

Indirect Potentiometry for Very Slow Chelate-Forming Metal Ions in Water-Organic Solvent Mixtures

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If rates of chelate formation reactions or chelate displacement reactions are slow at ordinary temperature, these reactions are usually carried out under high temperature or boiling. However, in the case of water-organic solvent mixtures, the solvent composition changes due to the evaporation of the organic solvent. Therefore, indirect potentiometry utilizing a chelate displacement reaction independent of solvent composition and ionic strength was proposed for the determination of metal ions with very slow chelate formation in water-organic solvent mixtures. As an application example of this method, the determination of Cr(III), in which chelate formation occurs very slowly, was performed using Cu^{II}-EDTA as a chelate displacing agent and a cupric ion-selective electrode as an indicator electrode.

Keywords: Indirect potentiometry, Chelate displacement reaction, Very slow chelate-forming metal ions, Water-organic solvent mixtures

1. Introduction

Chelating agents such as EDTA are widely used in various methods for determinations of metal ions. In potentiometry, since there are no electrodes responding directly to the chelating agent, metal ion selective electrodes and metal electrodes, *e.g.*, the silver electrode¹⁾, are being used in the potentiometric titration. On the other hand, various indirect potentiometric methods utilizing a complexation reaction have also been developed for the determination of metal ions. The indirect potentiometry will be divided roughly into three methods. In the first, chelatometric titration is performed with the addition of metal chelate²⁾ or metal ion³⁾ as an indicator. In the second method, a residual reactant is measured after a reaction. There are methods using the calibration curves of

the complexing anion addition volume *vs.* concentration of metal ion to be determined until a certain electromotive force (emf) is attained⁴⁾. The third method measures an ion generated by a reaction, *i.e.*, there are methods employing the chelatometric titration of the released metal ion⁵⁾ or using the calibration curve of the emf of the released metal ion *vs.* log[concentration of metal ion to be determined]⁶⁾⁷⁾ by means of a chelate displacement reaction.

With the various features, above methods are useful for the determination of metal ions. However, above methods, except for the titrimetry²⁾³⁾⁵⁾ using only the emf change at end point, must be carried out the measurement under the constant ionic strength, *i.e.*, under the constant activity coefficient of the ion, because the emf value may be concerned in the calculation for determination. Measurements in a water-organic solvent

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mixture must be also carried out under constant solvent composition so that the transfer activity coefficient⁸⁾ of the ion may not change. In addition, neither changes in ion association⁹⁾ nor a liquid junction potential can be disregarded, if the solvent composition changes¹⁰⁾. Recently we reported indirect potentiometry for the determination of metal ions without dependence on the solvent composition and ionic strength of these solutions. We solved such problems by using chelate displacement reactions in aqueous solution¹¹⁾ and water-organic solvent mixtures¹²⁾. However, in a slow chelate displacement reaction that needs heating or boiling in the case of water-organic solvent mixture, the indirect method of our previous paper¹²⁾ cannot be applied because it causes change in the solvent composition by evaporation of organic solvent during the measurement operation. Based on these considerations we investigate indirect potentiometry not dependent on the solvent composition and ionic strength for the determination of metal ions with very slow chelate formation in water-organic solvent mixtures.

2. Principle of determination

A certain volume V_r of aqueous solution (hereafter called reactant) containing a metal chelate NL, where N is a metal ion and L a chelating ligand, of concentration c_r is added to sample of water-organic solvent mixture (hereafter called mixed solvent) of volume V_x and concentration c_x of analyte metal ion M with a low chelate displacement reaction rate. In this case, it is necessary that the added volume of reactant satisfies the condition $V_r > c_x V_x / c_r$. This solution is boiled in order to accelerate the reaction.

Then, the chelate displacement reaction is shown by $M + NL \rightleftharpoons N + ML$ supposing that M (or N) forms only 1:1 complexes with L and if the equilibrium constant of this reaction is large and NL has a large excess over M, then N quantity that is equal to M is released.

After the chelate displacement reaction had proceeded, the volume of the solution is exactly adjusted to V_{m0} at a temperature equal to the sample in the beginning (hereafter called measuring-solution). After the measuring-solution of volume

V_{m1} was transferred to the measurement cell and the N-selective electrode-reference electrode pair was immersed in the cell, it is titrated with the aqueous solution (hereafter called a diluent) of a certain ionic strength, where the titration volume is v_d . The emf in additions of the diluent, E_1 , are given by the following equation:

$$E_1 = E^0 + S \log \frac{c_x (V_x / V_{m0}) V_{m1}}{\alpha_N^d \omega^d (V_{m1} + v_d)} + S \log y_N + E_j \quad (1)$$

where the superscript d denotes an addition of the diluent. E^0 , S , y_N , E_j , α_N and ω are the standard potential difference of the N-selective electrode to the reference electrode (the liquid junction potential difference of the liquid junction contacted by the solution is not contained herein), the response slope of the N-selective electrode, the activity coefficient of N, the liquid junction potential difference generated where the liquid junction contacts the solution, the side-reaction coefficient¹³⁾ of N and the volume coefficient, respectively.

After the diluent is added up to v_{d0} , the measuring-solution of volume V_{m2} is again added to the solution in the cell. This solution is continuously titrated with the aqueous solution that has an ionic strength equal to the diluent and contains N at the concentration c_s (the aqueous solution is hereafter called a standard), where the titration volume is v_s . The emf in additions of the standard, E_2 , are given by the following equation:

$$E_2 = E^0 + S \log \frac{c_x (V_x / V_{m0}) (V_{m1} + V_{m2}) + c_s v_s}{\alpha_N^s \omega^s (V_{m1} + V_{m2} + v_{d0} + v_s)} + S \log y_N + E_j \quad (2)$$

where the superscript d denotes an addition of the standard.

Next, the conditions in which the solvent composition of the solution after addition of the diluent becomes equal to that of the standard are as follows. The volume fractions of the measuring-solution with additions of the diluent, ϕ_1 , and the standard, ϕ_2 , are given, respectively, by following equations.

$$\phi_1 = \frac{V_{m1}}{\omega^d (V_{m1} + v_d)} \quad (3)$$

$$\phi_2 = \frac{V_{m1} + V_{m2}}{\omega^s (V_{m1} + V_{m2} + v_{d0} + v_s)} \quad (4)$$

When ϕ_1 is equal to ϕ_2 , the following equation is obtained from equations (3) and (4).

$$v_s = [1 + (V_{m2}/V_{m1})]v_d - v_{d0} \quad (5)$$

Therefore, if the diluent and standard are aqueous solutions and these are identical ionic strengths, the solvent composition and ionic strength of the solution become identical in both titration points, i.e., v_d and v_s , satisfying Eq.(5). By substituting v_s of Eq.(5) and $\omega^s = \omega^d$ in Eq.(2), the following equation is obtained.

$$E_2 = E^0 + \text{Slog} \frac{c_x(V_x/V_{m0})V_{m1} + c_s\{v_d - v_{d0}/[1 + (V_{m2}/V_{m1})]\}}{\alpha_N^s \omega^d(V_{m1} + v_d)} + \text{Slog} y_N + E_j \quad (6)$$

Since Eqs.(1) and (6) become the potential equations for solutions of same ionic strength and same solvent composition from the derivative condition of Eq.(5), each y_N and E_j in both equations will have the same value. In addition, when the side-reaction relating to N can be disregarded or $\alpha_N^d = \alpha_N^s = 1$, α_N^d and α_N^s become the same value. Therefore, from Eqs.(6) and (1), the following equation is obtained:

$$10^{\Delta E/S} = 1 + \frac{c_s}{c_x(V_x/V_{m0})V_{m1}} \{v_d - v_{d0}/[1 + (V_{m2}/V_{m1})]\} \quad (7)$$

where

$$\Delta E = E_2 - E_1 \quad (8)$$

If the values of E_1 and E_2 corresponding to v_d and v_s that satisfy Eq.(5) are read off from titration curves of the diluent and standard, c_x is determined from the slope of the linear plots of $10^{\Delta E/S}$ vs. $\{v_d - v_{d0}/[1 + (V_{m2}/V_{m1})]\}$ by Eq.(7).

3. Experimental

3.1 Apparatus

An Orion (Model EA-940) mV/pH meter (measurement precision ± 0.1 mV) was used with an Orion 94-29BN model cupric ion-selective electrode and Horiba 2535A model reference electrode (3.3 mol dm⁻³ KCl silver-silver chloride electrode of double junction /sleeve type). Response slope of the cupric ion-selective electrode was 29.6 ± 0.1 mV decade⁻¹ in aqueous solution and water-ethanol mixture at 25°C, and the lower limit of linear response was almost 5.7 pCu ($\equiv -\log [\text{Cu}^{2+}]$). Thus, 29.6 mV decade⁻¹ was used as the value of the response slope for all determining calculations. To the external cylinder solution of the reference electrode, 1 mol dm⁻³ NH₄NO₃ was used and the sleeve liquid junction had to be handled as follows

in order to obtain the result with good reproducibility. By moving the sleeve in the measurement every time, the sleeve part was filled with the new external cylinder solution. The external cylinder solution leaked to the sleeve outside was wiped with paper-tissue (Wipers S-200) and the sleeve part would thus be perfectly immersed in the solution for measuring.

The measuring cell was a brown beaker with a jacket in order to avoid a photo-effect of the cupric ion-selective electrode¹⁴⁾ and was kept at a constant temperature of 25 ± 0.1 °C by running water at constant temperature through the jacket. The solution in the measuring cell was stirred with a magnetic stirrer. An electrically heated water bath was used for heating the solution. The additions of the diluent and standard were performed with two micro-burets.

3.2 Reagents and preparation of solutions

Chromium nitrate (III) of 99.9% purity (Wako Pure chemical Industries, Ltd.) was used as a chromium (III) source. Chelate solutions of Cu^{II}-EDTA were prepared from Na₂Cu^{II}-EDTA (Dotite reagent). All other reagents used were of analytical reagent grade. In order to avoid the generation of hydroxo-complexes or hydroxides of metal ions and the decrease of conditional stability constants of chelate complexes, pH buffer (0.15 mol dm⁻³ acetic acid-0.04 mol dm⁻³ sodium acetate) of pH 4 was added to the measuring-solution, diluent and standard. Ionic strengths of the diluent and standard were adjusted to 0.54 mol dm⁻³ with NaClO₄, whereas the ionic strength of the pH buffer was 0.04 mol dm⁻³. All solutions were prepared using deionized and distilled water at 25°C.

4. Results and Discussion

4.1 Application

In application of this method, chromium (III) with a very slow rate of complexation was chosen as the metal ion to be determined in mixed solvents, and Cu^{II}-EDTA as a chelate displacing agent. A cupric ion-selective electrode was used as the indicator electrode. The conditional stability constants of Cu^{II}-EDTA and Cr^{III}-EDTA are $\log K'_{\text{CuL}} = 10.5$ and $\log K'_{\text{CrL}} = 15.1$ at pH 4 and 20°C,

where L means EDTA¹³⁾.

4.2 Effect of reactant concentration to chelate displacement reaction rate

The chelate displacement reaction was carried out at different mole ratios $c_r V_r / (c_x V_x)$ between Cu^{II} -EDTA and $\text{Cr}(\text{III})$ in aqueous solution. The result was shown in the Fig.1. As can be seen in Fig.1, the time until a constant emf was attained increased with the decrease in sample concentration and a decrease in the ratio $c_r V_r / (c_x V_x)$. Constant emf was reached in a short time at $c_r V_r / (c_x V_x)$ ratios of 50 and 100 with the samples of 1×10^{-3} and 1×10^{-4} mol dm^{-3} $\text{Cr}(\text{NO}_3)_3$. In the sample with 1×10^{-5} mol dm^{-3} $\text{Cr}(\text{NO}_3)_3$, constant emf was reached after about 4 hours at a $c_r V_r / (c_x V_x)$ ratio of 100 and was not even reached after 5 hours at a $c_r V_r / (c_x V_x)$ ratio of 10. Therefore, the mole ratio must be made at least 50 in order to facilitate the reaction.

4.3 Effect of solvent composition to chelate displacement reaction rate and removal of organic solvent

In a previous paper¹²⁾, it was recognized that the chelate displacement reaction in mixed solvents, i.e., water-protic solvent (ethanol) and water-aprotic solvent (1,4-dioxane), is considerably slower than in aqueous solution, but a difference in the reaction rate could hardly be observed between these mixed solvents. Then, the chelate displace-

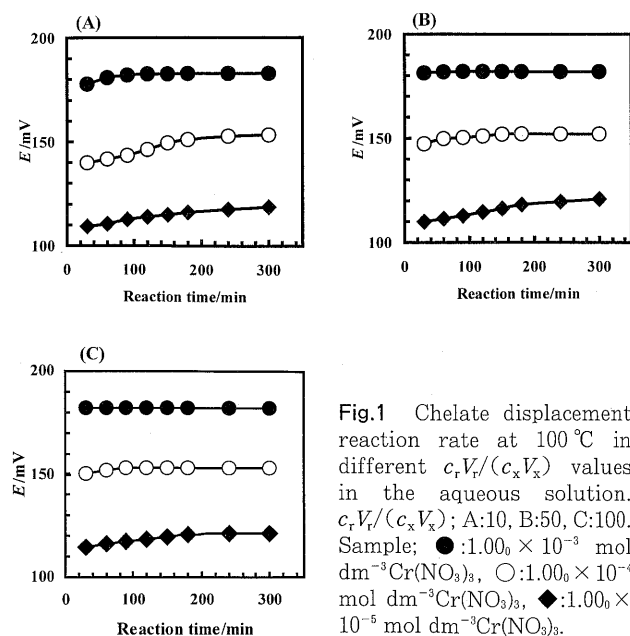


Fig.1 Chelate displacement reaction rate at 100 °C in different $c_r V_r / (c_x V_x)$ values in the aqueous solution. $c_r V_r / (c_x V_x)$; A:10, B:50, C:100. Sample; $\bullet$: 1.00×10^{-3} mol dm^{-3} $\text{Cr}(\text{NO}_3)_3$, $\circ$: 1.00×10^{-4} mol dm^{-3} $\text{Cr}(\text{NO}_3)_3$, $\blacklozenge$: 1.00×10^{-5} mol dm^{-3} $\text{Cr}(\text{NO}_3)_3$.

ment reaction rate between $\text{Cr}(\text{III})$ and Cu^{II} -EDTA in the water-ethanol mixture was examined as following: The changes in emfs against chelate displacement reaction time of $\text{Cr}(\text{III})$ samples containing 0, 20 and 60 vol% ethanol were measured at constant solvent composition under reflux. Reaction conditions were the same as in the aqueous solution system except the reflux. The result is shown in Fig.2. The ratio $c_r V_r / (c_x V_x)$ was

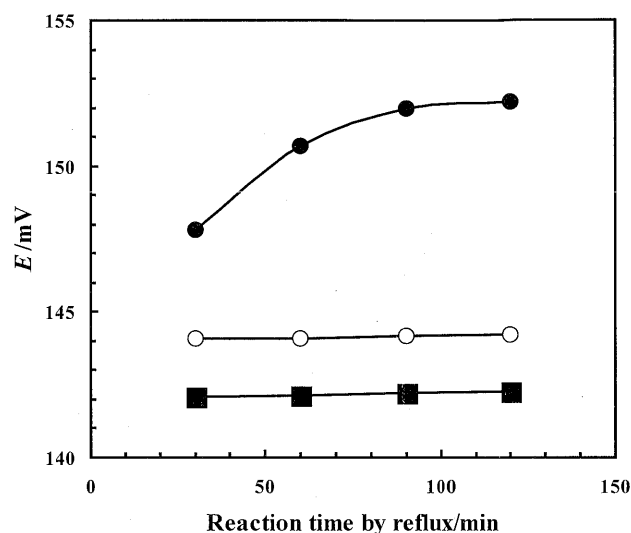


Fig.2 Effect of the organic solvent on the chelate displacement reaction rate between $\text{Cr}(\text{III})$ and Cu^{II} -EDTA under boiling and reflux. $\bullet$: aqueous solution, $\blacksquare$: 20 vol% ethanol, $\circ$: 60 vol% ethanol. Samples: 1.00×10^{-4} mol dm^{-3} $\text{Cr}(\text{NO}_3)_3$. $c_r V_r / (c_x V_x) = 100$.

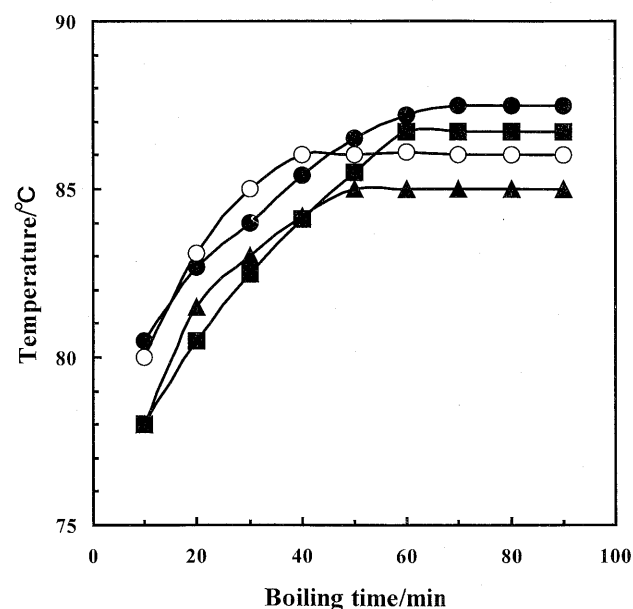


Fig.3 Relationship between boiling time and temperature of water-ethanol mixtures. Content of ethanol (vol%): $\bullet$: 20, $\circ$: 40, $\blacktriangle$: 60, $\blacksquare$: 80.

adjusted to 100. Fig.2 shows that changes in the emf against reaction time are not recognized in 20vol% and 60vol% ethanol, and it is therefore obvious that chelate displacement reactions did not take place. Based on these results, it seems necessary to remove the ethanol from mixed solvents by boiling or distillation beforehand. In order to determine the boiling time which the ethanol is removed from mixed solvents, the changes in temperature against boiling time were measured on 20-80vol% ethanol solutions (boiling water was appropriately added during the interval for volume adjustment). The result is shown in Fig.3. As can be seen from the figure, all mixed solvents retained a constant temperature after about one hour. It is therefore shown that the ethanol in the mixed solvent was evaporated in the boiling process.

4.4 Measurement procedure of chromium (III) in water-ethanol mixture

The water-ethanol mixture sample solution of 100 cm³ (V_x) was taken up in a conical flask of 200 cm³. The ethanol in this solution is almost completely removed by boiling for over one hour, while the solution volume is kept almost constant

by the addition of warm water. 10 cm³ HNO₃ (1.0 mol dm⁻³) and 10 cm³ reactant (Na₂Cu^{II}-EDTA aqueous solution) were added to this solution, and the solution was then heated in a water bath of 100 °C until the reaction finished. In this interval, HN O₃ was added in order to avoid a formation of hydroxo-complexes or hydroxide of Cr(III) upon heating of the solution. After the solution was partially cooled, 10 cm³ NaOH (1.0 mol dm⁻³) and 20 cm³ buffer solution of pH 4 (1.5 mol dm⁻³ acetic acid-0.4 mol dm⁻³ sodium acetate) were added. The solution was then transferred to a volumetric flask of 200 cm³, cooled to the same temperature as all other solutions and adjusted to volume (200 cm³, V_{m0}) with water (this is called the measuring-solution).

The titration procedure was carried out as follows. The measuring-solution of 50 cm³ (V_{m1}) was taken up in the measuring cell, the electrode pair was immersed, and after the addition of 5 cm³ diluent from the micro buret the emf was measured. Continuous titration up to a volume of 10 cm³ (v_{d0}) was done at 0.5 cm³ intervals, and emfs were measured for each titration point. This solution was then added to an identical measuring-solution of 50 cm³ (V_{m2}), the emf was measured, and it was titrated in 1 cm³ increments up to 10 cm³ with the standard, and emfs for each titration point were measured. The titration data of diluent

Table 1 Experimental data for chromium (III) determination^a

v_d/cm^3	E_1/mV	v_s/cm^3	E_2/mV	$\Delta E/\text{mV}$	$v_d-5.00^b/\text{cm}^3$	$10^4 \Delta E/29.6^c$
5.00	133.0	0.00	133.0	0.0	0.00	1.00
5.50	132.9	1.00	135.1	2.2	0.50	1.19
6.00	132.8	2.00	137.1	4.3	1.00	1.40
6.50	132.7	3.00	139.0	6.3	1.50	1.63
7.00	132.7	4.00	140.1	7.4	2.00	1.78
7.50	132.6	5.00	141.3	8.7	2.50	1.96
8.00	132.6	6.00	142.6	10.0	3.00	2.18
8.50	132.5	7.00	143.7	11.2	3.50	2.39
9.00	132.5	8.00	144.7	12.2	4.00	2.58
9.50	132.4	9.00	145.7	13.3	4.50	2.81
10.00	132.3	10.00	146.5	14.2	5.00	3.02

a. Sample : $1.00_0 \times 10^{-4} \text{ mol dm}^{-3} \text{ Cr}(\text{NO}_3)_3$ in 60% ethanol.

b. $v_d - v_{d0} [1 + (V_{m2}/V_{m1})] = v_d - 10.00 / [1 + (50/50)] = v_d - 5.00$.

c. $S = 29.6 \text{ mV decade}^{-1}$.

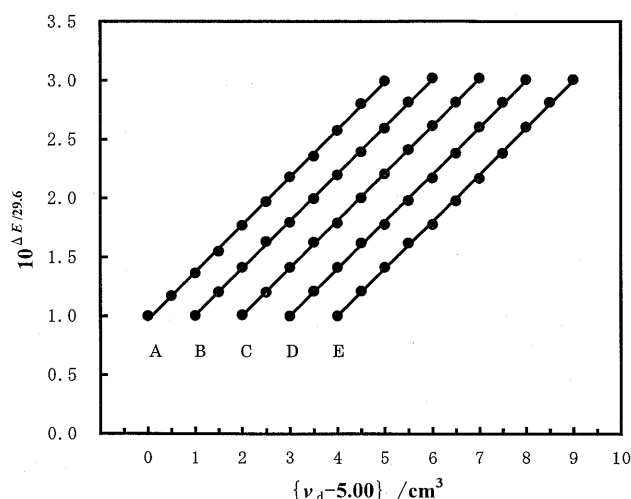


Fig.4 Examples of linear plots for chromium (III) determination. Samples: $1.00_0 \times 10^{-4} \text{ mol dm}^{-3} \text{ Cr}(\text{NO}_3)_3$. A: aqueous solution, B:20, C:40, D:60, E:80 vol% ethanol. The plots for B-E are parallel shifted by 1-4 cm³, respectively, the $\{v_d-5.00\}$ axis for graphic presentation.

Table 2 Results of chromium (III) determinations in water-ethanol mixtures^a

$c_{\text{Taken}}/\text{mol dm}^{-3}$	Content of ethanol, vol%	$c_{\text{Found}}/\text{mol dm}^{-3}$	Error ^b , %	RSD ^c , %
Reactant: $1 \text{ mol dm}^{-3} \text{Na}_2\text{Cu}^{\text{II}}\text{-EDTA}$; standard: $1.00_0 \times 10^{-2} \text{ mol dm}^{-3} \text{Cu}(\text{NO}_3)_2$ ^d				
(1) $1.00_0 \times 10^{-3 \text{ e}} (6 \times 10^{-3})^g$	0	$1.00_5 \times 10^{-3}$	0.5	0.2
	20	$0.99_6 \times 10^{-3}$	-0.4	0.2
	40	$1.00_3 \times 10^{-3}$	0.3	0.7
	60	$1.00_4 \times 10^{-3}$	0.4	0.6
	80	$1.00_7 \times 10^{-3}$	0.7	0.2
Reactant: $1 \times 10^{-1} \text{ mol dm}^{-3} \text{Na}_2\text{Cu}^{\text{II}}\text{-EDTA}$; standard: $1.00_0 \times 10^{-3} \text{ mol dm}^{-3} \text{Cu}(\text{NO}_3)_2$ ^d				
(2) $5.00_0 \times 10^{-4 \text{ f}} (3 \times 10^{-3})^g$	0	$5.02_9 \times 10^{-4}$	0.6	0.7
	20	$4.99_4 \times 10^{-4}$	-0.1	0.2
	40	$4.97_7 \times 10^{-4}$	-0.5	0.5
	60	$4.97_4 \times 10^{-4}$	-0.5	0.6
	80	$5.00_2 \times 10^{-4}$	0.0	0.5
(3) $1.00_0 \times 10^{-4 \text{ e}} (6 \times 10^{-4})^g$	0	$1.00_3 \times 10^{-4}$	0.3	1.0
	20	$0.99_6 \times 10^{-4}$	-0.4	0.3
	40	$1.00_0 \times 10^{-4}$	0.0	1.0
	60	$0.99_7 \times 10^{-4}$	-0.3	0.3
	80	$1.00_0 \times 10^{-4}$	0.0	0.3
Reactant: $1 \times 10^{-2} \text{ mol dm}^{-3} \text{Na}_2\text{Cu}^{\text{II}}\text{-EDTA}$; standard: $1.00_0 \times 10^{-4} \text{ mol dm}^{-3} \text{Cu}(\text{NO}_3)_2$ ^d				
(4) $5.00_0 \times 10^{-5 \text{ f}} (3 \times 10^{-4})^g$	0	$4.97_4 \times 10^{-5}$	-0.5	0.2
	20	$4.99_4 \times 10^{-5}$	-0.1	0.5
	40	$4.99_9 \times 10^{-5}$	0.0	0.4
	60	$4.99_8 \times 10^{-5}$	0.0	0.9
	80	$5.01_8 \times 10^{-5}$	0.4	0.9
(5) $1.00_0 \times 10^{-5 \text{ e}} (6 \times 10^{-5})^g$	0	$0.99_3 \times 10^{-5}$	-0.7	0.2
	20	$1.00_0 \times 10^{-5}$	0.0	0.9
	40	$1.00_2 \times 10^{-5}$	0.2	0.5
	60	$0.99_9 \times 10^{-5}$	-0.1	0.4
	80	$0.99_8 \times 10^{-5}$	-0.2	0.4

a. Based on three samples.

b. $\{(c_{\text{Found}}/c_{\text{Taken}})-1\} \times 100$.

c. Relative standard deviation.

d. Diluent and standard contain acetate buffer of pH 4, and ionic strengths of these solutions were adjusted to 0.54 mol dm^{-3} with NaClO_4 . Ionic strength of the acetate buffer is 0.04 mol dm^{-3} .e. $V_x=100\text{cm}^3$, $V_r=10\text{cm}^3$, $c_r V_r/(c_x V_x)=100$.f. $V_x=100\text{cm}^3$, $V_r=25\text{cm}^3$, $c_r V_r/(c_x V_x)=50$.g. Ionic strength (mol dm^{-3}) of samples.

addition volumes (v_a) of 5-10 cm³ and standard addition volumes (v_s) of 0-10 cm³ were obtained by this procedure and will be utilized for determining the calculation (see Eq.(5)).

4.5 Results of chromium (III) determination in water-ethanol mixture

The experimental data and linear plots based on Eq.(7) for Cr(III) determination are shown in Table 1 and Fig.4, respectively. The linear plots showed a good linearity regardless of sample concentration and solvent composition. The correlation coefficient of these straight lines had an average of 0.9995, which is not different from the aqueous solution system. Results of Cr(III) determinations in various solvent compositions are shown in Table 2. The error and RSD were less than $\pm 1\%$ and 1% , respectively, for all determinations. Systematic variations of error and RSD resulting from the decrease in sample concentration and the increase in organic solvent content could not be recognized, average errors in concentration and RSD were $0.0 \pm 0.6\%$ and $0.5 \pm 0.4\%$, respectively, for samples containing ethanol of 20–80% (n=20), and were $0.0 \pm 0.3\%$ and $0.5 \pm 0.3\%$, respectively, for samples without ethanol (n=5). These results for samples containing ethanol are almost the same as found with samples without ethanol.

5. Conclusion

The results prove that the indirect determination of metal ions in a mixed solvent as well as in an aqueous is possible by applying this method when the chelate displacement reaction rate is very slow. This was shown with the example of Cr(III) determination. Since chelate displacement reactions slow down in mixed solvent, this method will be useful for the determination of common metal ions

in such mixed solvent. In addition, it is advantageous that this method does not depend on ionic strength and solvent composition of sample solution.

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