# Conductometric Titration of Cation Exchange Resins

By Tunetaka SASAKI and Ayako INABA

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## Introduction

There have been various methods to determine the exchange capacities of exchangers, for example,the analysis of the supernatant obtained from the salt solution added in large excess to exchanger(1) or the analysis of the effluent of salt solution coming from a column of exchanger.(2) (3) But these methods give no information about the exchange tendency or dissociation degree of exchange groups. The potentiometric method(4) (5) (6) (7) and some other means(8) have also been reported for the determination of the above mentioned quantities. But these are often complex in procedure

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(2) R. J. Myers J. W. Eastes and F. J. Myers, *J. Ind. Eng. Chem.*, **33**, 697 (1941).

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and the detailed experimental results have not been available for discussion.

The present paper deals with the relatively simple method of conductometry and also with the analysis of its results for the determination of both exchange capacity and tendency of resins.

## Experimental

**Sample.**—The resins used included: (A) Dowex 50; (B) phenoxyacetic acid–formaldehyde; (C) Amberlite IR-C 50; (D) hydroquinone-formaldehyde; (E) phenolsulfonic acid–formaldehyde; (F) sulfonated coal. In these resins each of (A), (B), (C) and (D) had only one kind of exchange group, namely (A) had $SO_3H$ group, (B) and (C) COOH, and (D) phenolic OH. (E) had two kinds of groups, $SO_3H$ and OH, and (F) was supposed to have more than two kinds of groups. (A), (C) and (E) were commercial products and the others were prepared as follows. (B) was prepared by condensation of phenoxyacetic acid and fromaldehyde with hydrochloric acid as catalyst, and (D) by condensation of hydroquinone and formaldehyde with sodium hydroxide as catalyst with the subsequent promotion of the polymerization by heating in each case. (F) was prepared from bituminous coal of Takashima coal mine by treating with hot mixture of conc. sulfuric acid and potassium bichromate with a trace of mercuric sulfate as catalyst. These resins were used as grains of 48∼100 mesh size excepting (C) of 20∼30 mesh which condition was adopted because this resin was easily ground into very minute particles unsuitable for our purpose. The resins were converted into H-form by rinsing with 2 *N* sulfuric acid solution before using.

**Titration.**—From one to five g. of swollen resin and 50 cc. of conductivity water were introduced in a 200cc. glass vessel and the whole mixture were titrated with 0.5 *N* sodium hydroxide solution conductometrically. In this process, sodium hydroxide solution was gradually added, one cc. at each time, with constant stirring and conductivity of the supernatant was determined after each addition under the equilibrium condition. Time required to attain the equilibrium was about 5∼10 min., although in the case of some resins it became as long as 30 min. in the final stage of titration. To avoid the effect of carbon dioxide, air free from it and saturated with water vapor was passed through the solution during the titration. Moreover suitable corrections were made when the case required.

## Results and Discussion

(1) Results of measurements for (A), (B) and (C) resins were shown in Fig. 1. Here $x$ was the adsorption value in terms of eqivalent of sodium ion per 1000 cc. swollen resin and $u$ was the equilibrium concentration of solution in terms of equivalent of sodium ion remaining in 1000 cc. of solution together with resin.

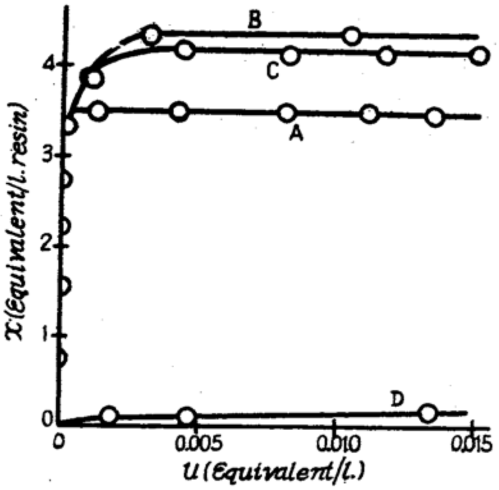

Fig. 1.—Exchange adsorption of NaOH by Dowex 50 (A), phenoxy. resin (B), Amberlite IR-C 50 (C), and hydroquinone resin (D).

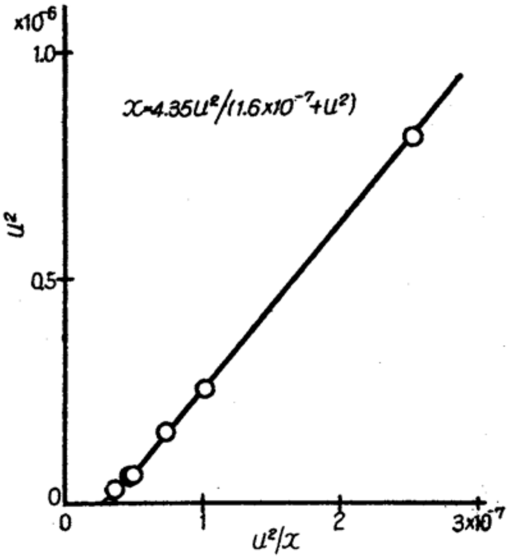

Fig. 2.—Exchange equilibrium for (B) resin.

Generally, when the cation exchanger in H-form is treated with sodium hydroxide solution, the equilibrium

$$\mathrm{RH + Na^+ + OH^- \underset{K}{\rightleftharpoons} RNa + H_2O}$$

is established. Here RH and RNa represent the exchanger in H-form and Na-form respectively, and $K$ denotes an equilibrium constant. In this case if mass action law is applicable, the relation

$$[R\dot{H}]\,[Na^+]\,[OH^-]/[RNa] = K$$

is obtained. [ ] represents the concentration of the substance inscribed. This relation is expressed in the terms of $u$ and $x$ as follows:

$$x = au^2/(K+\dot{u}^2) \text{ or } u^2 = au^2/x - K \qquad (1)$$

Here $a$ denotes a maximum adsorption value. Using the data for (B) resin, $u^2$ and $u^2/x$ were calculated. A fairly linear relation was obtained between them (Fig. 2). In the cases of (A) and (C) resins, similar relations were obtained. From these relations constant $a$ and $K$ were calculated (Table 1). Theoretical curves corresponding to the equation (1) were drawn using these $a$ and $K$ values (solid lines in Fig. 1), which showed good coincidence with the experimental results. Thus the adsorption isotherm (1) was considered to be sufficient to acccount for the results obtained. According to such a reasoning, the exchanger can conveniently be characterized by two factors, namely, $a$, the exchange capacity and $K$, the exchange tendency as has been generally accepted.(4) (9) (10) In fact, the value of $K$ for (A) resin having $SO_3H$ group is an order of $10^{-11}$, while the values are $10^{-7} \sim 10^{-8}$ for (B) and (C) resins both having only COOH group. From these results it is concluded that $SO_3H$ group has a stronger exchange tendency than that of COOH group, which is of course in accord with results obtained by others.(4) (5) Fluctuation of the value of $K$ for (B) and (C) resins, both having COOH group, may be ascribed to the difference in molecular structure and degree of gelation of these resins.

Table 1

Exchange Equilibrium Constants of Exchange Groups in Several Exchangers

| Resin | Exchange groups | | | | |
|---|---|---|---|---|---|
| | OH | COOH | | $SO_3H$ | |
| | $k$ | $a$ eq./l. | $K$ eq.$^2$/l.$^2$ | $a$ eq./l. | $K$ eq.$^2$/l.$^2$ |
| Amb. IR-C 50 | | 4.22 | $2.4\times10^{-8}$ | | |
| Phenoxy. resin | | 4.35 | $1.6\times10^{-7}$ | | |
| Dowex 50 | | | | 3.51 | $1.2\times10^{-11}$ |
| Hydroquinone resin | *ca.* 1.7 | | | | |
| Ph. sulf. resin | 27 | | | 1.34 | $2.0\times10^{-9}$ |
| Sulf. coal | 51.5 | 0.27 | $3.5\times10^{-8}$ | 0.75 | $1.0\times10^{-9}$ |

(2) Results obtained for (D) resin was shown in Fig. 1. $u^2 \sim u^2/x$ curve is linear excepting in the region of small $u$ value. In this connection it is worth while to refer to phenol formaldehyde resin. Novolack resin which was prepared by condensation using acid catalyst and showed low polymerization degree, was soluble in alkaline solution and so it was of no ure as an exchanger, while a resin such as Bakelite which was prepared by alkaline catalyst, and which showed high polymerization degree, was insoluble in alkaline solution, but it was again useless as an exchanger because of its no exchange capacity. We can however, expect the existence of the phenol formaldehyde resin having intermediate properties of being insoluble and showing weak exchange tendency. Considering from the results of such a phenol resin and (D) resin, it may be said that OH group of the resin generally shows very weak function, giving large value of $K$. The value of $K$ may also suffer fluctuation due to the variety in molecular structure of the resin. Such a weak adsorption can conveniently be expressed by $x' = ku$ as shown in gradual increase in $x'$ in the region of large $u$ value in Fig. 1, though the equation (1) rather gives $x = ku^2$ in the case of $K \gg u^2$. It must be noted that the case may not be a mere adsorption, but for the present purpose this is not a matter of importance as the equation $x' = ku$ is sufficient to characterize the behavior of phenolic OH group of the resin.

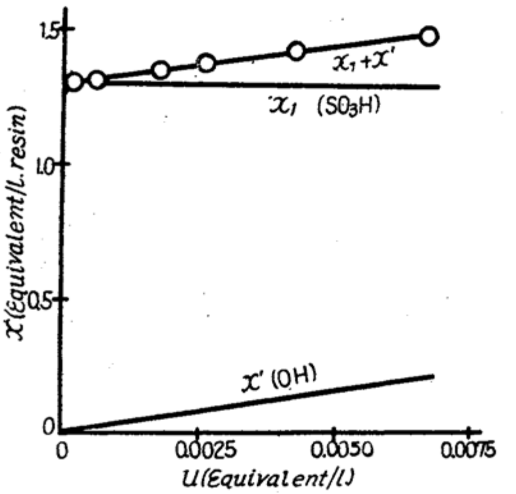

Fig. 3.—Exchange adsorption by phenolsulfonic acid formaldehyde resin (E).

(3) The results of experiments for (E) resin was shown in Fig. 3 (marked with ○). This

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adsorption curve shows steep inclination in the small $u$ region with subsequent and abrupt change in direction which can be interpreted as an existence of a strong exchange group perhaps of $SO_3H$. After the sudden change in direction, the amount of adsorption still increases gradually and linearly with equilibrium concentration. This gradual increase may be ascribed to the existence of OH group, for which the above equation $x'=ku$ $(k=27)$ may be given. Then, the remaining part of adsorption, $x-x'$ may be ascribed to $SO_3H$ group and for this part the value of $a$ and $K$ were determined by the similar method as mentioned above (Table 1). The theoretical curves thus obtained for $SO_3H$ and OH were shown in Fig. 3 ($x_1$ and $x'$ respectively), the resultant curve $(x_1+x')$ of which fairly coincide with experimental results. It can be concluded from such an analysis of the experimental results, that the (E) resin contains two kinds of exchange groups and no more group of any kind is necessary for the explanation. The value of $K$ for $SO_3H$ of this resin is hundred times greater than that of (A) resin, which is again explained by the difference in structure between these resins as in the case of COOH. We can, however, make clear distinction in order of magnitude of $K$ between $SO_3H$ and COOH.

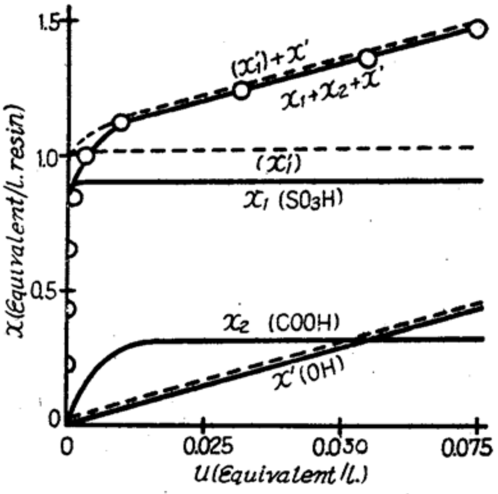

Fig. 4.—Exchange adsorption by sulfonated coal (F).

(4) The results obtained for sulfonated coal (denoted by ○ in Fig. 4) also showed linear increase in adsorption in the region of large equilibrium concentration. From the linear part of this curve we obtained $x'=ku$ $(k=51.5)$ for phenolic OH group. Using this value of $k$, the values of $x'$ and $x-x'$ accordingly were calculated for each concentration. We then attempted to explain this remainder part by supposing only one kind of exchange group. From the values of $a$ and $K$ thus obtained, and also from $k$ for OH group, two adsorption curves ($x'_1$ and $x'$ respectively) were drawn, the resultant $(x'_1+x')$ of which however did not coincide so well with the experimental results (Fig. 4). Therefore it was considered that at least two kinds of exchange groups other than OH took part in this case. Then, from the initial part of $u^2 \sim u^2/(x-x')$ plot, the constants $a_1$ and $K_1$ for stronger group were obtained (Table 1). Using these constants the corresponding adsorption amounts $x_1$ were calculated by equation (1) and from $u^2 \sim u^2/(x-x'-x_1)$ plot, the constants $a_2$ and $K_2$ for another exchange group were determined (Table 1). The adsorption amount $(x_2)$ due to the latter group, was also calculated using $a_2$ and $K_2$, and plotted together with $x_1$ against $u$ (Fig. 4). The resultant $x_1+x_2+x'$ thus obtained plotted against $u$ closely coincided with the experimental results. From such a reasoning it can be concluded that sulfonated coal has two different types of exchange groups in addition to phenolic OH group. These two groups are supposed to be $SO_3H$ and COOH, when we consider the facts that the constant $K_1$ and $K_2$ measured fall in the region of the order of magnitude of $K$ estimated in the earlier part of this paper for such exchange groups mentioned.

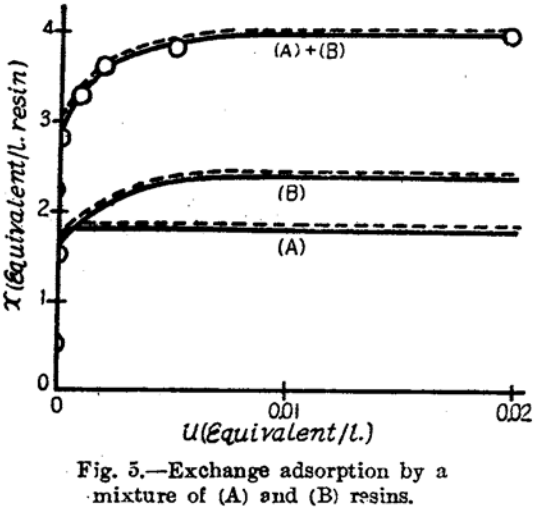

Fig. 5.—Exchange adsorption by a mixture of (A) and (B) resins.

(5) The results of measurement for (A) and (B) resins were shown in Fig. 5. The sum (solid line (A)+(B)) of the each adsorption amount of the two resins (solid lines (A) and (B)) calculated from the constants $a$ and $K$

Table 2

Exchange Equilibrium Constant of a Mixture of Dowex 50 and Phenoxy. Resin

| | Values calcd. from the separate determination | Values calcd. by the analysis of the results for mixed resin |
|---|---|---|
| Phenoxy. resin (COOH) | $a=2.18$ eq./l<br>$K=1.6\times10^{-7}$ eq.$^2$/l.$^2$ | $a=2.39$<br>$K=1.0\times10^{-7}$ |
| Dowex 50 ($SO_3H$) | $a=1.75$<br>$K=1.2\times10^{-11}$ | $a=1.76$<br>$K=3.2\times10-10^{11}$ |

which were previously determined by the separate measurement, agreed well with the experimental results (indicated by circles) for their mixture. The values of $a$ and $K$ obtained by the analysis of the experimental results for the resin mixture and the adsorption curves corresponding to them (dotted lines in Fig. 5) also coincided well with those obtained by the separate determination. These circumstances have some bearing upon the fundamental assumption in the present experiment that the total exchange capacity of an exchanger is the sum of the exchange capacities of each component exchange groups, although the lack of similarity between mechanical mixture of two different types of resins and the mixture of two different exchange groups in molecular scale, still leaves some questions behind.

(6) Finally, we should like further to note a few points. It is inevitable that the basic assumption made for the derivation of equation (1), namely, the substitution of the analytical concentration of sodium hydroxide, which was determined directly from conductometry in this experiment, for the concentrations of $Na^+$ and $OH^-$, introduces considerable error in the dilute region of sodium hydroxide. From this point, direct potentiometric determination of $OH^-$ concentration is rather desirable. However, this paper emphasizes the applicability of the simple conductometric method generally applied to the solution of a larger concentration. Consideration of activity in place of concentration is neglected for simplicity, which must be taken into account for precise discussion.

It has been reported that the dissociation constant of polymer electrolyte should be very complex in character,(11) however, the existence of the mean dissociation constant might still be considered. With the change in molecular structure and the degree of gelation of the resin, mutual effects of exchange groups are affected and the dissociation constant of the groups or the equilibrium constant $K$ fluctuates. However, the fluctuation due to these factors is small compared with that due to the variation in exchange groups. The exchange group can therefore be identified by the value of $K$.

## Summary

Cation exchange resins in H-form each having only one kind of exchange group were titrated with sodium hydroxide solution conductometrically. The results were analysed, and exchange capacity and tendency of each exchange group were determined. A mixture of two resins, each having one kind of exchange group was titrated. The analysis of the results gave adsorption values which agree well with that expected from the determination for the separate resin. From the titration results for more complex cation exchange resins the number of the sorts of exchange groups was estimated and each group was identified.

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*Department of Chemistry, Faculty of Science,*
*Kyushu University, Fukuoka*

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