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"Elasticity Index" for the Connecting Groups of Double-Chain Amphiphiles Bearing Two Hydrophilic Groups

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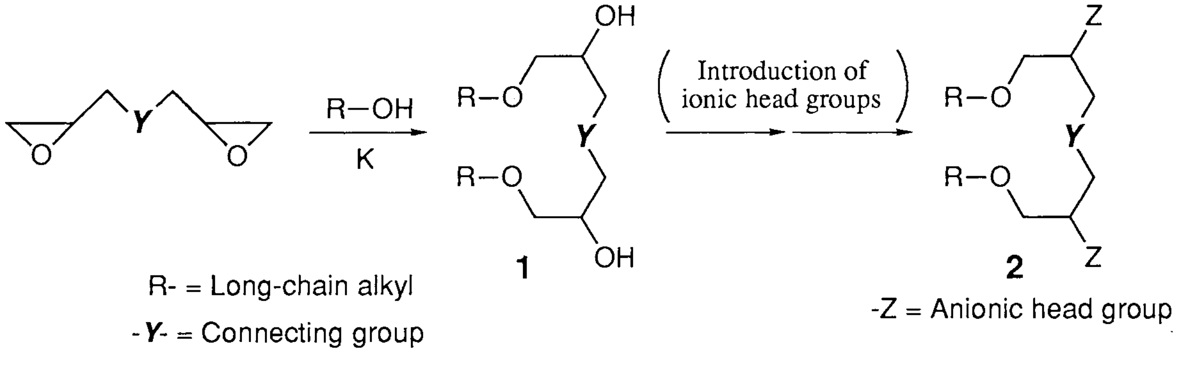
The surface pressure-area (π-A) isotherms for a series of double-chain diols derived from diepoxides were measured. A new parameter, "Elasticity Index", is proposed to explain the effect of the connecting group between the two lipophilic chains of double-chain amphiphiles on the behavior of their monolayer films at the air-water interface.

Multi-chain amphiphiles have been fascinating many researchers in a variety of fields such as synthetic, biomimetic, colloid, and polymer chemistries for fifteen years. However, it is no exaggeration to say that the research topics are for the most part concerned with the formation of bilayer vesicles in water and their application to biomimetic systems or molecular devices. Unfortunately, systematic investigation of water-soluble micelles made from the multi-chain amphiphiles has been out of the focus of interest.

We have been studying a design, preparation, and clarification of properties of many types of double- or triple-chain amphiphiles bearing two ionic groups which can form various molecular assemblies from micelles to bilayer vesicles.1) In the course of this study, we have found these water-soluble amphiphiles show many unique surface-active properties which cannot be achieved by the simple modification of the structure of general surfactants consisting of one lipophilic chain and one ionic head group. In the case of the double-chain *bis*(anionic) surfactants (**2**) derived from diepoxides, the structure of the connecting group (-Y-) between the two lipophilic chains has great influence on the surface-active properties of these types of compounds.1d)



In this letter, a new methodology for the analysis of the monolayer behavior of double-chain amphiphiles bearing two hydrophilic groups is introduced to clarify the effect of the connecting group on the orientation manner of molecules adsorbed at the air-water interface. Investigation of the adsorptive manner of surfactants on the surface is also necessary to understand their surface-active properties.2) The target compounds to measure the monolayer behavior in this study are water-insoluble double-chain diols (**1**) which are synthetic precursors of compounds **2**. The alkyl chain is fixed at a decyl group (R = $C_{10}H_{21}$), because we have mainly studied various properties of a series of surfactants **2** bearing two decyl chains. The connecting groups are derived from *bis*(2,3-epoxypropyl) ether, ethylene glycol-, di(ethylene glycol)-, tri(ethylene glycol)-, catechol-, and hydroquinone diglycidyl ethers [-Y- = $-O(CH_2CH_2O)_n-$ (n = 0-3), -O-(*o*-C_6H_4)-O-, and -O-(*p*-C_6H_4)-O-].[3]

The diols **1** were dissolved in benzene (*ca.* 1 g L^{-1}) and were spread on the water (18 MΩcm) evenly from the solution. A computer-controlled film balance system (Nippon Laser & Electronics Lab. type NL-LB80S-MTC) was used for measuring surface pressure (π) as a function of molecular area (A). The π-A isotherms were recorded in an equilibrium-relaxation compression mode (surface-compression conditions: permitted range of equilibration surface pressure per one compression step = 0.5 mN m^{-1}, compression step time = 10 s, and waiting time of equilibration surface pressure per one compression step = 10 s), and the temperature of the subphase was maintained at 25 ± 0.5 °C.[4]

Figure 1 clearly shows a dramatic change in the π-A isotherms depending on the structure of the connecting group of **1**. We use two parameters to characterize the π-A isotherms: one is the liftoff area (A_L, the molecular area value on the isotherm where the curve emerges from the base line, *i.e.*, $\pi = 0$) and the other is the limiting area (A_∞) which was proposed by Menger.[5] The A_∞ value is calculated by regression analysis of the following equation concerning a two-dimensional variation of a nonideal gas law:

$$\pi[A - A_\infty(1 - k\pi)] = nRT$$

where π and A are the observed pressure and molecular area, respectively, and k is a constant. This equation is generally applicable to the liquid-like region of the monolayer film (the 5-15 mN m^{-1} region for every **1**). The A_L, A_∞, and (A_L - A_∞) values for the compounds **1** are summarized in Table 1.

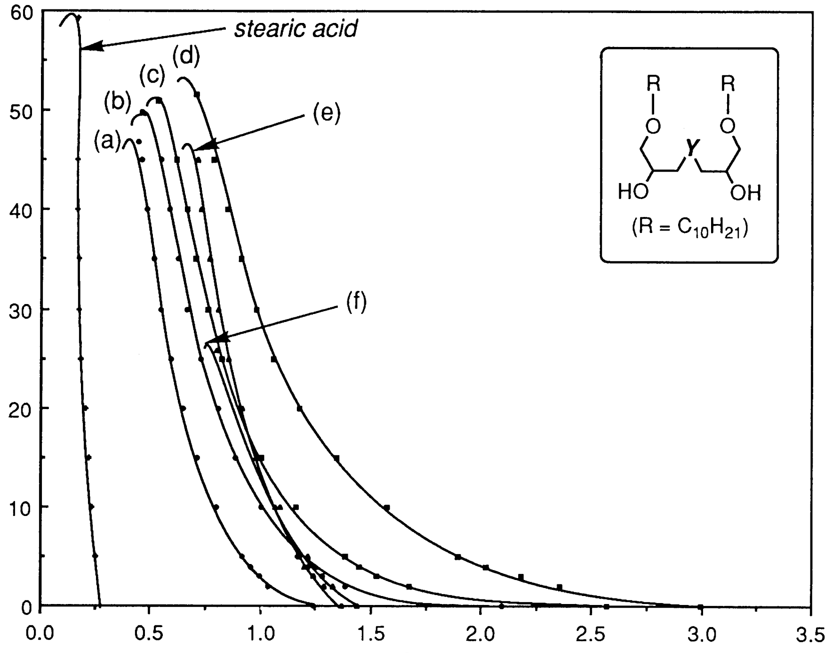


Fig. 1. π-A isotherms of monolayer films of compounds **1**. The structures of the connecting group (-Y-) are as follows: (a) -O-, (b) $-OCH_2CH_2O-$, (c) $-O(CH_2CH_2O)_2-$, (d) $-O(CH_2CH_2O)_3-$, (e) -O-(*o*-C_6H_4)-O-, and (f) -O-(*p*-C_6H_4)-O-.

Table 1. Liftoff areas A_L, limiting areas A_∞, and $A_L - A_\infty$ values for compounds **1**

Compd	-Y-	A_L	A_∞	$A_L - A_\infty$	Compd	-Y-	A_L	A_∞	$A_L - A_\infty$
		nm^2 molecule^{-1}					nm^2 molecule^{-1}		
1a	-O-	1.24	0.89	0.35	**1d**	$-O(CH_2CH_2O)_3-$	3.10	1.53	1.57
1b	$-OCH_2CH_2O-$	2.11	1.12	0.99	**1e**	-O-(*o*-C_6H_4)-O-	1.37	1.25	0.12
1c	$-O(CH_2CH_2O)_2-$	2.55	1.29	1.26	**1f**	-O-(*p*-C_6H_4)-O-	1.44	1.29	0.15

In a series of compounds bearing one oxygen, mono- or oligo(oxyethylene) connecting group (**1a-d**), the A_L, A_∞, and ($A_L - A_\infty$) values increase with an increase in the number of oxyethylene units within the range of this study. This tendency is reasonably explained considering that the oligo(oxyethylene) connecting moiety flexibly spreads on the surface. On the other hand, the A_L values for compounds bearing a benzene moiety (**1e** and **1f**) are only a little larger than that of the diol bearing an ether oxygen as "-Y-" (**1a**). The ($A_L - A_\infty$) values for **1e** and **1f** are much smaller than those of the diols bearing a mono- or oligo(oxyethylene) connecting group (**1b-d**). We deduce from these results that the ($A_L - A_\infty$) values reflect the degree of flexibility of the connecting group on the surface.

The A_L means the area per molecule at which interaction between adjacent molecules in the monolayer begins to be observed in the film compression process.6) Therefore, the A_L and the A_∞ represent the maximum area and the minimum area per adsorbed molecule in the monolayer, respectively, in the range from the gaseous behavior to a liquid-like behavior of the film.

If both areas are assumed to be a circle and if each diameter is taken to be ϕ_L (for a liftoff area circle) or ϕ_∞ (for a limiting area circle), the ratio of ϕ_L to ϕ_∞ should physically represent the extent of "elasticity" for the connecting group in the horizontal direction at the air-water interface (Fig. 2). So we use this ratio, that is, the "Elasticity Index (*E. I.*)" as a measure of estimating the flexibility of the connecting group.

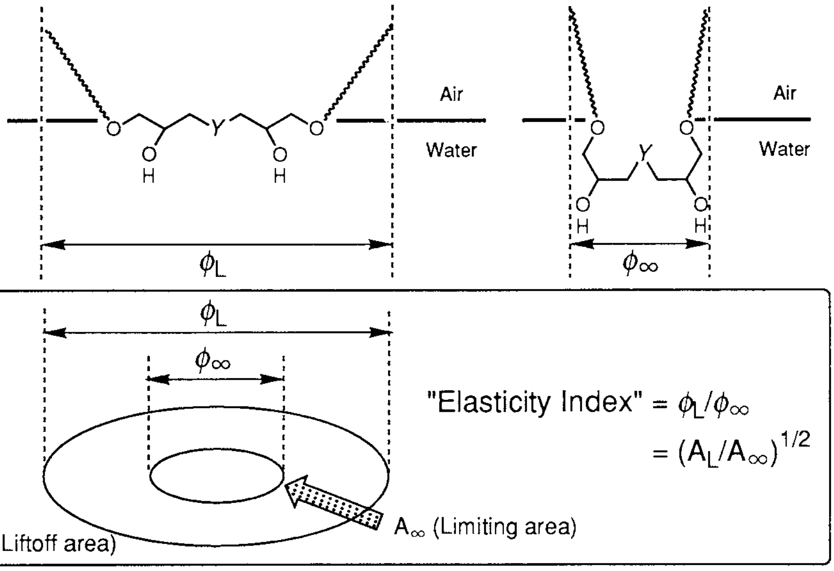


Fig. 2. Stylized illustration of the concept of "Elasticity Index".

Figure 3 illustrates the "Elasticity Index (*E. I.*)" for a series of diols in this study. The *E. I.* for the compound derived from ethylene glycol diglycidyl ether (**1b**) is much larger than that for the diol bearing one oxygen atom in the connecting group (**1a**). The *E. I.* values gradually increase with an increase in the number of oxyethylene units (**1b-d**). It can be said that these results reflect both the degree of hydration to the ether oxygens and good flexibility of the oligo(oxyethylene) group at the air-water interface. The *E. I.* values for diols bearing a benzene ring (**1e** and **1f**) are very small, which clearly indicates that the connecting group containing a benzene ring acts as a rigid segment on the surface. Measurement of the π-A isotherms for the monolayer films of other double-chain diols bearing various types of connecting groups is now in progress to clarify the scope and limitation of the concept of "Elasticity Index".

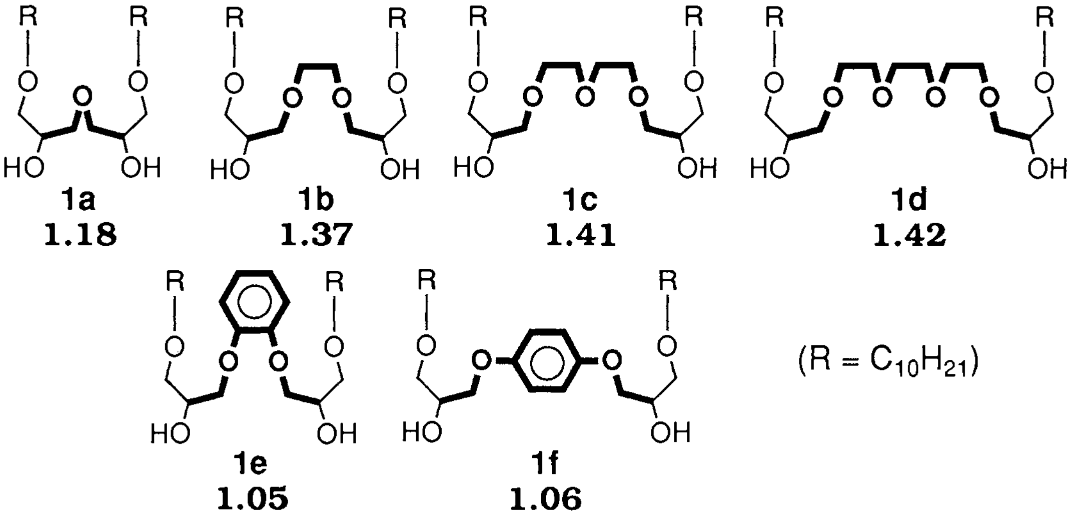


Fig. 3. "Elasticity Index" values for various connecting groups of compounds **1** bearing two decyl groups as hydrophobic chains.

References

1) For example, a) M. Okahara, A. Masuyama, Y. Sumida, and Y.-P. Zhu, *J. Jpn. Oil Chemists' Soc. (YUKAGAKU)*, **37**, 746 (1988); b) Y.-P. Zhu, A. Masuyama, and M. Okahara, *J. Am. Oil Chemists' Soc.*, **67**, 459 (1990); c) Y.-P. Zhu, A. Masuyama, Y. Kirito, M. Okahara, and M. J. Rosen, *ibid.*, **69**, 626 (1992); d) Y.-P. Zhu, A. Masuyama, Y. Kobata, Y. Nakatsuji, M. Okahara, and M. J. Rosen, *J. Colloid and Interface Sci.*, **158**, 40 (1993).
2) M. J. Rosen, "*Surfactants and Interfacial Phenomena*," Wiley, New York (1989), pp. 33-107.
3) All compounds **1** were prepared by the procedures mentioned in Ref. 1b. They were purified repeatedly by silica gel column chromatography with a hexane:acetone gradient eluent system until no contaminant peak was detected in their TLC and in their ^{1}H-NMR (400 MHz) spectra. Satisfactory microanalyses were obtained for all purified **1**.
4) A film balance experiment requires a delicate operation. We made the measurement carefully according to the guidelines of the operation described previously (Ref. 5). The measurement of the π-A isotherm for each compound was carried out *at least five times* to confirm its reproducibility.
5) F. M. Menger, M. G. Wood, Jr., S. Richardson, Q. Zhou, A. R. Elington, and M. J. Sherrod, *J. Am. Chem. Soc.*, **110**, 6797 (1988).
6) F. M. Menger, S. D. Richardson, M. G. Wood, Jr., and M. J. Sherrod, *Langmuir*, **5**, 833 (1988).

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