Thermochimica Acta, 57 (1982) 301–308
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

HEATS OF ION-EXCHANGE ON DOWEX 50W OF ALKALI METAL CATIONS. THERMAL EFFECTS OF LONG DURATION IN THESE EXCHANGE SYSTEMS

M. ZAMORA, E. ROJAS and J. ALGABA

Departamento de Termologia, Facultad de Fisica, Universidad de Sevilla, Seville (Spain)

(Received 2 March 1982)

ABSTRACT

An experimental device for the calorimetric measurement of enthalpies of cation-exchange is described, giving the values of these enthalpies for K^+/H^+, Na^+/H^+, H^+/Li^+, K^+/Li^+, Na^+/Li^+ and K^+/Na^+ exchange systems on Dowex 50W with several degrees of cross-linking. Weak thermal effects of long duration have been found in these exchange processes. The influence of the exchange system and cross-linking of the resin is studied.

INTRODUCTION

The heat of ion-exchange of 50W type resins has been measured calorimetrically by several authors [1–6] who all found that, in the exchange process, equilibrium is restored in some minutes. However, Heumann and Patterson [7], using a continuous recording Tian–Calvet-type calorimeter detected thermal effects for up to 4 h. This disagreement in the time to arrive at equilibrium cannot be imputed either to the different types of calorimeters, or the diverse experimental techniques used, but rather it must be implicit in the exchange process. On the other hand, kinetic studies [8] predict a time to reach equilibrium in these systems from seconds to several hours, depending on the exchange system, degree of cross-linking, grain size, and concentration of the external solution.

In this paper values of the heat of ion-exchange are given with special consideration to the relative values of these "long-lasting thermal effects". The influence of cross-linking and the exchange system on these thermal effects are also studied. The experimental arrangement used has been designed to point out these effects and the calorimeter is a Tian–Calvet type with a high accuracy detection system to show the descending terminal powers of the ion-exchange processes.

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MATERIALS

The resins used were Dowex 50W with X-2, X-4, X-8 and X-12 degrees of cross-linking and 50/100 mesh of nominal particle size, supplied by Serva-Fenbiochemical. The solutions used for the exchange as well as for the conditioning of the resins were prepared from HCl, KCl, NaCl and LiCl A. G. supplied by Merck.

CALORIMETRIC APPARATUS

The calorimetric measurements were carried out at 298.15 K using an isothermal Tian–Calvet type differential calorimeter which has been described elsewhere [9]. The calorimeter output is first amplified by a Teckelec TE 921 microvoltmeter and then goes to a Hewlett-Packard 3052 A data

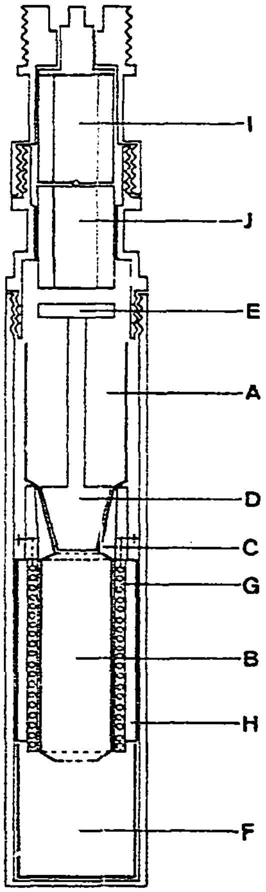

Fig. 1. Schematic diagram of the reaction cell.

processing system. The whole system has a sensitivity to thermal effects of 0.3 μW and was designed to detect weak thermal phenomena over long periods of time.

The reaction cell used for the cation-exchange process is shown schematically in Fig. 1. It is made of glass and consists of an upper receptacle A which contains, at the beginning of the experiment, the solution of the cation to be exchanged, and a column B, where the resin is placed between two wafers of spun glass. Communication between the two parts occurs by means of a tapered emery joint C which contains a glass plug D, to which a piece of ferromagnetic material E is solidly attached. The solution produced by the exchange is collected in a platinum receptacle F.

Column B is fitted into an electric heating element G of anti-inductively wound manganin which is used to calibrate the system in each trial. This heating element is embedded in a piece of copper H which improves thermal contact.

Plug D is opened by means of the attraction of piece E produced by rotation of magnet I with respect to magnet J which is stationary. Both magnets are of the sintered type and are placed between two polar pieces. Friction between the magnets is minimized by placing a steel ball between them. The entire assembly is enclosed in a cylindrical stainless steel vessel which assures that it is hermetically sealed.

EXPERIMENTAL PROCEDURE

About 0.4 g of the resin in the required cationic form is placed in the column, soaked in, and in equilibrium with a chloride solution of its own cation. This solution has the same concentration (0.2 mole dm^{-3}) as that in receptacle A, so that thermal effects due to changes of concentration in the liquid phase are minimized.

The exchange processes were carried out following the order of affinity of the resins used for the cations, $K^+ > Na^+ > H^+ > Li^+$, so that the added cation is the one of higher affinity; thus, the exchanges studied were K^+/H^+, Na^+/H^+, K^+/Na^+, H^+/Li^+, K^+/Li^+ and Na^+/Li^+.

The process of exchange is initiated by raising the plug and letting about 1 cm^3 of the upper solution flow through the bed of resin. Once the process has finished the part of the resin that has undergone the exchange is a perfectly defined portion that should be considered completely exchanged [10]. This assures that the total measured heat represents the integral heat of exchange.

A thermogenetic analysis [11] of the thermograms was performed using as transference function of the calorimeter that obtained from calibration data.

This was possible because the placement of the heating element for calibration made the generation of heat comparable in the two cases. This analysis has shown that the long-lasting thermal effects may be studied directly on the thermogram, as the relaxation time of the exchange process is much longer than that of the calorimeter.

The fundamental source of error in the measurements issues from the stability of the zero line of the calorimeter, so that the estimated error is in the order of 2–3%, depending on the duration of the process and the average value of the weak heat flow at the end.

The values of the enthalpies of exchange have been corrected for the relative apparent molal heat contents of the electrolyte solutions used [12]. They have also been corrected for spurious thermal effects due to the opening of the plug and the solution flow through the resin bed using values obtained in blank experiments.

Once the process of exchange has finished, the external solution is eliminated by running distilled and deionized water through the bed of resin. The metallic cations of the resinate are then recovered by adding 1 mole dm^{-3} HCl solution. This solution is dried by evaporation, dissolved in water and the cations are analyzed with a Perkin-Elmer 460 spectrophotometer. However, when the exchanged cation is H^+, it is recovered by replacing it with a 1 mole dm^{-3} KCl solution and then titrating it using a standard sodium hydroxide solution.

RESULTS AND DISCUSSION

Two typical thermograms are shown in Fig. 2 and indicate that the exchange process has a high power first stage followed by another of long duration and decreasing power. This indicates that the time required to reach equilibrium is much longer than that reported in the literature.

Since the characteristic time of the calorimeter is 40 min, the long-lasting thermal effects will be represented as the ratio, Ω, of the heat evolved after 40 min from the initiation of the experiment, and the total heat liberated in the process, in per cent. Values of Ω are given in Table 1 where it is shown that its contribution to the total heat becomes important due essentially to the long duration of the process. Ω shows a strong dependence on the exchange system, but this dependence is weaker with cross-linking.

With these influences, some consequences must be noted: (a) it seems that relative sizes of hydrated ions do not affect Ω values, as can be observed in Table 1, knowing that the sequence of these sizes is $H^+ > Li^+ > Na^+ > K^+$; (b) a comparative study of the different exchanges shows a dependence between Ω and the electrolyte used. Thus, for the K^+/H^+, K^+/Li^+ and

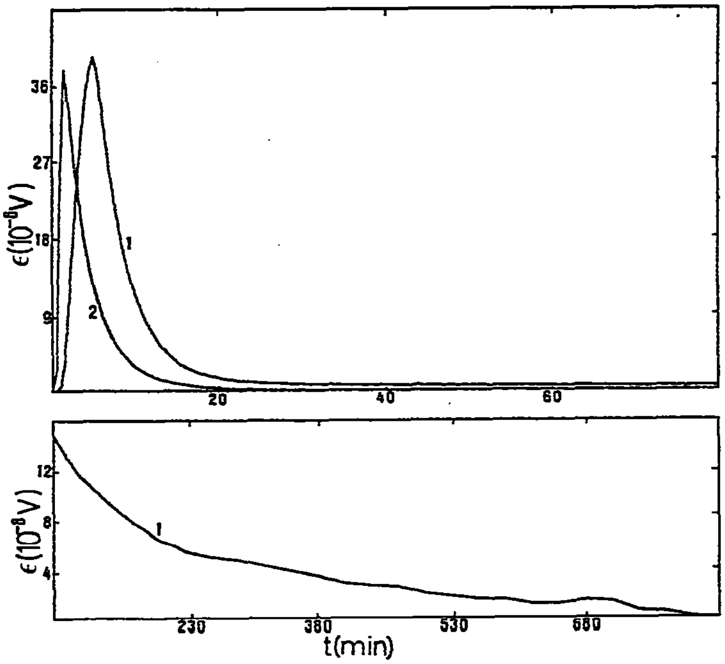

Fig. 2. Calorimeter output, ϵ, plotted against time, t. Curve 1, H^+/Li^+ exchange on Dowex 50W X-8, (with the final part enlarged); curve 2, electric calibration.

TABLE 1

Enthalpies of cation-exchange on Dowex 50W
Uncertainties are the standard deviations of the means.

Exchange system	Resin cross-linking X	No. of determinations n	$-\Delta H$ (kJ mole^{-1})	Long-lasting thermal effects (%) Ω
K^+/H^+	2	3	4.33±0.01	7
	4	3	5.78±0.05	6
	8	3	8.15±0.03	11
	12	3	10.96±0.02	17
Na^+/H^+	2	3	1.69±0.02	0
	4	5	2.57±0.02	0
	8	5	3.97±0.07	3
	12	3	4.78±0.01	7
H^+/Li^+	2	3	1.54±0.02	17
	4	3	1.75±0.03	21
	8	3	2.55±0.03	26
	12	3	3.41±0.01	37
K^+/Na^+	2	2	1.83±0.03	7
	8	3	2.78±0.01	9
K^+/Li^+	2	3	5.43±0.04	9
	8	3	9.60±0.04	11
Na^+/Li^+	8	3	4.97±0.02	2

K^+/Na^+ systems, where the electrolyte is KCl, the Ω values are of the same order. For the Na^+/H^+ and Na^+/Li^+, where NaCl has been used, the Ω values are similar, but different from those above. Finally, the highest Ω values correspond to the H^+/Li^+ system, with HCl as electrolyte.

Table 1 shows the enthalpies of exchange of the K^+/H^+, Na^+/H^+ and H^+/Li^+ systems for X-2, X-4, X-8 and X-12 degrees of cross-linking and those of the K^+/Li^+ and K^+/Na^+ systems for X-2 and X-8 only. In all cases the concentration of the external solution was 0.2 mole dm^{-3}.

The enthalpies of exchange measured and those given in the literature for exchanges similar to those made here are given in Table 2. As a general observation, the values obtained here are somewhat higher than those in the literature; the differences generally being larger when long-lasting thermal effects are greater. In the Na^+/H^+ system, where these effects are negligible, our values are lower.

Data shown in Table 1 are plotted in Fig. 3, which shows an increase, in absolute value, of the enthalpies with a rise in the degree of cross-linking. The lines adjusted to the experimental data show negative curvatures for the K^+/H^+ and Na^+/H^+ systems, and a positive one for the H^+/Li^+ system.

In interpreting this behaviour, the effect of variation in cross-linking on the internal solution of the resins must be considered. A decrease in the water content of the resin takes place when the exchanger cross-linking increases. Thus, there may be changes in hydration of the exchanging

TABLE 2

Comparison of enthalpies of cation-exchange with data from the literature

Exchange system	X	$-\Delta H$ (kJ $mole^{-1}$)							
		Ref. 1	Ref. 2	Ref. 3	Ref. 4	Ref. 5	Ref. 6	This work	Ω
K^+/H^+	4				5.14			5.78	7
	8			7.78	8.46			8.15	9
	12						7.74	10.96	17
Na^+/H^+	2		1.92					1.69	0
	4		3.60					2.57	0
	8	4.68	4.94	4.60		4.68		3.97	3
H^+/Li^+	4					1.02		1.75	21
	8			1.34		2.21		2.55	26
K^+/Na^+	2		1.21					1.83	8
	8		2.30					2.78	9

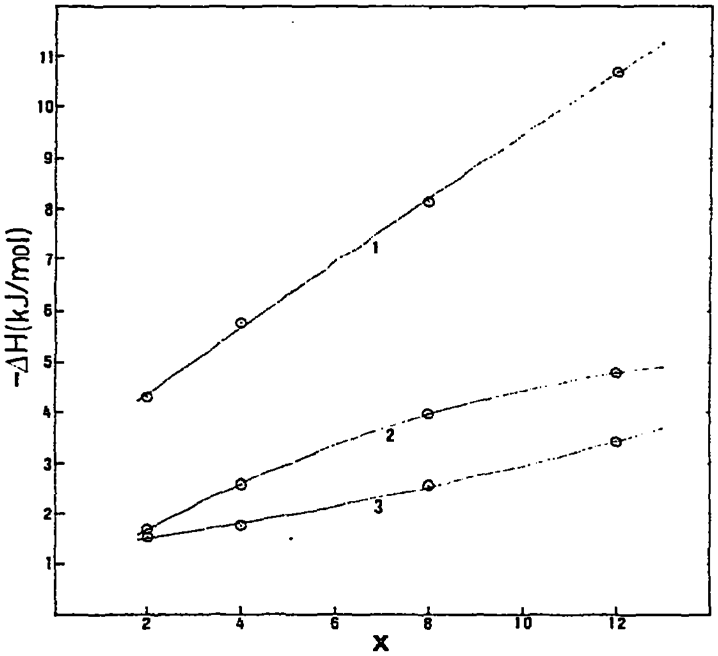

Fig. 3. Enthalpies of cation-exchange as a function of the cross-linking for various exchange systems, 1, K^+/H^+; 2, Na^+/H^+; 3, H^+/Li^+.

cations. These changes will be larger for the cations with a larger hydration number.

The changes in $-\Delta H$, shown in Fig. 1, are consistent with the above arguments, since the general shape of the lines could result from an increasing influence of the cross-linking on the hydration of the exchanging cations. The magnitude of this influence will depend on the difference in hydration, in the external solution, of the cations implicated in the exchange process. These differences decrease in the order $K^+/H^+ > Na^+/H^+ > H^+/Li^+$.

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