CHEMISTRY LETTERS, pp. 585-588, 1976. Published by the Chemical Society of Japan

LIQUID-LIQUID EXTRACTION OF VARIOUS METAL IONS WITH POLYETHYLENEGLYCOL AND ITS DERIVATIVES

Takeshi SOTOBAYASHI*, Toshio SUZUKI*, and Shigemasa TONOUCHI**
* Department of Chemistry, Faculty of Science, Niigata University, Niigata 950-21
**Environmental Research Institute of Niigata Prefecture, Niigata 950-21

Polyethyleneglycol (PEG) and its derivatives of high molecular weight, including polypropyleneglycol, were found to be used as extractants for the liquid-liquid extraction of small amounts of various metal ions. Their extraction with these extractants were studied from thiocyanate and iodide solutions. The extraction power of these extractants increased with the increasing number of ehtylene-oxide groups in PEG's. The extractability of metal ions from their thiocyanate solution increased in the following order:
Zn(II) > Mo(V) > Co(II) > Fe(III) > V(IV) > Cu(I) > Hg(II) > Cd(II) > Pb(II) > Ni(II)

More recently it was found that PEG, its derivatives and polypropyleneglycol (PPG) were successfully used as extracting reagents for the liquid-liquid extraction of small amounts of Co(II) and U(VI) from their thiocyanate solutions. The results of Co(II) extraction were briefly reported in this journal[1)] and the extraction behaviors of some actinides will be published elsewhere[2)]. Based on these findings, is now in progress a systematic investigation on the extraction behaviors of various metal ions from their thiocyanate, iodide or nitrate solution with varying acidities and salt concentrations. In this paper we will briefly describe some extraction features of ten metal ions especially heavy metal ions, with PEG, its derivatives and PPG. Further, we will demonstrate the dependence of the extractability of each metal ion on the number of ethylene-oxide groups in the respective extractants.

Polyoxyethylene-type extractants used are almost the same as those used previously[1)], and they are shown as follows:

(1) Alcohols; PEG's and PPG's

(2) Ethers; Polyoxyethylene(POE) monoalkyl ether (Brij 35 and 58), and POE alkylphenyl ether (Triton X-100)

(3) Esters; POE sorbitan monooleate (Tween 80)

All other reagents used were of reagent grade. As stock solutions of ten metal ions, were used "Standard solutions of metal ions for atomic aborption spectrophotometry" (1000 ppm in each metal ion, from Wako Pure Chemicals Ltd. Co.). These standard solutions were appropriately diluted to use for the extraction experiments.

The experiments were made on a two-phase organic aqueous extraction system, a 1,2-dichloroethane solution of each extractant mentioned above (1.0%, w/v) and an aqueous salt solution (thiocyanate or iodide) with a constant acidity (0.1 N in HCl). Metal ion concentrations of the aqueous phases were all 100 ppm for each metal ion except for Hg(II) (10 ppm in Hg). It was found that a shaking time for 5 min was sufficient to reach the extraction equilibrium by preliminary experiments. The percentage extraction of each metal ion was determined by measuring the respective metal ion concentrations of the aqueous or the organic phase. All metal ion concentrations were measured by an atomic absorption spectrophotometer (Jarrel Ash AA-1 and AA-8200) with a flameless atomizer (Hitachi HFA type)and a spectrophotometer (Shimazu UV-201) with a flameless atomizer (Hitachi HFA type).

Since it was already found that PEG of high molecular weight showed a high extractability of Co(II), more than 99%,[1)] it was further attempted to investigate an extraction feature of PEG for various metal ions. Ten metal ions, as shown in Table 1, were extracted from 2.0 M ammonium thiocyanate solution in a 0.1 N mineral acid into a 1,2-dichloroethane solution of PEG. The average molecular weight of PEG used ranged from 200 to 20000. Table 1 shows the percentage extraction of each metal ion in the order of increasing extractability. The molybdenum was extracted 3 hours after the addition of ascorbic acid (50 mg/ 10-ml aqueous phase) to reduce Mo(VI) to Mo(V). From this table the ten metal ions were classified into two main groups, a higher extractable group and a lower extractable one. The former consists of Zn(II), Mo(V), Co(II), Fe(III) and V(IV), and the latter, Cu(I), Hg(II), Cd(II), Pb(II) and Ni(II). The dependency of the extractability on the molecular weight of PEG was more remarkable in the higher extractable group than in the lower one.

Table 1. Extraction of metal ions with PEG's of various molecular weights from thiocyanate solution

Metal ions	Percentage extraction PEG					
	(200)	(600)	(1000)	(2000)	(7500)	(20000)
Zn(II)	11	95	>99	100	100	100
Mo(V)	54	87	91	>99	>99	>99
Co(II)	23	66	87	97	>99	>99
Fe(III)	5	9	34	73	95	98
V(IV)	0	0	8	34	81	81
Cu(I)	0	3	7	23	42	42
Hg(II)	12	13	11	13	14	14
Cd(II)	0	1	2	7	11	13
Pb(II)	0	2	3	6	9	9
Ni(II)	0	0	—	0	0	0

The extractions of the ten metal ions with some available PEG derivatives were carried out under the same extraction conditions as those in the case of the PEG extractions mentioned above. The results are presented in Table 2, together with the percentage extraction of each metal ion with PEG 1000. From this table it will be clearly seen that the extractability of each metal ion with alkyl or alkylphenyl derivatives of PEG was higher than that for PEG, when the number (n) of ehtylene-oxide groups in the respective polyoxyethylene chain of these extractants was nearly equal to each other; for example, the percentage extraction of Fe(III) with Brij 58 (n=20, 92%) was higher than that of PEG 1000 (n=23, 34%). It should be noted that the extractabilities of Cu(I) and Hg(II) for the PEG derivatives were higher by a factor of about 5 than those for the PEG.

Table 2. Extraction of ten metal ions with some PEG derivatives from thiocyanate solution

Metal ions	Percentage extraction				
	Triton X-100 (n=10)	Brij 35 (n=23)	Brij 58 (n=20)	Tween 80 (n=20)[3]	PEG 1000 (n=23)
Zn(II)	100	100	100	100	$>$99
Mo(V)	85	99	99	$>$99	91
Co(II)	99	99	99	98	87
Fe(III)	80	92	92	90	34
Hg(II)	45	56	68	44	11
V(IV)	18	75	56	43	8
Cu(I)	26	38	28	16	7
Pb(II)	13	12	10	8	2
Cd(II)	4	—	7	—	3
Ni(II)	0	0	0	—	—

Five metal ions of the lower extractable group for the PEG-thiocyanate system were subjected to the extraction experiments from 1.0 M iodide solution in 0.1 N HCl into a 1,2-dichloroethane solution of PEG (1.0%, w/v) of various molecular weights. The results are summarized in Tables 3 (PEG's) and 4 (PEG derivatives); these five metal ions are listed in the order of increasing extractability. It will be clearly seen from these tables that this group of metal ions showed a higher extractability as compared with that in case of the extraction from thiocyanate solution and that even PEG 200 gave a high percentage extraction of 77% for Hg(II). The order of increasing extractability was similar to that for the PEG-thiocyanate system except for Cu(I).

Metal ions of the higher extractable group were extracted on a PPG-thiocyanate system, and metal ions of the lower extractable one were also done on a PPG-iodide system, whereby the aqueous concentrations of thiocyanate and iodide were 2.0 and 1.0 M, respectively, and the aqueous acidity was 0.1 N in HCl. Table 5 shows the percentage extraction of each metal ion in the order of increasing extractability, together with that for PEG 1000 (n=23). It was found that a little more extractable with PPG than with PEG for Fe(III) and Cu(I), when the degree of polymerization (n) of propylene oxide is nearly equal to each other.

Table 3. Extraction of some metal ions with PEG's of various molecular weights from iodide solution

Metal ions	Percentage extraction PEG					
	(200)	(600)	(1000)	(2000)	(7500)	(20000)
Hg(II)	77	95	95	99	99	99
Cd(II)	0	39	92	99	99	99
Pb(II)	2	43	51	98	99	99
Cu(I)	1	11	29	57	92	92
Ni(II)	3	3	—	2	3	1

Table 4. Extraction of metal ions with some PEG derivarives from iodide solution

Metal ions	Percentage extraction		
	Triton X-100 (n=10)	Brij 58 (n=20)	Tween 80 (n=20)[3]
Hg(II)	99	99	99
Cd(II)	99	99	99
Pb(II)	94	97	90
Cu(I)	89	89	74
Ni(II)	0	0	—

Table 5. Extraction of metal ions with some PPG's of various molecular weights

Metal ions	Percentage extraction PPG			PEG
	(1000, n=17)	(3000, n=17)	(4000,n=23)	(1000, n=23)
	(from thiocyanate solution)			
Zn(II)	99	100	100	99
Co(II)	94	97	98	87
Fe(III)	74	83	84	34
Mo(V)	81	81	81	91
V(IV)	10	10	10	8
	(from iodide solution)			
Hg(II)	99	99	99	95
Cd(II)	90	91	91	92
Pb(II)	84	60	62	51
Cu(I)	54	55	54	29

References

1) T. SOTOBAYASHI, T. SUZUKI and K. YAMADA, Chem. Lett., 1976, 77.
2) T. SOTOBAYASHI, T. SUZUKI and H. KUDO, J. Radioanal. Chem., in press.
3) This value (n) shows the average total number of ethylene oxide groups in a Tween 80 molecule.

(Received April 7, 1976)