} = l_0(1 + l_1'[\text{Cl}^-])/X \qquad (3)$$

from equation (2), the definition of β_1, and where $l_1' = l_1\beta_1/l_0$. Values for ϕ could be obtained from experimental results by means of the relation

$$\phi = \nu(a' - a\delta)/ma. \qquad (4)$$

Since in the experiments $C_{\text{Mn}} \ll C_{\text{Cl}}$, $[\text{Cl}^-]$ was obtained with sufficient accuracy from the relationship $[\text{Cl}^-] \approx C_{\text{Cl}} = C_{\text{Cl}}'/\delta$. One could thus obtain corresponding values of ϕ and $[\text{Cl}^-]$ which must satisfy equation (3).

In order to determine the desired stability constants β_j, use was made of two new parameters, *viz.*:

$$\phi_1 = (l_0\phi^{-1} - 1)/[\text{Cl}^-], \qquad (5)$$
$$f = (l_0\phi^{-1}\{(\beta_1 - l_1')[\text{Cl}^-] - 1\} + 1)/[\text{Cl}^-]^2. \qquad (6)$$

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[9] Kraus, Michelson, and Nelson, *J. Amer. Chem. Soc.*, 1959, **81**, 3204.

By substitution of the value of ϕ from equation (3) the following relationships are obtained:

$$\phi_1 = \frac{\beta_1 - l_1' + [\mathrm{Cl}^-]X_2}{(1 + l_1'[\mathrm{Cl}^-])} \tag{7}$$

$$f = \frac{\beta_1(\beta_1 - l_1') - \beta_2 + [\mathrm{Cl}^-]\{X_2(\beta_1 - l_1') - X_3\}}{(1 + l_1'[\mathrm{Cl}^-])} \tag{8}$$

Since $X_j = \sum_{i=j}^{n} \beta_i[\mathrm{Cl}^-]^{i-j}$ is always a monotonic increasing function of $[\mathrm{Cl}^-]$,

$$\phi_1^0 = \lim_{[\mathrm{Cl}^-]\to 0} \phi_1 = \beta_1 - l_1', \tag{9}$$

$$f^0 = \lim_{[\mathrm{Cl}^-]\to 0} f = \beta_1(\beta_1 - l_1') - \beta_2. \tag{10}$$

The necessary graphical extrapolations can be made as illustrated in Fig. 1. By combining equations (5), (6), and (7), it can be shown that

$$f = \beta_1\phi_1 - X_2. \tag{11}$$

Then, if
$$\Delta f = f - f^0, \quad \text{and } \Delta\phi_1 = \phi_1 - \phi_1^0,$$

$$\Delta f/[\mathrm{Cl}^-] = (\beta_1\Delta\phi_1/[\mathrm{Cl}^-]) - \beta_3 - \beta_4[\mathrm{Cl}^-]. \tag{12}$$

In the present study a plot of $\Delta f/[\mathrm{Cl}^-]$ against $\Delta\phi_1/[\mathrm{Cl}^-]$ is a straight line (cf. Fig. 2) even with the higher values of $[\mathrm{Cl}^-]$. It appears, therefore, that $\beta_4 \approx 0$ under the conditions of our experiments. The stability constant β_1 follows from the slope of the rectilinear plot, and β_3 may be evaluated from the intercept. The value of β_2 may be obtained from equation (10).

As our work has been performed at an appreciable acidity, there should be no complications due to hydrolysis of the hydrated Mn^{2+} ion ($K_\mathrm{H} \approx 2{\cdot}5 \times 10^{-11}$) or to the formation of hydroxy-halide complexes.

EXPERIMENTAL

Manganese-54 of high specific activity was supplied as the chloride in aqueous solution by the Radiochemical Centre, Amersham. The tracer was converted into perchlorate by repeated evaporation with small quantities of perchloric acid, and a stock solution was made up. Afterwards tests for traces of chloride were carried out periodically and were always negative. Solutions of hydrochloric and perchloric acid used in the work were prepared from "AnalaR" materials.

The cation-exchange resin Zeo-Karb 225 (8% DVB; 30—50 mesh) was transformed into the H^+-form, dried over "Anhydrone," and stored in a closed bottle. The exchange capacity was found to be 3·64 milliequiv. per g. of "Anhydrone"-dried resin.

Distribution measurements were performed by mechanically shaking solutions (10 ml., ν) of manganese complexes ($7{\cdot}6 \times 10^{-6}$M), made up from stock radiomanganese, hydrochloric acid, and perchloric acid, with portions (0·75 g., m) of dry resin in 50-ml. Pyrex tubes fitted with ground-glass stoppers. All experiments were performed at 20° ± 1°. Shaking was for at least 36 hr. to ensure attainment of equilibrium. After equilibration, 2 ml. of each aqueous phase were accurately pipetted into standard Polythene counting cups and counted at constant geometry with a NaI(Tl) γ-ray scintillation counter (type 1186A). The background count was subtracted from the measured counting rates to give the corrected activities, a. The corrected counting rate of a standard reference solution of known manganese concentration was also determined at frequent intervals, to yield values for a'. No adsorption of radiomanganese on the walls of vessels was detected.

The swelling factor, δ, was determined by shaking $\nu = 10$ ml. of standard halogen acid with $m = 0{\cdot}75$ g. of resin and determining the change in hydrogen-ion concentration after equilibration. The value was always found to be 0·95.

RESULTS AND DISCUSSION

The experimental results for the effect of hydrochloric acid concentration on the cation-exchange distribution, and the functions used in evaluating stability and other constants, are given in Table 1. Application of the graphical procedures is illustrated in Figs. 1 and 2. In order to obtain satisfactorily consistent series of functions, it was necessary to carry out a certain amount of curve-fitting within the limits of counting

TABLE 1.

[Cl⁻] (mole/l.)	$10^3\phi$ (l./g.)	ϕ_1 (mole/l.)$^{-1}$	f (mole/l.)$^{-2}$	$\Delta f/[\text{Cl}^-]$ (mole/l.)$^{-3}$	$\Delta\phi_1/[\text{Cl}^-]$ (mole/l.)$^{-2}$
0	59·97	(0·871)	(1·557)	—	—
0·01815	59·02	0·8563	1·492	−3·581	−0·815
0·03629	58·18	0·8443	1·438	−3·279	−0·736
0·07281	56·57	0·8244	1·343	−2·911	−0·640
0·1080	55·14	0·8111	1·277	−2·593	−0·556
0·1455	53·74	0·7968	1·204	−2·426	−0·510
0·1815	52·48	0·7863	1·151	−2·237	−0·467
0·2164	51·32	0·7790	1·104	−2·093	−0·425
0·2540	50·15	0·7709	1·066	−1·933	−0·394
0·2912	49·05	0·7653	1·030	−1·812	−0·363
0·3621	47·05	0·7598	0·9694	−1·626	−0·308
0·4274	45·28	0·7590	0·9230	−1·483	−0·262
0·4837	43·92	0·7555	0·8967	−1·365	−0·239
0·5788	41·72	0·7558	0·8574	−1·209	−0·199
0·6411	40·41	0·7550	0·8386	−1·121	−0·181

$C'_{\text{Mn}} = 7\cdot6 \times 10^{-6}$M.

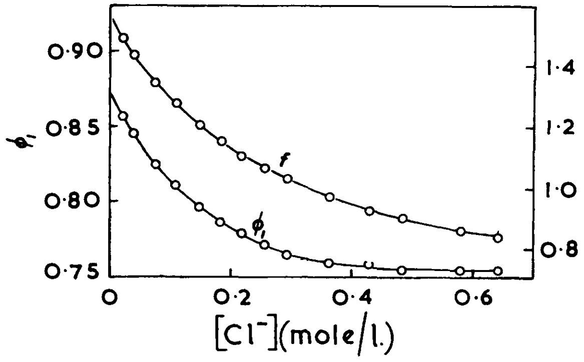

FIG. 1. Evaluation of $\phi_1{}^0$ and f^0 for the manganese(II) chloride system.

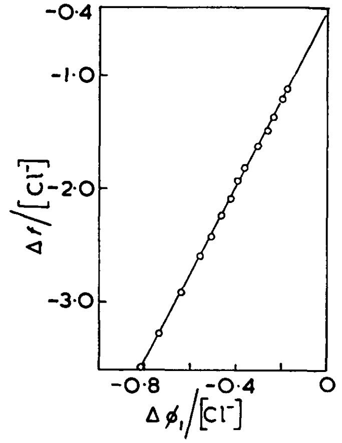

FIG. 2. Evaluation of β_1, β_2, and β_3 for the manganese(II) chloride system.

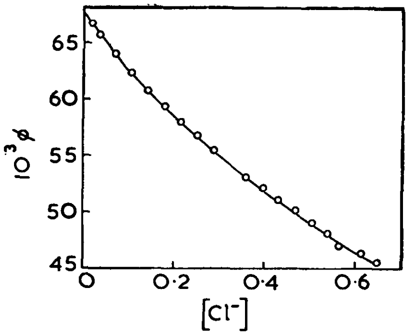

FIG. 3. Cation-exchange distribution of radio-manganese(II) with the resin Amberlite IR-120 (H⁺).

errors ($\pm 0{\cdot}5\%$). Final values obtained for the overall stability constants β_j and the step constants $K_j = \beta_j/\beta_{j-1}$ are listed in Table 2.

TABLE 2.

Stability constants for manganese(II) chloride complexes, valid for 20° and 0·691M-perchloric acid.

β_1	β_2	β_3	K_1	K_2	K_3
$3{\cdot}85 \pm 0{\cdot}15$	$1{\cdot}80 \pm 0{\cdot}1$	$0{\cdot}44 \pm 0{\cdot}08$	3·85	0·47	0·24

In addition to the experiments with Zeo-Karb 225, similar measurements were made with the cation-exchange resin Amberlite IR-120 in the H^+-form. Results for the effect of hydrochloric acid concentration on the distribution of radiomanganese with this other resin are plotted in Fig. 3. The curve shown in the diagram has been computed from equation (3), with the stability constants of Table 2, $l_0 = 67{\cdot}70 \times 10^{-3}$, and $l_1' = 2{\cdot}966 \times 10^{-3}$. It is apparent that the cation-exchange distribution variations with both Zeo-Karb 225 and Amberlite IR-120 are compatible with the stability constants derived in the present work. The uncertainties in the values for the stability constants given in Table 2 have been estimated from the results of several calculations of values for β_j by the use of a relaxation method (see Appendix).

Our study provides no evidence for the existence of the ion $MnCl_4^{2-}$ in solution in the range $[Cl^-] \leqslant 0{\cdot}64$M, though crystalline compounds $[Ph_3MeAs]_2[MnCl_4]$ and $[Et_4N]_2[MnCl_4]$ have been prepared[10] which are uni-bivalent electrolytes in solvents such as nitromethane.

Studies of the solvent extraction of tracer manganese from aqueous chloride solutions and of the Raman spectra and structure of manganese(II) chloride complexes in solution will be reported later.

APPENDIX

Relaxation methods[11] have recently been used in computing stability constants[12] from results obtained by various procedures.[13] The application of such a method to the present study is illustrated here.

Equation (3) may be rearranged in the form

$$\beta_1\phi[Cl^-] + \beta_2\phi[Cl^-]^2 + \beta_3\phi[Cl^-]^3 - \beta_1 l_1[Cl^-] - (l_0 - \phi) = 0.$$

Since values of ϕ, $[Cl^-]$, and l_0 are known from experimental results, this is an equation containing four unknowns, β_1, β_2, β_3, and $(\beta_1 l_1)$. Hence, by taking four sets of corresponding values for ϕ and $[Cl^-]$ and using the extrapolated value for l_0 a set of simultaneous equations can be set up. For typical data obtained on using the resin Zeo-Karb 225, four such equations may be written as:

$$\begin{aligned}
10{\cdot}712\beta_1 &+ 0{\cdot}1944\beta_2 + 0{\cdot}00353\beta_3 - 181{\cdot}5\beta_1 l_1 - 9{\cdot}68 = R,\\
5{\cdot}955\beta_1 &+ 0{\cdot}643\beta_2 + 0{\cdot}06946\beta_3 - 108\beta_1 l_1 - 4{\cdot}83 = S,\\
17{\cdot}037\beta_1 &+ 6{\cdot}169\beta_2 + 2{\cdot}234\beta_3 - 362{\cdot}1\beta_1 l_1 - 12{\cdot}92 = T,\\
2{\cdot}4148\beta_1 &+ 1{\cdot}3976\beta_2 + 0{\cdot}80894\beta_3 - 57{\cdot}88\beta_1 l_1 - 1{\cdot}825 = U,
\end{aligned}$$

where R, S, T, and U are residuals. A unit relaxation operations table may then be constructed in which the matrix of the coefficients is the transpose of the matrix of the original equation.

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[10] Gill and Nyholm, *J.*, 1959, 3997.

[11] Shaw, " An Introduction to Relaxation Methods," Dover Publns., New York, 1953.

[12] Watkins and Jones, *J. Inorg. Nuclear Chem.*, 1961, **16**, 187.

[13] Leden, *Z. phys. Chem.*, 1941, *A*, **188**, 160; Bjerrum, " Metal Ammine Formation in Aqueous Solution," P. Haase, Copenhagen, 1957; Eriksson and Ringbom, *Acta Chem. Scand.*, 1953, **7**, 1105; Eriksson, *ibid.*, p. 1146; DeFord and Hume, *J. Amer. Chem. Soc.*, 1951, **73**, 5321; DeFord, Hume, and Cave, *ibid.*, p. 5323.

This Table shows the change in the residual brought about by a unit change in an unknown. For the present example the unit operations table results in:

	$\Delta(R)$	$\Delta(S)$	$\Delta(T)$	$\Delta(U)$
$\Delta\beta_1$	10·712	5·955	17·04	2·415
$\Delta\beta_2$	0·1944	0·643	6·17	1·398
$\Delta\beta_3$	0·00353	0·0695	2·234	0·8089
$\Delta(\beta_1 l_1)$	−181·5	−108	−362·1	−57·88

	R	S	T	U
$\Delta\beta_j = \Delta(\beta_1 l_1) = 0$	−9·68	−4·83	−12·92	−1·825
$\Delta(\beta_1 l_1) = 0·1$	−27·83	−15·56	−49·13	−7·613
$\Delta\beta_1 = 3·0$	4·306	2·305	1·99	−0·368
$\Delta(\beta_1 l_1) = 0·1$	−13·844	−8·495	−34·22	−6·156
$\Delta\beta_1 = 0·75$	−5·81	−4·0288	−21·44	−4·3448
$\Delta\beta_2 = 1·5$	−5·5184	−3·0643	−12·185	−2·2478
$\Delta\beta_3 = 0·44$	−5·5168	−3·0337	−11·202	−1·8919
$\Delta\beta_2 = 0·3$	−5·4585	−2·8408	−9·351	−1·4005
$\Delta\beta_1 = 0·1$	−4·3873	−2·2453	−7·647	−1·159
$\Delta(\beta_1 l_1) = -0·021$	−0·5758	0·02273	−0·0429	−0·01545
$\Delta\beta_3 = 0·0191$	−0·5757	0·024057	−0·0002	0·0000

The relaxation table is then constructed; one way is annexed. After the residuals have been reduced suitably, the values for the stability constants and the other unknown constant $(\beta_1 l_1)$ are obtained by summing the changes which have been made in each of the variables. In the present example: $\beta_1 = \sum\Delta\beta_1 = 3·85$, $\beta_2 = \sum\Delta\beta_2 = 1·8$, $\beta_3 = \sum\Delta\beta_3 = 0·459$, and $(\beta_1 l_1) = \Sigma\Delta(\beta_1 l_1) = 0·179$.

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