Anion Exchange Adsorption of Some Metals from Mixed Solvents[1]

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Recently K.A. Kraus and his coworkers[2] have carried out an extensive study on anion exchange adsorption of a number of metallic elements from a hydrochloric acid solution and its related media.

In the present paper, anion exchange adsorption data for zinc(II) and copper (II) from organic solvent—hydrochloric acid mixtures are described and the effect of the addition of the organic solvents are discussed.

Experimental

Materials. — The anion exchanger used was polystyrene-divinylbenzene quarternary amine resin Dowex 1-X8, supplied as beads of 50-100 mesh. The resin was cycled twice with 1N sodium hydroxide and then with 1N hydrochloric acid; after complete conversion into the chloride form it was thoroughly washed with deionized water. The chloride resin was dried to constant weight in a desiccator over silica-gel. The resin thus obtained was found to have a capacity of 3.29 milliequiv. per gram. Dowex 1-X4 resin which was conditioned and dried in the same manner had a capacity of 3.15 milliequiv. per gram.

The organic solvents such as methanol, ethanol, *n*-propanol and acetone were all of "JIS"* first class grade and purified by distillation. Concentrated hydrochloric acid of "JIS" special class quality was used without further purification. Dilute hydrochloric acid was prepared from distillate of azeotropic mixture. Other chemicals are all of "JIS" special class grade and purified by distillation or recrystallization when necessary.

The zinc tracer** was ^{65}Zn ($T_{1/2}=250$ days). An aliquot of the hydrochloric acid solution was dried up and preserved as 0.1 M perchloric acid solution. The absorption characteristic and cation anion exchange chromatographic behavior showed that the tracer was of satisfactory purity.

Measurement of Adsorbability. — The adsorbability of the elements was measured by the equilibrium method and the results were described in terms of distribution coefficient K_d defined as amount of element per gram resin/amount per milliliter solution. In the measurement of K_d of zinc(II), a known weight of dry resin was added to 30 or 40 ml. of mixed solvents and was left overnight until swelling equilibrium was attained. Then 1 ml. of the tracer solution was added and the resulting solution was shaken mechanically in a thermostat at 25±0.1° for three hours. The supernatant solution was pipetted using filter-tubes packed with glass-wool and the radioactivity was measured with a Kobe Kogyo's dipping type G.M. counter of scale-of-64. Factors such as the geometry and the self-absorption were kept as constant as possible. From the resultant decrease in radioactivity of the solution, the values of distribution coefficients were calculated. Preliminary experiments revealed that the constancy of K_d values was attained when the loading of the resin was kept less than ca. 0.5 % of resin capacity.

The distribution coefficient of copper(II) was estimated in the same manner as in the case of zinc(II) except that the decrease in the concentration was measured photometrically using carbamate method[3] (436 mμ). Extinction and spectra were measured by means of a Hitachi's EPU-2 spectrophotometer. The amount of copper was taken so as to be less than 1 % loading with respect to the resin capacity.

The chloride ion concentration was determined by titration with 0.1 or 0.01 N silver nitrate solution using Goodall and Mellor's dead-stop method[4].

Results and Discussion

Adsorption of Zinc(II) from Mixed Solvents.—In Fig. 1, distribution coefficients of zinc(II) in hydrochloric solution containing 30 and 60 % (v/v) methanol were plotted against the molarity of hydrochloric acid (curve 2 and 3). For comparison, the adsorbability in a hydrochloric acid solution was shown by curve 1, which seems to conform very closely to Kraus's[2].

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[1] Presented at the Symposium on the Complex Compound Chemistry, October 27, 1956, Tokyo.

[2] For example, K. A. Kraus and G. E. Moore, *J. Am. Chem. Soc.*, **75**, 1460 (1953); K. A. Kraus, F. Nelson and G W. Smith, *J. Phys. Chem.*, **58**, 11 (1954); K. A. Kraus and F. Nelson, Peaceful Uses of Atomic Energy, Proceedings of the International Conference in Geneva, Vol. VII, 113 (1955) United Nations.

* Japan Industrial Standard.

** Zn-65 (P-1) obtained from U. S. Atomic Energy Commission. The specific activity was 261 mC./g. Zn. on Dec. 23, 1955.

[3] E. B. Sandell, "Colorimetric Determination of Traces of Metals" 304 (1950) Interscience Publishers, Inc., New York.

[4] R. R. Goodall and N. Mellor, *Anal. Chim. Acta*, **5**, 373 (1952).

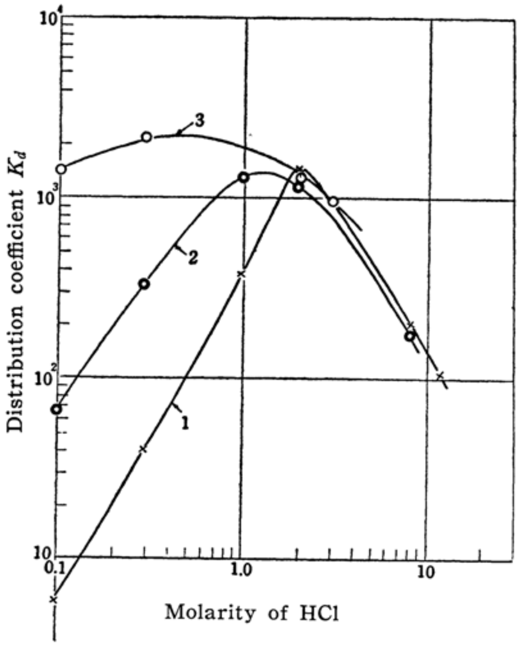

Fig. 1. Anion exchange adsorption of Zn(II).
1. in HCl solution
2. in HCl-30% (v/v) methanol mixture
3. in HCl-60% (v/v) methanol mixture

It is clear that the addition of methanol increases the adsorbability of zinc (II) in the range of lower hydrochloric acid concentrations, i. e. less than 2 M, while in a higher concentration, the effect is not clear. An interesting feature of the results is that the more the concentration of the hydrochloric acid is decreased, the more pronounced the effect and, at the same time, adsorption maxima shift to lower hydrochloric acid concentration.

In order to see the details of the relation between the adsorbability and the concentration of the organic solvent, the distribution coefficient of zinc(II) in various mixed solvents containing methanol, ethanol, *n*-propanol or acetone was examined at constant hydrochloric acid concentration i.e. 0.1 M. The results were summarized in Fig. 2.

The addition of these materials was found to be likewise effective for increasing of the adsorbability of zinc(II). In general the straight line relation between the logarithm of distribution coefficient and the concentration of organic solvents was observed in the range up to at least ca. 60 %. The order of the effect to increase the adsorbability of zinc(II) on the weight bases is:

Acetone≧ethanol>methanol>n-propanol

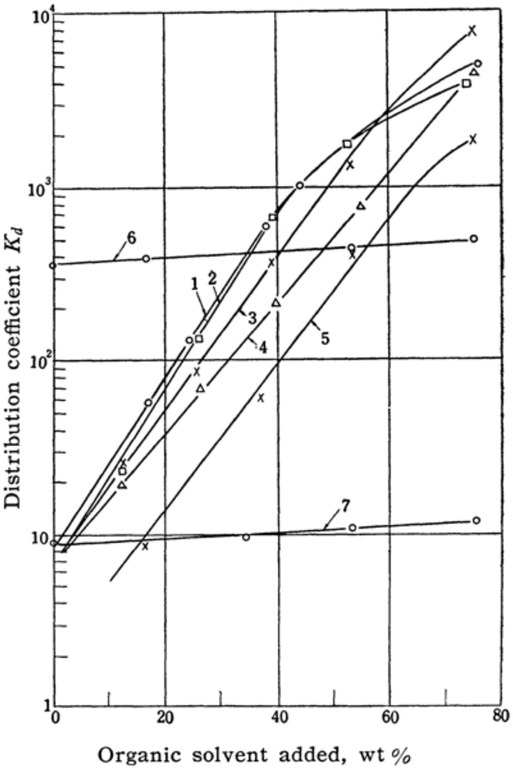

Fig. 2. Effects of various organic solvents on the anion exchange adsorption of Zn(II) in 0.1 M HCl.
1. Acetone
2. Ethanol
3. Methanol
4. *n*-Propanol
5. Methanol(Dowex 1-X4)
6. RNO_3+Cl^-, $\mu=0.003$, (NaCl) Methanol
7. RNO_3+Cl^-, $\mu=0.1$, (KNO_3) Methanol

The experimental data using less cross-linked resin (Dowex 1-X4) in methanol-hydrochloric acid media were also plotted in Fig. 1 (curve 5). The result is very similar to those of 8 % cross-linked resin except that the lower K_d values were obtained.

In the cation exchange equilibria involving alkali and alkaline earth metal ions, Sakaki and Kakihana[5] had previously pointed out that the effect of addition of an alcohol depends, as a first approximation, on the dielectric constants of mixed solvents and is indifferent to the kind of alcohol added, i.e. methanol or ethanol. In the authors' experiments, this relation

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[5] T. Sakaki and H. Kakihana, *Kagaku* (*Science*), **23**, 71 (1953).
T. Sakaki, This Bulletin, **28**, 217, 220 (1955).

was also proved to hold in the media containing methanol and ethanol but the relation no longer holds in cases of other solvents as is seen in Fig. 3.

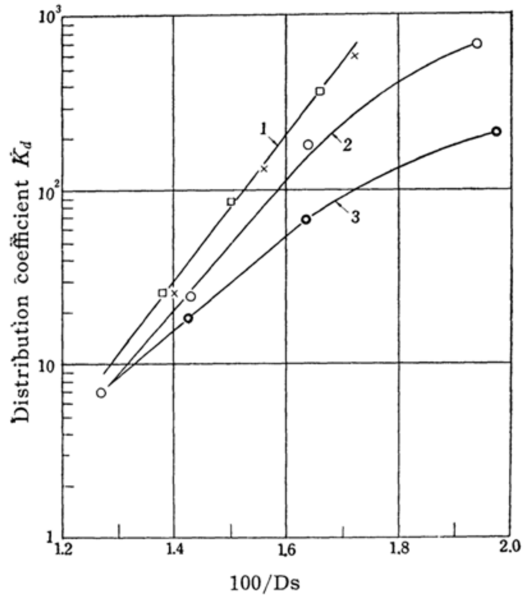

Fig. 3. Relation between K_d of Zn(II) and dielectric constants of solutions in at 0.1 M HCl.
1. Methanol (-×-×-), Ethanol (-□-□-)
2. Acetone
3. *n*-Propanol

Then as a base of comparison, a simple ion, i.e. a chloride ion was equilibrated to the nitrate resin in methanol-water mixtures (curves 6 and 7 in Fig. 2). In this case, the solvent effect was found to be slight as compared with the case described above.

Kraus[2)] suggested that in the elements which show adsorption functions with maxima such as zinc(II), cadmium(II) and gallium(III), the portion of increasing absorbability with increasing hydrochloric acid concentrations is due to the formation of the negatively charged complexes and that the maxima occur at approximately those hydrochloric acid concentrations where the negatively charged complexes become predominant. In view of this, all the experimental data described above seem to imply that the addition of organic solvents favors the dehydration of aquated zinc ions and consequently favors the stepwise formation of negatively charged chloro-complexes as may be expressed by the following set of equations,

$$Zn(H_2O)_4^{2+}+Cl^- \longrightarrow ZnCl(H_2O)_3^{+}+H_2O$$
$$ZnCl(H_2O)_3^{+}+Cl^- \longrightarrow ZnCl_2(H_2O)_2+H_2O$$
$$ZnCl_2(H_2O)_2+Cl^- \longrightarrow ZnCl_3(H_2O)^-+H_2O$$
$$ZnCl_3(H_2O)^-+Cl^- \longrightarrow ZnCl_4^{2-}+H_2O$$

Adsorption of Copper(II) from Mixed Solvents.—According to Kraus[2)], the adsorbability of copper(II) from hydrochloric acid solution is relatively weak, showing a flat maximum in ca. 7 M hydrochloric acid (the elution constant E=ca. 0.1). The results of our measurements up to 8 M hydrochloric acid are shown by curve 1 in Fig. 4, which seems to be in fairly good agreement with Kraus's results. The effect of addition of methanol to this system is summarized in Fig. 4, (curves 2, 3, 4).

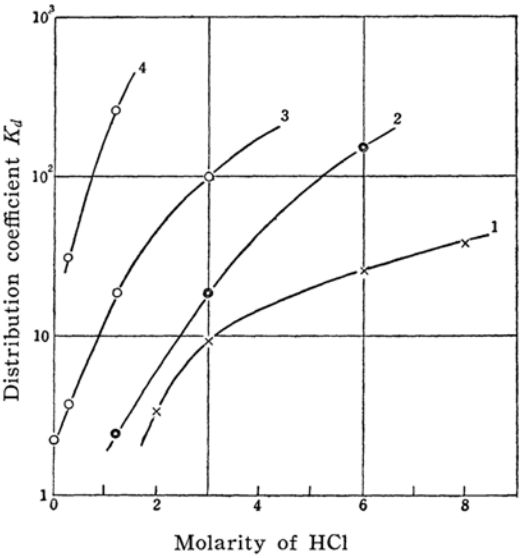

Fig. 4. Effect of methanol addition on the anion exchange adsorbability of Cu(II).
1. HCl only
2. 30% (v/v) methanol
3. 60% (v/v) methanol
4. 80% (v/v) methanol

In comparison to the case of zinc(II), the increase in the adsorbability of copper(II) in the presence of methanol was observed up to higher hydrochloric acid concentrations: This fact seems to suggest that the negatively charged complexes of Cu(II) are not completely formed throughout the range of hydrochloric acid concentration studied.

This may also be understood by the adsorption spectra of the copper(II) solution in the ultraviolet region*. As is seen

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* The absorption spectra of chloro-complexes of zinc (II) in the ultraviolet region could be detected only in the range of higher zinc(II) concentration (more than 1 M) where the constancy of K_d can no longer hold and the experimental results are not comparable with each other.

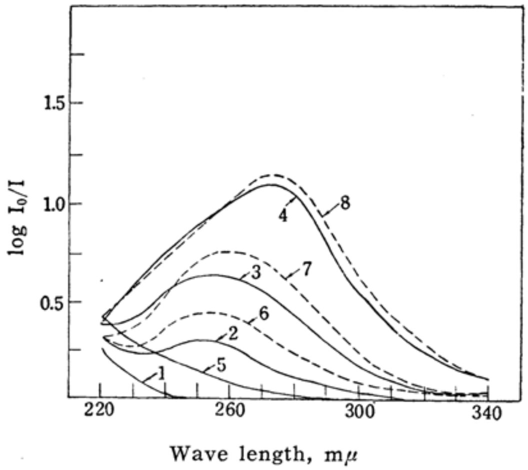

Fig. 5. Absorption spectra of Cu(II) in HCl or HCl-methanol mixtures.
$Cu(ClO_4)_2$, 4×10^{-4} M, Cell, 10 mm
1. in water
2. 1.2 M HCl
3. 3.0 M HCl
4. 5.0 M HCl
5. 80% (v/v) methanol
6. 1.2 M HCl-30% (v/v) methanol
7. 1.2 M HCl-60% (v/v) methanol
8. 1.2 M HCl-80% (v/v) methanol

from the curves 6, 7 and 8 in Fig. 5, the increase of methanol concentration in the 1.17 M hydrochloric acid solution of copper (II) resulted in the increasing formation of chloro-complexes in just the same manner as in increasing the concentration of hydrochloric acid in the absence of methanol (curves 2, 3, 4).

Katzin and Gebert⁶⁾ have found the adsorption of various inorganic salts onto anion exchange resin from their solution in acetone and suggested as a possible mechanism that the salts of transition elements might be adsorbed as complex anions. On the other hand, Davies and Owen⁷⁾ have postulated the possibility of the passage of the salts from acetone solutions into the resin phase from the standpoint of unequal partition of the solvents between both phases.

However, it was ascertained that tracer scale calcium chloride ($^{45}CaCl_2$*) in 0.1 M hydrochloric acid-methanol solution showed only negligible adsorption in the range less than 80% methanol. Therefore, under the conditions of our experiments, where the content of water is relatively high, the pronounced effect of increase in the adsorbability of zinc(II) and copper(II) might, if not completely, be explained by the dehydration effect of organic solvents added.

The remarkable rise in the adsorbability of the elements in the regions of relatively low hydrochloric acid concentrations may be of great use in the anion exchange separation of the elements which show only slight adsorption in dilute hydrochloric acid solutions and also in their rapid determination using the methods other than radiometry, e.g., complexometric titration⁸⁾.

Summary

1) It was found that the addition of some organic solvents such as methanol, ethanol, *n*-propanol and acetone to the hydrochloric acid solution of zinc(II) and copper(II) increases the anion exchange adsorption of the elements in the range of relatively low hydrochloric acid concentrations (less than 2 M). In the 0.1 M hydrochloric acid solution, the straight line relation between log K_d and concentration of organic solvent was observed up to ca. 60%.

2) In the case of copper(II), this effect of increasing the adsorbability was observed up to higher hydrochloric acid concentrations i.e., at least 8 M, which seems to reflect that the adsorption maximum occurs at a higher hydrochloric acid concentration than in the case of Zn(II).

3) It was suggested that these solvent effects may be, as a first approximation, explained by the increase in the formation of negatively charged chloride complexes of the metals as a consequence of the decrease in the tendency for solvation of metallic ions in mixed solvents.

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6) L. I. Katzin and E. Gebert, *J. Am. Chem. Soc.*, **75**, 801 (1953).

* Ca-45 (P-2) ($T_{1/2}$=164 days), obtained from Atomic Energy Commission of U. S. A.. Its specific activity was 14.59 mC./g. solid on Feb. 10, 1955.

7) C. W. Davies and B. D. R. Owen, *J. Chem. Soc.*, **1956**, 1676.

8) For example, G. Schwarzenbach, "Die komplexometrische Titration" 2nd Ed. (1956), Ferdinand Enke Verlag, Stuttgart.