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COMPLEXOMETRIC TITRATIONS BASED ON THERMOCHROMISM

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Based on the thermochromism observed for the metal complexes of Xylenol Orange, complexometric titrations of Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} ions were successfully carried out in a lower pH region where the titrations at room temperature were impossible so far.

Copper(II) complex of 3,3'-bis[N,N-bis(carboxymethyl)aminomethyl]-o-cresolsulfonphthalein (Xylenol Orange, XO) is thermochromic in aqueous media.[1] The complexes of other triphenylmethane complexons with various divalent metal ions were also confirmed to be thermochromic.[2] These phenomena are primarily ascribed to a protolytic equilibrium between a complex having an uncoordinated phenolic hydroxyl group AH and a complex having a coordinated phenolate group A,

$$AH \overset{K}{\rightleftharpoons} A + H. \qquad (1)$$

AH is predominant at lower temperatures and A at higher temperatures. The orange color of the solution containing Cu(II)-XO complex in the pH region near the pK of Eq. 1 changes to reddish violet upon heating. The effect of heating the solution corresponds to the effect of elevating the pH of the solution.

We tried to carry out the complexometric titrations of Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} ions based on this phenomenon in a lower pH region where the ordinary titrations at room temperature were impossible so far. A 1.0×10^{-3} mol dm^{-3} XO solution of highest purity[3] was used as an indicator.

Figure 1 shows the % recovery of the metal ions at various pH adjusted with acetate buffers at 50 and 75 °C. The hatched regions in the figures correspond to the pH region where the ordinary complexometric titration can be carried out with XO as an indicator.[4] The scheme of the complexometric titration based on the thermochromism of the XO-complexes is summarized as follows:

$$n\,M + XO' \rightleftharpoons \begin{pmatrix} M_nxo & \text{(a high-temperature form)} \\ K \uparrow\downarrow H & \\ M_nxoH & \text{(a low-temperature form)} \end{pmatrix} \xrightarrow{n\,Y'} n\,MY + XO'. \qquad (2)$$

M_nxoH and M_nxo correspond to AH and A in Eq. 1, respectively.

In the lower pH region where AH is predominant, the complexometric titrations with XO as an indicator cannot be carried out at room temperature, since the colors of both AH and XO' are yellow. However, upon heating, the color of the solution

containing metal complexes changes to reddish violet in the pH region near the pK value of Eq. 2. Under this condition the color of the solution distinctly changes from reddish violet or reddish yellow to yellow at the end-point of the titration.

Table 1 shows the pH range for each metal ion where the complexometric titration can be carried out at 75 °C. For the metal concentrations used in the present work (ca. 2 x 10^{-4} mol dm^{-3}), the conditional stability constants of the EDTA complexes are sufficiently large for the performance of the complexometric titrations.

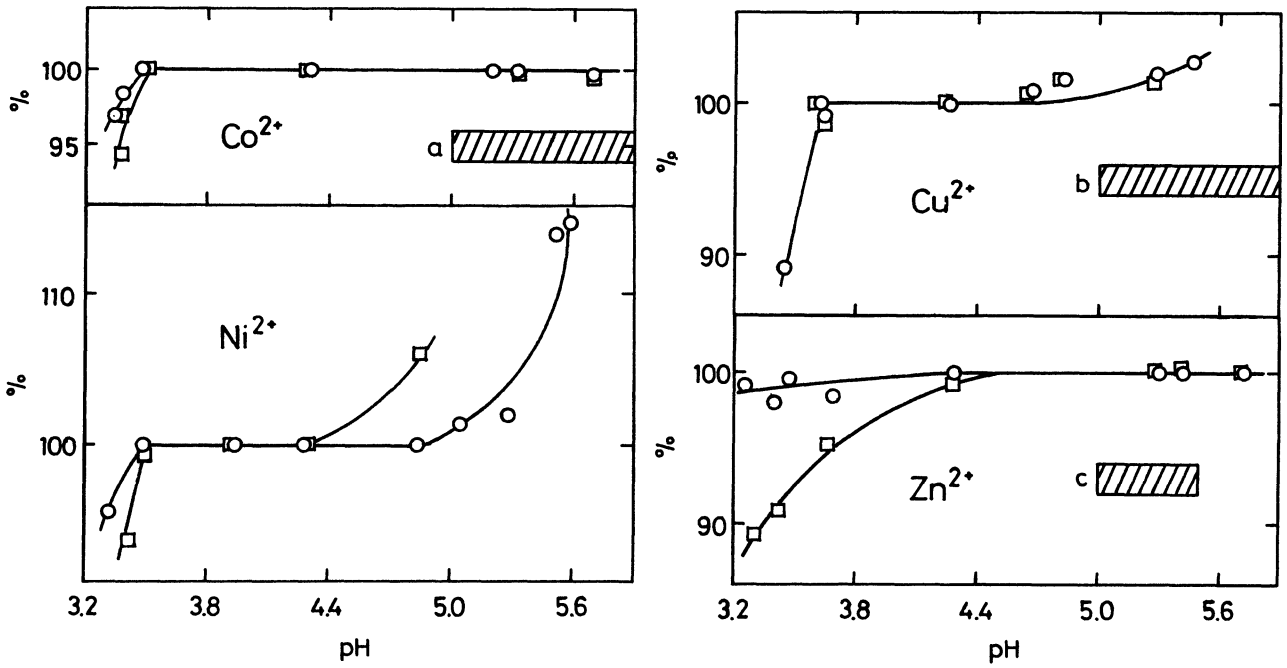

Fig. 1. pH-Dependence of the % recovery for the metal ions at 50 (□) and 75 °C (○) The hatched region shows the range of the pH where the complexometric titrations have been reported to be possible (a) at high temperature, (b) at room temperature by the addition of o-phenanthroline, and (c) at room temperature.[4] About 2 x 10^{-4} mol dm^{-3} metal ions were used.

Table 1. pH-Ranges where the titrations are possible at 75 °C within 100 ± 1 %.

Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
3.5 - 6.0	3.5 - 4.9	3.7 - 4.7	3.8 - 6.0

REFERENCES

1) M. Yamada, Bull. Chem. Soc. Jpn., 49, 1023 (1976).
2) S. Nakada, M. Yamada, T. Ito, and M. Fujimoto, Chem. Lett., 1977, 1243.
3) M. Yamada and M. Fujimoto, Bull. Chem, Soc. Jpn., 49, 693 (1976); S. Nakada, M. Yamada, T. Ito, and M. Fujimoto, ibid., 50, 1887 (1977).
4) G. Schwarzenbach and H. Flaschka, "Die komplexometrische Titration", 2nd ed, Ferdinand Enke Verlag, Stuttgart (1965).
5) L. G. Sillén and A. E. Martell ed, "Stability Constants, Supplement No. 1", Special Publication No. 25, The Chemical Society, London (1970).

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