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The Liquid-Liquid Extraction of Zinc with Polyethylene Glycol and Poly(oxyethylene)-type Nonionic Surfactants

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Synopsis. The Zn(II) extraction was made from its acidic thiocyanate solution, using polyethylene glycol and its mono(alkylphenyl) ether as extractants. The effects of the number of oxyethylene groups ($-O-CH_2-CH_2-$) per molecule and of the kind of the counter cation of thiocyanate on the extractability are described, together with some other factors affecting the Zn(II) extraction.

Recently polyethylene glycol (PEG) and its derivatives have been found to useful as extractants in the liquid-liquid extraction of heavy metal and actinoid ions, and their extraction behavior has been briefly reported.[1—3] In the present paper, somewhat detailed results will be reported on the extraction behavior of a trace amount of Zn(II) from hydrochloric-acid solutions of several alkali and alkaline earth metal thiocyanates into some polar organic-solvent solutions of PEG and several poly(oxyethylene)-type nonionic surfactants.

Experimental

Reagents and Apparatus. The PEG, with a nominal molecular weight of 7500 ($HO(EO)_nH$, n: The number of oxyethylene groups (EO's), abbreviated as PEG 7500), and poly(oxyethylene)($-O-CH_2-CH_2-$, POE) mono[(6-methylheptyl)phenyl] ether ($C_8H_{17}C_6H_4O(EO)_n$, $n=10$, abbreviated as Triton X-100) were supplied by the Wako Pure Chemicals Co., and the POE mono(nonylphenyl) ethers ($C_9H_{19}C_6H_4O(EO)_nH$, $n=10$—120, abbreviated as NS (10—120), by the Nippon Oils & Fats Co. All these reagents were used for the extraction experiments without further purification. ^{65}Zn was used as a radioactive tracer to determine the distribution ratio of Zn(II) extraction, while the ^{65}Zn radioactivity was measured by means of a well-type NaI(Tl) detector (2.5 × 3.0 in.) equipped with a multi-mode scaler (Aloka).

Extraction Procedure. Take 10 ml of an acidic aqueous thiocyanate solution containing a small amount of Zn(II) and 10 ml of a given organic solvent solution of a PEG or POE surfactant into a stoppered centrifuging tube, and then shake the tube for 2 h at 25±0.5 °C. It was proved by the preliminary experiment that the shaking time of 2 h was sufficient to attain the extraction equilibrium. After centrifuging, the radioactivity of a 5 ml aliquot of each phase was measured. The distribution ratio(D) of Zn(II) was determined by means of the radioactivity ratio of the two phases.

Results and Discussion

Effect of Organic Diluent. The extractability of Zn(II) was measured using various organic solvents as the diluent of PEG 7500 or Triton X-100, the results are shown in Table 1, together with the dielectric constants of the organic solvents used. As may be seen from this table, a polar diluent with a high dielectric constant (>10), like nitrobenzene and 1,2-dichloroethane(DCE), gave a high percentage extraction, but *o*-dichlorobenzene, with a dielectric constant of only 9.93, yielded a very low % E-value of 1.6. Thus, a 1,2-DCE solution of the extractant was used as the organic phase in this work.

TABLE 1. EFFECTS OF ORGANIC SOLVENTS

Solvent	Dielectric constant	Percentage extraction (%)	
		PEG 7500	Triton X-100
Nitrobenzene	34.8	>99	>99 (>99)a)
1,2-Dichloroethane	15.1	>99	84.5 (>99)
o-Dichlorobenzene	9.93	1.6	94.8 (—)
Chlorobenzene	5.61	0.2	68.9 (>99)
Benzene	2.28	<0.1	16.8 (95.6)
Toluene	2.37	<0.1	13.6 (45.3)
Xylene	2.57	<0.1	— (15.6)
Carbon tetrachloride	2.23	<0.1	— (6.5)

Aqueous phase: 0.2 M KSCN, 0.01 M HCl, 0.001 M surfactant. a) Aqueous phase: 1.0 M KSCN, 0.01 M HCl, 0.05 M Triton X-100.

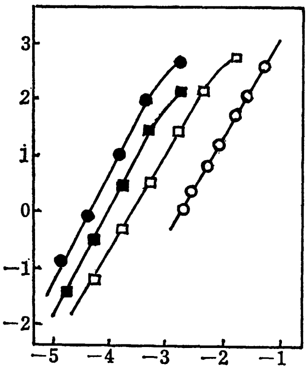

Fig. 1. Effect of surfactant concentration on the Zn(II) extraction.
Aqueous phase: 0.01 mol dm^{-3} HCl, 1.0 mol dm^{-3} thiocyanates. ●: KSCN, ■: NH_4SCN, □: NaSCN, ○: LiSCN. Organic phase: Triton X-100 in 1,2-DCE (w/v %).

Effect of the Extractant Concentration in the Organic Phase and the Kind of the Counter Cation of Thiocyanate in the Aqueous Phase. Figure 1 shows four log-log plots of the distribution ratio(D) of Zn(II) *vs.* the concentration (w/v %) in the organic phase of Triton X-100 for 4 different acidic aqueous phases, each containing an alkali metal and ammonium thiocyanates (1.0 mol dm^{-3}). When compared with each other at a given Triton X-100 concentration in the organic phase, the distribution ratios for these aqueous phases (4 thiocyanates) increased in the following order:

$$LiSCN < NaSCN < NH_4SCN < KSCN.$$

The log-log plots for Li^+, Na^+, NH_4^+, and K^+ give

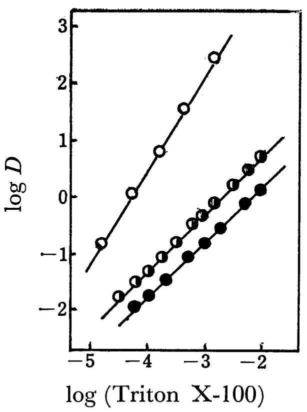

Fig. 2. Effect of surfactant concentration on the Zn(II) extraction.
Aqueous phase: 0.01 mol dm^{-3} HCl, 0.5 mol dm^{-3} thiocyanates. ○: $Ba(SCN)_2$, ◑: $Ca(SCN)_2$, ●: $Mg(SCN)_2$. Organic phase: Triton X-100 in 1,2-DCE.

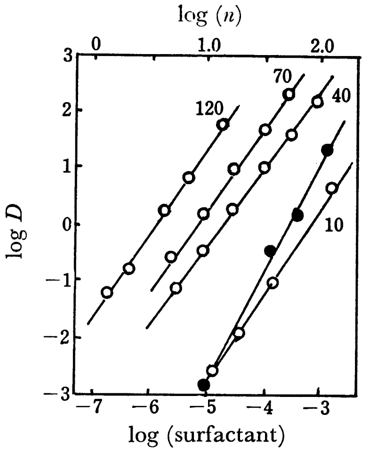

Fig. 3. Effect of the number(n) of EO's per molecule. Aqueous phase: 0.5 mol dm^{-3} HCl, 1.0 mol dm^{-3} NH_4SCN. Organic phase: NS(10—120) in 1,2-DCE. ○: log *D* *vs.* log (surfactant), ●: log *D* *vs.* log (*n*). (The figures refer to the number of EO's.)

straight lines with slopes of 1.7, 1.7, 1.9, and 2.0 respectively. The plots for Na^+, however, show a tendency to deviate a little from their straight lines at high Triton concentrations of more than 10^{-2} mol dm^{-3}, the plots for NH_4^+ and K^+ show a similar tendency at concentrations of more than 10^{-3} mol dm^{-3}. Such a deviating tendency is not observed in the plot for Li^+, not even at high Triton concentrations of up to 8×10^{-2} mol dm^{-3}. In Fig. 2 the distribution ratio of Zn(II) is plotted against the concentration in the organic phase of Triton X-100, with the respective 0.01 mol dm^{-3} HCl solutions of 3 alkaline earth metal thiocyanates (1.0 mol dm^{-3}) being used as the aqueous phases. It can clearly be seen in Fig. 2 that the log-log plot for the aqueous phase of $Ba(SCN)_2$ has a slope of 1.7, about twice those for the aqueous $Mg(SCN)_2$ and $Ca(SCN)_2$ systems, and rather similar to those for the aqueous alkali metal thiocyanates (2.0—1.7). The *D*-value for the aqueous $Ba(SCN)_2$ system was larger than those for the $Mg(SCN)_2$ and $Ca(SCN)_2$ systems by a factor of at least 10—10^4 in the Triton X-100 concentration in the organic phase studied. The *D*-value for the aqueous phases of the these alkaline earth metal thiocyanates increased in this order:

$$Mg(SCN)_2 < Ca(SCN)_2 \ll Ba(SCN)_2.$$

Effect of the Number of EO's Per Molecule. Zn(II) was extracted from its 0.5 mol dm^{-3} HCl solution of NH_4SCN (1.0 mol dm^{-3}) with NS(10—120) in 1,2-DCE. Figure 3 shows the log-log plots of the distribution ratio(*D*) of Zn(II) *vs.* the formal molar concentration in the organic phase of NS (10—120), or the number of EO's per molecule. As can clearly be seen, at a given concentration in the organic phase of NS (10—120) the *D*-value increased with an increase in the EO number; the *D*-value for NS (120) was more than 10^4 times larger than that for NS(10), whereas the EO number for NS(10) is 12 times larger than that for NS(120). This finding is consistent with the U(VI) extraction dependence on the EO number for a series of PEG's of various molecular weights (200—20000)[3].

References

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