$$C^{13}O_2 + EtMgI \longrightarrow CH_3CH_2C^{13}OOH \qquad (1)$$

$$CH_3CH_2C^{13}OOH \xrightarrow{LiAlH_4} CH_3CH_2C^{13}H_2OH \qquad (2)$$

$$CH_3CH_2C^{13}H_2OH \xrightarrow{P + I_2} CH_3CH_2C^{13}H_2I \qquad (3)$$

$$CH_3CH_2C^{13}H_2I \xrightarrow[\text{Couple}]{\text{Cu-Zn}} CH_3CH_2C^{13}H_3 \qquad (4)$$

Ordinary propane of almost 100% purity has been prepared from acetone in 70% yield by electrolytic reduction. This reaction may be useful in preparing propane-2-C^{13} since $CH_3C^{13}OCH_3$ has been prepared starting with $BaC^{13}O_3$ in 89% yield by Grosse and Weinhouse.[3]

---

(3) Grosse and Weinhouse, *Science*, **104**, 402 (1946).

U. S. BUREAU OF MINES
4800 FORBES STREET
PITTSBURGH 13, PENNA.
RECEIVED DECEMBER 4, 1950

Study on the Relation between *p*H of Ion Exchange Resin Phase and the Composition of Solution at Equilibrium

BY MASATAKE HONDA

An essential investigation in ion exchange reactions is a study of the activities of the ions adsorbed by the ion exchange resin. In this work the hydrogen ion activity (*p*H) in the resin phase was determined with appropriate *p*H indicators which were adsorbed as ions.

The experimental data presented in this paper as well as in previous work[1,2] involve the following considerations.

(1) It is assumed that the exchange reaction is purely ionic. The interior of the resin phase is taken as a homogeneous system analogous to a solution. The equilibrium condition for exchange between two ions has been frequently explained by the membrane equilibrium condition,[3] namely, that the chemical potentials of any component in the resin and liquid phases should be equal at equilibrium. Thus for such components as HA, MOH, MA or H_2O where A and M are monovalent anions and cations, respectively, it is true that

$$a_{Hr}a_{Ar} = a_{Hs}a_{As} \qquad (1a)$$
$$a_{Mr}a_{OHr} = a_{Ms}a_{OHs} \qquad (1b)$$
$$a_{Mr}a_{Ar} = a_{Ms}a_{As} \qquad (1c)$$
$$a_{Hr}a_{OHr} = a_{Hs}a_{OHs} = K_w \qquad (1d)$$

where a_{Hr} is the activity of hydrogen ion in the resin phase and a_{Hs}, the activity in the solution, and so on.

(2) The adsorption of an acid (anion) or alkali (cation) by the resin can be considered as a neutralization reaction which takes place in the resin phase. When any exchange resin has adsorbed a definite amount of an ion at equilibrium, *i.e.*, when the activity of the adsorbed ion is at a definite value, the *p*H in the resin phase should take a fixed value. The presence of a small amount of neutral salt hardly influences the *p*H and the salt concentration in the resin phase is always lower than in solution.[3] This negative adsorption can be attributed to the higher concentration of the common adsorbed ion in the resin phase according to (1c). For an anion exchange resin this leads to

$$a_{Hr} = f_1(a_{Ar}) \qquad (2a)$$

or for a cation exchange resin

$$a_{Hr} = f_2(a_{Mr}) \qquad (2b)$$

From 1 and 2

$$a_{Ar} = f_3(a_{Hs}a_{As}) \qquad (3a)$$
$$a_{Mr} = f_4(a_{Ms}a_{OHs}) = f_5(a_{Hs}/a_{Ms}) \qquad (3b)$$

where a_{Ar} and a_{Mr} are determined by the amount of adsorption.

In a previous study[1] a weak anion exchange resin (*m*-phenylenediamine-HCHO, cyanamid type) was used. In the presence of a salt of the anion it was found that at equilibrium the amount of adsorption (exchange capacity of the anion in m. eq./g.) was determined by the product of the activities of the hydrogen ion and anion in solution, *i.e.*, (3a) is obeyed.

For the adsorption of acetate ion in the presence or absence of 0.002, 0.02 or 0.2 *N* sodium acetate, the relation between *p*H − log a_{acetate} in the solution and the amount of adsorption in the range 0.2 to 3 m. eq./g. obeyed (3a). Here the value of $a_{Hs}a_{As}/a_{HAs}$ is a constant for any weak acid. Because of the addition of sodium acetate, the concentration of HAs (acetic acid) can be regarded as invariable. Hence, the exchange capacity for acetate ion was independent of the concentration of sodium acetate. Relation (3a) was also confirmed for the adsorption of chloride ion in the presence or absence of 0.01 *N* sodium chloride and in dilute zinc chloride solution in the presence of an excess of zinc oxide, on the above resin and later[2] on a *m*-phenylendiamine-HCHO resin or for Amberlite IR-4B (Rohm and Haas Co.).[2] It has been pointed out that the data of Kunin[4] for Amberlite IR-4B satisfy (3a).[1]

In another paper[2] a semi-quantitative study was made of the equilibrium relations between composition of solution, amount of adsorption, and *p*H of the resin. Colorless or faintly colored cation or anion exchange resins, of both weak and strong types, were utilized with appropriate indicators such as sulfonephthaleins or azo dyestuffs.

A more quantitative study is presented here. According to 2 and 3 the amount adsorbed at equilibrium is constant when a_{Hr} is constant and at the same time for anion exchange we have

$$pH_s + pA_s = \text{constant} \qquad (4a)$$

and for cation exchange

$$pH_s - pM_s = \text{constant} \qquad (4b)$$

The following data validate these relations if it is assumed that a_{Hr} for the resins equilibrated with various solutions are equal when the resins have attained the same color caused by the adsorption of an indicator whose transition point is near a_{Hr}.

Experimental

Each set of experiments was performed simultaneously at room temperature (20 to 25°). pH_s was measured po-

---

(1) M. Honda, *J. Chem. Soc. Japan*, **71**, 183, 405 (1950); Kagaku no Ryôiki (*J. Japan. Chem.*), Extra Ed. No. **1**, 19 (May, 1949); *cf. C. A.*, **44**, 6753g (1950).

(2) M. Honda, *J. Chem. Soc. Japan*, **71**, 440 (1950).

(3) O. Samuelson, Ph.D. Dissertation, Horsal, Sweden, 1944.

(4) R. Kunin and R. J. Myers, THIS JOURNAL, **69**, 2874 (1947).

tentiometrically (quinhydrone electrode) or colorimetrically.

Strong Cation Exchange Resin.—A colorless exchanger of polystyrolsulfonic acid[3] was prepared. Commercial, colorless polystyrol was cut in pieces, treated with chlorosulfonic acid for one day at room temperature, then slowly poured into water and allowed to stand overnight. A colorless, or faintly yellow, gelatinous cation exchanger resulted. It was converted to the NaR type with excess sodium acetate solution, washed with water, crushed, and screened in to 30 to 60 mesh size in water. Dry weight was measured after dehydration over calcium chloride. A 5-ml. bed volume of the wet exchanger in water adsorbed 0.05 ml. of 0.1% solution of dimethylaminoazobenzene in 90% alcohol. The neutral NaR resin is yellow but readily changes to red by washing with distilled water because of slight hydrolysis of adsorbed sodium ion. Five ml. of resin and 20 ml. of sodium chloride solution were bottled in a flask. The color was adjusted to the pink orange transition point of the indicator by the use of a minimum amount of 0.1 *N* hydrochloric acid or sodium hydroxide. This adjustment is so delicate that there is no considerable change in either a_{Nas} or a_{Nar}. The stable condition of exchange equilibrium was obtained in a short time by shaking the flask. The $p\mathrm{H}_s$ was then measured. Since the adsorbed indicator was not eluted by washing or by change of $p\mathrm{H}_s$, the above procedure and measurement could be repeated with the resin. The results are summarized in Table I.

TABLE I

EQUILIBRIUM BETWEEN SODIUM–POLYSTYROLSULFONATE[a] AND SODIUM CHLORIDE SOLUTIONS

Concentration of solution, *N* NaCl	pHs	pNas	pHs − pNas	Swelling volume,[c] ml./g.
1.0	3.6	0.2[b]	3.4	9
0.3	3.9	0.6[b]	3.3	11
.1	4.3	1.1[b]	3.2	14
.03	4.7	1.5	3.2	15
.01	5.0	2.0	3.0	17
.003	5.5	2.5	3.0	17
.001	6.2	3.0	3.2	17

[a] The adsorbed amounts of Na^+ in all cases were equal to 4.4 m. eq./g. [b] At higher concentrations of NaCl solution the activity coefficient of single Na^+ (or Cl^-) was used. [c] The change of swelling volume with salt concentration will slightly influence the $p\mathrm{H}_s$–$p\mathrm{Na}_s$.

Analogous experiments were repeated for other cations. Metallic chloride solutions were percolated through the bed of exchanger until saturated with the metallic ion. The exchanger was then mixed with metallic salt solution. For 0.1 *N* solutions of Li^+, Na^+, $\mathrm{NH_4}^+$, K^+, Ag^+ (as nitrate), Ca^{++} and Ba^{++} the measured $p\mathrm{H}_s$ values were, respectively: 4.2, 4.2, 4.1, 4.0, 3.0, 3.6 and 3.0.

Strong Anion Exchange Resin.—Amberlite IRA-400[5,6] (Rohm & Haas Co.) was employed. It was 30 to 50 mesh in size and pale yellow in color. It was treated with 5% sodium hydroxide and washed almost completely with carbon dioxide free distilled water. It was dried in a slow stream of carbon dioxide free air. One-tenth-gram sample of the ROH type resin, 1.5 ml. of 0.1 *N* hydrochloric acid, 0.5 ml. of 0.04% aqueous solution of thymol blue and 20 ml. of sodium chloride solution were mixed in stoppered bottles. Although the indicator did not diffuse in to the centers of the granules, it was completely adsorbed by the resin. For these cases the color adjustments to dark green with hydrochloric acid took a rather long time. Table II presents the results.

TABLE II

EQUILIBRIUM BETWEEN AMBERLITE IRA-400 (RCl)[a] AND SODIUM CHLORIDE SOLUTIONS

Concentration of solution, *N* NaCl	pHs	pCls	pHs + pCls
1.0	8.8	0.2	9.0
0.1	7.7	1.1	8.8
.01	6.9	2.0	8.9
.001	6.1	3.0	9.1
.000	4.6	*ca.* 4.3[b]	*ca.* 8.9

[a] The adsorbed amounts of Cl^- were equal to 1.5 m. eq./g. [b] By nephelometry.

Analogous experiments for other anions were performed at concentrations of 0.1 molar using 1 ml. of 0.02% indicator solution per gram of resin. Thymol blue or phenol red were the indicators. The RCl type resin was treated with 0.1 *M* salt solution. For 0.1 *M* solution (or mixture of 0.1 *M* solutions) of potassium fluoride; sodium chloride; potassium bromide; potassium iodide; potassium nitrate; potassium sulfate; sodium acetate and acetic acid; disodium hydrogen phosphate and orthophosphoric acid the measured $p\mathrm{H}_s$ values with thymol blue indicator at a yellowish-green color were, respectively: 7.4, 7.5, 7.6, 8.2, 7.8, 7.5, 7.4 and 7.6. For phenol red indicator at an orange color the $p\mathrm{H}_s$ values were, respectively: 6.4, 6.5, 6.7, 7.0, 6.6, 6.5, 6.0 and 6.2. For this indicator the amount of chloride ion adsorbed was 1.6 m. eq./g.

Weak Anion Exchange Resin.—Amberlite IR-4B[4] (Rohm & Haas Co.) at 20 to 50 mesh and orange in color was employed. The inherent color of this exchanger made it somewhat difficult to observe the transition point of the indicator. Two-tenths gram of resin in the ROH form was colored with 0.2 ml. of 0.02% aqueous phenol red solution or 0.6 ml. of 0.04% aqueous thymol blue and then treated with 20 ml. of hydrochloric acid and sodium chloride solutions. The results are summarized in Table III.

TABLE III

EQUILIBRIUM BETWEEN AMBERLITE IR-4B (RCl) AND SODIUM CHLORIDE SOLUTION

Concentration of solution, *N* NaCl	pHs	pCls	$p\mathrm{H}_s$ + $p\mathrm{Cl}_s$
With thymol blue indicator (1.2 m. eq./g.)			
1.0	8.1	0.2	8.3
0.1	7.2	1.1	8.3
.01	6.4	2.0	8.4
.001	5.5	3.0	8.5
.000	4.7	*ca.* 4.0[a]	*ca.* 8.7
With phenol red indicator (3.2 m. eq./g.)			
1.0	6.4	0.2	6.6
0.1	5.6	1.1	6.7
.01	4.7	2.0	6.7
.001	3.7	3.0	6.7
.000	3.2	*ca.* 3.5[a]	*ca.* 6.7

[a] By nephelometry.

From these experiments and others[2] it was noticed that the $p\mathrm{H}_r$ was roughly equal to $p\mathrm{H}_s + p\mathrm{Cl}_s$ or $p\mathrm{H}_s - p\mathrm{Na}_s$ for any exchanger in those cases where the adsorbed indicator showed the same pH in the resin as in the aqueous solution. This leads to the possible assumption that the numerical values of $p\mathrm{Cl}_r$ or $p\mathrm{Na}_r$ are almost negligible with regard to the value of the $p\mathrm{H}_r$.

DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE, ST. PAUL'S UNIVERSITY
IKEBUKURO, TOKYO, JAPAN
RECEIVED JULY 10, 1950

An Enzymatic Synthesis of *sym*-Bis-(N-carbobenzoxy-L-alanyl)-hydrazine

BY FREDERICK W. HOLLY, JOSEPH J. CAHILL, JR., AND KARL FOLKERS

In an attempt to prepare N-carbobenzoxy-L-alanine hydrazide from N-carbobenzoxy-DL-alanine by application of the method described for an enzymatic synthesis of N-carbobenzoxy-L-glutamic

---

(5) R. Kunin and F. X. McGarvey, *Ind. Eng. Chem.*, **41**, 1265 (1949).

(6) The Amberlite resins were obtained through the courtesy of Mr. R. Kunin.