On the Relation Between Viscosity and Critical Micelle Concentration of Detergent Solutions. II.[1] Viscosity and Diffusion Coefficient of Non-ionic Detergent Solutions[2]

By Haruhiko OKUYAMA and Kiyoshi TYUZYO[3]

(Received November 4, 1953)

Introduction

In the first paper, we proposed the method of determining the first and second critical micelle concentration (CMC) and two kinds of intrinsic viscosity from the analysis of viscosity of various ionic detergent solu-

---

[1] The first paper of this investigation is: N. Sata and K. Tyuzyo, This Bulletin, **26**, 177 (1953).

[2] Presented before the sixth Annual Meeting of the Chem. Soc. of Japan in Kyoto, April, 1953.

[3] Present Address: Research Laboratory, Dai-Nippon Celluloid Co., Ltd., Sakai City, Osaka, Japan.

tions¹⁾. In this paper, the results concerning the aqueous solutions of non-ionic detergents are presented. Namely, not only viscosity of the solutions is measured, but also diffusion coefficient is investigated. This latter method is especially effective in determining CMC and molecular weight of micelle in the present case because this method is remarkably simplified on account of negligible action of diffusion potential in the case of non-ionic detergents, in contrast with ionic detergents⁴⁾.

Samples and Experimental Methods

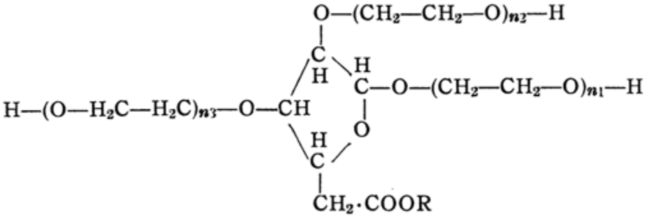
(1) **Samples:** Several kinds of non-ionic detergents (made by Kao-Soap Co. Ltd.) were used. We used series of polyoxyethylene sorbitan (Emasol) and polyoxyethylene-ether (Emulgen). These have such structures as shown below, and the coexistence of hydrophilic group and hydrophobic group in the same molecule causes the surface activity.

Emulgen

$R—O—(CH_2—CH_2—O)_n—H$

R: Alkyl radical

Emasol



R: Alkyl radical

Pure samples of Kao-Soap Co. Ltd. were used. These contain a small quantity of water, metal salt and polyoxyethylene as the impurities. The content of water is less than 1%⁵⁾ and quantity of metal ion is too minute to hinder the measurement of viscosity and diffusion⁶⁾. It was very difficult to remove polyoxyethylene and so we left it as it was.

(2) **Viscosity:** Viscosity was measured by an ordinary Ostwald's viscometer at 30±0.05°C. The falling time of distilled water was 127.14 sec. Each Sample was measured three times and the averaged value was adopted. But, moreover, at lower concentration (below 1%), measurement was performed with freshly prepared solutions for three times, then the averaged value was obtained.

(3) **Partial Specific Volume:** Partial specific volume was determined by Ostwald's picnometer of 5 cc content at 30±0.05°C.

(4) **Diffusion Coefficient:** Diffusion coefficient was measured by the schlieren method using the cylindrical lens as was already shown⁷,⁸⁾. This time, its accuracy was increased by using the improved diffusion cell. The temperature was 25±0.05°C. The diffusion coefficient at each concentration was obtained by the differential diffusion method⁹⁾. The limiting concentration-gradient of our new cell was about 0.3 weight per cent, but we measured it at the concentration-gradient of 0.5~1% considering the requirement of accuracy.

Results

(1) **Partial Specific Volume:** The temperature was 30±0.05°C. Partial specific volume of 1% solution is shown in the Table I.

TABLE I. PARTIAL SPECIFIC VOLUME OF 1% SOLUTION OF NON-IONIC DETERGENT AT 30°C

Substance	ρ (g/cc)	V (cc/g)
Emasol 1112	0.9972	0.849
Emasol 1115	0.9964	0.934
Emasol 1120	0.9966	0.916
Emasol 1130	0.9971	0.864
Emasol 3130	0.9978	0.796
Emulgen 120	0.9964	0.934

(2) **Viscosity:** Fig. 1 shows the relative viscosity-concentration curve of detergents at 30±0.05°C. For Emasol 1120, 1130, and Emulgen 120, the η_{sp}/C vs. C-curve becomes minimum at C_1 as is shown in the Fig. 2, but for others, η_{sp}/C simply increases with concentration.

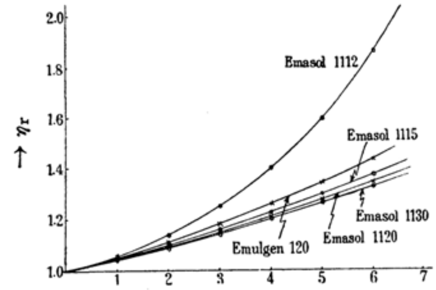


Fig. 1. Dependence of relative viscosity on concentration of several non-ionic detergent solutions.

Now, according to the first paper, the second CMC (C_2) and intrinsic viscosity ($[\eta_1]$,

---

4) G. S. Hartley and C. Robinson, *Proc. Roy. Soc.*, **A134**, 20 (1931).

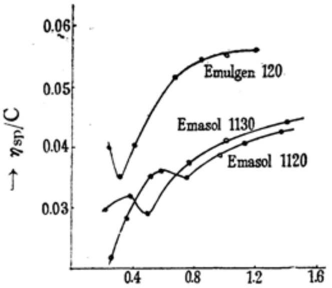
5) Results of the analysis of water content by Mr. R. Muneyuki of Shionogi-Seiyaku Co., Ltd., were as follows:
Emasol 1112,1.9; Emasol 1115,3.26; Emasol 1120,0.6; Emasol 1130,0.7; Emulgen 120,19.4 mg./g.

6) Results of the measured electric conductivity of several aqueous solutions were as follows:
Emasol 1112, specific electric conductivity of
1% aqueous solution $=6\times10^{-5}$
3% aqueous solution $=2\times10^{-4}$
Emulgen 120, 3% aqueous solution $=2\times10^{-4}$
Potassium chloride 2/10000 N aqueous solution $=2\times10^{-5}$
1/1000 N aqueous solution $=1.5\times10^{-4}$

7) O. Lamm, *Nova Acta Regiae Soc. Scien. Upsal.* IV, **10**, No. 6 (1937); J. S. L. Phillipot, *Nature*, **141** 283 (1938).

8) N. Sata, H. Okuyama, K. Tyuzyo, *Kolloid-Z.* **121**, 46 (1951).

9) L. G. Longsworth, *J. Amer. Chem. Soc.*, **69**, 2510 (1947).



→ C (in wt %)

Fig. 2. Relation between η_{sp}/C and C of Emasol 1120, 1130 and Emulgen 120.

$[\eta_2]$) are obtained from the Fig. 3 and the following equation. Namely,

$$\eta_{sp}{}^0/C^0=\frac{(\eta_r/\eta_{r\,min})-1}{C-C_1}\quad ....(1)$$

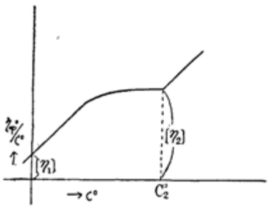


Fig. 3. Determination of C_2, $[\eta_1]$ and $[\eta_2]$.

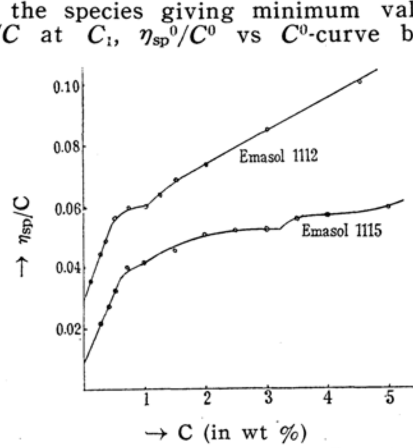
According to the Equation 1, if we replot the curve for $\eta_{sp}{}^0/C_0$ and C^0, Fig. 3 is obtained. From the curve, the values of C_2 $[\eta_1]$, $[\eta_2]$ are gained.

$$[\eta_1]=\lim_{C^{0\to 0}}(\eta_{sp}{}^0/C^0)\ ....(2)$$

$$[\eta_2]=\lim_{C^{0\to C_2{}^0}}(\eta_{sp}{}^0/C^0)\ ....(3)$$

$$C_2=C_1+C_2{}^0\ ....(4)$$

For the species giving no minimum values of η_{sp}/C, the analogous curve as the Fig. 3 is obtained as is shown in the Fig. 4. Therefore C_2 $[\eta_1]$, $[\eta_2]$ values can easily be gained, although C_2 is not so clear as in the case of ionic detergents except Emasol 1112. But, for the species giving minimum values of η_{sp}/C at C_1, $\eta_{sp}{}^0/C^0$ vs C^0-curve becomes minimum at $C^0=1$ (Fig. 5). Therefore, $[\eta_1]$, $[\eta_2]$ cannot be obtained. $C^0{}_2$ is adopted as the concentration where $\eta_{sp}{}^0/C^0$ vs C^0-curve bends. The above results are summarized in the Tab. II. In the Table, C_1 (Dif.) is the concentration where the diffusion coefficient suddenly decreases as will be shown later.



→ C (in wt %)

Fig. 4. Relation between η_{sp}/C and C of Emasol 1112 and Emasol 1115.

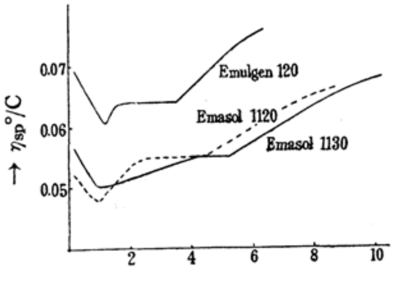


Fig. 5. Relation between $\eta_{sp}{}^0/C^0$ and C° of Emasol 1120, 1130 and Emulgen 120.

TABLE II CMC OF NON-IONIC DETERGENTS

Substance	C_1 (wt %)	C_2	C_1 (Dif.)
Emasol 1112	0～0.3	1.10	0～0.3
Emasol 1115	0～0.3	3.25	0～0.5
Emasol 1120	0.75	5.25	0～2
Emasol 1130	0.50	5.50	0～1
Emasol 3130	0～0.3	1.50	....
Emulgen 120	0.31	3.81	0～1

(3) **Diffusion Coefficient:** In order to examine the accuracy of the diffusion cell, the diffusion of 0.1n potassium chloride solution in water was measured at 20±0.05°C. The diffusion coefficient calculated from the second moment method[10] was 168.4×10^{-7}. This value is satisfactorily consistent with the results of O. Lamm[11] (166.6×10^{-7}) and Cohen, Bruin[12] (167.5×10^{-7}). As the accuracy of our instrument was found quite satisfactory from the above check-experiment, the following experiments were performed.

As the method of determining the diffusion coefficient from the first and second moment is too laborious and moreover very accurate data are not required in our case, the simplest inflection point method was adopted. Namely,

$$D\mu=\mu^2/2t.\,G^2\ ....(5)$$

where μ is the x-coordinate at the inflection point of a diffusion curve.

The results are shown in Fig. 6. Diffusion coefficient extrapolated to the zero concentration ($D_0(30)$) at 30°C, calculated from the following equation:

$$D_{T1}/D_{T2}=\eta_2T_1/\eta_1T_2\ ....(6)$$

where η is the viscosity of solvent, T the absolute temperature provided that the volume of the micelle is independent of temperature, is shown in the Tab. III. It is clear from the Fig. 6 that the diffusion

---

[10] H. Neurath, *Chem. Rev.*, **30**, 357 (1942).

[11] O. Lamm, loc. cit.

[12] Cohen, Bruin, *Z. Phys. Chem.*, **103**, 347 (1923).

TABLE III DIFFUSION COEFFICIENT EXTRAPOLATED TO THE ZERO CONCENTRATION AT 30°C

Substance	Emasol 1112	Emasol 1115	Emasol 1120	Emasol 1130	Emulgen 120
$D_0(30)\times 10^7$	5.92	8.08	8.93	10.1	12.3

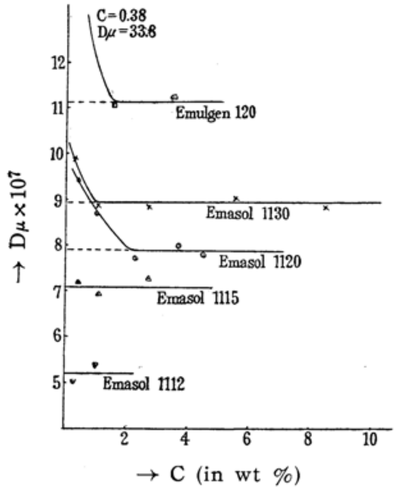


Fig. 6. Dependence of diffusion coefficient on concentration.

coefficient suddenly increases at low concentration for Emasol 1120, 1130, and Emulgen 120, but not for Emasol 1112, and 1115. Moreover, above a certain concentration, the diffusion coefficient is constant and independent of concentration. The concentration region where the diffusion coefficient suddenly increases is shown in the fourth column of Tab. II.

In the next place, the influence of electrolyte on the diffusion was examined. The addition of electrolyte to the aqueous solution of ionic detergent results in the decrease of the diffusion potential and at the same time, in the increase of the micelle size. Therefore, as a result, the diffusion coefficient decreases remarkably. But, for the aqueous solution of non-ionic detergents, the diffusion potential is small and the interaction between electrolyte and hydrophilic group is not so strong as in the case of ionic detergents. Therefore it may be supposed that the influence of electrolyte on diffusion is not so striking as in the case of ionic detergents.

TABLE IV

INFLUENCE OF ELECTROLYTE ON THE DIFFUSION OF NON-IONIC DETERGENT: EMASOL 1112, 1.5 % TO 0.75 %

KCI concentration (mol/1)	$D\mu\times 10^7$
0	5.20
0.005	4.90
0.05	4.66
0.2	2.90
0.4	2.75

The used sample was Emasol 1112 and this sample was dissolved in the potassium chloride solutions of various concentrations. Diffusion of 1.5 % to 0.75 % solution was measured at 25°C. Results are shown in the Tab. IV. It is clear from the Table that diffusion coefficients moderately decrease with the increase of electrolyte concentration.

Discussion

(1) It is clear from Tab. II that the concentration at which η_{sp}/C becomes minimum is satisfactorily consistent with the concentration at which the diffusion coefficient suddenly varies. As it is rational that the rapid change of diffusion coefficient is due to the formation of micelle, it can be concluded that the concentration at which η_{sp}/C becomes minimum is CMC even for non-ionic detergents. Therefore the phenomenon that η_{sp}/C becomes minimum at CMC is the common property for both ionic and nonionic detergents and is based not only on the coulombic electrostatic interaction but also on the dipole interaction.

In the next place, it is not clear whether the diffusion coefficient becomes abnormal at C_2 (concentration at which $\eta_{sp}{}^0/C^0$ bends) or not, but at least for Emasol 1130, the diffusion coefficient is constant through C_2 and this fact is different from that of sodium oleate[13].

For Emasol 1112, 1115 (CMC is very low.), $\eta_{sp}{}^0/C^0$ vs C^0-curve is quite analogous to ionic detergents (Fig. 3). On the contrary, Emasol 1120, 1130, and Emulgen 120 show abnormality in the lower concentration region (Fig. 5).

(2) After completion of micelle formation, the diffusion coefficient is constant and independent of concentration. This phenomenon is also found in ionic detergents[14, 15]. It is possible that the concentration dependence of diffusion due to the hydrodynamic and thermodynamic interaction[16] compensates with the volume effect. In this case, the diffusion coefficient is apparently

---

[13] H. Okuyama, S. Saito and K. Tyuzyo, Presented before the 4th Annual Meeting of the Chemical Society of Japan in Tokyo, April, 1951. To be published elsewhere.

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

[15] O. Lamm, *Kolloid-Z.*, **98**, 45 (1942).

[16] S. J. Singer, *J. Chem. Phys.*, **15**, 341 (1947). A. F. Schick and S. J. Singer, *J. Phys. and Colloid Chem.*, **54**, 1028 (1950).

constant in spite of the change of micellar volume. But this possibility is very small and micellar volume may perhaps be constant and independent of concentration.

The region where the diffusion coefficient varies suddenly covers a considerable concentration range. It cannot be concluded from this fact that the process of micelle formation is fairly gradual, because the region where the diffusion coefficient varies suddenly has a moderate width of concentration range even for ionic detergents.

(3) The influence of electrolyte on diffusion is moderately remarkable although not so much as in the case of ionic detergent.17) The diffusion coefficient of Emasol 1112 in 0.4n potassium chloride solution is one-half what it is in pure water. This means that micellar molecular weight (M_m) becomes about eight times as great. Moreover, Emasol 1112 was dissolved in 1n, 2n, 3n, 4n aqueous solutions of potassium chloride in the concentration of 10 % and was allowed to stand still for 24 hours. Then the 1n solution was almost transparent; the turbidity increased with increasing potassium chloride concentration, the 4n solution being very turbid. This behavior corresponds to the so-called "salting out" phenomenon. From this and above results, it is reasonable to consider that increase of micellar volume and salting out are equivalent phenomena in this case. It seems to be probable that with addition of electrolyte, the hydrophilic property of colloidal particles decreases and they combine with each other, increasing in size and finally they precipitate. We think this concept more probable than that the size is constant and its solubility decreases. It seems to be reasonble to classify "salting out" as follows: (a) Particle size is constant and its solubility decreases. (b) Particle size increases with the increase of electrolyte concentration. This difference may be based upon the degree of separation of hydrophilic and hydrophobic radicals in the same molecule.

(4) Assuming the micelle as a sphere, micellar molecular weight is calculated from the following equation18)

$$M_m = \frac{(RT)^3}{162\,\pi^2\eta^3 N_A{}^2 D_0{}^3 V} \quad \cdots\cdots\cdots(7)$$

where D_0 is the diffusion coefficient extrapolated to the zero concentration, V the specific volume of the micelle which may be substituted by the partial specific volume. Results are shown in Tab. V. These values may have no important meaning, but the values of several ten thousand to hundred thousand suggest that moderately large micelles exist. This corresponds to the fact that CMC is comparatively low and may be based on the weak hydrophilic property of non-ionic detergents compared with ionic detergents.

TABLE V MICELLAR MOLECULAR WEIGHT OF NON-IONIC DETERGENT

Substance	Emasol 1112	Emasol 1115	Emasol 1120	Emasol 1130	Emulgen 120
$D_0\times10^7$	5.9	8.1	8.9	10.1	12.3
$M_m\times10^{-4}$	28.9	10.1	7.8	5.8	3.1

Summary

(1) Partial specific volume, viscosity, diffusion coefficient of the aqueous solutions of non-ionic detergents are measured.

(2) η_{sp}/C becomes minimum at CMC and this concentration is quite consistent with the concentration where diffusion coefficient varies suddenly. It is interesting that this is the common phenomenon for ionic and non-ionic detergents.

(3) The form of $\eta_{sp}{}^0/C^0$ vs C^0-curve is analogous to that described in the first report and the second CMC (C_2) is also obtained but some abnormality occurs in the part of low concentrations for the substance of which CMC is high.

(4) After the completion of micelle formation, diffusion coefficient stays constant and is independent of concentration which suggests that micellar volume is constant and independent of concentration.

(5) The influence of an electrolyte on the diffusion is examined and a new idea of the mechanism of "salting out" is proposed.

(6) Micellar molecular weight is calculated from the diffusion coefficient assuming that a micelle is spherical.

Lastly, we heartily thank Prof. Dr. N. Sata for his kind instruction and Mr. S. Saito for his helpful suggestions. We also express our sincere thanks to Mr. R. Muneyuki of Shionogi-Seiyaku Co. Ltd. who afforded us several valuable samples and data, and Kao-Soap Co. Ltd. for offering some samples.

Department of Chemistry,
Faculty of Science,
Osaka University, Osaka

---

17) H. Okuyama and K. Tyuzyo, Presented before the Colloid Symposium held by the Chem. Soc. of Japan in Tokyo, November, 1951.

18) H. Neurath, loc. cit.