On the Relation between Viscosity and Critical Micelle Concentration of Detergent Solutions*

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(Received August 2, 1952)

Introduction

The viscosity of detergent solutions has been investigated for a long time, but almost all investigations before 1935 were carried out in the region of concentrated solutions owing to the insufficient knowledge about the structure of micelles in this period.(1) Thereafter, there was also no research which dealt with the relation between viscosity and micelle-structure. In 1939, Hess, Philippoff and Kiessig found a method of determining critical micelle concentration (CMC) of soap solutions from their viscosity and measured viscosities of several soap solutions for a wide range of concentration.(2) Although this is a remarkable investigation, it did not yet try to discuss the size and shape of micelle from viscosity data, because the systematic investigation of micelle-structure began gradually at that period.

However, after 1940, new interesting phenomena (e. g., solubilization,(3) spectral dye(4)) were found and several new physical methods (e. g., long spacing X-ray diffraction,(5) light scattering(6)) were applied to the micelle-investigation, so that knowledges concerning micelle increased suddenly. We can remember the

* Part of this paper was presented at the 5th Annual Meeting of the Chemical Society of Japan, April, 1952 in Tokyo.

(1) E. L. Lederer, "Kolloidchemie der Seifen" 1932, S. 141.

(2) K. Hess, W. Philippoff and H. Kiessig, *Kolloid-Z.*, **88**, 40 (1939).

(3) J. W. McBain and R. C. Merrill, *Ind. Eng. Chem.*, **34**, 915 (1942).

(4) M. L. Corrin and W. D. Harkins, *J. Am. Chem. Soc.*, **69**, 679 (1947).

(5) W. D. Harkins, R. W. Mattoon and M. L. Corrin, ibid., **68**, 220 (1946).

(6) P. Debye, *J. Colloid Sci.*, **3**, 407 (1948).

discovery of 1st and 2nd CMC, theories of spherical, cylindrical and lamellar micelle, etc.

Therefore it seems necessary to review the existing many viscosity data again, under the light of the new structural theory of micelles.

We want to remark first the superiority of the viscosity-method in comparison with other methods of CMC-determination; secondly describe our new simple method of determining 1st and 2nd CMC from viscosity and finally discuss the relation between molecular weight of micelle and characteristic constants concerning viscosity which we have newly discovered.

Comparison of Variable Methods of Determining CMC

Variable methods have been proposed hitherto for CMC-determination, and it is convenient to classify them as follows. (Table 1) In the 2nd and 3rd column are expressed the possibilities of various methods to determine 1st and 2nd CMC respectively in which positive and negative use is expressed with ⊕ and ⊖. In the 4th column are tabulated the possibilities of giving the information concerning the shape of micelle. The 5th column shows the accuracy of the methods in which many ⊕ signs express higher accuracy. The 6th column shows the degree of the experimental difficulty of the method and also number of ⊕ signs corresponds to its degree. Moreover, methods are classified in (I) and (II) groups before the 1st column. To (I) belong the methods which cause the change of the state of micelle at the measurement and also the change of CMC. (Generally, CMC falls by adding other substances.) (II) contains methods which cause no changes relatively.

Investigating Table 1, it is clear that light scattering is the best, and spectral dye method is the simplest. 2nd CMC can be determined only by diffusion and X-ray method. Moreover, there are a few methods which give some information about the shape of micelle. From all view points, we could conclude that light scattering method is the best among many methods. But this method requires an especially precise experiment under troublesome conditions and is not easy to perform. After all, there is no method which gives 1st and 2nd CMC, shape of micelle and moreover is easy to perform. The new viscosity method which we propose, gives 1st and 2nd CMC and has the possibility of giving the information concerning size of micelle, if very high accuracy is not demanded. That is why we insist upon this new viscosity method as a practical and useful one. (Viscosity method in Table 1 is not ours but that of Hess and others.)

The Method of Determining 1st CMC from Viscosity

Hess, Philippoff and Kiessig were the first who found the method of determining CMC from

Table 1

Methods of Determining CMC

	Method	1st CMC	2nd CMC	Size & Shape of Micelle	Accuracy of Method	Difficulty of Method	Literature
(I)	Solubilization	+	−	−	++	++	(7)
	Spectral Dye	+	−	−	++	+	(4)
	Diffusion	+	+	+	+	+++	(8), (9), (10)
(II)	Osmotic Coefficient	+	−	−	+	++	(11)
	Conductivity	+	−	−	+	++	(12)
	Density	+	−	−	+	+	(9), (13)
	Viscosity	+	−	−	+	+	(2)
	Surface Tension	+	−	−	+	+	(14)
	Light Scattering	+	−	+	+++	+++	(15), (16)
	X-rays	−	+	+	+	+++	(2), (17)
	Membrane Potential	+	−	−	+	++	(18)
	Flow Birefringence	−	−	+	+	+++	(19)

(7) R. S. Stearns, H. Oppenheimer, E. Simon and W. D. Harkins, *J. Chem. Phys.*, **15**, 496 (1947).

(8) G. S. Hartley and D. F. Runnicles, *Proc. Roy. Soc.*, **A168**, 420 (1938).

(9) R. J. Vetter, *J. Phys. Colloid Chem.*, **51**, 262 (1947).

(10) H. Okuyama, S. Saito and K. Tyuzyo, presented at the 4th Year Meeting of the Chemical Society of Japan in Tokyo, 1952.

(11) J. W. McBain and A. P. Brady, *J. Am. Chem. Soc.*, **65**, 2072 (1943).

(12) J. W. McBain, Frontiers in Colloid Chemistry, p. 113 (1951).

(13) K. A. Wright and H. V. Tartar, *J. Am. Chem. Soc.*, **61**, 544 (1939).

(14) A. E. Alexander, *Trans. Faraday Soc.*, **38**, 248 (1942).

(15) P. Debye, *J. Phys. Colloid Chem.*, **53**, 1 (1949).

(16) P. Debye, Ann. N. Y. Acad. Sci., **51**, 575 (1949).

(17) R. W. Mattoon, R. S. Stearns and W. D. Harkins, *J. Chem. Phys.*, **16**, 644 (1948).

(18) C. W. Carr, W. F. Johnston and I. M. Kolthoff, *J. Phys. Colloid Chem.*, **51**, 636 (1947).

(19) H. A. Scheraga and J. K. Backus, *J. Am. Chem. Soc.*, **73**, 5103 (1951).

η_r (relative viscosity) or $1/[\eta]$ ($[\eta]$ is the solpe of η_r vs. C-curve.) We have already discovered that η_{sp}/C_m vs. concentration curve of Potassium-caprate becomes minimum at 1st CMC[10]. (η_{sp}: specific viscosity $=\eta_r-1$, C_m: soap conc. in mol./l.) Further examining the existing data, we found, almost without exceptions, the curve with one maximum and minimum as Fig. 1. Namely, η_{sp}/C_m becomes minimum at some value of C_m, i. e. C_{m1}, and C_{m1} value is somewhat lower than C'_{m1} which is obtained from the knick of η_r, in many cases. Moreover, η_{sp}/C_m becomes maximum in lower part of C_{m1} in many cases. As the examples, we show the data of Dodecylamine-hydrochloride at 20° and 30°C. in Fig. 2[20] and

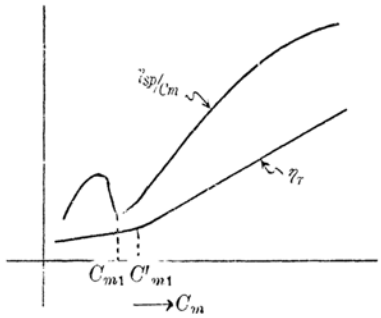


Fig. 1

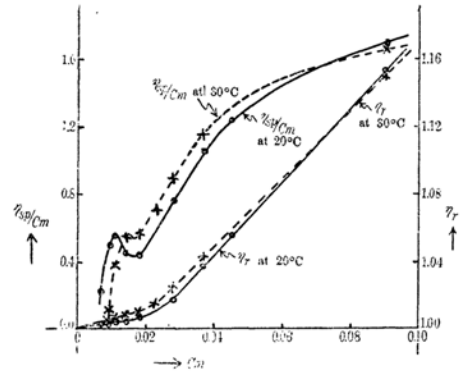


Fig. 2.—Dodecylamine-hydrochloride at 20 and 30°C. (K. Tyûzyô)

Table 2

1st CMC determined by the new Viscosity-Method

Substance	Temp. (°C)	1st CMC(A)	CMC from η_r	C_{m1}	Author	Literature
Na-caprylate	20	—	(0.36)	0.07(E)	Lamm, Högberg (1940)	(21)
Na-nonylate	20	0.22	0.22	0.24	Hess, Philippoff Kiessig (1939)	(2)
Na-caprate	20	0.10	0.12(B)	0.10(B)	Lamm, Högberg (1940)	(21)
K-caprate	20	0.10	0.08(C)	0.07(C)	Okuyama, Tyuzyo Saito (1951)	(10)
Na-laurate	20	0.025	0.096	0.031	Hess, Philippoff Kiessig (1939)	(2)
Dodecylamine-HCl	20	0.0132	0.023	0.015	Tyuzyo (1951)	(20)
	30	0.0132	0.020	0.016	Tyuzyo (1951)	(20)
Na-dodecyl-sulfate	40	0.010	0.012	0.012	Wright, Tartar (1939)	(13)
	70	0.012	0.017	0.014	Wright, Tartar (1939)	(13)
Na-oleate	20	0.001	0.23(D)	—(D)	Hess, Philippoff Kiessig (1939)	(2)
Hexanolamine-caprylate	20	—	0.35	0.26	Gonick (1946)	(22)
Aerosol-MA	25	—	0.029	0.027	Vetter (1947)	(9)

(A) 1st CMC in the 3rd column is the average value derived from the several different methods.

(B) Sodium-caprate has two minimum and the larger one coinsides with 1st CMC.

(C) In Potassium-caprate, CMC from η_r is closer to 0.10 than C_m, but in this case, 0.044 n KOH is added as the swamping electrolyte for diffusion and so CMC must somewhat fall. Therefore, the method of η_{sp}/C_m is not inferior than the one of η_r even in this case.

(D) 1st CMC of Sodium-oleate cannot be determined from viscosity method becaues its value (0.001) is too small. The value (0.23) of Hess and others is very large. Perhaps they mistook 2nd CMC for 1st CMC. (Also see Section 4.)

(E) C_{m1} of Sodium-carylate is too small contrary to expectation.

(F) Sodium-dodecylsulfate has no minimum at 50 and 60°C. It has only a knick at 70°C.

(G) Both Sodium-capronate and Sodium-valeriate have no minimum. It seems probable that there exist no micelles in the studied range of concentration.

(20) K. Tyuzyo, Unpublished.

(21) O. Lamm and H. Högberg, *Kolloid-Z.*, **91**, 10 (1940).

(22) E. Gonick, *J. Am. Chem. Soc.*, **68**, 177 (1946).

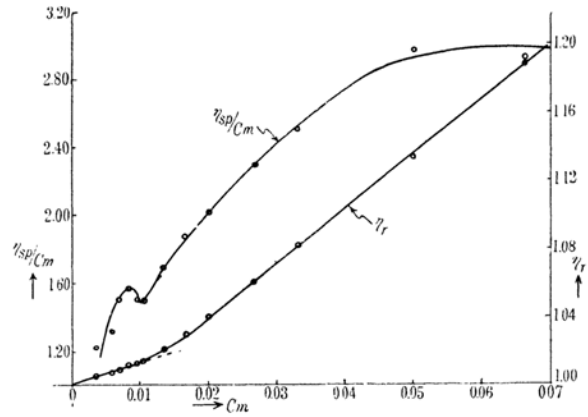


Fig. 3.—Na-dodecylsulfate at 20°C.
(Hess, Philippoff, Kiessig)

Sodium-dodecylsulfate at 20°C. in Fig. 3.[2] All the numerical data are summarized in Table 2. From Tab. 2, we see that the coincidence of C_{m1} and 1st CMC from other methods is satisfactory. Moreover, because C_{m1} corresponds to the distinct "minimum" of η_{sp}/C_m vs. C_m curve, it could be determined more accurately than the rather vague "knick" of η_r.

The Method of Determining 2nd CMC from Viscosity

2nd CMC is defined with the concentration where I-band in X-ray diffraction begins to appear,[17] but almost no other physico-chemical properties are investigated in such a region of high concentration. Only a few abnormalities were found in diffusion measurement.[9][10]

Now, we can presume that above 1st CMC, concentration of detergent monomer in solution which is in equilibrium with micelle is almost constant and unchanged.[16] Accordingly, we make the following operations.

$$C_m^\circ = C_m - C_{m1} \tag{1}$$

$$\eta_{sp}^\circ/C_m^\circ = (\eta_r^\circ - 1)/(C_m - C_{m1}) = (\eta_r/\eta_{r\min})^{-1}/(C_m - C_{m1}) \tag{2}$$

where,

C_m°: detergent concentration defined with equation (1)
C_m: detergent concentration in mol./l.
C_{m1}: 1st CMC derived from above viscosity method
$\eta_{r\min}$: relative viscosity of solution against water at 1st CMC

If we plot $\eta_{sp}^\circ/C_m^\circ$ against C_m°, we obtain the curve as Fig. 4 almost without exceptions.[23] As the examples, we have shown in Fig. 5 and Fig. 6

(23) There are only few data on the viscosity measurement over the wide range of concentration, and so in some cases we connect two independent data.

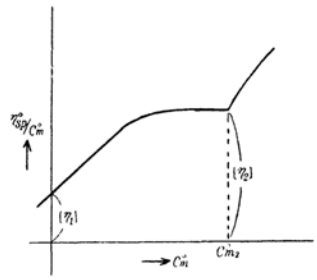


Fig. 4.

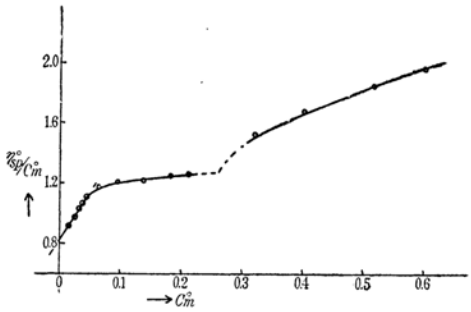


Fig.5.—Na-nonylate at 20°C.
(Hess, Philippoff, Kiessig)

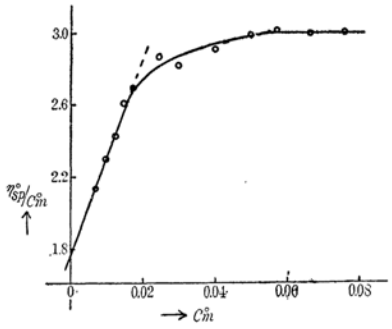


Fig. 6.—Na-dodecylsulfate at 20°C.
(Hess, Philippoff, Kiessig)

the results of sodium-nonylate and sodium-dodecylsulfate.[2] From the figures, we see that $\eta_{sp}^\circ/C_m^\circ$ increases linearly with C_m° as long as C_m° is small and thereafter passing a knick, converges to the constant value, i. e. $[\eta_2]$ in Fig. 4. Then the second and more sharp knick appears when C_m° reaches to some value, i. e. C_{m2}° from where $\eta_{sp}^\circ/C_m^\circ$ increases suddenly again. After all, $[\eta_1]$ and $[\eta_2]$ are defined with the following equations.

$$[\eta_1] = \lim_{C_m^\circ \to 0} (\eta_{sp}^\circ/C_m^\circ) \tag{3}$$

$$[\eta_2] = \lim_{C_m^\circ \to C_{m2}^\circ} (\eta_{sp}^\circ/C_m^\circ) \tag{4}$$

The meaning of $[\eta_1]$ and $[\eta_2]$ will be explained in the next section. Moreover, we have C_{m2} from the next equation.

Table 3

2nd CMC determined by the new Viscosity-Method

Substance	Temp. (°C.)	C_{m2}(*) in wt. %	2nd CMC in wt. %	Method of determining 2nd CMC	Author	Literature
Na-nonylate	20	9~10	—	—	—	—
K-caprate	—	—	22.9	X-rays	Mattoon, Stearns, Harkins (1948)	(17)
K-laurate	20	10.7~13.1	12.20	X-rays	〃 〃 〃	〃
K-myristate	20	8.0~10.7	7.16	X-rays	〃 〃 〃	〃
Na-palmitate	60	5.6~ 6.7	—	—	—	—
Na-stearate	60	3.1~ 3.7	—	—	—	—
Na-dodecyl-sulfate	40	6~9	4~5	X-rays	Hess, Philippoff Kiessig (1939)	(2)
	70	6~9				
Na-oleate	20	4.39	7.2	Viscosity	Hess, Philippoff Kiessig (1939)	(2)
			4~5	X-rays	〃 〃 〃	〃
			5~6	Diffusion	Okuyama, Tyuzyo, Saito (1951)	(10)
Aerosol-MA	25	2.99	4.5	Partial specific Volume	Vetter (1947)	(9)
			2.5	Diffusion	〃	〃

(*) In many cases, $\eta_{sp}^{\circ}/C_m^{\circ}$ vs. C_m° curve gives no sharp knick so that C_{m2} is expressed in an extended range and not a fixed value. For this fact, the method itself is not responsible but the insufficiency of the experimental data is the real reason.

$$C_{m2}=C_{m1}+C_{\mu 2}^{\circ} \qquad (5)$$

In the Table. 3 are shown C_{m2}-values from above method and the existing values of 2nd CMC. It will be understood from the table that our C_{m2} values fairly coincide with 2nd CMC obtained from other methods. This method of determining 2nd CMC seems to be quite satisfactory at the present stage. (The data of X-rays are not quite accurate themselves.)

Table 4

Values of $[\eta_1]$ and $[\eta_2]$

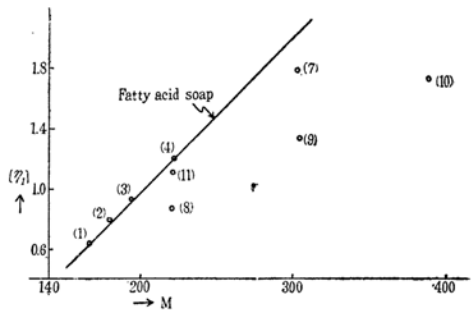
Substance	M	Temp. (°C.)	$[\eta_1]$	$[\eta_2]$
Na-caprylate	166.21	20	0.65	0.87
Na-nonylate	180.23	20	0.81	1.28
Na-caprate	194.25	20	0.67	—
	〃	20	1.19	—
K-caprate	210.35	20	0.87	—
Na-laurate	222.30	20	1.18	(2.2)
K-laurate	238.40	20	—	2.6
K-myristate	266.48	20	—	3.3
Na-Palmitate	278.42	60	—	2.0
Na-stearate	306.48	60	—	2.5
Na-dodecylsulfate	302.37	20	1.78	3.0
		40	2.23	2.65
		70	1.94	2.57
Dodecylamine-HCl	221.80	20	0.88	2.0
		30	0.94	1.9
Na-oleate	304.34	20	1.35	—
		20	—	3.81
Aerosol-MA	388.46	25	1.73	1.84
Hexanolamine-caprylate	221.80	25	1.13	—

The Meaning of $[\eta_1]$ and $[\eta_2]$

We tabulate in Table. 4 $[\eta_1]$ and $[\eta_2]$ values obtained from above method. M in the second column of the table is the molecular weight of the detergent monomer. $[\eta_1]$ would be the related quantity to the micelle molecular weight (M_m) from the analogy of high polymer solutions. But unfortunately, M_m has hardly ever been measured accurately up to this time. And so it is impossible to compare $[\eta_1]$ with M_m directly. Therefore, for convenience, we plotted $[\eta_1]$ and $[\eta_2]$ against M (monomer molecular weight) in Fig. 7 and Fig. 8.

The following facts are recognizable from these figures.

(a) Fatty acid anionic soap series lie almost on the straight line.



(1) Na-caprylate; (2) Na-nonylate; (3) Na-caprate; (4) Na-laurate; (5) K-laurate; (6) K-myristate; (7) Na-dodecyl-sulfate; (8) Dodecylamine-HCl; (9) Na-oleate; (10) Aerosol MA; (11) Hexanolamine-caprylate

Fig. 7.—Relation between $[\eta_1]$ and M.

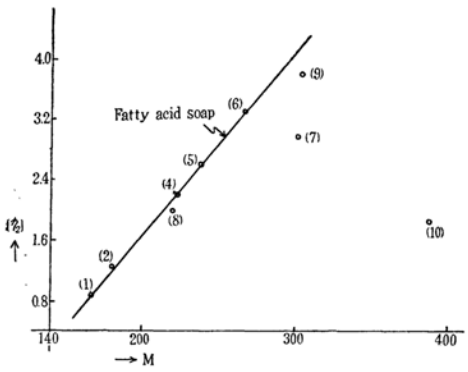


Fig. 8.—Relation between $[\eta_2]$ and M

(b) $[\eta_1]$ of sodium-oleate is exceptionally small, whereas its $[\eta_2]$ is not very small.

(c) $[\eta_1]$ and $[\eta_2]$ of sodium-dodecylsulfate are both abnormally small.

(d) $[\eta_1]$ of dodecylamine-hydrochloride is smaller than that of anionic soap, but $[\eta_2]$ is almost equal.

(e) $[\eta_1]$ and $[\eta_2]$ of aerosol-MA (sodium-methylamyl-sulfosuccinate) are both much smaller than those of ordinary fatty acid soap.

Discussion

(I) The phenomenon that η_{sp}/C_m becomes minimum at C_{m1} (Section 3) may probably be due to the result of the electrostatic interaction, owing to the strong electrolytic character of soap molecules. (η_{sp}/C_m of polyelectrolyte solutions passes generally a minimum value at some concentration.) However, most recently, R. Goto, N. Koizumi and T. Sugano found that η_{sp}/C_m of polyethleneoxide-monoalkylether solutions (nonionic detergent) also reaches a minimum in the neighbourhood of CMC.[24] Therefore, this phenomenon seems to be common to ionic and nonionic detergent which cannot be explained simply with the electrostatic force. We have no adequate explanation for this phenomenon.

(II) It is very particular that $\eta^{\circ}_{sp}/C^{\circ}_m$ converges to $[\eta_2]$. This is a completely different behavior compared with high polymer solutions of which η_{sp}/C_m is proportional to the square of concentration and so increases very rapidly in the region of high concentration. There seem to be three cases.

(i) Micellar size increases with concentration, but its shape does not change.

(ii) Shape changes with increasing concentration, whereas its size stays unchanged.

(iii) Size increases and shape also changes with increasing concentration.

Which of those three possibilities is most reasonable cannot still be decided. The recent investigation of flowbirefringence of detergent solutions[19] seems to be important in order to aquire some information of the micelle size and shape at moderately high concentration. At present, there is no direct means to determine both micellar size and shape simultaniously over wide range of concentration. Our discussion therefore is obliged to be limited to the indirect one. The most effective method, i. e. light scattering, can decide M_m only at low concentration and is not applicable at high concentration. Moreover, in the condition without adding electrolyte, it is impossible to dicide the micelle shape from the assymmetry of the scattered light, because micelle is too small in this condition. On the other hand, X-ray method gives some information of micelle size and shape at high concentration, but cannot be applied to low concentration. With diffusion method, it is necessary to add some swamping electrolyte in the soap solution, nevertheless micelle size is given only under some assumptions concerning hydration. At any rate, for detailed analysis of th above phenomena, many experimental data are still lacking.

(III) It must be remarked that $[\eta_1]$ and $[\eta_2]$ and M (monomer molecular weight) has a linear relation for fatty acid homologue. The fact that sodium-oleate dislocates the linearity could be explained from abnormal physical properties of oleic acid based on its cis-configuration. For example, it has abnormal low meltingpoint (14°C.) and high density (0.895). Aerosol-MA dislocates also, but it is natural if we remember that its micelle is quite different from ordinary soap because its monomer has the hydrophilic group nearly at the center. The difference between cationic and anionic soap micelles may be based upon the difference of the hydrophilic character of their hydrophilic group. The difference between sodiumdodecylsulfate and fatty acid soap is due also to the same cause. If M_m of several detergents are measured accurately by the light scattering, we can expect that the relation such as $[\eta_1]=KM_m^n$ may be concluded from those data.

Summary

(1) Several methods of determining CMC are compared and criticised.

(2) A new method of determining 1st CMC from viscosity is experimentally established.

(24) R. Goto, N. Koizumi and T. Sugano, presented at the 5th Annual Meeting of the Chemical Society of Japan in Tokyo, 1952.

(3) A new method of determining 2nd CMC from viscosity is established by transforming concentration and viscosity in the new variables.

(4) Of each soap, characteristic constants $[\eta_1]$ and $[\eta_2]$ are discovered, and it is shown that a definite relation is concluded between these values and monomer molecular weight.

(5) The theoretical explanation of these newly found phenomena has not yet been made.

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