Adsorption of Protium and Deuterium Oxides on Cation Exchange Resins

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The adsorption of protium and deuterium oxides at 298.15 K on the lithium, sodium, potassium, and barium forms of Dowex 50W-X8 cation exchanger was studied. In the whole humidity range the resinates adsorb larger mol amounts of H_2O than of D_2O. In the low humidity range the observations fit well the two parameter B.E.T. isotherm. The Gibbs energy changes of transfer of the resinates from H_2O to D_2O were $\Delta G_t = 2400$ J/mol. About 2200 J/mol of this is believed to be caused by the anions. Thus, in their interactions with the isotopically different waters the resinates resemble ordinary salts. The relative magnitudes of the ΔG_t values reveal different surface effects between the resin matrix bound sulfonate groups and the two kinds of water.

The cation exchangers based on strong sulfonic acid resins are polyelectrolytes with their negative charge bound to the resin matrix. A special feature of these resinates is their great ability to adsorb water even from the vapor phase.[1] The purpose of this study was to examine, if there are any differences in this feature when the ordinary water, protium oxide, is replaced with the isotopically different kind of water, deuterium oxide.

EXPERIMENTAL

The cation exchange resin used was a commercial sulfonated polystyrene resin Dowex 50W-X8, 50 to 100 mesh, manufactured by Dow Chemicals Co. The resin in the H^+ form was first washed with methanol in a Soxhlet apparatus and then with distilled water. The exchange capacity determined by a standard titrimetric method[2] was 5.060 mmol/g dry acid form resin, which gives a molecular weight of 197.6. (One mol of resin is defined as the amount

which contains a number of sulfonic acid groups equal to Avogadro's number.) Portions of the resin were converted to salt forms in a column using a tenfold amount of Merck's analytical grade lithium, sodium, potassium, and barium chlorides. According to the manufacturer, Norsk Hydro-elektrisk Kvaelstofaktieselskab, the deuterium fraction of the heavy water employed in the experiments was 0.997.

The isopiestic measurements were conducted in a stainless steel humidistat shown in Fig. 1. It was modified from the type described by Boyd and Soldano[3] to facilitate rapid weighings below a balance without opening the vessel. The basic part of the humidistat was a 5 l pot with a 3 cm wide rim with eight fastening bolts (A) and a channel for an O-ring seal (B). The cover was furnished with holes for the fastening bolts, a plastic window (C), and eight pipes (D) which could be closed with rubber plugs. The air in the humidistat was stirred with a paddle stirrer (E) and slave magnets (F) fixed to it. The stirrer was rotated with a master magnet (G) driven at one revolution per second by a small synchronous electric motor. A proper saturated salt solution was placed in a nickel dish (H) which was stirred at times with a glass rod. The samples were in eight open porcelain crucibles (I) equipped with metal wire bails. The whole humidistat was sub-
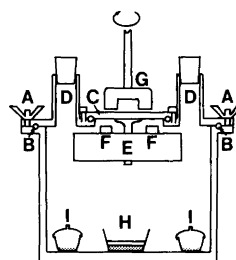

Fig. 1. The isopiestic apparatus.

merged up to the rim in a constant temperature water bath (25.00 ± 0.05 °C) below the balance.

For each ionic form two samples were used, and their dry weights (0.6 to 1.0 g) were determined after drying for 24 h at 120 °C. The dry samples and the first saturated salt solution were placed in the humidistat, which in the case of the deuterium oxide run was predried with phosphorus pentoxide, the vessel was closed tightly and placed in the water bath. To determine the water uptake of a sample the plug of the respective pipe (D) was removed, a hook-ended wire was threaded through to grip the bail on the crucible, and the sample was weighed in the humidistat below the balance. Because this procedure did not change the humidity of the isopiestic apparatus, it greatly speeded up reaching an equilibrium. When constant weights were registered, the salt solution was replaced with the next one. To avoid the effect of possible hysteresis the experiments were performed in such a succession that every second equilibrium was approached from below, every second from above. The relative humidities of the saturated salt solutions in D_2O were taken from the paper by Becker et al.[4] The corresponding values for the H_2O solutions were from the measurements by Stokes and Robinson.[5]

RESULTS

Since the samples were rather big, and the porcelain crucibles did not conduct heat well, the samples reached constant weights fairly slowly, typically in a week. The equilibrium was reached more slowly from above than from below, and more

slowly with D_2O than with H_2O, which is, no doubt, caused by the slower diffusion of D_2O through the resin matrix. Further, the equilibrium was established slower with increasing molecular weight of the counter ion. Especially with the barium resinate such a slowness caused a distinct hysteresis effect at some humidities.

The results of the experiments are given in Table 1, each the mean of two samples consistent within a few hundredths of mol/mol resinate. For a more convenient comparison the lithium resinate data are presented also in Fig. 2. The results are most accurate in the low humidity range; in higher humidities the experimental points may differ from the average adsorption curves by as much as 0.1 to
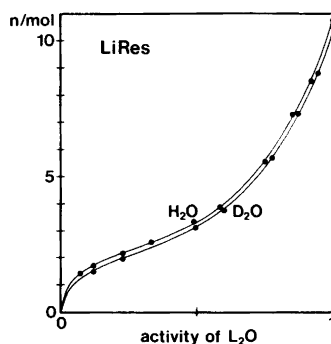

Fig. 2. The amounts of H_2O and D_2O adsorbed on one mol of the lithium resinate at various relative humidities at 298.15 K.

Table 1. The amounts of protium and deuterium oxides adsorbed by resinates at 298.15 K expressed in mol of water species per mol of resin. For $BaRes_2$ the molecular weight of 265.3 was used.

Resinate	Saturated salt solution and its relative vapor pressure										
		NaOH	LiCl	KAc	$MgCl_2$	KNO_2	NaBr	NaCl	KCl	KNO_3	L_2O
	H_2O	0.070	0.113	0.222	0.330	0.482	0.582	0.751	0.842	0.920	1.000
	D_2O		0.116	0.226		0.495	0.598	0.771	0.865	0.943	1.000
LiRes	H_2O	1.41	1.67	2.13	2.55	3.31	3.81	5.50	7.29	8.44	10.71
	D_2O		1.50	1.93		3.12	3.74	5.65	7.34	8.75	10.42
NaRes	H_2O	1.37	1.62	2.00	2.35	3.03	3.36	4.65	6.18	7.16	9.54
	D_2O		1.43	1.84		2.82	3.24	4.71	6.22	7.44	9.20
KRes	H_2O	1.16	1.37	1.67	1.95	2.49	2.73	3.63	4.60	5.61	7.99
	D_2O		1.20	1.53		2.28	2.57	3.61	4.82	5.80	7.49
$BaRes_2$	H_2O	1.38	1.59	1.92	2.13	2.74	2.89	3.45	4.24	5.69	6.12
	D_2O		1.39	1.79		2.43	2.61	3.35	4.29	4.62	5.49

0.2 mol/mol resinate. In this study as in the earlier ones [3,6,7] the adsorption from the vapor phase gave lower values for 100 % relative humidity than those obtained with a centrifugal method from water solution.[8] During the D_2O run the dry weights of the resinates increased by 1 to 3 mg/g resinate, which, however, is negligible compared with other experimental errors. The effect is due to the deuteration of the resin matrix found in an earlier study.[9] The present adsorption curves are similar to the sigmoidal curves obtained by other investigators. In the case of lithium, sodium, and potassium the H_2O adsorption can be directly compared with the results of Boyd and Soldano,[3] and the agreement is good. For the D_2O adsorption no comparative values were found in the literature.

DISCUSSION

Each of the resinates studied adsorbs larger mol amounts of protium oxide than of deuterium oxide in the whole humidity range. The difference is produced already at the steeply rising low humidity part of the adsorption curves, where the water is thought to be used mainly to form hydration shells on sulfonate groups.[3,7] Then the water dipoles preferably orient themselves with hydrogen ends towards the negatively charged sulfonate groups, and we may expect differences in the behavior of various kinds of water. When the relative humidity is raised the cations, too, begin to be hydrated but the orientation of the water dipoles is the opposite and there are no special differences between the different kinds of water. Thus, the difference of the adsorption curves remains essentially constant in the plateau range, and the situation continues in the higher humidities, where adsorption takes place on the nonionic resin matrix.

As Gregor and his coworkers stated [6] the Raoult's law diagrams like Fig. 3 reveal special features of the binary system resin-water. At low water mol fractions the components behave as if they were completely miscible. Where the water activity becomes one the components become completely immiscible. Thus, there is a solubility gap in the range corresponding to dilute solutions of ordinary electrolytes. According to Fig. 3, the system exhibits a large negative deviation from Raoult's law indicating strong interactions between the resinates and the two waters. As the deviation is larger for H_2O, the resinate binds H_2O more tightly than D_2O.
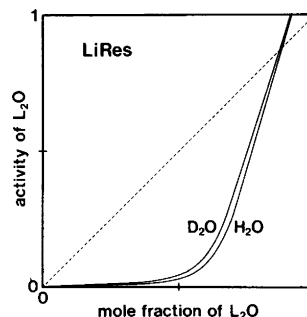
Fig. 3. The Raoult law diagrams of the system L_2O-LiRes.

The Raoult's law relations for a number of salt solutions in protium and deuterium oxides can be calculated from the osmotic coefficients reported by Kerwin [10] and Rasaiah.[11] Because the ordinary salts have limited solubilities, only the upper right corner in the Raoult's law diagram is reached.

In the case of alkali halides and zink sulfate the D_2O and H_2O curves lie very close to one another and generally the former curve is to the right of the latter one. Cesium chloride and zink sulfate, however, resemble the resinates in that the D_2O curves lie to the left of the H_2O curves. This does not, however, prove any deeper relationship between the mentioned salts and resinates. The same comparison can also be made by calculating the osmotic coefficients for the resinate solutions. Then it must be noted that the sulfonate groups bound to the resin matrix have no osmotic effect.[6] According to such calculations the osmotic coefficients for the resinates are larger in H_2O than in D_2O as in the case of cesium chloride and zink sulfate.

The measurements provide data for calculating free energy changes of adsorption.[6,12,13] According to the Gibbs-Duhem equation, the Gibbs energy change for a process, where a dry resinate adsorbs water isothermally up to the relative humidity of 100 %, is

$$\Delta G = -RT \int_0^1 \frac{n}{a} \, da \qquad (1)$$

In this equation n is the number of water moles adsorbed at the water activity a, R is the gas constant and T the absolute temperature. The integral can be evaluated best with graphic integration by plotting n/a against a.

Table 2. The B.E.T. parameters and Gibbs energy changes for adsorption of different kinds of water on resinates.

		B.E.T. parameters		Gibbs energy changes	
		C	n_m	ΔG J/mol	ΔG_t J/mol
LiRes	H_2O	35.78	1.808	-26100	
	D_2O	30.75	1.657	-23660	2440
NaRes	H_2O	50.14	1.647	-24870	
	D_2O	39.49	1.529	-22170	2700
KRes	H_2O	60.25	1.357	-21040	
	D_2O	51.43	1.235	-18640	2400
BaRes$_2$	H_2O	165.83	1.466	-29130	
	D_2O	175.38	1.339	-27110	2020

For calculations the observations were first plotted in a large scale and the best fitting adsorption curves (Fig. 2) were drawn considering the possible hysteresis. The two parameter B.E.T. isotherm[14] was found to represent the observations very well in the low humidity range. The equation of this isotherm is

$$\frac{a}{1-a}\frac{1}{n} = \frac{1}{Cn_m} + \frac{(C-1)a}{Cn_m} \qquad (2)$$

where a and n are the same quantities as above, C and n_m are parameters. The observations were fitted to eqn. (2) by least squares, and the parameters are given in Table 2. The missing points for $a(D_2O)$ $=0.330$ were estimated from the large scale adsorption curves. In the B.E.T. isotherm theory the parameter n_m is the amount of the adsorbate needed to form a monomolecular layer. From the n_m values we can estimate that the adsorption areas of the resinates are 320 to 570 m^2/g, which is very reasonable. The point must not, however, be taken too literally, since we get smaller areas with D_2O than with H_2O.

The integrals (1) were calculated with Simpson's formula. In the range $a=0-0.35$ the B.E.T. isotherm values were used. The integral can be evaluated also at the lower limit, because $\lim_{a\to 0} n/a = Cn_m$. In the range above $a=0.35$ the n values were taken from the large scale adsorption curves. The calculated Gibbs energy changes are given in Table 2 and their cumulation with increasing relative humidity cal-

culated with the trapeze rule in Fig. 4. The errors of the Gibbs energy changes are estimated to be a few hundred J/mol at most, except for the barium resinate, which is less accurate.

The difference $\Delta G_t = \Delta G(D_2O) - \Delta G(H_2O)$ is the Gibbs energy change for the transfer process

$$MRes(H_2O) \to MRes(D_2O) \qquad (3)$$
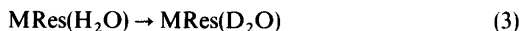
where the adsorbed protium oxide is replaced with deuterium oxide. Within the experimental errors the ΔG_t values for the resinates are the same, 2400 J/mol. They are somewhat larger than, but of the same sign as, those obtained for ordinary salts.[15,16] The Gibbs energy changes of transfer of metal ions are believed to be only a few hundred J/mol.[16]
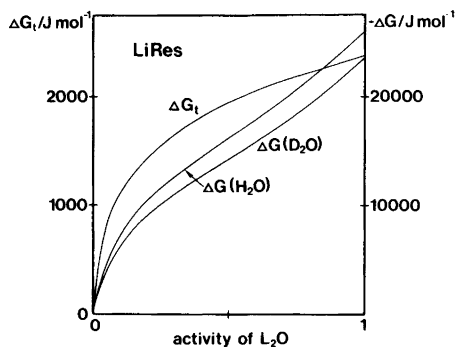

Fig. 4. The cumulative Gibbs energy changes of adsorption for the lithium resinate.

Thus, the transfer of the resin matrix bound sulfonate groups from H_2O to D_2O causes a Gibbs energy change of about 2200 J/mol. It is larger than obtained for other anions[16] giving evidence of special surface effects in this case. The fact that a larger part of the ΔG_t value of a resinate is due to the anion is seen also from Fig. 4: ΔG_t increases very steeply just in the low humidity range, where the hydrate shells of the sulfonate groups are being filled.

The present adsorption experiments show that the resinates of strong sulfonic acid cation exchangers are rather normal electrolytes in their interactions with the isotopically different kinds of water. As usual, the isotopic effects are mainly due to the anions. The magnitude of the transfer Gibbs energies suggests, however, that there are special surface effects between the resin matrix bound sulfonate groups and the two kinds of water.

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