

Registry No. DMSO, 67-68-5; benzene, 71-43-2; toluene, 108-88-3; 1,3-dimethylbenzene, 108-38-3; 1,3,5-trimethylbenzene, 108-67-8; methoxybenzene, 100-68-3.

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## Sorption and Separation of Divalent Metals by a Macromolecular Resin Containing Organophosphorus Acids

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Studies have been conducted on the equilibrium distribution of divalent zinc ion between aqueous solution and macromolecular resin impregnated with phosphoric acid bis(2-ethylhexyl ester) (D2EHPA). The mechanism of Zn(II) sorption on the impregnated sorbent is different from that for the solvent extraction, being expressed by a simple ion-exchange reaction, with the equilibrium constant of 0.036 kg of sorbent/dm<sup>3</sup>. The separations of Zn(II)/Cu(II) using D2EHPA-impregnated sorbent and of Co(II)/Ni(II) by the resin impregnated with (2-ethylhexyl)phosphonic acid mono(2-ethylhexyl ester) (EHPNA) have also been conducted in a batch operation. It was found that the selective sorptions of Zn(II) to Cu(II) and of Co(II) to Ni(II) can be attained satisfactorily with the separation factors of 55.2 and 6.73, respectively.

### Introduction

The fields of application of ion exchange for separation are extremely widespread from the treatment of low-cost materials such as water to the purification of expensive pharmaceutical derivatives. There is a need for specific ion-exchange materials having high affinities to the objective substances.

Extractant-impregnated sorbents and Lewextrel resins have had special attention because of their great potential for highly selective separation and concentration of metal ions from aqueous solutions (1-4); their features and applications are reviewed by Warshawsky (5). Compared with typical chelating resins, impregnated sorbents have some advantages such as simplicity in preparation, high selectivity, and complete desorbability. The most attractive feature of this type of the

sorbent is in the availability of an extractant fitted in with a metal separation system; furthermore, the sorption characteristics can be evaluated from previous data on the solvent extraction.

In a previous work (6), we studied the equilibrium sorption and separation of Zn(II) by a tri-*n*-octylamine-impregnated sorbent. These showed that the stoichiometric relation of the sorption equilibrium follows that of the solvent extraction, and Zn(II) could be separated from Cu(II) continuously in a column operation.

The present study has been made on the sorption and separation characteristics of divalent metals by sorbents impregnated with two organophosphorus acid reagents: D2EHPA and EHPNA as phosphoric and phosphonic acid type extractants, respectively. Solvent extraction using these extractants has been studied extensively for the separation of lanthanoids and transition-metal ions.

### Experimental Section

**Preparation of Impregnated Sorbent.** Two types of organophosphorus acid reagents, D2EHPA (Tokyo Kasei Co., Ltd.) and EHPNA (trade name PC-88A; Daihachi Chemicals Industry Co., Ltd.), were used as active components without further purification. Amberlite XAD-2 (Organo Co., Ltd.), washed with acetone and water, and fractionated in the particle size range of 500-710  $\mu\text{m}$  prior to the impregnation with an extractant, was used as a matrix resin.

A sorbent impregnated with each extractant was prepared as follows. An appropriate volume of 0.1 M solution of the extractant in *n*-hexane was mixed with a given weighed amount of XAD-2, and the diluent was then evaporated in a rotary evaporator. Subsequently the impregnated sorbent was placed in a vacuum at 50 °C for 2 h to be sure of the complete

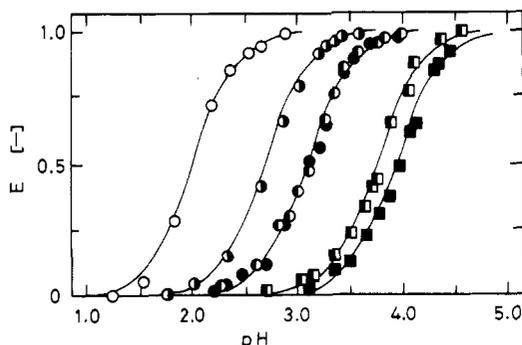


Figure 1. Effect of equilibrium pH on the sorption ratio  $E$  of divalent metal ions with organophosphorus acid-impregnated sorbents ( $S = 1.0 \times 10^{-4}$  kg,  $V = 2.0 \times 10^{-2}$  dm<sup>3</sup>, and  $c_0 = 1.0 \times 10^{-4}$  mol/dm<sup>3</sup>): O,  $\bullet$ ,  $\square$ ,  $\blacksquare$ , [D2EHPA]<sub>s,0</sub> = 0.75 mol/kg of sorbent;  $\square$ ,  $\blacksquare$ , [EHPNA]<sub>s,0</sub> = 0.76 mol/kg of sorbent; O, Zn;  $\bullet$ , Cu;  $\square$ , Co;  $\blacksquare$ , Ni.

evaporation of the diluent. The amount of extractant held within the sorbent was determined from a change in the weight of the resin before and after the impregnation.

**Sorption and Separation of Metal Ions.** All the experiments were carried out batchwise; the sorption equilibrium was attained by shaking 0.10 g of the sorbent and 20 cm<sup>3</sup> of an aqueous metal solution in a 50 cm<sup>3</sup> glass-stoppered flask for 20 h using a mechanical shaker (Yamato, BT-25) maintained at  $25 \pm 2$  °C. The aqueous solution of divalent metal was prepared by dissolving the metal chloride in deionized water, its pH value being adjusted by the addition of a small amount of HCl or NaOH. In some cases, buffer solution was used. The equilibrium value of the solution pH was measured with a pH meter; the initial and equilibrium concentrations of metal in the aqueous phase were determined by atomic absorption spectroscopy. The amount of metal ion retained in the sorbent was calculated on the basis of a mass balance.

## Results and Discussion

**Sorption Equilibria.** Figure 1 shows the sorption ratio  $E$  of divalent metal ions by the two impregnated sorbents as a function of the equilibrium pH for each solution. The sorption ratio was defined as

$$E = 1 - (c/c_0) \quad (1)$$

where  $c_0$  and  $c$  denote the initial and equilibrium concentrations of the metal in the aqueous phase, respectively.

The characteristic curves are analogous to each other, exhibiting a strong pH dependence of the sorption. As the sorptibility of D2EHPA-impregnated sorbent, the following sequence is observed for these ions:



In addition, Fe(III) ion was more strongly sorbed; thus, the curve located around pH 1.0, though the data are not given. It is well known that D2EHPA is a preferential extractant for cobalt over nickel. However, no significant difference is observed between the sorption curves of Co(II) and Ni(II) in Figure 1. This limited separation may be due to the lack of the solvent effect compared with the case of solvent extraction.

Further experiments were made of the sorption equilibria of Co(II) and Ni(II) by the sorbent impregnated with EHPNA. As Figure 1 shows, although the sorption characteristics shifted to a higher pH region, a significant difference is observed between the two metal ions as is reported in the solvent extraction.

Figure 2 shows the relationship between the equilibrium pH and distribution ratio  $D$  defined as

$$D = m/c \quad (2)$$

$$m = (c_0 - c)V/S \quad (3)$$

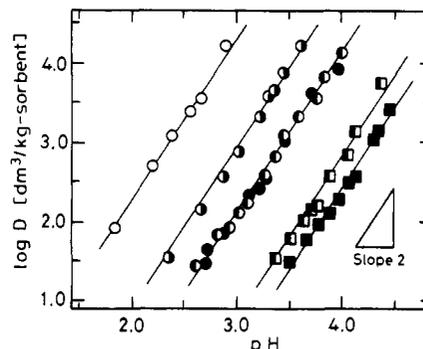


Figure 2. Effect of equilibrium pH on the distribution ratio of various divalent metal ions. Symbols are the same as in Figure 1.

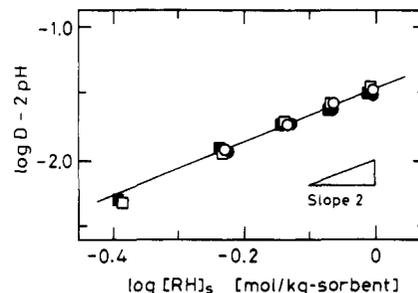


Figure 3.  $\log D - 2\text{pH}$  versus D2EHPA content in the sorbent for Zn(II) sorption ( $S = 1.0 \times 10^{-4}$  kg,  $V = 2.0 \times 10^{-2}$  dm<sup>3</sup>, and  $c_0 = 1.0 \times 10^{-4}$  mol/dm<sup>3</sup>):  $\square$ ,  $\blacksquare$ , for 0.02 M buffer solution of chloroacetic acid/sodium chloroacetate; O, pH 2.2;  $\bullet$ , pH 2.0;  $\square$ , pH 2.4;  $\blacksquare$ , pH 2.6.

where  $m$  denotes the metal content in the sorbent phase,  $V$  the volume of the aqueous phase, and  $S$  the mass of the sorbent. Equation 2 can be combined with eq 1 to yield

$$E = D/(D + V/S) \quad (4)$$

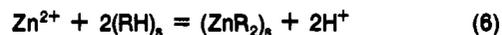
The results for various divalent metal ions lie on each straight line of slope 2. If an ion-exchange reaction takes place in the sorbent, then the plot of  $\log D$  versus equilibrium pH should give a straight line having a tangent which corresponds to the charge of metal species in the aqueous phase.

For the solvent extraction of Zn(II) by D2EHPA in kerosene, Huang and Juang (7) reported that the extraction chemistry has the overall stoichiometry



where RH denotes D2EHPA.

In the sorption on D2EHPA-impregnated sorbent, on the other hand, we assumed that the chemistry can be expressed by a simple ion-exchange reaction:



$$K_{\text{ex}} = [\text{ZnR}_2]_s [\text{H}^+]^2 / [\text{Zn}^{2+}] (\text{RH})_s^2 \quad (7)$$

Combining eqs 2 and 7, one obtains

$$\log D - 2\text{pH} = 2 \log [\text{RH}]_s + \log K_{\text{ex}} \quad (8)$$

where  $[\text{RH}]_s$  denotes the D2EHPA content in the sorbent, given as  $[\text{RH}]_s = [\text{RH}]_{s,0} - 2[\text{Zn}]_s$ , and  $[\text{RH}]_{s,0}$  the initial content.

The results obtained for the sorption of Zn(II) are shown in Figure 3 as a plot of  $\log D - 2\text{pH}$  vs  $\log [\text{RH}]_s$  according to eq 8. The data points are on a straight line with a slope of 2, regardless of aqueous solutions with or without buffer action.

From the above discussion, it can be concluded that the extractant in the sorbent exists as the monomer. This leads to the ion-exchange reaction, eq 6, for the sorption of Zn(II); then the value of equilibrium constant  $K_{\text{ex}}$  was found to be 0.036 kg of sorbent/dm<sup>3</sup>. In Figures 2 and 3 the solid lines for

Table I. Values of  $K_{ex}$  for the Sorption of Zn(II), Cu(II), Co(II), and Ni(II) by Two Extractant-Impregnated Sorbents

	Zn(II)	Cu(II)	Co(II)	Ni(II)
D2EHPA-Impregnated Sorbent				
$K_{ex}$ , kg/dm <sup>3</sup>	$3.64 \times 10^{-2}$	$1.56 \times 10^{-3}$	$2.48 \times 10^{-4}$	$2.38 \times 10^{-4}$
EHPNA-Impregnated Sorbent				
$K_{ex}$ , kg/dm <sup>3</sup>			$1.11 \times 10^{-5}$	$4.59 \times 10^{-6}$

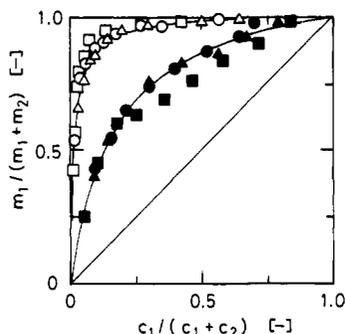


Figure 4. Relationship between fractional concentrations of metal ions in aqueous phase and sorbent phase for both binary systems of Zn/Cu and Co/Ni: O,  $\Delta$ ,  $\square$ , Zn/Cu systems 1, 2, and 3, respectively;  $\bullet$ ,  $\blacktriangle$ ,  $\blacksquare$ , Co/Ni systems 1, 2, and 3, respectively.

the Zn(II) sorption represent the calculated ones in terms of the value of  $K_{ex}$ .

Furthermore, for Cu(II), Co(II), and Ni(II), assuming the same ion-exchange reaction as eq 6, we can obtain the  $K_{ex}$  value for each sorption equilibrium; these values are listed in Table I.

**Separation of Zn(II)/Cu(II) and Co(II)/Ni(II).** The application of the impregnated sorbent to the separation of metal ions was examined for two binary systems of Zn(II)/Cu(II) using D2EHPA-impregnated sorbent and of Co(II)/Ni(II) by EHPNA-impregnated sorbent in the batch operation.

Figure 4 shows the equilibrium relation between the fractional concentrations in both phases: a plot of  $m_1/(m_1 + m_2)$  against  $c_1/(c_1 + c_2)$ , where subscripts 1 and 2 denote the respective metal species. The experimental conditions in the present study are listed in Table II, where we used two 0.05 M buffer solutions: chloroacetic acid/sodium chloroacetate for the Zn(II)/Cu(II) system and acetic acid/sodium acetate for the Co(II)/Ni(II) system. For the two systems the equilibrium data locate on each convex curve, which will be described later; little significant effect of the initial concentration of the total metal ions and the equilibrium pH on the selectivity is observed in the range measured. In the present experiments, the sorbents used were in the H form of each extractant, and the metal loading during the sorption was no more than 0.088 mol/kg of sorbent for the Zn/Cu system and 0.040 mol/kg of sorbent for the Co/Ni system. This implies that D2EHPA-impregnated sorbent has a high selectivity for the separation of Zn(II) from Cu(II); Zn(II) in aqueous solution is preferentially sorbed and recovered by use of the present sorbent. Also, Co(II) can be separated preferentially from Ni(II) by using EHPNA-impregnated sorbent. The data of the separation are tabulated in Table II.

We here defined the separation factor  $\alpha$  as

$$\alpha = (m_1/c_1)/(m_2/c_2) \quad (9)$$

The values of  $\alpha$  are also given in Table II, which were determined from the reciprocal plots of  $m_1/(m_1 + m_2)$  against  $c_1/(c_1 + c_2)$ . From Figure 4, it is evident that the experimental data for both systems can be represented with the solid lines calculated from the average separation factors of 55.2 for the Zn/Cu system and of 6.73 for the Co/Ni system.

It should be noted that the separation factor  $\alpha$  for cosorption given by eq 9 is higher than that calculated from the values of

Table II. Extent of the Separation and Separation Factor for Zn(II)/Cu(II) and Co(II)/Ni(II) Systems<sup>a</sup>

aqueous phase	sorbent phase	aqueous phase	sorbent phase
$c_{Zn^{2+}}$	$m_{Zn}$	$c_{Co^{2+}}$	$m_{Co}$
$c_{Zn^{2+}} + c_{Cu^{2+}}$	$m_{Zn} + m_{Cu}$	$c_{Co^{2+}} + c_{Ni^{2+}}$	$m_{Co} + m_{Ni}$
Zn/Cu 1		Co/Ni 1	
0.020	0.543	0.096	0.436
0.042	0.781	0.154	0.551
0.059	0.833	0.208	0.660
0.095	0.891	0.302	0.744
0.130	0.911	0.393	0.807
0.174	0.946	0.519	0.880
0.266	0.982	0.637	0.935
0.351	0.969	0.801	0.985
0.565	1.000		
$c_{t,0} = 4.9 \times 10^{-4}$		$c_{t,0} = 4.7 \times 10^{-4}$	
pH 2.52, $\alpha = 59.1$		pH 4.54, $\alpha = 7.17$	
Zn/Cu 2		Co/Ni 2	
0.037	0.663	0.093	0.411
0.050	0.785	0.145	0.542
0.082	0.849	0.221	0.656
0.100	0.869	0.301	0.756
0.142	0.928	0.427	0.838
0.201	0.958	0.565	0.868
0.301	0.980	0.671	0.935
0.499	0.989	0.789	0.988
0.645	1.000		
$c_{t,0} = 1.0 \times 10^{-4}$		$c_{t,0} = 1.1 \times 10^{-4}$	
pH 2.52, $\alpha = 53.5$		pH 4.52, $\alpha = 6.83$	
Zn/Cu 3		Co/Ni 3	
0.015	0.434	0.054	0.250
0.022	0.575	0.106	0.460
0.025	0.740	0.174	0.606
0.038	0.797	0.254	0.637
0.049	0.865	0.368	0.686
0.074	0.927	0.471	0.761
0.136	0.962	0.583	0.838
0.283	0.988	0.718	0.897
0.425	0.991	0.839	0.986
$c_{t,0} = 4.8 \times 10^{-4}$		$c_{t,0} = 5.6 \times 10^{-4}$	
pH 3.04, $\alpha = 53.0$		pH 4.22, $\alpha = 6.19$	

<sup>a</sup>  $S = 1.0 \times 10^{-4}$  kg,  $V = 2.0 \times 10^{-2}$  dm<sup>3</sup>, [D2EHPA]<sub>s,0</sub> = 0.75 mol/kg of sorbent for Zn/Cu systems, and [EHPNA]<sub>s,0</sub> = 0.77 mol/kg of sorbent for Co/Ni systems.

$K_{ex}$  or  $D$  for single metal sorption as  $K_{ex,1}/K_{ex,2}$  (or  $D_1/D_2$ ): 23.3 for Zn to Cu and 2.42 for Co to Ni (see Table I). Thus, the selective separation of divalent metals is possible by using these impregnated sorbents. Especially, Zn(II) was satisfactorily separated from Cu(II) by use of D2EHPA-impregnated sorbent in the batch operation. To realize a continuous operation, the applicability of organophosphorus acid-impregnated sorbent to column separation is now being undertaken.

## Conclusion

Studies were made of the sorption equilibrium and separation of divalent metal ions from aqueous solution by two types of organophosphorus acid-impregnated sorbents, and the following conclusions were obtained.

The mechanism of Zn(II) sorption by D2EHPA-impregnated sorbent is expressed in terms of a simple ion-exchange reaction unlike the extraction. The equilibrium constant was found to be 0.036 kg of sorbent/dm<sup>3</sup>.

The selective separation of Zn(II)/Cu(II) and Co(II)/Ni(II) was attained satisfactorily with the average separation factors of 55.2 for the former and of 6.73 for the latter in a batch operation.

## Glossary

$c$  concentration in aqueous phase, mol/dm<sup>3</sup>  
 $D$  distribution ratio defined by eq 2, dm<sup>3</sup>/kg of sorbent

$E$	sorption ratio defined by eq 1
$K_{ex}$	equilibrium constant defined by eq 7, kg of sorbent/dm <sup>3</sup>
$m$	content in the sorbent, mol/kg of sorbent
$S$	mass of the sorbent, kg
$V$	volume of aqueous phase, dm <sup>3</sup>
[ ]	concentration in aqueous phase or content in the sorbent, mol/dm <sup>3</sup> or mol/kg of sorbent
$\alpha$	separation factor defined by eq 9

#### Subscripts

org	organic phase
s	sorbent phase
t	total

0	initial
1, 2	metal species

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## Vapor-Liquid Equilibrium for Chlorodifluoromethane + Dimethyl Ether from 283 to 395 K at Pressures to 5.0 MPa

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Vapor-liquid equilibrium conditions ( $p$ - $T$ - $x$ - $y$ ) of the binary mixture chlorodifluoromethane (R22) + dimethyl ether (DME) have been measured for the first time along six isotherms (three subcritical and three supercritical). The mixture forms a negative (maximum boiling) azeotrope which persists to the critical line. Direct observations were made of points on the critical line. The two lower temperature isotherms are fitted to a temperature-dependent Redlich-Kister excess Gibbs free energy model. The equal area method has been used to test the thermodynamic consistency of the two lower temperature isotherms. A brief description of the apparatus is given.

### Introduction

An understanding of the vapor-liquid equilibria (VLE) of mixtures whose components have strong specific interactions (association and solvation) is important to applications such as the production of synthetic fuels (1), supercritical fluid extraction (2), and development of alternative refrigerant mixtures (3, 4). A number of theories have been developed to allow calculation of the vapor-liquid equilibria of associating and solvating mixtures at high pressure (>1 MPa), but they have mostly been applied to associating systems due to the scarcity of high-pressure VLE data for solvating mixtures (5-7). The few experimental high-pressure VLE studies of solvating mixtures generally contain sparse and scattered data (8-10). This laboratory has undertaken a program to provide VLE data of solvating binary mixtures over a wide temperature and pressure range (11, 12) in order to test the ability of theories being developed to describe the thermodynamics of mixtures with strong specific interactions (5-7).

The purpose of this work is to examine the pressure,  $p$ , temperature,  $T$ , liquid composition,  $x$ , and vapor composition,  $y$ , dependence of the vapor-liquid equilibria of the solvating

mixture chlorodifluoromethane (R22) + dimethyl ether (DME) from room temperature to the critical region. This mixture has been used commercially as an aerosol propellant. The thermodynamic consistency of the results has been examined using a maximum likelihood method and an equal area method.

### Experimental Section

A schematic diagram of the apparatus is shown in Figure 1. A detailed description of the apparatus and procedures is given elsewhere (11). It is a dual recirculating apparatus designed to operate isothermally from 283 to 520 K and at pressures to 40 MPa. The apparatus can be divided into three functional sections: (1) the pressure generation section, (2) the equilibrium section, and (3) the sampling section.

In the pressure generation section, the two components to be studied are distilled from individual supply cylinders into Ruska screw pumps. The screw pumps are then used to pressurize and pump the pure fluids into the equilibrium section.

The equilibrium section consists of a sapphire tube pressure cell, two magnetically driven reciprocating pumps, and two sample traps housed in an insulated thermostated oven. The equilibrium cell is made from a 3.18-cm-o.d., 1.27-cm-i.d., 10.2-cm-long sapphire tube (Union Carbide Corp.) sealed by a Bridgman unsupported area seal with a Teflon gasket (13). To establish equilibrium, the two magnetically driven pumps are used to circulate the vapor and liquid phases.

The oven is maintained at constant temperature using an electric ceramic heater coupled with a finned heat exchanger connected to a thermostated liquid bath (Brinkmann Model RM20). The temperature is maintained within  $\pm 0.02$  K using a software implemented proportional-integral-derivative (PID) controller. A 12-in. fan is used to circulate air in the oven to minimize temperature gradients. The temperature of the equilibrium cell is measured with an accuracy of 0.002 K on IPTS-68 using a platinum resistance thermometer (Leeds and Northrup Model 8164) placed in a hole drilled concentrically in the top of one of the flange bolts of the equilibrium cell.

Data acquisition and temperature control are implemented using a general-purpose interface bus (GP-IB) system consisting

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