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34. Toyozo Uno and Koichiro Miyajima: Determination of Surface-active Agents. VII.[*2] Differential Determination of Cationics and Nonionics in Mixture.[*3]

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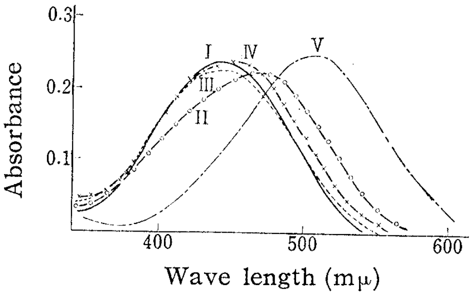
Only a few papers have been reported on the determination of cationics and nonionics in mixture. They are, gravimetry with phosphotungstate after separation of the mixture with ion-exchange resin,[1)] and the determination using a combination of Schönfeldt's method and either Epton's or Hartley's method.[2)] In the preceding papers,[3~5)] the volumetric determinations of cationics and nonionics using sodium tetraphenylborate (STB) and pH indicators were reported. Based on the differences of the principles in the determinations of cationics and nonionics, differential determination of these surfactants was established.

Determination of Cationics in Nonionics



I 1 ml. of 0.0001M MO and 9 ml. of 0.01M cetyl trimethyl ammonium chloride solution (pH: 5.8)
Ⅱ 1 ml. of 0.0001M MO and 9 ml. of H_2O (pH: 5.8)
Ⅲ 1 ml. of 0.0001M MO and 9 ml. of 0.01M nonylphenol with 40 units of ethylene oxide solution (pH: 5.8)
Ⅳ 1 ml. of 0.0001M MO and 9 ml. of 0.001M nonylphenol with 40 units of ethylene oxide solution (pH: 5.8)
V 1 ml. of 0.0001M MO and 9 ml. of H_2O (pH: 2.8)

Fig. 1. Absorption Spectra of Methyl Orange (MO) in Cationics and Nonionics Solution

The absorption spectra of Methyl Orange (MO) in cationics and nonionics solution are shown in Fig. 1. The absorption spectrum of MO in cationics solution is shown with curve I, which has the absorption maximum at 440 mμ, and this solution does not develop its acidic color even at pH 3 when the concentration of cationics solution is over the CMC. MO at pH 5.8 and pH 2.8 shows curve Ⅱ and V, having the absorption maximum at 465 and 505 mμ respectively. Curve Ⅲ is the absorption spectrum of MO in 0.01M of nonionics solution, whose maximum was observed at 440 mμ as in cationics solution. However, when the concentration of nonionics was lowered to 0.001M the absorption spectrum of MO turned to curve Ⅳ, and in 0.0001M solution of nonionics the absorption spectrum was in accord with the curve Ⅱ. When the pH values of the solutions corresponding to curves Ⅲ and Ⅳ are changed to pH 3, MO showed its acidic color unlike the case of cationics solution. It seems that the type of a bond between

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[*1] Yoshida-konoe-cho, Sakyo-ku, Kyoto (宇野豊三, 宮島孝一郎).
[*2] Part Ⅵ: This Bulletin, **11**, 80 (1963).
[*3] This work was presented at the Kinki Branch Meeting of Pharmaceutical Society of Japan, December, 1961.
1) C.C.T. Chinnick, P.A. Lincoln: World Congress on Surface Active Agents. Section 2. 41 (1954).
2) M. Kurata, S. Inoue: Yakugaku, **6**, 96 (1957).
3) T. Uno, K. Miyajima: Yakugaku Zasshi, **80**, 153 (1960).
4) *Idem*: This Bulletin, **11**, 75 (1963).
5) *Idem*: *Ibid.*, **11**, 80 (1963).

MO and nonionics is different from that of MO and cationics. The absorption spectrum of MO in the mixed solution of cationics and nonionics agrees with that of MO in cationics solution. With respect to the reaction with STB, precipitation was scarcely observed in nonionics solution in the absence of barium chloride. Therefore the auther's method previously reported for the determination of cationics would be applicable to the determination of cationics in nonionics with little error in the absence of barium chloride. This method was applicable to the determination of various kinds of cationics in nonionics and the results obtained are shown in Table I. The accuracy of this method is about ± 1%.

Table I. Determination of Cationics in Nonionics

Cationics	Cationics added (mg.)	Cationics alone		Plus nonionics	
		Found (mg.)	Recovery (%)	Found (mg.)	Recovery (%)
Hexadecyl trimethyl ammonium bromide	38.05	37.22	97.82	37.47	98.46
Tetradecyl trimethyl ammonium bromide	34.33	33.67	98.08	33.44	98.40
Dodecyl trimethyl ammonium bromide	38.21	38.04	99.55	38.16	99.85
Tetradecyl dimethyl benzyl ammonium bromide	48.72	47.96	98.45	48.34	99.02
Dodecyl dimethyl benzyl ammonium bromide	40.52	40.48	99.88	40.50	99.95
Octyl dimethyl benzyl ammonium bromide	35.96	35.72	99.29	35.66	99.15
Benzethonium chloride	52.50	51.70	98.44	52.00	99.05

Cationics : 10 ml. of $0.01M$ sample solution
Nonionics : 10 ml. of $0.001M$ nonylphenol with 30 units of ethylene oxide solution

Experimental

Method Procedure——To 10∼20 ml. of the sample solution, 2∼3 drops of $0.0001M$ MO solution were added, the solution was adjusted to pH 3 with HCl, and this solution was titrated with $0.001M$ standard STB solution with mechanical stirring until the red color of MO appeared.

Materials and Reagents——Surface-active compounds and reagents used in this experiment were as same as the one used in the preceding papers.[3,4] Preparation of reagents followed the method described in the preceding papers.[3,4]

Discussions

1) Concentration of cationics solution.

Table II. Effect of the Concentration of Cationics Solution

Cationics (ml.)	Cationics (mg.)		Recovery (%)	Cationics (ml.)	Cationics (mg.)		Recovery (%)
	Added	Found			Added	Found	
10	38.05	37.47	98.46	0.1	0.38	0.31	81.72
5	19.03	18.73	98.46	0.05	0.19	—	—
1	1.91	1.86	97.38				

Cationics : $0.01M$ cetyl trimethyl ammonium bromide solution
Nonionics : 10 ml. of $0.001M$ nonylphenol with 30 units of ethylene oxide solution

As shown in Table II, good results were obtained at about $0.001M$ concentration as converted to concentration of cationics. This value almost agreed with that of cationics alone. Therefore it seems that a limit of titration depends upon the CMC of the cationics solution.

2) Molar ratio of cationics and nonionics in mixture.

As shown in Table III, titration could be carried out when a molar ratio of cationics to nonionics was greater than 1/2. Because in this titration, solubilization of cationics-STB precipitate with nonionics took place unlike in the case of cationics alone, and the recognition of color change of MO became difficult. This solubilization began to take

Table III. Results obtained when the Molar Ratio of Cationics and Nonionics was changed

Nonionics	$0.01M$ CTABr[c] (ml.)	CTABr (mg.) Added	Found	Recovery (%)
NP 30[a]	10	38.05	37.47	98.46
NP 30	5	19.03	18.82	98.87
NP 30	1	3.81	3.14～3.52	82.43～92.45
LA 20[b]	10	38.05	37.47	98.46
LA 20	5	19.03	18.65	98.00
LA 20	1	3.81	3.14～3.52	82.43～92.45

a) NP 30 : Nonylphenol with 30 units of ethylene oxide
b) LA 20 : Lauryl alcohol with 20 units of ethylene oxide
c) CTABr : Cetyl trimethyl ammonium bromide
Nonionics : 10 ml. of $0.01M$ solution

place in the mixed solution of 1 to 1 mole, and became complete in the mixed solution of 1 mole of cationics and 3 mole of nonionics.

3) Results obtained with different nonionics.

Table IV. Determination of Cationics in Various Nonionics

Nonionics	CTABr (mg.) Added	Found	Recovery (%)	Nonionics	CTABr (mg.) Added	Found	Recovery (%)
NP 40[a]	38.05	37.50	98.56	LA 20[b]	38.05	37.50	98.56
NP 30	38.05	37.47	98.46	LA 15	38.05	37.47	98.46
NP 20	38.05	37.47	98.46	LA 10	38.05	37.50	98.56
NP 10	38.05	37.47	98.46				

a) NP 40 : Nonylphenol with 40 units of ethylene oxide
b) LA 20 : Lauryl alcohol with 20 units of ethylene oxide
Nonionics : 10 ml. of $0.001M$ solution
Cationics : 10 ml. of $0.01M$ solution

As shown in Table IV, difference in nonionics gave no influence on the determination of cationics.

4) Results obtained when different indicators were used.

Table V. Results obtained when Different Indicators were used

Indicator	CTABr (mg.) Added	Found	Recovery (%)	pH range	Color change
Methyl orange	38.05	37.47	98.46	2.0～3.1	pink-yellow
Bromophenol blue	38.05	37.47	98.46	3.0～4.6	yellow-blue
Congo red	38.05	38.13	100.21	3.2～5.2	blue-red
Tropaeoline OO	38.05	37.47	98.46	1.3～3.0	pink-yellow
Thymol blue	38.05	37.36	98.18	1.2～2.8	pink -yellow

Cationics : 10 ml. of $0.01M$ cetyl trimethyl ammonium bromide solution
Nonionics : 10 ml. of $0.001M$ nonylphenol with 30 units of ethylene oxide solution

As shown in Table V, five dyes such as MO, Bromophenol Blue, Congo Red (CR), Tropaeoline OO, and Thymol Blue could be used as an indicator for this titration. A higher value was obtained with CR, as in the case of cationics. However, this is not due to the interaction of nonionics with CR.

5) Effect of the hydrogen ion concentration of the solution.

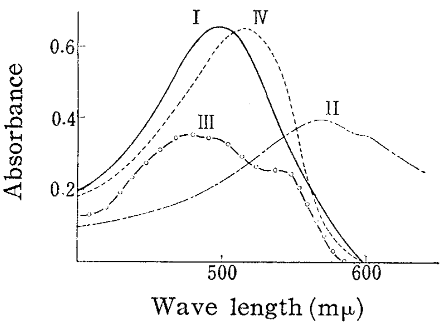
An effect of the hydrogen ion concentration was investigated to the mixed solution of cationics and nonionics using MO as an indicator, and as shown in Table VI, similar results were obtained to the case of determination of cationics alone. However in this case, titration could be carried out even at lower pH values (pH : 2.0～3.0) in comparison with the case of determination of cationics.

Table VI. Effect of the Hydrogen Ion Concentration of the Solution

pH value of the solution		CTABr (mg.)		Recovery
Before titration	After titration	Added	Eound	(%)
3.4	3.7	36.06	35.43	98.25
3.0	3.1	36.06	35.28	97.82
2.7	2.9	36.06	35.28	97.82
2.5	2.6	36.06	35.28	97.82
2.3	2.4	36.06	35.28	97.82
1.9	2.0	36.06	35.28	97.28
1.5	1.6	36.06	35.22	97.00
1.0	1.1	36.06	34.69	96.40

Cationics : 10 ml. of 0.01M cetyl trimethyl ammonium chloride solution
Nonionics : 10 ml. of 0.001M nonylphenol with 30 units of ethylene oxide solution

Determination on Nonionics in Cationics



I 2 ml. of 0.0001M CR and 8 ml. of H_2O (pH : 5.8)
II 2 ml. of 0.0001M CR and 8 ml. of H_2O (pH : 2.8)
III 2 ml. of 0.0001M CR and 8 ml. of 0.01M cetyl trimethyl ammonium chloride solution (pH : 5.8)
〃 2 ml. of 0.0001M CR and 8 ml. 1 of to 1 mixed solution of 0.01M cetyl trimethyl ammonium chloride solution and 0.01M nonylphenol with 40 units of ethylene oxide (pH : 5.8)
IV 2 ml. of 0.0001M CR and 8 ml. of 0.01M nonylphenol with 40 units of ethylene oxide solution (pH : 5.8)

Fig. 2. Absorption Spectra of Congo Red (CR) in Cationics and Nonionics solution

The absorption spectra of CR are shown in Fig. 2. As stated in the previous paper,[4] CR interacted with nonionics at more than 10^{-4} molor concentration of nonionics. In Fig. 2, curves I and II are the absorption spectra of CR at pH 5.8 and 2.8, having absorption maximum at 500 and 570 mμ respectively. Curve IV is the absorption spectrum of in nonionics solution, having its maximum at 515 mμ. Curve III is the spectrum of CR in either cationics solution or a mixed solution of cationics and nonionics at pH 5.8, showing its maximum at 475 mμ. It was shown that CR combined

Table VII. Determination of Nonionics in Cationics

Nonionics	Nonionics added (mg.)	Nonionics alone		Plus cationics	
		Found (mg.)	Recovery (%)	Found (mg.)	Recovery (%)
NP 40[a]	19.81	19.23	97.1	18.64	94.1
NP 30	15.42	14.99	97.2	14.57	94.5
NP 20	10.81	10.50	97.0	10.11	93.5
NP 10	6.61	6.61	100.0	6.54	99.0
LA 20[b]	10.29	9.82	95.6	9.99	97.1
LA 15.4	8.28	8.06	97.3	7.74	93.5
LA 10	6.06	6.24	102.9	6.06	100.0

a) NP 40 : Nonylphenol with 40 units of ethylene oxide
b) LA 20 : Lauryl alcohol with 20 units of ethylene oxide
Cationics : 1 ml. of 0.01M cetyl trimethyl ammonium chloride solution
Nonionics : 10 ml. of 0.001M solution

with cationics preferentially in the mixed solution, by the fact that the absorption spectrum of CR in mixed solution agreed with that in cationics solution. Therefore if the mixed solution was titrated after an addition of barium chloride at pH 3, the color change took place at an equivalent point of cationics, and a determination of nonionics became difficult. To remove this inconvenience, nonionics was titrated after an addition of STB solution which was equivalent to cationics. Consequently, nonionics was determined without interfered by cationics, and results were shown in Table VII. The accuracy of this titration was ±5%.

Experimental

Method Procedure——To 10~20 ml. of sample solution, the same volume of standard STB solution consumed with the titration of cationics was added. To this solution 2~3 drops of 0.001*M* CR solution and 2~10 ml. of 0.1*M* $BaCl_2$ solution were added. This solution was adjusted to pH 3 with HCl, and titrated with standard STB solution until the pink color turned to blue-purple.

Materials and Reagents——Surface-active compounds and reagents used in this experiment were as same as those used in the preceding papers.[4,5] Preparation of reagents was also carried out as described previously.[3]

Discussion

1) Effect of the hydrogen ion concentration of the solution.

Table VIII. Effect of the Hydrogen Ion Concentration of the Solution

pH value of the solution		CTACl (mg.)		Recovery
Before titration	After titration	Added	Found	(%)
3.40	—	—	—	—
3.20	3.50	15.42	14.83	96.2
2.90	3.05	15.42	14.83	96.2
2.60	2.80	15.42	14.83	96.2
2.50	2.75	15.42	14.83	92.2
2.25	2.40	15.42	14.20	92.0
2.02	2.25	15.42	—	—

Cationics : 10 ml. of 0.01*M* cetyl trimethyl ammonium chloride solution
Nonionics : 1 ml. of 0.01*M* nonylphenol 30 units of ethylene oxide solution

As shown in Table VIII, better results were obtained between pH 2.5~3.0, similary to the case of the determination of nonionics alone.

2) Molar ratio of nonionics and cationics in mixture.

Table IX. Results obtained when the Molar Ratio Nonionics and Cationics was changed

NP 40 solution	Nonionics (mg.)		Recovery
	Added	Found	(%)
10 ml. of 0.001*M* solution	19.81	19.95	100.7
5 ml. of 0.001*M* solution	9.91	9.76	98.5
2.5 ml. of 0.001*M* solution	4.96	4.82	97.1
1 ml. of 0.001*M* solution	1.98	1.83	92.6
10 ml. of 0.01*M* solution	198.1	199.3	100.6

Cationics : 10 ml. of 0.01*M* cetyl trimethyl ammonium chloride solution

Good results were obtained when a molar ratio of nonionics/cationics was greater than 1/40. At a ratio of less than 1/50, the precipitation of nonionics-barium-STB coprecipitated with the precipitate of cationics-STB, and the coagulation point of the precipitate no longer agreed with the point of color change of CR, unlike the case of nonionics alone. On the other hand, titration could be carried out at about 0.001*M* concentration as converted to the concentration of nonionics similary to the case of nonionics alone.

3) Other effects on the titration

The volume of barium chloride solution was fixed by the results of the determination of nonionics alone. Any other dyes useful for this titration could not be found.

The authers wish to express their thanks to Mr. S. Okuda and Sanyo Yushi CO. Ltd., for the gift of nonionics.

Summary

A volumetric determination of cationics and nonionics in mixtures was established with sodium tetraphenylborate as a titrant using Methyl Orange and Congo Red as indicators. For the determination of cationics, this method could be applied to a mixture of one mole of cationics and two moles of nonionics with an error of ±1%. For the determination of nonionics, this method could be applied to a mixture of one mole of nonionics and forty moles of cationics with an error of ±5%.

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35. Hiroshi Fujiwara, Takatsuka Yashiki, and Tokunosuke Kanzawa :

Rheology of the Pharmaceutical Suspension. III. Effects of Some Additives on Viscous Behavior of Barium Sulfate-Water System.

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In the previous paper,[1] flow properties of barium sulfate suspensions in various concentrations were studied with rotational viscosimeter and it was clarified that the flow properties of the suspensions are classified into several types according to the concentration of barium sulfate, that is, Bingham flow, negative shear-rate thixotropy, and pseudoplastic flow.

In this paper, the effects of adding some high polymers such as sodium carboxymethylcellulose (Na-CMC), methylcellulose (MC), and polyvinylpyrrolidone (PVP) to the suspension in order to disperse the particles finely and to prevent the sedimentation were studied.

Experimental

1) Sample

$BaSO_4$: The same product as described in the previous paper.
Na-CMC : High type of Na-CMC (Hercules Co.).
MC : Marpolose M600 (Matsumoto Fat Co.).
PVP : NPK-30 (Wako Pure Chemicals Co.).

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[1] H. Fujiwara, T. Yashiki, T. Kanzawa : Takeda Kenkyusho Nempo, **20**, 65 (1961).