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Indirect Determination of CTMAB with Sodium Chloride and Ammonium Thiocyanate by Floatation and Separation of Zinc

Quan Min LI*, Hai Xin BAI, Wen Ying LÜ

College of Chemistry and Environmental Science, Henan Normal University, Key Laboratory of Environmental Science and Engineering Education Commission of Henan Province, Xinxiang 453002

Abstract: A new method for indirect determination of cetyl-trimethyl ammonium bromide (CTMAB) with NaCl and NH_4SCN by floatation and separation of zinc has been studied. The study shows that Zn(II) can associate with NH_4SCN and CTMAB to form insoluble ternary ion-association complex, and the precipitate can float on the surface of the liquid phase. A good linear relationship is observed between the floatation yield (E%) of Zn(II) and the amount of CTMAB. On the ground, CTMAB can be indirectly determined by determining E% of Zn(II). The results were satisfactory.

Keywords: Cetyl-trimethyl ammonium bromide, ammonium thiocyanate, floatation, zinc.

Cetyl-trimethyl ammonium bromide (CTMAB) is a very useful cationic surfactant, so the study on determination of CTMAB assumes great importance. A small amount of CTMAB is generally determined by spectrophotometry basing CTMAB combines with triazide to form colored binary ion-association complex[1-3]. However, those methods of determination of CTMAB have disadvantages of small linear range, need of special reagent, determination in base environment, *etc*. In this paper, indirect determination of CTMAB with NaCl and NH_4SCN by floatation and separation of Zn(II) was investigated. The method is superior to those methods reported in the references 1-3 since its simplicity, rapidity, reliability, wide linear ranges, no synthesis of special reagents, determination in acid environment (pH1.0~6.0), suffering from little interference of common cations or anions, *etc*. The method was successfully applied to determine CTMAB in water samples with satisfactory results.

Experimental

Reagents and Instruments

Metal ions standard solutions and buffer solutions were prepared by reference 4. Solution of 0.1 mol/L NH_4SCN, 1×10^{-2}mol/L CTMAB and 1×10^{-3}mol/L 4-(2-

*E-mail: mercy606@sohu.com

pyridyllaxo) resorcinol (PAR) (dissolved in ethanol)were prepared respectively. A model 722 grating spectrophotometer was used.

Procedure

A given amount of metal ion, NH_4SCN solution and CTMAB were added to a 25mL graduated colorimetric tube. Then the pH was adjusted with buffer solution (pH=4.0) and the mixture was diluted to 10 mL. 1.00 g of NaCl was added and the mixture was shaken thoroughly before standing for a while. Then the mixture separated into floatation phase and salt-water phase. 1.00 mL of the aqueous salt, 1.00 mL of 1×10^{-3}mol/L PAR, 3.00 mL of 0.1mol/L sodium tetraborate were added into a 25 mL volumetric flask. After diluting to the mark, the absorbency was read at 495 nm against the reagent blank. Then the floatation yield (E%) of Zn(II) was calculated. Based on E% of Zn(II), the amount of CTMAB can be obtained from the calibration curve.

The precipitate of floatation phase was dissolved and the concentration of Zn(II) was determined in the solution by using the above color development reaction method. The results agreed well with each other.

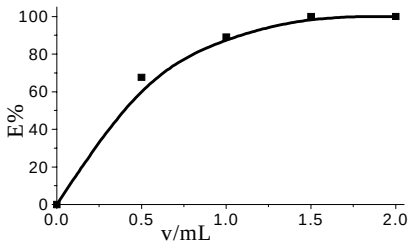
Results and Discussion

Influence of amount of NH_4SCN and CTMAB on E% of Zn(II)

Figure 1 and **Figure 2** show the influence of the amount of NH_4SCN and CTMAB on the E% of Zn(II), respectively. In the presence of 1.50 mL of NH_4SCN and 0.80 mL of CTMAB, E% of Zn(II) is 100%. In order to ensure Zn(II) was floated completely, 2.50 mL of NH_4SCN and 1.00 mL of CTMAB were selected for all further studies.

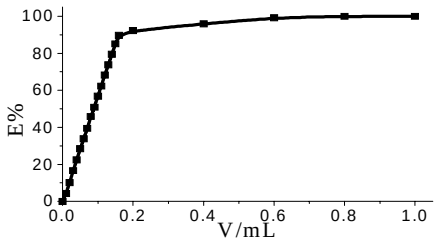
Figure 2 also shows that there is a very good linear relationship between floatation yield (E%) of Zn (II) and the amount of CTMAB. Therefore, the amount of CTMAB can be determined indirectly by determining E% of Zn(II).

Figure 1 Influence of NH_4SCN



Zn(II):50 μg; c(NH_4SCN): 0.1 mol/L; CTMAB(1.0×10^{-2}mol/L): 1.0 mL; Total volume: 10 mL; NaCl: 1.0 g

Figure 2 Influence of CTMAB



Zn^{2+}: 50 μg; c(CTMAB): 1.0×10^{-2}mol/L;NH_4SCN (0.10mol/L): 2.50 mL;Total volume: 10 mL; NaCl: 1.0 g

Reactive mechanism of floatation of Zn(II)

The aforementioned results show that Zn(II) cannot be floated without either NH_4SCN or CTMAB. Only with the simultaneous existence of NH_4SCN and CTMAB, Zn(II) can associate with them to form insoluble ternary ion-association complex. Hence, the mechanism of floating Zn(II) can be described as follows,

$$(1)\ Zn^{2+} + 4SCN^{-} \rightarrow [Zn(SCN)_4]^{2-}$$
(Water phase) (Water phase)

$$(2)\ [Zn(SCN)_4^{2-}] + 2CTMAB^{+} \rightarrow [Zn(SCN)_4^{2-}] \bullet (CTMAB^{+})_2$$
(Water phase) (Floatation phase)

Influence of different salts on E% of Zn(II)

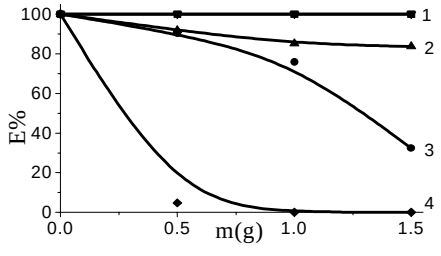
Figure 3 shows that NaCl and KBr do not affect E% of Zn(II), while large amount of $(NH_4)_2SO_4$, KI and $NaNO_3$ have different effects. The reason may be that increment in amount of salt reinforces the ionic strength and increases the solubility of the precipitate. So E% of Zn(II) is decreased. Compared with other salts, KI has the most remarkable effect on E% of Zn(II). Probably because I^- is big and has much stronger hydrophobicity, thereby it can associate with $CTMAB^+$ to form $CTMAB^+ \bullet I^-$. Consequently it can consume more $CTMAB^+$ which can associate with $[Zn(SCN)_4]^{2-}$ to form insoluble ion-association complex. In the experimental course, we also found that Zn(II) can be floated more quickly and completely, the interface of liquid-solid was much clearer than before. Therefore, 1.00g of NaCl was selected for all further studies.

Influence of acidity and temperature on E% of Zn(II)

We studied the influence of different acidity (pH1.0~6.0) on E% (E%) of Zn(II). The results showed that the acidity did not influence E% of Zn(II) in pH range of 1.0~6.0.

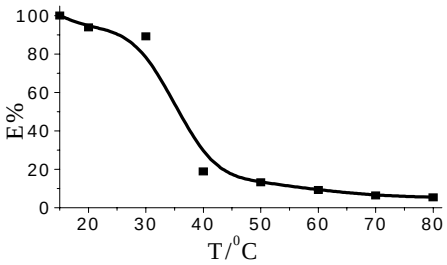
Figure 4 shows that E% of Zn(II) decreases with the increase in temperature. The E% of Zn(II) decreases from 100% to 5% or so when the temperature is increased from 15°C to 80°C. So 15°C was selected for all further studies.

Figure 3 Influence of different salts



Zn^{2+}: 50 μg; NH_4SCN (0.10mol/L): 2.50 mL; CTMAB(1.0×10^{-2}mol/L): 1.00 mL; Total volume: 10 mL; 1.NaCl; KBr; 2.$NaNO_3$; 3.$(NH_4)_2SO_4$; 4.KI

Figure 4 Influence of temperature



Zn(II):50 μg;NH_4SCN(0.10mol/L):2.50 mL;CTMAB(1.0×10^{-2}mol/L):1.00 mL; Total volume: 10 mL;NaCl:1.0 g

Calibration curve

Under the selected conditions, using 200 μg of Zn(II), a calibration curve for CTMAB was constructed. A very good linear relationship was observed between E% of Zn(II) and the amount of CTMAB. The linear equation obtained by least-squares analysis was found to be E (%)= -0.433+28.50x, where x represents the amount (10^{-6}mol) of CTMAB, with a correlation coefficient r =0.9999.

Influence of co-existing ions on determination of CTMAB

Under the above experimental conditions and relative deviation less than ±5%, most of common anions and cations (NH_4^+, K^+, Na^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mg^{2+}, Pb^{2+}, Fe^{3+}, Co^{2+}, Cd^{2+}, Ni^{2+}, Mn^{2+}, Al^{3+}, Cr^{3+}, PO_4^{3+}, SiO_3^{2-}, SO_4^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, CO_3^{2-}, $C_2O_4^{2-}$, NO_3^-, F^-, Cl^-, Br^-, Ac^-, As(III,V), *etc*) did not affect the determination of CTMAB. 65-fold tartrate and 1/20 fold SDS, 1/130 fold TritonX-100 did not interfere with the determination.

Sample Analysis

Determination of CTMAB in water sample

Some of these permitted ions were added into CTMAB solution to make up composed water sample. The results of analysis were satisfactory (**Table1**). The standardized added method was applied in determining CTMAB in the wastewater. The results summarized in **Table 2** confirm the validity of this proposed method.

Table 1 Analytical results of composed sample

Samples	Added (10^{-6}mol/10 mL)	Found (10^{-6}mol/10 mL)	RSD (%)	Recovery (%)
1	1.00	0.996 0.987 1.00 1.01 1.01	0.98	99.54~101.0
2	2.00	1.98 2.01 2.03 2.00 2.02	0.96	98.61~101.1

Table 2 Analytical results of wastewater (n=5)

Wastewater	Determined	Added (10^{-6}mol/10mL)	Found (10^{-6}mol/10mL)	RSD (%)	Recovery (%)
CTMAB	0	1.00	0.988	0.98	98.75
		1.50	1.46	0.97	97.33
		2.00	2.08	0.96	103.9

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