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Heat of Ion Exchange Reaction as Determined by Means of Flow Micro-Calorimetry. I. Cation Exchange in Aqueous System

Tetsuo Morimoto, Hiromitu Naono,† Kuniji Nōso,* and Yasumasa Shigetomi*
Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama 700
**Department of Chemistry, Okayama College of Science, Ridai-cho, Okayama 700*

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The applicability of flow micro-calorimetry to the measurement of ion exchange heat was investigated by use of H-form resin of Dowex 50W×4 having a low degree of cross-linking. It was found that: accurate measurement of ion exchange heat can be performed by means of flow micro-calorimetry; the data obtained include additional heat effects such as heats of invasion and dilution; the effects can be exactly analyzed experimentally and eliminated for calibrating the data of pure ion exchange heat. The ion exchange heat thus obtained for the H-form resin and alkali metal ions was found to agree with the results obtained by means of heat of immersion measurements.

A number of fundamental studies have been carried out on ion exchange phenomena as regards the origin of selectivity of ion exchangers.[1–3] Combining the calorimetric data and the selectivity coefficients on ion exchange phenomena, Cruickshank and Meares,[4] Myers and Boyd,[5] and Boyd *et al.*[6] developed the thermodynamics of ion exchange reactions and attempted to elucidate the exchange phenomena in terms of the properties of ions and the structure of resins. In order to measure the ion exchange heat, they adopted the same calorimetric technique as that used for the measurement of immersion heat. The heat of ion exchange reaction can be measured step by step over the whole range of loading on one kind of ion.

A report has been given on flow micro-calorimetry[7] for the measurement of heat of adsorption from solution, which makes it possible to measure sensitively a small amount of heat evolved in a solid-liquid system.

The present paper deals with the applicability of flow micro-calorimetry to the measurement of ion exchange heat of alkali metal ions with H^+ ions, by use of a cation exchange resin, Dowex 50W×4, made of poly(styrene sulfonate) and having relatively homogeneous sites for the exchange of alkali metal ions.

Experimental

Materials. Poly(styrene sulfonate) type resin, Dowex 50W×4 was used as a cation exchanger. The resin was washed with dilute hydrochloric acid until the well-defined H-form was ensured, followed by washing with distilled water. The total exchange capacity of the resin thus treated was 4.35 meq/g for alkali metal ions. Alkali metal chlorides of guaranteed grade were employed for the preparation of electrolyte solutions.

Ion Exchange Calorimetry. The apparatus was essentially the same as that used for the measurement of heat of adsorption from solution.[7] Figure 1 shows a diagram of the flow micro-calorimeter. The main part of this apparatus consists of a liquid column chromatograph, JLC-2A (Japan Electron Optics Laboratory Co., Ltd.). The resin (0.1 ml in apparent volume) was sandwiched by glass beads (65—100 mesh) and placed in a bed in the same position as that of both detection and reference columns. A coiled platinum resistance wire of 0.1 mm in diameter and 25 cm in length was embedded in the sample bed of the detection column, used for the calibration of the heat evolved by ion-exchanging. Change in temperature caused by ion exchange reaction or passage of electrical current through the platinum wire was detected with a thermistor connected by copper leads to a Wheatstone bridge, another arm of which was constructed by a similar thermistor placed in the reference column so that the calorimeter operates as a type of twin calorimeter. All the reacting solutions or water were forced to flow through the sample bed with a constant rate, 0.36 ml/min, by use of a constant flow pump.

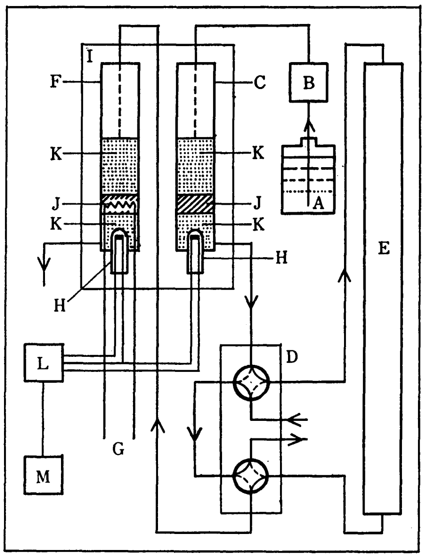

Fig. 1. Flow micro-calorimeter for the heat of ion exchange reaction. A, Reservoir for water; B, constant flow pump; C, reference column; D, exchange valves; E, reservoir for solution; F, detection column; G, calibration heater; H, thermistor; I, metal thermostat; J, ion exchange resin; K, glass beads; L, amplifier; M, recorder.

The procedure for ion exchange calorimetry was carried out as follows. After the attainment of thermal equilibrium, the H-form resin set in the columns was washed with distilled water by passing through with the flow pump, until a constant base line was attained. Then, a certain amount of electrical energy was supplied to the platinum heater, the temperature rise being recorded. The calibration measurements were repeated by supplying various amounts of electrical energy. Next, the flowing liquid was converted from water into an electrolyte solution by means of exchange valves (Fig. 1). The heat

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† Present address: Department of Chemistry, Faculty of Science, Kwansei Gakuin University, Uegahara, Nishinomiya, Hyogo 662.

liberated by the exchange of alkali metal ions with H^+ ions in the resin was recorded. All the measurements of ion exchange heat were carried out at 30 °C and within a reproducibility of $\pm 5\%$. The amount of ions which underwent exchange was determined by titrating the eluted solution with a standard 0.01 M NaOH solution.

Results and Discussion

Figure 2 shows the peaks corresponding to the heats generated when various amounts of electrical energy were supplied under a flow rate, 0.36 ml/min, of water. Here, the rate of heat generation was 0.076 J/min. The relation between the peak area (Fig. 2) and the electrical energy supplied is shown in Fig. 3. We see that the peak area is proportional to the electrical energy supplied, and that the straight line passes the origin of the co-ordinates. A preliminary test[7] showed that the slope of the calibration curves does not depend upon the rate of heat generation, but varies with the flow rate of liquid. Thus, the flow rate of liquid was kept constant during the course of the experiment.

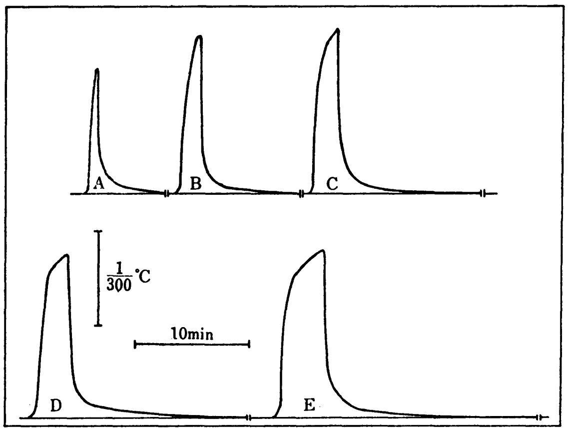

Fig. 2. Calibration peaks at 30 °C.
Peaks, A, B, C, D, and E were obtained by supplying electrical energy of 0.1515, 0.3063, 0.4690, 0.6188, and 0.7653 J respectively.

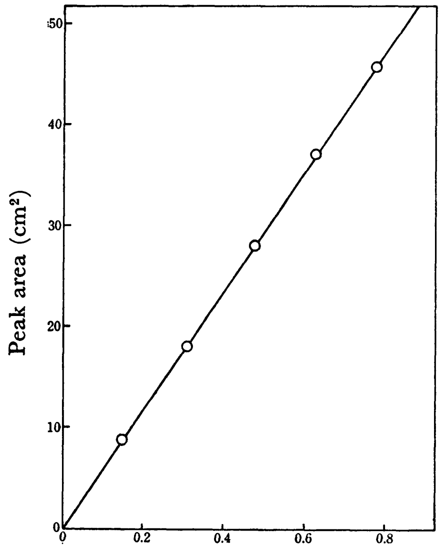

Fig. 3. Relation between peak area and electrical energy supplied.

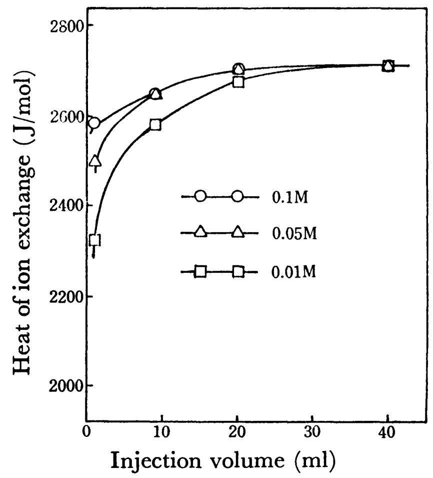

Fig. 4. Dependence of heat of ion exchange (Na^+) upon injection volume.

Figure 4 shows the molar heat of ion exchange (J/mol) as a function of the injected volume of 0.05 M solution to a constant amount (0.1 ml) of the resin. The heat evolution due to ion exchange reaction increases with increasing amount of solution injected and reaches a constant value when the volume of injected solution exceeds 10 ml. Such a slight heat evolution at the initial stage of injection may be due to partial exchange of ions at a slightly greater distance from the position of thermistor as compared to the cases where the volume of injected solution exceeds 10 ml. Thus, the measurement on the molar heats of ion exchange reaction was carried out by injecting 40 ml solution.

Figure 5 shows a few peaks obtained when the flowing liquids were exchanged successively by means of the exchange valves in the order: water, electrolyte solution, water. Preliminary tests showed that the higher the concentration of the solution and the greater the atomic weight of the ions injected, the steeper the peaks, whereas the peak area, obtained on a given alkali ion species are the same irrespective of the concentration of the solution. The peaks were obtained by injecting 40 ml of 0.05 M solution of Li^+, Na^+, and K^+ ions, and 60 ml of 0.035 M solution of Rb^+ and Cs^+ ions, respectively. The results show that the exchange reaction of alkali metal ions with H^+ ions in the H-form resin is exothermic except for the case of Li^+ ions. A small endothermic peak appeared after the flowing liquid was changed from an electrolyte solution to water except for the case of Li^+ ions.

Concerning these phenomena, the following experiment was carried out. The H-form resin set in the detection column of the calorimeter was converted to the Na-form by flowing a sufficient amount of NaCl solution, washed with water completely, and subjected to the injection of 40 ml of 0.05 M NaCl solution. When washing with water and injection of NaCl solution were repeated, the same recording was obtained as shown in each underlying curve in Fig. 5. The results show that a pair of small peaks appear, exothermic at the initial

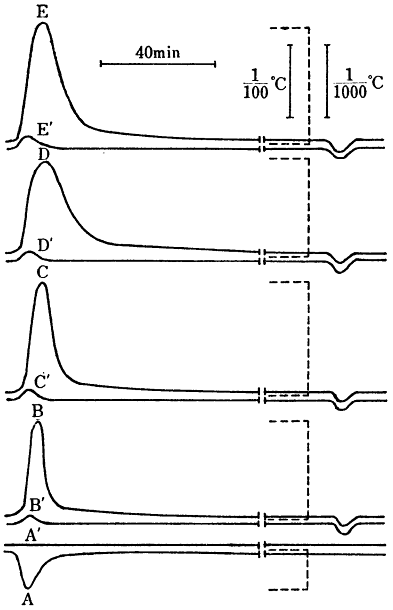

Fig. 5. Heat of ion exchange reaction of alkali metal ions with $\mathrm{H^+}$ ions in resin. A, $\mathrm{Li^+}$; B, $\mathrm{Na^+}$; C, $\mathrm{K^+}$; D, $\mathrm{Rb^+}$; E, $\mathrm{Cs^+}$. Curves A′, B′, C′, D′, and E′ (sensitivity 1/1000 °C) show the heat generation when a solution was injected to the resin containing the same cation species. Peaks directed upward mean "exothermic" and directed downward "endothermic".

stage just after the injection of a solution, and endothermic at the initial stage of washing, except for the case of $\mathrm{Li^+}$-loading, where a nearly straight line appears. The areas of both peaks appearing in a curve are almost the same, being also lose to the area of endothemic peaks appearing at the latter part of the corresponding main run. The heat evolution which took place was too small to be detected. However, it appeared when the concentration was high, the sign being the same as that of heat of ion exchange reaction. The same phenomenon was also found when a solution of $\mathrm{H^+}$ ions was injected into the H-form resin, the sign of heat generation being the same as that in the case of $\mathrm{Li^+}$ ions. It is not easy to find the cause of the occurrence of such small peaks. The ion exchange reaction might be accompanied by a weak interaction of ions in solution with the field of exchanging sites such as invasion or adsorption which may involve hydration and dehydration of ions concerned. We could infer that the small endothermic peaks appearing in the process of washing with water are due to physical interaction such as desorption of ions from the network of resin. The main peak of exchange reaction might be determined by exchange reaction and physical interaction. In order to obtain the energy of pure exchange reaction, we should subtract the contribution of the weak interaction from the total heat effects.

In the present system, the boundaries between water and electrolyte solution would be formed every time the exchange valves are operated, moving in the detection column through the position of the temperature sensing element. Since the diffusion of ions or dilution of the solution would gradually take place near the boundaries during the course of liquid flow, a small amount of heat generation can be expected when a moving boundary layer passes through the position of the thermistor. In order to test the heat generation by dilution, the layer of resin was replaced by glass beads which are considered not to act upon neutral alkali chloride solution. The exchange operation of the valves was carried out as before. No visible peaks appeared when the concentration of the solution was 0.05 M.

Table 1. Ion exchange heat of alkali metal ions with Dowex 50WX4, H-form cation exchange resin

Metal ion	Quantity exchanged (meq)	Heat evolved (J)	Ion exchange heat (J/mol)
$\mathrm{Li^+}$	0.1558	−0.196	−1260(−920.5)
$\mathrm{Na^+}$	0.1549	0.432	2790(3598.2)
$\mathrm{K^+}$	0.1589	0.730	4590(5313.7)
$\mathrm{Rb^+}$	0.1546	0.815	5270(—)
$\mathrm{Cs^+}$	0.1524	0.876	5750(6192.3)

Ion exchange heats in parenthesis were calculated from those by Boyd *et al.*,6) which were obtained by exchanging any alkali metal ions for $\mathrm{Na^+}$ ions in Na-form Dowex 50 WX4.

The molar heat of ion exchange of alkali metal ions with $\mathrm{H^+}$ ions in the H-form resin was obtained by calibrating the heat of invasion. The results are listed in Table 1 together with those reported by Boyd *et al.*6) The molar heats agree with those obtained by the other method. The ion exchange heat depends strongly upon the extent of ion loading particularly in highly cross-linked resin. In the latter case, the heat of ion exchange is high at the initial loading of ions, decreases gradually with increasing loading of ions and sharply near 60—80 % loading. On the other hand, the exchanger, Dowex 50 W×4, is of relatively low extent of cross-linking, representing only a small dependence of the exchange heat upon ion loading. This makes us convince the coincidence of two kinds of data on ion exchange heat, *i.e.* of differential heats reported by Boyd *et al.* and intergral heats.

References

1) R. L. Gustafson and J. A. Lirio, *J. Phys. Chem.*, **72**, 1502 (1968).

2) K. E. Becker, S. Lindenbaum, and G. E. Boyd, *J. Phys. Chem.*, **70**, 3834 (1966).

3) G. E. Boyd and A. Schwarz, *J. Phys. Chem.*, **71**, 1355 (1967).

4) E. H. Cruickshank and P. Meares, *Trans. Faraday Soc.*, **53**, 1289 (1957).

5) G. E. Myers and G. E. Boyd, *J. Phys. Chem.*, **60**, 521 (1956).

6) G. E. Boyd, F. Vaslow, and S. Lindenbaum, *J. Phys. Chem.*, **68**, 590 (1964).

7) T. Morimoto and H. Naono, *Bull. Chem. Soc. Jpn.*, **45**, 700 (1972).