AN EVALUATION OF CROWN COMPOUNDS IN SOLVENT EXTRACTION OF METALS*

W. J. McDowell and R. R. Shoun
Chemical Technology Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830 USA

SUMMARY

CONF-770907--4

The cyclic polyethers or crown ethers are known to form adducts with

some alkali and alkaline earth compounds, and the selectivity of complex

formation is reported to be related to the match between the size of the

metal ion and the size of the hole in the crown ether. These early

observations suggested that appropriate compounds of this type might be

highly selective solvent extraction reagents for substances of interest in

process applications; therefore tests were conducted in which we attempted

to extract mineral acid salts into water-immiscible solutions of crown ethers.

A number of tests of extraction from aqueous nitrate, chloride,

hydroxide, thiocyanate, and perchlorate systems gave very low distributions

of the metal ion (alkali, alkaline earth, and actinide) to a benzene-- or

chloroform--crown ether phase, and the relative distribution did not usually

agree with the extraction order expected from a match between ion size and

crown ether hole size. These results, plus early work reporting successful

extraction from picrate systems and of complex formation in homogeneous

alcohol-water systems, suggest that successful extraction of metal ions

into a water-immiscible organic solution of crown ethers depends on the ability to solvate the anion in the organic phase. Experiments in which an organic-soluble anion, di(2-ethylhexyl) phosphate, was provided in the organic phase resulted in increased alkali metal extraction and an order of extraction of K > Rb > Cs > Li > Na rather than the order Li > Na > K > Rb > Cs expected for di(2-ethylhexyl) phosphoric acid alone. This indicates a contribution of the crown ether to the selectivity and also supports the importance of anion solvation in crown-ether extraction.

The addition of an organic phase distributing phenol (nonylphenol) or alcohol (2-ethylhexanol) to the crown ether solution increased the extraction of alkali metal chlorides markedly, presumably because of increased solvation of the chloride ion. The benzene--crown ether--2-ethyl-hexanol system was studied systematically. The extraction of KCl from 2 $\underline{M}$ $MgCl_2$ solutions was found to vary with alcohol concentration with a first-power dependence at low concentrations and a second-power dependence at high concentrations. Crown ether concentration dependence was first power over the concentration range tested. These and supporting data indicate an organic-phase species containing one crown ether and one to two alcohol molecules per KCl molecule. KCl extraction increased as ionic strength and/or chloride concentration increased but increased only slightly with HCl concentration at constant ionic strength.

AN EVALUATION OF CROWN COMPOUNDS IN SOLVENT EXTRACTION OF METALS*

W. J. McDowell and R. R. Shoun
Chemical Technology Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

AN EVALUATION OF CROWN COMPOUNDS IN SOLVENT EXTRACTION OF METALS*

W. J. McDowell and R. R. Shoun
Chemical Technology Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

ABSTRACT

Unexpectedly low results were obtained for extraction of chlorides, perchlorates, nitrates, and thiocyanates of alkalis, alkaline earths, and actinides from aqueous solutions by water-immiscible solutions of crown ethers. The expected preference for ions matching the crown ether hole-size was not seen here or in solubilizing dry alkali chlorides. Addition of an organic-soluble acid increased alkali extraction, with preference for the ion sized to fit the crown ether. Addition of an organic-soluble alcohol or phenol increased extraction of KCl. Alcohol system results indicated an adduct of one crown ether and one or two alcohol molecules per KCl.

INTRODUCTION

It has been amply demonstrated that crown ethers such as those shown in Table 1 are able to form adducts with alkali metal salts and, under some conditions, to solubilize these salts into organic solvents where it would normally be impossible to dissolve the salt.[1,2] Evidence has been presented indicating that the alkali metal ion in these adducts is situated in the hole in the crown ether ring and that the stability of the adduct formed depends on the correspondence between the size of the ion and the size of the hole in the crown ether.[1]

Although most of the early work with crown ether complex formation used homogeneous alcohol-water systems, a number of more recent studies of relative binding of alkali metal ions have involved extraction of metal salts from aqueous phases into water-immiscible solutions of the crown ethers. The anion most commonly used in these studies was picrate.[3-8] In addition, dicyclohexyl-18-crown-6 has been used as the extractant in a countercurrent liquid-liquid distribution system for the separation of calcium isotopes as calcium chloride.[9] These facts suggest that crown ethers could be useful specific reagents for two-phase solvent extraction systems. Therefore, consistent with our present interests, most of the work reported here (both that of others and our own) will be concerned with the applicability of crown ethers to liquid-liquid extraction systems.

Special anions such as picrate would not be desirable in the kind of extraction system we want to consider. Chloride or some other mineral acid would be more suitable. Further requirements of a suitable extraction system would include: (1) adequate solubility in a solvent of high flash point (and preferably of low toxicity), such as dodecane or diethylbenzene, (2) very low distribution to the aqueous phase (e.g., $\leq 10^{-6}$ $\underline{M}$), and (3) ability to extract the compound or compounds of interest with a distribution coefficient greater than 1, preferably greater than 10. The purpose of this work was to examine the available crown ethers for applicability, within such criteria, to liquid-liquid extraction systems of interest in hydrometallurgical and related applications.

EXPERIMENTAL

Dicarboxydinaphthyl-18-crown-6 and bis dinaphthyl-18-crown-6 were supplied by D. J. Cram.* Dicyclohexyl-18-crown-6, dibenzo-18-crown-6, 18-crown-6, and 15-crown-5 were obtained from the Aldrich Chemical Company and the Parish Chemical Company. All these compounds were used as received. Dicyclohexyl-18-crown-6 from more than one source was used in this work. However, in each set of experiments for determining a specific effect (e.g., reagent dependence, order of extraction) only one batch of reagent was used so that results are internally consistent, although cross-comparison of extraction coefficients under the same conditions shows more scatter than would be expected from considering individual studies. Di(2-ethylhexyl)

---

*Department of Chemistry, UCLA.

phosphoric acid was obtained from the Virginia-Carolina Chemical Company
and was purified by a copper precipitation method prior to use.[10]   Other
chemicals used were of the usual reagent grade quali-y.

Equilibrations were done in small separatory funnels and vials.
The equilibrated phases were analyzed by radiochemical and atomic absorption
methods.

RESULTS AND DISCUSSION

General Screening Tests

The crown ethers used in this study and their approximate solubilities
in benzene or chloroform are listed in Table 1. Each compound is shown
structurally and is identified both by name and by an abbreviated form,
which is used throughout the remainder of this paper. Two solvents, benzene
and chloroform, were used here as in previous survey work because they avoid
some solubility limitations and thus facilitate intercomparison of reagents;
however, neither of them meets our requirements for practical process
applications. Table 1 also shows the distribution of several metal salts
from aqueous solutions to the crown ether solutions. Although the distribu-
tion coefficients ($D = [M]_{org}/[M]_{aq}$) are uniformly and disappointingly low,
the results do suggest some specific effects. Compound CDN18-C-6 extracted
salts from hydroxide systems essentially as would be expected because of
its carboxylic acid groups; on the other hand, the reversal in order of
extractability of sodium and potassium from that expected for a carboxylic
acid alone[11] seems to imply that the structure of the crown ether has an

effect. A similar reversal in the expected order of extractability of potassium and calcium[12] observed in neutral chloride and nitrate systems provides further evidence of such an effect. High selectivity for strontium over barium and potassium has been noted by Helgeson, Timko, and Cram for a similar compound with a carboxy functional group.[13]

Compounds BisDN18-C-6, 18-C-6, DB18-C-6, and 15-C-5 extracted so little of the alkalis and alkaline earths from dilute aqueous solutions that work with them was suspended. The subsequent systematic investigation used primarily DC18-C-6.

As an adjunct to the liquid-liquid extraction investigation, the relative solubilization of the alkali and alkaline earth chlorides was tested in the presence of minimum amounts of water; that is, the nominally dry salts were contacted with an organic crown ether solution. The results are shown in Table 2. The expected size relationship that has been reported for other systems[1,2] does not seem to have any discernible effect on the order of solubilization of these chloride salts under these conditions. Maximum loadings obtained in the tests with 0.1 $\underline{M}$ DC18-C-6 in benzene were 50% when the group I elements were mixed, 30% when the group II elements were mixed, and 10% and 35% for lithium and calcium, respectively, when tested separately. This can be compared with potassium permanganate, which is reported to solubilize in DC18-C-6 in a 1:1 mole ratio.[14] The only case in our tests in which loading approached a 1:1 mole ratio was the calcium extraction from 2 $\underline{M}$ calcium thiocyanate solution.

Prompted by the apparent difficulty of solvating the mineral acid anions into the organic phase, experiments were designed in which an

organic-phase-soluble anion was present. Di(2-ethylhexyl) phosphoric acid

HDEHP) is known to extract the alkali metals (although with low distribu-

tion coefficients) in the order Li > Na > K > Rb > Cs.[15] Solutions containing

0.1 $\underline{M}$ HDEHP and 0.4 $\underline{M}$ DC18-C-6 were equilibrated at pH 4.8 (HDEHP 50% in

the salt form) with a solution that was 0.1 $\underline{M}$ in each of the alkali metal

nitrates. In these tests the order of extraction was found to be K > Rb >

Cs > Li > Na (Table 3).

Perhaps the most pertinent observation to be made from the above tests

is that anions such as nitrate, chloride, perchlorate, and hydroxide are

very difficult to solvate into crown ether solutions in the diluents chosen.

Thiocyanate, being a large anion, is somewhat easier to solvate, and we can

conclude from the work of others that permanganate and picrate are even

more readily solvated. It is reasonable to expect large anions of an organic

character such as picrate to be easily solvated into organic phases. Thus,

in order to utilize crown ethers as extractants, either an organophilic

anion must be supplied for the metal ion or provisions must be made for solvating

the inorganic anion into the organic phase.

Alcohols as Anion Solubilizers

In the early work with the crown ethers, complexes with alkali metal

salts were frequently formed in mixtures of alcohol and water in which

both the salt and the crown ether were soluble. Further, it was noted by

Pedersen and Frensdorff[1] that the addition of small amounts of methanol greatly increased the amount of salts solvated by crown ether solutions. Thus they hyphothesized that alcohol or some analogous compound might take part in the complex, possibly serving to complete the solvation sphere of the cation or solvate the anion. Some of our early experiments in which 10% butanol was added to a benzene solution of crown ether produced a two- to three-fold increase in potassium extraction from 0.01 $\underline{M}$ KCl, suggesting that a water-immiscible alcohol in the organic phase might effectively promote the extraction of alkali salts of the mineral acids by crown ether solutions. This opinion was subsequently reinforced by information obtained from Y. Marcus,[16] in which he reported significant enhancement of salt solubilization by crown ethers using a number of alcohols and other hydrogen bonding compounds. These pieces of information led us to examine a mixed alcohol-crown ether system in some detail.

The 2-Ethylhexanol--DC18-C-6 System

Figure 1 shows the effect of varying the 2-ethylhexanol content of the benzene diluent on potassium extraction from 2 $\underline{M}$ MgCl$_2$-0.01 $\underline{M}$ KCl by 0.1 $\underline{M}$ DC18-C-6. In this figure, log D_K (D_K = [K]$_{org}$/[K]$_{aq}$) is plotted vs log volume percent of alcohol (proportional to molarity). The average slope is 1.5, approaching slope 1.0 at low alcohol concentration, and approaching 2.0 at the higher alcohol concentration. The effect of nonylphenol on potassium extraction is similar (Fig. 2), the slope of a comparable plot being about 1.0; however, higher concentrations were not tested because

of the viscosity of the nonylphenol. These data indicate that the alcohol and phenol are similarly and strongly involved in the formation of the KCl-crown ether adduct in the organic phase and suggest the formation of an organic-phase species containing one mole of alcohol or phenol at low concentrations and possibly more at higher concentrations. Analyses show that very little $MgCl_2$ is extracted in this system; only 2.7×10^{-4} $\underline{M}$ magnesium is found in 0.1 $\underline{M}$ DC18-C-6 in 75% 2-ethylhexanol--25% benzene when equilibrated with 2 $\underline{M}$ aqueous $MgCl_2$.

Since DC18-C-6 contains no ion exchange sites, the extraction of potassium must involve the extraction of chloride, and a general equation for this extraction could be:

$$K^+ + Cl^- + nDC18\text{-}C\text{-}6 + mROH \rightarrow \frac{1}{x} (nDC18\text{-}C\text{-}6 \cdot KCl \cdot mROH)_x, \tag{1}$$
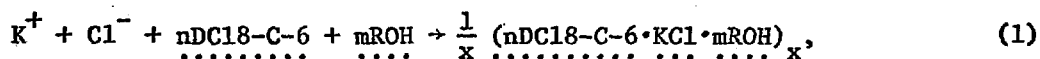
in which dotted underlines indicate an organic-phase species, ROH represents the alcohol, and possible association of the organic-phase adduct into an x-fold aggregate is provided for. Figure 3 shows a plot of log $[K]_{org}$ vs log $[K]_{aq}$ in a system where the aqueous phase is 2 $\underline{M}$ $MgCl_2$ and the organic phase is 0.1 $\underline{M}$ DC18-C-6 in 75% 2-ethylhexanol--25% benzene. The initial slope of this curve is 1.0, which indicates that, if potassium is unassociated in the aqueous phase, then the complex is also unassociated in the organic phase and the value of x is 1.

The dependence of potassium extraction from 2 $\underline{M}$ $MgCl_2$ on the concentration of DC18-C-6 in 25% benzene--75% 2-ethylhexanol is shown in Fig. 4. These data yield a slope of almost exactly 1.0, indicating (since polynuclear

complexes are ruled out) the association of one mole of potassium (as KCl) with one mole of DC18-C-6 in this system over the concentration range used here. This is in agreement with reported data indicating a one-to-one association in similar crown ether adducts.[1,2]

Figures 5 and 6 show acid dependence and ionic strength dependence, respectively, of KCl extraction by 0.1 $\underline{M}$ DC18-C-6 in 25% benzene--75% 2-ethylhexanol. In both cases, however, the aqueous-phase chloride concentration increases along with the ionic strength variable since we knew of no "inert" anion to substitute for chloride. Thus, Fig. 5 suggests that the acid dependence, if any, is slight. The nature of the extractant does not lead one to expect an increased extraction due to increased acid concentration; therefore, we suspect that what appears to be a small positive acid dependence may be related to the small chloride concentration increase. However, plotting log D_K vs log [Cl] from these data yields a slope greater than the expected value of 1, suggesting that changes in the medium, or activity effects, may also be contributing to the observed increase in D_K. Figure 6 likewise probably reflects primarily the change in chloride concentration or activity.

CONCLUSIONS

Although crown ethers form complexes with alkali and alkaline earth compounds in homogeneous alcohol-water systems and extract the picrate salts of these elements in two-phase systems, they extract the common mineral-acid salts very poorly and not in the order expected from the size of the ion relative to the size of the crown ether hole. Solubilization of the anion appears to be critical in the extraction of salts by crown ethers; i.e., providing a means of solubilizing the anion appears to be necessary. The latter can be accomplished by using an alcohol as the main component of the organic diluent. A study of KCl extraction from $MgCl_2$ solutions by DC18-C-6 in 75% 2-ethylhexanol--25% benzene suggests a reaction such as:
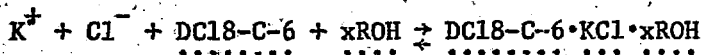
$$K^+ + Cl^- + DC18\text{-}C\text{-}6 + xROH \rightleftharpoons DC18\text{-}C\text{-}6 \cdot KCl \cdot xROH$$

where x is 1 or 2.

NOTATION LIST

BisDN18-C-6 = bis dinaphthyl-18-crown-6

CDN18-C-6 = dicarboxydinaphthyl-18-crown-6

DB18-C-6 = dibenzo-18-crown-6

DC18-C-6 = dicyclohexyl-18-crown-6

D_K = distribution coefficient for potassium

$= [K]_{org}/[K]_{aq}$

D_m = distribution coefficient for the metal, M
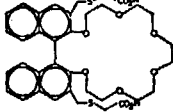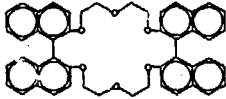
$= [m]_{org}/[M]_{aq}$

15-C-5 = 15-crown-5
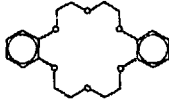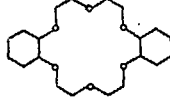
18-C-16 = 18-crown-6

HDEHP = di(2-ethylhexyl)phosphoric acid

REFERENCES

1. Pedersen, C.J. and Frensdorff, H.K., Angew.Chem.Intern.Ed.Engl. 1972, 11, 16.

2. Lehn, J.M., Structure and Bonding 1973, Vol.16, 1-70, Springer-Verlag, New York.

3. Frensdorff, H.K., J.Am.Chem.Soc. 1971, 93, 4684.

4. Pedersen, C.J., Fed.Proc. 1968, 27, 1305.

5. Sadakane, A., Iwachido, T. and Toei, K., Bull.Chem.Soc.Jpn. 1975, 48, 60.

6. Danesi, P.R., Meider-Gorican, H., Chiarizia, R. and Scibona, G., J.Inorg. Nucl.Chem. 1975, 37, 1479.

7. Rais, J. and Selvcky, P., Check Patent No. 149403, July 15, 1973.

8. Rais, J., Kyrs, M. and Kadlecova, L., in Proceedings of International Solvent Extraction Conference 1974, Vol. 2, 1705-15.

9. Jepson, B.E. and DeWitt, R., J.Inorg.Nucl.Chem. 1976, 38, 1175.

10. McDowell, W.J., Perdue, P.T. and Case, G.N., J.Inorg.Nucl.Chem. 1976, 38, 2127.

11. Nikolaev, A.V. et al., Izv.Sib.Otd.Akad.NaukSSSR 1972, 5, 52.

12. McDowell, W.J. and Harmon, H.D., J.Inorg.Nucl.Chem. 1969, 31, 1473.

13. Helgeson, R.C., Timko, J.M. and Cram, D.J., J.Am.Chem.Soc. 1973, 93, 3023.

14. Sam, D.J. and Simmons, J.F., J.Am.Chem.Soc. 1972, 94, 4024.

15. McDowell, W.J., J.Inorg.Nucl.Chem. 1971, 33, 1067.

16. Marcus, Y., Personal communication, 1976.

Table 1. Screening Tests With Crown Ether Solutions

	ORGANIC SOLUTION					
	DICARBOXY DINAPHTHYL 18-CROWN-6 (CON18-C-6)	BIS DINAPHTHYL 18-CROWN-6 (BISDN18-C-6)	18-CROWN-6 (18-C-6)	DIBENZO 18-CROWN-6 (DB18-C-6)	DICYCLOHEXYL-18-CROWN-6 (DC18-C-6)	15-CROWN-5 (15-C-5)
AQUEOUS SOLUTION[a]	0.01 M in CHCl$_3$	0.01 M in CHCl$_3$	0.1 M in benzene	0.01 M in benzene	0.1 M in benzene	0.1 M in benzene

DISTRIBUTION COEFFICIENTS, $D_M = [M]org / [M]aq$

0.1 M HNO$_3$[b]	Sr, Ce, Am $\}$ <10^{-4} ; Cs 0.007				Am <10^{-4}	
2 M HNO$_3$[b]	Sr, Ce, Am $\}$ <10^{-4} ; Cs 0.035				Am <10^{-4}	
NEUTRAL NITRATE	Ca <10^{-4} ; K 0.22	K, Ce $\}$ <10^{-4}			K <10^{-4}	
HYDROXIDE	Na 0.95 ; K 2.58 ; Ca 1.86 ; Sr 2.65 ; Ba 2.05	Na, K, Ba $\}$ <10^{-4} ; Ca 0.1 ; Sr 0.001	Na, K, Sr, Ba $\}$ <10^{-4}	Na, K, Sr, Ba $\}$ <10^{-4}	K, Ba $\}$ <10^{-4}	
NEUTRAL CHLORIDE	Ca <10^{-4} ; K 0.21	K, Ce $\}$ <10^{-4}			K <10^{-1}	
4 M LiClO$_4$[b]					Zn, Eu $\}$ <10^{-4} ; Ce 0.13 ; Am 0.0007	
THIOCYANATE, 2 M[c]					Li 0.020 ; Na 0.023 ; K 0.035 ; Ce 0.049	Li 0.014 ; Na 0.0066 ; K 0.014 ; Ce 0.0056 ; Ba 0.0097

ABBREVIATIONS: _/ = ETHYLENE ;)C-C((H$_2$, H$_2$) ; V = METHYLENE CH$_2$; = CYCLOHEXYLENE ; = BENZO ; = NAPHTHALENE.

TOPO = TRI-N-OCTYLPHOSPHINE OXIDE

[a] 0.01 M 0.1 M EXCEPT AS OTHERWISE NOTED.

[b] TEST CATIONS AT TRACER LEVELS.

[c] 18-C-6 LOADING FROM 58 TO 94%, AND 15-C-5 LOADINGS FROM 11 TO 28% FROM THIOCYANATE SOLUTIONS.

Table 2. Relative solubilization of chloride salts by crown ether solutions

Organic phase	Conc. order in organic	Solids phase
0.1 M DC18-C-6 in C_6H_6	Ca >> Li > Sr > Na > K > Ba > Mg > Rb > Cs	Individual salts
0.1 M 15-C-5 in C_6H_6	Na > Li > K > Rb > Ba > Ca > Cs > Sr >> Mg	Individual salts
0.01 M BisDN18-C-6 in $CHCl_3$	K ≈ Na > Li > Rb > Cs and Ca > Mg > Sr >> Ba	Mixed within groups
0.1 M 18-C-6 in C_6H_6	Rb > Li > Cs > K > Na and Ca > Mg > Sr > Ba	Mixed within groups
0.1 M DB18-C-6 in C_6H_6	Na > K ≈ Li > Rb >> Cs and Ca > Mg > Sr > Ba	Mixed within groups
0.1 M DC18-C-6 in C_6H_6	Li >> K ≈ Rb > Cs > Na and Ca > Sr > Mg > Ba	Mixed within groups
0.1 M DC18-C-6 in C_6H_6	Li > Sr > Ca > Rb > K > Na > Cs > Ba > Mg	All mixed

Table 3. Effect of crown ether on order of extraction of alkali metals
by HDEHP

| Alkali metal | Extraction relative to Cs | | Extraction coefficient with crown ether[b] |
	Without crown ether[a]	With crown ether[b]	
Li	8.2	0.46	0.023
Na	2.6	0.40	0.020
K	1.2	7.2	0.36
Rb	0.87	3.2	0.16
Cs	1.0	1.0	0.05

[a]See Ref 14; organic phase was 65% in the salt form.

[b]0.1 $\underline{M}$ HDEHP, 0.4 $\underline{M}$ DC18-C-6; total alkali ion concentration in aqueous phase, 0.5 $\underline{M}$.

FIGURE CAPTIONS

Fig. 1. Potassium extraction from 2.0 $\underline{M}$ MgCl$_2$ by 0.1 $\underline{M}$
DC18-C-6 in benzene--2-ethylhexanol as a function of the volume
percent of alcohol.

(ORNL DWG 77-529)

Fig. 2. Potassium extraction from 2.0 $\underline{M}$ MgCl$_2$ by 0.1 $\underline{M}$
DC18-C-6 in benzene-nonylphenol as a function of the volume percent
of phenol.

(ORNL DWG 77-526)

Fig. 3. Equilibrium organic-phase potassium vs aqueous-phase
potassium. Extraction was from MgCl$_2$ by 0.1 $\underline{M}$ DC18-C-6 in 25% benzene--
75% 2-ethylhexanol.

(ORNL DWG 77-528)

Fig. 4. Potassium extraction as a function of DC18-C-6 concentration
in 25% benzene--75% 2-ethylhexanol. Aqueous phase was 2 $\underline{M}$ MgCl$_2$.
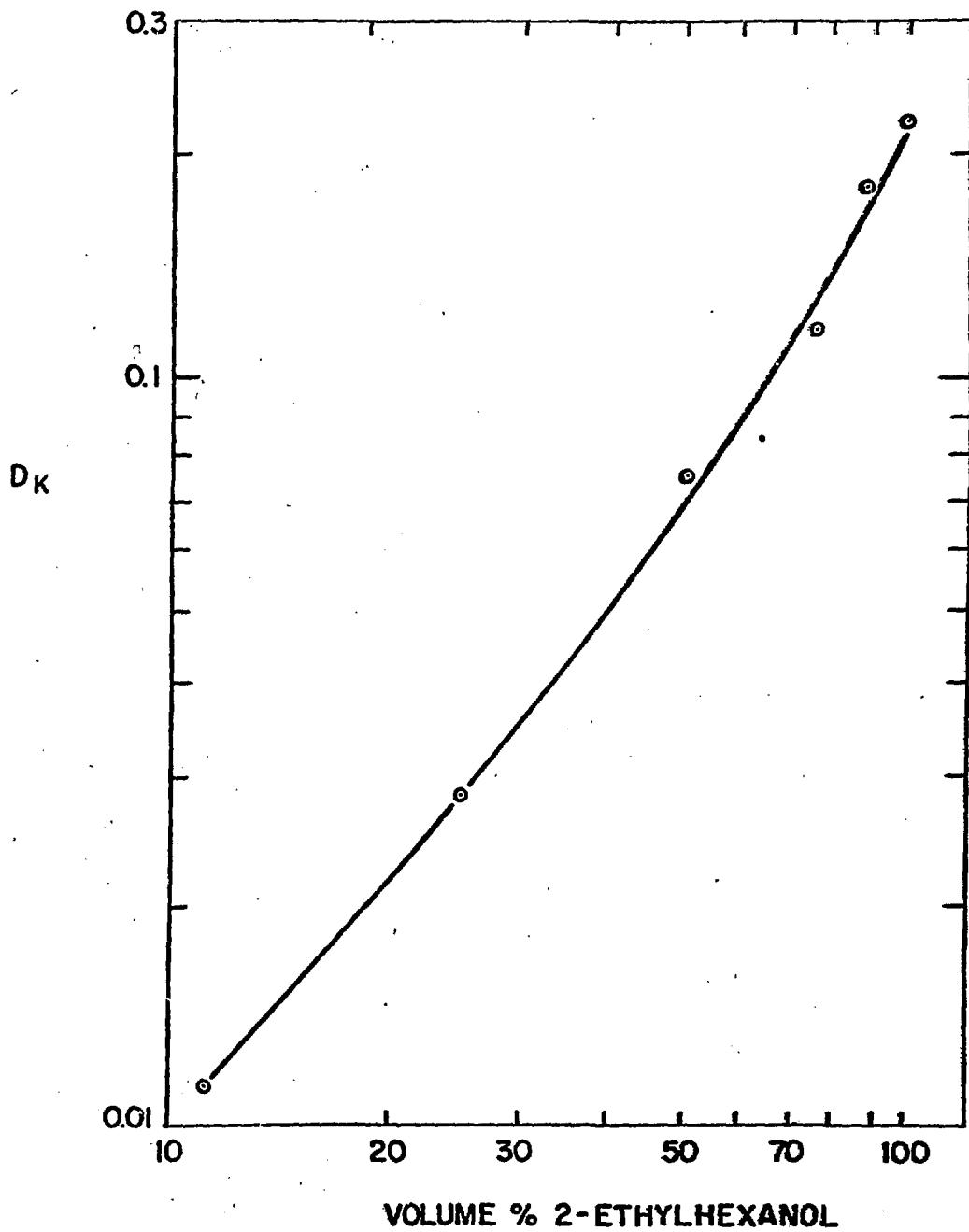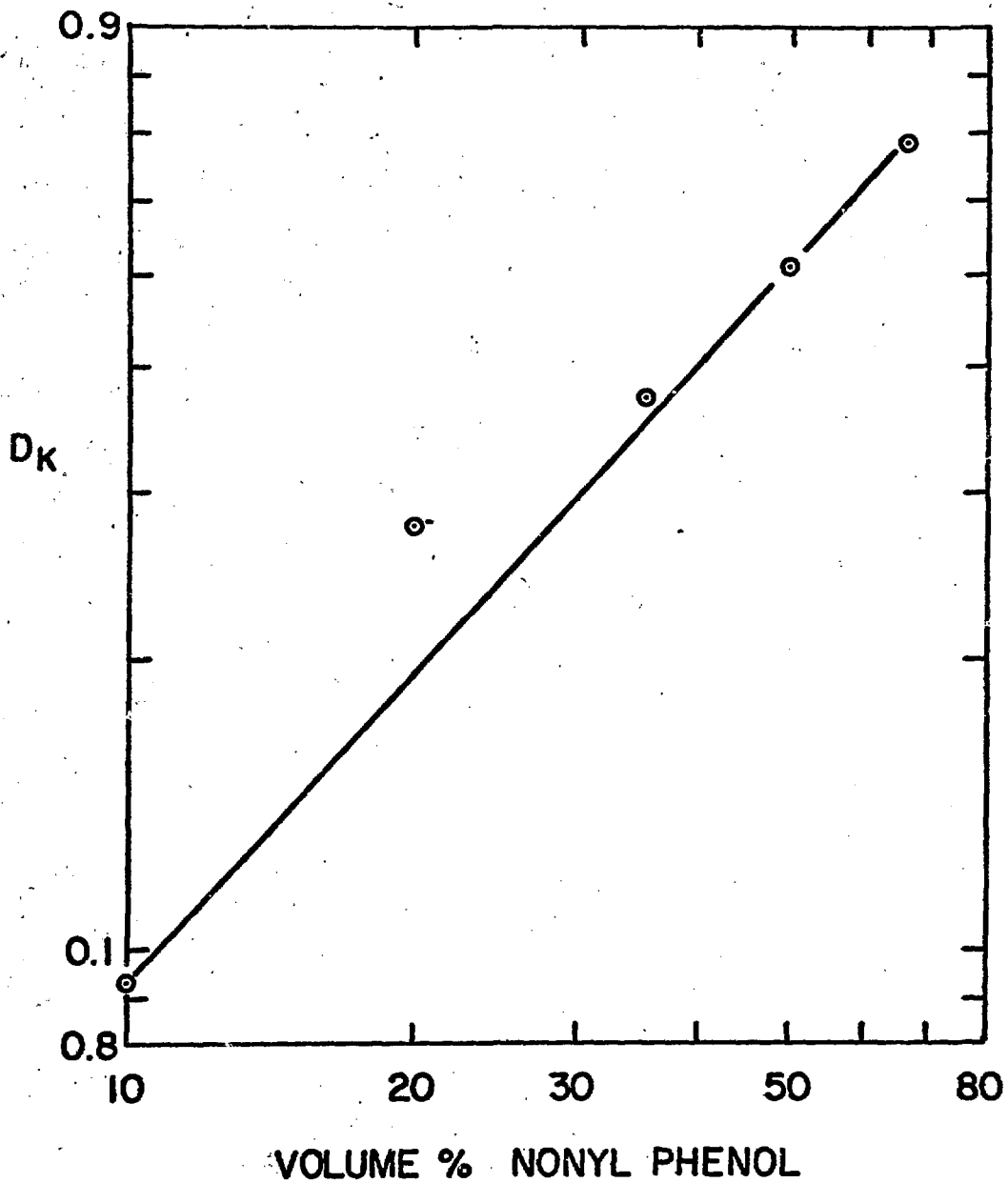
(ORNL DWG 527)

Fig. 5. Acid dependence of potassium extraction by DC18-C-6 in 25%
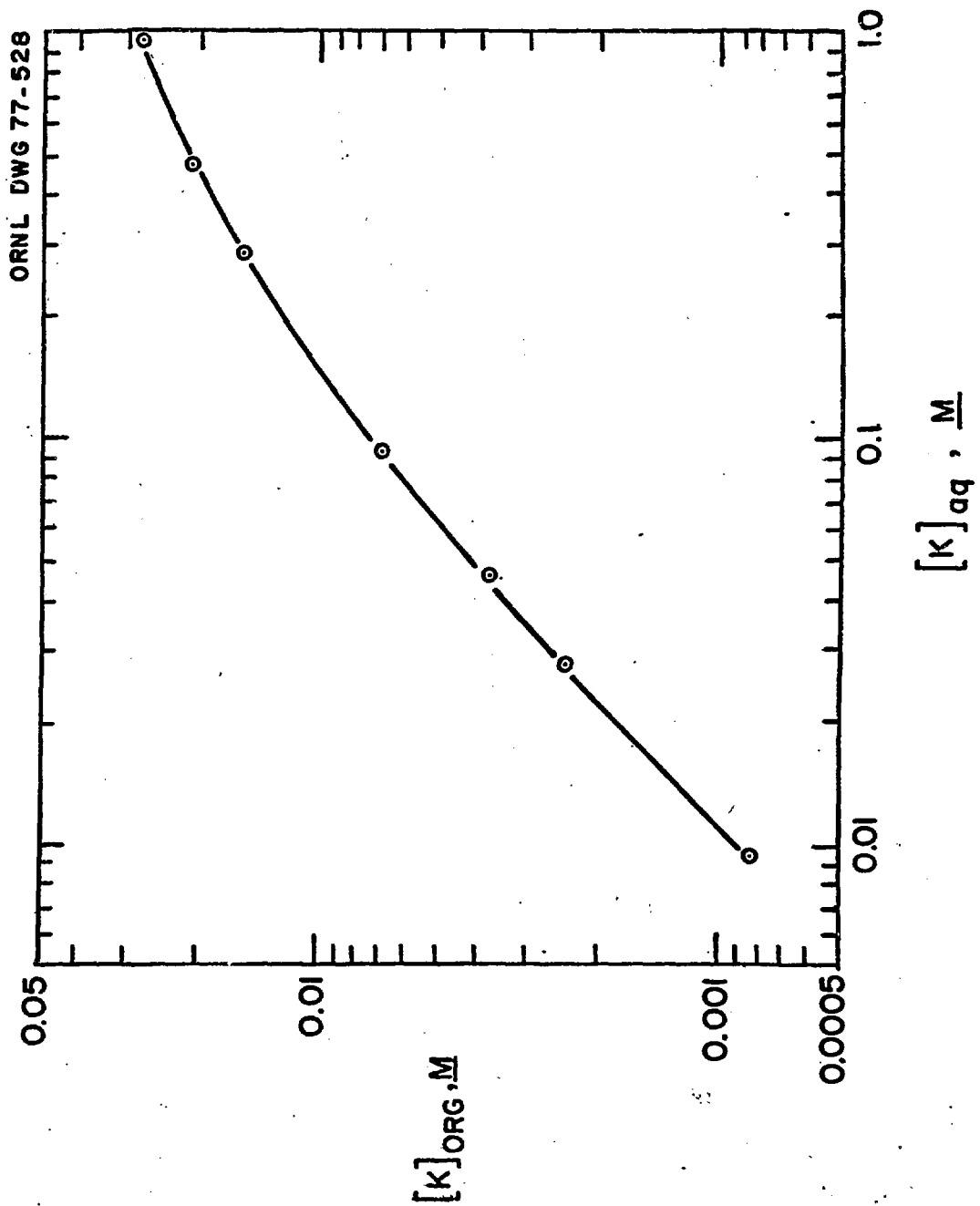benzene--75% 2-ethylhexanol at ionic strength of 6.

(ORNL DWG 77-531)

Fig. 6. Potassium extraction by DC18-C-6 in 25% benzene--75% 2-ethyl-
hexanol as a function of aqueous ionic strength. MgCl$_2$ concentration was
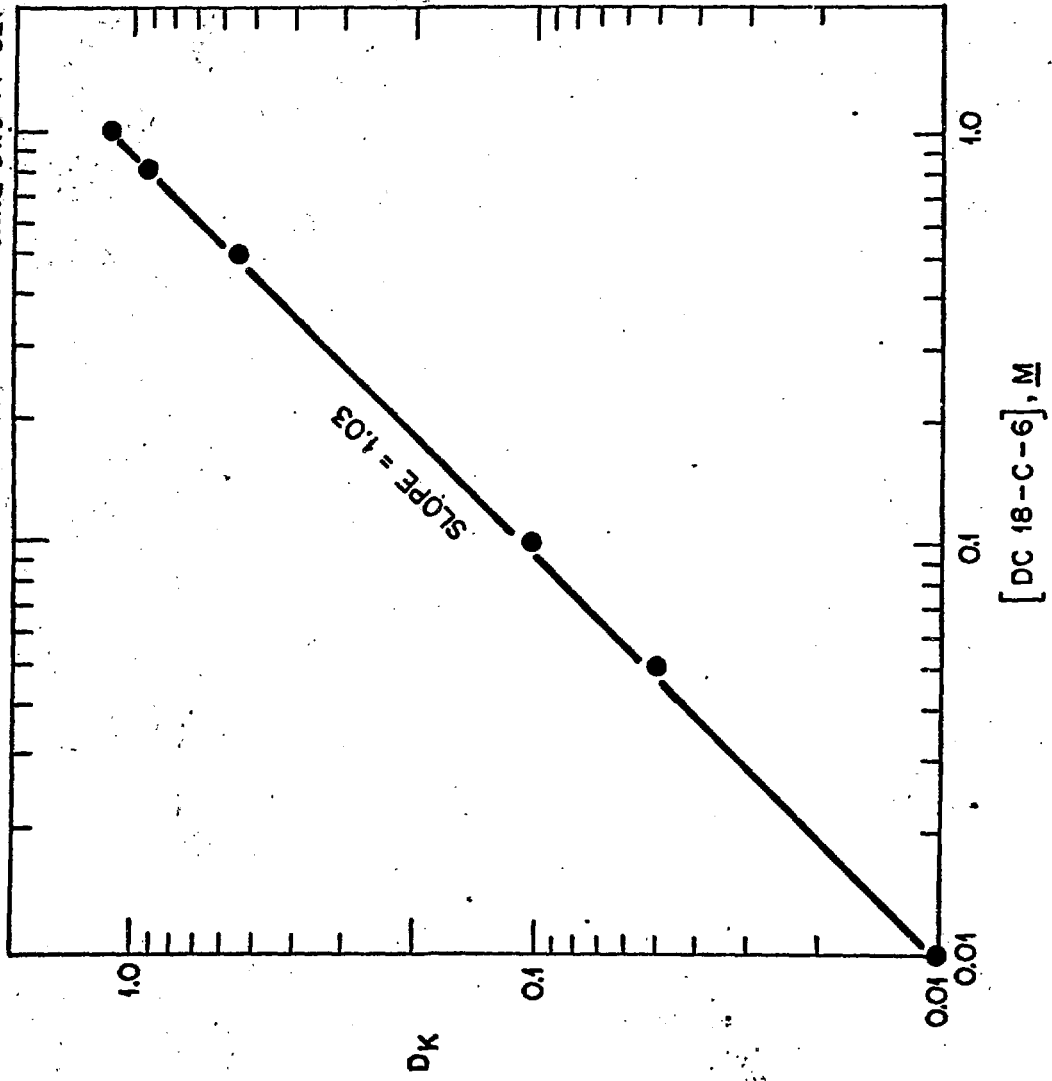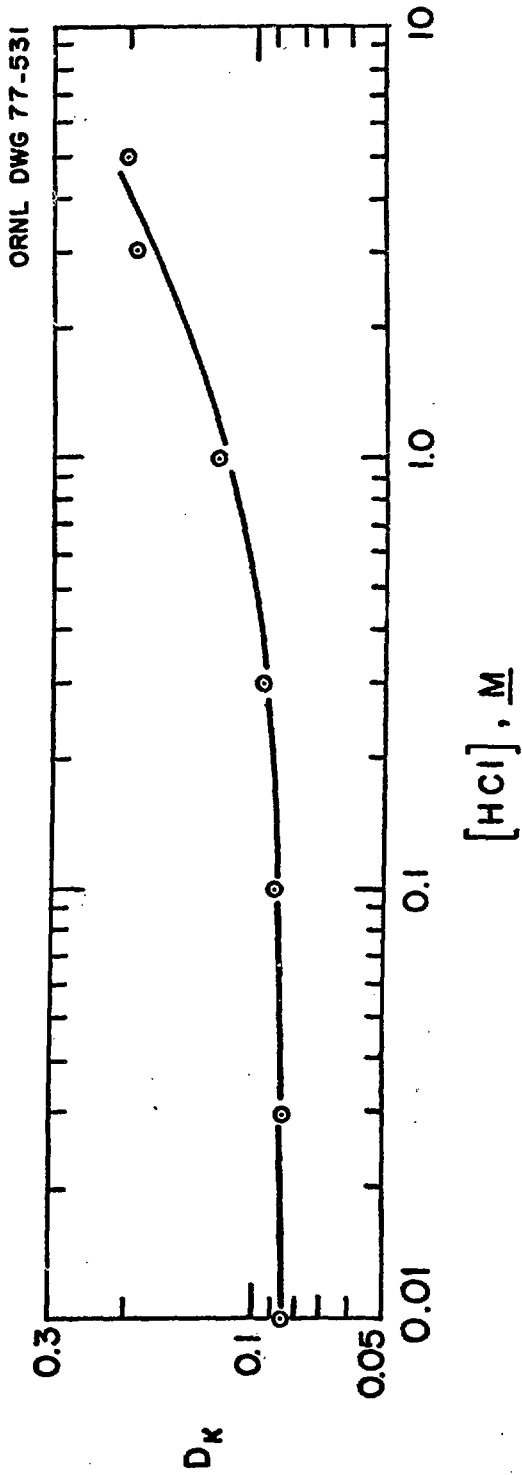0.03 to 3.3 $\underline{M}$.

(ORNL DWG 77-530)

VOLUME % 2-ETHYLHEXANOL

VOLUME % NONYL PHENOL

ORNL DWG 77-528

ORNL DWG 77-531

ORNL DWG 77-530 RI