Ion-Pair Extraction by Use of Liquid Crystals as Extracting Solvent

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By using a liquid crystal, 4-cyano-4'-hexylbiphenyl (abbreviated as CHB), as an extracting solvent, the following ion-pair extraction reaction was investigated: $(Q \cdot ClO_4)_o + (Pi^-)_w \rightleftharpoons (Q \cdot Pi)_o + (ClO_4^-)_w$ (Q^+: cationic species such as Crystal Violet (CV^+), Methylene Blue (MB^+) and tetrabutylammonium (TBA^+); Pi^-: picrate anion; subscripts o and w denote organic and aqueous phases, respectively). The above extraction equilibrium was confirmed to hold in the case of a liquid crystal (CHB) solvent as well as in an ordinary solvent (hexylbenzene/cyanobenzene 1:1 mixture for comparison; abbreviated as MIX). The dependence of the extraction constant on the temperature was investigated. Only in the CV^+-CHB system, the extraction constant discontinuously changed around a phase transition temperature of CHB (29°C; nematic/liquid). When an MIX solvent was used, such a phenomenon was not observed; the extraction constant gradually increased with an increase in temperature. The effect of the molecular orientation of the extracting solvent is discussed.

Keywords   Ion-pair extraction, extracting solvent, liquid crystal, phase transition

Liquid–liquid extraction of the ion-pair association complex (ion-pair extraction) is widely used in analytical and separation chemistry.[1-3] The effect of the extracting solvent on the extractability has been one of the major subjects in studies concerning ion-pair extraction, and has usually been discussed in terms of solvent polarity, solubility parameter, and/or hydrogen-bonding power.[4-10]

However, the influence of the molecular shape and orientation of the solvent has not yet been studied.

Anisotropic liquids, such as liquid crystals, have not been used in ion-pair extraction reactions. A carrier-mediated liquid membrane transport has been reported which involves a polymer/liquid crystal composite membrane, being capable of thermocontrolling the transport rate via a solid–liquid crystal phase transition.[11] However, the phase transition phenomena between the liquid crystal and an isotropic liquid have not yet been dealt with in solvent extractions and related studies.
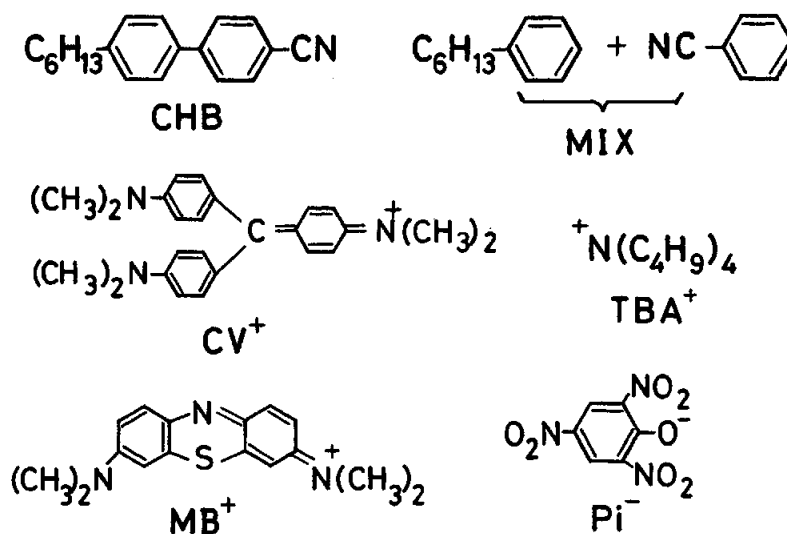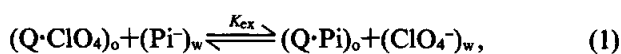

Fig. 1   Structures of solvents and ionic species used in this study.
CHB, 4-cyano-4'-hexylbiphenyl; MIX, hexylbenzene/cyanobenzene
1:1 mixture; CV^+, Crystal Violet; TBA^+, tetrabutylammonium; MB^+,
Methylene Blue; Pi^-, picrate.

In this study, we investigated the following extraction reaction by the use of liquid crystal as an extracting solvent:

$$(Q \cdot ClO_4)_o + (Pi^-)_w \xrightleftharpoons{K_{ex}} (Q \cdot Pi)_o + (ClO_4^-)_w, \quad (1)$$

where Q^+ and Pi^- represent a cationic species (Crystal Violet (CV^+), Methylene Blue (MB^+), and tetrabutylammonium (TBA^+)) and picrate anion, respectively, and subscripts o and w denote the organic and aqueous phases, respectively. As a liquid crystal, 4-cyano-4'-hexylbiphenyl (abbreviated as CHB) was used, which is a thermotropic liquid crystal in the nematic state around room temperature; the phase transition temperatures are 14°C (solid/nematic, T_{SN}) and 29°C (nematic/liquid, T_{NL}). The structutes of the solvents and ionic species used in this study are summarized in Fig. 1.

Experimental

Reagents

CHB (Merck) was purified by silica gel column chromatography (eluent: chloroform). Other chemicals were of reagent grade and were used without further purification.

Extraction procedure

An aqueous buffered solution (1 ml; 10 mM (M= mol/dm³) Na_2CO_3–$NaHCO_3$ buffer; pH 10) containing a 0.1 mM cationic species (CV^+ chloride, MB^+ chloride, or TBA^+ chloride), 0.1 mM sodium picrate, and 10 – 50 mM sodium perchlorate was shaken with an organic solvent (1 ml; CHB or mixed solvent (hexylbenzene/cyanobenzene 1:1; abbreviated as MIX)) for 18 h in a thermostated bath (15, 20, 25, 30, 35 or 40°C; ±0.1°C). After a phase-separation procedure was rapidly carried out, the concentration of the picrate in aqueous phase was determined by spectrophotometry (λ_{max}=358 nm) using a Hitachi 556 instrument.

Results and Discussion

Extraction equilibrium

The extraction constant, K_{ex}, of reaction Eq. (1) can be given as

$$K_{ex} = [Q \cdot Pi]_o [ClO_4^-]_w / [Q \cdot ClO_4]_o [Pi^-]_w. \quad (2)$$

Equation (2) can be rewritten logarithmically as

$$\log([ClO_4^-]_w / [Q \cdot ClO_4]_o)$$

$$= \log K_{ex} - \log([Q \cdot Pi]_o / [Pi^-]_w). \quad (3)$$

The distribution of the cationic species, such as MB^+ and CV^+, into the aqueous phase was confirmed to be

negligibly small when the extraction procedure was performed. Further, the concentration of perchlorate added to the aqueous phase was in large excess compared to that of other relatively lipophilic anions, such as chloride. Accordingly, when the extraction procedure is carried out, the reaction depicted in Eq. (1) is presumed to predominantly occur. Thus, $[Q \cdot Pi]_o$, $[Q \cdot ClO_4]_o$ and $[ClO_4^-]_w$ are given as follows:

$$[Q \cdot Pi]_o = [Pi^-]_{w,initial} - [Pi^-]_w, \quad (4)$$

$$[Q \cdot ClO_4]_o = [Q^+]_{w,initial} - [Q \cdot Pi]_o, \quad (5)$$

and

$$[ClO_4^-]_w = [ClO_4^-]_{w,initial} - [Q \cdot ClO_4]_o. \quad (6)$$

Therefore, the values of $\log([ClO_4^-]_w / [Q \cdot ClO_4]_o)$ and $\log([Q \cdot Pi]_o / [Pi^-]_w)$ in Eq. (3) can be derived experimentally.

Liquid crystal as an extracting solvent

Figure 2 shows a plot of $\log([ClO_4^-]_w / [Q \cdot ClO_4]_o)$ against $-\log([Q \cdot Pi]_o / [Pi^-]_w)$ in the extraction reactions performed at 25°C by use of a CHB solvent. Extraction reactions with the MIX solvent were carried out for a comparison, and the results are also indicated in Fig. 2; the solvent consists of hexylbenzene and cyanobenzene (1:1), which have fragmentary structures of the CHB molecule. All of the plots in Fig. 2 give straight lines with a slope of unity, suggesting that the reaction depicted in Eq. (1) is taking place exactly.

By considering the phase transition temperatures, CHB is in the nematic state at 25°C. Thus, the extraction equilibrium, Eq. (1) proved to hold under the
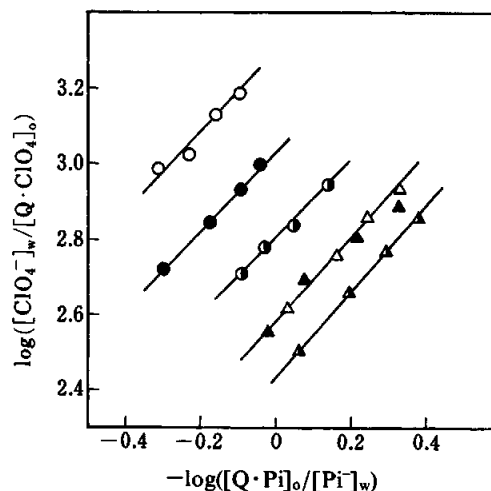

Fig. 2 Extraction equilibrium at 25°C. ○, CV^+-CHB; ●, MB^+-CHB; ◑, TBA^+-CHB; △, CV^+-MIX; ▲, MB^+-MIX; ▲, TBA^+-MIX systems (e.g., CV^+-CHB system means the extraction reaction Eq. (1) by use of CV^+ as Q^+ and of CHB as solvent).

liquid crystal state of the solvent as well as in the ordinary solvent.

Table 1 summarizes the extraction constants (log K_{ex}; at 25°C) derived from Eq. (3). The liquid crystal solvent

Table 1 Extraction constant at 25°C (log K_{ex})

Q^+	Extracting solvent	
	CHB	MIX
CV^+	3.3	2.6
MB^+	3.0	2.6
TBA^+	2.8	2.4

(CHB) tended to exhibit a higher extraction constant than the MIX solvent in all three systems of CV^+, MB^+ and TBA^+.

Temperature dependence of the extraction reaction

Figure 3 shows a plot of $\log([ClO_4^-]_w/[Q\cdot ClO_4]_o)$ against $-\log([Q\cdot Pi]_o/[Pi^-]_w)$ ($Q^+=CV^+$) performed at various temperatures (15-40°C). Similar plots for the extraction reaction ($Q^+=TBA^+$) are indicated in Fig. 4. All of the plots in Figs. 3 and 4 are straight lines with a slope of unity. It was found that the extraction equilibrium did not change under the temperature conditions (15-40°C), *i.e.*, Eq. (1) holds both under the liquid crystal state of CHB and under the liquid state of CHB.

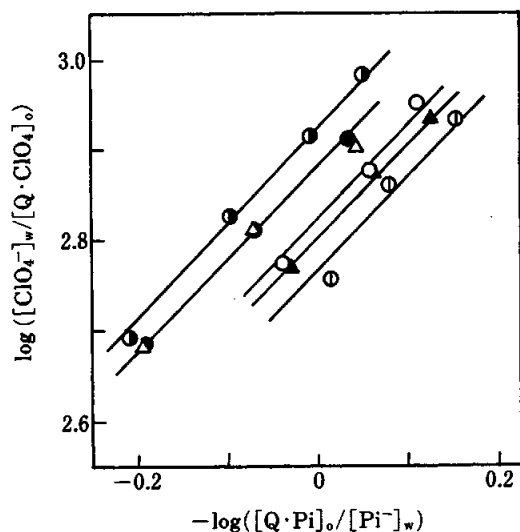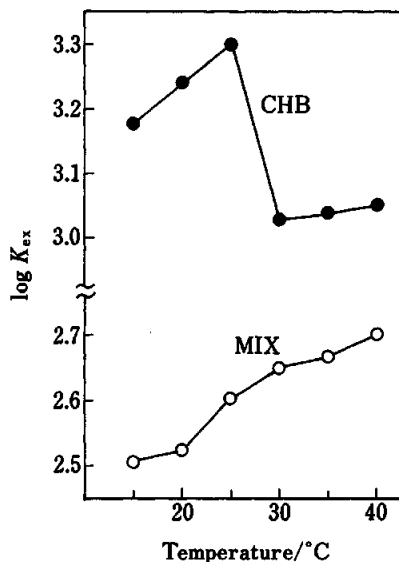Fig. 3 Extraction equilibrium (CV⁺-CHB system) at various temperatures. ①, 15°C; ▲, 20°C; ○, 25°C; ◑, 30°C; △, 35°C; ●, 40°C.

Fig. 4 Extraction equilibrium (TBA⁺-CHB system) at various temperatures. Symbols are the same as those in Fig. 2.

Fig. 5 Dependence of log K_{ex} on temperature ($Q^+=CV^+$). CHB (●) and MIX (○) were used as solvent.
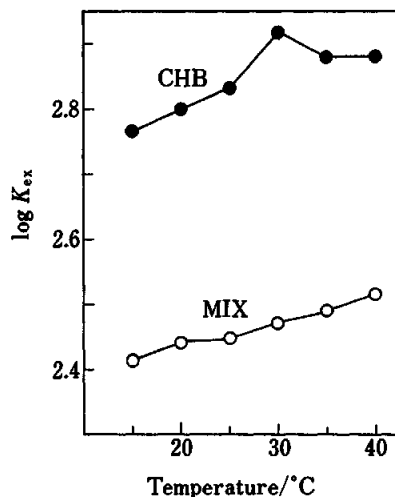

Fig. 6 Dependence of log K_{ex} on temperature ($Q^+=TBA^+$). CHB (●) and MIX (○) were used as solvent.
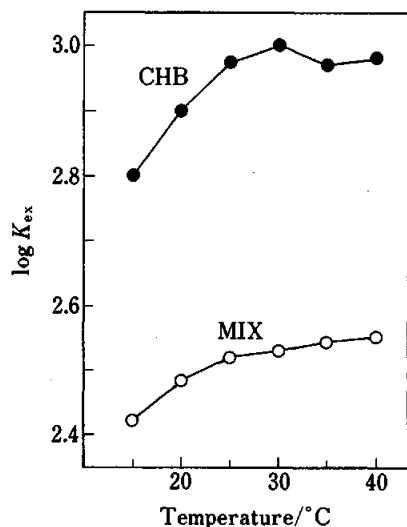
Fig. 7 Dependence of $\log K_{ex}$ on temperature ($Q^+=MB^+$). CHB (●) and MIX (○) were used as solvent.

The values of $\log K_{ex}$ in the CV^+-CHB system and in the TBA^+-CHB system are graphically summarized in Figs. 5 and 6 as a function of the temperature, respectively. In the case of the CV^+-CHB system (below T_{NL}; 15–25°C), the extraction constant gradually increased with an increase in the temperature, whereas a considerable depression in the $\log K_{ex}$ value was observed near T_{NL} (29°C). However, in the TBA^+-CHB system, such a depression in $\log K_{ex}$ was not observed; the extraction constant gradually increased between 15–30°C, while slightly decreasing above 30°C.

The temperature dependence of the extraction reaction, the MB^+-CHB system, was also investigated (Fig. 7)[12], indicating a similar behavior to that observed in the TBA^+-CHB system. Further, we investigated the temperature dependence of the extraction reactions by the use of a MIX solvent; Figs. 5, 6 and 7 additionally display the plots of $\log K_{ex}$ against temperature in the CV^+-MIX system, the TBA^+-MIX system and the MB^+-MIX system, respectively.[12] The extraction constants in these systems were slowly increased throughout all temperatures used.

Molecular orientation effect of the extracting solvent

In the case of the CV^+-CHB system, the extraction behavior were remarkably different from each other under the anisotropic liquid crystal state and under the isotropic liquid state (Fig. 5). It is considered that the phase transition of the solvent causes a destruction of the molecular orientation and a variation in the chemical and physical properties, such as the dielectric constant, leading to a change in the extraction constant. The extraction reaction, Eq. (1), is an anion-exchange reaction between spherical (in shape) perchlorate and plane (in shape) picrate. The extractability of picrate was higher in the liquid crystal state than in the liquid state. Further, as can be seen in Table 1, the CV^+-CHB

system exhibited a higher extractability compared to other systems. These results suggest that the highly plane shaped ion-pair complex, CV^+-picrate, favors liquid crystal state solvents to liquid state solvents.

In both the TBA^+-CHB system and the MB^+-CHB system, no distinct change in the extraction behavior was observed at T_{NL}; the extraction constant was gradually increased with an increase in the temperature, being almost constant above T_{NL} (Figs. 6 and 7). The ion-pair complexes formed with TBA^+ and MB^+ are considered to be less plane in shape than that with CV^+; this would account for the lack of distinct behavior change at T_{NL}.

When the MIX solvent was used, such a plateau part of the plot (above T_{NL}) was not observed, i.e., the increase in $\log K_{ex}$ continued throughout all temperatures (Figs. 5–7). Accordingly, it seems adequate that, even in the TBA^+-CHB system and the MB^+-CHB system, the effect of the phase transition of the solvent exists to some extent.

In this study, by using a liquid crystal as the extracting solvent, we have verified the effect of the molecular orientation of a solvent on the ion-pair extraction reaction. Anisotropic liquids, such as liquid crystal, have not been used in solvent extraction studies. Rather little consideration has been given to the structural aspects of the extracting solvent, such as the effects of molecular shape and orientation. Obviously, the novel-type solvent effect presented in this study may open a new possibility in solvent extraction chemistry (e.g., thermocontrol of the extractability), which certainly deserves further exploration.

References

1. K. Tôei, *Anal. Chem.*, 3, 479 (1987).
2. H. Green, *Talanta*, 20, 139 (1973).
3. K. L. Cheng, K. Ueno and T. Imamura, "*Handbook of Organic Analytical Reagents*", CRC Press, Boca Raton, 1982.
4. R. Diamond and J. Bucker, *J. Phys. Chem.*, 69, 1565 (1965).
5. W. Müller and R. Diamond, *J. Phys. Chem.*, 70, 3469 (1966).
6. H. Freiser, *Anal. Chem.*, 41, 1354 (1969).
7. T. Higuchi, A. Michaels and J. H. Rytting, *Anal. Chem.*, 43, 287 (1971).
8. H. M. N. H. Irving and R. H. Al-Jarrah, *Anal. Chim. Acta*, 63, 79 (1973).
9. E. Iwamoto, K. Ito and Y. Yamamoto, *J. Phys. Chem.*, 85, 894 (1981).
10. A. Ohki, X-L. Xiao, Y. Fujino and M. Takagi, *Anal. Sci.*, 2, 293 (1986).
11. S. Shinkai, K. Torigoe, O. Manabe and T. Kajiyama, *J. Am. Chem. Soc.*, 109, 4458 (1987).
12. It was confirmed in several runs that the extraction equilibrium, Eq. (1), exactly occurred.