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Surface Activities of Nonionic Polymeric Surfactants

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The relationship between surface activity and molecular structure has been studied for the nonionic polymeric surfactants which have 2,3,4 or 6 branches of polypropylene glycol-polyethylene glycol (PPG-PEG) chain in their molecules. A linear relation, $1/\Delta\gamma = A + B \cdot x/y$ has been found to hold for each series, where $\Delta\gamma$ is the surface tension depression of surfactant solution of a given concentration from that of water, x/y is the molecular structure index, in which x is the weight percent of PEG group in a molecule and y is the molar weight of PPG part, and A and B are constatns. Constant A, being equal to 0.025 cm/dyn, is independent of the concentration and the number of PPG-PEG branches and corresponds to the reciprocal of surface tension lowering of an aqueous solution of infinitely large PPG polymer. Constant B decreases linearly with the logarithm of molar concentration, and increases with the number of branches. It also depends on the hydrophilic nature of the central group of molecule.

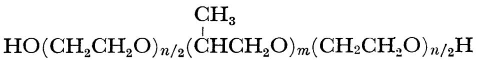
Recently, numerous nonionic surfactants have been prepared for various practical purposes, and the selection of surfactant has become much simpler by application of the HLB system proposed by Griffin.(1) Studies have been made on the relation between the HLB value and the molecular constitution of nonionic surfactants.(2) However, the relation between molecular structure and surface activity is not yet clear.

As regards nonionic surfactants, block copolymer (PPG-PEG) composed of polypropylene glycol (PPG) and polyethylene glycol (PEG) has recently attracted attention in relation to theoretical and practical problems. These surfactants are favorable for studying the relation between molecular structure and surface activity, because a slight difference in nature of the hydrophobic propylene glycol unit (PG) of the PPG group and the hydrophilic ethylene glycol unit (EG) of the PEG group makes a delicate control of surface activity possible by the change of degree of polymerization of PG and EG. In the present study we tried to obtain systematic information on the relation between surface activity and molecular structure for this type of polymer surfactants, from the study of surface tension lowering of the solution.

Experimental

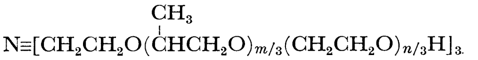
Materials. PPG-PEG type of surfactants employed in the present study are of the following molecular structure:

"Pluronic" m, n (2-branch series)



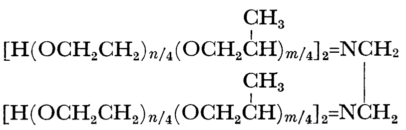
$$HO(CH_2CH_2O)_{n/2}(\overset{CH_3}{\overset{|}{C}}HCH_2O)_m(CH_2CH_2O)_{n/2}H$$

"Trinic" m, n (3-branch series)



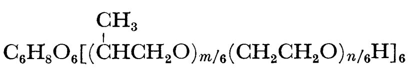
$$N\equiv[CH_2CH_2O(\overset{CH_3}{\overset{|}{C}}HCH_2O)_{m/3}(CH_2CH_2O)_{n/3}H]_3$$

"Tetronic" m, n (4-branch series)



$$\begin{array}{l} [H(OCH_2CH_2)_{n/4}(OCH_2\overset{CH_3}{\overset{|}{C}}H)_{m/4}]_2{=}NCH_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ [H(OCH_2CH_2)_{n/4}(OCH_2\overset{CH_3}{\overset{|}{C}}H)_{m/4}]_2{=}NCH_2 \end{array}$$

"Hexonic" m, n (6-branch series)



$$C_6H_8O_6[(\overset{CH_3}{\overset{|}{C}}HCH_2O)_{m/6}(CH_2CH_2O)_{n/6}H]_6$$

in which m and n are the average degrees of polymerization of PG and EG, respectively. The Pluronic and Tetronic series were obtained from Asahi Denka Industry Co., and the rest from Nihon Surfactant Industry Co. The Trinic, Tetronic and Hexonic series may be regarded as having 3, 4 and 6 branches of PPG-PEG chains of equal average length in respective molecules and the Pluronic series is conventionally seen to have two branches. The Hexonic series is the ether derivative of sorbitol. The surfactants investigated are listed in Table 1.

Polypropylene glycols, glycerine polyoxypropylene ethers and trimethylolpropane polyoxypropylene ethers of molecular weights ranging from 260 to 2500 were used as samples having no hydrophilic PEG group.

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1) W. C. Griffin, *J. Soc. Cosmet. Chem.*, **1**, 311 (1949).

2) W. C. Griffin, *Soap, Sanit. Chem.*, **27**, No. 11, 128 (1951); *Amer. Perfumer*, **65**, No. 5, 26 (1955). J. T. Davies, *Proc. 2nd Intern. Congr. Surface Activity*, **1**, 426 (1957).

TABLE 1. THE POLYPROPYLENE GLYCOL-POLYETHYLENE GLYCOL (PPG-PEG) BLOCK COPOLYMER SURFACTANTS, THEIR MOLECULAR STRUCTURE INDICES (x/y) AND EQUILIBRIUM SURFACE TENSIONS (γ_∞) OF AQUEOUS SOLUTIONS AT 25.8°C

Series	Trade No.	m	n	x/y	γ_∞ (dyn/cm)		
					1×10^{-4} (mol/l)	1×10^{-5} (mol/l)	1×10^{-6} (mol/l)
Pluronic (2-branch)	F-88	40	300	0.0366		47.4	49.1
	F-68	28	210	0.0523	46.7	47.3	50.1
	F-38	16	120	0.0916	51.8	55.8	59.7
	L-64	28	31	0.0164	36.0	39.0	41.0
	L-62	28	13	0.0283	39.3	42.1	47.5
Trinic (3-branch)	20.30	20	30	0.0384	46.0	50.6	54.5
	20.50	20	50	0.0479	46.6	51.4	57.3
	20.100	20	100	0.0589		53.9	51.1
	20.150	20	150	0.0638	49.4	54.6	56.2
	20.190	20	190	0.0661		54.1	59.2
	33.100	33	100	0.0330	45.4	48.0	
	33.150	33	150	0.0369	45.3	49.4	51.5
	50.30	50	30	0.0100	36.1	37.8	41.0
	50.100	50	100	0.0194	40.2	42.9	46.3
	50.150	50	150	0.0224	43.3	45.3	48.1
	50.200	50	200	0.0243	44.3	46.3	49.4
	50.300	50	300	0.0266	46.6	48.9	51.3
Tetronic (4-branch)	304	12	14	0.0641	48.5	50.2	54.1
	501	29	7	0.0086	37.5	39.0	42.3
	504	29	32	0.0263	42.4	44.4	47.0
	508	29	217	0.0498	50.5	52.5	54.0
	701	46	11	0.0054	33.2	34.9	37.3
	702	46	20	0.0091	34.6	36.6	37.9
	707	46	182	0.0277	46.5	48.7	51.1
	904	69	74	0.0111	35.5	36.5	39.3
	908	69	501	0.0211	40.7	46.0	53.0
Hexonic (6-branch)	6000.30	91	30	0.0030			33.6
	6000.60	91	60	0.0051		33.2	34.8
	6000.120	91	120	0.0078	33.3	33.6	36.8

These samples were also obtained from Asahi Denka Industry Co.

In order to remove water and impurities having low boiling points, all the samples had been vacuum dried for about 48 hr until their weights became constant at room temperature. Solutions were prepared immediately after purification.

Aqueous solutions of 1×10^{-4}, 1×10^{-5} and 1×10^{-6} mol/l were made by dissolving the substances in water which had been obtained by refluxing a solution of $KMnO_4$ and NaOH in ion-exchanged water for about 15 hr in a borosilicate glass apparatus and then distilling.

Method. The equilibrium surface tension lowering from pure water was measured and taken as a parameter of surface activity. Since the surface tension of an aqueous surfactant solution of a concentration below the critical micelle concentration usually changes gradually over a long period after the surface is freshly formed,[3] a method should be adopted which allows a continuous measurement over a long period with minimum disturbance of the system under examination. For this purpose, a modified Wilhelmy plate method was used.[4]

The vessel containing the solution was a Petri-dish of 6.5 cm in diameter and 1.5 cm in depth, the edge of which was coated smoothly with paraffin for the purpose of bringing an aqueous surface level higher than the rim of the vessel and for avoiding contamination creeping in from the outer wall.

The solution was introduced into the vessel immediately after preparation. After about 1 hr a fresh surface was formed by sweeping off the surface of the solution in the vessel with a paraffin-coated glass barrier in order to keep the bulk aging effects constant. Surface tension was measured with time about 1 min after the sweep of the aqueous surface. Throughout the measurement, the temperature was controlled to 25.8±0.2°C in an air thermostat, which also served to prevent evaporation.

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3) G. C. Nutting, F. A. Long and W. D. Harkins, *J. Amer. Chem. Soc.*, **62**, 1496 (1940). K. L. Sutherland, *Aust. J. Chem.*, **12**, 1 (1959).

4) M. Nakamura and T. Sasaki, *J. Sci. Instrum.*, **44**, 855 (1967).

Results and Discussion

It was confirmed that for all surfactant solutions the surface tension generally decreases with time and does not attain an equilibrium value even 120 min after the formation of a fresh surface, as illustrated by Tetronic 46, 20 in Fig. 1. Concerning the time dependence of surface tension of surfactant solution, some empirical relations have been reported: Lange[5] used the equation

$$\gamma = \gamma_0 - (\gamma_0 - \gamma_\infty)/(b/t^{1/2} - 1) \qquad (1)$$

and Boutaric and Berthier[6]

$$\gamma = \gamma_\infty + (\gamma_0 - \gamma_\infty)e^{-\alpha t}. \qquad (2)$$

The present authors propose another equation of the following type

$$\gamma = \gamma_\infty + a/t - b/t^2. \qquad (3)$$

In the above three equations, γ and γ_∞ are the surface tension of a solution at time t and at equilibrium respectively, γ_0 that of the solvent, and a, b and α are constants. To evaluate γ_∞, Eq. (3) is transformed into

$$t \cdot \frac{d\gamma}{dt} + 2\gamma = 2\gamma_\infty + a/t \qquad (4)$$

and $t \cdot d\gamma/dt + 2\gamma$ is plotted against $1/t$, $t \cdot d\gamma/dt$ being graphically obtained from the $\gamma - t$ plot. The extrapolated value of $t \cdot d\gamma/dt + 2\gamma$ at $1/t = 0$ gives $2\gamma_\infty$ as Fig. 2 shows. Table 1 shows γ_∞, the values thus obtained for the surfactants studied. The value $\Delta\gamma = \gamma_0 - \gamma_\infty$ is taken as a measure of surface activity, where $\gamma_0 = 71.8$ dyn/cm is the surface tension of water at 25.8°C. A linear relationship is found to hold between the reciprocal of $\Delta\gamma$ for each concentration and the molecular structure index x/y, as shown in Fig. 3, where x is the weight percent of hydrophilic PEG group in the molecule and y is the molar weight of PPG part. This plot is well expressed by

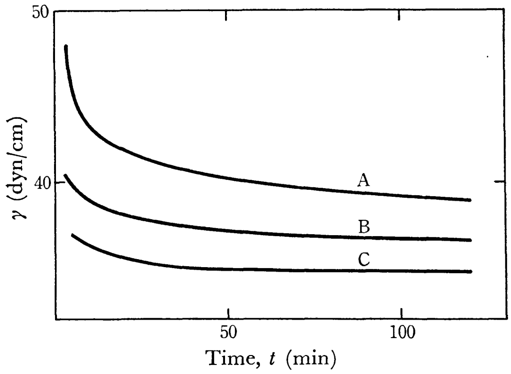

Fig. 1. Surface tension (γ) of the aqueous solutions of Tetronic 46, 20.
Concentration: A, 1×10^{-6}; B, 1×10^{-5}; C, 1×10^{-4} mol/l

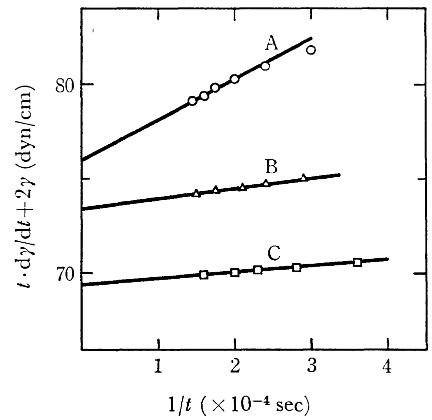

Fig. 2. $t \cdot d\gamma/dt + 2\gamma$ *vs.* $1/t$ plot for Tetronic 46, 20.
Concentration: A, 1×10^{-6}; B, 1×10^{-5}; C, 1×10^{-4} mol/l

$$1/\Delta\gamma = A + B \cdot x/y, \qquad (5)$$

where A and B are constants. In Fig. 3, plots scatter in the region of large values of $1/\Delta\gamma$ due to the small values of $\Delta\gamma$ observed. Constant A which is equal to 0.025 cm/dyn turned out to be independent of the concentration and the number of PPG-PEG branches. It depends only on the nature of hydrophobic group in a polymer chain, in this case PPG, as will be mentioned later. The value B was found to depend on both the concentration and the number of PPG-PEG branches.

Constant B, when compared at the same concentration, is indistinguishable with respect to 3- and 4-branch series, while the value for 2-branch series is slightly smaller than the value for 3- and 4-branch series. Further it was found that B decreases linearly with the logarithm of concentration C for 2-, 3- and 4-branch series as shown in Fig. 4. Thus we obtain the relations

$$B = -1.1 \log C - 0.41 \qquad (6)$$

for 2-branch series and

$$B = -1.3 \log C - 0.45 \qquad (7)$$

for 3- and 4-branch series, where C is expressed in mol/l. By substituting Eqs. (6) and (7) into Eq. (5), the surface tension lowering $\Delta\gamma$ can be expressed as a function of the structure index x/y and the concentration C for these series: The relation for 2-branch series is

$$1/\Delta\gamma = 0.025 - (1.1 \log C + 0.41)x/y \qquad (8)$$

and that for 3- and 4-branch series is

$$1/\Delta\gamma = 0.025 - (1.3 \log C + 0.45)x/y \qquad (9)$$

In these equations $\Delta\gamma$ can be taken as the measure of surface activity, at a given concentration C.

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5) H. Lange, *Proc. 3rd Intern. Congr. Surface Activity*, **1**, 279 (1960).

6) A. Boutaric and P. Berthier, *J. Chim. Phys.*, **36**, 1 (1939).

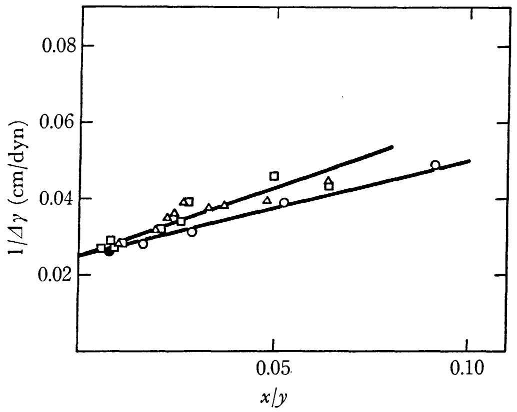

Fig. 3(a)

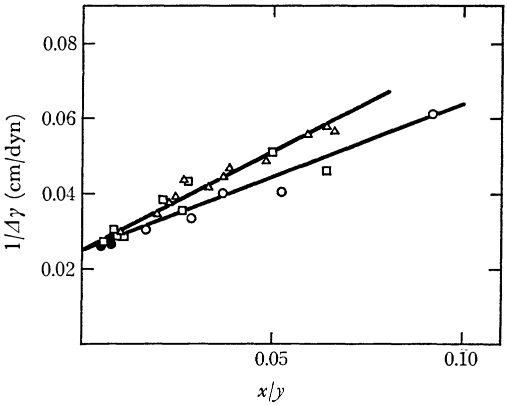

Fig. 3(b)

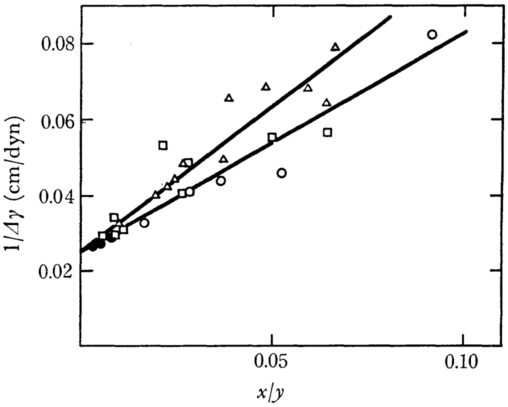

Fig. 3(c)

Fig. 3. Surface tension lowering ($\Delta\gamma$) *vs.* molecular structure index (x/y) plot for Pluronic (○), Trinic (△), Tetronic (□) and Hexonic (●) (2-, 3-, 4- and 6-branch) series.

Concentration: (a), 1×10^{-4}; (b), 1×10^{-5}; (c), 1×10^{-6} mol/l

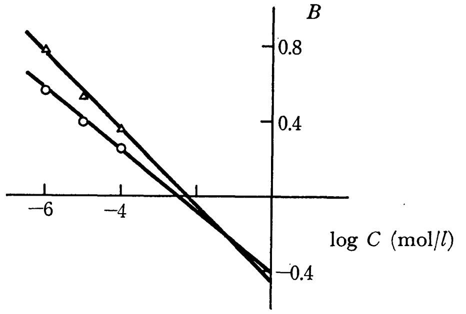

Fig. 4. Constant B *vs.* concentration C plot for Tetronic (4-branch), Trinic (3-branch) (both △) and Pluronic (2-branch) (○) series.

As to 6-branch series, since all samples employed are those of small values of the molecular structure index x/y, it is difficult to confirm the applicability of Eq. (5) and to obtain the exact values of constant B. But the value $1/\Delta\gamma$ is seen to approach 0.025 cm/dyn, the value of constant A in Eq. (5),with the decrease of x/y for the substance of this series.

Constant A should correspond to $1/\Delta\gamma$ for a polymer having no hydrophilic PEG group or having PEG groups with hydrophobic PPG groups of infinitely high molecular weight. The surface activity of PPG is considered to depend on molecular weight, since the surface tension of aqueous PPG solution has been reported to depend on the molecular weight.[7] To study further details of the constants A and B, the surface tensions of polypropylene glycol (PPG) series, glycerine polyoxypropylene ether (GP) series, and trimethylolpropane polyoxypropylene ether (TP) series, as the samples having no PEG groups, were measured under the same conditions as for the above surfactants. The relation between the surface tension lowering $\Delta\gamma$ thus obtained and the molar weight y of PPG or PPG part of the molecule for each series is shown in Fig. 5. No distinction is seen between the surface activity of PPG

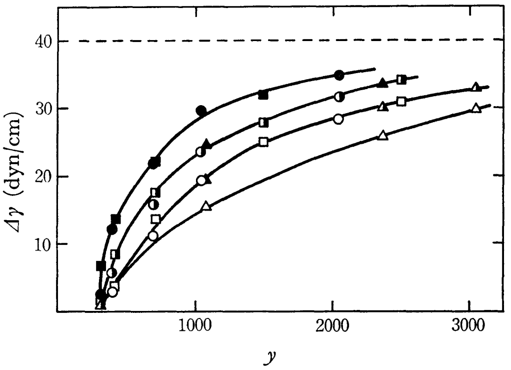

Fig. 5. Surface tension lowering ($\Delta\gamma$) *vs.* molar weight (y) plot.

	1×10^{-4}	1×10^{-5}	1×10^{-6} mol/l
PPG	●	◑	○
GP	▲	◭	△
TP	■	◨	□

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[7] Y. Nemoto, H. Funahashi, K. Kunugi and M. Kashima, *Yukagaku*, **14**, 246 (1965).

and TP series and the less surface activity of GP series, where the surface tension of GP is equal to that of the PPG or TP solution of the concentration, being about one tenth of the GP solution.

The fact that the GP series is less surface active than the TP series shows some other factors than those mentioned above affecting surface activity. It is evident that these two series differ only in the central group of their molecules. Therefore it may be presumed that the surface activity of polymeric surfactant is also affected by the nature of its central group to which polymer branches are attached. It is conceivable that glycerine is more hydrophilic than trimethylolpropane so that GP is less surface active then TP. The fact that the plots of PPG and TP series, differing in the number of branches, fall on the same curve suggests the effect of central groups on the surface activity. Thus, it may be concluded that the surface activity decreases with either the increase of branching or the degree of hydrophile of the central group.

It is seen in Fig. 5 that when the molecular weight increases towards infinity, the surface tension lowering is seen to approach a constant value (broken line in Fig. 5), 40 dyn/cm, for each curve; the value taken to be equal to $1/A$ in Eq. (5). This may indicate the constant A being independent of the value of x under the condition of $y=\infty$, and it can naturally be concluded that Eq. (5) can not be applied exactly if the value y is too small; a small value of y might give a larger value of A, as presumed from Fig. 5.

From the results of the above PPG polymers and their ethers it may be quite reasonable to consider that the difference of B in Eqs. (6) and (7) depends not only on the number of branches as was mentioned in the earlier section but also on the nature of the central groups. The fact that both the molecules of 3- and 4-branch series tend to ionize to a certain extent, while 2-branch series has no such ionizing nitrogen atom, can be taken at least as the cause of the difference in surface activity. The fact that 3- and 4-branch series show a similar surface activity (Eq. (9)) in spite of the difference in branching suggests a more hydrophobic nature of the central group of the latter series, since the increase in number of branches from 3 to 4 should be balanced with the stronger hydrophobic nature of the central group of the latter in order to keep the same surface activity.

In conclusion, the surface activities of the nonionic polymeric surfactants of PPG-PEG derivatives type depend upon the ratios of the amount of PPG to that of PEG groups, the molecular weights, the number of branches, and the nature of central group. Constant A in Eq. (5) depends only on the nature of hydrophobic group in polymer chain. In the present case it is the reciprocal of the surface tension lowering of the PPG polymer having a sufficiently large molecular weight. Constant B is in linear relationship with the logarithm of the surfactant concentration; it also depends upon the molecular structure of the surfactant, particularly the number of PPG-PEG branches and the hydrophilic nature of the central group to which they are attached.