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Liquid Crystal Orientation on Inorganic Surfaces

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It has been known empirically that some kinds of liquid crystal align perpendicular to inorganic flat surface such as In_2O_3 film. The authors clarified in the previous paper that this phenomena was due to perpendicular adsorption of amphiphilic impurities contained in the liquid crystal to the substrate surfaces. In this paper, the authors evaluate the adsorbabilities of various amphiphilic materials to inorganic surfaces by using a chromatographic effect and investigate the correlation between the adsorbability and the liquid crystal orientation. From the results, it is found that the perpendicular alignment of liquid crystal is induced when polarities of the amphiphilic material and substrate surface are both strong. It is also found that there is evident relation between the polarity and IEPS (Isoelectric Point of Solid Surface) which is a measure of basicity of the surface. This fact suggests that adsorption of the amphiphilic impurity to the surface is due to the acid-base interaction.

I. INTRODUCTION

Understanding of liquid crystal molecular orientation on flat inorganic surface is important not only as a physical problem but also in application to display devices. Several researchers have tried to explain the mechanism of liquid crystal orientation.[1–6] However, they could not explain all the experimental results without contradiction.[7,8] This contradiction was considered to be due to the lack of considering about the effect of impurities contained in the liquid crystal material. Actually, we have found that the orientation of some liquid crystal changed by degradation. In order to examine the intrinsic orientation of liquid crystals without influence of impurity, the impurity must be eliminated from the liquid crystal. For this purpose, the authors[9] considered a method to eliminate impurities from the liquid crystals by applying the principle of chromatography using a special

sandwich cell as shown in Figure 1. As both sides of the cell are opened, liquid crystal material is introduced by capillary action from one side of it, in this case, from the left-hand side. By this process, impurity adsorbs on the surface near the introducing hole, and hence the molecular orientation of liquid crystal induced by the adsorbed impurity is observed in this region. On the other hand, liquid crystal orientation without influence of the impurity can be observed at the front region, that is, right-hand side of the cell. We have named this cell the liquid crystal chromatographic cell. Liquid crystal-chromatography is useful not only in removing impurity from liquid crystal but also in evaluating the amount of the impurity and its adsorbability to the surface by the length l_1 of the impurity adsorbed region, because l_1 decreases with increase of the adsorbability as well as decrease of the impurity concentration. In addition, the length l_1 depends on the cleanliness of the surface.

By using this liquid crystal-chromatography, the authors have examined molecular orientation of various liquid crystals without influence of impurity on In_2O_3 surface. As a result, all liquid crystals were found to align parallel to the surface at the front region of the liquid crystal-chromatographic cell though some liquid crystals align perpendicularly in the usual cell. Therefore, it was concluded that the orientation of pure liquid crystal on the inorganic surface was parallel alignment, and that the perpendicular alignment was caused by impurities. This kind of impurity

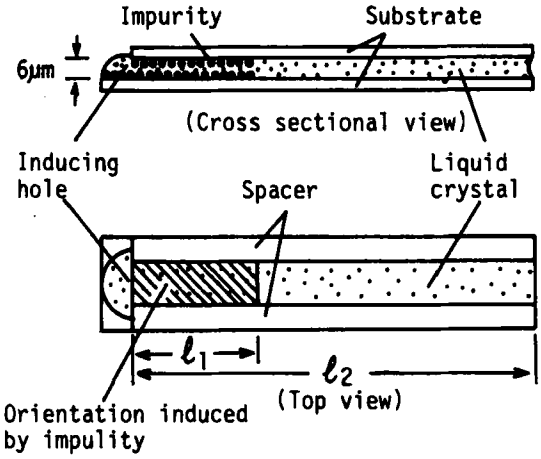


FIGURE 1 Liquid crystal chromatographic cell.

was considered to be amphiphilic material with polar and nonpolar groups at both ends of the molecule as shows in Figure 2a. When liquid crystals with this kind of impurity exist on the polar surface, molecules of the impurity are adsorbed perpendicular to the surface as shown in Figure 2b, and hence liquid crystal molecules align perpendicular to the surface according to the amphiphilic molecules.

The adsorption of amphiphilic material is based on some interaction between the polar groups of the amphiphilic materials and the polar surface. Then, in this paper, the relationship among polarity of substrates, amphiphilic materials and liquid crystal orientation are investigated by using the chromatographic effect, and the mechanism of the adsorption are discussed.

II. EXPERIMENTAL RESULTS AND DISCUSSION.

Table I shows amphiphilic materials used in the experiments, where nonpolar substituents of them are commonly normal alkyl groups with 17 or 18 carbons. All of these materials were purchased from Tokyo Kasei Kogyo Co., Ltd. Polarity of the amphiphilic materials are measured by using the usual thin layer chromatography.[10] That is, the polarity of the solute was evaluated by a replacement ratio R which denotes ratio of replaced distance of the solute, l_1, and developed distance of solvent, l_2, as shown in Figure 3. This R-value depends on the adsorbability of non-polar group as well as the polar group in the amphiphilic materials. In this experiment, however, the non-polar group of each compound is unified to alkyl group with almost the same length as mentioned before, so that it depends only on the characteristics of the polar substituent in it. According to the prin-

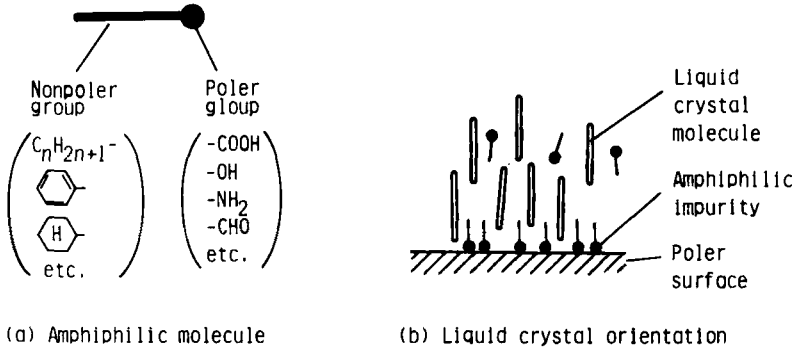


FIGURE 2 Structure of amphiphilic molecule and its effect on the liquid crystal orientation.

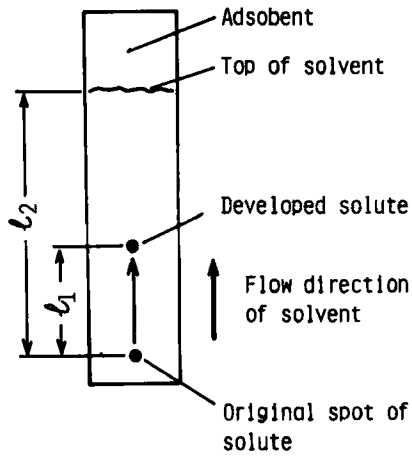
TABLE I

Amphiphilic materials and their polarity

Molecular structure	Symbol	R*	
ⓐ $C_{18}H_{37}N^+(CH_3)_3Cl^-$	N^+Cl^-	0.00	Strong polarity
ⓑ $C_{18}H_{37}SO_3Na$	SO_3Na	0.02	
ⓒ $C_{18}H_{37}NH_2$	NH_2	0.43	
ⓓ $C_{17}H_{35}COOH$	COOH	0.86	
ⓔ $C_{18}H_{37}OH$	OH	0.97	Weak polarity
ⓕ $C_{17}H_{35}CN$	CN	1.00	

*Determined by thin layer chromatography

ciple of adsorption chromatography, smaller R-value corresponds to the stronger polarity. For the developing plate, slide glass covered with silica-gel powder with fluorescent material (BF-5 of Wako Pure Chemical Industries Ltd.) was used. Ethanol solution of each amphiphilic material was spotted and it was developed by using acetone solvent (the thin layer-chromatography grade, Wako Pure Chemical Industries Ltd.). Detection of developed spot was made as follows. Sulfonic acid was sprayed on the developed plate, followed by heat treatment at 150°C for 10 min to oxidize organic solute. As BF-5 fluoresces weakly under irradiation of ultra violet light, developed spot could be observed either by dark spot or bright



$$R = l_1/l_2$$

FIGURE 3 Definition of replacement ratio R in the thin layer chromatography.

fluorescent spot according to their strength of fluorescence. R-values of surface active compounds obtained by these methods are shown in Table I. Adsorbability of these compounds decreases in the order of ⓐ to ⓕ.

Table II shows the substrates on which liquid crystal orientation was investigated. Aluminum ① and gold ⑧ were evaporated by resistance heated tungstenum wire at 5 X 10^{-6} Torr. Surface of the aluminum film is generally considered to change to Al_2O_3 because the surface is easily oxidized in the air. SiO ⑦ was evaporated by resistance heated aluminum basket. The starting material was silicon monoxide powder of 350 mesh produced by Mitsuwa Pure Chemicals Ltd. In_2O_3 coated soda-lime glass ② was obtained from Matsuzaki Sinkuu Co., Ltd. Soda-lime glass ④ is usual slide glass of 1.5 mm thickness. Heat-treated soda-lime glass ③ is a slide glass heat-treated at 500°C for 60 min in the air. Here, the authors have confirmed that sodium ion concentration of the usual soda-lime glass was considerably low at the surface compared to that of the bulk but it increased by heat treatment (see Appendix).

SiO_2 film ⑥ is prepared as follows. First, organic compound of silicon dioxides (Si-85000 of Tokyo Ohka Kogyo Co., Ltd.) is deposited by dipping a substrate in the 50 vol% ethanol solution. Then, the substrate is heated at 150°C for 15 min and then at 550°C for 15 min. The SiO_2 film deposited by this procedure is about 600 Å in thickness. It is necessary to clean the surface prior to the experiments on molecular orientation on it, because surface pollution affects the characteristic of adsorption significantly. The authors have already clarified that argon ion bonbardment was one of the most effective method in removing the pollution by using the liquid crystal chromatography.[11] Therefore, all substrate surfaces shown in Table II were cleaned by this method under the condition of the argon pressure of about 10^{-3} Torr and the accelerated voltage of 3.5 kV. In

TABLE II

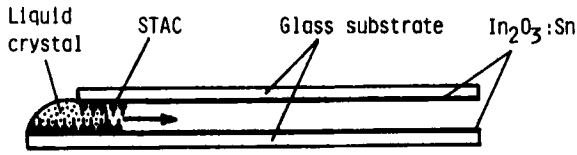
Substrates and their polarity

Substrate	Symbol	R*	
① Al evaporated glass	Al	0.01	↑ Strong
② In_2O_3 coated glass	In_2O_3	0.02	polarity
③ Heat-treated soda-lime glass (500°C, 1 hr)	Heated glass	0.07	
④ Soda-lime glass	Soda glass	0.19	
⑤ Pyrex glass	Pyrex	0.26	
⑥ SiO_2 coated glass	SiO_2	0.36	
⑦ SiO evaporated glass	SiO	0.49	Weak
⑧ Au evaporated glass	Au	1.00	↓ polarity

*Obtained by liquid crystal chromatography

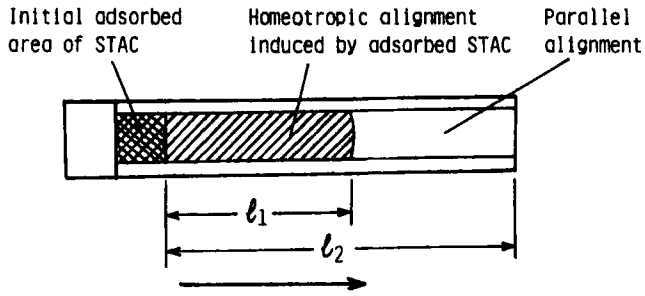
the case of heat-treated soda-lime glass, however, this cleaning was done before heat-treatment, because sodium ion migrates readily under the influence of electric fields produced by ion-beam irradiation upon the glass surface.[12]

Polarity of the substrate surface was measured by the liquid crystal chromatographic cell as shown in Figure 4. In this case, a small area of the substrates is previously covered with a monolayer of stearyltrimethylammonium chloride (STAC, Table I ⓐ) as solute, which was adsorbed by retraction method as mentioned later. As an adsorbent, nematic liquid crystal 4,4′-di(*n*-butyl)-azoxybenzene (BAB) purchased from Fuji Color Co., Ltd. was used. This liquid crystal is confirmed to align parallel to all substrates listed in Table II, which indicate that it does not contain any amphiphilic impurities inducing perpendicular alignment.[9] When the liquid crystal was introduced between the substrates, the adsorbed region of STAC was transferred by the flow of the liquid crystal in consequence of



(a) Cross section of the liquid crystal chromatography

(STAC : $C_{18}H_{37}N^{+}(CH_3)_3\,Cl^{-}$)



(Flow direction of the liquid crystal)

$R = \ell_1/\ell_2$

(b) Definishion of R

FIGURE 4 The liquid crystal chromatographic cell used in the experiments and definition of the replacement ratio R.

chromatographic effect. As the adsorbed STAC tend to align the liquid crystal perpendicular to the surface and hence adsorbed region of STAC was easily observed as a dark region between crossed polarizers. The transferred ratio R was defined as shown in Figure 4 as was in the thin layer-chromatography. In this case, smaller R corresponds to stronger polarity of the substrate surface.

The results are shown in Table II. It is found that the polarity of soda-lime glass becomes strong by heat-treatment. This is considered to be due to increase of sodium ion concentration at the surface as is shown in Figure 7 in Appendix.

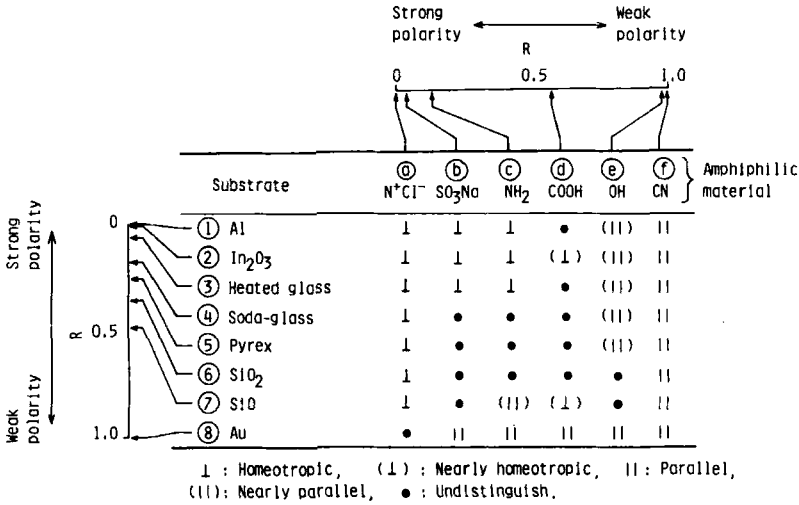
In order to examine the effect of amphiphilic materials on liquid crystal orientation, various substrate surfaces are coated with a monolayer of amphiphilic materials, and liquid crystal orientation on them is observed. The monolayer is made on the substrate by the retraction method[13] for the compound ⓐ and by the Langmuir-Blodgett method[14] for compounds ⓑ ~ ⓔ. In the case of the retraction method, each substrate was dipped into 2×10^{-4} mol/l aqueous solution for 5 min, and was withdrawn from it at a rate of 1 mm/min so that the substrate coated with the adsorbed monolayer emerged dry. Langmurir-Blodgett method can be applied to the compounds which are insoluble in water and form monolayer on the surface of water. The procedure is as follows: Nylon string is floated on deionized water to divide its surface into two regions. Then, benzene solution of a compound (concentration of about 5×10^{-3} mol/l) is dropped in one region. After the evaporation of benzene, oleic acid is dropped in the other region. This compound is called "piston oil" because it pushes the string at a constant pressure which makes the amphiphilic compound form a densely-packed monolayer. By dipping the substrate into the water through this layer followed by withdrawing it slowly, the monolayer was transferred to the substrate surface. For compound ⓕ, however, the monolayer was not formed by either method. Therefore, the following conventional method was used. The substrate was dipped into a 10^{-3} mol/l concentration of ethanol solution and then it was withdrawn at a rate of 3 mm/s. In this case, the adsorption of the compound ⓕ was ascertained by measuring the difference of contact angles[8] exhibited by a sessile water drop. The details of this method are described in Ref. 15.

Liquid crystal used in the experiment is BAB. Table III shows the results of the liquid crystal orientation for every combination of the substrates and amphiphilic materials.

Strength of porality of the substrates and the amphiphilic materials are also shown in this table by R-values. It is seen from this table that homeotropic alignments are induced when the polarity of both amphiphilic materials and substrates are strong.

TABLE III

Orientation of liquid crystal BAB on the substrate surfaces treated with various amphiphilic materials

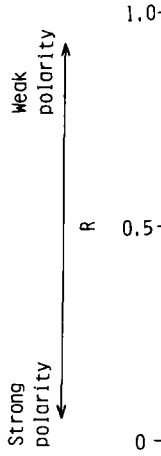


Next, the polarity of various oxide surfaces, soda-lime glass and heat-treated one (at 400°C for 60 min) was measured by using the liquid crystal-chromatography. All of the oxide materials used in this experiment were purchased from Tokyo Kasei Kogyo Co., Ltd. These materials were evaporated onto soda-lime glasses by electron-beam evaporation at a pressure of 5×10^{-6} Torr. Thickness of the film was 1000 ~ 3000 Å and evaporation rate was about 40 Å/s. Liquid crystal 50CB was used in this table. MgO, Al_2O_3 and In_2O_3 exhibits small R or strong polarity. The polarity of soda-lime glass becomes strong by heat-treatment. As mentioned previously, it is due to migration of sodium ions to the surface.

Liquid crystal orientation on these substrate surfaces was also investigated. Liquid crystals used in this experiment were BAB, *p*-methoxybenzylidene-*p*-*n*-butylaniline (MBBA) and *p*-heptylcyanobiphenyl (7CB). The results are shown in the right column in Table IV. It becomes clear that MBBA and 7CB with amphiphilic impurities align homeotropically to the surface with strong polality. Therefore, in order to obtain stable parallel alignment for these liquid crystals, polarity of the substrate surface must be weak enough. Therefore, in the actual liquid crystal cell, diffusion of sodium ions to the surface must be prevented and the polar ITO electrode must be covered with some material or weak polarity. In the usual commercial liquid crystal cells, SiO_2 is empirically used as the surface layer. This is because the polarity of SiO_2 is weak as shown in Table IV. By the way, CeO_2 and WO_3 are better materials than SiO_2 in the sense of weak polarity.

TABLE IV

Polarity of various surfaces and liquid crystal orientation on them



Oxide material	Liquid crystal orientation		
	BAB	MBBA	7CB
Au	∥	(∥)	(∥)
CeO_2	∥	(∥)	(∥)
WO_3	∥	(∥)	(∥)
SiO_2	∥	(∥)	(∥)
Soda-glass	∥	(∥)	(∥)
SnO_2	∥	(∥)	•
ZrO_2	∥	⊥	⊥
Heated-glass	∥	⊥	⊥
In_2O_3	∥	⊥	⊥
Al_2O_3	∥	⊥	⊥
Al	∥	⊥	⊥
MgO	∥	⊥	⊥

⊥ : Homeotropic, ∥ : Parallel
(∥) : Nearly parallel, • : Undistinguish

Finally, the mechanism of interaction between polar groups of amphiphilic materials and polar substrate surfaces is investigated.

First, the relationship between group dipole moment of the amphiphilic materials[15] and their R-values is examined. As shown in Table V, there is no relation between them, and hence it is found that dipole-dipole interaction is not dominant.

Next, correlation between IEPS (Isoelectric Point of Solid Oxide)[16] and R-values is examined. The IEPS is a parameter which indicates basicity of

TABLE V

Amphiphilic materials and their group dipole moment

Amphiphilic material	Group dipole moment[15]	R*	
ⓐ $C_{18}H_{37}N(CH_3)_3Cl$	—	0.00	Strong polarity
ⓑ $C_{18}H_{37}SO_3Na$	—	0.02	
ⓒ $C_{18}H_{37}NH_2$	1.5	0.43	
ⓓ $C_{17}H_{35}COOH$	1.6	0.86	
ⓔ $C_{18}H_{37}OH$	1.7	0.97	
ⓕ $C_{17}H_{35}CN$	3.5	1.00	

*Obtained by thin layer-chromatography (Adsorbent: acetone)

the surface and is defined as follows. When solid oxide with a surface hyderxy group is immersed in water, some part of the hydroxy group binds protons as shown in Figure 5a and some part of it dissociates into ions as shown in Figure 5c. The equilibrium depends on the basicity of the oxide and is shifted by changing pH-value. The IEPS is defined by pH at which the net surface charge is zero.

Figure 6 shows the relation between R-values of the oxide surface and their IEPS. It is seen from this figure that there is clear correlation between them. These results indicate that the adsorption is based on the acid-base interaction.

III. CONCLUSION

The effects of amphiphilic materials on the liquid crystal orientation on inorganic surfaces were investigated using the chromatographic effect.

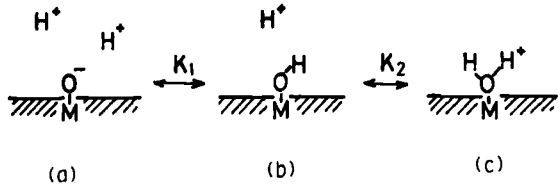


FIGURE 5 Surface structure of solid oxide in water.

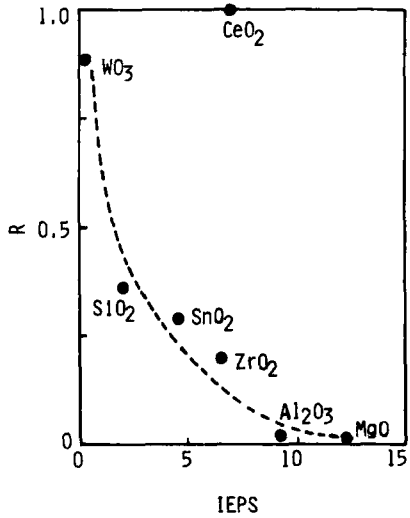


FIGURE 6 Relation between R-values and IEPS of the oxide surfaces.

From the results, it was found that the perpendicular alignment of liquid crystal on inorganic surfaces is due to the orientational adsorption of the amphiphilic impurity. In this case, the stronger the polarities of both substrate surface and amphiphilic impurity, the stronger the adsorbability becomes, and the tendency toward perpendicular alignment of the liquid crystal increases. Typical surfaces with strong polarity are In_2O_3, Al_2O_3 and MgO, and those with weak polarity are CeO_2 and WO_3.

Considering the results mentioned above, the stable homogeneous alignment is obtained by using stable liquid crystal material without amphiphilic impurities and/or covering the substrate surface with a material of weak polarity.

Finally, evident correlation between polarity and IEPS of various oxide surfaces was found, which indicates that the adsorption of amphiphilic materials on polar surfaces is based on the acid-base interaction.

APPENDIX: FLAME PHOTOMETRY OF SODIUM IONS

The compositional profile of sodium ions in the soda-lime glass before and after various treatments was measured as follows:

(1) Soaking the soda-lime glass in the 0.2 wt pct aqueous solution of HF and measuring the etched depth with a multiple beam interference microscope (Nippon Kogaku Co., Ltd.).

(2) Evaporating the water and HF completely, and then adding 10 cc of distilled water to the residual solid containing sodium ions to obtain an aqueous solution of the sodium ions.

(3) Analyzing the strength of D-spectrum of sodium ions in the solution by flame photometry (Shimazu Industry Co., Ltd.).

The quantity of sodium ions in the solution can be found by comparing the strength of the spectrum with that of standard solution. The measured concentration of the sodium ions in the solution corresponds to the sum of the sodium ions in the soda-lime glass from the initial surface to depth t. Denoting this value as $A(t)$, the sodium ion concentration $C(t)$ as a function of the depth t is given by

$$C(t) = \frac{dA(t)}{dt} \tag{1}$$

Therefore, $C(t)$ can be obtained from the inclination of the t dependence of $A(t)$. The result for an untreated soda-lime glass is shown in Figure 7a. The concentration of sodium ions at the surface is rather low compared to that of the bulk. This compositional profile agrees well with the results

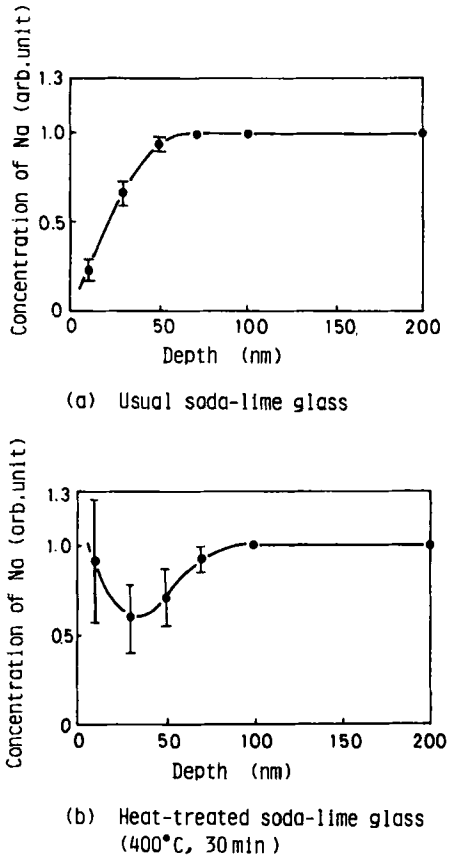


FIGURE 7 Compositional profile of sodium ions in soda-lime glass.

obtained by secondary ion microanalysis.[17] Figure 7b shows the results for heat-treated soda-lime glass (400°C, 30 min). In this case, the concentration of sodium ions increases at the surface which is considered to be due to migration of the ions from the bulk.

Acknowledgment

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