

# METAL SORPTION CHARACTERISTICS OF A MACROMOLECULAR RESIN CONTAINING D2EHPA

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## Introduction

Macromolecular resins containing an extractant within their polymer lattice provide the best use of the advantages of both solvent extraction and ion exchange<sup>9, 10</sup>. A significant feature of this type of sorbents is the availability of an extractant reagent suitable for the separation of metal ions from a dilute solution, for which conventional solvent extraction is unfavorable.

The preparation of sorbent containing an extractant is roughly classified into two methods. One is to soak a polymeric resin (*e.g.*, Amberlite XAD series) in a diluent containing a desired extractant and then evaporating the diluent (extractant-impregnated sorbent, abbreviated as ImSorb hereinafter)<sup>5, 6, 8</sup>. The other is to add an extractant to a mixture of styrene monomers during bead polymerization with DVB, which has been developed by Bayer A.G. and is called Levextrel resin<sup>3, 4, 7, 11</sup>.

In previous works, we studied the divalent metal sorption characteristics of di-(2-ethylhexyl) phosphoric acid (D2EHPA)-ImSorb in batch<sup>1</sup> and column<sup>2</sup> opera-

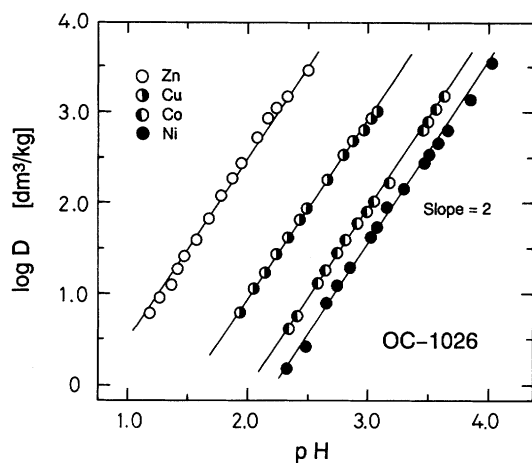
tion modes. The present study was made to elucidate whether the sorption behavior varies with the two different methods for preparation of extractant-containing resins or not, using both Levextrel resin and ImSorb containing D2EHPA.

## 1. Experimental

### 1.1 Preparation of sorbent

Levextrel resin containing D2EHPA was kindly supplied by Mitsui Toatsu Fine Chemicals, Inc. (trade name Lewatit OC-1026), and was used without further purification. The content of D2EHPA in OC-1026 was determined to be 1.14 mol/kg-dry OC-1026 by titrating the amount of D2EHPA eluted with methanol from the sorbent; the water content was found to be 12 wt%. The properties of Levextrel resin are available elsewhere<sup>7</sup>. D2EHPA-ImSorb which containing 0.77 mol D2EHPA/kg-dry ImSorb was prepared by the same method as described in the previous paper<sup>1</sup>, and was used for the study of sorption isotherm and column operation.

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**Fig. 1** Effect of equilibrium pH on distribution ratio of metals with OC-1026.  $W = 4.4 \times 10^{-4}$  kg,  $[M]_0 = 5.0 \times 10^{-4}$  mol/dm<sup>3</sup>

## 1.2 Sorption equilibrium

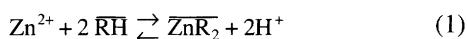
An aqueous solution of divalent metal was prepared by dissolving an appropriate amount of each metal chloride in deionized water. Its pH value was adjusted by adding a small amount of HCl or NaOH. In some cases a buffer solution was used.

Sorption equilibrium was attained by shaking the sorbent and an aqueous metal solution (20 cm<sup>3</sup>) in a 50-cm<sup>3</sup> glass-stoppered flask over 20 hr, using a mechanical shaker (EYELA, CTP-100). Both the initial and equilibrium concentrations in the aqueous phase were determined by atomic absorption spectroscopy. The amount of metal retained in the sorbent was then calculated on the basis of a mass balance. All the experiments were done at 298 K.

## 2. Results and Discussion

### 2.1 Sorption equilibrium

In a previous paper<sup>1)</sup> we showed that the stoichiometric relation of Zn(II) sorption on D2EHPA-ImSorb can be expressed in terms of a simple ion exchange reaction:



where the overbar denotes the sorbent phase and RH is D2EHPA. The equilibrium constant,  $K_{ex}$ , and the distribution ratio,  $D$ , are expressed as

$$K_{ex} = \frac{[\overline{\text{ZnR}_2}][\text{H}^+]^2}{[\text{Zn}^{2+}][\overline{\text{RH}}]^2} \quad (2)$$

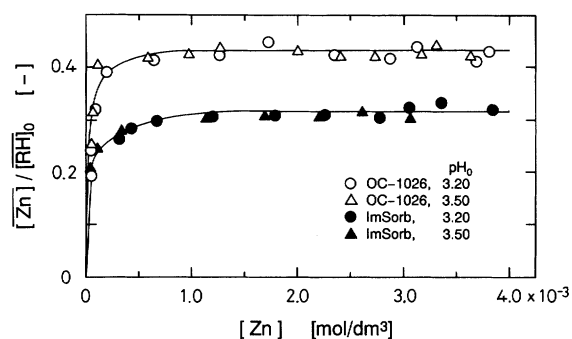
$$D = \frac{[\overline{\text{Zn}}]}{[\text{Zn}]} = K_{ex} \frac{[\overline{\text{RH}}]^2}{[\text{H}^+]^2} \quad (3)$$

**Figure 1** shows the distribution ratio  $D$  of four divalent metals on OC-1026 as a function of the equilibrium pH. The results yield straight lines with a slope of 2 according to Eq. (3). Providing that the sorption chemistry on OC-1026 is the same as that on ImSorb, we can obtain the values of  $K_{ex}$ . These values are listed in **Table 1** along with the values for the sorption on ImSorb<sup>1)</sup>.

**Table 1.** Values of  $K_{ex}$  for sorption of divalent metals

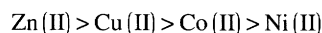
	Zn (II)	Cu (II)	Co (II)	Ni (II)
Lewatit OC-1026				
$K_{ex}$ [kg/dm <sup>3</sup> ]	$2.51 \times 10^{-2}$	$6.92 \times 10^{-4}$	$6.76 \times 10^{-5}$	$2.83 \times 10^{-5}$
D2EHPA-Impregnated Sorbent*				
$K_{ex}$ [kg/dm <sup>3</sup> ]	$3.64 \times 10^{-2}$	$1.56 \times 10^{-3}$	$2.48 \times 10^{-4}$	$2.38 \times 10^{-4}$

\*: from ref. 1)



**Fig. 2** Sorption isotherms of Zn (II) with both OC-1026 and ImSorb.  $[M]_0 = 5.0 \times 10^{-3}$  mol/dm<sup>3</sup>, 0.20 mol/dm<sup>3</sup> buffer solution

The following sequence of the sorptibility is observed in the present systems:

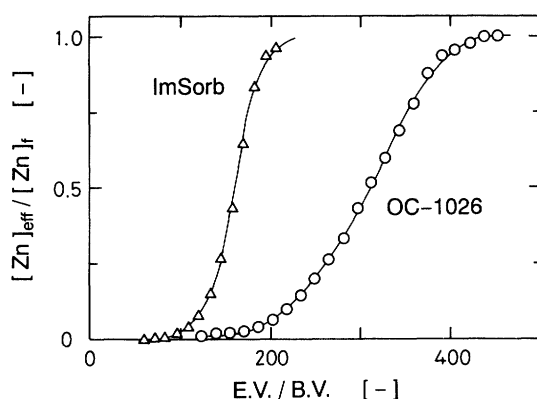


This order is in agreement with that of ImSorb and with the extractability of D2EHPA as well. However, the values of  $K_{ex}$  on OC-1026 are smaller than those on ImSorb. In **Fig. 1** the solid lines represent the calculated ones from the determined values of  $K_{ex}$ .

In contrast with the sorption mechanism provided above, Juang and Su<sup>5)</sup> determined the equilibrium constants of D2EHPA-ImSorb for some divalent metals using the same stoichiometric relation as for solvent extraction with D2EHPA, which is different from the simple ion exchange.

**Figure 2** shows the sorption isotherms of Zn (II) on OC-1026 and ImSorb from buffer solutions of chloroacetic acid/sodium chloroacetate (0.2 M), indicating that the two sorbents give Langmuir-type isotherms. The maximum uptake of Zn (II) on OC-1026 corresponds to 44 % of the D2EHPA content, which is somewhat smaller than the value of 50 % predicted from Eq. (1). The shortage of ion exchange capacity may be due to the fact that D2EHPA in OC-1026 is liable to be eluted from the solid phase into the buffer solution<sup>2)</sup>. The uptake on ImSorb is smaller compared with OC-1026. This suggests the existence of unavailable D2EHPA in the sorbent, which does not participate in the sorption reaction owing to a steric hindrance or an occlusion.

To examine the sorption characteristics in a continuous mode, the breakthrough curve for Zn (II) sorption was determined using a glass column (I.D. 10 mm) packed with 2.0 g of the fresh sorbent. After condi-



**Fig. 3** Breakthrough curves for Zn (II) sorption with both OC-1026 and ImSorb.  $B.V. = 4.4 \text{ cm}^3$ ,  $F = 0.87 \text{ cm}^3/\text{min}$ ,  $[M]_i = 4.9 \times 10^{-4} \text{ mol/dm}^3$ , pH 2.50

tioning with the blank solution, an aqueous metal solution was fed at the bottom of the column with OC-1026 (upflow) or at the top of the column with ImSorb (down-flow). Typical breakthrough curves are shown in **Fig. 3**. When compared with the ImSorb column, OC-1026 has a later breakthrough point and provides a more gentle slope of the breakthrough curve. Considering that the D2EHPA content is different in the two, OC-1026 is found to have much higher capacity for Zn (II) sorption than ImSorb, even in a column operation.

## 2.2 Separation from binary metal solution

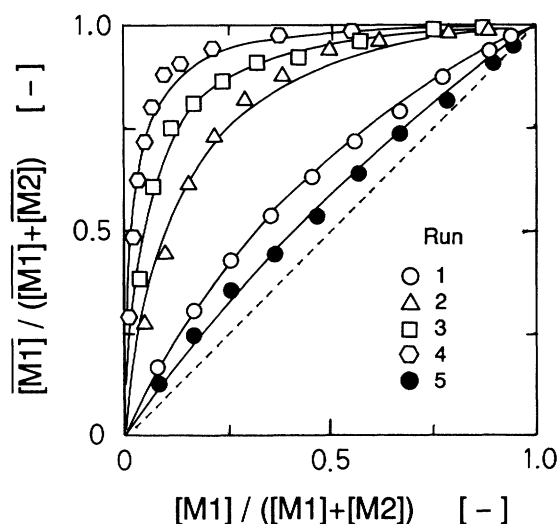
The application of OC-1026 to mutual separation of metals was examined for binary metal systems in a batch mode. **Figure 4** shows the relationship between the fractional concentrations of metals in aqueous and sorbent phases under experimental conditions shown in **Table 2**. The equilibrium data located on each convex curve show the selective sorption of Co (II) over Ni (II), Cu (II) over Co (II), Cu (II) over Ni (II), and Zn (II) over Cu (II) according to the sequence of the sorptibility of OC-1026, as described above. In Fig. 4 the separation of Co (II) and Ni (II) on ImSorb is also plotted with the closed symbol.

To evaluate the mutual separation quantitatively, the separation factor  $\alpha$  was defined as

$$\alpha = ([M1] / [M1]) / ([M2] / [M2]) \quad (4)$$

where M1 and M2 represent the respective metal species. Values of  $\alpha$  were determined so as to best fit the experimental data, and the results are listed in Table 2. For the separation of Co (II) and Ni (II), OC-1026 has a little larger value of  $\alpha$  than ImSorb does. The solid lines in Fig. 4 represent the calculated results from these  $\alpha$  values.

The separation factor can also be expressed as  $K_{ex,1}/K_{ex,2}$ , and the calculated ones from the  $K_{ex}$  values in Table 1 are also listed in Table 2. It can be seen that the calculated values,  $K_{ex,1}/K_{ex,2}$ , reasonably agree with the experimental ones. This means that the degree of separation can be estimated from the results of the single-metal



**Fig. 4** Relationship between fractional concentrations of metals in aqueous and sorbent phases.  $W = 4.4 \times 10^{-4} \text{ kg}$  for OC-1026,  $W = 5.0 \times 10^{-4} \text{ kg}$  for ImSorb,  $[M]_0 = 1.0 \times 10^{-4} \text{ mol/dm}^3$ ,  $0.05 \text{ mol/dm}^3$  buffer solution

**Table 2.** Separation factors for binary metal systems

Run	M1	M2	pH	$\alpha$	$K_{ex,1}/K_{ex,2}$
Lewatit OC-1026					
1	Co	Ni	3.0	2.11	2.39
2	Cu	Co	2.6	8.61	10.2
3	Cu	Ni	2.7	19.8	24.5
4	Zn	Cu	2.2	43.4	36.2
D2EHPA-Impregnated Sorbent					
5	Co	Ni	3.0	1.42	1.04

sorption, at least in the concentration region studied.

## Conclusions

Metals sorption and separation characteristics of a commercial sorbent OC-1026 were examined with a view to comparing with a homemade D2EHPA impregnated sorbent (ImSorb). The equilibrium constants for Zn, Cu, Ni and Co as divalent metals were determined on the basis of the same ion exchange mechanism as obtained for ImSorb in the previous study. The resin has the advantage that the ion exchange capacity is higher than that of ImSorb in both batch and column operations. Furthermore, it was found that the separation factor in a binary metal system can be estimated from each equilibrium constant.

## Nomenclature

$B.V.$	= bed volume of the column	$[\text{cm}^3]$
$D$	= distribution ratio defined by Eq. (3)	$[\text{dm}^3/\text{kg}]$
$E.V.$	= effluent volume	$[\text{cm}^3]$
$F$	= flow rate	$[\text{cm}^3/\text{min}]$
$K_{ex}$	= equilibrium constant defined by Eq. (2)	$[\text{kg}/\text{dm}^3]$
$M$	= metal species	
$V$	= volume of aqueous phase	$[\text{dm}^3]$
$W$	= dry weight of OC-1026 or D2EHPA-ImSorb	$[\text{kg}]$

$\alpha$  = separation factor defined by Eq. (4) [-]  
 $[ ]$  = concentration in aqueous or sorbent phase  
 [mol/dm<sup>3</sup>], [mol/kg]

#### <Subscripts>

$eff$  = effluent  
 $f$  = feed  
 $0$  = initial

#### <Superscripts>

— = sorbent phase

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