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Color Reaction among Gallein, Thorium(IV) and Lanthanum(III) in the Coexistence of Amphoteric and Nonionic Surfactants, and Its Application to the Determination of These Ions[1]

ITSUO MORI,* YOSHIKAZU FUJITA, KINUKO FUJITA, TAKESHI TANAKA,
YOZO KOSHIYAMA, and HIROSHI KAWABE

Osaka University of Pharmaceutical Sciences, 2-10-65, Kawai,
Matsubara, Osaka 580, Japan

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Color reaction systems among thorium(IV) {Th(IV)}, lanthanum(III) {La(III)} and xanthene derivative such as gallein (gall), in the coexistence of amphoteric and nonionic surfactants were studied, and spectrophotometric determinations of these metal ions (0—50 μg of Th(IV) or La(III)/10 ml) at 620 nm by using gall–Th(IV)–La(III) ternary complex in the coexistence of sodium *N*-lauroylsarcosine (LS) as an amphoteric surfactant and Brij-35 as a nonionic surfactant were developed. The influences of foreign ions in this proposed method were greatly reduced (to 1/2—1/10) in comparison with the method in the presence of cationic surfactant alone.

Keywords——spectrophotometry; thorium(IV); lanthanum(III); gallein; Brij-35; sodium *N*-lauroylsarcosine; color reaction system; amphoteric surfactant; nonionic surfactant

We have already reported[2] spectrophotometric determinations of thorium(IV) {Th(IV)} and samarium(III) {Sm(III)} or lanthanum(III) {La(III)} by using xanthene derivatives (gallein(gall), tetrachlorogall(T.Cl.gall), Pyrogallol Red (PR))–Th(IV)–Sm(III) or xanthene–Th(IV)–La(III) ternary complex in the presence of a cationic surfactant. On the other hand, various surfactants have been used for the color reaction systems between dyes such as Xylenol Orange (XO), PR, Pyrocatechol Violet (PV), *o*-hydroxyhydroquinonephthalein (Qnph), gall and various metal ions such as aluminum(III), iron(III), and Th(IV). These include cationic surfactants such as hexadecylpyridinium chloride (HPC) and *N*-hexadecyltrimethylammonium chloride (HTAC), an anionic surfactant, sodium dodecyl sulfate (SDS), and nonionic surfactants such as Triton X-100, Tween-20(LT-221), poly(vinylalcohol) (PVA), Brij-35, *etc.* The use of combinations of two or three surfactants in the color reaction systems or spectrophotometric determinations has been discussed; for example, anionic and cationic surfactants, nonionic and cationic surfactants, and nonionic and nonionic surfactants, *etc.*[3] Nevertheless, the use of amphoteric surfactants in these color reaction systems has not been considered in detail.

In this paper, the color reaction systems among various xanthene dyes, Th(IV) and La(III) in combinations of various surfactants—nonionic, cationic, anionic and amphoteric surfactants—were studied. Spectrophotometric determinations of these metal ions were developed by using the gall–Th(IV)–La(III) ternary complex in the coexistence of sodium *N*-lauroylsarcosine (LS) as an amphoteric surfactant and Brij-35 as a nonionic surfactant.

Experimental

Reagents and Apparatus——Solutions of 1.0×10^{-3} M gall (Merck Chemical Co., Ltd.), PV (Dojindo Co., Ltd.), XO (Dojindo Co., Ltd.) and Qnph[4] were prepared by dissolving these dyes in methanol. Working solutions of 5.0×10^{-4} M Th(IV) and rare earth elements(III) were prepared as described in previous reports.[2] Solutions of 2.0%

LS (Tokyo Kasei Kogyo Co., Ltd.) and 2.0% Brij-35 (Kishida Chemical Co., Ltd.) were prepared by dissolving the compounds in water. A 2.0×10^{-1} M sodium acetate–acetic acid buffer solution (pH 4.2) was used for the pH adjustments. All the other reagents and materials were of analytical grade, and deionized water was used throughout.

Recommended Procedure——Th(IV) or La(III) (0—50 μg) was placed in a 10 ml volumetric flask, then 0.15 ml of 2.0% LS solution, 1.0 ml of 2.0% Brij-35 solution, 1.5 ml of 1.0×10^{-3} M gall solution, and 1.0 ml of 5.0×10^{-4} M La(III) for the determination of Th(IV) or 0.5 ml of 5.0×10^{-4} M Th(IV) for the determination of La(III) were added. The pH of the final solution was adjusted to about pH 4.2 with 2.0 ml of Walpole acetate buffer solution. The mixture was diluted to 10 ml with water to make solution A, which was kept at 60 °C for 20 min together with the reference solution {gall solution (solution D), gall–La(III) solution (solution C) or gall–Th(IV) solution (solution B)}, and cooled to room temperature for 10 min. The absorbance of solution A was measured at 620 nm against solution C for the determination of Th(IV). For the determination of La(III), the absorbance of solution A was measured at 620 nm against solution B.

Results and Discussion

Figure 1 shows the absorption spectra of solutions A (gall–Th(IV)–La(III)solution), B (gall–Th(IV) solution), C (gall–La(III) solution) and D (gall solution) in the presence of Brij-35 or HPC alone, and in the coexistence of LS and Brij-35. The color reaction systems between gall and Th(IV), or gall and La(III) were enhanced by the presence of La(III) or Th(IV), respectively, and the difference of absorbance between solutions A and C, or solutions A and B in the coexistence of LS and Brij-35 was greater than that in the presence of HPC or Brij-35 alone.

The effect of xanthene dyes such as gall, Qnph, PV, XO, *etc.* in the dye–Th(IV)–La(III) color reaction systems was examined under the standard conditions; gall was superior to the other dyes in terms of sensitivity, stability and catalytic reaction. As shown in Table I and Fig. 1, the simultaneous use of amphoteric and nonionic surfactants was the most effective. Among the various amphoteric surfactants tested, including betaine-type LS, AM-301(lauryldimethylaminoacetic acid betaine, Nihon Chemicals Co., Ltd.), AM-101, AM-103, *etc.*, LS was found to be the best in the coexistence of Brij-35. Maximum and constant absorbance was obtained upon the addition of more than 0.10 ml of 2.0% LS solution to the final volume of 10 ml. On the other hand, solution A in the presence of LS alone was unstable,

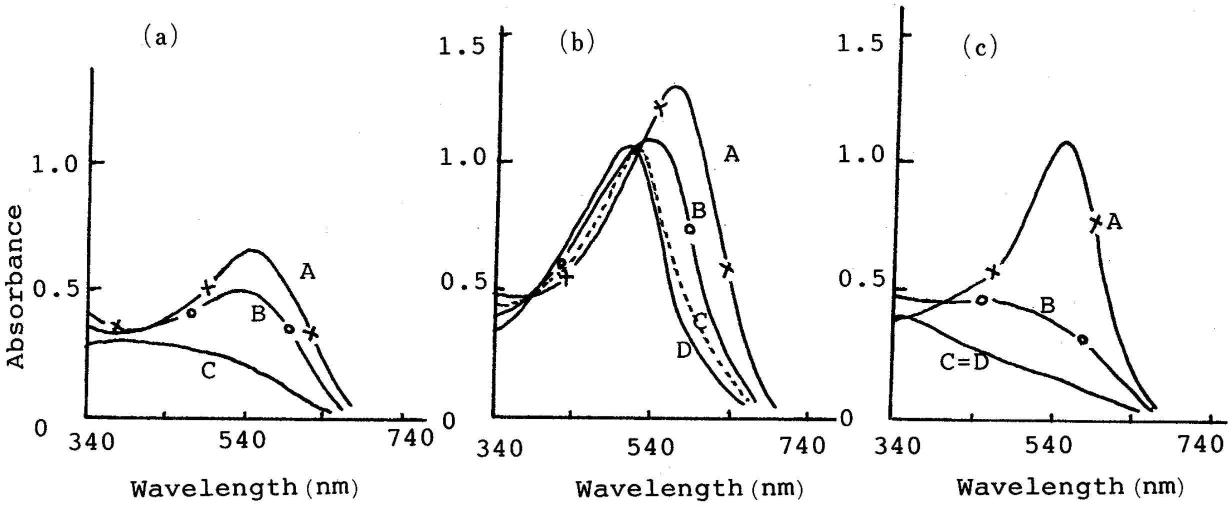

Fig. 1. Absorption Spectra of Gall, Gall–La(III), Gall–Th(IV) and Gall–La(III)–Th(IV) Solutions in the Presence of Brij-35 Alone or HPC Alone, and in the Coexistence of LS and Brij-35

(a) Brij-35 (0.2%). (b) HPC (1.0×10^{-3} M). (c) LS+Brij-35 (0.13%, 0.2%). Th(IV), La(III), 2.5×10^{-5} M; gall, 1.5×10^{-4} M; Brij-35 (0.2%)+LS (about 0.13%); curve A, solution A; curve B, solution B; curve C, solution C; curve D, solution D. The pH values of all these solutions were approximately 4.2; water was used as a reference.

TABLE I. Effects of Various Surfactants in This Color Reaction System

	None	Brij-35	HPC	SLS	LS	HPC+SLS	LS+HPC	LS+Brij-35
Max nm	595	605	610	a)	a)	a)	605	620
Absorbance	0.395	0.518	0.751	a)	a)	a)	0.150	0.975

	LS+Tween	LS+Triton	LS+PVP	AM-101+Brij-35	AM-301+Brij-35	AM-103+Brij-35
Max nm	590	610	a)	570	610	610
Absorbance	0.583	0.546	a)	0.033	0.710	0.441

Th(IV), 2.0×10^{-5} M; HPC, 5.0×10^{-3} M; nonionic surfactant, 0.2% La(III), 2.5×10^{-5} M; gall, 1.5×10^{-4} M; LS, 0.15 ml of 2.0% LS solution/10 ml; reference, solution B. *a*) The solution was turbid.

TABLE II. Sensitivity, Linear Range of Calibration Curve and Reproducibility for Th(IV) or La(III) Determination by Using Gall–Th(IV)–La(III) Ternary Complex

Method	pH range	nm	Linear range μg/10 ml	Sensitivity: Sandell scale μg/cm²	Sensitivity: ε	Coefficient of variation (*n*=5) %
1	3.0—4.5	620	Th(IV) 0—50	0.005	4.9×10^4	1.0
			La(III) 0—50	0.002	2.1×10^4	1.1
2	3.0—4.5	610	Th(IV) 0—70	0.006	3.8×10^4	1.0
3	3.0—4.5	580	Th(IV) 0—70	0.008	2.3×10^4	0.9

Method 1: proposed method, gall–LS–Brij-35. Method 2: HPC alone, gall–HPC. Method 3: Brij-35 alone, gall–Brij-35.

resulting in gradual precipitation. The simultaneous use of Brij-35 together with LS was the most effective in terms of sensitivity and reproducibility among various nonionic surfactants—PVA, poly(*N*-vinyl-pyrrolidone) (PVP), gum arabic, gelatin, Tween-20(LT-221), *etc.*

Among the rare earth elements tested—La(III), Ce(III), Sm(III), *etc.*, La(III) was the most effective with respect to sensitivity. A nearly constant difference of absorbance at 620 nm between solutions A and B was obtained by using 1.5×10^{-4} M gall and 5.0×10^{-5} M La(III) for Th(IV) as the final concentrations. Further, a constant and stable difference of absorbance at 620 nm between solutions A and C was obtained by using 1.5×10^{-4} M gall and 2.5×10^{-5} M Th(IV) for La(III) as the final concentrations.

The effects of temperature and standing time were examined. Maximum and constant difference of absorbances between solutions A and C, or A and B was obtained by heating these solutions at 60 °C for 20 min then cooling to room temperature for 10 min.

In the determination of Th(IV) and La(III), Beer's law was obeyed over the range of 0—50 μg per 10 ml of Th(IV) or La(III). Table II shows the apparent molar absorptivities, reproducibilities, and linear range of calibration curves, *etc.* obtained by using gall–HPC solution, gall–Brij-35 solution and gall–LS–Brij-35 solution (proposed method).

Interference by various ions was studied by using 23.2 μg of Th(IV). The coexistence of small amounts of copper(II), lead(II), mercury(II), aluminum(III), iron(III), tin(IV), tungstic acid, titanium(IV), fluoride ions, *etc.* resulted in positive errors, as shown in Table III. However, the interference of these metal ions could be overcome by addition of iminodiacetic acid (IDA), sulfosalicylic acid (Sulf.sal), L-ascorbic acid (Ascorb), *etc.*

Table III. Effect of Foreign Ions on the Determination of Th(IV)

Foreign ions	Added		Absorbance at	Permissible molar ratio		Masking agents[b]
		μg/10 ml	620 nm	Foreign ion/Th	Method 1/method 2[a]	
None	—	—	0.495	—	—	—
Al(III)	Nitrate	0.1	0.510	1/30	4	Sulf. sal
Fe(III)	Sulfate	0.3	0.504	1/25	4	Ascorb
Sn(IV)	Sulfate	0.8	0.514	1/30	2.5	IDA
Ti(IV)	Nitrate	0.6	0.495	1/8	10	IDA
U(VI)	Nitrate	1.2	0.510	1/30	4	IDA
Sm(III)	Nitrate	0.9	0.504	1/20	2	IDA
Cu(II)	Nitrate	7.9	0.504	1	2	IDA
Pb(II)	Nitrate	1.1	0.521	1/30	4	IDA
Hg(II)	Nitrate	5.0	0.510	1/8	2	IDA
Citrate	Sodium	2.6	0.504	1/10	2	
F^-	Sodium	0.2	0.532	1/25	1	
PO_4^{3-}	Potassium	2.4	0.478	1/25	2	
$S_2O_3^{2-}$	Sodium	700.0	0.510	50	10	
CN^-	Potassium	32.5	0.520	1/2	5	

Th(IV) taken, 23.2 μg/10 ml; La(III), 5.0×10^{-5} M; gall, 1.5×10^{-4} M; Brij-35, 1.0 ml of 2.0% Brij-35 solution/10 ml; LS, 0.15 ml of 2.0% LS solution/10 ml; pH 4.2; reference, solution B. *a*) Permissible molar ratio of method 1 (proposed method) : method 2 (gall–HPC method). *b*) Sulf. sal, 5.0×10^{-4} M; IDA, 1.0×10^{-3} M; Ascorb, 5.0×10^{-4} M.

Although further investigation is necessary for the color reaction systems, the molar ratios of Th(IV) to gall in this proposed method were found to be 1 : 2 in the presence of La(III), and 2 : 3 in the absence of La(III) by the molar ratio and continuous variation methods.

In conclusion, color reaction systems among gall, Th(IV) and La(III) in the presence of sulfactant alone or combinations of surfactants were studied. The simultaneous use of LS as an amphoteric surfactant and Brij-35 as a nonionic surfactant was more effective in terms of sensitivity and reproducibility than the method using gall and HPC. Further, the influences of foreign ions were reduced to 1/2—1/10 in comparison with gall–HPC method. An amphoteric surfactant such as LS may be useful for color reaction systems involving xanthene dyes, metal ions and surfactants.

References

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