May, 1988] *Bull. Chem. Soc. Jpn., 61, 1761—1765 (1988)*

Conductometric Determination of Some Metal Ions Using Oxine as Reagent

Mohamed Tarek Mohamed Zaki,* Wageh Georgy Hanna, and Mohamed Hossam Fawzy
Department of Chemistry, Faculty of Science, Ain Shams University,
Abbassia, Cairo, Egypt
(Received January 26, 1987)

A simple and sensitive conductometric method for the determination of copper(II), iron(II) and (III), aluminum(III), chromium(III), gold(III), platinum(IV), vanadyl, zirconyl, and uranyl ions with oxine solution in ethanol-water system is described. An average recovery of 100.3% with standard deviation not exceeding 0.4% is observed. The effect of solvent, shape of titration curves and molar ratio of the chelates are studied. The proposed method shows good agreement with the conventional EDTA titration using metallochromic indicators. The advantage over the conventional method is discussed.

Despite the wide application of conductance measurement as a tool for end point detection of acid-base reactions, little attention has been given to complex formation reactions. Conductometric determination of water hardness,[1] divalent metal ions with EDTA[2] or CDTA,[3] silver and mercury ions with cyanide ion[4] and copper(II) chloride with lithium chloride in *N,N*-dimethylformamide[5] have been described.

In the present investigation, oxine (8-hydroxyquinoline) was succesfully used as a chelating agent for the conductometric determination of some metal ions in ethanol-water system (2:1).

Experimental

Reagents. All chemicals used were of analytical grade. The determined metal salts were of the chloride type except for iron (II), vanadyl and zirconyl ions which were of the sulfate type. Bidistilled water of specific conductance, 1.82×10^{-4} S m^{-1} was used throughout. 0.1 M† oxine stock solution in ethanol-water solvent (2:1) was prepared and potentiometrically standardized with a base.[6] 10^{-2} M stock solutions of aqueous metal ions were prepared and standardized using EDTA and metallochromic indicators.[7]

Apparatus. The YSI Model 32M conductance meter [Yellow Spring Co., Inc. (USA)] was used. The measuring range was from 1.0 to 200.0 microsiemens with a maximum error of ±0.2%. Model YSI 3417 cell was used with cell constant K=100/m.

Procedure. 10.0 ml of 10^{-3} M aqueous metal salt solution was transferred to a 50-ml beaker contained 20.0 ml absolute ethanol. The conductance cell was immersed in the solution, which was titrated with 10^{-2} M oxine solution. The conductance was determined after each addiction of the oxine solution. Stirring after each addition was carried out. For an ordinary conductometric titration, a few readings on each side of the anticipated end point are enough. The end point was determined from a graphical plot of conductance vs. milliliters of oxine solution added. All conductance measurements were carried out at 25 °C.

Results and Discussion

Conductometric titration of metal ions with EDTA in buffer media has been described.[2] However, the presence of high electrolyte concentration affects the end point detection because of the relatively small change in conductance values determined against a relatively high background conductance of the buffer system.[7]

In the present investigation, a conductometric study of the interaction of some metal ions with oxine in absence of buffer has been carried out.

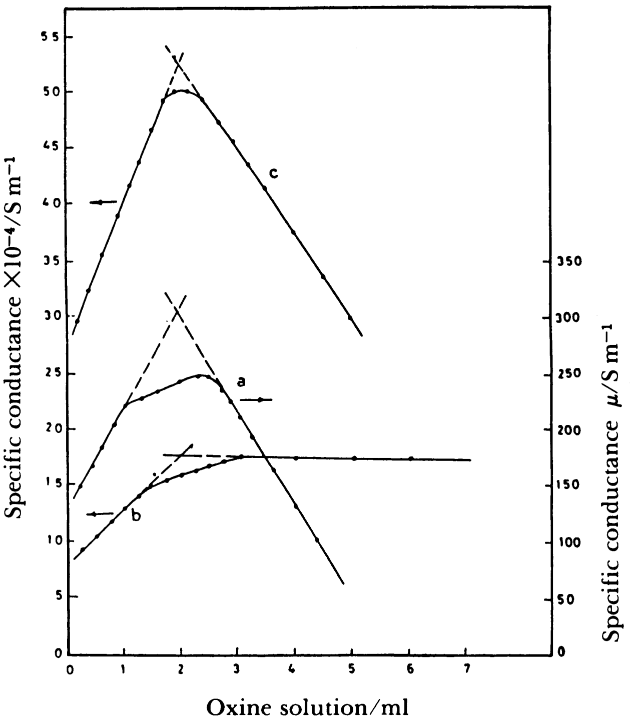

Fig. 1. Conductometic titration curves of (a) 10^{-3} M aqueous copper(II) chloride with 10^{-2} M ethanolic oxine solution, (b) 10^{-3} M ethanolic copper(II) chloride with 10^{-2} M ethanolic oxine solution, and (c) 10^{-3} M copper(II) chloride with 10^{-2} M oxine in ethanol-water system (2:1).

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† 1 M=1 mol dm^{-3}.

Effect of Solvent. Exploration of the conductometric titration of aqueous copper(II) chloride with ethanolic oxine solution was carried out (Fig. 1-a). However, a wide curvature around the end point was noticed. This is attributed to the formation of a precipitated chelate in aqueous medium. The presence of a precipitate affects conductance value due to the fact that accuracy depends on the speed of precipitation, composition and solubility of the precipitate.

A small curvature around the end point was observed in the titration of ethanolic copper(II) or iron(III) solutions with ethanolic oxine solution (Figs. 1-b and 2-b). However, most of the metal salts studied were insoluble in ethanol.

To overcome the problems of chelate and free metal ion solubility, an ethanol–water system (2:1) was used to prepare the oxine solution and as a medium for the titration.

Shape of Titration Curves. The shape of the titration curve depends on all the species present during the titration. Factors such as viscosity, dielectric constant, solvation, ion-pair association and proton transfer change the shape of the curve.

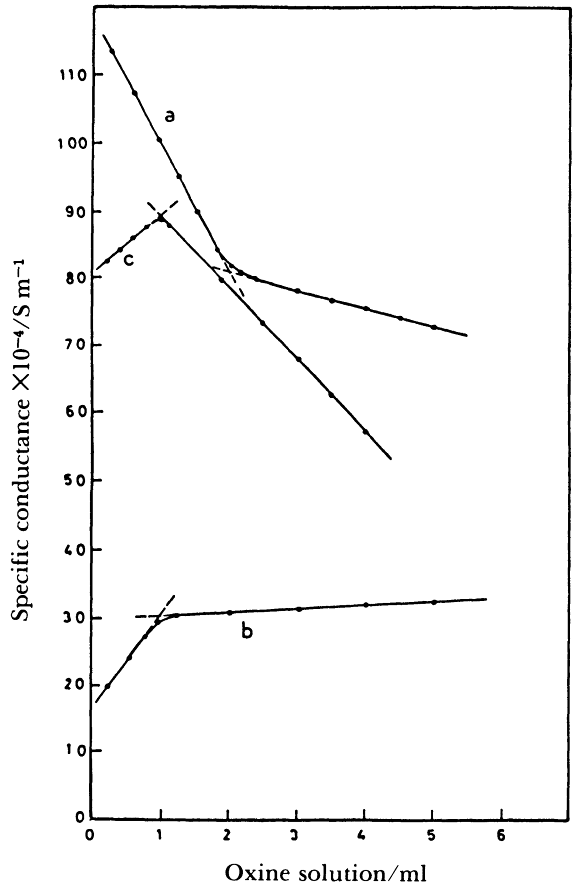
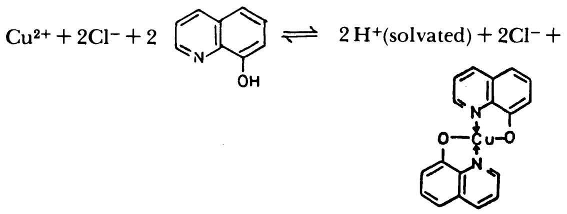


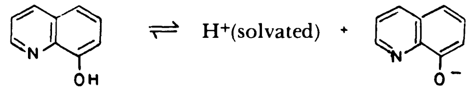
Fig. 2. Conductometric titration curves of (a) 10^{-3} M iron(III) chloride with 10^{-2} M oxine in ethanol–water (2:1), (b) 10^{-3} M ethanolic iron(III) chloride with 10^{-2} M ethanolic oxine solution, and (c) 10^{-2} M iron(III) chloride with 0.1 M oxine in ethanol–water system (2:1).

The conductometric titration of 10^{-3} M copper(II) chloride with 10^{-2} M oxine solution in ethanol–water system (2:1) was performed (Fig. 1-c). The results show an obvious maximum in the conductance curve at a copper(II)–oxine mole ratio of 1:2. The reaction may be represented by the equation:

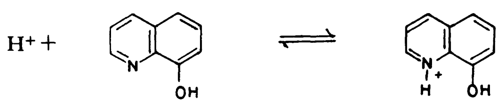


The specific conductance increased at first because each copper(II) ion is replaced by two solvated protons. The interaction of the protons with the solvent depend on the ratio of ethanol–water used.[8]

It was expected that the conductance values would remain constant or slightly increase after the equivalence point, due the the partial dissociation of oxine solution added:



However, after the equivalence point, the conductance of the solution decreased. The decrease may be due to the interaction of the protons available in the titration medium with the added oxine solution:



Measurement of the pH before and after the end point shows an increase of about 0.25 pH units indicating the probability of the above reaction. In addition, titration of 10^{-2} M hydrochloric acid in ethanol–water solvent (2:1) with 10^{-2} M oxine solution shows a continuous decrease of specific conductance.

The species which presumably existed before, at, and after the equivalence point are given in Table 1. Similar titration curves were observed for the titration of iron(II), aluminum(III), and vanadyl ions with oxine.

A different behavior in the conductometric titration curve of 10^{-3} M iron(III) chloride with 10^{-2} M oxine solution in ethanol–water solvent was observed (Fig. 2-a). The specific conductance continuously decreased throughout the titration. However, the two rectilinear curves formed gave an easily detected end point. The ions which presumably present through out the titration are given in Table 2. The decrease of conductance before the end point may be attributed to the replacement of the highly mobile iron(III) ions,

Table 1. Species Involved in the Conductometric Titration of Copper(II) Chloride with Oxine Solution in Ethanol-Water (2:1)

Species present before addition of oxine:	$Cu^{2+} + 2\ Cl^-$
	$\downarrow + 2$ oxine
Species present at the equivalence point:	$2\ H^+$(solvated) $+ 2\ Cl^- + [Cu(oxine)_2]$
	$\downarrow + 2$ oxine
Species present after the equivalence point:	$2\ Cl^- + 2\ [H\text{-}oxine]^+ + [Cu(oxine)_2]$

Table 2. Ions Involved in the Conductometric Titration of Up to 10^{-3} M Iron(III) Chloride with 10^{-2} M Oxine in Ethanol-Water System (2:1)

Ions present before addition of oxine:	$Fe^{3+} + 3\ Cl^-$
	$\downarrow +2$ oxine
Ions present at the equivalence point:	$2\ H^+$(solvated) $+3\ Cl^- + [Fe(oxine)_2]^+$
	$\downarrow +2$ oxine
Ions present after the equivalence point:	$2\ [H\text{-}oxine]^+ + 3\ Cl^- + [Fe(oxine)_2]^+$

Table 3. Speies Involved in the Conductometric Titration of 10^{-2} M Iron(III) Chloride with 0.1 M Oxine in Ethanol-Water System (2:1)

Species present before addition of oxine:	$FeCl_2^+ + Cl^+$
	$\downarrow + 1$ oxine
Species present at the equivalence point:	$[FeCl_2(oxine)] + Cl^- + H^+$(solvated)
	$\downarrow + 1$ oxine
Species present after the equivalence point:	$[FeCl_2(oxine)] + Cl^- + [H\text{-}oxine]^+$

which show abnormally high molar conductance in this medium, by solvated protons and $[Fe(oxine)_2]^+$ ions. The molar conductance of iron(III) chloride in ethanol-water solvent (2:1) is greater than that of hydrochloric acid over the same concentration range of titration. The observed low molar conductance of the formed acid in this solvent is in accordance with that for sulfuric acid in the same solvent.[9] After the end point, the decrease in conductivity is relatively small compared with that noticed in the titration of copper(II)-oxine. This may be attributed to the presence of the charged $[Fe(oxine)_2]^+$ chelate.

However, increasing the concentration of iron(III) chloride ten folds reversed the shape of the titration curve before the end point. Figure 2-c represent the titration of 10^{-2} M iron(III) chloride with 0.1 M oxine solution under identical experimental conditions. This behavior could be explained on the view of incomplete ionization of iron(III) chloride at this relatively higher concentration in the following manner:

$$FeCl_3 \rightleftharpoons FeCl_2^+ + Cl^-$$

Evidence in support of incomplete dissociation as uni-univalent electrolyte in acetone was reported.[10] Also, lanthanum chloride behaves similarly in ethanol.[11] Table 3 shows the expected ions throughout the titration stages. The increase in conductance values before the end point may be attributed to the replacement of Fe Cl_2^+ ion by H^+(solvated) ion.

A study of the concentration effect for copper(II) chloride solutions was carried out. No change of the shape of the titration curve of 10^{-2}—10^{-3} M copper(II) chloride with 10^{-1}—10^{-2} M oxine solution were observed. Titration of less than 10^{-3} M copper(II) chloride was not successful.

Similar titration curves to (Fig. 2-a) were observed for the titration of 10^{-3} M chromium(III), gold(III), platinum (IV), zirconyl and uranyl solutions with 10^{-2} M oxine solution using the same experimental conditions.

Metal-Ligand Mole Ratio of the Chelates. The mole ratio of metaloxine chelates were determined from the conductometric titration curves (Table 4-a). It was found that copper(II), platinum(IV), and zirconyl ions form (1:2) chelates with oxine. On the

Table 4-a. Conductometric Determination of Some Metal Ions Using 10^{-3} M Oxine Solution in Ethanol–Water System (2:1)

Metal ion	Weight taken	Weight found	Recovery	Standard deviation	Metal–ligand ratio of chelate
	mg	mg	%	%	
Copper(II)	0.755	0.754	99.9	0.1	1:2
	0.755	0.756	100.0		
	1.511	1.509	99.9		
	1.511	1.510	99.9		
Aluminum(III)	0.284	0.284	100.0	0.4	1:1
	0.284	0.285	100.5		
	0.568	0.569	100.2		
	0.568	0.570	100.3		
Chromium(III)	0.494	0.495	100.2	0.2	1:1
	0.494	0.495	100.2		
	0.988	0.988	100.0		
	0.988	0.989	100.1		
Gold(III)	1.970	1.965	99.7	0.3	1:1
	1.970	1.966	99.8		
	3.940	3.932	99.8		
	3.940	3.933	99.8		
Platinum(IV)	2.262	2.260	99.9	0.1	1:2
	2.262	2.261	100.0		
	4.524	4.525	100.0		
	4.524	4.524	100.0		
Vanadyl	0.510	0.511	100.2	0.4	1:1
	0.510	0.511	100.2		
	1.020	1.021	100.1		
	1.020	1.022	100.2		
Zirconyl	0.910	0.909	99.9	0.3	1:2
	0.910	0.911	100.1		
	1.820	1.822	100.1		
	1.820	1.824	100.2		
Uranyl	2.380	2.377	99.9	0.1	1:1
	2.380	2.381	100.0		
	4.760	4.763	100.1		
	4.760	4.761	100.0		

Table 4-b.

Metal ion	Weight taken	Weight found	Recovery	Standard deviation	Metal–ligand ratio of chelate
	mg	mg	%	%	
Iron(II)	0.532	0.549	103.2	3.7	1:1
	0.532	0.550	103.4		
	1.064	1.097	103.1		
	1.064	1.098	103.2		
Iron(III)	0.588	0.587	99.8	0.2	1:2
	0.588	0.587	99.8		
	1.176	1.175	99.9		
	1.176	1.176	100.0		
Iron(III)[a]	5.880	5.856	99.6	0.4	1:1
	7.840	7.816	99.7		
	8.820	8.794	99.7		
	11.760	11.740	99.8		

a) 0.1 M oxine soution is used as titrant.

other hand, iron(II), chromium(III), aluminum(III), gold(III), vanadyl, and uranyl ions form (1:1) chelates with the ligand. The mole ration of iron(III)-oxine chelate depends on the original iron(III) concentration (Table 4-b). It was found that up to 10^{-3} M iron (III) forms a (1:2) chelate with oxine while a higher concentration forms a (1:1) chelate. The metal ion octet in the chelate is completed with solvent molecules.

Sensitivity and Precision Down to 0.3 mg of metal ions were successfully determined by conductometric titration with 10^{-2} M oxine solution. The titrant concentration was about ten times that of the metal ion solutions to minimise dilution effect on conductance values throughout the titration. Moreover, dilution correction was carried out using the equation:

$$L_{\text{corrected}} = L_{\text{observed}} \times [(V_1 + V_2)/V_1]$$

where L is the conductance, V_1 the initial volume in the cell and V_2 the volume of added titrant.

Analysis of the data show an average recovery of 100.3% with a standard deviation not exceeding 0.4% (four determinations for each metal ion). However, an average recovery of 103.2% with a standard deviation of 3.7% was observed for the titration of iron(II) sulphate (Table 4-b). The high recovery may be due to the partial oxidation of iron(II) ions. Iron(II) forms (1:1) chelate with oxine whereas low concentrations of iron(III) form (1:2) chelates (Table 4-b).

All experiments have been carried out in a medium of low ionic strength. However, real samples may contain indifferent ions. A study of potassium chloride effect on the conductometric titration curves showed that the method is applicable up to ten fold potassium chloride concentration. Attempts to determine silver(I), thallium(I), nickel(II), palladium(II), zinc(II), magnesium(II), barium(II), calcium(II), strontium(II), cerium(IV), and molybdenum(VI) were unsuccessful.

Conclusion

The conductometric titration results were in good agreement with the conventional titrimetric method of EDTA using metallochromic indicators. Moreover, the proposed method has the advantage of eliminating the buffer medium and the back titration technique required for some of the measured ions with the conventional method.

We would like to acknowledge the assistance of Dr. W. H. Lee, Department of Chemistry, Surrey University, Guildford, U. K., for his valuable advice.

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