NOTES

The Extraction of Molybdenum(VI) with Long-chain Alkylamine

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Solvent extraction with long-chain alkylamine has found wide application in a number of fields, especially in the recovery or separation of metals. The amine extraction of metal ions has been widely investigated by Coleman *et al.*[1] and by Ishimori *et al.*[2-4]; the latter have given numerous data on the extraction of a number of elements, which were determined radiometrically using Primene JM-T, Amberlite LA-1, and tri-isooctylamine as extractants.

The experiments described below deal with the extraction of molybdenum(VI) from hydrochloric, sulfuric, and nitric acid solutions with each salt of Amberlite LA-2 in kerosene, and with the back-extraction of the organic molybdenum with several aqueous back-extractants.

Experimental

Amberlite LA-2 was diluted to a concentration of 0.1 M with kerosene, washed with hydrochloric acid and sodium hydroxide alternatively, and converted to hydrochloride, sulfate, or nitrate by equilibrating it with each respective acid of 1 M; then it was used for the extraction of molybdenum.

The ammonium molybdate solution (25 m*l*) containing 10 mg of molybdenum and varying amounts of hydrochloric, sulfuric, or nitric acid was equilibrated with an equal volume of the corresponding LA-2 salt solution. The residual molybdenum in the aqueous phase was determined titrimetrically with permanganate after the reduction of molybdenum to Mo(III) by the use of a liquid zinc amalgam, or colorimetrically by means of the thiocyanate - tin(II) chloride method.[5]

Results and Discussion

Figure 1 shows the percentage of the extraction of molybdenum(VI) *vs.* the initial acid concentration in the aqueous phase. From slightly acidic solutions, molybdenum(VI) is extracted in Amberlite LA-2 salt solutions. Since molybdenum(VI) is known to be present as the polymolybdate anion in neutral or weak acid solutions, the extracted species at such low acidities are presumably LA-2 polymolybdates. However, the extractability decreases abruptly with an increase in the acidity, and the extraction reaches almost zero at 2 M of nitric and 4 M of sulfuric acid. Thereafter, in both acid media, molybdenum(VI) remains not extracted over virtually all the acidity range investigated (both up to 6 M). These decreases in extractability may be attributed to the formation of inextractable cationic species such as MoO_2^{2+} and to the competition of acid anions for the amine. In the case of the hydrochloric acid medium, the extraction, after reaching a minimum at about 3 M, rises again and gives a plateau of about 65% at acidities between 6 and 9 M.

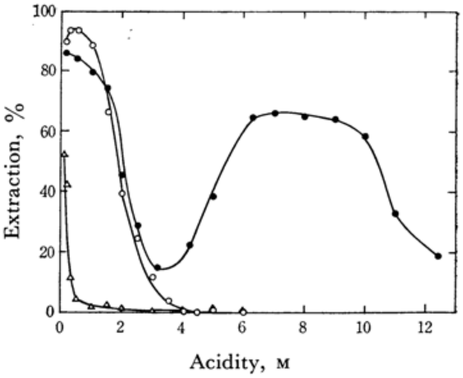

Fig. 1. Acid dependence of extraction of Mo(VI).
●: HCl, ○: H_2SO_4, △: HNO_3

Such extraction behavior of molybdenum(VI) in the LA-2 system bears an appreciable resemblance not only to that in Amberlite LA-1 or triisooctylamine systems given by Ishimori *et al.*,[2-4] but also to that in adsorption on a resinous anion

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[1] C. F. Coleman, K. B. Brown, J. G. Moore and D. J. Crouse, "2nd. United Nations International Conference on the Peaceful Uses of Atomic Energy," Paper No. 510 (1958).

[2] T. Ishimori and E. Nakamura, JAERI Rep. 1047 (1963).

[3] T. Ishimori *et al.*, JAERI Rep. 1062 (1964).

[4] T. Ishimori *et al.*, JAERI Rep. 1106 (1966).

[5] E. B. Sandell, "The Colorimetric Determination of Traces of Metals," Interscience Publishers, New York (1950), p. 453.

exchanger studied by Kraus *et al.*6) and Heitner-Wirguin *et al.*7) The last-named investigators reported the strong uptake of molybdenum(VI) at a low concentration of hydrochloric acid, although this has not been clearly described by Kraus *et al.* or by Ishimori *et al.* The results shown in Fig. 1 imply the presence of anionic chlorocomplex species of molybdenum(VI) in hydrochloric acid, and the absence of such extractable nitrato- or sulfatocomplexes in at least the acidities investigated. The neutral or anionic complexes of molybdenum(VI) in hydrochloric acid have been proposed by Chauveau,8) Neumann *et al.*,9) and Heitner-Wirguin *et al.*6)

The molybdenum extracted in the organic phase could be almost completely recovered by the use of aqueous alkali, such as sodium hydroxide, carbonate, and ammonia water. For instance, when the extraction was carried out at 1 M of hydrochloric acid, all the molybdenum could be back-extracted with 0.5 M sodium hydroxide; 1 M sodium carbonate gave a back-extraction of 99 to 100% regardless of the acidity at the extraction. On the other hand, sodium chloride of 2 M or less gave no satisfactory back-extraction.

The above data suggest two methods for the concentration of a dilute molybdate solution by the use of the alkylamine; one of them includes the extraction of molybdenum from a strong hydrochloric acid solution, and the other, from a slightly acidic solution. It would be expected that the latter would be more effective than the former because of its higher extraction and the ease of back-extraction.

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6) C. Heitner-Wirguin and R. Cohen, *J. Inorg. Nucl. Chem.*, **27**, 1989 (1965).

7) K. A. Kraus, F. Nelson and G. E. Moore *J., Am. Chem. Soc.*, **77**, 3972 (1955).

8) F. Chauveau, *Compt. rend.*, **242**, 2154 (1956).

9) H. M. Neumann and N. C. Cook, *J. Am. Chem. Soc.*, **79**, 3062 (1956).