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THERMAL STUDIES ON THE DEHYDRATION OF POLYSTYRENE-DIVINYLBENZENE-TYPE ION EXCHANGERS

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SUMMARY

Thermal studies on fully swollen polystyrene–divinylbenzene-type resins, variously cross-linked Dowex 50W (Li^+) resins and Dowex 1-X8 (Cl^-, Br^-, I^- and NO_3^-) resin forms have been carried out. Thermogravimetric analysis of the resins showed that apparently all of the water was lost in one step between 300 and 383°K. Isothermal kinetic data for the resins best fitted the contracting envelope equation. Nearly 70% of the total water in the resins, corresponding to the osmotic water in the resin phase, was lost at a constant rate. The activation energies for this part of the dehydration for Li^+ and NO_3^- resins were greater and those for Cl^-, Br^- and I^- resins were smaller than the enthalpy of evaporation of normal water. This indicates a more ordered state of water in Li^+ and NO_3^- resins and a more disordered state in Cl^-, Br^- and I^- resins than in normal water. These results are discussed in terms of a generally accepted model for the structure of aqueous electrolyte solutions.

INTRODUCTION

The development of synthetic organic ion exchangers started in the 1940s and by the mid-1950s it had been established that the ions inside the moderately and low cross-linked exchangers of the polystyrene–divinylbenzene (PS–DVB) type were fully hydrated[1]. The excess water in the exchanger which is not part of the hydration sphere of counter ions has been described as "free water" or osmotically imbibed water[2,3]. So far no serious attempt has been made to investigate the thermodynamic state or structure of this water. The existence of a high concentration of ions and the swelling pressure inside the resin phase make the water inside the swollen resins a very interesting substance from the point of view of electrolyte solutions. Currently accepted ideas about the structure of electrolyte solutions consider the water to exist in the following three forms[4]: (i) water in the hydration sphere of ions, (ii) water in between the hydration sphere and bulk water, and (iii) bulk "free" water. The high ionic concentration inside the exchanger phase virtually rules out the possibility of "normal" bulk water existing in the exchanger phase. This situation suggests that the study of water inside the exchanger phase could provide more information about the ion–water interactions in the first and second categories.

In this study, thermoanalytical techniques have been employed to investigate the properties of water inside the exchanger phase. The results of thermogravimetric and isothermal studies on the dehydration of fully swollen, strongly acidic cation exchangers, Dowex 50W (Li^+) (with 4, 8 and 12% DVB contents) and a fully swollen strongly basic anion exchanger, Dowex 1-X8 (Cl^-, Br^-, I^- and NO_3^-) are presented.

EXPERIMENTAL

Materials

Dowex 1-X8 and Dowex 50W with 4, 8 and 12% DVB contents were supplied by J. T. Baker (Pennsylvania, PA, U.S.A.). The resins were conditioned in the usual way by recycling through the Na^+/H^+ cycle for the cation exchangers and the OH^-/Cl^- cycle for the anion exchanger. The resins were finally converted into the Li^+ form (cation exchangers) and Cl^-, Br^-, I^- and NO_3^- forms (anion exchanger). The maximum water uptake and capacity per gram of oven-dried resin (ODR) are given in Table I.

TABLE I

MOISTURE CONTENTS AND CAPACITIES OF VARIOUS ION-EXCHANGE RESINS

Resin	*Ionic form*	*Water content (g/g ODR)*	*Capacity mequiv./g ODR*	*Water content (moles/equiv.)*
Dowex 50W-X4	Li^+	1.849	4.9	20.96
Dowex 50W-X8	Li^+	1.05	4.90	11.90
Dowex 50W-X12	Li^+	0.757	4.83	8.70
Dowex 1-X8	Cl^-	0.834	3.75	12.37
Dowex 1-X8	Br^-	0.614	3.21	10.63
Dowex 1-X8	I^-	0.425	2.79	8.46
Dowex 1-X8	NO_3^-	0.668	3.41	10.88

Thermal studies

A Stanton thermobalance (HT model) coupled with a Stanton-Redcroft linear variable temperature programmer (LVP-C model) was used for taking the thermograms. Generally 200-mg samples were used for taking thermograms both as a function of temperature (up to 500°K) and under isothermal conditions. The constancy of temperature when the balance was operated in the isothermal mode was checked by using an additional thermocouple (Pt–Pt–13% Rh) located very near the sample and connected through a cold junction to a millivolt potentiometer.

Thermogravimetric curves were recorded at a constant heating rate of 1°K/min (Fig. 1). Apparently all of the water was lost in one step in the temperature range 298–383°K. There was an additional weight loss with the anion exchanger beyond 450°K, a feature which was absent for the cation exchangers. It is well-known that cation exchangers are thermally more stable than anion exchangers, which decompose above·473°K[5], and the additional weight loss with the anion exchanger is attributed to thermal decomposition. No detailed study was made of this decomposition step. Isothermal decomposition curves were recorded at 343, 353, 363 and 373°K. Above 373°K the dehydration rates were too rapid to give any useful data.
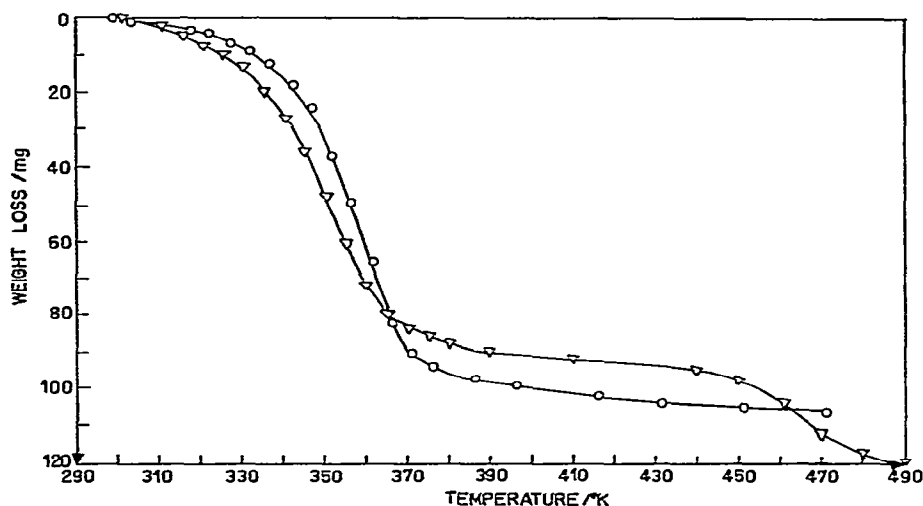
Fig. 1. Weight loss as a function of temperature. $\bigcirc$, Dowex 50W-X8 (Li$^+$); $\triangledown$, Dowex 1-X8 (Cl$^-$).

RESULTS

The variation of weight loss with temperatures was studied with constant sample size, particle size and container geometry. These factors appear to be important in reactions of the type[6]

$$\text{Solid (A)} \rightarrow \text{Solid (B)} + \text{gas}$$

as they influence the removal of gaseous products from the reaction zone. The rate of reaction in such instances reaches a maximum when gaseous products are absent and decreases continuously to zero as the pressure approaches the equilibrium pressure. During the removal of (osmotic) water from the resins at the temperatures used, the equilibrium vapour pressure is high and the convective flow of air through the furnace effectively reduces it to zero. However, this may not be true when the equilibrium vapour pressure of water is low.

The other problem in carrying out solid-state kinetics isothermally is that of the sample attaining the temperature of interest in a time interval that is small in comparison with the lifetime of the reaction. Discarding of the first 10% of the data on the degree of conversion, α, to the anhydrous state (which corresponded to the first 5–10 min of the experiment, depending on the temperature) was found to be adequate for obtaining kinetic information at a specific temperature.

Kinetic analysis of data

The important mathematical models that have been frequently used for the kinetic analysis of the dehydration of crystalline salt hydrates are as follows:
(i) Unimolecular decay equation[7]

$$-\ln(1 - \alpha) = kt \quad .$$

(ii) Avrami-Erofeev equation[8]

$$-\ln(1-\alpha) = (kt)^n \qquad n = 2,3, \ldots$$

(iii) Contracting envelope equation[7]

$$1-(1-\alpha)^{1/n} = kt \qquad n = 2,3, \ldots$$

where α = fraction of reaction completed at time t.

As the materials used in this study were spherical beads of an amorphous gel, it was not obvious which mathematical model would be appropriate. Therefore, all three equations were tried in an attempt to fit the dehydration curves. Representative curves for Dowex 50W-X8 (Li^+) at 353°K are shown in Fig. 2. Similar behaviour was observed in other instances. It is obvious that the unimolecular decay equation does not describe the data. The Avrami–Erofeev equation when applied in the form log [$-$ log $(1-\alpha)$] versus log t gave a good straight line, but with non-integral values of n. As n should be a whole number according to the model used for the derivation of these equations, these non-integral values of n indicate that the present experimental conditions do not correspond to the model which is the basis for these
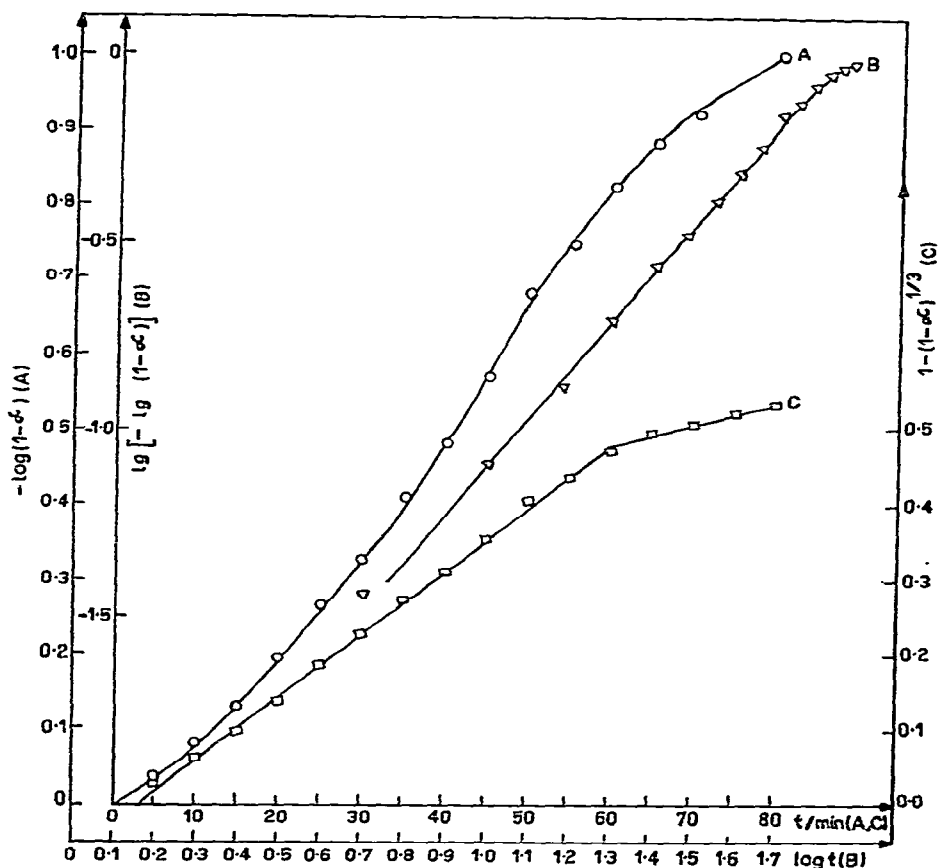

Fig. 2. Rate equations applied to the dehydration of Dowex 50W-X8 (Li^+) at 353°K. A, Unimolecular decay; B, Avrami–Erofeev equation; C, contracting envelope equation.

equations[9]. The contracting envelope equation, when plotted in the form $1 - (1 - \alpha)^{1/3}$ *versus t (i.e.,* with $n = 3$), gives very good linear plots up to $\alpha = 0.7$. There is a sharp decrease in the dehydration rates when α is greater than 0.7 (see Discussion). This equation was then used to analyse the data for all of the resins, and plots for two typical cases at various temperatures are given in Figs. 3 and 4. Arrhenius plots for the various resins are shown in Fig. 5. The activation energies for the dehydration process up to $\alpha = 0.7$ obtained from these plots are summarized in Table II.
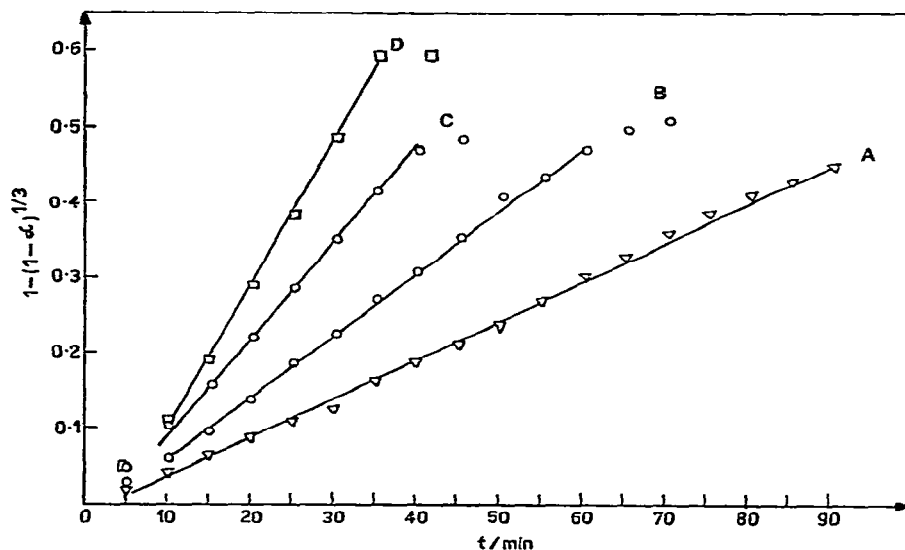

Fig. 3. $1 - (1 - \alpha)^{1/3}$ *versus t* plots for the dehydration of Dowex 50W-X8 (Li⁺) at A, 343°K; B, 353°K; C, 363°K; and D, 373°K.
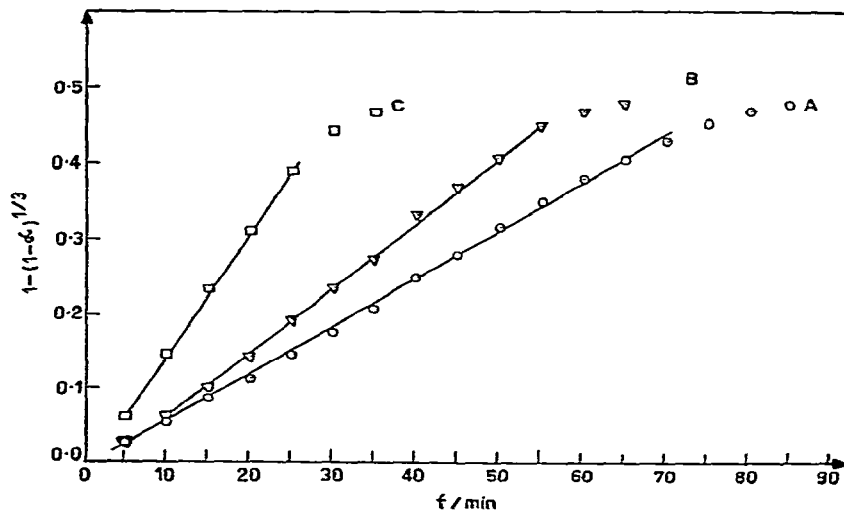

Fig. 4. $1 - (1 - \alpha)^{1/3}$ *versus t* plots for the dehydration of Dowex 1-X8 (Cl⁻) at A, 343°K; B, 353°K; and C, 373°K.

TABLE II

ACTIVATION ENERGIES AND RATE CONSTANTS FOR THE DEHYDRATION OF VARIOUS IONIC FORMS OF ION EXCHANGERS

| Resin	Ionic form	Rate constant (min^{-1})				Activation energy $(kJ/mole)$
		$343°K$	$353°K$	$363°K$	$373°K$	
Dowex 50W-X4	Li^+	0.00534	0.00823	—	0.0173	
Dowex 50W-X8	Li^+	0.00515	0.00816	0.0122	0.0188	43.2
		0.00548	0.00793	0.0125	—	
Dowex 50W-X12	Li^+	0.00558	0.00837	0.0124	—	
Dowex 1-X8	Cl^-	0.0061	0.00926	0.0133	0.0163	40.2
Dowex 1-X8	Br^-	0.00723	0.0101	0.014	0.0193	34.3
Dowex 1-X8	I^-	0.0106	0.0137	0.0173	—	25.7
Dowex 1-X8	NO_3^-	0.00728	0.0110	0.0163	—	41.7
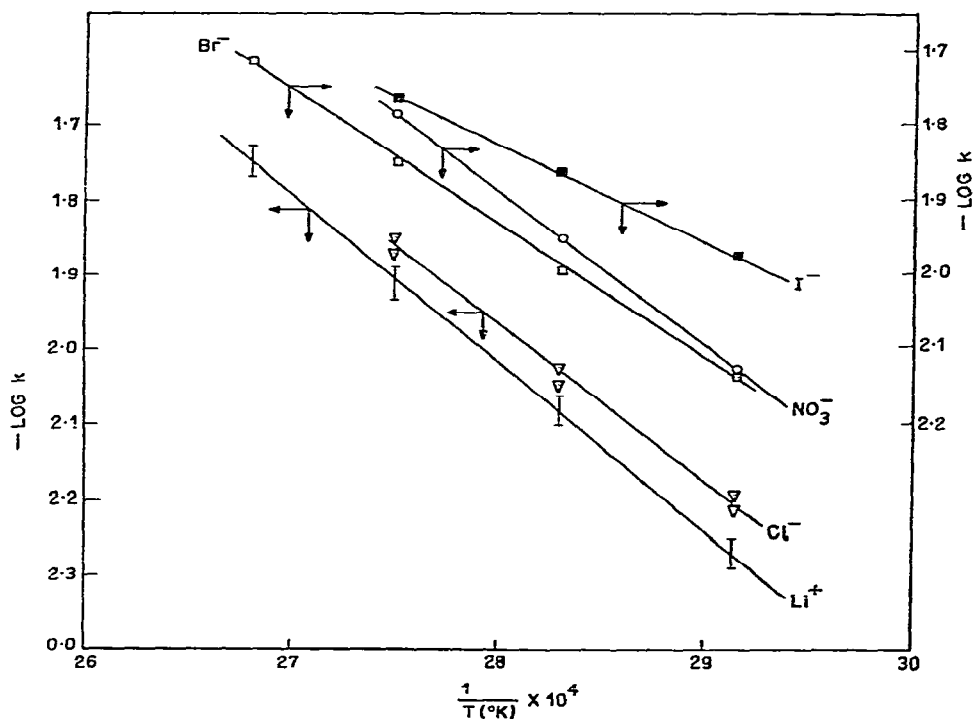
Fig. 5. Arrhenius plots for various resins. Bars represent the range of values obtained for variously cross-linked Li^+-form resins.

DISCUSSION

The physical model underlying the contracting envelope equations is that the reaction takes place at the surface of the unreacted core. It is assumed that there is no concentration gradient across the product layer. The dehydration of fully swollen spherical ion exchanger beads conforms very closely to this model and water, evapo-

rating from the surface, is removed from the reaction zone by a convective flow of air. The surface of the hydrated resin moves inwards as the reaction progresses. The water vapour moves freely out of the dry (product) zone and is lost to the atmosphere. The applicability of the contracting envelope equation, developed primarily for solid-state reactions, to the dehydration of ion-exchange resins is therefore not surprising.

It can be clearly seen from Figs. 3 and 4 that there is a sudden change in the slope at α values greater than 0.7, which indicates a sharp drop in the reaction rates. Earlier studies on the water sorption isotherms for these resins have shown that 70–80% of the total water content of the resins constitutes the so-called osmotic water and is taken up at water activities greater than 0.6–0.7[2,3]. On the other hand, the remaining water, which is taken up at low water activities, is part of the hydration shells of the ions. The low water vapour pressures, when this water is being removed during the dehydration process, may not permit the effective removal of released water vapour from the reaction zone. This inefficient removal of the product from the reaction zone could result in a lowering of the reaction rates.

The results of the experiments with resins in the Li^+ form containing different amounts of water (different cross-linking or equilibrated with lower activity) are given in Table II, and show the following:

(1) Dehydration rates and activation energies for the first part of the dehydration process are independent of resin cross-linking.

(2) The α values at which the dehydration rates decrease follow the sequence 4% DVB ($\alpha = 0.86$) > 8% DVB ($\alpha = 0.8$) > 12% DVB ($\alpha = 0.75$). This is also the sequence for the amount of osmotic water in these resins[2,3].

(3) The amount of water left in the Li^+ resins, when the k values decrease sharply, is independent of resin cross-linking, within experimental error (4% DVB, 2.9; 8% DVB, 2.4, 2.6*; 12% DVB, 2.2 mole/equiv.). The amount of water in the hydration shells of ions in these resins has also been shown to be independent of resin cross-linking in an earlier study[3].

(4) In the experiment in which Dowex 50W-X8 (Li^+) was equilibrated isopiestically with a water activity of about 0.65, the rate constant at 353°K (0.0075 min^{-1}) was comparable to those observed for the fully swollen resin (0.008 min^{-1}). This indicates that the lower water vapour pressure prevailing in the former instance does not prevent the effective removal of water vapour from the reaction zone. These results strongly suggest that the sharp decrease in k is associated with the water of ionic hydration from the resin being lost at a much lower rate than osmotic water and the dehydration process up to $\alpha \approx 0.7$ represents the removal of osmotic water. However, it is not possible to say so with certainty as the dehydration process beyond $\alpha \approx 0.7$ could not be studied. Nevertheless, the dehydration process up to $\alpha \approx 0.7$ can be discussed.

The activation energies for the dehydration of the resins (up to $\alpha \approx 0.7$) follow the sequence $Li^+ > NO_3^- >$ normal water $\geqslant Cl^- > Br^- > I^-$, which implies that ca. 70% of the water in the Br^- and I^- forms of resins is present in a more disordered state and in the Li^+ and NO_3^- forms in a more ordered state than in ordinary water. The more disordered state of water in the Br^- and I^- forms of the resins is consistent with their known structure-breaking character in aqueous solutions[4,10]. Cl^- also

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* Value obtained with Dowex 50W-X8 (Li^+) equilibrated with water activity ≈ 0.65.

falls in its proper place in this sequence. On the other hand, the more ordered state of osmotic water in Li^+-form resins in comparison with normal water is consistent with the structure-making character of Li^+ in aqueous solutions.

The structure-making character of NO_3^- indicated by the present study is surprising. Infrared studies of NO_3^- in aqueous solutions indicated the presence of two strong hydrogen bonds between nitrate ion and water molecules[11-13]. X-ray studies, however, suggest that nitrate ions interact weakly with a large number of water molecules[14]. This study supports the latter view as it suggests that water molecules around the nitrate ions are present in a slightly more ordered state than in ordinary water.

In conclusion, the dehydration of the ion-exchange resins (up to 70%) follows the contracting envelope equation. The solvent in the exchanger phase is primarily influenced by the osmotically active counter ions; hence a study of the exchanger phase provides a means for studying the properties of single ions. It has also been shown that the water in the ion exchanger is not present as normal water but is either more structured or less structured, depending on the structure-making or structure-breaking characteristics of the counter ions. Part of the total water in the resins (20–30%), apparently the water in the hydration shells of the counter ions, could not be studied owing to very slow rates of dehydration at that stage. More detailed and different types of experiments will be required for studying the properties of this part of the total water.

ACKNOWLEDGEMENTS

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