A Method for Estimation of the Hydration Numbers of Ions in Ion Exchange Resins

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A method for estimation of the hydration numbers of ions in ion exchange resins is proposed on the basis of the measurement of the amount of the solvent adsorbed isopiestically on the resin. The sulfonated cation exchange resins, Dowex 50-X4 (4% DVB resin), Diaion SK (8% DVB), Dowex 50-X16 (16% DVB) and Diaion SK-X24 (24% DVB) of sodium form, were used in mesh sizes of 50 to 200. They were dried at 50°C in vacuo. The resins were placed in the small dishes of stainless steel and were contacted with the solvent vapor under the pressure of about 3 mmHg. Ethanol-water and dioxane-water mixtures were used as the solvent systems. The concentrations of the organic solvents were in the range of 0 to 99.6% (v/v). The equilibrium of each isopiestic experiment had been attained in three days in a thermostat at 25 ±0.5°C.

The total amount of solvents adsorbed on the resin was determined gravimetrically. The solvent composition on the resin was determined by the following ways: in the ethanol-water system the solvents adsorbed on the resin were eluted with water and the amount of ethanol in the eluate was measured colorimetrically[1]. In the dioxane-water system, the solvents on the resin were distilled completely

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[1] B. Lange, "Kolorimetrische Analyse", Verlag Chemie, Weinheim (1956), p. 334.

and the refractive index of the distilled solution was measured.

The distribution coefficient of the solvents, $K_o{}^w$, is defined as

$$K_o{}^w = \frac{\overline{m}_w \cdot m_o}{\overline{m}_o \cdot m_w} \tag{1}$$

where $\overline{m}$ and m denote the concentrations of the solvents in the resin and the solution phases, respectively, and subscripts w and o represent water and the organic solvent.

The distribution of the solvents between the resin and the solution phases is thermodynamically given as follows*:

$$\ln \frac{\bar{a}_w \cdot a_o}{\bar{a}_o \cdot a_w} = \frac{\pi}{\boldsymbol{RT}}(\bar{v}_o - \bar{v}_w) \tag{2}$$

where $\bar{a}$ and a denote the activities of the solvents in the resin and the solution phases, respectively, and $\bar{v}$ is the partial molal volume of the solvent in the resin phase. π is the swelling pressure of the resin.

It may be considered that the solvent adsorbed on the resin is devided to two different parts: the one I is the solvents solvating to the functional groups (sulfonic acid groups) and their counter ions (sodium ions), another II is the solvents condensed on the exchange sites which become solvophilic by the solvation of the exchange groups. The fact that the resin particles without functional groups do not adsorb the solvent shows that the solvent is not adsorbed on the resin skeleton. We assume that only water molecules can solvate to the ions even in the considerably high concentration of the organic solvent in the solution phase (probably up to about 80%).

From these considerations Eq. 1 may be rewritten as follows:

$$K_o{}^w = \frac{(\overline{m}_{w_I} + \overline{m}_{w_{II}})}{\overline{m}_{o_{II}}} \cdot \frac{m_o}{m_w} \tag{3}$$

where subscripts I and II denote part I and part II described above.

Being different from the case in which the resin is derectly dipped in the solvents, it is observed that the resin scarcely swells in the equilibrium with the solvent vapor. From this observation, we assume that π in Eq. 2 is very small, or

$$\frac{\pi}{\boldsymbol{RT}}(\bar{v}_o - \bar{v}_w) \simeq 0 \tag{4}$$

As the water molecules solvated to the functional groups are fixed and hardly move, the fugacities of the solvents in the resin phase which is equilibrated with the vapor phase may be proportional to the molar fractions of the solvents in part II. It is assumed that the activities of the solvents in the solution phase are proportional to their molar fractions, the following equation is derived from Eqs. 2 and 4:

$$\ln \frac{\bar{a}_{w_{I,II}} \cdot a_o}{\bar{a}_{o_{II}} \cdot a_w} \simeq \ln \frac{\overline{N}_{w_{II}} \cdot N_o}{\overline{N}_{o_{II}} \cdot N_w} = \ln \frac{\overline{m}_{w_{II}} \cdot m_o}{\overline{m}_{o_{II}} \cdot m_w} \simeq 0 \tag{5}$$

where $\overline{N}$ and N denote the molar fractions of the solvents in the resin and the solution phases, respectively, and hence

$$\frac{\overline{m}_{w_{II}}}{\overline{m}_{o_{II}}} \simeq \frac{m_w}{m_o} \tag{6}$$

Applying Eqs. 3 and 6, the hydration number per one functional group and its counter ion (sodium ion), $\overline{H}$, is calculated readily by the following equation:

$$\overline{H} = \frac{(1-m_o)\overline{W}_o}{1000\,EM_w m_o}(K_o{}^w - 1) \tag{7}$$

where $\overline{W}_o$ is the weight of the organic solvent adsorbed on the resin (gram), E denotes the exchange capacity (meq.) of the resin used, M_w is the molecular weight of water and m_o represents the concentration of the organic solvent given in the scale of weight percentage.

In Fig. 1 the hydration numbers are plotted against the concentrations of ethanol for the variously cross-linked resins. The similar results can be obtained in the dioxane-water system.

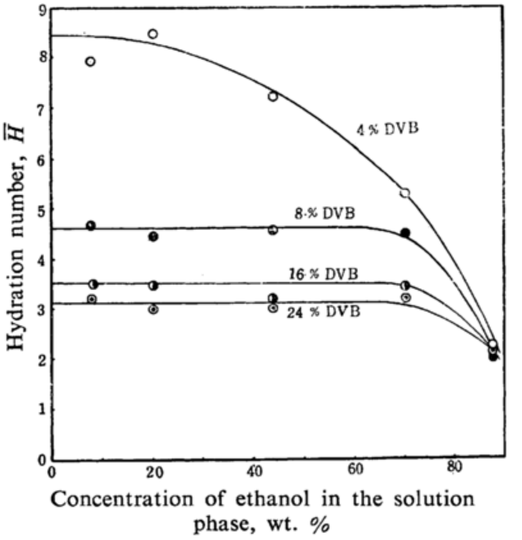

Fig. 1. Hydration number per one functional group and its counter ion (sodium ion) of the cross-linked sulfonic acid resins in the various concentrations of ethanol.

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* Cf. H. Kakihana, H. Ohtaki and T. Nomura, *Bull. Tokyo Inst. Tech., Series-B*, No. 1, 1 (1960); H. Kakihana, T. Nomura and H. Ohtaki, ibid., No. 1, 14 (1960).

The numbers extrapolated to zero concentration of the organic solvents may correspond to the hydration numbers of the ions on the ion exchange resins equilibrated with the saturated water vapor. The values of the numbers are listed in Table I. The agreement of the results obtained in the cases of ethanol-water and dioxane-water systems is satisfactory.

TABLE I. HYDRATION NUMBERS, $\overline{H}$, EXTRAPOLATED TO ZERO CONCENTRATION OF THE ORGANIC SOLVENTS

Resins	Ethanol-water	Dioxane-water	Mean
4% DVB resin	8.3	8.4	8.4
8% DVB resin	4.6	4.5	4.6
16% DVB resin	3.5	3.7	3.6
24% DVB resin	3.1	3.0	3.1

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