Polysoap as a New Titrant for the Determination of Sodium Dodecylbenzenesulfonate by Colloid Titration

Toshiro Ono, Haruo Miyata, and Kyoji Tôei*

Department of Chemistry, Faculty of Science, Okayama University, Tsushima-naka 3-1-1, Okayama 700

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A colloid titration method for the determination of sodium dodecylbenzenesulfonate (LAS) with poly(4-vinyl-1-pentylpyridinium bromide) (polysoap) is described. The end-point detection is based on the measurement of turbidity, the transmittance at 420 nm or 680 nm being used for the determination. The most successful results were obtained by titrating LAS ($1—7.5\times10^{-4}$ N) with 2.5×10^{-3} N polysoap solution. The purity of commercial LAS was found to be 81—84%.

Colloid titration is widely used for the determination of polyelectrolytes. Usually, Cat-Floc (poly(diallyldimethylammonium chloride)) and PVSK (potassium poly(vinyl sulfate)) are used as polycationic and polyanionic titrants, respectively.[1] Anionic surfactants, however, can not be titrated with Cat-Floc, since Cat-Floc can not form polyion complexes with anionic surfactants stoichiometrically.

When a long aliphatic chain is introduced into the polycation to enhance the bonding strength of polycationic titrants with sodium dodecylbenzenesulfonate, the chain is combined firmly with the dodecyl group of the surfactant by hydrophobic bonding. An attempt was made to synthesize a cationic titrant by introducing methyl, ethyl, propyl, butyl, pentyl, hexyl, or octyl group into poly(4-vinylpyridine) in order to form poly(4-vinyl-1-alkylpyridinium halide). The longer the chain, the stronger the bonding strength, the solubility in water decreasing. No standard solution of hexyl and octyl derivatives (2.5×10^{-3} N) can be prepared since they are hardly soluble in water. Thus, poly(4-vinyl-1-pentylpyridinium bromide)(polysoap), synthesized by Menschutkin's reaction,[2] was used as a new cationic titrant. It can combine with sodium dodecylbenzenesulfonate (LAS) stoichiometrically. For the titration of LAS, turbidimetry[3] was used to observe the end-point at wavelengths 420 or 680 nm. Titration was carried out slowly near the end-point.

Experimental

Synthesis of Polysoap. Poly(4-vinyl-1-pentylpyridinium bromide) was synthesized as follows: An equimolecular mixture of pentyl bromide(3 M) and 4-vinylpyridine(3 M) in nitrobenzene was refluxed at 100 °C for several hours. After steam distillation to remove the nitrobenzene and the unreacted reagents, polysoap was obtained as a solid.

Apparatus. Turbidity was measured with a Metrohm Spectrocolorimeter E 1009 equipped with a titration cylinder cell(diameter 35 mm), titration curve being recorded with a Metrohm Potentiograph E 336. pH was measured with a Hitachi-Horiba M 5 pH meter.

Reagents. PVSK solution. Potassium poly(vinyl sulfate) (Wako Pure Chemical Industries Ltd., degree of esterification 92.6%) was dissolved in distilled water to prepare a 2.5×10^{-3} N solution. The factor of the PVSK solution was determined by titrating a standard solution of 2.5×10^{-3} N hexadecylpyridinium chloride monohydrate,[4] stored for several days over a silica gel desiccator, using Toluidine Blue as an indicator.

Polysoap solution. Poly(4-vinyl-1-pentylpyridinium bromide) was dissolved in distilled water to prepare a 2.5×10^{-3} N solution. The solution (10 ml) was diluted to 50 ml with distilled water in a 100 ml cylinder cell and titrated automatically with the standardized PVSK solution using Toluidine Blue as an indicator. The titration speed was 0.37 ml min^{-1}. The end-point was indicated by the inflection point of the transmittance at 630 nm.

Sample Solutions. Standard LAS solution. Standard LAS (Wako Pure Chemical Industries Ltd., purity>99%) was dried *in vacuo* at about 50 °C, and weighed. The standard LAS solution was prepared by dissolving the LAS in distilled water to a constant volume.

Other LAS sample solutions were prepared in the same way as described above.

Titration Procedure of LAS. LAS solution was titrated directly with 2.5×10^{-3} N polysoap solution. A sample solution (2.5×10^{-3} N, 10 ml) in a 100 ml cylinder cell was diluted to 50 ml with distilled water, and titrated with the polysoap solution under mechanical stirring. In order to follow the course of titration, the transmittance at 420 or 680 nm was measured and recorded automatically. It is important to maintain a titration speed of 0.37 ml min^{-1} near the end-point.

Results and Discussion

Standardization of Polysoap. Figure 1 shows the influence of pH on the titration of polysoap with a standard solution of PVSK. The values of meq g^{-1} are constant (3.77 meq g^{-1}) in the pH range 5.0—9.5, decreasing gradually above 9.5. Since the polysoap is quaternary ammonium salt, the values of meq g^{-1} should be constant over the whole pH range 0—14. Actually, however, the pH range is restricted. This

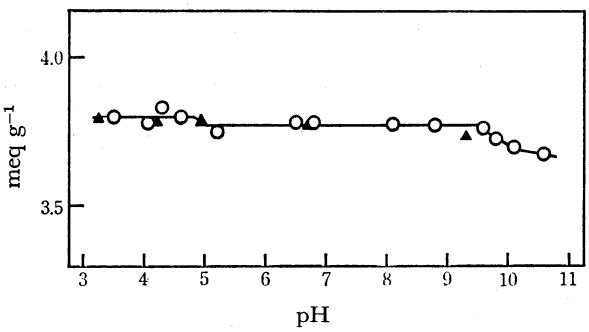

Fig. 1. Colloid titration results of polysoap. Titrant: 1×10^{-3} N PVSK. Titrating solution: 2×10^{-4} N polysoap. ○ Colorimetric, ▲ conductometric.

Table 1. Titration values of standard LAS solution

LAS total concn	Polysoap normality ($N \times 10^3$)					
	2.5	1.25	1	0.5	0.25	0.125
75×10^{-5} N	2.84 meq g^{-1} (99.$_1$%)					
50	2.85(99.$_1$)					
25	2.85(99.$_5$)	2.78(97.$_1$)				
20			2.76(96.$_4$)			
15	2.85(99.$_2$)					
12.5		2.78(97.$_1$)		2.74(95.$_5$)		
10	2.85(99.$_1$)			2.73(95.$_2$)		
7.5		2.77(96.$_5$)		2.74(95.$_5$)		
5		2.79(97.$_2$)		2.72(94.$_8$)	2.68(93.$_5$)	
2.5						2.69(93.$_5$)

Standard LAS (Wako Pure Chemical Industries, Ltd.; purity: more than 99%).

suggests that the quaternarized reaction is incomplete, the titration results of 3.77 meq g^{-1} corresponding to 96.7% of the expected value, 3.90 meq g^{-1}. The results obtained by the conductometric method[4] with platinum electrodes coincide with those of the photometric method as shown in Fig. 1.

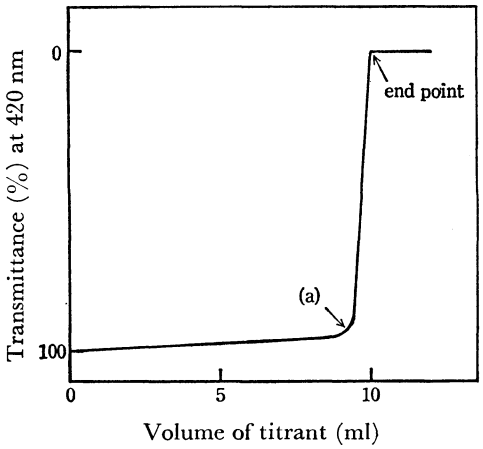

Fig. 2. Turbidimetric titration curve. Titrant: 1×10^{-3} N polysoap. Titrating solution: 2×10^{-4} N LAS(purity: more than 99%).

Turbidimetric Titration of LAS. Figure 2 shows a titration curve for LAS (50 ml of 2×10^{-4} N) titrated with polysoap solution (1×10^{-3} N). The turbidity measured at 420 nm increases gradually with the progress of titration. Near the end-point the transmittance decreases abruptly. The end-point was determined by the point where the reaction between polysoap and LAS finishes completely and the transmittance becomes zero. The titration curve is reproducible. The titration speed is 0.55 ml min^{-1} until point (a) in Fig. 2, and subsequently, 0.37 ml min^{-1}. When the titration speed is faster than 0.37 ml min^{-1} near the end-point, the results are not reproducible since the rate of reaction between polysoap and LAS is slow. When the concentration of LAS is above 2.5×10^{-3} N LAS, the wavelength 680 nm is preferable.

The titration results at various pH values are shown in Fig. 3. A constant value was obtained in the pH range 4.5—10.5. For determination of the purity of LAS,

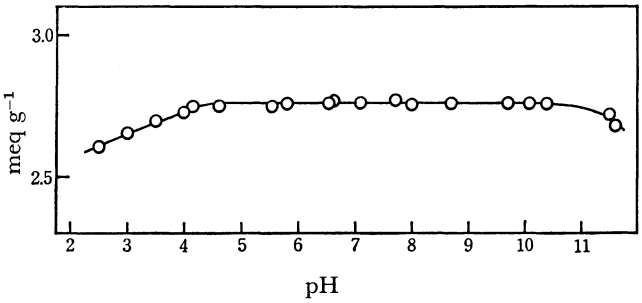

Fig. 3. Coloid titration results of LAS. Titrant: 1×10^{-3} N polysoap. Titrating solution: 2×10^{-4} N LAS.

the LAS solution can be used as it is because of its neutrality. Titration values of the standard LAS solution are given in Table 1. The concentration of LAS and polysoap is shown to have an effect on the titration value, when lower than 7.5×10^{-5} and 1.25×10^{-3} N respectively, the results becoming lower than the calculated value. Titration is impossible when the concentration of polysoap and LAS becomes higher than 10^{-2} and 10^{-3} N, respectively, since the solution becomes strongly turbid from the beginning of titration. The concentration of polysoap and LAS should be 2.5×10^{-3} and $1—7.5 \times 10^{-4}$ N, respectively.

Purity of LAS. The purity of samples was determined under the conditions described above with a 2.5×10^{-3} N polysoap solution. The results of the analysis of commercial LAS are given in Table 2. The

Table 2. Determination of the purity of LAS samples

Sample	LAS		Polysoap		LAS purity %
	concentration mg/ml	amount ml	normality $N \times 10^3$	amount ml[a]	
A	88.2/100	10.00	2.402	3.74±0.01	35.3
B_1	432.2/500	10.00	2.434	9.99±0.01	98.0
B_2	89.5/100	10.00	2.402	8.85±0.01	82.8
C	218.8/250	10.00	2.434	8.45±0.02	81.9
D	85.6/100	10.00	2.434	8.23±0.01	81.6
E	91.3/100	10.00	2.434	8.96±0.02	83.2
F	90.6/100	10.00	2.402	9.03±0.01	83.4

a) Average value of three determinations.

purity of Sample A, over twenty years old, was an abnormally low 35.3%. B_1 was an ultra pure reagent (Tokyo Kasei Kogyo Co., Ltd.). The others were of chemical pure grade, the purity being 81—84%.

Other Anionic Surfactants. As described in JIS K 0102-1974, sodium bis(2-ethylhexyl) sulfosuccinate (SSS) is used as a standard substance for the determination of anionic surfactants in water. SSS can also be titrated by the present method. The purity of SSS was found to be 95.7%. This is in line with the value 96.3% confirmed by the Japan Oil Chemists' Society.

On the other hand, the titration values of sodium dodecyl sulfate (LS) varied with the concentration of LS. The titration curve of sodium myristate show no clear end-point. These anionic surfactants can not form stable polyion complexes with polysoap.

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