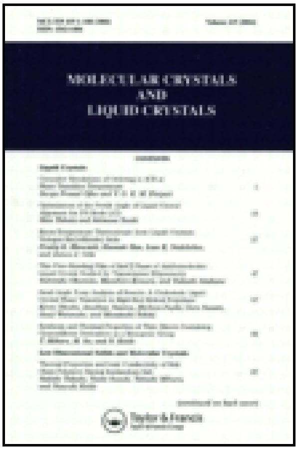

Molecular Crystals and Liquid Crystals

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Liquid Crystal Alignments and Surface Energy

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Liquid Crystal Alignments and Surface Energy

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The relationship between molecular alignments, surface tension (γ_L) of nematic liquid crystals and critical surface tension (γ_C) of surfaces are examined for various surface structures using thirteen types of alkoxysilanes $RSi(OC_nH_{2n+1})_3$. As the results, Creagh's conception that the perpendicular alignments are induced when $\gamma_C < \gamma_L$, and parallel alignments are induced when $\gamma_C > \gamma_L$ was found to be not necessarily correct. Moreover, Porte's theory which gave the theoretical basis to Creagh's conception was examined, and it is clarified that the prerequisite for the theory is not generally realized.

1 INTRODUCTION

Liquid crystal display devices have recently been developed. These devices require the uniform molecular alignment on the glass surfaces for their quality and/or function. Then, various methods for obtaining the uniform alignment have been proposed by many workers, but the mechanism of molecular alignment have not yet been well-understood.

The molecular alignments of nematic liquid crystals have been considered to depend on (1) physicochemical interactions such as hydrogen bonding. van der Waal's interactions, or dipole-dipole interactions between liquid crystal molecules and the glass surface and (2) mechanical interactions relating to the surface topology and anisotropic elasticity of liquid crystal molecules. The former interactions seems to play a dominant role in orienting molecules parallel or perpendicular to the glass surfaces, but the latter interactions seems to play an auxiliary role, that is, it determines the orientation of molecules in the case of parallel alignment.[1] Recently, several investigations[1–4] tried to predict quantitatively the molecular alignment by using critical surface tension γ_C of the substrate and surface tension γ_L of the liquid crystal as a measure of the physicochemical interactions. However, Haller[5] argued against this theory from experimental results.

In this paper, we make various surface structures by surface treatment with several alkoxysilanes $RSi(OC_nH_{2n+1})_3$, and examine the relationship between molecular alignment and surface tension.

2 HISTORICAL PERSPECTIVE

The relationship between molecular alignment and surface tension was first explained by Creagh *et al.*[2] as follows:

a) When the surface energy of a substrate is relatively low, the intermolecular force among liquid crystal molecules is stronger than the force across the interface. Then, the longer axis of nematic molecules are aligned perpendicular to the surface so as to maximize their intermolecular interactions.[6]

b) When the critical surface tension γ_C of a solid is greater than the surface tension γ_L of a liquid crystal, the force across the interface dominates. Therefore, surface free energy is minimized if liquid crystal molecules are packed flat, that is, aligned parallel to the substrate.

c) The relationship described above was confirmed by observing the molecular alignment of MBBA(*p*-methoxybenzylidene-*p*′-*n*-butylaniline) on a carbon- or lecithin-coated surface.

Later, Kahn *et al.*[1] defined the value

$$\Delta\gamma = \gamma_L - \gamma_C \qquad (1)$$

as a measure of the free energy responsible for liquid crystal alignment. If $\Delta\gamma > 0$, the perpendicular alignment is obtained but if $\Delta\gamma < 0$, a parallel one is obtained. These results supported the Creagh's conception. But Kahn's paper did not give detailed experimental data.

Dubois *et al.*[3] observed the molecular alignments of six types of nematic liquid crystals on five kinds of polymeric surfaces, critical surface tension of which was <22–40 dyn/cm. They summarized experimental results as follows. When γ_C is very low compared with γ_L, perpendicular alignment is effectively induced. Conversely, when γ_C is very high parallel alignment is observed.

Funada *et al.*[7] observed the molecular alignments of five kinds of liquid crystals on nine types of surfaces and summarized the results as follows. Molecular alignments depend on contact angle ϕ between liquid crystal and surface. When $\phi \geq 36°$ perpendicular alignment is induced, but when $\phi \leq 36°$ parallel alignment is observed.

Porte[4] dealed quantitatively with surface energy and examined molecular alignment. Surface tension $\gamma_L(\theta)$ of liquid crystal is defined as a function of a tilt angle θ of alignment from the line normal to the surface, and then interfacial tension between liquid crystal molecules and the substrate surface is written by

$$\gamma_{LS}(\theta) = \gamma_S + \gamma_L(\theta) - W(\theta), \tag{2}$$

where γ_S is the surface tension of the substrate, and $W(\theta)$ the work of adnesion. Assuming the first approximation that the interaction force is only dispersion force, $W(\theta)$ can be expressed by[8]

$$W(\theta) = 2(\gamma_L(\theta) \cdot \gamma_S)^{1/2}. \tag{3}$$

Thus

$$\gamma_{LS}(\theta) = \gamma_S + \gamma_L(\theta) - 2(\gamma_L(\theta) \cdot \gamma_S)^{1/2}. \tag{4}$$

Liquid crystal molecules are aligned so as to minimize $\gamma_{LS}(\theta)$, then, we have

$$\frac{\partial \gamma_{LS}(\theta)}{\partial \theta} = \frac{\partial \gamma_L(\theta)}{\partial \theta} \left[1 - \left(\frac{\gamma_S}{\gamma_L(\theta)}\right)^{1/2}\right] = 0 \tag{5}$$

Here, assuming Creagh's interpretation[9] that:

$$\gamma_L(0) < \gamma_L(\theta) < \gamma_L(\pi/2), \tag{6}$$

Eq. (5) gives the following typical cases.

a) $\gamma_S < \gamma_L(0)$: perpendicular alignment.
b) $\gamma_L(0) < \gamma_S < \gamma_L(\pi/2)$: tilted alignment.
c) $\gamma_L(\pi/2) < \gamma_S$: parallel alignment.

If Eq. (3) is valid, we can replace γ_S by γ_C. Then, these results are in good agreement with Creagh's conception without considering θ-dependence of γ_L. Porte confirmed that results described above consistent with experimental observation of alignment of MBBA on the surfaces with various values of γ_S, which are made by treatment with various alkylmonoamines.

Haller[5] observed alignments of three types of liquid crystals on the substrate treated with four organic surfactants, and did not support Creagh's conception.

3 EXPERIMENTS

3.1 Liquid crystals and surfactants

Table I shows molecular structure of liquid crystals used in the experiments reported here. Among them, I-2, 3, 4, 8, IV-1, 4 are synthesized from para derivative benzaldehydes and anilines. IV-1 and the others are purified by several times of vacuum distillation and recrystallization, respectively, so that their clearing temperatures coincided with the values given in literatures.[10–12] The other liquid crystals in Table I were purchased from Fuji Color Co., Ltd., and their clearing temperatures were confirmed to agree with literatures.[11–14] Table II shows molecular structure, solvents and sources of alkoxysilanes used in the experiments.

Cell substrates used in the measurements are SnO_2-coated slide glass plates etched partially with zinc powder and hydrochloric acid. A typical procedure of surface treatments is as follows:

1) Immersing of the substrate in a dilute solution of alkoxysilane for 15 min.

2) Drying at room temperature

3) Heating at 130°C for 20 min.

In this process, alkoxygroup ($-OC_nH_{2n+1}$) is adsorbed on the substrate, then the treated surface is covered with the left part of molecular structures shown in Table II.

TABLE I

Liquid crystals used in the experiments

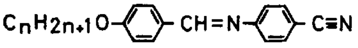
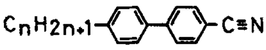
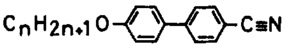
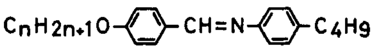
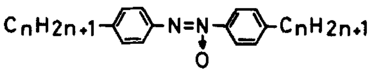
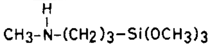
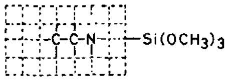
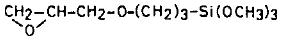
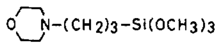
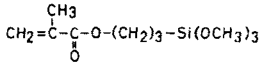
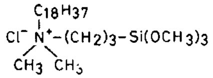
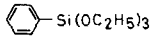
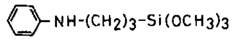
Type	Molecular structure	Symbol Type ← n →
I		I—1,2,3,4,6,8,10
II		II—5,6,7
III		III—5,7
IV		IV—1,4
V		V—4

TABLE II

Alkoxysilanes used in the experiments

Alkoxysilane	Symbol	Molecular structure	Solvent	Source
N-methyl-3-aminopropyl-trimethoxysilane	MAP	 $CH_3\text{-}\overset{H}{N}\text{-}(CH_2)_3\text{-}Si(OCH_3)_3$	water	A
N-β(aminoethyl)γ-aminopropyl-trimethoxysilane	AAMS	$NH_2\text{-}(CH_2)_2\text{-}NH\text{-}(CH_2)_3\text{-}Si(OCH_3)_3$	water	B
γ-aminopropyl-triethoxysilane	AES	$NH_2\text{-}(CH_2)_3\text{-}Si(OC_2H_5)_3$	$(\text{water})_2(\text{methanol})_{3x}$	C
Polyaminotrimethoxysilane	PAMS		water	D
γ-glycidoxypropyl-trimethoxysilane	GMS		water	B
γ-morpholinopropyl-trimethoxysilane	MOMS		water	B
γ-methacryloxypropyl-trimethoxysilane	MEMS	 $CH_2=\overset{CH_3}{C}\text{-}\underset{O}{\overset{}{C}}\text{-}O\text{-}(CH_2)_3\text{-}Si(OCH_3)_3$	$(\text{water})_6(\text{methanol})_x$	B
Methyltrimethoxysilane	MMS	$CH_3\text{-}Si(OCH_3)_3$	water	B
Pentyltriethoxysilane	PES	$C_5H_{11}\text{-}Si(OC_2H_5)_3$	$(\text{water})_2(\text{methanol})_{9x}$	C
N,N-dimethyl-N-octadecyl-3-aminopropyltrimethoxysilyl chloride	DMOAP	 $Cl^-\ \overset{C_{18}H_{37}}{N^+}(CH_3)_2\text{-}(CH_2)_3\text{-}Si(OCH_3)_3$	water	D
Phenyltriethoxysilane	PHES		$(\text{water})_3(\text{methanol})_x$	C
N-phenyl-3-aminopropyl trimethoxysilane	PHAMS		$(\text{water})_5(\text{methanol})_{3x}$	B
γ-mercaptopropyl trimethoxysilane	MCMS	$HS\text{-}(CH_2)_3\text{-}Si(OCH_3)_3$	$(\text{water})_7(\text{methanol})_{3x}$	B

In the column of solvent, subscript indicates weight ratio, and x indicates concentration of alkoxysilane in wt%.

Source:
- A Dow Corning Corp.
- B Shin-Etsu Chemical Co, Ltd.
- C Tokyo Kasei Kogyo Co., Ltd
- D Toray Silicone Co., Ltd.

3.2 Surface tension measurements

Surface tension is measured using the du Noüy ring method[15] and its value is normalized by applying the correction factor given by Harkins and Jordan.[16]

3.3 Critical surface tension measurements

Critical surface tension was proposed by Zisman[17] as a measure of wettability of solid surface, and is experimentally determined by following procedure. First, contact angle ϕ of various organic liquids to the surface is measured. Then, the critical surface tension γ_C is obtained from a plot of $\cos\phi$ versus γ_L extrapolated to a zero contact angle as shown in Figure 1(a).

Contact angle is determined using light-reflecting method[18] as shown in Figure 1(b). In this apparatus, a light source and a slit can be rotated together around a drop of liquid.

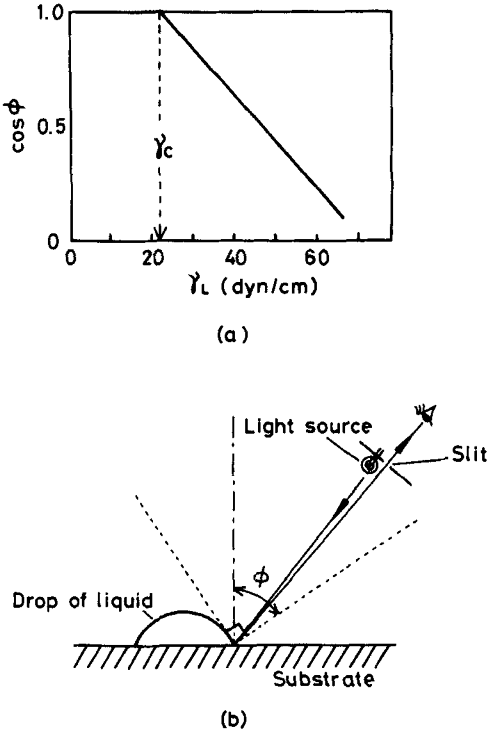


FIGURE 1 Determination of critical surface tension.

When the light source and the slit are placed just above the drop, the reflected image of the light source can be seen on the drop through the slit. Then, the light source is rotated to the plane slowly until the reflected image suddenly disappears. This rotation angle gives contact angle.

4 RESULTS

Figures 2 and 3 show critical surface tension (γ_C) and molecular alignments of various liquid crystals on the glass surface treated with AAMS and MOMS as a function of alkoxysilane concentration. For AAMS, γ_C increases with alkoxysilane concentration in "a" region, but is flat in "b" and "c" regions. However, for MOMS, "c" region does not appear. It seems that "b" and "c" regions correspond to the closed packing state in which the alkoxysilane chains align parallel and perpendicular to the glass surface, respectively. On this point of view, the fact that "c" region does not appear for MOMS is considered to be due to strong absorbed groups at both ends of MOMS molecule.

Comparing molecular alignments with critical surface tension in Figures 2 and 3 we can see the following facts.

1) Molecular alignments change according to a, b, c regions for AAMS, and a, b regions for MOMS.

2) For high γ_C region, most of the liquid crystals show parallel alignments.

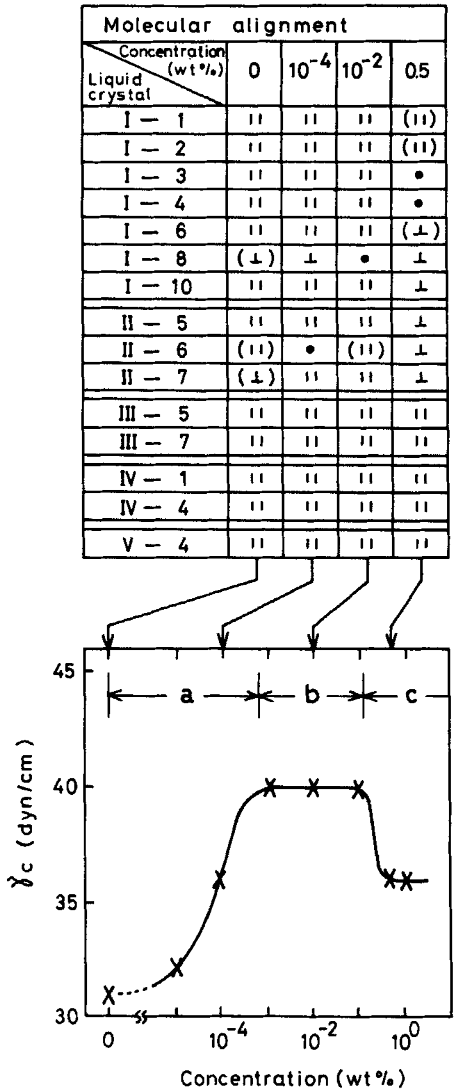
These results are in good agreement with Creagh's conception qualitatively. Next, we measured the surface tension of liquid crystals II–5, IV–1 and V–4 at 20°C. Results obtained are shown in Table III. Creagh's conception predicts that these three liquid crystals align parallel to the surfaces treated by using AAMS or MOMS of a concentration more than about 10^{-4} wt %, and perpendicular to the surfaces treated with that less than about 10^{-4} wt. %. But the experimental results shown in Figures 2 and 3 did not agree with the prediction described above.

Next, we measured critical surface tension and contact angle, and observed molecular alignments of II–5, IV–1 and V–4 on glass and SnO_2-coated

TABLE III

Surface tension of liquid crystals at 20°C

Liquid crystal	γ_L(dyn/cm)
II – 5	34.4
IV – 1	34.2
V – 4	32.6



Molecular alignment

Concentration (wt%) / Liquid crystal	0	10^{-4}	10^{-2}	0.5
I — 1	‖	‖	‖	(‖)
I — 2	‖	‖	‖	(‖)
I — 3	‖	‖	‖	●
I — 4	‖	‖	‖	●
I — 6	‖	‖	‖	(⊥)
I — 8	(⊥)	⊥	●	⊥
I — 10	‖	‖	‖	⊥
II — 5	‖	‖	‖	⊥
II — 6	(‖)	●	(‖)	⊥
II — 7	(⊥)	‖	‖	⊥
III — 5	‖	‖	‖	‖
III — 7	‖	‖	‖	‖
IV — 1	‖	‖	‖	‖
IV — 4	‖	‖	‖	‖
V — 4	‖	‖	‖	‖

FIGURE 2 Critical tension γ_c and molecular alignment on AAMS treated surface as a function of AAMS concentration. ‖: parallel alignment, ⊥: perpendicular alignment, (‖), (⊥): nearly parallel, nearly perpendicular alignment, or alignment changes near the nematic-isotropic transition temperature, ●: undistinguished alignment.

Molecular alignment				
Concentration (wt%) / Liquid crystal	0	10^{-4}	10^{-2}	10^{0}
I — 1	∥	∥	∥	∥
I — 2	∥	∥	∥	∥
I — 3	∥	∥	∥	∥
I — 4	∥	∥	∥	∥
I — 6	∥	∥	∥	∥
I — 8	(⊥)	(∥)	∥	∥
I — 10	∥	∥	∥	∥
II — 5	∥	∥	∥	∥
II — 6	(∥)	(∥)	•	•
II — 7	(⊥)	•	∥	∥
III — 5	∥	∥	∥	∥
III — 7	∥	∥	∥	∥
IV — 1	∥	∥	∥	∥
IV — 4	∥	∥	∥	∥
V — 4	∥	∥	∥	∥

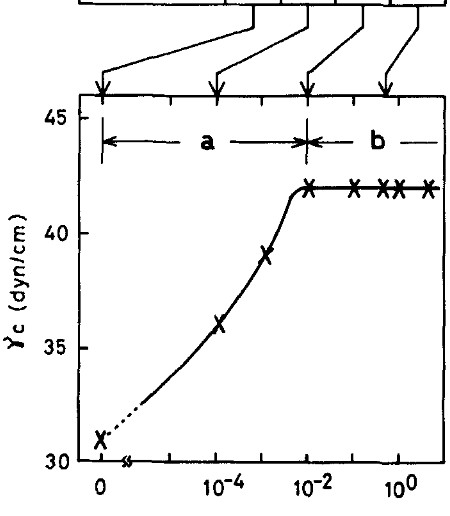


FIGURE 3 Critical surface tension γ_c and molecular alignment on MOMS treated surface as a function of MOMS concentration.

TABLE IVa

Critical surface tension γ_C, molecular alignment and contact angle on the glass surfaces treated with 0.5 wt % solution of various alkoxysilanes

No.	Alkoxy-silane	γ_c (dyn/cm)	Molecular alignment and contact angle					
			II-5 (γ_L = 34.4 dyn/cm)		IV-1 (γ_L = 34.2 dyn/cm)		V-4 (γ_L = 32.6 dyn/cm)	
1.	MCMS	42	•	0°	•	0°	∥	0°
2.	PHAMS	42	(∥)	0°	∥	0°	∥	0°
3.	MOMS	42	∥	0°	∥	0°	∥	0°
4.	GMS	38.5	∥	0°	∥	0°	∥	0°
5.	AES	38	⊥	0°	∥	0°	∥	0°
6.	AAMS	36	⊥	0°	∥	0°	∥	0°
7.	PHES	32	∥	16°	∥	15°	∥	8°
8.	MEMS	31	(∥)	<5°	∥	<5°	∥	11°
9.	MAP	29	⊥	16°	∥	15°	∥	12°
10.	PAMS	26	(∥)	37°	∥	39°	∥	25°
11.	MMS	23	∥	47°	(∥)	45°	∥	40°
12.	DMOAP	23	⊥	55°	⊥	56°	⊥	46°
13.	PES	22	⊥	44°	•	42°	∥	36°

surfaces treated with 0.5 wt % alkoxysilane solutions. Results obtained are summarized in Table IV, Figures 4 and 5. In Figures 4 and 5, γ_C is larger than γ_L at the right-handed side of the broken line, and γ_C is smaller than γ_L at the left-handed side. Then, if Creagh's conception is valid, it is expected that parallel alignment is observed at the right-handed side of the broken line and perpendicular alignment at the left-handed side. But, results fall short of the above-described expectation. Moreover, the relationship between molecular alignment and contact angle reported by Funada also cannot be found.

These facts show that Creagh's conception is not generally realized.

5 DISCUSSION

The reasons why Creagh's conception cannot be generally recognized are considered as follows.

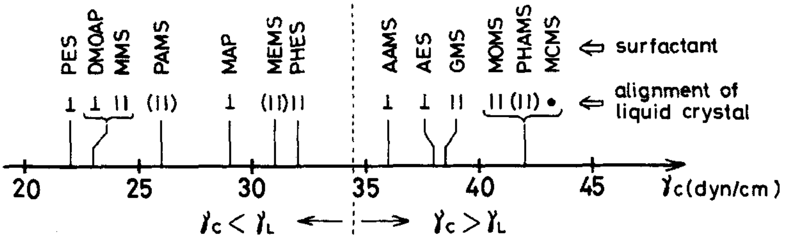
TABLE IVb

Critical surface tension γ_C, molecular alignment and contact angle on the SnO_2-coated glass surfaces treated with 0.5 wt % solution of various alkoxysilanes

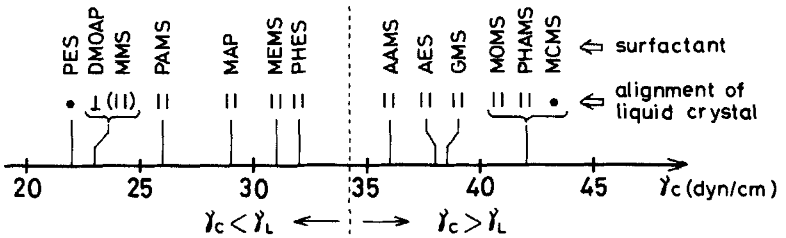
No.	Alkoxy silane	γ_c (dyn / cm)	Molecular alignment and contact angle					
			II-5 (γ_L = 34.4 dyn / cm)		IV-1 (γ_L = 34.2 dyn / cm)		V-4 (γ_L = 32.6 dyn / cm)	
1.	MCMS	45	∥	0°	∥	0°	∥	0°
2.	PHAMS	45	∥	0°	∥	0°	∥	0°
3.	MOMS	45	∥	0°	∥	0°	∥	0°
4.	GMS	45	∥	0°	∥	0°	∥	0°
5.	AES	43	⊥	0°	∥	0°	∥	0°
6.	AAMS	38	⊥	0°	∥	0°	∥	0°
7.	PHES	44	(∥)	0°	∥	0°	∥	0°
8.	MEMS	41	∥	0°	∥	0°	∥	0°
9.	MAP	34	⊥	25°	∥	21°	∥	<5°
10.	PAMS	31	(∥)	24°	∥	24°	∥	<5°
11.	MMS	31	∥	24°	(∥)	24°	∥	18°
12.	DMOAP	24	⊥	55°	⊥	56°	⊥	46°
13.	PES	25	•	36°	∥	37°	∥	33°

1) Equation (6) in Porte's theory, which seems to give the theoretical basis to Creagh's conception, is not always valid. For example, since Bouchiat[19] showed that the molecules of MBBA are tilted at an angle θ of about 15° from the line normal to the free surface and those of PAA(*p*-azoxyanisole) are about 90°, γ_L does not obviously become minimum at $\theta = 0°$ as given by Eq. (6) for at least MBBA and PAA. We also observed alignments on free surface of liquid crystals used in the experiments reported here, and confirmed that $\theta \neq 0$ for I-1, I-2, I-3, I-4, I-6, IV-1, IV-4 and V-4. Hence, it is obvious that Eq. (6) is not always valid in all cases.

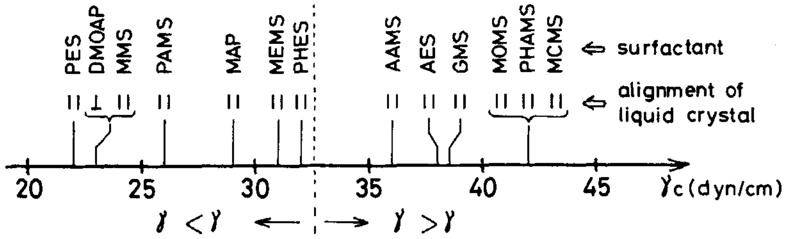
2) Porte's theory is based on the assumption that the interaction between liquid crystal molecules and surfaces is only dispersion force as mentioned above. However, as most surfactant and almost all liquid crystals have polar groups, dipole interactions such as dipole-dipole or dipole-induced dipole interactions cannot be neglected. Therefore, Eq. (3) derived from the assumption cannot be generally applicable and γ_S cannot be replaced by γ_C.



(a) II-5 (γ_L = 34.4 dyn/cm)



(b) IV-1 (γ_L = 34.2 dyn/cm)

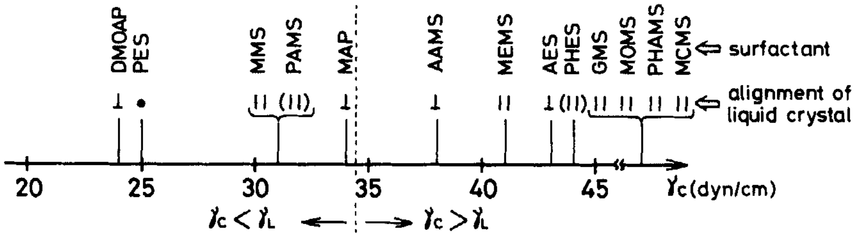


(c) V-4 (γ_L = 32.6 dyn/cm)

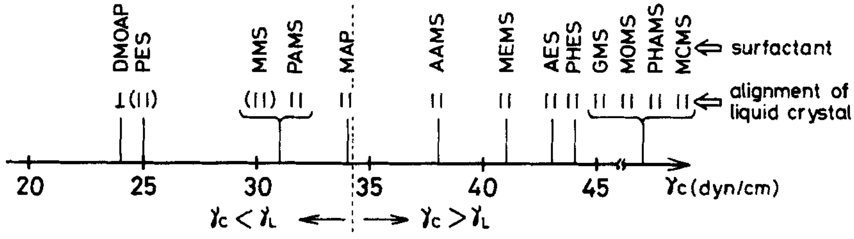
FIGURE 4 Relationship between γ_C and molecular alignments of liquid crystals on the glass surfaces treated with alkoxysilanes.

By the way, liquid crystals I-8, I-10, II and III align perpendicular ($\theta = 0$) to the free surface as stated in (1). These liquid crystals have common end groups, that is, a cyano group and a relatively longer aklyl chain, which are strong polar and nonpolar groups, respectively. Therefore, these liquid crystals have somewhat amphiphilic characteristics, which seems to be related to the perpendicular alignment. Then, Eq. (6) may be valid for only such an amphiphilic liquid crystal. Details of this point are being investigated.

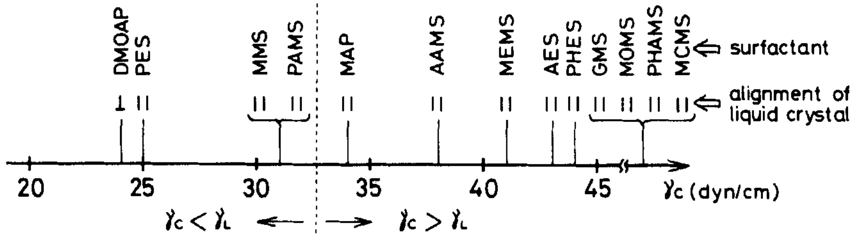
Next, we examined the reason why Creagh's conception did not contradict their experimental results in spite of difficulty described above. All of the



(a) II-5 (γ_L = 34.4 dyn/cm)



(b) IV-1 (γ_L = 34.2 dyn/cm)



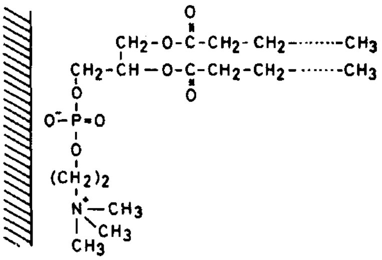
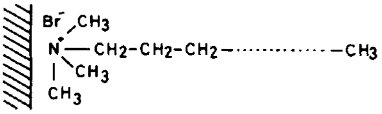
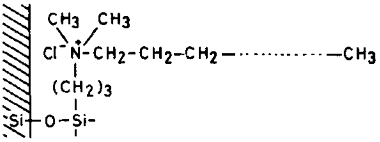
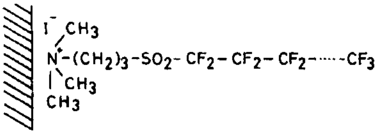
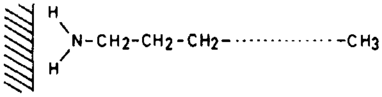
(c) V-4 (γ_L = 32.6 dyn/cm)

FIGURE 5 Relationship between γ_C and molecular alignments of liquid crystals on the SnO_2-coated surfaces treated with alkoxysilanes.

low energy surfaces used by Creagh, Funada and Porte except the surface of PTFE, have a long hydrocarbon or fluorocarbon chain elongated from the surface of substrate as shown in Table V (surface structure of PTFE is unknown). From the fact that liquid crystal molecules tended to align perpendicularly on these surfaces, Creagh concluded that there was interdependence between the low energy surface and liquid crystal perpendicular alignment. However, not only hydrocarbon or fluorocarbon chains but also short ones such as MMS and PES actually make low energy surfaces. Though critical surface tension of substrates treated with MMS and PES

TABLE V

Surface structures which were reported to have low critical surface tension

Worker	Surface	Surface structure
Creagh et al.[2]	lecithin treated surface	
Funada et al.[7]	hexadecyltrimethylammonium bromide treated surface	
	N,N-dimethyl-N-octadecyl-3-aminopropyltrimethoxysilyl chloride (DMOAP) treated surface	
	N-perfluorooctylsulphonyl-3-aminopropyltrimethylammonium iodide treated surface	
	polytetrafluoroethylene (PTFE) film surface	unknown
Porte[4]	alkylmonoamine treated surface	

is efficiently low compared with surface tension of liquid crystals, perpendicular alignments are not obtained.

Since Eqs. (3) and (6) are not generally applicable as mentioned above, molecular alignment should be considered as follows: The molecular alignment is determined by θ which minimizes the interfacial tension between liquid crystal and substrate surface, that is,

$$\frac{\partial \gamma_L(\theta)}{\partial \theta} - \frac{\partial W(\theta)}{\partial \theta} = 0 \tag{7}$$

$$\frac{\partial^2 \gamma_L(\theta)}{\partial \theta^2} - \frac{\partial^2 W(\theta)}{\partial \theta^2} > 0 \tag{8}$$

In order to solve Eqs. (7) and (8), it is necessary to obtain θ-dependence of γ_L and W, but is now unknown and further clarification is required.

By the way, the perpendicular alignments on the surface shown in Table V may be due to interlacing hydrocarbon or fluorocarbon chains with liquid crystal molecules. The perpendicular alignment of several liquid crystals at "c" region in Figure 2 may be also due to the same mechanism. In this case, θ dependence of $W(\theta)$ will be dominant in Eq. (7) and inequation (8), and of course $\theta = 0$ will satisfy these expressions.

6 Conclusion

We made various surface structures using thirteen kinds of alkoxysilanes, and measured critical surface tension and observed molecular alignments of liquid crystals. The results obtained clarified that Creagh's conception is not generally applicable.

We examined Porte's theory which provided the theoretical basis to Creagh's conception, and consequently clarified that the prerequisite for this theory was not generally realized.

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