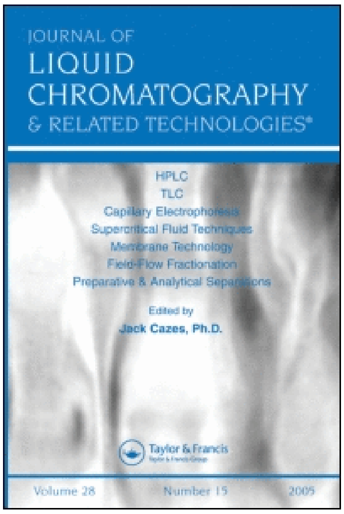

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LIQUID MEMBRANE TRANSPORT OF HEAVIER RARE EARTH METAL IONS BASED ON CPC RESULTS WITH DI(2-ETHYLHEXYL)PHOSPHORIC ACID

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ABSTRACT

The behaviors of heavier rare earth metal ions in bulk liquid membrane transport systems were examined for Gd^{3+}, Tb^{3+}, Dy^{3}, Ho^{3+}, Er^{3+}, Tm^{3}, Yb^{3+} and Lu^{3+} ions. The liquid membrane transport system was constructed by aq. HCl/$CHCl_3$ containing Di(2-ethylhexyl)phosphoric acid/aq. HCl. The optimum concentration of HCl in the aqueous phase with respect to the rate of transport for these ions increased with the atomic number of the rare earth elements. This trend of transport behaviors was on the same line observed for lighter rare earth ions in the preceding work. Difference in the rate of transport can be used for selective liquid membrane transport of several sets of combination with these ions.

INTRODUCTION

In the papers previously reported we have shown that the separator-(or carrier-)aided Centrifugal Partition Chromatography (CPC)(1) can be regarded as(2) a type of multistage liquid membrane transport (LMT) system. It is because the key processes in these techniques can be represented by a common equilibrium as described in eq. 1:(2-4)

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

where S denotes a substrate and a sample in LMT and CPC, respectively, and Y a carrier in LMT and a separator in CPC, respectively. The symbol [S----Y] represents the interacting states in the liquid membrane (LMT) or in the stationary phase (CPC).

This concept was tested for lighter series of rare earth (RE) metal ions, i.e., La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, and Eu^{3+}.(4) In the last study the LMT system was constructed by the two phase liquid system which was almost the same as used in CPC. Namely, the aqueous phase (the source and receiving phases in LMT, and the mobile phase in CPC) was HCl solution and the organic phase (the liquid membrane in LMT and the stationary phase in CPC) was n-heptane containing di(2-ethylhexyl)-phosphoric acid (D2EHPA). The results showed that the LMT and CPC were well correlated, and selective LMT was attained for several combinations of the lighter RE ions.(4)

In the preceding work(5) we examined the CPC behaviors of heavier RE ions (Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}, and Lu^{3+}) by using D2EHPA as separator in $CHCl_3$ stationary solvent. The CPC separation results (summarized in TABLE 1 of the ref. 5) indicated that

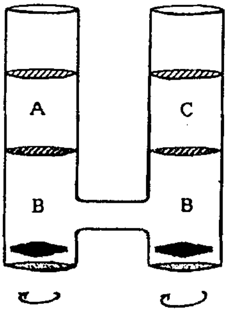

FIGURE 1. An H-type apparatus used in LMT experiments. A: source phase, B: liquid membrane, C: receiving phase.

there were considerably high values of separation factor ( ) for these RE ions.

This paper refers to the investigation of LMT behaviors of these heavier RE ions by the use of LMT system corresponding to the last CPC experiments.(5) The results indicate that there are several sets of RE combinations which can be used for selective LMT procedures such as ion sensing devices.

EXPERIMENTAL

Materials: The reagents used in this work were identical as described in the preceding paper.(5)

Apparatus: Detection of RE metal ions in the aqueous phase was carried out with a Shimadzu double beam spectrophotometer Model UV-180 and a Hitachi-Horiba pH meter Model F-7 II.

Liquid membrane transport procedures: An H-type glass apparatus (Figure 1) was immersed in a thermo-statted

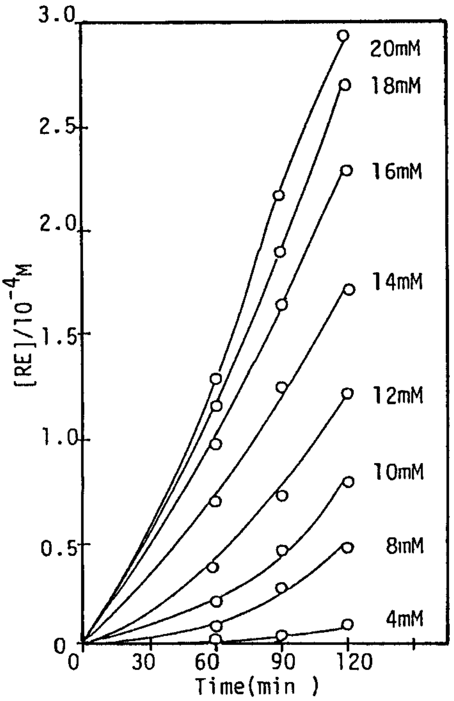

FIGURE 2. Effect of concentration of D2EHPA on the rate of transport of Ho^{3+} ion at 30°C. $[Ho^{3+}]$: 5 mM, [HCl] in aq. phases: 0.03 N.

bath, where the phases A (5 mL) and C (5 mL) are aqueous source and receiving phases containing HCl (0.01-0.20 N), respectively, and the phase B (15 mL) is the liquid membrane composed of $CHCl_3$ solution containing D2EHPA (2-20 mM) as carrier. The concentration of RE ions in the source phase was 1-10 mM. The liquid membrane phase was gently stirred (150 rev) by the aid of a Yanaco Rotating Electrode Head Model P10-RE equipped with a small magnet.

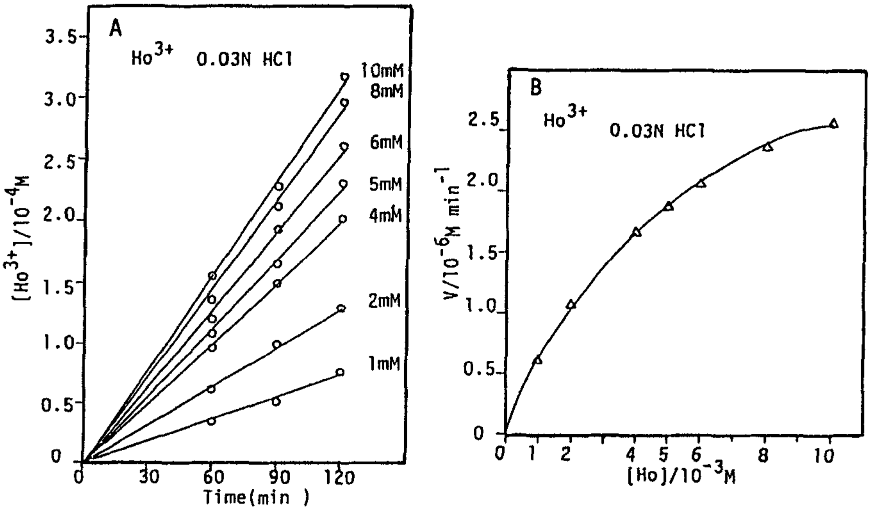

FIGURE 3. Effect of initial concentration of Ho^{3+} ion on the rate of transport. (a) $[Ho^{3+}]$ in the receiving phase vs. time. (b) Apparent transport rate constant vs. initial $[Ho^{3+}]$. [D2EHPA]: 15 mM, [HCl] in the aq. phases: 0.03 N.

The aliqots of the receiving aqueous phase were taken up after 60, 90, and 120 min, diluted and analyzed spectroscopically at 580 nm as described in the report of corresponding CPC.(5)

RESULTS AND DISCUSSION

The experiments of LMT were carried out by employing almost identical procedures as reported previously,(4) except for the use of an H-type apparatus and chroloform organic phase as liquid membrane. The constitution of the two liquid phase system was almost comparable to that of the corresponding CPC. Namely,

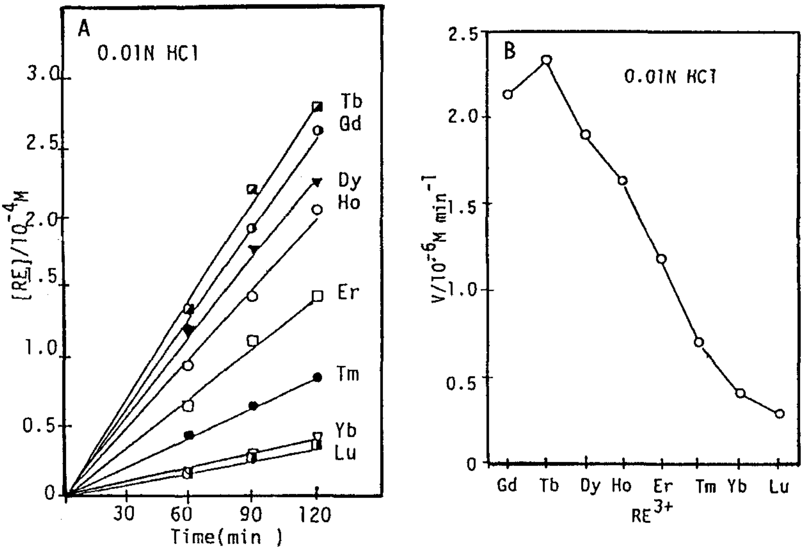

FIGURE 4. LMT of RE ions with D2EHPA carrier and 0.01 N aqueous HCl phases at 30°C. (a) Transport rate data. (b) Transport rate constants vs. atomic number of RE.

the source and receiving phases were aqueous HCl solutions (corresponds to the mobile phase in CPC), and the liquid membrane was a chloroform solution of D2EHPA (corresponds to the stationary phase in CPC).

Effect of Concentration of D2EHPA in Chloroform: It was confirmed that no transport was observed when a liquid membrane without D2EHPA was used. The typical results of effect of D2EHPA concentrations on the rate of transport for Ho^{3+} ion are shown in Figure 2. The rate increased steeply with increase in D2EHPA concentration from 8 to 16 mM, and the rate enhancing effect became smaller at concentrations higher than 18 mM D2EHPA.

Effect of Initial Substrate Concentration on the Transport Rate: The effect of initial substrate concentration on the rate of transport is exemplified by the case of Ho^{3+} ion at a D2EHPA concentration of 15 mM and a HCl concentration of 0.03 N (Figure 3). The apparent rates of transport (V) were calculated from the slopes of time-concentration plots. The general trend in the effect of initial substrate concentration on V was similar to the cases of lighter RE ions in the previous work.(4)

Effect of Concentration of HCl in the Aqueous Source Phase on the Transport Rates of RE Ions: As In the case of LMT of lighter RE ions,(4) the concentration of HCl in the aqueous source phase was of prime importance for transport of heavier RE ions. From Figures 4 to 8 the variations of transport rates of RE ions from Gd^{3+} to Lu^{3+} with change in the HCl concentration are illustrated. The relations of V vs. atomic number of RE ions are shown for some selected HCl concentrations (Figures 4b, 6b, and 7b).

Correlation Between LMT and CPC: Figure 9 summarizes the behaviors of heavier RE ions examined in this work by plotting V vs. HCl concentration. Underneath are the corresponding CPC chromatograms(5) obtained with identical two phase system as LMT. The HCl concentrations which give rise to good separation of the RE ions in CPC produce considerably large difference in V values in LMT. The optimum V values in LMT were shifted directing to higher HCl concentrations with increase of atomic number of RE ions as observed in the cases of lighter series of RE ions.(4) In CPC the optimum peak separation with reasonable peak shapes was also obtained at

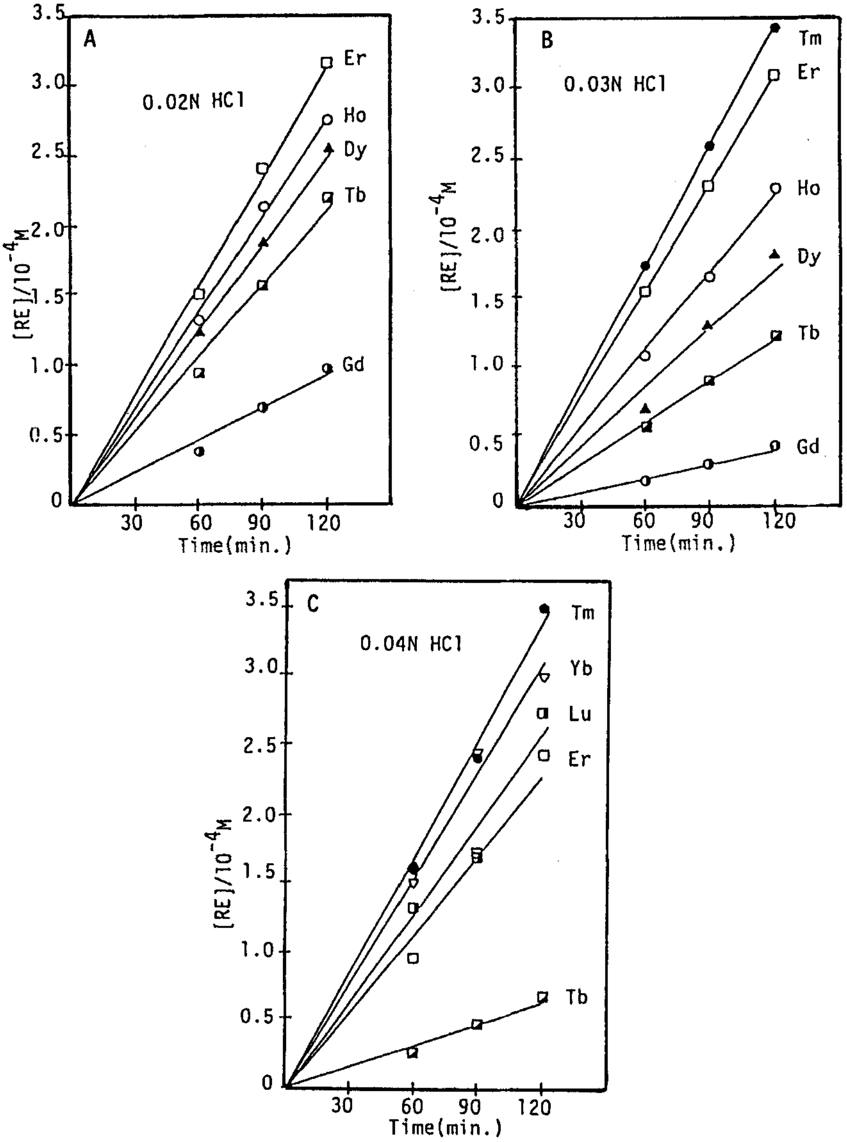

FIGURE 5. LMT of RE ions with D2EHPA carrier at 30°C. Concentration of HCl in the aqueous phases. (a) 0.02 N, (b) 0.03 N, and (c) 0.04 N.

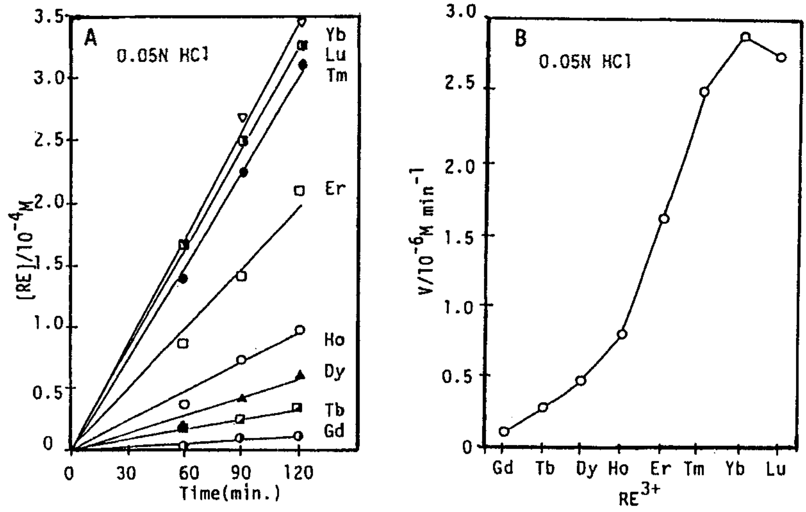

FIGURE 6. LMT of RE ions with D2EHPA carrier and 0.05 N aqueous HCl phases at 30°C. (a) Transport rate data. (b) Transport rate constants vs. atomic number of RE.

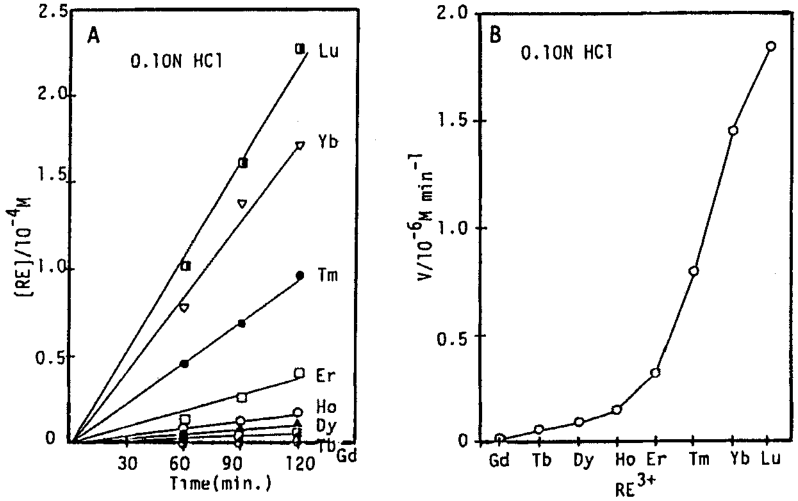

FIGURE 7. LMT of RE ions with D2EHPA carrier and 0.10 N aqueous HCl phases at 30°C. (a) Transport rate data. (b) Transport rate constants vs. atomic number of RE.

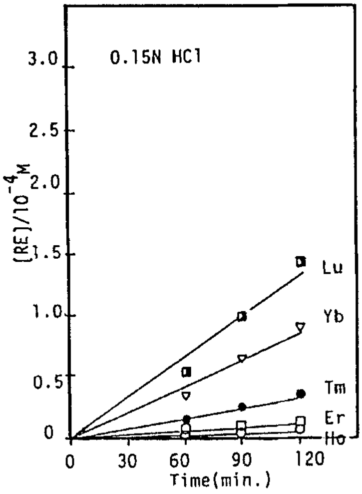

FIGURE 8. LMT of RE ions with D2EHPA carrier and 0.15 N aqueous HCl phases at 30°C.

higher HCl concentrations as increase in the atomic number of RE ions. In these respect, the behaviors of heavier RE ions in LMT and CPC are well correlated.

The phenomena of that maximum V values in LMT are present with respect to HCl concentration seem to be associated with broad peaks in CPC.(5) At a HCl concentration higher than its maximum the equilibrium (eq. 2) will be shifted toward left. In this situation the substrate ion cannot transferred into the liquid membrane so easily, resulting in a low transport rate. On the other hand, this situation corresponds to fast elution of a sample in CPC according to the expectation described in TABLE 1 of the previous paper.(4) In fact, the leading edge of a very broad peak in CPC became to start immediately after the dead time as increasing the

TABLE 1. COMPARISON OF LIQUID MEMBRANE TRANSPORT DATA AT 30°C WITH CENTRIFUGAL PARTITION CHROMATOGRAPHIC DATA AT 25°C.

RE_1	RE_2	Concn. of HCl (N)	LMT (V_1/V_2)	CPC (α)
Gd	Tb	0.03	2.98	4.21
Gd	Tb	0.04	2.61	3.66
Dy[a]	Ho[a]	0.06	1.76	0.94
Ho[a]	Er[a]	0.06	2.06	1.43
Er	Tm	0.10	2.53	4.05
Tm	Yb	0.10	1.84	3.79
Tm	Yb	0.12	2.05	1.20
Yb	Lu	0.12	1.33	0.61

a) At 45°C.

HCl concentration.(5) At the same time the elution of tailing edge of the peak became faster with increase in

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

HCl concentration.

TABLE 1 is a comparison of CPC and LMT data for adjacent pairs of RE ion by the use of almost comparable two liquid phase conditions. The data are also illustrated in Figure 10. Except for the Tm^{3+}/Yb^{3+} pair (0.10 N HCl), a considerably good correlation between the ratio of rate constants (V_1/V_2) in LMT and the separation factor (α) in CPC was obtained. This fact supports our assumption that the key equilibria in LMT and CPC are common, i.e., eq. 2.

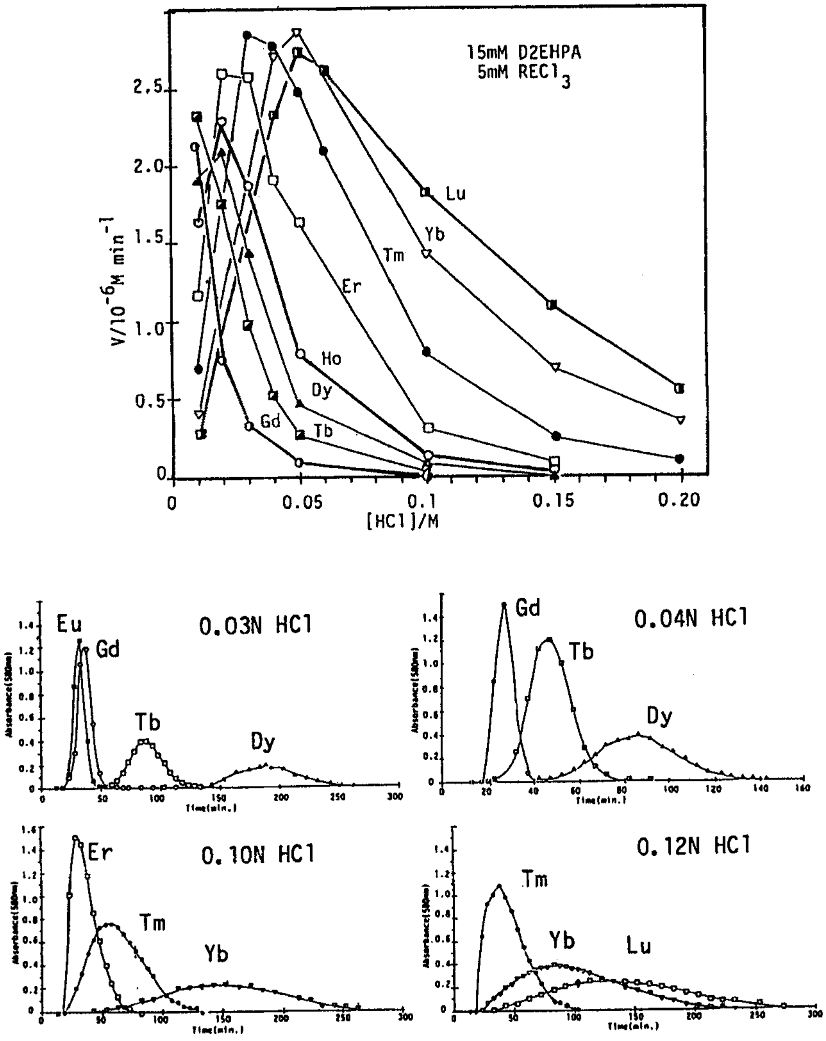

FIGURE 9. Relation between transport rate constant and HCl concentration for a series of heavier RE ions (Top diagram). The corresponding typical CPC chromatograms (ref. 5) are shown underneath.

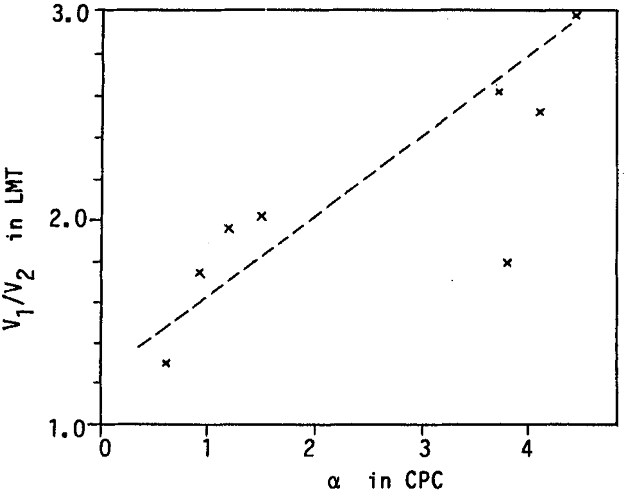

FIGURE 10. Correlation between (V_1/V_2) in LMT and α in CPC.

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

	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Gd	--	yes[a]	yes[b]	yes[b]	yes[e]	yes[g]	yes[i]	yes[m]
Tb		--	sl[c]	yes[d]	yes[f]	yes[g]	yes[i]	yes[n]
Dy			--	sl[c]	yes[c]	yes[h]	yes[j]	yes[o]
Ho				--	yes[c]	yes[h]	yes[k]	yes[p]
Er					--	sl[c]	yes[l]	yes[q]
Tm						--	yes[l]	yes[r]
Yb							--	sl[s]

with a)0.02 N, b)0.02-0.03 N, c)0.05 N, d)0.03 N, e)0.02-0.05 N, f)0.03-0.05 N, g)0.03-0.06 N, h)0.05-0.06 N, i)0.01 N, and 0.04-0.07 N, j)0.04-0.1 N, k)0.02 N and 0.05-0.1 N, l)0.1 N, m)0.01 N and 0.03-0.1 N, n)0.01 N and 0.04-0.1 N, o)0.05-0.1 N, p)0.02 N and 0.05-0.1 N, q)0.02 and 0.1 N, r)0.03 and 0.1 N, and s)0.1-0.15 N aq.-HCl.

Selective LMT for Heavier RE Ions: From Figure 9 one can find several combinations of RE ions which are promising for selective LMT processes such as ion sensing by the use of D2EHPA. Figure 9 shows that in some cases it is possible to revert the order of transport of RE ion sets. For example, in the case of Yb^{3+}/Gd^{3+} pair Yb^{3+} is selectively transported with 0.04-0.07 N HCl aqueous phases, but Gd^{3+} can be selectively transported with 0.01 N HCl. It is also the similar cases for Yb3+/ Tb^{3+}, Yb^{3+}/Ho^{3+}, Lu^{3+}/Gd^{3+}, Lu^{3+}/Tb^{3+}, Lu^{3+}/Ho^{3+}, and Lu^{3+}/Er^{3+} pairs. The LMT selectivities are also tabulated in TABLE 2 for convenience.

Conclusion

Liquid membrane transport of heavier rare earth metal ions from Gd^{3+} to Lu^{3+} was facilitated by di(2-ethylhexyl)phosphoric acid as well as that of lighter series (La^{3+}-Eu^{3+}).(4) Thus, the behaviors of a whole series of rare earth metal ions in the bulk liquid membrane transport system was unveiled throughout by completion of this work. All of the rare earth metal ions were found to be in accord with a common equilibrium represented by eq. 2. The chemical processes in Centrifugal Partition Chromatography of the whole series of rare earth metal ions with the corresponding two liquid phase system containing D2EHPA also follow the same equation.(5) Hence, the correlation between LMT and CPC was almost satisfactory. This fact supports our original concept that CPC can be regarded as a kind of multistage LMT system.(2,3)

CPC behaviors of these metal ions have been reported(6) by using EHPA and the key process has been supposed to be an equilibrium essentially the same as eq. 2, and the CPC behaviors were found to closely resemble to those employing D2EHPA.(5) So, we can dare to propose that LMT of rare earth metal ions by the use of EHPA carrier will give a result quite similar to that of this work using D2EHPA.

It is notable that a highly familiar and costless phosphate carrier such as D2EHPA (and probably also EHPA) was shown to be able to realize selective LMT of several combinations of rare earth metal ions. This fact will encourage to develop more sophisticated ion-sensing molecular systems in rare earth metal applications. Combination of macrocyclic structures(7) and phosphate group may be a candidate of an effective carrier.

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