

measurements was $\pm 5\%$. For comparison, the earlier measurements of Eversole and others (1) and the Nernst limiting value are included in Table I. At 0.35 molar, the present data and those of Eversole and others differ by approximately 5%, which is approximately the experimental error of the diaphragm cell measurements. A convenient empirical correlation of the differential diffusivities of CuSO_4 in water at 25° C. is:

$$D/D_0 = 1 - 0.52C^{1/5}; \quad 0 \leq C \leq 1.4$$

Differential diffusion coefficients for water in *n*-butyl alcohol are listed in Table II. The precision of the measurements was $\pm 6\%$. Randall, Longtin, and Weber have reported much larger diffusivities for this system (3). However, their data are almost certainly incorrect, since the

values reported are two orders of magnitude greater than any other liquid diffusion coefficients in the literature.

LITERATURE CITED

- (1) Eversole, W., Kindswater, H., Peterson, J., *J. Phys. Chem.* **46**, 370 (1942).
- (2) Hammond, B.R., Stokes, R.H., *Trans. Farad. Soc.* **49**, 890 (1953).
- (3) Randall, M., Longtin, B., Weber, H., *J. Phys. Chem.* **45**, 343 (1941).
- (4) Stokes, R.H., *J. Am. Chem. Soc.* **72**, 763 (1950).
- (5) *Ibid.*, p. 2243.

RECEIVED for review May 14, 1962. Accepted September 17, 1962. This work was carried out with the support of the National Science Foundation.

Water-Content Isotherms for a Sulfonic Acid–Styrene-Divinylbenzene, Cation-Exchange Resin at 110° and 130°C.

ROBERT E. ANDERSON

Physical Research Laboratory, The Dow Chemical Co. Midland, Mich.

Water-content isotherms were determined for Dowex 50W-X8 cation-exchange resin in the potassium form at 110° and 130° C. over a water vapor pressure range from 0 to 22 mm. of Hg using a carrier gas method.

SEVERAL investigators have published data on the water content of the sulfonated styrene-divinylbenzene, cation-exchange resins as a function of the partial pressure of water vapor present at temperatures of 25° and 50° C. (1, 2, 4). These studies have included such resin variables as ionic form and relative crosslinking. More recently, Wymore has shown that this water-holding property makes these resins promising desiccants (5). Use of the resins as desiccants will involve a cyclic process in which the resin takes on water at ambient temperatures from a liquid or gas stream and is then regenerated by stripping the water from it at a higher temperature. The efficiency of such a regeneration is dependent on the equilibrium water content of the resin as a function of the partial pressures of water vapor present at temperatures above 100° C. Since no such data have been published, the present work was carried out.

The work was limited to the potassium form of a cation-exchange resin of average crosslinkage, Dowex 50W-X8. The potassium form of the resin has been shown to be the most useful as a desiccant in that it combines stability, good equilibrium capacities, and good kinetic properties (5).

EXPERIMENTAL

A carrier gas method was used for the determination of the high temperature isotherms. A known amount of resin in a thermostated chamber was allowed to equilibrate with a flow of nitrogen containing a known partial pressure of water vapor. The weight of the resin at equilibrium was determined and the water content calculated. The water vapor content of the carrier gas was varied to obtain the isotherms over the desired range.

A sample of Dowex 50W-X8 resin in the 100 to 200 mesh size was used. This resin in the hydrogen form had an exchange capacity of 5.05 meq. H^+ per dry gram, and when fully swollen and centrifuged, contained 54.9% water. The resin was converted to the potassium form with an excess of potassium carbonate and thoroughly rinsed. The 100 to 200 mesh size was used to give faster equilibration times.

The experimental train had four major components. The gas supply system consisted of a cylinder of nitrogen with a flow-regulating valve and a rotameter. An average flow rate of 20 ml./min. was used.

The nitrogen stream was adjusted to the desired water-vapor level by passing it through two 250-ml. gas-washing bottles, each two-thirds filled with standardized sulfuric acid. The sulfuric acid was analyzed by titration of a weighed sample before it was placed in the saturator. As a check, a sample of the acid from the second gas-washing bottle was analyzed at the end of a run using a particular strength of acid. In all cases these two analyses agreed within experimental error. A mist knock-out chamber consisting of a gas-washing bottle filled with glass helices was used in series with the saturator bottles. All three of these bottles were completely immersed in a constant temperature bath which could be set at either 25° or 30° C. and held to $\pm 0.1^\circ \text{C}$. The water vapor pressure in the nitrogen stream at a given temperature and sulfuric acid concentration was obtained from the literature (3).

The equilibration and weighing chamber was immersed in a constant temperature bath containing a silicone heat-exchange fluid. The gas entering passed through a spiral heat exchanger immersed in the bath before entering the equilibration chamber. The resin sample (about 0.5 gram) was placed in a small platinum dish and suspended in the

Table I. Water-Content of Dowex 50W-X8 Cation Exchange Resin in the Potassium Form at 110° and 130° C.

Equilibrium Water-Vapor Pressure, Mm. Hg	Water Content, %, on dry basis			
	110° C.	Order No. ^a	130° C.	Order No. ^a
1.7	0.56	6	0.25	7
2.3	0.72	5	0.34	4
5.6	1.06	9	0.56	8
8.6			0.72	1
11.4	1.57	2	0.93	3
16.6	1.82	11	1.07	10
22.2	2.12	12	1.38	13

^a Chronological order of determination.

Table II. Water-Content of 8% Cross-linked Potassium Polystyrene Sulfonate Resin at 25° C.

Equilibrium Water-Vapor Pressure, Mm.Hg	Water Content, % on dry basis	
	25° C.	50° C.
0.14	4.22	
0.52	5.11	
1.19	6.15	
1.25		2.96
2.06	7.41	
2.55		3.71
3.20	8.22	
4.77	9.19	
5.36		4.60
6.82	10.80	
9.71		5.63
10.52	14.15	
15.84	22.22	
18.04	25.20	

lower part of the equilibration chamber by a length of No. 35 Nichrome wire which passed out of the chamber through a short length of capillary tubing.

The weight of the resin sample was determined by a double-pan analytical balance mounted directly above the equilibration chamber. One pan was removed and replaced with a ballast to which was attached the wire supporting the resin sample. With this arrangement the resin could be weighed with a reproducibility of ± 0.1 mg. by counting swings. Special care had to be taken to keep the system properly aligned and free of dirt.

The fact that the equilibration chamber was open to the atmosphere through the capillary exit for the supporting wire offered the possibility for back diffusion of room air into the chamber. This apparently was not a problem as the weighings obtained were quite insensitive to changes in room temperature or humidity although these did go through fluctuations during the course of the work. The weighings were very sensitive to small changes in the conditions in the saturator bottles.

The resin sample was dried at 110° C. in a vacuum oven before being placed in the equilibration chamber. While the resin was exposed to room humidity for less than a minute in the process of being placed in position, in some cases it was found to have picked up as much as 0.5% of water. Therefore, the true dry weight of the sample was determined by holding the equilibration chamber at 130° C. and passing a nitrogen stream through it which had been dried over P_2O_5 until the sample came to a constant weight.

Since the actual changes in the water content of the resin sample from one set of conditions to the next was usually only a few milligrams, equilibration was obtained in a few hours. When two successive weighings taken over a

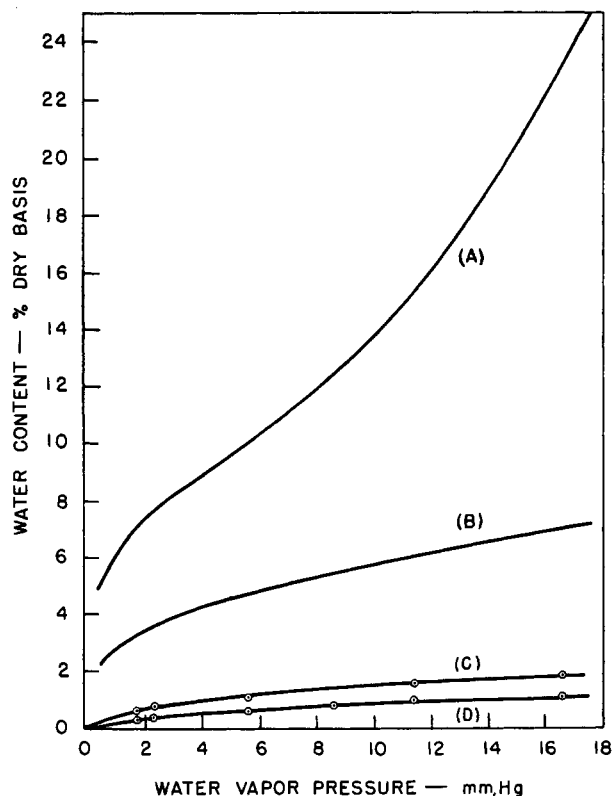


Figure 1. Water-content isotherms for sulfonic acid ion-exchange resin of 8% crosslinkage in K^+ form

A. 25° C. (4) C. 110° C.
B. 50° C. (4) D. 130° C.

period of at least 8 hours did not vary by more than 0.1 to 0.2 mg., equilibrium was assumed.

A total of 14 data points were obtained to give isotherms at 110° and 130° C. up to a partial water vapor pressure of 22 mm. Hg. One of these 14 points was not consistent in that it did not fall on a smooth curve plot of the data and was discarded. The remaining data are shown in Table I and Figure 1. The chronological order of the collection of the data points is indicated in the table. There is no indication of the slight hysteresis effect reported at 25° C. (2, 4).

Values of Table II were calculated from Waxman's original data (4) and used for curves A and B in Figure 1. These isotherms are shown along with the two high-temperature isotherms. The high temperature isotherms give the residual water content of the resin when regenerated with air of known relative humidity. Once this degree of regeneration is known, the low temperature isotherms allow the estimation of the minimum water content which can be obtained in a gas product stream at working temperatures. These resins are unique, reversible, and stable desiccants that can be regenerated to useful levels at moderate temperatures using available air.

LITERATURE CITED

- (1) Boyd, G.E., Soldano, B.A., *Z. Electrochem.* 57, 162 (1953).
- (2) Dickel G. Hartmann, J.W., *Z. Phy. Chem.* 23, 1 (1960).
- (3) International Critical Tables, Vol. III, E.W. Washburn, ed., p. 303, McGraw-Hill, New York, 1928.
- (4) Waxman, M.H., thesis for the Ph.D., Polytechnic Institute of Brooklyn, 1952.
- (5) Wymore, C.E., *Ind. Eng. Chem., Product Research Develop.* 1, 173 (1962).

RECEIVED for review May 14, 1962. Accepted September 24, 1962.