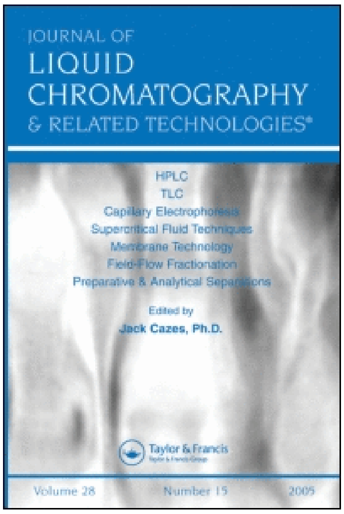

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LIQUID-MEMBRANE TRANSPORT OF RARE EARTH METAL IONS FACILITATED BY DI(2-ETHYLHEXYL) PHOSPHORIC ACID: COMPARISON WITH THE RESULTS OF CORRESPONDING CENTRIFUGAL PARTITION CHROMATOGRAPHY

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ABSTRACT

Selective liquid-membrane transport of rare earth metal ions were found to be effectively attained by the use of di(2-ethylhexyl)phosphoric acid (D2EHPA) carrier. This finding was obtained on the basis of the idea that liquid-membrane transport phenomena would be basically correlated with those of "separator-aided centrifugal partition chromatography", a separation technique based on the counter-current continuous extraction method. For the rare earth metal ion samples direct comparison of liquid-membrane transport with the corresponding centrifugal partition chromatography by employing the same two-phase liquid systems both containing D2EHPA showed that a close parallelism in the results obtained with the two separation systems.

INTRODUCTION

The selective liquid-membrane transport (LMT) of rare earth metal (RE) ions is a challenging problem for developing new techniques for a variety of analytical tools including RE ion-selective sensors. Izatt, et al. have reported the liquid-membrane transport of Eu^{2+} ion with a crown-ether carrier.(1) The present article is referred to selective LMT of lighter RE metal ions with D2EHPA carrier, which was attained based on the corresponding counter-current type chromatographic behaviors.

Recently we developed a technique of "carrier(or separator)-aided centrifugal partition chromatography (CPC)",(2) which is an extension of centrifugal counter-current continuous extraction method.(3) The classical counter-current distribution method(4) has been developed as continuous extraction technique in which a mixture of sample solutes distributes between two immiscible liquid phases (solvents) simply by the difference in partition coefficients. However, when a separating reagent or a carrier compound added in the stationary liquid phase of the centrifugal partition chromatography (CPC) plays a crucial role for the separation in problem, the chromatography becomes to have an fundamental common aspect with the LMT system(5) in view of that both of these separation systems involve the following chemical process (eq 1)(6,7):

$$\begin{tikzcd} S + Y \arrow[r] & {[S\text{---}Y]} \arrow[r] & Y + S \arrow[ll, bend left] \end{tikzcd} \qquad (1)$$

where, S denotes a sample molecule in CPC and a substrate molecule in LMT, Y is a separator in CPC or a carrier in LMT, and [S---Y] designates any type of interactions between S and Y leading to an effective separation or molecular recognition.

The "carrier(or separator)-aided CPC" can effectively be used when the sample components have identical or closely similar partition-coefficients for the two-solvent pair used. The example is that alkali metal picrates were able to separate(2) with a separator of benzo-crown ether which had been known as an effective carrier in selective LMT of the alkali metal picrates.(5)

The research field of LMT has been extensively developed in a past decade, but one frequently encounters difficulty for finding out an effective carrier for selective transport of neutral molecules or ions with larger size, and the researchers have been imposed to design complicated carrier molecules. Recently, on the basis of the result of CPC data, we achieved the selective transport of picric acid and p-nitrophenol by using a simple and costless compound of butan-1-ol.(6) At the same time we also proved(6) a direct correlation between CPC and LMT in the two liquid-phase system used.

More recently, we found that lighter rare earth metal ions can be effectively separated by CPC containing di(2-ethylhexyl)phosphoric acid (D2EHPA) as separator.(8) Hence, in the present work we applied the same liquid system to LMT aiming to test the selective transport of RE^{3+} ions with this costless carrier molecule of D2EHPA.

Fundamental Aspects of Relation Between CPC and LMT:

Actually there is a common chemical behavior of eq. 1 between LMT and CPC. However, when the mechanistic difference between LMT and CPC (Figure 1) is considered, the results of LMT and CPC are expected to be more complex as summarized in TABLE 1.(7) In TABLE 1 it is assumed, for simplification, that partition effects of the solvent are completely negligible: no transport

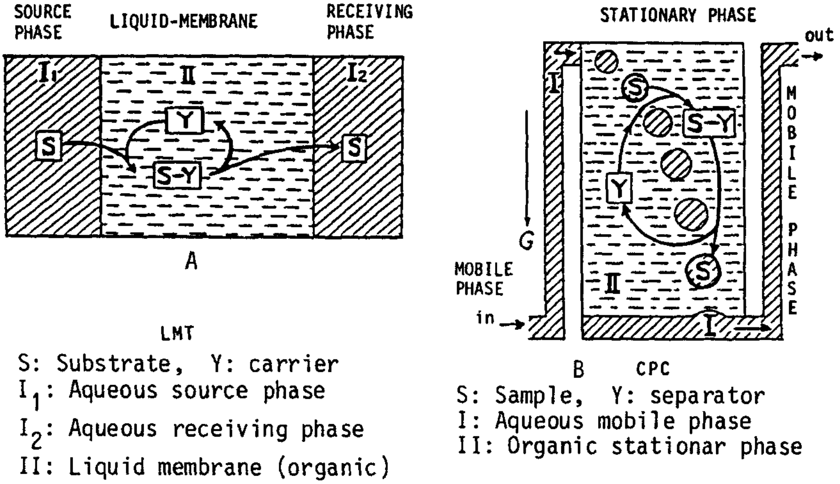

Figure 1. Fundamental illustrations of LMT and CPC. For simplification only shown are the systems of organic phases as liquid-membrane and stationary phase. A: LMT system with aqueous source and receiving phases. B: CPC system with aqueous mobile phase in a descending mode.

TABLE 1. GUIDE-LINE TABLE FOR PREDICTING THE RESULTS OF CPC AND LMT ON THE BASIS OF PHASE TRANSFER PROCESSES.(7)

	Phase Transfer Processes		CPC	LMT
No.	(in) aq. org.	(out) org. aq.	(Retention Value)	(Rate of Transport)
1	no	----	very low	no transport
2	ready	ready	low	high
3	ready	difficult	high(tailing)	low
4	difficult	ready	low(leading)	low
5	difficult	difficult	very broad peak	very low
6	interphase only	----	high or low (depends on the partition coefficient)	no transport

through a liquid-membrane occurs in the absence of the carrier molecule, and retention volume of the sample agrees with the value of the dead volume if a stationary phase containing the solvent alone is used in the corresponding CPC. Hence, we also assume that the results of LMT (as rate of transport) and CPC (as retention time) solely depend on the interaction equilibria in the formation and dissociation of the [S---Y] state, and that the phase-transfer processes involved in both systems depend only on these equilibria. (For practical comparison of the data of LMT with CPC, the interaction equilibria are conventionally and roughly designated as "ready" and "difficult", and "rapid" and "slow" instead of more correct descriptions of "small or large equilibrium constants".)

As can be seen from the TABLE 1, the results of LMT and CPC will correlate well in the cases-2 and -3. The examples of these cases are behaviors of alkali metal picrates with crown ether(1) and of nitrophenols with butan-1-ol.(6) However, in the other cases-1, -4 and -5 the correlation between LMT and CPC data will not be straightforward. In our preliminary tests stronger [S---Y] interactions such as acid-base interaction as for dl-mandelic acid (S) with brucine (Y) was found to be the case-3 with significant peak-broadening in CPC.(9)

Since the interaction of the RE ions with D2EHPA is a type of acid-base interaction (eq 2) and significant peak broadening was observed in CPC,(8) we supposed the behavior in these substrate/carrier pairs might be classified into the case-3 or -4.

$$3(HG)_2 + RE^{3+} \rightleftharpoons RE(HG_2)_3 + 3H^+ \qquad (2)$$

$$G = (\text{2-ethylhexyl-O})_2P(=O)OH$$

If it is the case-3, it seemed possible to realize selective transport of the RE ions by LMT with D2EHPA carrier, but if it is the case-4 only slow transport would be observed. Further, if there are other factors other than eq 1, correlation between LMT and CPC might be much complicated. Then, we tested the LMT of RE ions by the use of the same two-liquid phase systems as used in the preceding work on CPC separation of RE ions.(8)

EXPERIMENTAL

Materials:(8) Lighter rare earth (RE) metal ions were obtained from commercial suppliers and used without further purification: $LaCl_3 \cdot 7H_2O$ (Wako, first grade), $CeCl_3 \cdot 7H_2O$ (Wako, >98%), $PrCl_3 \cdot 7H_2O$ (Kanto, first grade), $NdCl_3 \cdot 6H_2O$ (Wako, >97%), $SmCl_3 \cdot 6H_2O$ (Nakarai, first grade) and $EuCl_3 \cdot 6H_2O$ (Nakarai, extra pure grade). Di-(2-ethylhexyl)phosphoric acid (D2EHPA) (Nakarai, 99%), n-heptane (Nakarai, extra pure grade), xylenol orange (Wako, analytical grade) and hexamethylenetetramine (Wako, extra pure grade) were used without further purification. Deionized water was used throughout the experiments.

Apparatus: For analysis of RE ions a Hitachi Spectrograph Model 200-20 was used, and pH measurements were carried out with a Horiba pH meter Model H-7LD. Centrifugal partition chromatography was performed as in the case of the preceding paper(8) by using a Centrifugal Partition Chromatograph-L.L. Model NMF (Sanki Engineering, LTD) apparatus with cartridges of Model 240W.

Liquid membrane transport procedures: A double-cylinder glass apparatus (Figure 2) was designed for liquid-

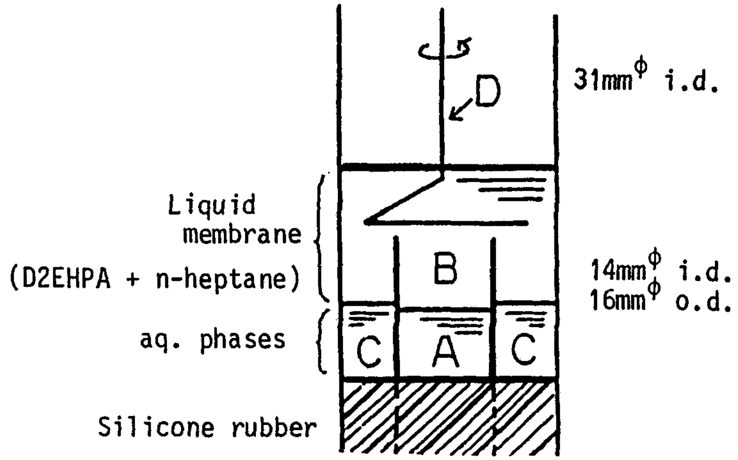

Figure 2. LMT apparatus for upper liquid-membrane system.

membrane transport experiments in which liquid-membrane is the upper organic layer (15 ml, 0-0.10M D2EHPA in n-heptane) and source (containing 3-30 mM $RECl_3$) and receiving phases are constructed in the two lower aqueous layers (each 5 ml, 0.01-0.20M aq.-HCl), respectively. The upper layer was stirred (ca. 150 rpm) at the top of the layer at room temperature with a stainless-steal stirring bar connected with a Yanako electrode-head motor (Model P10-RE) which was rotated by a variable-rotation motor Model K-1033 (TOP, LTD).

Analysis of RE ions in aqueous fractions: Analysis of RE ions in the source and receiving phases were carried out at 5 min's intervals as described in the preceding paper.(8) From each fraction 2 ml-aliquots were taken, and aqueous solutions of 5.60 x 10^{-4} M xylenol orange (XO)(1 ml) and 0.5 M hexamethylenetetramine hydrochloride buffer (2 ml) were added, resulting in 5 ml of aqueous solutions of pH 5.6 containing 1.12 x 10^{-4} M of XO and 0.2 M hexamine buffer. Concentrations of the RE ions thus color-developed were determined from the intensities of absorption spectra at 420 nm(10), by comparing with the pre-calibrated values.

Chromatographic procedures:(8) Three cartridges (Model 240W: high resolution type) containing 400 microcells per cartridge were equipped in series (total 1200 microcells). A 0.1M D2EHPA solution of in n-heptane (total ca. 40 ml n-heptane containing 1.3 g of D2EHPA) was used as stationary phase, and and a given concentration of aqueous HCl solution (mobile phase, elution speed (1.12 ± 0.02 ml min^{-1})) was pumped through the microcells in a descending fashion under centrifugal force (800 rpm). The sample (0.54 ml) was charged through the sample injecting valve. Analytical procedures of RE ions were identical with those employed in the liquid-membrane transport experiments.

RESULTS AND DISCUSSION

LMT of Rare Earth Metal Ions Under Constant Initial HCl Concentration:

When n-heptane solvent alone was used as the liquid-membrane without D2EHPA, no transport was observed for all of the RE ions. Namely, the transport of the RE ions was confirmed to be facilitated only when the substrates interact with this carrier compound in the liquid-membrane.

In principle, the effect of carrier concentration can be dual: [1] at high concentration of D2EHPA in n-heptane the rate of transfer from aqueous source phase

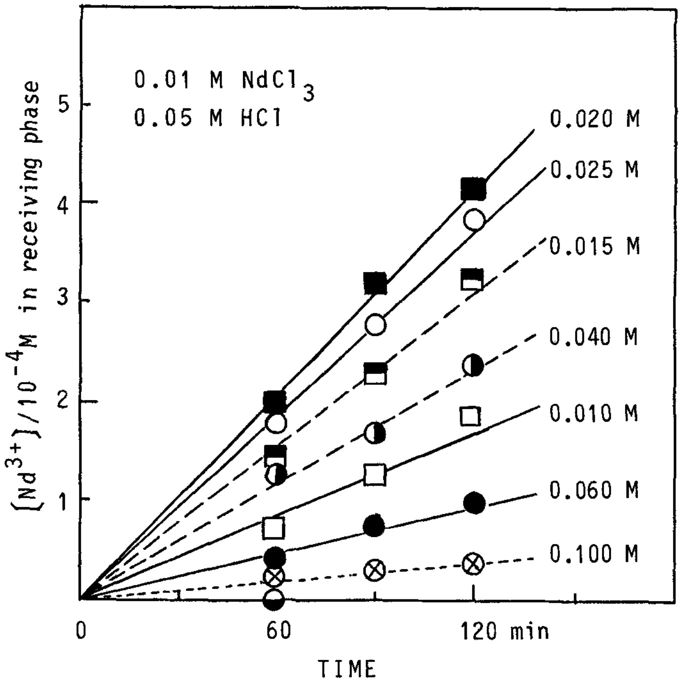

Figure 3. Effect of carrier concentration on the time-profile of transport of $NdCl_3$. $NdCl_3$: 0.01 M in 0.05 M aq.-HCl. Liquid-membrane: D2EHPA in n-heptane.

to liquid-membrane will be increased, resulting in higher rate of transport. [2] But, when excess amounts of carrier are present, the rate of transfer from the organic phase to the aqueous receiving phase will be decreased, leading to lower transport rate. By using 0.01 M $NdCl_3$ in 0.05 M aq.-HCl solution as a typical substrate, the effect of carrier concentration on the transport rate was tested (Figure 3). The apparent rate (V) of transport were estimated from slopes of the time profiles of Figure 3, and they are plotted against the

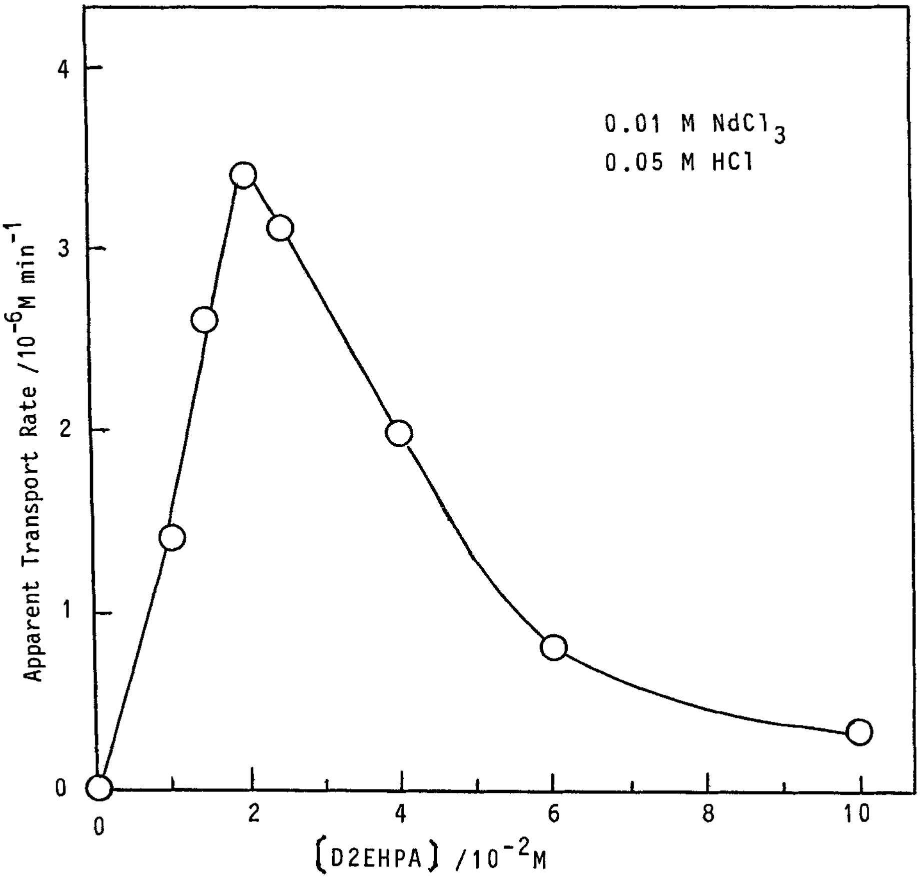

Figure 4. Plot of apparent rates (V) vs. carrier concentrations for $NdCl_3$ (cf. Fig. 3).

carrier concentrations (Figure 4). From these results the optimum carrier concentration was established as 0.02 M.

Rate of transport of a substrate through a liquid-membrane also depends on the initial concentration of substrate in the source phase. In general, the higher rate is attained with the higher substrate concentration. For the case of $NdCl_3$ in 0.05 M aq.-HCl solution the relation between the rate of transport and the initial substrate concentration was found as illustrated in Figure 5. The result of Figure 5 suggests that the substrate concentrations higher than 0.01 M cause a rapid saturation of the substrate in the liquid-membrane and it exceeds the ability of the system to give a smooth diffusion from the organic phase to the receiving aqueous phase, resulting in unexpectedly large fluctuations of the rate data. Hence, we chose 0.01 M substrate concentration (the turning point in Figure 5c) as an optimum.

Dependence of Initial HCl Concentrations in the Source Phase on the Transport Rate of RE Metal Ions:

In view of the chemical mechanism of interaction between RE^{3+} ions with D2EHPA (eq 2), transport behaviors in our system were expected to depend on the initial concentration of HCl in the aqueous source phase. Concentration of HCl in aqueous phase was, in fact, also the key factor in the CPC of RE^{3+} ions by employing the corresponding two-phase system.(8)

As expected, our LMT systems were strongly affected by the concentration of HCl in the source phase (Figure 6). With 0.01 M HCl the transport rates of all RE^{3+} ions were very low and a slight selectivity was observed only for La^{3+} (Figure 6a,b). However, with 0.05 M HCl the rates increased significantly for Nd^{3+}, Pr^{3+} and Ce^{3+} ions, and less extents for Sm^{3+}, La^{3+} and Eu^{3+} ions (Figure 6c,d). With 0.10 M HCl the transport rates of La^{3+}, Ce^{3+}, Pr^{3+} and Nd^{3+} ions slowed down but those of Sm^{3+} and Eu^{3+} ions increased (Figure 6e,f). With 0.15 M HCl the behaviors of ions were somewhat modified from those shown in Figure 6e,f: the transport rate of Eu^{3+} ion was considerably higher than that of Sm^{3+} ion (Fi-

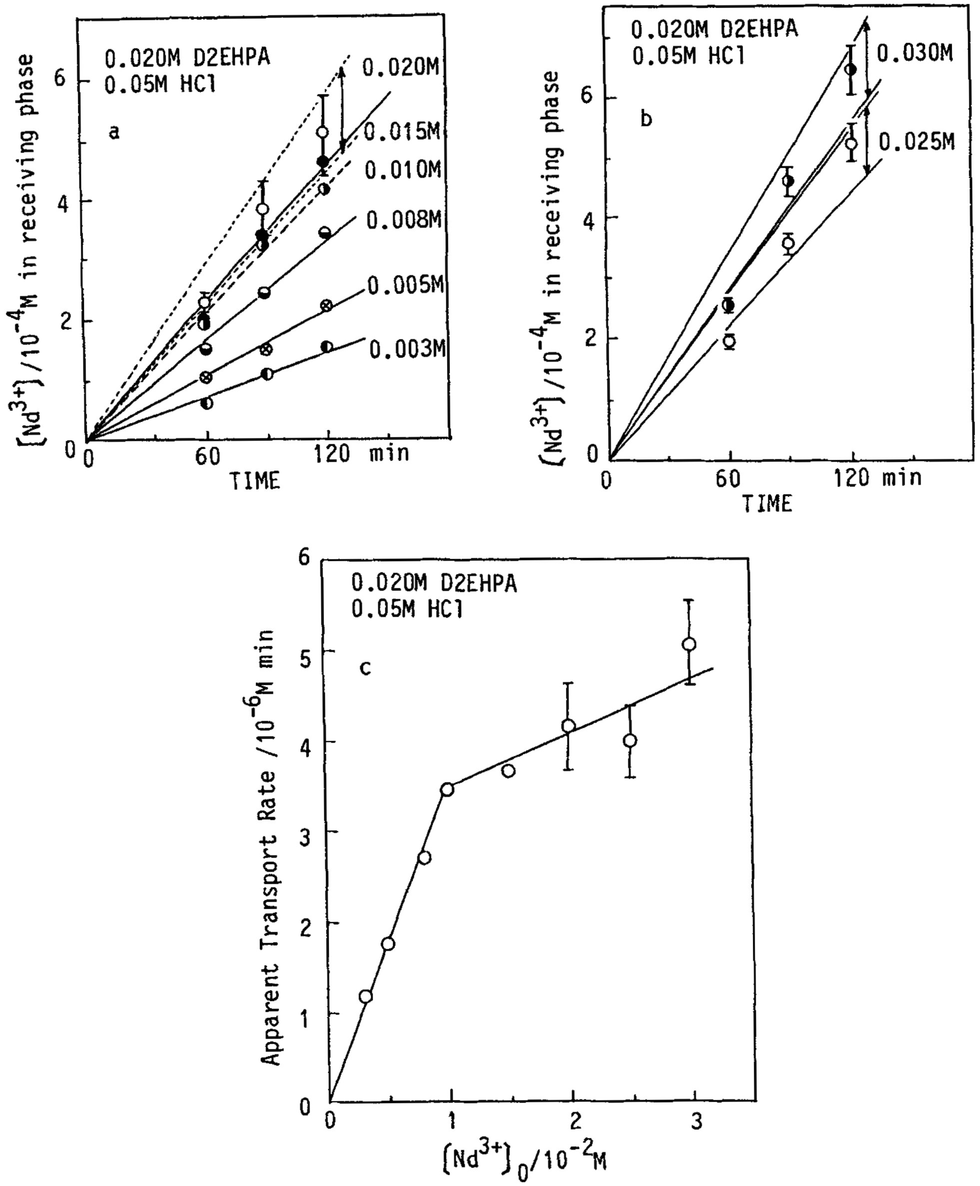

Figure 5. Effect of initial substrate concentration on the transport rate of $NdCl_3$. HCl concentration: 0.05 M, and carrier concentration in the liquid-membrane: 0.02 M in heptane. (a) Time-profile for 0.003-0.020 M. (b) Time-profile for 0.025-0.030 M. (c) Plot of apparent rates (V) vs. initial substrate concentrations.

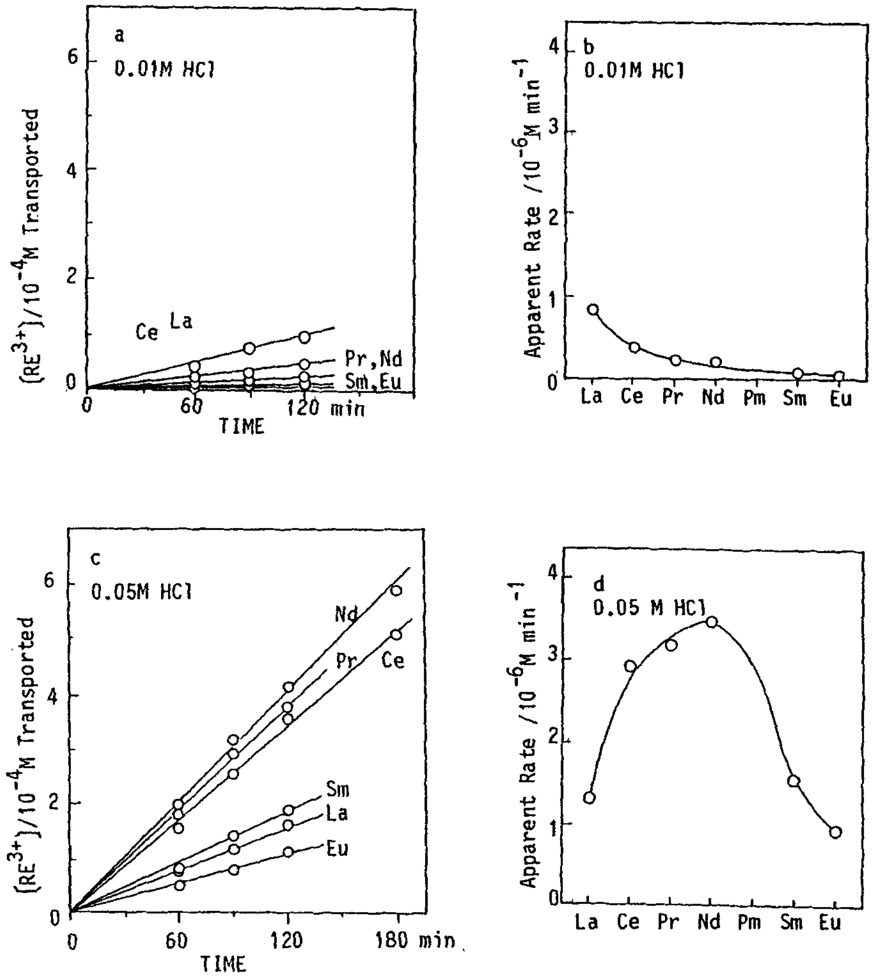

Figure 6. Effects of HCl concentration on the transport rates of a series of RE^{3+} ions. Carrier concentration in the liquid-membrane: 0.02 M in heptane. Substrate concentration: 0.01 M in aq.-HCl solution. (a), (c), (e), (g) and (i) show time-profiles, and (b), (d), (f), (h) and (j) show the corresponding apparent rates (V) vs. HCl concentration. (a) 0.01 M HCl. (b) 0.01 M HCl. (c) 0.05 M HCl. (d) 0.05 M HCl. (e) 0.10 M HCl. (f) 0.10 M HCl. (g) 0.15 M HCl. (h) 0.15 M HCl. (i) 0.20 M HCl. (j) 0.20 M HCl.

(continued)

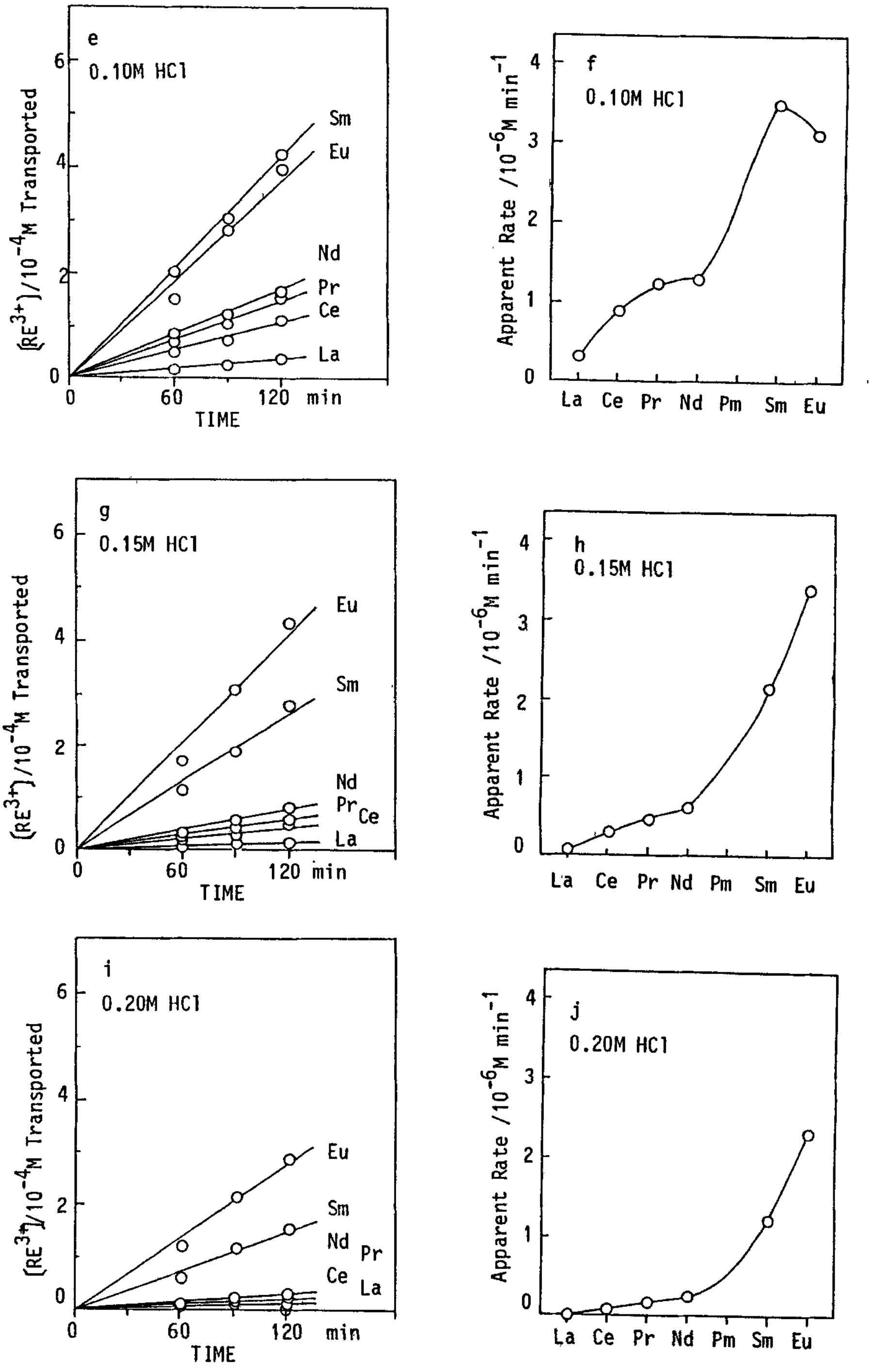

Figure 6 (continued)

TABLE 2. SELECTIVITIES IN LIQUID-MEMBRANE TRANSPORT FOR PAIRS OF RE^{3+} IONS.

	La	Ce	Pr	Nd	Sm	Eu
La	--	yes[a]	yes[a]	yes[a]	yes[b]	yes[c]
Ce		--	slight	slight	yes[b]	yes[c]
Pr			--	slight	yes[b]	yes[c]
Nd				--	yes[b]	yes[c]
Sm					--	yes[d]

With a) 0.05 M, b) 0.10-0.15 M, c) 0.15 M, d) 0.20 M aq. -HCl.

gure 6g,h). With 0.20 M HCl transport rates of all of the RE^{3+} ions decreased, but the selectivity of Sm^{3+} or Eu^{3+} ion from other RE^{3+} ions remained effective (Figure 6i,j). Figure 7 summarizes the dependences of transport rate on the HCl concentration for all of the RE^{3+} ions tested. Under these concentrations it is possible to realize selective transport for various pairs of RE^{3+} ions as summarized in TABLE 2.

Comparison of LMT with CPC for RE Metal Ions:

Our LMT results of RE^{3+} ions by using D2EHPA carrier in heptane indicate that La^{3+} is most effectively transported with 0.03 M HCl; Nd^{3+}, Pr^{3+}, and Ce^{3+} with 0.05 M HCl; Sm^{3+} with 0.10 M HCl; and Eu^{3+} with 0.15 M HCl, i.e., the optimum HCl concentrations for individual RE^{3+} ions increase roughly with the increasing order of atomic number of RE^{3+} metal ions (Figure 7).

In the preceding study we observed(8) that results of the corresponding CPC of the RE metal ions used here were well correlated with the corresponding extraction results.(11) And in many cases LMT behaviors have been shown to correlate with those of the corresponding extraction experiments. Our CPC results also showed that

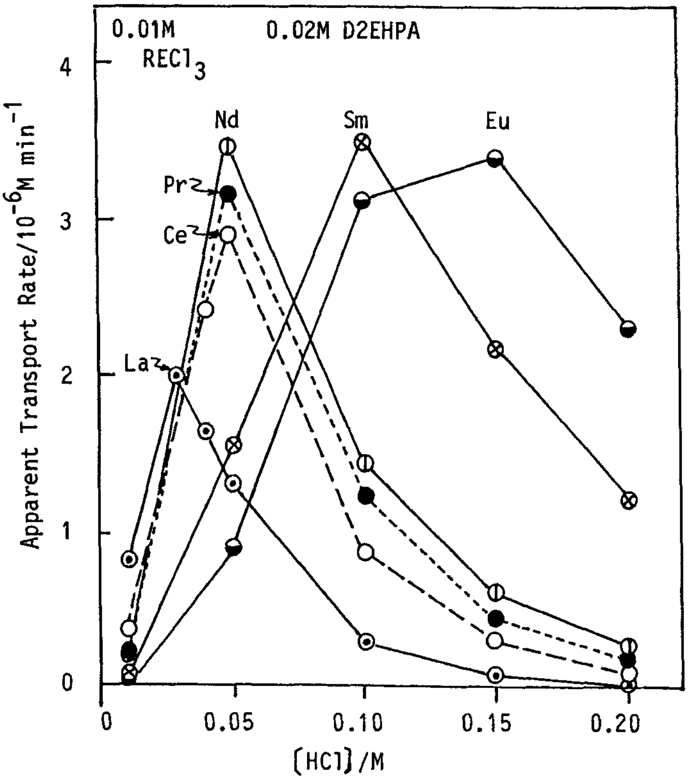

Figure 7. Summary of effects of HCl on the transport rates of a series of lighter RE^{3+} ions.

the optimum HCl concentrations was increased with the atomic number of RE^{3+} ions as shown in Figure 8. This behavior is well consistent with our present observations in the corresponding LMT systems.

The facts that no transport in LMT was observed without D2EHPA, and that no effective retention times were recorded in CPC in the absence of D2EHPA,(8) indicates that our LMT and the corresponding CPC systems satisfy the assumption of complete neglect of the partition effect due to the mother solvent. Namely, both the LMT and CPC systems examined are almost solely the results of interaction of [S---Y] in the organic phases.

Hence, we can conclude that the behaviors of RE^{3+} ions in the presence of D2EHPA belong to the case-3 of TABLE 1 as expected, and any other significant factors is not involved in the major parts of the phase transfer processes between the aqueous and organic phases. It is important that although significant peak broadening is observed in CPC (case-3), its direct application to the LMT systems leads to achievement of promising selective ion transport. In TABLE 3, relative transport rates obtained in the LMT system using n-heptane solution of D2EHPA and aqueous HCl solution are compared with the separation factors (α) obtained in the corresponding CPC. Both of the results show qualitatively parallel trends in selectivity of adjacent couples of RE^{3+} ions.

Then, it can be derived a further important prediction that many types of carrier compounds other than D2EHPA, which have been used in the related extraction

TABLE 3. COMPARISON OF RELATIVE TRANSPORT RATES (V(RE2)/V(RE1)) IN LMT WITH SEPARATION FACTORS (α) IN CPC.[a]

RE_1	RE_2	LMT[b]		CPC[c]	
		[HCl] (M)	$V(RE_2)/V(RE_1)$	[HCl] (M)	α
La	Ce	0.05	2.2	0.05	4.0 ± 0.1
Ce	Pr	0.05-0.10	1.2 ± 0.2	0.05	1.7
Pr	Nd	0.05-0.10	1.1 ± 0.1	0.06	1.4
Nd	Sm	0.10	2.4	0.12	9.2 ± 0.1
Sm	Eu	0.15	1.6	0.15	2.3

a) Organic phase: n-heptane solution of D2EHPA; Aqueous phase: aq.-HCl solution. b) 0.02 M D2EHPA. c) 0.10 M D2EHPA.(8)

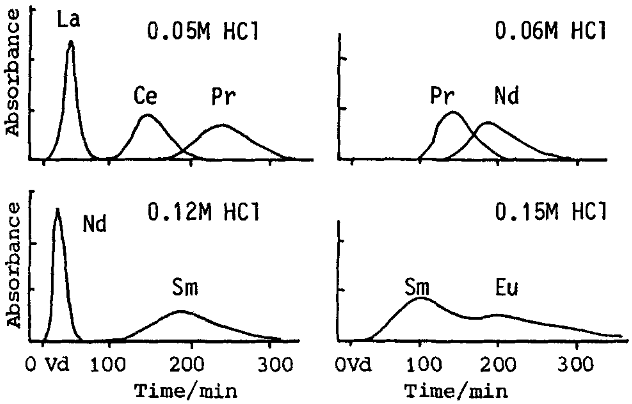

Figure 8. D2EHPA-aided CPC separations of lighter $RECl_3$ used in this report. Cited from the preceding report (ref. 8). Stationary phase: 0.1 M D2EHPA in n-heptane. Mobile phase: aq.-HCl solution. Centrifugation: 800 rpm at r.t. Elution: descending mode. Microcells: 400 x 3 = 1200.

procedures for refining RE ions, will be effectively applied to selective LMT techniques leading to some useful sensors for RE ions in future. Since several types of structurally simple and costless compounds have been used in the extraction techniques, it seems not always necessary to design the guest-recognizing host molecules having complicated structures, in cases of practical applications of LMT system are aimed.

More recently we have observed that the separation of Er^{3+} and Yb^{3+} (the 2nd heaviest RE metal) can be readily attained by CPC with D2EHPA in $CHCl_3$.(12) This means that the selective LMT of a series of heavier RE metal ions will also be realized relatively readily by the use of a liquid-membrane containing D2EHPA in $CHCl_3$. This study is now underway.

CONCLUSION

According to our idea that LMT and "separator-aided CPC" are basically correlated each other, selective LMT of lighter RE^{3+} ions were found to be attained with a simple and costless carrier of D2EHPA. In this case the considerably good correlation between CPC and LMT was observed. On extending our present observations it may be realized selective LMT of heavier RE metal ions including Er^{3+}/Yb^{3+} pair.

Since LMT and CPC techniques are based on the extraction behaviors, a variety of costless, simple and effective carriers can be used for sensing applications of LMT in future. This will cover the selective transport of a versatile molecular and ionic substrates which has been highly difficult with macrocyclic host carriers.

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REFERENCES

(1) Brown, P. R., Izatt, R. M., Christensen, J. J., and Lamb, J. D., Transport of Eu^{2+} in a H_2O-$CHCl_3$-H_2O liquid membrane system containing the macrocyclic polyether 18-crown-6, J. Membrane Sci., 13, 85, 1983.

(2) Araki, T., Kubo, Y., Toda, T., Takata, M., Yamashita, T., Murayama, W., and Nunogaki, Y., Carrier-aided centrifugal partition chromatography for preparative-scale separations, Analyst, 110, 913, 1985.

(3) (a) Murayama, W., Kobayashi, T., Kosuge, Y., Yano, H., Nunogaki, Y., and Nunogaki, K., A new centrifu-

gal counter-current chromatograph and its application, J. Chromatogr., 239, 643, 1982. (b) Itoh, Y., Weinstein, M. A., Aoki, I., Harada, R., Kimura, E., and Nunogaki, K., The coil planet centrifuge, Nature (London), 212, 985, 1966.

(4) Craig, L. C., and Craig, D., Technique of Organic Chemistry, Vol. 3, Interscience, New York, 1952.

(5) (a) Reusch, C. F., and Cussler, E. L., Selective membrane transport, AIChE J., 19, 736, 1973. (b) Wong, K. H., Yagi, K., and Smid, J., Ion transport through liquid membrane facilitated by crown ethers and their polymers, J. Membrane Biol., 18, 379, 1974.

(6) Araki, T., Kubo, Y., Takata, M., Gohbara, S., and Yamamoto, T., Selective liquid-membrane transport of nitro-phenols by a simple and costless carrier. An application of the results of centrifugal partition chromatography, Chem. Lett., 1987, 1011, 1987.

(7) Araki, T., Centrifugal countercurrent extraction method (Ensin koryu-bunpai Chushutu-hou), Kagaku (Chemistry), 41, 512, 1986.

(8) Araki, T., Okazawa, T., Kubo, Y., Ando, H., and Asai, H., Separation of lighter rare earth metal ions by centrifugal counter-current type chromatography with di-(2-ethylhexyl)phosphoric acid, J. Liquid Chromatogr., 11, 267, 1988.

(9) Araki, T., and Kubo, Y., Correlation between multistage liquid-membrane transport system and centrifugal liquid-liquid partition chromatography, Prepr. 1st. CPC Colloquium, Jan. 13, Kyoto, Japan, p.7, 1986.

(10) Ueno, K., Kireito Tekitei-hou (Chelate Titration Methods), Nanko-do, Tokyo, Kyoto, p.133, 1979.

(11) Pierce, T. B., Peck, P. F., and Hobbs, R. S., The separation of the rare earths by partition chromatography with reversed phases. Part II. Behaviour of individual elements on HDEHP-corvic columns, J. Chromatogr. , 12, 81, 1963.

(12) Araki, T., Okazawa, T., Kubo, Y., Asai, H., and Ando, H., Further results on behaviors of rare earth metal ions in centrifugal partition chromatography with di(2-ethylhexyl)phosphoric acid, J. Liquid Chromatogr., submitted.