On the Relation between Viscosity and Critical Micelle Concentration of Detergent Solutions. III. Relations between Micellar Molecular Weight, Viscosity and Critical Micelle Concentration of Detergent Solutions

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Various methods are proposed for measuring micellar molecular weight (M_m) in detergent solutions; namely, X-ray diffraction[1,2], diffusion[3,4], osmotic coefficent[5] and light scatering[6,7]. Each method has its own characteristic and M_m obtained from various methods are quite different from each other[5]. However, recently, several light scattering investigations were made and accurate M_m values were obtained. This method seems to be the only one that has sure theoretical background.

It is shown in this paper that a kind of empirical relation is established between critical micelle concentration (CMC) and and association number (n) measured by the light scattering method. Using this relation, new empirical equations are proposed which hold between micellar molecular weight (M_m) and two kinds of intrinsic viscosity ($[\eta_1]$ and $[\eta_2]$) proposed in the first paper of this series. Further, some discussions are made concerning the characteristic behavior of viscosity in the range of low concentration of detergent solutions.

Relation between Association Number (n) and Critical Micelle Concentration (CMC)

In Table I are summarized the values of M_m*, association number (n) measured by the light scattering method and CMC (C_c). As both n and C_c are expected to be dependent mainly upon affinity of detergent molecules for solvent, n is plotted against $\log(1/C_c)$. The result is shown

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[1] R. W. Matoon, R. S. Stearns and W. D. Harkins, *J. Chem. Phys.*, **16**, 644 (1948).

[2] D. E. Andersen and G. B. Carpenter, *J. Am. Chem. Soc.*, **75**, 850 (1953).

[3] R. J. Vetter, *J. Phys. Colloid Chem.*, **51**, 262 (1947).

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[5] W. Phillippoff, *Trans. Faraday Soc.*, Discussion, No. 11, 96 (1951).

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* Whether M_m is independent of detergent concentration or not is not clear at present. (K. Sasaki, S. Saito and H. Okuyama, This Bulletin., **29**, 186 (1957)) M_m obtained from light scattering is the value at C_c and so M_m which appears in our discussion also means the one at CMC.

TABLE I

ASSOCIATION NUMBER, MICELLAR MOLECULAR WEIGHT AND CMC

Number	Substance	Temperature	Solvent	n	M_m	$C_c\times 10^3$ (mol./l.)	Literature
1	Na-Octane-sulfonate	23	water	25.4	5500	155	8)
2	Na-Decane-sulfonate	30	water	40	9900	38	〃
3	Na-Dodecane-sulfonate	40	water	54	14700	11	〃
4	Na-Tetradecane-sulfonate	60	water	80	24000	3.3	〃
5	Na-Decyl-sulfate	23	water	50	13000	31	〃
6	Na-Dodecyl-sulfate	23	water	71	20500	8	〃
7	Na-Tetradecyl-sulfate	23	0.01 M NaCl	138	43500	1.9	〃
8	Dodecyl trimethyl ammonium-Br	23	water	50	15400	14.4	〃
9	Dodecyl trimethyl ammonium sulfate	23	water	65	17900	16.6	〃
10	Mg-Octane-sulfate	23	water	51	10400	110	〃
11	Mg-Decane-sulfate	60	water	103	24000	20	〃
12	Mg-Dodecane-sulfate	60	water	107	28500	3.3	〃
13	Didodecyl dimethyl ammonium-Cl	60	0.003 M NaCl	206	43000	0.1	〃
14	Triton X-100	—	water	139	90000	0.9	9)
15	Dodecylamine-HCl	—	water	59	12300	14.0	6)
16	Dodecylamine-HCl	—	0.016 M NaCl	99	20500	11.6	〃
17	Dodecylamine-HCl	—	0.046 M NaCl	152	31400	8.2	〃
18	Decyl trimethyl ammonium-Br	—	water	36	10080	70	〃
19	Decyl trimethyl ammonium-Br	—	0.013 M KBr	38	10600	67.2	〃
20	Dodecyl trimethyl ammonium-Br	—	water	50	15400	15.1	〃
21	Dodecyl trimethyl ammonium-Br	—	0.013 M KBr	56	17200	10.5	〃
22	Tetradecyl trimethyl ammonium-Br	—	water	75	25200	3.4	〃
23	Tetradecyl trimethyl ammonium-Br	—	0.013 M KBr	95	31900	1.76	〃
24	Hexadecyl trimethyl ammonium-Br	—	0.013 M KBr	170	61700	—	〃

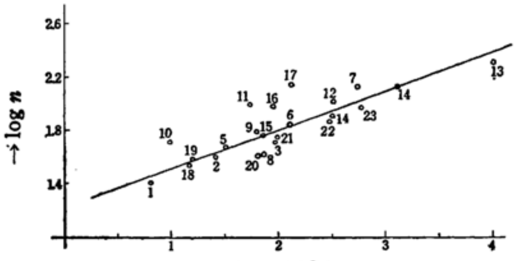

Fig. 1. Relation between log n and log $(1/C_c)$.

in Fig. 1. In this case it is necessary to use mol./l. as unit of CMC. The number in the figure corresponds to that of Table I.

1) A linear relationship between n and log $(1/C_c)$ approximately holds, independent of the presence of added electrolytes.

2) The linear relationship between n and log $(1/C_c)$ is especially satisfactory in the case where the counter ion is univalent, independent of the sign of charge of the detergent ion, with the exception of No. 16 and 17. That relation does not seem to hold when the counter ion is bivalent. (e. g., No. 10, 11, 12)

3) A definite conclusion can not be given as to non-ionic detergent because of the lack of available data. But, Triton-100 (No. 14) follows the linear relationship satisfactorily. When M_m instead of n is plotted against log $(1/C_c)$, deviation is quite large. The fact that the linear relation holds only for n vs. C_c plot and not for M_m vs. C_c one, seems to show that the direct measure of interaction between detergent molecules and solvent is not M_m but n.

The micelle formation of non-ionic detergent is different from that of ionic detergent in many respects. Especially, CMC is not clear because of polymolecularity of the monomer. Therefore, the linear relationship observed in the case of ionic detergent may not always be applicable to non-ionic detergent[10,11]. Further investigation is necessary in order to clarify the applicability of a similar relation to non-ionic detergent.

4) The linear relationship between n

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8) H. V. Tartar and A. L. M. LeLong, *J. Phys. Chem.*, **59**, 1185 (1955).

9) L. M. Kushner and W. D. Hubbard, ibid., **58**, 1163 (1954).

10) R. Goto, N. Koizumi, N. Hayama and T. Sugano, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **74**, 994 (1953) (in Japanese).

11) S. Kuroiwa, K. Shimizu and Y. Yano, *J. Chem. Soc. Japan., Ind. Chem. Sec.* (*Kogyo Kagaku Zassi*), **58**, 859 (1956) (in Japanese).

and $\log(1/C_c)$ is satisfactorily expressed by the following equation.

$$n=\beta_1\times(1/C_c)^{\alpha_1} \qquad (1)$$

where $\alpha_1=0.29$, $\beta_1=17.0$

The Eq. (1) is shown graphically in Fig. 1. Approximate values of n and M_m can be obtained from C_c using Eq. (1).

5) It is well known that a linear relationship holds between $\log C_c$ and the number of carbon atoms (N) in a hydrogen chain of a detergent molecule for each homologue[12,13]. Namely,

$$\log C_c=-\alpha_2 N+\beta_2 \qquad (2)$$

where α_2, β_2 are characteristic constants for a given homologue.

As seen in Eqs. (1) and (2), a linear relationship may hold between $\log n$ and N for each homologue. Fig. 2 shows a relation between $\log n$ and N. A linear relationship between them is clear from the figure. That is,

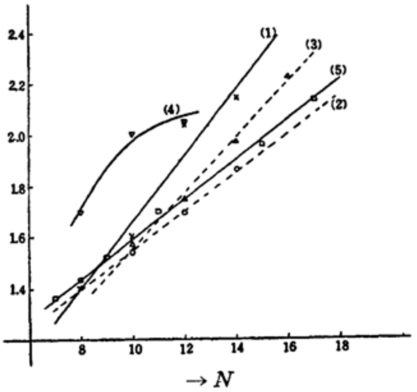

Fig. 1. Relation between $\log n$ and N.
- (1) Na-alkylsulfonate in water[8]
- (2) Alkyl trimethyl ammonium bromide in water[6]
- (3) Alkyl trimethyl ammonium bromide in 0.0130 M KBr[6]
- (4) Mg-alkylsulfonate in water[8]
- (5) Na-alkyl carboxylate in water*

$$\log n=-\alpha_3 N+\beta_3 \qquad (3)$$

where $\alpha_3=0.29\alpha_2$, $\beta_3=17.0-0.29\beta_2$. It can be noted that α_1 and β_1 in Eq. (1) are common constants for all homologues, on the contrary that α_2, α_3, β_2 and β_3 in Eq. (2) and (3) are characteristic constants for each homologue.

6) Several theoretical approaches have been made concerning CMC[6,14], but a satisfactory result has not been obtained yet. CMC can be given by Eq. (4), according to Ooshika's recent treatment[15].

$$kT\log C_c=Z\sqrt{w_e w_s}-w_m \qquad (4)$$

where w_e, w_s and w_m are constants for each detergent, and are related with Coulombic repulsive energy, van der Waals' attractive energy and surface energy, respectively.

However, as the relation w_e, w_s, w_m and n is not clear, Eq. (1) can not be derived from Eq. (4). Recently, Hutchinson et al.[16] regarded micelle formation as phase change and obtained Eq. (5) using Clausius-Clapeyron relation.

$$\log C_c=-H_m/RT+A \qquad (5)$$

where A and H_m are constants and H_m is the heat of micelle formation.

Therefore, an equation similar to Eq. (1) could be obtained, if H_m were linearly related with $\log n$. However, log CMC vs. $1/T$ is not linear even in a narrow range of temperature but generally convex upwards[17], and Eq. (5) can not be applied satisfactorily. Theoretical explanation of general empirical equation (1) should be made in future.

Relation between Micellar Molecular Weight (M_m) and Intrinsic Viscosity

A simple method for determining C_c from solution viscosity was proposed by the present author[18]. This method was also confirmed to be applicable to non-ionic detergent, recently[10,11,19].

Moreover, the authors presumed the possibility of the existence of some relationships between M_m and two kinds of intrinsic viscosity, $[\eta_1]$ and $[\eta_2]$ determined from solution viscosity[18]. Now it is possible to compute the approximate value of M_m from C^o using Eq. (1). Therefore, the above relationships can be tested.

According to the first paper of this series, $[\eta_1]$ and $[\eta_2]$ are defined by the following equations,

$$\eta^0_{sp}/C^0=\frac{(\eta_r/\eta_{r\ \mathrm{min}})-1}{C-C_1} \qquad (6)$$

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[12] H. B. Klevens, *J. Phys. Colloid Chem.*, **52**, 130 (1948).

[13] M. E. L. McBain and E. Hutchinson, "Solubilization" Academic Press Inc., New York, p. 40 (1955).

* calculated from CMC using Eq. (1)

[14] M. Nakagaki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **72**, 113 (1950); **73**, 801 (1951) (in Japanese).

[15] Y. Ooshika, *J. Colloid Sci.*, **9**, 254 (1954).

[16] E. Hutchinson et al., *Z. phys. Chem.*, Neue Folge **5**, 450 (1955).

[17] Ref. No. 12) may be refered for temperature variation of CMC.

[18] N. Sata and K. Tyuzyo, This Bulletin, **26**, 177, (1953).

[19] H. Okuyama and K. Tyuzyo, ibid., **27**, 259 (1954).

TABLE

INTRINSIC VISCOSITY AND

Number	Substance	Temperature	$[\eta_1]$	$[\eta_2]$	$C_c\times10^3$ (mol./l.)
1	Na-Caprylate	20	0.65	0.87	360
2	Na-Nonylate	20	0.81	1.28	220
3	Na-Caprate	20	1.19	—	100
4	K-Caprate	20	0.87	—	100
5	Na-Laurate	20	1.18	(2.2)	25
6	K-Laurate	20	—	2.6	20
7	K-Myristate	20	—	3.3	8
8	Na-Palmitate	60	—	2.0	3
9	Na-Stearate	60	—	2.5	0.8
10	Na-Dodecyl-sulfate	40	2.23	2.65	10
11	Na-Dodecyl-sulfate	70	1.94	2.57	12
12	Dodecylamine hydrochloride	20	1.08	2.0	13
13	Dodecylamine-hydrochloride	30	1.05	1.9	13
14	Na-Oleate	20	1.35	3.81	1
15	Aerosol MA	25	1.73	1.84	27
16	Hexanolamine-caprylate	25	1.13	—	260
17	Emasol 1112	30	2.59	5.17	3.5
18	Emasol 1115	30	1.00	5.20	3.0
19	Emasol 1120	30	—	6.71	6.2
20	Emosol 1130	30	—	9.13	3.1
21	Emulgen 120	30	—	7.25	2.9

(1) Literature 18) may be refered for $[\eta_1]$, $[\eta_2]$ of No. 1~No. 16.

(2) Literature 19) may be refered for $[\eta_1]$, $[\eta_2]$ of No. 17~No. 21.

$$[\eta_1]=\lim_{C^0\to0}(\eta_{sp}{}^0/C^0) \tag{7}$$

$$[\eta_2]=\lim_{C^0\to C^0{}_2}(\eta^0{}_{sp}/C^0) \tag{8}$$

were C_c is CMC and η_r is relative viscosity at CMC. They are shown in Fig. 3. The unit of concentration should neither be weight per cent. nor volume per cent. but mol./l.

In Table II are shown $[\eta_1]$, $[\eta_2]$ obtained by the above method, n and M_m being computed from Eq. (1), $n[\eta_1]$ and $n[\eta_2]$.

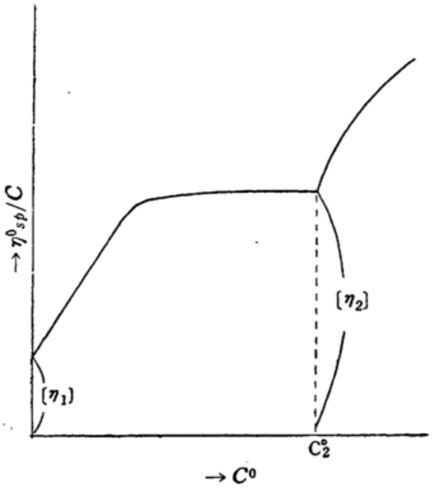

Fig. 3. Determination of C_2, $[\eta_1]$ and $[\eta_2]$.

When M_m is plotted against $[\eta_1]$ and $[\eta_2]$, definite relations can not be found but when M_m is plotted against $n[\eta_1]$ and $n[\eta_2]$, smooth curves can be obtained, regardless of their cationic, anionic and non-ionic nature*. To multiply $[\eta_1]$ and $[\eta_2]$ with n is equivalent to transform the unit of concentration from mol. of monomer/l. to mol. of micelle/l. Neither $\log M_m$ vs. $n[\eta]$ nor M_m vs. $\log n[\eta]$ is linear, but the following eqations apply between $\log M_m$ and $\log n[\eta]$.

$$\log M_m=0.41\{\log n[\eta_1]\}^2-0.39\{\log n[\eta_1]\}+3.47 \tag{9}$$

$$\log M_m=0.45\{\log n[\eta_2]\}^2-0.91\{\log n[\eta_2]\}+4.04 \tag{10}$$

M_m-value, $M_{m\ \mathrm{calc}}/M_m$ calculated from Eqs. (9) and (10) are shown in Table II. Experimental values and curves expressed by Eqs. (9) and (10) are shown in Fig. 4. Experimental and calculated values coincide fairly well with each other with a few exceptions. Therefore, n and M_m can be calculated from $[\eta_1]$ and $[\eta_2]$, using Eqs. (9) and (10). It is very remarkable that the above relationships are generally applicable, regardless of their cationic, anionic

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* CMC obtained by different methods fluctuates cosiderably in the case of non-ionic detergent. The concentration where η_{sp}/C becomes minimum is adopted as CMC in this paper.

II

MICELLAR MOLECULAR WEIGHT

n	M_m	$n[\eta_1]$	$n[\eta_2]$	M^1_m from $[\eta]$	M^2_m from $[\eta]$	$\frac{M^1_{m\ \text{calc.}}}{M_m}$	$\frac{M^2_{m\ \text{calc}}}{M_m}$
23.2	3900	15.1	22.0	3800	4370	0.97	1.12
26.9	4900	21.8	27.9	4900	4580	1.00	0.94
33.4	6500	39.7	—	7940	—	1.22	—
33.4	7000	29.0	—	6030	—	0.86	—
50	11000	59.0	110	11800	11500	1.07	1.04
53	12600	—	138	—	14500	—	1.15
69	18400	—	228	—	25200	—	1.37
92	25700	—	184	—	20000	—	0.78
135	41400	—	338	—	41700	—	1.01
65	19600	145	172	35500	18200	1.81	0.93
62	18700	120	159	27600	16600	1.48	0.89
60	13300	65	120	12900	12600	0.97	0.95
60	13300	63	114	12600	11750	0.95	0.89
126	38300	170	480	44700	69200	1.17	1.80
49	19000	85	90	17800	9600	0.94	0.50
26	5600	29.4	—	6200	—	1.10	—
89	71800	231	461	69200	64600	0.96	0.90
91	90600	—	473	—	66200	—	0.73
74	90000	—	496	—	74200	—	0.83
91	151000	—	831	—	166000	—	1.10
93	99200	—	674	—	117500	—	1.18

(3) Solvent is water in all cases.

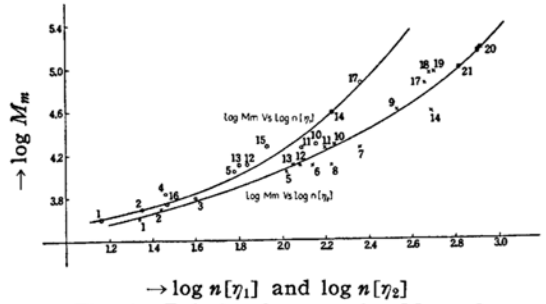

Fig. 4. Relation between log M_m and log $n[\eta_1]$, log $n[\eta_2]$.

and non-ionic nature. $n[\eta]$ is related with the degree of solvation, shape and size of micelle and electro-viscous effect. Theoretical explanationof Eqs. (9) and (10) may be quite difficult, because of uncertainty of the relation between above factors and M_m*.

On the Remarks for the Characteristic Behavior of Viscosity at CMC

We have shown that η_{sp}/C becomes minimum at CMC when η_{sp}/C of the detergent solution is plotted against concentration as is shown in Fig. 5—a and b[18,19]. The complete explanation for this phenomenon has never been performed until now, but it is natural that this is due to adsorption of detergent molecules to the wall of viscometer, if we consider the following terms.

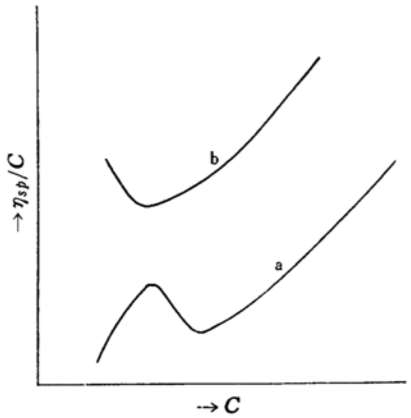

Fig. 5. Dependence of η_{sp}/C on concentration.

1) This phenomenon always appears, for both ionic- and non-ionic detergent. Therefore, it is different from the abnormality of viscosity in dilute solutions of polyelectrolytes which is due to

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* K. J. Mysels[20] discussed charge effect for determining M_m from light scattering, but data are too few and the conc usion can not fundamentlly influence the above results. Therefore, charge effect was neglected in this paper.

20) K. J. Mysels, *J. Colloid Sci.*, **10**, 507 (1955).

the result of electric repulsion and high polymer characteristics.

2) The phenomena are recently often found that η_{sp}/C becomes minimum at some concentration in the case of extremly dilute solutions of non-electrclytic high polymers[21]. It is generally recognized that this phenomenon is due to the result of adsorption of polymer molecules to the wall of viscometer[22].

3) In general, detergent molecules have high adsorbability to the interface as is evident from their nature. Moreover, the action of lowering interfacial tension is especially remarkable in dilute solutions and interfacial tension becomes almost constant, passing through CMC[23]. These phenomena seem to indicate that monomers of a detergent have a great adsorbability but micelles of a detergent have quite small.

Then, it is expected that characteristic minimum of η_{sp}/C at CMC can be explained from the above view-point of adsorption on the wall of viscometer but further details of explanation cannot be given in the present situation.

Summary

1) The following equation is found between association number (n) and critical micelle concentration (C_c in mol./l.) in detergent solutions

$$n=17.0\times(1/C_c)^{0.29}$$

This relation holds, independent of anionic and cationic detergents and added electrolytes.

2) The following equations are found between micellar weight (M_m) and two kinds of intrinsic viscosity ($[\eta_1]$ and $[\eta_2]$) already reported in the previous paper.

$$\log M_m=0.41\{\log n[\eta_1]\}^2-0.39\{\log n[\eta_1]\}+3.47$$

$$\log M_m=0.45\{\log n[\eta_2]\}^2-0.91\{\log n[\eta_2]\}+4.04$$

These relations are applicable, not only to ionic- but also to non-ionic detergents.

3) Discussions are made on the cause of characteristic behavior of viscosity at CMC. This phenomenon seems to be due to adsorption of detergent molcules to the wall of viscometer.

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[22] H. G. Fendler, H. Rohlender and H. A. Stuart, *Makromol. Chem.*, **18/19**, 385 (1956); O. E. Öhrn, *J. Poly. Sci.*, **17**, 137 (1955).

[23] J. Powney and C. C. Addison; *Trans. Faraday Soc.*, **34**, 372 (1938); L. Schedlovsky and L. Ross, Jr., C. W. Jakob, *J. Colloid Sci.*, **4**, 25 (1949).