perties for some vapour chromatographic purposes.

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Note on the Sorption Rate of Water Vapour in Almost Dry Ion Exchangers

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This note will draw attention to some aspects of the sorption rate of water vapour in organic cation exchangers. The results were obtained when the beta ray transmission technique was used to follow (*in situ*) the sorption properties of various solids towards vapours[1]. Another note describes the sorption of organic vapours by organic cation exchangers[2]. It was shown that the sorption rate and attainment of equilibrium could be easily followed by measuring the transmission of a pencil of ^{32}P beta rays through a flat cell of the type described (in Ref.[1]) filled with the grainy ion exchange material. Such studies are nowadays facilitated by stable vibration-reed-electrometers and rapid recorders. The data presented below, however, have been obtained using ordinary weighing procedures.

The experiments were performed using several organic cation exchangers but the main efforts were concentrated on Dowex 50, 50—100 mesh grain size. The material

was treated according to standard practice with 3 N HCl until every trace of three-valent iron had been eluted. The resin was then transferred to the forms required by eluting with an excess of simple inorganic electrolytes in a pure form and containing the cation wanted, *e.g.* $Ca(NO_3)_2$, $RbNO_3$, etc. After complete expulsion of the acidic ions, the resin was treated with distilled water, transferred to weighed glass vessels and then carefully dried by successively heating until constant weight was obtained (highest temperature 105°C). A similar procedure was used with other cations to yield Dowex 50 in the following ionic forms: H^+, Rb^+, Cs^+, H_4N^+, $(CH_3)_4N^+$, Be^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Ce^{3+}, Fe^{2+}, Fe^{3+} and UO_2^{2+}.

Vessels containing a certain cation form of Dowex 50 were placed in air of a definite humidity. This was accomplished by using standard electrolytic solutions giving, after equilibrium, well-known relative humidities[3].
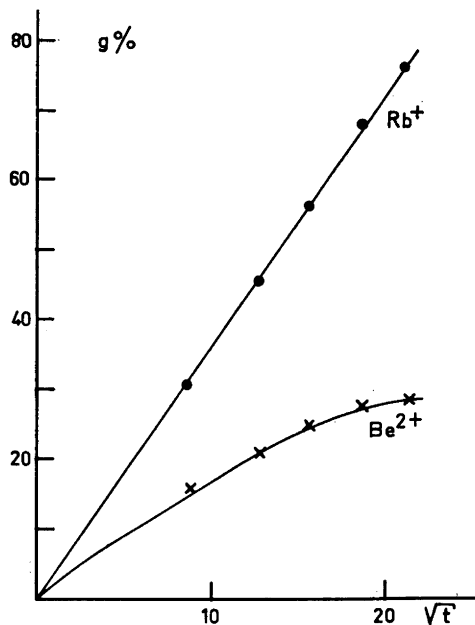

Fig. 1. Fractional attainment of equilibrium (*g*, in %) for water sorption on Dowex 50-Me as a function of $\sqrt{t}$ (*t* in min). The two cases of Me = Rb^+ and Be^{2+} are seen to behave somewhat differently.

The increase in weight was found as a function of time at a single temperature (23° ± 1) until apparent equilibrium was reached at a certain relative humidity (RH). Then a new step to a higher RH was taken and the resulting kinetics and equilibrium were studied. RH up to 90 % were studied. Especially at these high RH, equilibrium took a long time — up to two weeks — to become established.

The weight increase at a certain RH was divided by the final equilibrium weight increase under the same conditions in order to yield the "fractional attainment of equilibrium", g^4. The g-value did not follow any definite function of time. In some cases (especially for the alkali cations) it followed the wellknown $\sqrt{t}$-behaviour. Fig. 1 illustrates this behaviour for Dowex 50−Rb$^+$. In the same figure, another extreme is represented by Dowex 50−Be^{2+}. The best (but not exact) description was given by the known relation:

$$g = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{D \pi^2 n^2 t}{r_0^2}\right) \quad (1)$$

This equation was theoretically derived [5] for the case of diffusion controlled sorption into spherical grains of radius, r_0. (D is the diffusion coefficient of water in the material). Various factors seem to cause deviations from the conditions for which (1) was derived. One is certainly that the grain radius, r_0, increases during sorption. Microscopic examination revealed a very rapid increase of r_0 at the beginning of the exposure to water vapour followed by a slower one. (The grain diameter was found to increase with the ionic volume of the cation.) Some of the originally almost spherical grains became cracked (probably during drying) and thus many were only hemispheres.

For the above reasons, the evaluation of a diffusion coefficient from (1) for all the materials investigated would not correspond to reality. Therefore we simply take the g-value after a certain time for all the materials and represent this as a function of some cation property.

The most interesting behaviour is got by studying the kinetics of the step from the dry state to the state corresponding to RH 8.7 %. The sorption of water at equilibrium at this RH does not correspond to more than 10 % (for H$^+$) of the weight of the ion exchanger material. Usually about 5 % is obtained and so the regain at
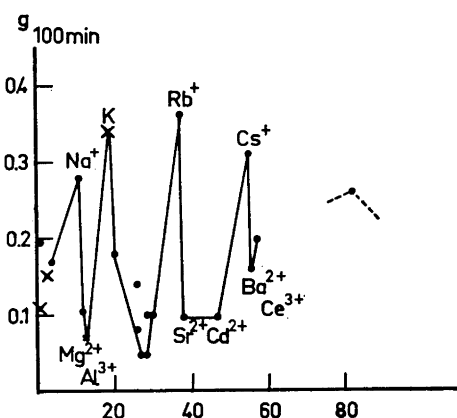
Fig. 2. g-Value for 100 min sorption of water at 8.7 % relative humidity starting from dry material. The g-value, as given as a function of the atomic number of the cation of the Dowex 50, exhibits a periodical character. (Points not explained are H$^+$ and Li$^+$ at the left end, and then after K$^+$, Ca^{2+}, Fe^{3+} (highest), Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}. Points to the right are Pb^{2+} and UO$_2^{2+}$).

equilibrium corresponds to a state of less than one water molecule per monomer unit (assumed to be (—CH$_2$-CH-⟨ ⟩SO$_3$Me)$_n$.

Thus we are justified in expecting the individuality of the different cations to appear under these conditions.

Fig. 2 shows the fractional attainment (g) figures (for 100 min sorption from the dry state) as a function of the atomic number of the counter ions of the ion exchanger. It is seen that a periodic function is obtained which to some extent resembles the behaviour of, *e.g.*, the atomic volume [6]. If similar studies are made for the steps involving higher RH's, the individuality of the cations disappears almost completely and the kinetics are nearly identical for all materials studied. Adsorption isoterms were obtained for the materials (and for other types of cation exchangers) but resemble those published by Gluechauf [7] and others and will therefore not be presented here.

Although too little systematic material is available, we feel justified in suggesting that the initial hydration is a dipole-ion interaction involving the cation of the ion

exchanger (and also the sulphonic acid anion).

A complete description of the sorption rate might necessarily involve the interaction energy for the process considered as an activation energy for the diffusion coefficient. If so, a larger ion would exhibit a smaller activation energy and hence a larger sorption rate (or diffusion coefficient). The results of Fig. 2 could then be reasonably connected with the periodicity of the atomic volumes. As for the latter, the ion charge must also be taken into account. Among the alkalis, the sorption rate increases with increasing (crystallographic) ion volume in accordance with the above picture. Unfortunately, the result for $Z > 45$, was obtained with a different batch of Dowex 50 and so no conclusions can be drawn from the result for cesium. The complete description might also contain entropy factors. These are apparently not known for the systems studied here. Following the picture given above it is reasonable that, under wetter conditions, the sorbing water molecules would mainly interact with water already sorbed, thus roughly explaining why the individuality of the counter ions disappears in such a case.

A more complete study of these phenomena would seem to be of interest. The temperature dependence of the sorption rate might give a clue for the interpretation of the interaction mechanism suggested.

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Sheet Ion Exchangers as Resistance Gauges for Moisture in Gases

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The sulphonation of sheets, rods, tubes or any shape of solid polystyrene yields a thin layer of polystyrene sulphonic acid [1], a well-known cation exchange material. Many other ways of forming a sheet ion exchanger are possible [1] or conceivable.

It has been found that the electrical resistance of this material is a good measure of the relative humidity in air. The ion exchange groups may be saturated by Na^+-ions for instance, so that the moisture detector is less likely to be affected by materials sorbed from the gas which may cause precipitation *etc.* The ion exchange layer of course is a hydrophilic substance, the moisture content of which is a function of the water partial pressure in the surrounding gas if equilibrium prevails. The conductance of the sheet ion exchanger will increase with increasing moisture content and so the resistance of an exchanger unit will be an appropriate measure of the moisture content. At constant temperature, it will after calibration with standard salt solutions [2] be a good moisture detector. Changing the temperature of course changes both the equilibrium conditions and conductance and must be corrected for by recalibration.

Practical exchanger units can be made by simply clamping two platinum electrodes on a sulphonated piece of polystyrene or better by winding a double spiral on a sulphonated (sodium ion-saturated) rod or hole cylinder using two wires of platinum (stainless steel was found to corrode in the long run), the wires being separated by about 0.5 mm or so. The wires should be long in order to reduce the resistance.

A typical calibration curve is given in Fig. 1. At decreasing humidities, the resistance increases steadily; at very low figures, the resistance may be impractically high. The resistance is preferably measured at 1 000 Hz to avoid polarization phenomena at the electrodes. Such effects were often obtained when DC was used. Any of the common electrical circuits can be used