

Sorption of Organic Vapours in Organic Ion Exchanging Substances

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When it was shown that the transmission properties of beta particles through layers of matter possessing sorption properties (*e.g.* towards vapours) could be used to study these processes¹ (kinetics, equilibria), the author tried to find illustrative examples of how the method might be applied. Some of these examples have been published¹ but some others have not. Some of them concern the sorption properties of ion exchangers. The observations made were not pursued systematically but, as nothing similar has apparently been given in the literature, two short notes will be given. The present note concerns the sorption of organic vapours in ion exchanging materials. Another note will deal with water sorption kinetics.

Ion exchanging substances containing typical functional groups, *e.g.* SO_3^- , COOH , NH_2 , *etc.*, can to our present knowledge be considered to react within their whole volume at least for small ions (*cf.* Kunin and Myers²) in the liquid phase. It was therefore judged likely that they would have a very high "inner surface" (in about the same sense as is used for, *e.g.*, activated charcoal) and consequently be able to sorb polar molecules to a great extent, for example, when exposed to gases.

Simple experiments to test this idea were made by bubbling dry nitrogen from a tank tube through wash-bottles containing some organic liquids at room temperature. The gas stream (a few ml/sec) thereby becomes saturated (or very nearly so) and thus the sorption figures given correspond to the vapour pressure at room temperature under these conditions. Table 1 summarizes the observed percentage weight increase of the material when apparent equilibrium was reached.

Table 1. Equilibrium sorption of some organic vapours in ion exchangers at 21°C. The ion exchange material was present in a glass tube in grain form (50–100 Mesh) and was nearly dry at the beginning of the experiment.

Ion exchanger	Vapour	Percent weight increase referred to dry material
Wofatite KS—Na	Diethylether	15
»	»	21
Dowex 50-H	<i>n</i> -Butanol	43.1
»	»	4.7

From these few observations, it is indicated that the hydrophilic substances (*e.g.* the alcohols) are sorbed to a greater extent than a less hydrophilic one (*e.g.* benzene). It might from this evidence be assumed that ion-dipole interaction plays a role in the sorption process.

The sorption rate was interpreted in terms of spherical diffusion which gives as is well known³:

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 D}{\gamma_0^2} t\right)$$

where D is the diffusion coefficient of the organic molecule within the ion exchanger grains, t time, γ_0 grain radius and F fractional attainment of equilibrium.

The results are in rough accordance with this formula which is valid if the diffusion is rate-determining. The diffusion coefficient for benzene is about 12×10^{-10} cm²/sec and, for *n*-C₄H₉OH, 6×10^{-10} cm²/sec according to these estimates in Dowex 50-H. It was demonstrated that the sorption processes mentioned could be easily followed by beta ray transmission.

It might be added that it has been found in this laboratory that molecular iodine (as fission product ¹³¹I) is readily sorbed⁴ from the gas phase on an anion exchanger Dowex 2.

Obviously it would be of interest to study sorption equilibria and kinetics systematically for different types of ion exchangers. The sorption properties of ion exchangers normally used in liquid systems might find applications in certain cases. It might well be possible to use these pro-

perties for some vapour chromatographic purposes.

1. Westermark, T. *Some Applications of Beta Radiation. Transactions, Instruments and Measurements Conference, Stockholm 1949*, p. 308–314.
2. Kunin, R. and Myers, R. J. *Ion Exchange Resins*, John Wiley 1950 (Ch. 2).
3. Cf. e.g. Boyd, G. E., Adamson, A. W. and Myers, L. S. *J. Am. Chem. Soc.* **69** (1947) 2836.
4. Forberg, S., Westermark, T. and Holmquist, C.-E. *Sorption of fission product iodine from air on different materials with applications to nuclear reactor accidents (in course of publication)*.

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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 vapours¹. Another note describes the sorption of organic vapours by organic cation exchangers². It was shown that the sorption rate and attainment of equilibrium could be easily followed by measuring the transmission of a pencil of ³²P 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(NO₃)₂, RbNO₃, 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⁺, H₄N⁺, (CH₃)₄N⁺, Be²⁺, Mg²⁺, Sr²⁺, Ba²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Pb²⁺, Ce³⁺, Fe²⁺, Fe³⁺ and UO₂²⁺.

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 humidities³.

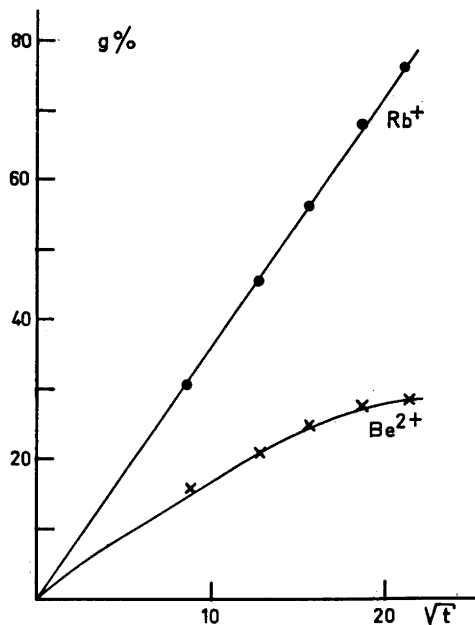


Fig. 1. Fractional attainment of equilibrium (g, in %) for water sorption on Dowex 50-Me as a function of \sqrt{t} (t in min). The two cases of Me = Rb⁺ and Be²⁺ are seen to behave somewhat differently.