A New Ion-exchange Method for the Determination of Polymerization Number of Metal Salt in Nonaqueous Solutions

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Although studies on ionic species present in solution with ion-exchange resins have been made by a number of workers, almost all of them have been on the determination of the ionic charge or stability constants of metal complexes, and polymerization equilibria have been left because of difficulties in theoretical treatment.

The polymerized molecule of a metal salt MA_a may be ionized in nonaqueous solvents of low dielectric constants in the following form:

$$2M_nA^0_{an} \rightleftharpoons M_nA^+_{an-1} + M_nA^-_{an+1} \qquad (1)$$

The equilibrium constant for Eq. (1) is written as

$$K_{ioniz} = \frac{[M_nA^-_{an+1}]^2}{[M_nA^0_{an}]^2} \qquad (2)$$

In such a solvent most part of the salt may remain unionized as the neutral $M_nA^0_{an}$ and the ionic species of higher charges $|i|\geqq 2$ may hardly be produced. In an anion exchange resin phase these neutral and cationic complexes may be converted into the anionic form $M_nA^-_{an+1}$ to a large extent by combining with the resin counter ion A^-. Under these conditions, the distribution coefficient of M is given in the following form:

$$D \equiv \frac{[\sum M]_R}{[\sum M]} \approx \frac{[M_nA^-_{an+1}]_R}{[M_nA^0_{an}]+2[M_nA^-_{an+1}]}$$

$$= \frac{[M_nA^0_{an}]_R}{[M_nA^0_{an}]} \cdot \frac{\beta_R}{1+2\sqrt{K_{ioniz}}} \cdot [A^-]_R \qquad (3)$$

where $\beta_R = [M_nA^-_{an+1}]_R/[M_nA^0_{an}]_R[A^-]_R$. Neglecting the neutral complexes of the metal salt present in the resin phase, uncomplexed $[A^-]_R$ is given as:

$$[A^-]_R = C - \frac{1}{n}[\sum M]_R \qquad (4)$$

where C represents the exchange capacity of the anion exchange resin. Assuming that $[M_nA^0_{an}]_R/[M_nA^0_{an}]$, K_{ioniz} and β_R are effectively constant, the following equation can be derived from Eqs. (3) and (4).

$$\log D = \log(C - \frac{1}{n}[\sum M]_R) + K \qquad (5)$$

where K is a constant. Hence by comparing the slope of experimental curve of log D vs $[\sum M]_R$ with those of theoretical curves obtained by inserting $n=1,2,\cdots$ into $\log(C-1/n[\sum M]_R)$ for corresponding $[\sum M]_R$, n can be presumed.

In case of $AlCl_3$-tetrahydrofuran (THF) solution, the following type of ionization is presumed from conductivity data.

$$2Al_nCl^0_{3n} = Al_nCl^+_{3n-1} + Al_nCl^-_{3n+1}$$

The experiment was carried out by passing $AlCl_3$-THF solutions of various concentrations through a small column containing 1 g of the resin Amberlyst A-27 Cl^- type of commercial particle size, followed by stripping the sorbed aluminum with diluted HNO_3 after equilibrium, and determining Al by EDTA titration. D was calculated in an ordinary way.

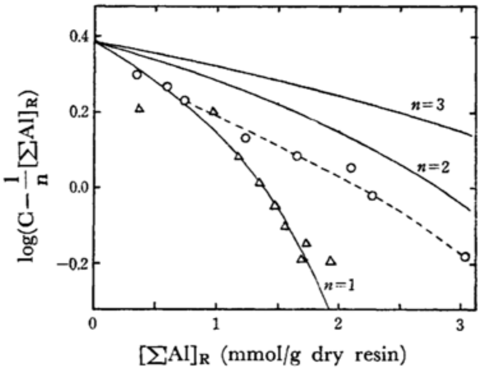

Fig. 1. The determination of the polymerization number "n" of $AlCl_3$ in THF by anion-exchange. ○: 24 hr △: 96 hr

The experimental plots of log D *vs.* $[\sum Al]_R$ are compared with the theoretical lines of log $(C-1/n[\sum Al]_R)$ *vs.* $[\sum Al]_R$ in Fig. 1. It may be seen from the graph that the dimer species $Al_2Cl^{0\mp1}_{6\pm1}$ is predominant in THF solution for the Al concentration range larger than 0.2 mol/*l* in solution 24 hr after the preparation of $AlCl_3$-THF stock solution, and the monomeric $AlCl^{0\mp1}_{3\pm1}$ is predominant for the whole concentration range of Al at 96 hr after. These results may indicate that the dimer or higher Al-Cl complexes are produced immediately after the solution of $AlCl_3$ and the Cl-bridge in $\rangle Al\langle^{Cl}_{Cl}\rangle Al\langle$ gradually disappears by the attack of THF molecules.

The proposed method seemed to be valid in the system of low polymerization number like metal salts dissolved in nonaqueous solvents. Details of this work will be reported later.