Preferential Adsorption of Protium and Deuterium Oxides from Solutions of Diethyl Ether and Ethyl Acetate on a Sodium Ion Exchanger

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Isotherms for the adsorption of H_2O and D_2O from solutions of diethyl ether and ethyl acetate on a sodium resinate at 298.15 K were determined as well as the activity curves of the two waters in these solvents. H_2O is adsorbed in larger mol amounts than D_2O, but in low D_2O concentrations the measurements were disturbed by a slow hydrogen exchange between D_2O and the resin matrix. Corrected to activity scale, the isotherms in both solvents are nearly identical. They resemble also the isotherms obtained for adsorption from gas phase, but with smaller slopes at low water activities due to smaller heats of swelling of the resin in liquid phase. The results fit well the two parameter BET isotherm at low activities. The Gibbs energy change of the resin swelling, $\Delta G = -16\,500$ J/(mol of the resin), is somewhat lower in absolute value than in gas phase. According to the isotherms, ion exchange resins are potential agents for dehydration of certain organic liquids.

A special feature of cation exchangers based on strong sulfonic acid resins is their great ability to adsorb water and to swell. In an earlier study[1] of certain resinates a distinct difference was found in the uptakes of H_2O and D_2O; the former is adsorbed in larger mol amounts from gas phase than the latter. In this study an analogous research is extended to liquid phase by examining preferential adsorption of the two waters from suitable organic liquids.

EXPERIMENTAL

An organic liquid suitable for this study must satisfy three conditions: (1) The solubility of water in the liquid must be limited but sufficient for analysis. (2) The liquid must be inert against water which in the case of D_2O means that no hydrogen exchange reaction occurs. (3) The liquid must not dissolve the adsorbent, an aromatic polymer. After consulting literature and performing preliminary tests diethyl ether and ethyl acetate, both common chemicals, were found suitable for the experiments. The slight decomposition of ethyl acetate reported in the literature[2] was not believed to affect the measurements. Merck's analytical grade solvents were used and before use they were purified by drying and distilling. The residual water was determined by titration and taken into consideration in calculations.

The resinate used in the experiments was a commercial sulfonated polystyrene resin Dowex 50W-X8, 50 to 100 mesh, in the sodium form. The resin originally in the hydrogen form was washed with methanol, analytical grade hydrochloric acid and distilled water. The resin was slowly converted to the sodium form in a column by using a tenfold amount of Merck's analytical grade sodium chloride. The exchange capacity of the hydrogen form resin determined by a standard titrimetric method[3] was 5.060 mmol per gram of dry resin which gives a molecular weight of 220.6 for the sodium resinate. (One mol of resin is defined as the amount which contains a number of sulfonic acid groups equal to Avogadro's number.) Before further use the resinate was dried overnight at 120 °C.

In the adsorption experiments weighed amounts of the solvent (20—40 g), the resinate (1—2 g) and H_2O or D_2O were put into plastic bottles which were closed with screw caps and rubber seals. The

bottles were placed in a thermostated (25.00±0.05 °C) mechanical shaker and shaken occasionally. The equilibrium was now reached more rapidly than in the isopiestic experiments[1] and samples of the liquid phases could be taken after three days.

The water contents of the samples were analyzed by the Karl Fischer method using a Metrohm E 547 automatic titrator. The accuracy of the titrations was $1-2\%$, but even some larger deviations were met with probably because of the evaporation of the solvents. The solubilities of the two waters in the organic liquids were measured similarly, taking samples after a week's shaking.

The activity curves of H_2O and D_2O were determined with an isopiestic method. Thin layers of the solvents (in some cases premoistened) and dishes of the proper saturated salt solution[1,4] were closed in tight glass jars. The jars were placed in a 25.00 °C water bath and gently tilted daily in order to mix the solvent layers. The L_2O concentrations of the organic phases were analyzed after the equilibration of three weeks.

To determine the maximum uptakes of L_2O, resin samples in sinter tubes were first saturated with H_2O or D_2O. The samples were then centrifuged dry of the exterior water[5] and submerged in L_2O saturated solvents in large closed test tubes. The same solvents were daily poured through the samples to ensure the equilibration. The wet and dry weights of the samples were determined after ten days. The results were corrected for the adsorption of the solvents, 5 mg of diethyl ether and 30 mg of ethyl acetate per one gram of the resinate, found in control experiments.

RESULTS AND DISCUSSION

The solubilities of H_2O in diethyl ether and ethyl acetate at 298.15 K were 0.687 and 1.878 mol per 1000 g of the solvent. The corresponding values for D_2O were a little smaller, 0.654 and 1.703 mol per 1000 g of the solvent, respectively. The H_2O solubilities expressed in weight per cent of H_2O per sample were 1.22 and 3.27 %, which agree well with the values of 1.2 % (20 °C) and 3.3 % (w/w) reported in the literature.[2] The maximum uptakes of H_2O and D_2O from both L_2O saturated solvents were 10.5 and 10.3 mol/(mol of the resinate), respectively. These are about the same values as obtained from pure liquid water species[6] but higher than in the case of adsorption from gas phase.[1]

The results of the adsorption experiments plotted against reduced concentrations[7,8a] c/c_0 are given in Fig. 1; c is the equilibrium concentration and c_0 the saturation concentration. H_2O is adsorbed to
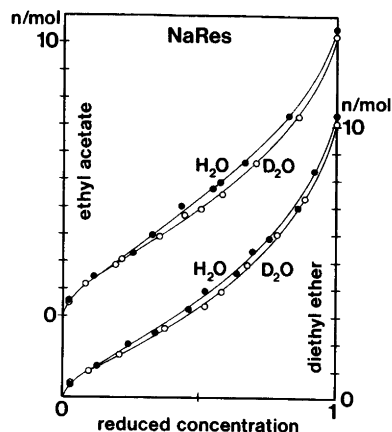

Fig. 1. The amounts of H_2O and D_2O adsorbed on one mol of the sodium resinate from diethyl ether and ethyl acetate at 298.15 K.

a larger extent than D_2O in both solvents, but in low water concentrations the isotherms join together. This can be accounted for with a slow hydrogen exchange between D_2O and the resin matrix observed already in some earlier studies.[1,9] Consequently, even in the case of D_2O the main adsorbed constituents in low D_2O concentrations are H_2O or HDO rather than D_2O. Near the saturation concentration the adsorption increases here very regularly showing that capillary condensation is absent. Comparison of the H_2O isotherms in the two solvents reveals the same effect as found in the study of H_2O adsorption on silica gel[7] by Bartell and Donahue: With decreasing solubilities of water in a solvent series the isotherms are flattened and at a lower level.

The isotherms of Fig. 1 rise more steeply than those obtained in adsorption from gas phase (cf. Fig. 3). It was concluded that the difference might be only apparent and due to the fact that the activity of the water species does not obey Raoult's law as plotting against reduced concentration presupposes. This was verified by determining the experimental activity curves presented in Fig. 2. The points were obtained using the activities of L_2O in some saturated salt solutions.[1,4] As a matter of fact, the salt solutions are also saturated with organic solvents but this probably does not much affect the L_2O activities. The activity curves show distinct positive deviations from Raoult's law. In ethyl acetate a slight difference in the activities of H_2O and D_2O can be found, but in
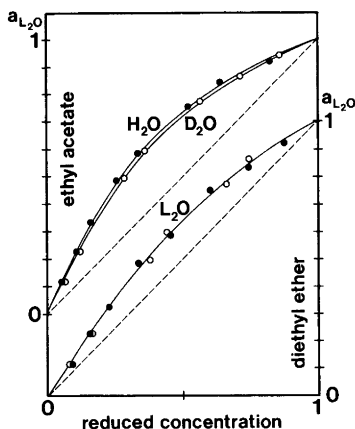
Fig. 2. The activity curves of the two kinds of water in diethyl ether and ethyl acetate at 298.15 K. Each observation point gives the relation between the L_2O activity of a saturated salt solution together with the composition of the organic solution in isopiestic equilibrium.

Fig. 3. The amounts of H_2O and D_2O adsorbed at 298.15 K on one mol of the sodium resinate from diethyl ether (below), ethyl acetate (middle) and gas phase (upper), plotted against the activity of the two waters.

diethyl ether the accuracy is not so good perhaps because of the heavy vaporization of the solvent; thus, only one curve was drawn.

When the activity curves of Fig. 2 were applied for the isotherms of Fig. 1, the new activity corrected isotherms of Fig. 3 were obtained. The isotherms of the gas phase adsorption[1] have also been reproduced for comparison. It is remarkable that in the case of both solvents the isotherms are now nearly identical and resemble also the isotherms of the gas phase adsorption, especially at higher activities. Thus, the adsorption of L_2O is essentially the same phenomenon in different media.

The difference between the liquid phase and the gas phase isotherms is largest at low water activities where L_2O is thought to be used mainly to form the hydration shells on sulfonate groups.[10,11] To examine the effect more closely the values of Fig. 3 were fitted to the two parameter BET isotherm.[1,8b] It represents the observations very well up to $a_{L_2O}=0.45$. The following parameters for H_2O were obtained: In diethyl ether $C=8.00$, $n_m=1.52$, and in ethyl acetate $C=10.21$, $n_m=1.44$. The smaller C values in the liquid phases compared with the gas phase value $C=50.1$ reveal that the heat of adsorption is lower in the former cases.[8b] The Gibbs energy changes of the adsorption (or resin swelling) were calculated as described earlier.[1] The results for H_2O in J/(mol of the resin)
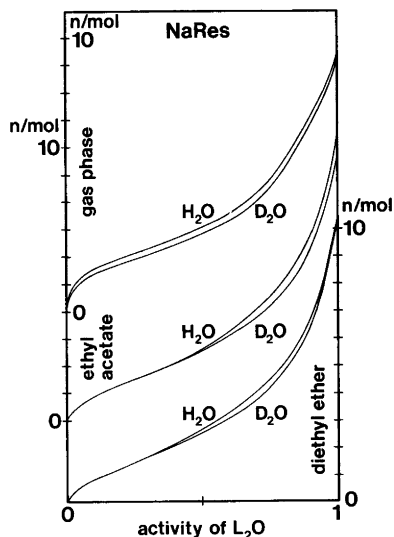
were $-16\,400$ in diethyl ether and $-16\,600$ in ethyl acetate. For D_2O they were somewhat lower, $-15\,600$ and $-16\,200$, respectively, but the possible hydrogen exchange reaction makes these values unreliable. Regarding the accuracy of the measurements the ΔG for H_2O is the same in both solvents and distinctly lower in absolute value than in the gas phase adsorption ($-24\,900$ J mol^{-1}). As the enthalpy term dominates in the ΔG value of the resin swelling,[12,13] it can again be concluded that the adsorption from liquid phase occurs with a smaller heat than from the gas phase.

Apart from the above theoretical points, the isotherms in Fig. 1 show that ion exchange resins are potential hydration agents for many organic liquids. Dehydration can be accomplished rather quickly without adsorbing significant amounts of the organic solvent, and after the treatment the resin is easy to dry for re-use. The smaller the solubility of water in the organic liquid is, the better is the dehydration ability.

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