

STUDIES ON ION EXCHANGE RESINS
V. ELECTROLYTIC REGENERATION OF ION EXCHANGE RESINS
(STUDIES IN POLYMERIC ELECTROLYTES. XXIX)

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Introduction

Although the regeneration of ion exchange resin is attainable by means of the electrolytic procedure, previous reports¹⁻⁴⁾ show that in many cases the current efficiency of electrolytic regeneration remains very low. According to Heymann-O'Donnel¹⁾ and Spiegler,²⁾ the fall of current efficiency is due to the increasing electric conductance caused by the formation of H⁺ ion or OH⁻ ion in resins during the progress of regeneration.

This paper covers the study of electrolytic regeneration of resin carried out with special attention to the current efficiency on the strongly basic resin "Amberlite IRA-400."

Experimental

1) *Apparatus:* As shown in Fig. 1, the apparatus used is of the same type as the ordinary electro-dialyser composed of three cells. The resin is packed in a middle cell having a capacity of ca. 3 cc separated from neighboring cells by means of perforated filter papers reinforced by a collodion or paraffine coating. Each of the neighboring cells having a capacity of ca. 40 cc is equipped with a perforated platinum electrode. The current is kept at a constant value below 30 mA during the electrolysis by adjusting the voltage between the electrodes over a range up to 500 V.

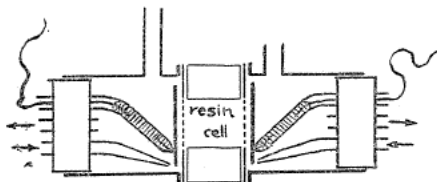


FIG. 1

2) *Procedures:* The experiments were carried out under the seven different conditions described below. In each experiment records were made of the magnitudes of the electrolyzing voltage, current, time, electric resistance, water flow rate in the cell, and hydraulic head required to give a definite flow rate. The resin, after the experiment, was subjected to chemical analysis. From these data, the mean current efficiency \bar{E} and the regeneration rate R were determined. The value of \bar{E} is the ratio of the quantity of electricity which served to effectually regenerate the resin to the total quantity of electricity; the value of R is the ratio of the re-

generated amount to the total exchange capacity of the whole resin in the cell.

Experimental Conditions :

With resin in chloride form

- a) the water in the cell was kept stationary
- b) the water was let to flow from the cathode cell to the anode cell at a rate of 1.5 cc/min.
- c) the water was let to flow as in b) at 8 cc/min.
- d) the water was let to flow at 16 cc/min. in the anode cell only
- e) 0.005 m.eq. of NaOH was added to the cathode cell, while other conditions were the same as d)
- f) the resin in the cell was separated vertically into two layers by means of a piece of perforated filter paper, while other conditions were the same as b)

With resin in sulfate form

- g) the same as b)

3) *Determinations of the total exchange capacity and the regenerated amount :*

The total exchange capacity was determined from the acid consumption of the completely regenerated resin sample by the ordinary method of volumetric titration and shown by the quantity of radicals in m.eq. for 1 g of bone-dried resin of salt form. The regenerated amount was also determined in the same way.

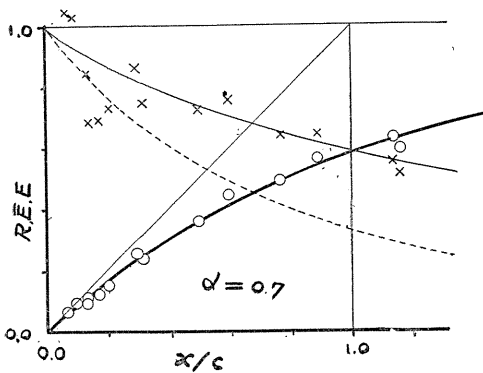


FIG. 2

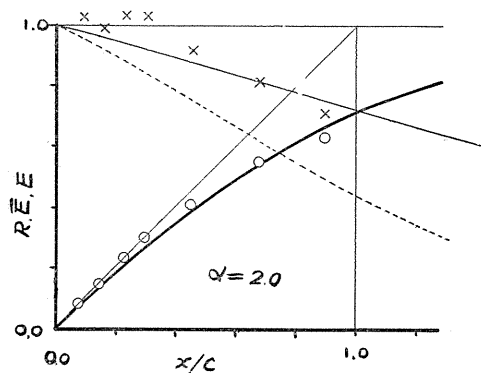


FIG. 3

Results

1) Total exchange capacity :

- 2.80 m.eq./1 g of dry resin for chloride form
- 2.96 m.eq./1 g of dry resin for sulfate form

2) Some preliminary experiments revealed that the magnitudes of the regenerating voltage and current had a slight influence, remaining within an experimental error, on the regeneration of resin.

3) Figs. 2 and 3 show the regeneration rate R and the mean current efficiency \bar{E} for experiments a) and b) respectively. In both the abscissa is given showing the ratio of the quantity of electricity passed through the cell x in m.eq. The points

are the observed values and the rigid lines, fine lines and broken lines show the calculated values of R , \bar{E} and E respectively, which are given by the equations (4) (6) and (5), described below.

4) The data of all experiments are summarized in Table 1.

5) In the experiment f), each part of the resin sample separated into two layers, 0.68 g in anode side and 0.57 g in cathode side, was subjected independently to the determination of regeneration rate and the following result was obtained for the condition of $x/c = 0.178$:

	regeneration rate
for the resin layer in anode side	7%
for the resin layer in cathode side	35%

6) When the regeneration proceeded to a considerable extent, the formation of small bubbles appeared in the resin cell, which seemed to have a remarkable influence on the flowing resistance of water as well as on the electric resistance of the cell.

Discussion

1) *Mechanism of Electrolytic Regeneration.* In the case of electrolysis of strongly basic resins, the electric current in the resin cell is supposed to flow only by the transportation of anions because the concentration of cations must be extremely low in the resin phase. The resin phase is, as a rule, supplied with OH^- ion formed by the dissociation of water from the cathode cell and simultaneously sends out towards the anode cell the anions (e.g. OH^- and Cl^- ions) of an exact corresponding amount. Now the authors propose a parameter m to indicate quantitatively the departing easiness, or the boundary mobility, with which an anion moves from the resin phase to the solution phase, and by α to designate the ratio of the m value of an anion to that of OH^- ion. The full meaning of the values, m and α , will be explained later.

Although, strictly speaking, the regeneration of resin varies with the location in the resin cell as shown by the experiment f), the authors assume for convenience that the regeneration proceeds uniformly throughout the whole resin and that the total amount of regeneration z depends only on the quantity of electricity passed through the resin phase x . Now, supposing that electricity or the quantity dx in m.eq. flows and the regeneration of the amount dz in m.eq. occurs at a certain time, the electricity dx must be transported at the boundary of the anode side by the departing of two kinds of anions, Cl^- and OH^- , from the resin phase to the solution phase. Since only the departing of Cl^- ion from the resin phase is considered to serve to regenerate, we can establish the following relation between dz and dx :

$$dz = \frac{m_{\text{Cl}^-} \cdot (c - z)}{m_{\text{Cl}^-} \cdot (c - z) + m_{\text{OH}^-} \cdot z} dx, \quad (1)$$

where c is the total exchange capacity of the resin and consequently the values of $c - z$ and z mean the concentrations of Cl^- ion and OH^- ion, respectively.

Integrating the equation (1) on the assumption that the ratio of departing easiness $\alpha = m_{\text{Cl}^-}/m_{\text{OH}^-}$ is kept constant, we have:

$$x/c = (1 - 1/\alpha) \cdot R + (2.303/\alpha) \cdot \log(1/(1 - R)), \tag{2}$$

$$\text{or} \quad 2.303 \log(1/(1 - R)) - R = \alpha \cdot ((x/c) - R), \tag{3}$$

where R shows the regeneration rate, z/c .

From these result, we can easily compute both the current efficiency E and the mean current efficiency \bar{E} , the latter of which is also determinable experimentally.

$$E = \frac{dz}{dx} = \frac{\alpha \cdot (1 - R)}{\alpha \cdot (1 - R) + R}, \tag{4}$$

$$\bar{E} = \frac{z}{x} = \frac{R}{(x/c)} = \int_0^x \frac{E}{x} dx. \tag{5}$$

2) Comparison of Calculated Data with Experimental Results.

By plotting the value of $2.303 \log(1/(1 - R)) - R$ against that of $(x/c) - R$ determined in the experiment a), we can find a good linearity between them, as shown in Fig. 4. This result indicates that the authors' opinion mentioned above is quite reasonable and that the parameter α can be determined as a constant value for a defined condition, e.g., $\alpha = 0.7$ for the experiment a) and $\alpha = 2.0$ for the experiment b). As is evident in Figs. 2 and 3, the calculated values of R and \bar{E} show a good agreement with the experimental results.

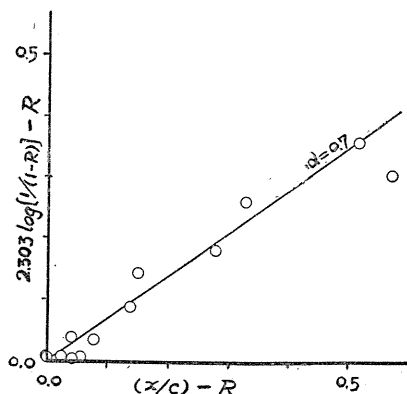


FIG. 4

Thus, the value of α is determined for each experiment and is shown in Table 1. together with values of R and \bar{E} obtainable for $x/c = 0.73$ and the electric resistance of the cell, r .

The curves of R , \bar{E} and E versus x/c are shown in Fig. 5 for $\alpha = 0.1, 1.0$ and 10 .

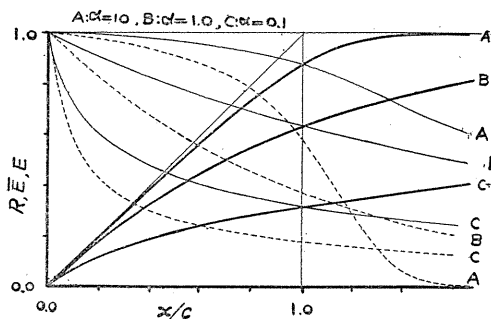


FIG. 5

TABLE 1

Expt.	a	b	c	d	e	g
α	0.7	2.0	8	1.7	0.8	2.5
R	0.48	0.58	0.68	0.59	0.49	0.60
\bar{E}	0.66	0.79	0.91	0.78	0.65	0.83
r (K Ω) ..	10	20	50	15	8	30

3) Meaning of the Parameter α . An inspection of Table 1. reveals that the magnitude of α depends chiefly on the water flow rate in the resin cell. Although an addition of alkali causes a remarkable fall of the electric resistance resulting in the decrease of the watt loss of electrolysis, it very slightly affects the magnitude of α .

The ratio of the electric conductances of the sample resin between its Cl^- form and OH^- form determined 0.13. Hence, the departing easiness or boundary mobility m is considered to be of quite a different nature from that of mere ionic mobility

in the interior of the resin. The values of m and α must evidently be determined by the boundary condition concerning both the resin phase and the solution phase of anode side.

When the water is allowed to stand still and there is no electrolysis, the following equilibrium condition must be established between the resin phase and the solution phase:

$$\frac{(\text{OH}^-)_R(\text{Cl}^-)_S}{(\text{Cl}^-)_R(\text{OH}^-)_S} = K, \quad (6)$$

where K is a equilibrium constant. During the electrolysis such an equilibrium state is never attainable although it may become a stationary state. The greater the deviation of electrolyzing state from the equilibrium state, or the lower the concentration of Cl^- ion in the solution phase, the easier the Cl^- ion departs from the resin phase and enters the solution phase. Thus the magnitude of α presumably larger as the water flow rate increases. Although the meaning of the parameter α is qualitatively explainable as described above, its quantitative evaluation seems impossible under the present circumstance.

Conclusion

The above results lead to the conclusion that the magnitude of the parameter α plays a most important role in the electrolytic regeneration of resin. By electrolyzing the resin through the water layers which are laid on both sides of the resin and letting the water flow fast to enlarge the value of α , we can improve the current efficiency of regeneration to an appreciable extent.

On the other hand such a procedure causes a remarkable increase in the electric resistance of the whole cell which results in an increase in watt loss. Therefore, in considering the electrolytic regeneration of resin for industrial purposes, further researches from another point of view are necessary.

References

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