Notes

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Toyozo Uno and Koichiro Miyajima : Volumetric Determination of Surface-active Quaternary Ammonium Salts using Marme's Reagent.*2

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In a previous paper,[1] it was reported that surface-active quaternary ammonium salts could be determined volumetrically with sodium tetraphenylborate (STB) as a titrant, using Methyl Orange as an indicator. Similarly, it was expected that potassium cadmium iodide[2] could also be used as a titrant in the determination of surface-active quaternary ammonium salts.

This paper deals with the procedure and discussion of conditions for this method. When a drop of *M*/200 Methyl Orange solution is added to the solution of the surface-active quaternary ammonium salts with long-chain alkyl group, an orange precipitate appears at first, but the precipitate immediately disperses in the solution and then disappears. This solution does not show the acid color of Methyl Orange even at pH 3.

As stated in a previous paper,[1] the ratio of Methyl Orange to the quaternary ammonium base is 1:1 in the orange complex. When potassium cadmium iodide solution is added to this solution, a white precipitate forms and increases gradually until the end-point where the acid color of Methyl Orange appears.

$$(R_4N)X + NaO_3SC_6H_4N{=}NC_6H_4N(CH_3)_2 \longrightarrow (R_4N)O_3SC_6H_4N{=}NC_6H_4N(CH_3)_2 + NaX \quad (1)$$

$$2(R_4N)X + K_2CdI_4 \longrightarrow (R_4N)_2CdI_4 + 2KX \quad (2)$$

$$2(R_4N)O_3SC_6H_4N{=}NC_6H_4N(CH_3)_2 + K_2CdI_4 \longrightarrow (R_4N)_2CdI_4 + 2KO_3SC_6H_4N{=}NC_6H_4N(CH_3)_2 \quad (3)$$

R : Alkyl X : Halogen

Chart 1.

This reaction is regarded to proceed as shown in Chart 1. Equation (1) represents the complex formation between Methyl Orange and quaternary ammonium salts. An excess of quaternary ammonium salt reacts with potassium cadmium iodide according to equation (2), and finally, Methyl Orange is set free from the complex and acid color of Methyl Orange appears according to equation (3).

Experimental

(**I**) **Method**——(1) Procedure : To 10～20 cc. of the *M*/50～*M*/500 sample solution a drop of *M*/200 Methyl Orange solution is added, the solution is adjusted to pH 3 with HCl, and titrated with *N*/100 K_2CdI_4 solution, stirring mechanically until the red color appears.
(2) Preparation of standard *N*/100 K_2CdI_4; 2.5611 g. of $3CdSO_4 \cdot 8H_2O$, 9.0 g. of KI, and 0.2 g. of Na_2SO_3 was dissolved in H_2O to make 1 L. pH value of this solution is 6.0.
(3) Determination of factor of *N*/100 K_2CdI_4 : To 20 cc. of *N*/100 K_2CdI_4 solution measured accurately, H_2O is added to make 100 cc., 0.1 cc. of Eriochrom Black T is added as an indicator, and

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1) T. Uno, K. Miyajima, H. Tsukatani : Yakugaku Zasshi, **80**, 153 (1960).
2) B. Budesinsky, E. Vanickova : Collection Czechoslov. Chem. Communs., **22**, 236 (1957).

adjusted to pH 10 with 2 cc. of NH_4OH-NH_4Cl buffer solution. This is titrated with $M/100$ EDTA solution standardized with $CaCO_3$, using Murexide as an indicator.

(II) **Results of Determination**——Results of determination are shown in Table I, and they agreed with these from the STB method.

Table I. Determination of Quaternary Ammonium Compounds

Quaternary Ammonium Compound	by $N/100$ K_2CdI_4 Method			by STB Method	
	mg./cc. (Added)	mg./cc. (Found)	Recovery (%)	mg./cc. (Found)	Recovery (%)
Hexadecyldimethylbenzylammonium bromide	4.602	4.550	98.87	4.555	98.97
Hexadecyltrimethylammonium bromide	3.828	3.741	97.72	3.748	97.90
Tetradecyldimethylbenzylammonium bromide	4.352	4.290	98.57	4.270	98.12
Tetradecyltrimethylammonium bromide	3.636	3.613	99.36	3.592	98.79
Dodecyldimethylbenzylammonium bromide	4.164	4.123	99.10	4.160	99.90
Dodecyltrimethylammonium bromide	2.275	2.270	99.78	2.276	100.04
Benzethonium chloride	4.275	4.182	98.46	4.180	98.43

(III) Discussion of Conditions——(1) Effect of the pH value of the solution : As shown in Table II, good results were obtained when pH value before titration is within 2.6~3.2, as in the STB method.

Table II. Effect of the pH Value of the Solution
(Sample solution : $M/100$ Benzethonium chloride)

pH Value		mg./cc.		Recovery (%)
Before titration	After titration	Added	Found	
3.2	3.8	4.273	4.182	98.46
3.0	3.3	4.273	4.182	98.46
2.8	3.0	4.273	4.182	98.46
2.6	2.6	4.273	4.182	98.46
2.4	2.4	4.273	4.069	95.18
2.2	2.2	4.273	3.842	89.87

(2) Effect of the concentration of the solution : When the concentration of the sample solution is $M/1000$, color change at the end-point is not sharp. Consequently, this method can be applied to solutions of above $M/500$ in concentration.

Table III. Effect of the Concentration of the Solution
(Sample solution : $M/100$ Benzethonium chloride)

Molar Concentration	mg./cc. (Added)	mg./cc. (Found)	Recovery (%)
$M/50$	4.275	4.182	98.46
$M/100$	2.133	2.100	98.45
$M/200$	1.055	1.039	98.49
$M/500$	0.838	0.825	98.44

(3) Indicator : One or two drops of $M/200$ Methyl Orange solution per 10 cc. of sample solution is sufficient for this titration. More than two drops of $M/200$ Methyl Orange make it difficult to recognize the end-point and cause positive error.

Other dyes were also tested as the indicator, but good results could not be obtained. Quaternary ammonium salts with 8 carbon atoms, such as octyldimethylbenzylammonium bromide, and octyltrimethylammonium bromide, which could be titrated by STB method, could not be titrated by this method. These differences are regarded to be based on the solubility and character of ammonium tetraphenylborate and $(NH_4)_2CdI_4$.

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