Two-Phase Mixed Indicator Method for the Determination of Zwitterionic Surfactants

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The two-phase, mixed indicator method for anionic surfactants has been modified and applied to zwitterionic surfactants. The modifications entail: (i) lowering the pH; (ii) adding 95% ethanol, and (iii) increasing the concentration of mixed indicator solution and adjusting the ratio of the indicators. By adjusting one parameter (the amount of 95% ethanol added), the method is applicable to different types of zwitterionic surfactants. Six different surfactants were examined; three were pure materials synthesized and purified in our laboratory, and the remaining three were commercial materials.

The two-phase mixed indicator titration method for the analysis of anionic surfactants was developed by Reid and coworkers (1,2) for the Commission Internationale d'Analyses of the Comité International des Dérivés Tensioactifs (70 Champs Elysees, Paris, France). This method was extended to shorter chain anionics by Li and Rosen (3). The Reid and coworkers two-phase titration method for anionic surfactants is also applicable to cationic surfactants. In addition, other titration methods exist for cationic surfactant determination (4,5). Recently, titration methods for polyoxyethylenated nonionics have been published (6,7). However, no titration technique exists for dilute solutions of zwitterionic surfactants.

In this study, the two-phase mixed indicator method for anionic surfactants (1,2) is modified for use with zwitterionic surfactants. The new method was tested on three pure zwitterionic surfactants and three commercial materials.

EXPERIMENTAL

Materials. Zwitterionic Surfactants: N-dodecyl-N-benzyl-N-methyglycine, $C_{12}H_{25}N^+(CH_2C_6H_5)(CH_3)CH_2COO^-$ (C_{12}BMG), > 98% purity, synthesized in this laboratory (8). 2-Pyridinium tetradecanoate (2PT), $C_{12}H_{25}CH(N^+C_5H_5)COO^-$ (Anal. Found: C, 74.75; H, 10.10; N, 4.56. Calcd: C, 74.71; H, 10.23; N, 4.59), and 2-pyridinium hexadecanoate (2PH), $C_{14}H_{29}CH(N^+C_5H_5)COO^-$ (Anal. Found: C, 75.55; H, 10.22; N, 4.15. Calcd: C, 75.63; H, 10.57; N, 4.20), synthesized in this laboratory (9). Miratraine CDMB, $RN^+(CH_3)_2CH_2COO^-$ (R = "coco" alkyl), average MW = 292, supplied by Miranol Chemical Co., Dayton, New Jersey, and used as received. Monateric LMAB, $RCONHC_3H_6N^+(CH_3)_2CH_2COO^-$ (RCO = "cocoyl"), average MW = 347, and Monalux CAO, $RCONHC_3H_6N^+(CH_3)_2O^-$ (RCO = "cocoyl"), average MW = 307, supplied by Mona Industries Inc., Paterson, New Jersey, and used as received.

Anionic Surfactant: Sodium dodecanesulfonate, $C_{12}H_{25}SO_3^-Na^+$ (Anal. Found: C, 52.99; H, 9.29; S, 11.74. Calcd: C, 52.92; H, 9.25; S, 11.77), purchased from Research Plus, Bayonne, New Jersey.

Indicators: Dimidium bromide (Burroughs Wellcome Co., Ltd., London, England); disulphine blue V (BDH Chemicals Ltd., Poole, England).

Acid Mixed Indicator Solution: Weigh 0.050 g dimidium bromide into a 50-ml beaker and dissolve it in 10-15 ml hot 10% (by volume) ethanol solution. Weigh 0.050 g disulphine blue V into a second 50-ml beaker and dissolve it in 10 ml hot 10% ethanol solution. Add the contents of the second beaker to that of the first and dilute to 25 ml with hot 10% ethanol

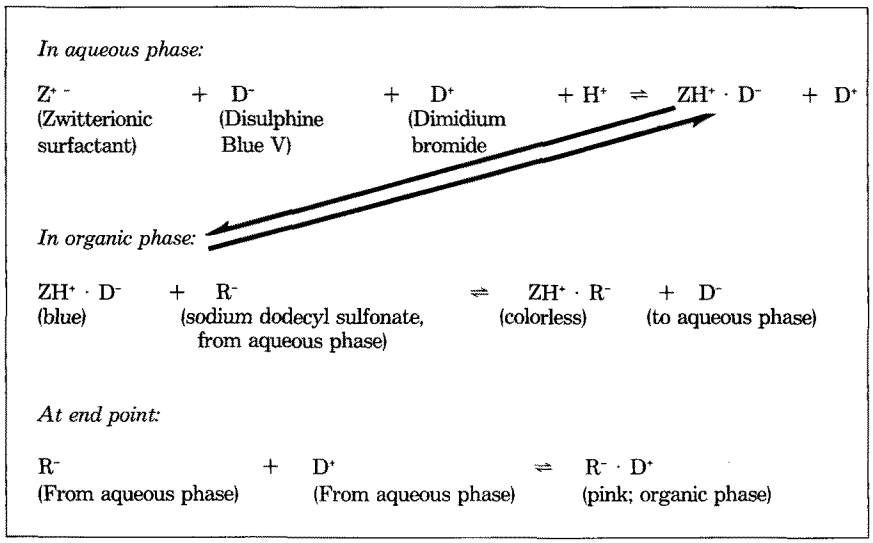

FIG. 1. Equilibria involved in the two-phase, mixed indicator titration method for zwitterionic surfactants.

solution. Transfer this solution to a brown bottle, add 100 ml distilled water, 10 ml 2.5 M H_2SO_4 and then 115 ml more of distilled water.

Analytical method. Ten ml of approximately 1×10^{-3} M zwitterionic surfactant solution was pipetted into a glass-stoppered 125-ml Erlenmeyer flask. To this was added 10 ml acid mixed indicator solution, 15 ml chloroform, 0.235 ml concentrated H_2SO_4, (from a 1-ml pipette graduated in 1/100 ml) and 5.0 ml 95% ethanol. The mixture was then titrated with standardized sodium dodecanesulfonate solution (approximately 1×10^{-3} M) with vigorous shaking after each addition, until the whole chloroform layer was lightly, but distinctly, pink. [The sodium dodecanesulfonate was standardized by titration against an approximately 1×10^{-3} M solution of Hyamine 1622, a cationic surfactant (Rohm and Haas Co., Philadelphia, Pennsylvania) whose concentration was determined by UV absorption (3).] This first titration was used along with the known concentration of the zwitterionic surfactant solution [determined by UV absorption for the purified materials (8,9) or from the manufacturer's value of percent actives for the commercial materials] to determine the proper amount of 95% ethanol to be used for a particular zwitterionic. If the % assay was below 100%, subsequent titrations were performed using more 95% ethanol (a rough guide is that for each additional 0.3 ml of 95% ethanol added, the % assay increases by 1%) until the correct amount of 95% ethanol (accurate to 0.1 ml) necessary to give 100% assay was determined. Care must be taken, however, since it is possible to over-calibrate the method and find more actives than are actually present (i.e. find a percent assay greater than 100%), as Tables 2 and 3 show. If this happens, some 95% ethanol must be removed to bring the percent assay back to 100%. If the percent assay was above 100% for the initial 5.0 ml 95% ethanol titration, subsequent titrations were performed using less 95% ethanol (removal of 0.3 ml of 95% ethanol lowers the % assay by approximately 1%) until the correct amount of 95% ethanol (accurate to 0.1 ml) necessary to give 100% assay was determined. This amount of 95% ethanol was then used for all further determinations of that particular zwitterionic surfactant.

Partitioning of surfactant between aqueous and organic phases. Five ml pure zwitterionic surfactant, 5 ml chloroform and 0.20_5 ml concentrated H_2SO_4 were added to a centrifuge tube. In a second centrifuge tube, 5 ml pure zwitterionic surfactant, 5 ml chloroform, 0.20_5 ml concentrated H_2SO_4 and 1 ml 95% ethanol were added. The mixtures in the tubes were shaken vigorously for 10 min and then allowed to stand in a constant temperature bath at 25 C until the two phases were clear (about 6 hr). Samples of the aqueous phases were analyzed by UV spectroscopy for the surfactant concentrations and the partition coefficients of the surfactant in each system thereby determined.

RESULTS AND DISCUSSION

Preliminary work was done using 5 ml surfactant solution. The following qualitative trends were found: (i) lowering the pH increases the percent assay; (ii) increasing the overall indicator concentration and increasing the amount of disulphine blue V relative to dimidium bromide increases the percent assay, and (iii) increasing the amount of 95% ethanol increases the percent assay.

The first of these trends is explained by looking at Figure 1, which shows the equilibria involved in this titration method. By lowering the pH, the equilibrium in the aqueous phase is shifted to the right (the zwitterionic surfactant is put in cationic form). This shift causes $ZH^+ \cdot D^-$ to form to a greater extent and, by the equilibria shown in the organic phase, causes more R^- to be used before the end point is reached. This results in a higher percent assay.

Increasing the overall indicator concentration and increasing the amount of disulphine blue V to dimidium bromide also shift the equilibrium in the aqueous phase in Figure 1 to the right, increasing the amount of R^- required to reach the end point and, consequently, the percent assay.

The third trend mentioned above is explained by the partitioning of the surfactant into the organic phase. By adding 95% ethanol, the polarity of the organic phase increases and the solubility of the surfactant in the organic phase increases, as is apparent from the data in Table 1. The increased solubility of the surfactant in the organic phase increases the concentration of $ZH^+ \cdot D^-$ there and consequently causes an increase in the percent assay.

Once these trends were determined, the method was extended to larger surfactant solution volumes in order to reduce the percent error inherent in the method. When 20 ml surfactant solution was used, the end point was so dark that it was impossible to see the transition from blue to pink in the orgainc phase. At 10 ml surfactant solution, however, the end point was sharp (1 or 2 drops produced a clearly discernible color change in the organic phase from blue to pink). Therefore, 10 ml surfactant solution was used in all subsequent work.

The results for the pure surfactants are given in Table 2, those for the commercial materials in Table 3. In all these titrations, 0.23_5 ml concentrated H_2SO_4 and 10 ml mixed indicator were used, as described in the analytical method above. The amount of 95% ethanol added was the adjustable parameter used to achieve a 100% assay. However, the range of optimal amount of 95% ethanol runs only from 7.6 ml needed for CAO to 4.2 ml for CMAB. Therefore, it is suggested to begin with 5.0 ml of 95% ethanol and to determine the optimal amount by adding or subtracting 95% ethanol

TABLE 1

Effect of Ethanol on Partitioning of Pure Zwitterionic Surfactants

Surfactant	Partition (coefficient)[a]	
	No added 95% ethanol	1 ml 95% ethanol added
C_{12}BMG	7.43	14.3
2PT	2.46	8.23
2PH	0.668	47.2

[a]Defined as the concentration in the organic phase divided by the concentration in the aqueous phase.

TABLE 2

Effect of 95% Ethanol on Assays of Pure Zwitterionic Surfactants

Surfactant	ml of 95% ethanol	% assay
C_{12}BMG	5.0	98_0
C_{12}BMG	5.9	100_0
C_{12}BMG	6.2	101_3
2PT	4.0	97_3
2PT	5.0	100_2
2PT	5.5	101_1
2PH	5.5	97_1
2PH	6.3	100_2
2PH	6.8	101_4

TABLE 3

Effect of 95% Ethanol on Assay of Commercial Zwitterionic Surfactants (30% active)

Surfactant	ml 95% ethanol	Experimental % actives
LMAB	3.2	29.2
LMAB	4.2	30.1
LMAB	5.8	31.7
CDMB	5.0	27.8
CDMB	6.5	30.1
CDMB	7.3	30.7
CAO	6.0	27.6
CAO	7.6	30.0
CAO	8.0	30.7

(according to the rough guide of 0.3 ml of 95% ethanol to cause a change of 1% in the assay) in subsequent trials. If the initial run gives an assay that is below 100%, more 95% ethanol is needed; if the assay is initially greater than 100%, some 95% ethanol must be removed.

Based on the drop volume of titrant and the error in reading the buret, this method is accurate to approximately $\pm 1_0$% once the optimal amount of 95% ethanol has been determined. A caveat is in order, however, because we noticed that a small amount of long-chain alcohol impurity in the titration makes the percent assay too high. For titrating commercial materials, therefore, a pure compound should not be used for determining the optimal 95% ethanol volume. Rather, a sample of the reaction product should be used for this purpose.

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ERRATUM

Several lines of type were inadvertently omitted from the last paragraph of "Biodegradation and Fish Toxicity of Nonionic Surfactants," written by Koichi Yoshimura and published on pages 1590 through 1596 of the December 1986 issue of the *Journal of the American Oil Chemists' Society*.

The paper should end this way:

. . . Although a quantitative explanation of the fish toxicity in the course of the river die-away test is not possible because of the lack of data of residual Met 1 and 2, the contribution of Met 1 and 2 is inferred to be high. Since 48-hr LC_{50} values of Met 1 and 2 were almost at the same level as intact APE, it is believed that little change in fish toxicity might have occurred within the biodegradation pathway from intact C_9APE_9 to Met 1. Because the fish survival rate attained 100% after 14 days, biodegradation intermediates such as Met 1 and 2 are considered to be further biodegraded (Fig. 2).