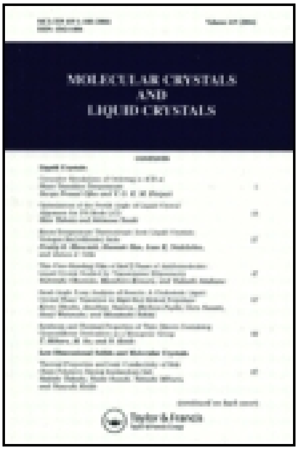

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Note on Electrodeposition of Metal in Electrochemical System Containing Nematogenic Compound

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Note on Electrodeposition of Metal in Electrochemical System Containing Nematogenic Compound†

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The electrodeposition of metal ion dissolved from the positive electrode on the negative electrode in a few nematic liquid crystal mediums under DC electric field was studied in this paper. The nematic liquid crystal compounds used were anysilidene—*p*-aminophenyl acetate and *p*-methoxybenzylidene—*p*′-*n*-butylaniline and *p*-cyano-*p*′-pentylbiphenyl, and the metals used as the positive electrode were Ag and Cu. The electrodeposition phenomena were observed in both nematic and isotropic phase of the medium. Plots of amount of Ag deposited against amount of electricity obeyed the Faraday equation, although the efficiency was only 7–26%.

INTRODUCTION

Various attempts to improve the properties of nematic liquid crystals for dynamic scattering (DS) displays have been done by many workers,[1-19] since the discovery of DS phenomenon.[1] In particular, it has been reported that dopants,[9-19] especially redox dopants,[9-16] are very useful in improving the dynamic scattering characteristics; the addition of dopant leads to the increase of conductivity anisotropy which lowers the threshold voltage and heightens the scattering levels, and to protracting the life time. On the other hand, the injection of metal ion from metal electrode itself have been little studied in the ne-

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matic liquid crystals medium to our knowledge, although most of the workers may be aware of this phenomenon. Because this phenomenon is a trouble problem on the DS display design, it seems to be studied mainly in a manufacturing step how to avoid this phenomenon. Actually this must be one factor of the lifetime in the display device, since the surface of electrode is spoiled by the metal electrodeposition. Recently we find that this phenomenon occurs intensely in some nematic liquid crystal cells as are described in this paper. The purpose of this paper is to report the electrodeposition of metal ion injected from the positive metal electrode on the negative metal electrode in the nematic liquid crystals medium under a direct-current (DC) electric field. The nematogenic compounds used are *p*-methoxybenzylidene—*p*′-*n*-butylaniline (MBBA), *p*-cyano-*p*′-*n*-pentylbiphenyl (CPB) and anisylidene—*p*-aminophenyl acetate (APAPA), and the electrode metals used are Ag, Au, Cu and Fe.

EXPERIMENTAL

MBBA was synthesized and purified by the same procedure as described previously.[20] CPB and APAPA were purchased from Merck Japan Ltd. and Tokyo Kasei Co. (Japan), respectively. APAPA was purified as follows; APAPA in benzene was washed thoroughly with 10% NaOH, and dried with anhydrous $CaCO_3$ for about 24 hours. The crystalline APAPA sample was recrystallized from *n*-hexane solution. The nematic temperature ranges were 21-47°C in MBBA, 23-35°C in CPB and 82-109°C in APAPA.

The electrodepositions of metal on the negative electrode were studied with various electrochemical systems designated as (negative electrode)metal| liquid crystal materials|metal(positive electrode) systems, under a nitrogen atmosphere. The above electrode system consisted of two parallel glass plates on which metal was deposited in vacuum. No other surface treatment was performed on the electrodes. Teflon spacer of 0.010 to 0.050 cm thick was packed between them. Measurements of DC current between the electrodes under various DC electric potentials were carried out with TOA CDR 12 Recorder with Function Unit (Type FU-36A) of Toa Electrics Ltd. (Japan). The amount of Ag/Cu deposited on the negative electrode in the (−)metal|liquid crystal materials|Ag/Cu(+) system was determined by the atomic absorption method.

RESULTS AND DISCUSSION

Variation of current with operation time under applied DC electric field was measured in several electrochemical systems containing nematogenic compound. The current intensity increased with time from the operation time of about a few minutes and leveled up during a few ten minutes. Then, the electrodeposition of metal on the negative electrode was observed. For example, we obtained a uniform and strong silver plating on the Au-electrode by applying the DC potential of 400 V/cm at 105°C for 30 minutes in the (−)Au| APAPA| Ag(+) system. The specific conductivities at the stationary state of electrodepositing in several systems are listed in Table I.

Figure 1 shows plots of logarithm of amount of Ag deposited, m, against logarithm of amount of electricity, $\int_0^t I dt$. Here, I is a current intensity at an operation time, t. Since the plots give a straight line with the slope of 1, they satisfy apparently the Faraday equation,

$$m = k \int_0^t I dt,$$

where k is the electrochemical equivalent.

Therefore, this electrodeposition phenomenon must be explained by an electrochemical process—a formation of Ag^+ (perhaps, liquid crystal molecule-Ag^+ complex) by a reaction at the positive Ag-electrode, its migration in the medium towards the negative electrode, and its charge transfer and deposition on the negative Au-electrode.[21] The efficiencies of electrodeposition in several systems are listed in Table I. The efficiencies are 7–26%. These low efficiencies can be caused by an existence of organic ions which would arise from an electrochemical decomposition of liquid crystal compound and/or impurities.[1-8]

TABLE I

Efficiencies of electrodeposition in several systems.

System	Efficiency %	Operation condition	Conductivity at the stationary state of electrodepositing $\times 10^{-9}$ ohm^{-1}·cm^{-1}
(−)Au|APAPA|Ag(+)	7	(a)	4.0
(−)Fe|APAPA|Ag(+)	7	(a)	2.0
(−)Au|APAPA|Cu(+)	10	(a)	3.5
(−)Au|CPB|Ag(+)	20	(b)	4.3
(−)Au|CPB|Cu(+)	18	(b)	0.38
(−)Au|MBBA|Ag(+)	24	(c)	0.55
(−)Fe|MBBA|Ag(+)	26	(c)	0.12
(−)Au|MBBA|Cu(+)	17	(c)	1.0

(a) Applied field: 400 V/cm, Electrode distance: 0.010 cm, Temperature: 93°C (nematic phase).

(b) Applied field: 400 V/cm, Electrode distance: 0.018 cm, Temperature: 28°C (nematic phase).

(c) Applied field: 800 V/cm, Electrode distance: 0.010 cm, Temperature: 65°C (isotropic phase).

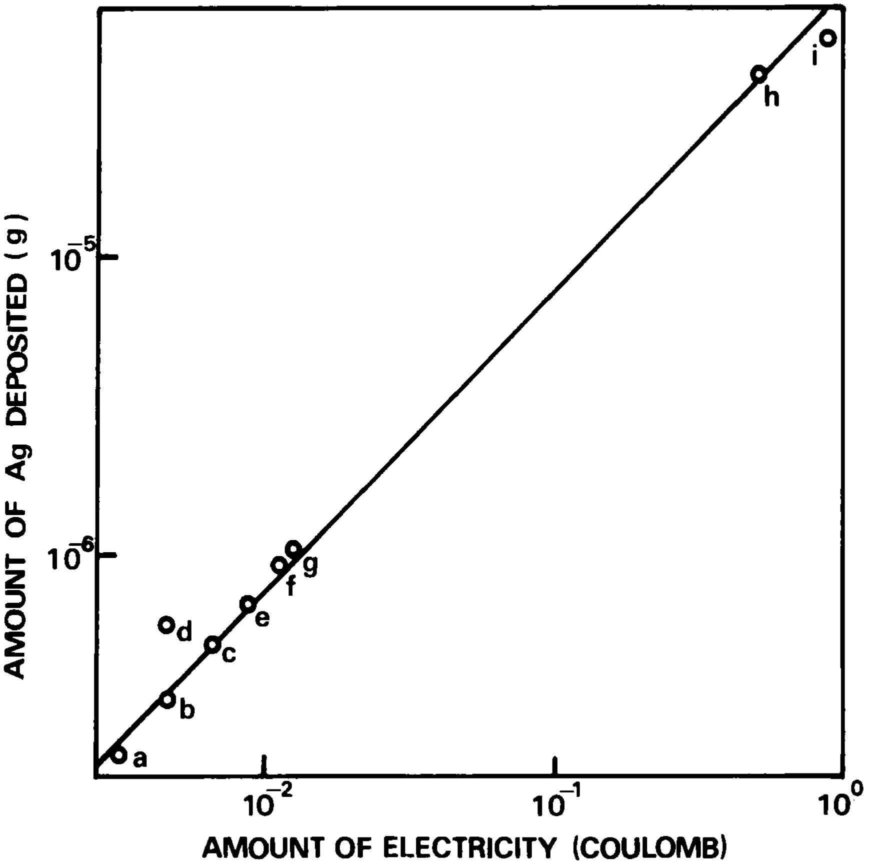

FIGURE 1 Plots of logarithm of amount of Ag deposited versus logarithm of amount of electricity under the potentiostatic field of 400 V/cm in (−)Au |APAPA| Ag(+) system. Operation temperature, a: 85°C, b: 93°C, c: 101°C, d: 107°C, e: 93°C, f: 107°C, g: 115°C, h: 120°C, i: 90°C, a–f and i: nematic phase, g and h: isotropic phase.

The electrodeposition was observed in both nematic and isotropic phases of liquid crystal materials, but not in the solid phase.

In conclusion, we observed that the electrodeposition of metal ion injected from the positive electrode on the negative electrode occurs intensely, when Ag or Cu was used as the positive electrode. Further studies on electrodeposition of metal in other systems and the mechanisms are going on in our laboratory.

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