

**Acknowledgment**

The authors express their thanks for the financial support from a Grant-in-Aid from the Ministry of Education, Science and Culture.

**Nomenclature**

$A$	= interfacial area	[m <sup>2</sup> ]
$C$	= concentration	[mol/dm <sup>3</sup> or mol/m <sup>3</sup> ]
$C_i$	= concentration at interface position	[mol/dm <sup>3</sup> or mol/m <sup>3</sup> ]
$J$	= flux	[mol·m <sup>-2</sup> ·s <sup>-1</sup> ]
$K_{H2O}$	= equilibrium constant of TH dimerization	[(dm <sup>3</sup> /mol) <sup>2</sup> ]
$K_{Mlm}$	= equilibrium constant of the complex (TOAHCl) <sub>l</sub> (MCl) <sub>p</sub> <sub>m</sub>	[in mol/dm <sup>3</sup> ]
$K_{ov}$	= overall mass transfer coefficient	[m/s]
$k_M$	= specific reaction rate of interfacial reaction for metal species $M$	[m <sup>4</sup> ·s <sup>-1</sup> ·mol <sup>-1</sup> ]
$k_m$	= mass transfer coefficient in membrane phase	[m/s]
$k_o$	= mass transfer coefficient in organic phase	[m/s]
$k_r$	= mass transfer coefficient for permeation through interfacial zone	[m/s]
$k_w$	= mass transfer coefficient in aqueous phase	[m/s]
$P$	= distribution ratio for single-metal extraction	[—]
$P^*$	= distribution ratio for simultaneous extraction of metal	[—]
$S$	= selectivity of separation	[—]
$t$	= time	[s]
$V$	= volume	[m <sup>3</sup> ]

$\phi$  = a coefficient to relate metal activity in neutral form to total concentration of metal in aqueous phase [—]

**<Superscripts>**

I, II = aqueous phase I, II

**<Subscripts>**

$i$  = interfacial position  
 $F$  = iron  
 $H$  = hydrochloric acid  
 $M$  = metal species  $M$   
 $N$  = TOA  
 $Z$  = zinc  
 Overline = organic phase

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## SELECTIVE SEPARATION OF METALS BY LIQUID MEMBRANE WITH MIXED CARRIERS

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**Key Words:** Liquid Membrane, Membrane Separation, Mixed Carriers, Tri-*n*-Octylamine, Di-2 Ethylhexyl Phosphoric Acid, Selective Separation, Iron and Zinc

Selective separation is usually performed with the help of a strong difference in the permeation rates of the solutes through a liquid membrane, where the solutes are transported through the membrane in co-current fashion. In this work we propose a method of obtaining the countercurrent transport of the solutes, by using a liquid membrane with two kinds of carriers which have different mechanisms of extracting the solutes. It was demonstrated that one carrier, TOA, transports the metals zinc and iron from one aqueous phase to the other while the other carrier, D2EHP, preferentially back-transport to the original aqueous phase the iron transported by TOA. An efficient separation of zinc and iron was performed with the help of these two carriers.

**Introduction**

One of the important uses of the liquid membrane is the selective separation of solutes. This is performed

with the help of the difference in the rates at which the solutes permeate through the membrane.<sup>4)</sup> The size of this difference depends upon the separation system. A strong difference is expected if we select a carrier with molecular-recognition function,<sup>5)</sup> but cannot be expected for usual carriers lacking such

Received October 24, 1983. Correspondence concerning this article should be addressed to M. Harada. N. Shiomi is now at Kanegafuchi Chem. Ind. Co., Ltd., Takasago 676.

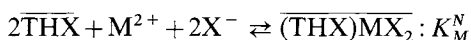
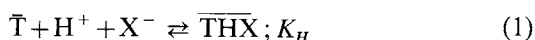
function.

The solutes to be separated simultaneously permeate through the membrane in the selective separation with the help of the difference in the permeation rates.<sup>4)</sup> Thus the selective separation can be effectively realized only when there exists a strong difference in the rates. More effective separation can be expected if the solutes to be separated permeate through the membrane in countercurrent fashion, as in the case of sodium-potassium permeation through a bio-membrane.<sup>1)</sup>

In this work we propose a method to realize the countercurrent transport of solutes through the membrane with mixed carriers. First, the principle of obtaining countercurrent flow is explained for an amine and another carrier, and the characteristics of the membrane operation are shown. Secondly, we demonstrate that an efficient selective separation can be performed with use of tri-*n*-octylamine and di-2-ethylhexyl phosphoric acid as the mixed carriers.

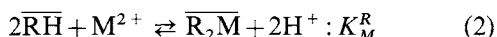
## 1. Characteristics of Liquid Membrane with Mixed Carriers

Consider two kinds of carriers. One is an amine of high molecular weight. The essential feature of extracting metals is described as



The counter anion  $X^-$  is taken up by the membrane phase from the aqueous phase when extracting metal species a and b. In this system, the agent which gives the driving force to the metal transport is the counter anion  $X^-$ .

The other carrier is, for example, a chelating agent or acidic organophosphorus compound.



Such carriers release hydrogen ion when extracting metals. Hydrogen ion gives the driving force to the metal transport.

The distribution of metals to the organic phase with these carriers mixed is expressed as follows, if no synergism between the carriers exists:

$$\bar{C}_M = K_M^N C_M C_X^2 (\overline{THX})^2 + K_M^R C_M C_H^{-2} (\overline{RH})^2 \quad (3)$$

$$P_M = \bar{C}_M / C_M = K_M^N C_X^2 (\overline{THX})^2 + K_M^R C_H^{-2} (\overline{RH})^2 \quad (4)$$

Figure 1 shows the distribution ratios in the extraction of metals by these mixed carriers, the conditions of calculation being given as follows in mol, dm<sup>3</sup> units:

$$\begin{aligned} K_a^N &= 10^4, & K_b^N &= 10^2, & K_a^R &= 10^{-3}, \\ K_b^R &= 10^{-2}, & K_H &= 10^8 \\ \bar{C}_N &= 0.1, & \bar{C}_R &= \text{variable} \end{aligned} \quad (5)$$

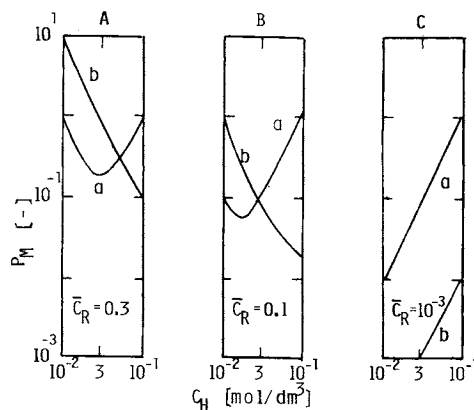


Fig. 1. Features of distribution of metal extraction by mixed solvents.

We assumed  $C_H = C_X$ , though  $C_H$  and  $C_X$  are independently variable. The distribution ratio is concave in shape. The ratios for two kinds of metals are determined by the amine when  $C_H$  is large or  $\bar{C}_R$  is small. The other carrier dominates the distribution ratios when  $C_H$  is small or  $\bar{C}_R$  is large. In the intermediate range, the functions of both carriers reveal themselves.

Figure 2 shows the separation trajectories for metals a and b for a liquid membrane containing two kinds of carriers. The calculation was performed by use of

$$dC_a^I / dC_b^I = (\bar{C}_a^I - \bar{C}_a^II) / (\bar{C}_b^I - \bar{C}_b^II) \quad (6)$$

with the concentrations in membrane phase contacted with aqueous phase  $J$ ,

$$\begin{aligned} \bar{C}_M^J &= K_M^N C_M^J (C_H^J)^2 [(\overline{THX})^J]^2 \\ &+ K_M^R C_M^J (C_H^J)^{-2} [(\overline{RH})^J]^2, \end{aligned}$$

$$J = \text{I, II}, \quad M = a, b$$

$$\bar{C}_R^J = \sum_M 2K_M^R C_M^J [C_H^J]^{-2} [(\overline{RH})^J]^2 + (\overline{RH})^J$$

$$\begin{aligned} \bar{C}_N^J &= \sum_M 2K_M^N C_M^J [C_H^J]^2 [(\overline{THX})^J]^2 \\ &+ (\overline{THX})^J + K_H^{-1} (C_H^J)^{-2} (\overline{THX})^J \end{aligned}$$

and with  $C_a^I = C_b^I = C_a^{II} = C_b^{II} = 10^{-3}$  mol/dm<sup>3</sup> at initial state.

The acid concentrations in both aqueous phases were assumed as

$$C_H^I = 0.1 \text{ mol/dm}^3 \quad \text{and} \quad C_H^{II} = 10^{-2} \text{ mol/dm}^3.$$

In the  $\bar{C}_R = 10^{-3}$  case, the trajectory starts from the initial phase point i and the metal a is preferentially transported towards aqueous phase II from aqueous phase I. This trend shows that the function of amine dominates the metal transfer, as is clear from Fig. 1C. The selective separation of metal a is attributed to the

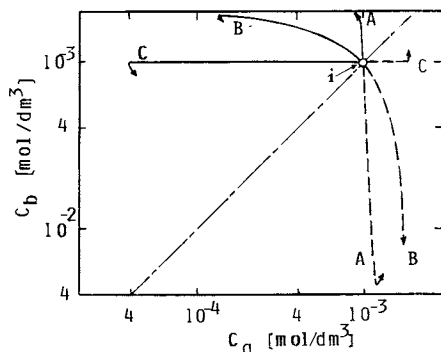


Fig. 2. Separation trajectories in batch operation of liquid membrane with mixed carriers. Conditions of calculation:  $C_H^I=0.1$ ,  $C_H^{II}=0.01$ ,  $\bar{C}_N=0.1$ ,  $C_{a0}^I=C_{b0}^I=C_{a0}^{II}=C_{b0}^{II}=10^{-3}$ ,  $V^I=V^{II}$ . A,  $\bar{C}_R=0.3$ ; B,  $\bar{C}_R=0.1$ ; C,  $\bar{C}_R=10^{-3}$ . These conditions, A, B and C, correspond to the ones shown in Fig. 1. A, B and C. Solid curves, aqueous phase I; broken curves, aqueous phase II.

strong difference in permeation rates between metals a and b.

In  $\bar{C}_R=0.3 \text{ mol/dm}^3$ , preferential permeation of metal b is observed due to the function of the chelating agent. As is clear from Fig. 1A, the permeation rate of metal a is very low.

In the intermediate range of  $\bar{C}_R$ , i.e.,  $\bar{C}_R=0.1 \text{ mol/dm}^3$ , the functions of both carriers reveal themselves as shown in Fig. 1B. Metal a is concentrated from aqueous phase I to phase II, while metal b is transported in the reverse direction to the transport of metal a. Therefore, the two metals are transported in countercurrent fashion in the membrane. The maximum selective separation has a horizontal trajectory in this situation when a single carrier, i.e., the amine, is involved in the membrane phase. In the case of mixed carriers, the trajectory of the selective separation has a negative slope, and more effective separation than that with the single-carrier system is observed in Fig. 2.

We assumed  $C_X=C_H$  in the above discussion. Generally,  $C_H$  and  $C_X$  are independently variable with use of acid and salt which involve common anion  $X^-$ . This increases the freedom of operation where the respective functions of the two carriers reveal themselves.

## 2. Experimental

### 2.1 Reagents

Tri-*n*-octylamine (TOA) supplied by Tokyo Kasei Co., Ltd. was used after purifying by usual procedures.<sup>1)</sup> We selected di-2-ethylhexyl phosphoric acid (D2EHP) as the other carrier. D2EHP was also supplied by Tokyo Kasei Co., Ltd. and was used without further purification. The other reagents used were of guaranteed grade and were used without purification. Water was purified by distillation.

### 2.2 Procedure

We selected zinc chloride and iron chloride as the metal species. These metals in aqueous solutions of hydrochloric acid were transported through the liquid membrane, which was the same as described in the previous report.<sup>4)</sup> The methods of analyzing these metals were also the same as described in the previous report.<sup>4)</sup> The diluent for the carriers was *n*-decane.

The equilibrium relationships were measured for zinc and iron extraction by both carriers and by the mixed carriers. The diluents for the carriers were *n*-decane or benzene. All experiments were performed at 25°C.

## 3. Experimental Results and Discussion

### 3.1 Equilibrium relationship

Figure 3 shows the equilibrium relationships of zinc and iron extractions. The open keys are the results obtained in the extraction of metals by D2EHP in *n*-decane. The broken curves are the distribution equilibria evaluated from the previous results<sup>4)</sup> in the TOA-in-benzene system, because TOA-hydrochloric acid complex does not dissolve in *n*-decane. The closed keys are the results obtained in the system, TOA-D2EHP mixed carriers in *n*-decane.

The distribution ratios of iron and zinc for the mixed carrier system almost agree with those for the TOA system, the broken curves in the high acid concentration range, where the amine dominates the equilibrium. In the lower acid concentration range, the distribution ratios for zinc and iron are much lower than those obtained in the system containing D2EHP only. This arises from the strong interference effect of both carriers. However, the pattern of the distribution ratios is similar to that shown in Fig. 1B, i.e., the concave distribution curves with respect to acid concentration. If we select proper conditions for the acid concentrations in the two aqueous phases, an efficient separation would be obtained with the help of the liquid membrane involving two kinds of carriers mixed.

### 3.2 Selective separation of zinc and iron

Figure 4 shows examples of the selective separation of zinc and iron mixture, obtained by operating the liquid membrane with the carriers in *n*-decane. The acid concentrations were selected by referring to the result shown in Fig. 3:

$$C_H^I=1.0, \quad C_H^{II}=0.1 \text{ mol/dm}^3$$

Initial concentrations of iron and zinc in the aqueous phases were set to agree with each other:

$$C_{F0}^I=C_{Z0}^I=C_{F0}^{II}=C_{Z0}^{II}=1 \times 10^{-3} \text{ mol/dm}^3$$

Separation trajectory A was obtained at the condition  $\bar{C}_N=0.05$  and  $\bar{C}_R=0.13 \text{ mol/dm}^3$ . This trajectory is almost horizontal through the initial phase

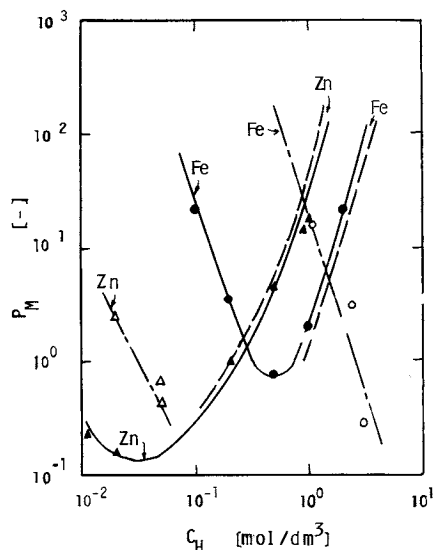


Fig. 3. Distribution ratios of zinc and iron in TOA and D2EHP systems. Closed keys, experimental for TOA–D2EHP mixed carriers in *n*-decane; open keys, experimental for D2EHP–*n*-decane system; broken curves, experimental for TOA in benzene system.  $\bar{C}_R=0.13$  mol/dm<sup>3</sup>,  $\bar{C}_N=0.05$  mol/dm<sup>3</sup>.

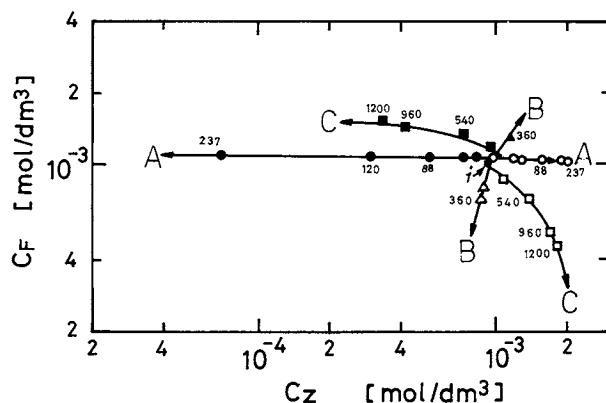


Fig. 4. Separation trajectories in batch operation of liquid membrane with TOA and D2EHP in *n*-decane.  $C_{H0}^I=1.0$ ,  $C_{H0}^{II}=0.1$ ,  $C_{F0}^I=C_{F0}^{II}=C_{Z0}^I=C_{Z0}^{II}=1.0 \times 10^{-3}$  mol/dm<sup>3</sup>,  $V^I=50$ ,  $V^{II}=36$  cm<sup>3</sup>. A,  $\bar{C}_N=0.05$ ,  $\bar{C}_R=0.13$  mol/dm<sup>3</sup>; B,  $\bar{C}_N=0$ ,  $\bar{C}_R=0.13$  mol/dm<sup>3</sup>; C,  $\bar{C}_N=0.02$ ;  $\bar{C}_R=0.13$  mol/dm<sup>3</sup>. Closed keys, aqueous phase I; open keys, aqueous phase II. The numerical values attached to the keys represent time in min.

point i, because the membrane was operated batchwise in this work, and the zinc was transported from aqueous phase I to phase II, but the iron was immobile. This feature of the trajectory shows that the amine carrier dominates the transport of zinc.

Trajectory B was obtained at  $\bar{C}_R=0.13$  and  $\bar{C}_N=0$  mol/dm<sup>3</sup>. In this case, the phosphoric acid preferentially transports iron from aqueous phase II to phase I. Zinc transport was weak due to lower flux of zinc than that of iron.

Trajectory C was obtained at  $\bar{C}_R=0.13$  mol/dm<sup>3</sup> and a little lower amine concentration than in trajec-

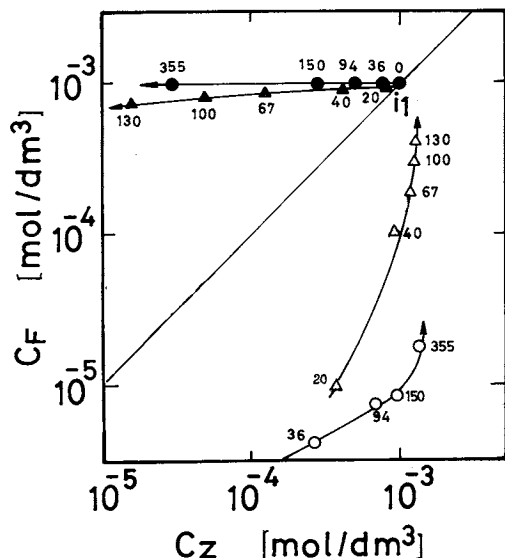
tory A, i.e.,  $\bar{C}_N=0.02$  mol/dm<sup>3</sup>. In this case, the functions of both carriers reveal themselves, and iron and zinc were transported in countercurrent fashion in the liquid membrane. The trajectory has a slope of about  $-1$  and a very effective separation can be observed.

It is interesting to examine the phase trajectories of the separation at the condition that one aqueous phase contains both metals and the other is free from metal. The trajectories at this condition are shown in Fig. 5. The triangle keys are the result obtained at  $\bar{C}_N=0.01$  mol/dm<sup>3</sup> and  $\bar{C}_R=0$ . In this case, the zinc flux is about 100 times larger than that of iron<sup>4)</sup> and comparatively efficient preferential transport of zinc can be observed. However, the leakage of iron to aqueous phase II is not neglected (see the trajectory for aqueous phase II). On the contrary, if we use the membrane with mixed carriers (The circle keys), the leakage of iron through the membrane is much weaker in the case of the TOA membrane.

Acid permeation through the membrane was negligibly weak in the experiments shown in Figs. 4 and 5. It is, therefore, concluded that selective separation of metals spontaneously proceeds with the help of the liquid membrane with mixed carriers.

Finally, we should mention the function of D2EHP. The concentrations of TOA and D2EHP in the trajectory A-experiment in Fig. 4 ( $C_H^I=1.0$ , and  $C_H^{II}=0.1$  mol/dm<sup>3</sup>) are taken to be the same as in the distribution experiment shown in Fig. 3. The distribution ratio  $P_M$  for iron at  $C_H=1.0$  mol/dm<sup>3</sup> is much less than the  $P_M$  value of iron at  $C_H=0.1$  mol/dm<sup>3</sup>, and the  $P_M$  value at  $C_H=1$  mol/dm<sup>3</sup> is much greater than that at  $C_H=0.1$  mol/dm<sup>3</sup> in the zinc case. This distribution pattern is similar to the B-case in Fig. 1. As expected from trajectory B in Fig. 2, more efficient separation than that in the trajectory A-experiment, i.e., a trajectory with negative slope, should be obtained under trajectory A-experimental conditions, if we take into account the equilibrium distribution relationship. In other words, the function of D2EHP of transporting iron is degraded in the trajectory A-experiment. The slow rate of reaction between iron and D2EHP<sup>3)</sup> is the reason why less effective separation was obtained in the trajectory A-experiment.

Synergism in the mixed carrier system, i.e., the degradation of extraction ability, is observed in Fig. 3 (compare the  $P_M$  values for the mixed carrier system with those for the single carrier D2EHP). This negative synergism is of particular importance in selective separation with the use of mixed carriers. In this work, separation experiments using benzene as the diluent for the mixed carriers were also performed. The experimental results for the benzene diluent system were similar to those for the *n*-decane system. It was, however, elucidated from the equilibrium



**Fig. 5.** Separation trajectories in batch operation of liquid membrane with TOA or TOA-D2EHP when  $C_{F0}^{\text{II}} = C_{Z0}^{\text{II}} = 0$ . Circle keys, experimental for TOA-D2EHP-mixed carriers at  $C_H^{\text{I}} = 1.0$ ,  $C_H^{\text{II}} = 0.1$ ,  $\bar{C}_N = 0.05$ ,  $\bar{C}_R = 0.13$ ,  $C_{F0}^{\text{I}} = C_{Z0}^{\text{I}} = 1.0 \times 10^{-3}$  mol/dm<sup>3</sup>,  $V^{\text{I}} = 50$ ,  $V^{\text{II}} = 35$  cm<sup>3</sup>. Diluent, *n*-decane. Triangle keys: experimental for  $C_H^{\text{I}} = 1.0$ ,  $C_H^{\text{II}} = 0.05$ ,  $\bar{C}_N = 0.01$ ,  $\bar{C}_R = 0$ ,  $C_{Z0}^{\text{I}} = C_{F0}^{\text{I}} = 1.0 \times 10^{-3}$  mol/dm<sup>3</sup>,  $V^{\text{I}} = 50$ ,  $V^{\text{II}} = 35$  cm<sup>3</sup>. Diluent, benzene. Closed keys: aqueous phase I. Open keys: aqueous phase II. The numerical values attached to the keys represent the time in min.

relationships for the systems with mixed carriers and single carrier in benzene that the extraction ability of D2EHP for metals was lowered and that negative synergism was much stronger than in the *n*-decane diluent system.

## Conclusion

A method of obtaining efficient selective separation of metals was proposed. The principle is to use the countercurrent transport of metals in the membrane, involving two kinds of carriers having different extraction mechanisms. It was demonstrated in liquid membrane operation that TOA transports zinc and iron from aqueous phase I to phase II and the iron transported by TOA is back-transported by D2EHP preferentially to the original aqueous phase. An efficient separation of zinc and iron can be performed

with the help of these two carriers.

## Acknowledgment

The authors wish to express their thanks for the financial support from a Grant-in-Aid of Scientific Research, Ministry of Education, Science and Culture.

## Nomenclature

$C_H$	= total concentration of acid in aqueous phase	[mol/dm <sup>3</sup> ]
$C_F$	= total concentration of iron	[mol/dm <sup>3</sup> ]
$C_M$	= total concentration of metal $M = a, b$	[mol/dm <sup>3</sup> ]
$\bar{C}_N$	= total concentration of TOA in membrane phase	[mol/dm <sup>3</sup> ]
$\bar{C}_R$	= total concentration of chelating agent or D2EHP in membrane phase	[mol/dm <sup>3</sup> ]
$C_Z$	= total concentration of zinc	[mol/dm <sup>3</sup> ]
$K_H$	= equilibrium constant for Eq. (1)	[in mol/dm <sup>3</sup> ]
$K_M^N$	= formation constant of amine-metal complex	[in mol/dm <sup>3</sup> ]
$K_M^R$	= formation constant of chelating agent-metal complex	[in mol/dm <sup>3</sup> ]
$P_M$	= distribution ratio for metal M	[—]
$V$	= volume of aqueous phase	[cm <sup>3</sup> ]

## <Superscript>

I, II = aqueous phases I and II

## <Subscripts>

$F$  = iron  
 $Z$  = zinc  
 $a, b$  = metal species a and b  
 $0$  = initial

## Superscripts

— = organic or membrane phase

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