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NUCLEAR MAGNETIC RELAXATION RATE AS INDICATOR IN COMPLEXIMETRIC TITRATIONS

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SUMMARY

Nuclear magnetic relaxation titration was applied for determinations of transition metal ions in aqueous solutions through complex formation. With EDTA, Co^{2+}, Cu^{2+}, Mn^{2+}, Fe^{3+} and Ni^{2+} were titrated; the simultaneous determination of Cu^{2+} and Mn^{2+} is possible. With NTA, single ion solutions, e.g. Mn^{2+}, and multiple ion solutions can be analysed. The influence of kinetic effects is shown and the possibility of determining ratios of equilibrium constants is discussed.

The nuclear magnetic relaxation rate can be used in chemical analysis as shown by Nothnagel and Weiss [1] and by Schlüter and Weiss [2, 3] (nuclear magnetic relaxation titration, n.m.r.t.). The nuclear magnetic relaxation times T_1 and T_2 of ^{1}H depend linearly on the concentration of paramagnetic ions in aqueous solutions. Furthermore, T_1 and T_2 are functions of the magnetic moment μ_{eff} of the paramagnetic ions in the solution, and of the gyromagnetic ratio of the protons, γ_H, and they are also properties of the solutions involved [1—3]. Restricting the experiments to measurements of T_1, which is measured more conveniently than T_2, the paramagnetic relaxation rate $(1/T_1)_p$ is given by

$$(1/T_1)_p = \sum_i a_i C_i \tag{1}$$

where C_i are the concentrations of the different paramagnetic ions in the solution and a_i the magnetic coefficients, $a_i = f(\mu_{eff}, \gamma_H, \ldots)$. In investigations of complexes in solutions, the concentration of the paramagnetic ions is constant and a correction for dilution effects has to be applied [3]. However, the complexing reagent changes the magnetic coefficients a_i of the ion considered to some extent. For example, the formation of $[Ni(CN)_4]^{2-}$ is accompanied by a strong change in μ_{eff} and thus by a large change in $(1/T_1)_p$ [1]. Much smaller but measurable changes of a_i were observed in compleximetric titrations with EDTA and NTA. Some single ion determinations are reported here and the use of n.m.r.t. in the simultaneous compleximetric determination of two different ions is discussed.

THEORY

Discussion is restricted to 1:1 complexes, $Me + L \rightleftharpoons MeL$, and it is assumed that the magnetic coefficient a (complexed ion) $\neq$ a (uncomplexed ion). Then it follows from eqn. (1):

$$(1/T_1)_p = \sum_i a_i C_i = a_{Me}\,[Me] + a_{MeL}\,[MeL] \qquad (2)$$

Taking the mass balance $[Me]_0 = [Me] + [MeL]$ into account,

$$(1/T_1)_p = a_{MeL}\,[Me]_0 + (a_{Me} - a_{MeL})\,[Me] = a_{Me}\,[Me]_0 + (a_{MeL} - a_{Me})\,[MeL] \qquad (3)$$

Equation (3) shows that $(1/T_1)_p$ of the protons in the solution changes if the difference in the magnetic coefficients is not zero: $a_{Me} \neq a_{MeL}$. Generally, the relaxation rate $(1/T_1)_p$ depends on both the aquo ions $Me(H_2O)_n$ and the complex ions MeL (for simplification the electric charge is neglected); eqn. (1) has to be written in the form:

$$(1/T_1)_p = \sum_i a_i C_i = \sum_{q=1}^{k} a_q C_{Me}^{(q)} + \sum_{r=1}^{m} a_r C_{MeL}^{(r)} \qquad (4)$$

For the practical application of n.m.r.t. in compleximetry, a linear change in $(1/T_1)_p$ as a function of the added ligand concentration [L] is wanted for both regions $[L] < [L]_{eq}$ (reaction line) and $[L] > [L]_{eq}$ (excess line), where eq denotes the equivalence point. This condition is fulfilled if the effective complex formation constant is sufficiently large. For mass balance, before the equivalence point is reached

$$[L] \approx 0; \quad [MeL] = [L]_0\left(\frac{V_L}{V_{tot}}\right); \quad [Me] = [Me]_0\left(\frac{V_0}{V_{tot}}\right) - [L]_0\left(\frac{V_L}{V_{tot}}\right) \qquad (5)$$

where V_0 is the initial volume containing $[Me]_0$, $[L]_0$ is the concentration of L in the standard solution, V_L the volume of the standard solution added, and $V_{tot} = V_0 + V_L$ the total volume of the reaction mixture. In this range the paramagnetic relaxation rate is then:

$$\left(\frac{1}{T_1}\right)_p = a_{Me}\,[Me]_0\left(\frac{V_0}{V_{tot}}\right) + (a_{MeL} - a_{Me})\,[L]_0\left(\frac{V_L}{V_{tot}}\right) = \left(\frac{1}{T_1}\right)_{p,o}\left(\frac{V_0}{V_{tot}}\right) + (a_{MeL} - a_{Me})\,[L]_0\left(\frac{V_L}{V_{tot}}\right) \qquad (6)$$

where $(1/T_1)_{p,o}$ is the initial paramagnetic relaxation rate in the paramagnetic solution. Above the equivalence point, $(1/T_1)_p$ stays constant as long as the ligand L is diamagnetic and the experimentally measured paramagnetic relaxation rate is corrected for dilution effects. Finally, for one kind of paramagnetic ion, after correcting the dilution effect,

$$\frac{V_{tot}}{V_0}\left(\frac{1}{T_1}\right)_p = a_{Me}\,[Me]_0 + (a_{MeL} - a_{Me})\,[L]_0\;V_L/V_0 \qquad (7)$$

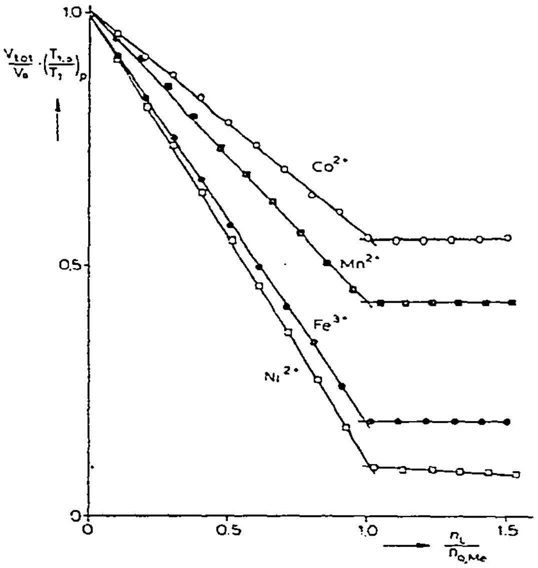
This equation shows linear dependence of the corrected relaxation rate $(V_{\mathrm{tot}}/V_0)\,(1/T_1)_p$ on the added volume V_L of the titrant.

RESULTS AND DISCUSSION

*Titrations with ethylenediamine-*N,N,N′,N′*-tetraacetic acid (EDTA)*

The determination of cations by titration with EDTA is based on the formation of soluble but undissociated chelate complexes. The equivalence point of the reaction is observed with an indicator which forms colored complexes with the metal ion that are less stable than the metal complexes with EDTA. During the formation of the complexes, protons are released and the conditions for the reaction (e.g. pH value) have to be chosen carefully. When the nuclear magnetic relaxation rate is the indicating method, the external conditions for the reaction are probably less critical if the effective constant of complex formation is sufficiently large.

Figure 1 shows the titration curves for Co^{2+}, Mn^{2+}, Fe^{3+}, and Ni^{2+} with the disodium salt of EDTA. The corrected and normalized paramagnetic relaxation rate, $(V_{\mathrm{tot}}/V_0)\,(T_{1,0}/T_1)_p$, is plotted as a function of the ratio of the mol number of the organic ligand to the initial mol number of para-



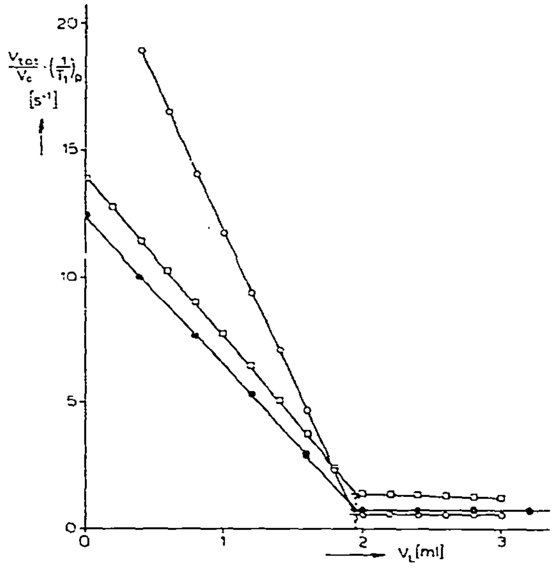


Fig. 1. N.m.r.t. of different transition metal ions with EDTA (disodium salt). The corrected and normalized proton relaxation rate, $(V_{\mathrm{tot}}/V_0)\,(T_{1,0}/T_1)_p$, is plotted as a function of the ratio of the mol number of the ligand to the mol number of the transition metal ion in solution.

Fig. 2. N.m.r.t. of Ni^{2+} with EDTA in different media. The corrected relaxation rate of the protons, $(V_{\mathrm{tot}}/V_0)\,(1/T_1)_p$, is plotted as a function of the volume of titrant (0.1 M EDTA, disodium salt). $V_0 = 10.0$ ml, $[Ni^{2+}]_0 = 0.0196$ M. ○ Ammoniacal solution; □ neutral solution; ● acetate buffer.

magnetic ions in the solution. This diagram shows the usefulness of n.m.r.t. in compleximetric titrations.

Titration of Ni^{2+} with EDTA. Details of the titration of Ni^{2+} with EDTA are shown in Fig. 2, where the corrected relaxation rate, $(V_{tot}/V_0)(1/T_1)_p$, is plotted as a function of the added volume V_L of 0.1 M EDTA solution, disodium salt. The influence of the medium (e.g. pH) on the n.m.r.t. of Ni^{2+} with EDTA was studied in ammoniacal solution, neutral solution, and acetate-buffered solution.

Independent of the particular pH, the volume-corrected relaxation rate changes linearly with the added volume of EDTA solution. In the three cases, 10.0 ml of 0.0196 M $NiSO_4$ were titrated with 0.1 M EDTA (Titriplex III, E. Merck, Darmstadt); the equivalence point was found at $V_{eq} = (1.96 \pm 0.01)$ ml which was the same as obtained in a control titration with murexide as indicator. Figure 2 shows that the pH of the solution is only of minor importance in determining V_{eq} by n.m.r.t., in contrast to the classical indicator method. The slopes of both the reaction line and the excess line, however, depend on the particular conditions chosen for the reaction. The sensitivity of the slope of the reaction line to the reaction conditions is probably due to the medium-dependent formation of different Ni^{2+} complexes (different magnetic factors a_i, see eqn. 1). For n.m.r.t. of Ni^{2+} with EDTA, an ammoniacal solution is the most useful.

N.m.r.t. of Cu^{2+} with EDTA. The n.m.r.t. of Cu^{2+} with EDTA is similar to the determination of Ni^{2+} by this method. In Fig. 3 the titration of

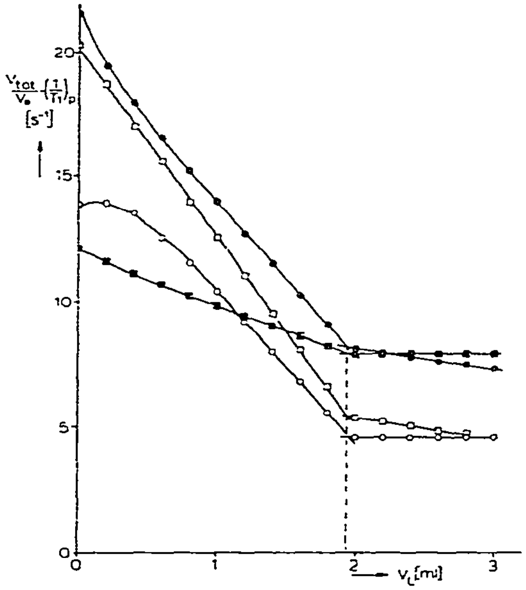
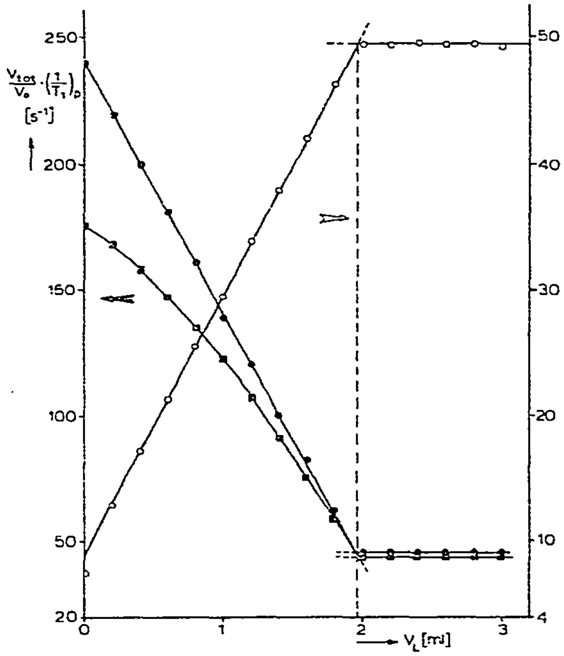


Fig. 3. N.m.r.t. of V_0 = 10.0 ml of 0.0195 M Cu^{2+} with the disodium salt of EDTA (0.1 M) in different media. ● Neutral solution, ▫ neutral solution + K_2SO_4; ○ acetate buffer; ▪ ammoniacal solution.

10.0 ml of 0.0195 M $CuSO_4$ with 0.1 M EDTA is shown for different reaction conditions. The equivalence point, independent of external conditions, was (1.95 ± 0.01) ml. However, in contrast to the titration of Ni^{2+}, deviations from linearity are found at the start of the titration. This is probably due to the formation of H^+ during the titration whereby the equilibria may be influenced. Another interesting point is that, depending on the conditions, different relaxation rates are found at the equivalence point. During the reaction not only the complex $Cu(EDTA)^{2-}$ but also other complexes are formed, particularly protonated complexes. This was proved by studying the proton spin lattice relaxation time T_1 in aqueous solution of $Cu(EDTA)^{2-}$ as a function of the H^+ concentration. At high proton concentrations (pH = 0 ... 1) the relaxation rate is about 9.0 s^{-1}. With increasing pH, $1/T_1$ decreases to about 4.5 s^{-1} (pH $\approx$ 6). Above pH 10, $1/T_1$ increases.

N.m.r.t. of Fe^{3+} with EDTA. Fe^{3+} forms very stable complexes with EDTA. A pH value of 2.5 and sulfosalicylic acid, tiron, or xylenol orange as indicator are common in classical compleximetry. N.m.r. titrations of 0.0196 M $Fe(NO_3)_3$ (10.0 ml) with 0.1 M EDTA were done in neutral solutions and in solutions acidified with 0.10 ml of 2 M HNO_3, or buffered with acetate. The results are given in Fig. 4. Again, the reaction medium is important. In the acidified solution, $(V_{tot}/V_0)\,(1/T_1)_p$ decreases by a factor of about 5 until the equivalence point is reached. However, in the buffered



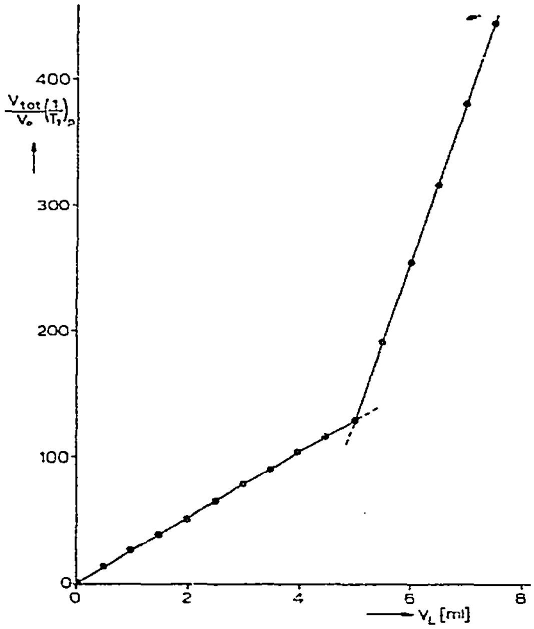


Fig. 4. N.m.r.t. of V_0 = 10.0 ml of 0.0198 M Fe^{3+} with the disodium salt of EDTA (0.1 M) in different media. ● Acidified solution; ■ neutral solution; ○ acetate buffer.

Fig. 5. N.m.r.t. of EDTA with Fe^{3+} solution (0.1 M $Fe(NO_3)_3$). V_0 = 10.0 ml of 0.05 M EDTA.

solution (V_{tot}/V_0) $(1/T_1)_p$ increases until the equivalence point is reached. In both cases the relaxation rate at the equivalence point is about the same (compare the two ordinates in Fig. 4). The large decrease of $(1/T_1)_{p,o}$ on the addition of a buffer solution is due to the formation of the complex $Fe_3(CH_3COO)_6O^+$. The almost identical excess lines are determined mainly by the influence of the Fe(EDTA) complex on the relaxation rate of the protons; therefore the pH is of minor importance. The n.m.r.t. curve for a pure $Fe(NO_3)_3$ solution is slightly bent, as the solution is partially hydrolysed. Protons produced during the titration shift the hydrolysis equilibrium. This explains the slight curvature of the reaction line. The reverse procedure — titration of an EDTA solution with an appropriate ionic solution — is also possible, as shown in Fig. 5. In this case, the effect is particularly pronounced because of the high effective magnetic moment of Fe^{3+}.

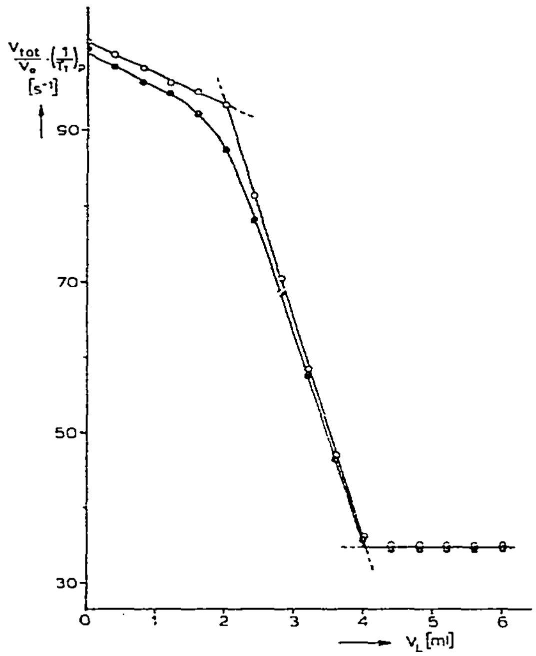
N.m.r.t. of Mn^{2+} *with EDTA.* The disodium salt of EDTA produces unreliable results because the protons released during titration prevent the complete formation of complexes at the equivalence point. With the tetrasodium salt good results were obtained.

N.m.r.t. of Co^{2+} *with EDTA.* The titration of Co^{2+} is similar to the Mn^{2+} titration, i.e. the tetrasodium salt of EDTA is required. The results are shown in Fig. 1. The complexation of Co^{2+} produces a smaller change in $(1/T_1)_p$ than Ni^{2+}, Fe^{3+}, or Mn^{2+}.

Simultaneous determination of several cations by n.m.r.t. with EDTA

EDTA forms very stable complexes with many polyvalent cations, so that it is not a selective reagent, although the selectivity can be increased by masking, pH control etc. As far as n.m.r.t. is concerned, the possibility of determining several cations directly without masking reagents, auxiliary complex-forming reagents, or variable pH, should be possible when the complex formation constants for the different cations in the solution differ by a factor of ca. 10^3, in the same way as for other instrumental methods. Also, the complex equilibria have to be reached quickly.

In mixtures of $Cu^{2+} + Mn^{2+}$, or $Ni^{2+} + Mn^{2+}$, the complexes Cu(EDTA) and Ni(EDTA) are formed before Mn^{2+} reacts with the chelating ligand EDTA. The magnetic coefficient a_i (see eqn. 1) for Mn^{2+} is quite different from the coefficients $a(Cu^{2+})$ and $a(Ni^{2+})$. N.m.r.t. of $Cu^{2+} + Mn^{2+}$ and of $Ni^{2+} + Mn^{2+}$ is possible; the results are shown in Fig. 6. At the beginning of the formation of Cu(EDTA) and Ni(EDTA), $(1/T_1)_p$ changes slowly. After complete complexation of Cu^{2+} in the mixture of $Cu^{2+} + Mn^{2+}$, the slope of the curve $(1/T_1)_p = f(V_L)$ changes abruptly and is quite steep in the range where Mn(EDTA) is formed. In the mixture $Ni^{2+} + Mn^{2+}$, the two steps are not so sharply separated, probably because of kinetic effects. The end of the complex formation of both $(Ni^{2+} + Mn^{2+})$—EDTA and $(Cu^{2+} + Mn^{2+})$—EDTA is marked by a very sharp change of $(1/T_1)_p = f(V_L)$. Further addition of EDTA changes the relaxation rate very little (the magnetic coefficients remain almost constant).



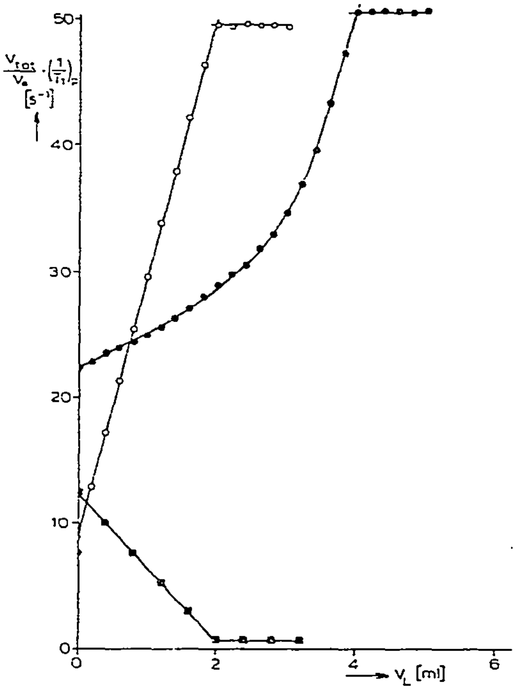


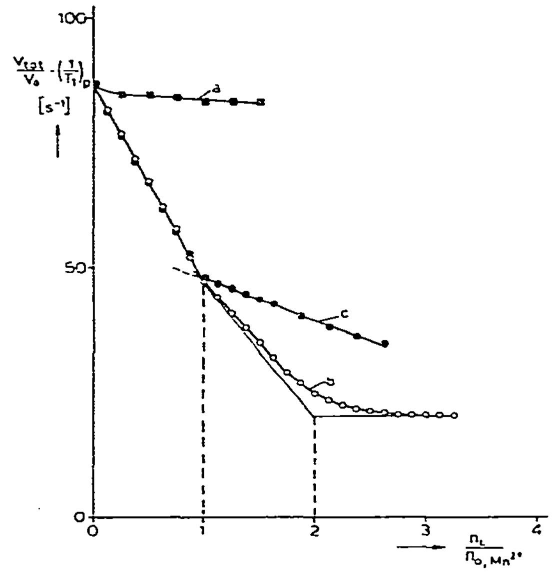
Fig. 6. Simultaneous titration of (Ni^{2+} + Mn^{2+}) and (Cu^{2+} + Mn^{2+}) with 0.05 M EDTA (tetrasodium salt). Initial volume: V_0 = 10.0 ml. ○ Cu^{2+} + Mn^{2+}, $[Cu^{2+}]_0 = [Mn^{2+}]_0 = 0.01$ M; ● Ni^{2+} + Mn^{2+}, $[Ni^{2+}]_0 = [Mn^{2+}]_0 = 0.01$ M.

Fig. 7. Simultaneous and individual titrations of Fe^{3+} + Ni^{2+} with 0.1 M EDTA (disodium salt) in acetate buffer solution. Initial volume: V_0 = 10.0 ml. ○ $[Fe^{3+}]_0 = 0.02$ M; ■ $[Ni^{2+}]_0 = 0.02$ M; ● $[Fe^{3+}]_0 = [Ni^{2+}]_0 = 0.02$ M.

Another example of a simultaneous n.m.r.t. is the determination of Ni^{2+} and Fe^{3+} in acetate-buffered solution of pH 4.62. The titration curve is shown in Fig. 7 together with those for the individual ions Ni^{2+} and Fe^{3+}. The titration curve of the mixture is the sum of the two individual titration curves.

N.m.r.t. with nitrilotriacetic acid (NTA)

NTA and its salts may be applied in compleximetric n.m.r.t., and complexes of the type MeL as well as MeL_2 are to be expected. In Fig. 8 the n.m.r.t. of Mn^{2+} with NTA is shown. Curve (a) was found with the disodium salt of NTA; complex formation is not complete and it is impossible to find the respective equivalence point. Satisfactory results were obtained with the trisodium salt of nitrilotriacetic acid. The hydrolysis equilibrium makes a solution of $N(CH_2COONa)_3$ strongly alkaline: $NTA^{3-} + H_2O = HNTA^{2-} + OH^-$. In the formation of metal complexes $Mn^{2+} + HNTA^{2-} = Mn(NTA)^- + H^+$, the H^+ ions formed are neutralized and the Mn^{2+} solution titrated is practically



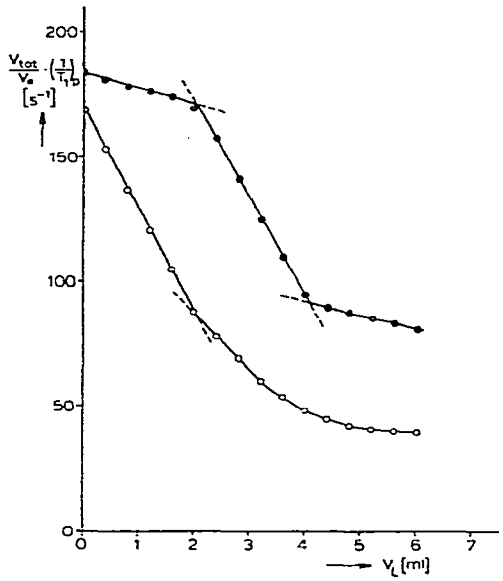


Fig. 8. N.m.r.t. of Mn^{2+} with nitrilotriacetic acid (NTA). Initial concentration of Mn^{2+}: 0.01 M. Initial volume of the solution: 10.0 ml. ■ Titration with disodium salt of NTA (0.1 M) (a); ○ titration with trisodium salt of NTA (0.1 M) (b); ● titration with trisodium salt of NTA (0.1 M) at pH 7.5 (borate) (c).

Fig. 9. Simultaneous titration of Ni^{2+} and Mn^{2+} with the trisodium salt of NTA (0.1 M). Initial volume: V_0 = 10.0 ml. ● $Mn^{2+} + Ni^{2+}$, $[Ni^{2+}]_0 = [Mn^{2+}]_0$ = 0.02 M; ○ Mn^{2+} alone, $[Mn^{2+}]_0$ = 0.02 M.

neutral until the complex formation is completed (a self-buffering system). Curve (b) in Fig. 8 shows the titration of Mn^{2+} with $N(CH_2COONa)_3$. The spin lattice relaxation rate of the protons decreases linearly with increasing concentration of the complex formed until the first equivalence point at $n_L/n_{o,Mn^{2+}} = 1$ is reached. Beyond this point, $Mn(NTA)^-$ reacts with a second ligand and forms the complex ion $Mn(NTA)_2^{4-}$. This reaction is not completed at the second equivalence point; the titration curve bends gently in this region.

The complex formation constant $K_2 = [MnL_2]/([MnL]\ [L])$ is clearly smaller than 10^6 l mol^{-1}. This limit is estimated because of the deviations of $(V_{tot}/V_0)\ (1/T_1)_p = f(n_L/n_{o,Me})$ from a straight line. A quantitative investigation of the curvature of the titration function $1/T_1 = f(n_L)$ should allow a calculation of K_2. To do so, the pH of the solution containing MnL^- was kept constant at 9.3 with a borate buffer, and $\log K_2 = 3.02 \pm 0.02$ (T = 25°C) was found. Dividing this value by the activity coefficient α_H of NTA, which takes the proton equilibria into account, gave $\log K_2 = 3.60 \pm 0.02$, in good agreement with the value $\log K_2 = 3.7 \pm 0.2$ determined by Schwarzenbach and Beidermann [4]. In a third experiment Mn^{2+} was titrated with $N(CH_2$-$COONa)_3$ at pH 7.5 (borate buffer). The results are shown in curve (c) of

Fig. 8; the curvature of $(1/T_1) = f(n_L/n_0)$ beyond $n_L/n_0 = 1$ is not visible in practice. This experiment reveals the importance of the proton concentration for the formation of $Mn(NTA)_2^{4-}$.

The trisodium salt of NTA can also be used for simultaneous titrations, e.g. for a solution of $(NiSO_4 + MnSO_4)$. At first, the complex $Ni(NTA)^-$, which is more stable than $Mn(NTA)^-$, is formed. Then $Mn(NTA)^-$ is formed before $Ni(NTA)^-$ reacts with NTA^{3-} to give $Ni(NTA)_2^{4-}$. These consecutive steps are indicated by the two breaks in the upper titration curve in Fig. 9. The lower curve represents the n.m.r.t. of Mn^{2+} alone with $N(CH_2COONa)_3$. First, the formation of $Mn(NTA)^-$ occurs (compare the slopes of the upper and lower curves). The second stage $Mn(NTA)^- + NTA \rightarrow Mn(NTA)_2^{4-}$ is represented by the bent part of the titration curve. The rather low equilibrium constant is responsible for this non-linear behavior (see above).

As a final example, the simultaneous titration of $(CaCl_2 + MnCl_2)$ with NTA was studied. There is only a small difference in the equilibrium constants of Ca^{2+} and Mn^{2+} with regard to the first and second complexing step. As expected, the individual equivalence points are no longer intercepts of straight lines but bent titration curves. From these curves ratios of equilibrium constants may be determined: $K_1(Mn(NTA)^-)/K_1(Ca(NTA)^-)$ and $K_2(Mn(NTA)_2^{4-})/K_2(Ca(NTA)_2^{4-})$. From the titration curve shown in Fig. 10, the deviations from the straight lines yield the equilibrium constants ($T = 25°C$): $K = K_1(Mn(NTA)^-)/K_1(Ca(NTA)^-) = 14.2$; $\log K = 1.15$; $K' = K_2(Mn(NTA)_2^{4-})/K_2(Ca(NTA)_2^{4-}) = 3.60$; $\log K' = 0.56$. These values are in good agreement with literature data: Mn^{2+}: $\log K_1 = 7.44$ [5], $\log K_2 = 3.7 \pm 0.2$ [4]. Ca^{2+}: $\log K_1 = 6.33$ [6], $\log K_2 = 3.43$ [7]. The values $\log K = 1.11$ and $\log K' = 0.27$ follow from these data.

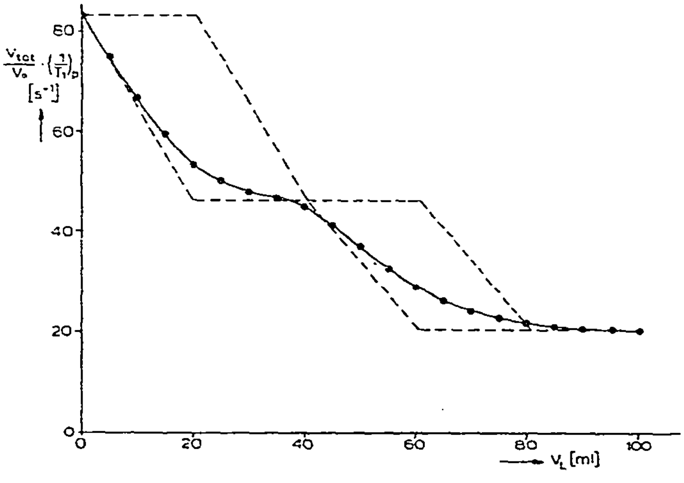


Fig. 10. Simultaneous titration of Mn^{2+} and Ca^{2+} with 0.05 M NTA (trisodium salt). Initial volume: $V_0 = 100.0$ ml. Initial concentrations: $[Mn^{2+}]_0 = [Ca^{2+}]_0 = 0.01$ M.

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