$10^4\,C$, where C is the concentration of CO_2 in moles/l. The change in refractive index due to CO_2 in a solution is consequently proportional to the concentration of the gas as would be expected.

It is evident from these results that if $\kappa < 2$, $-\delta n < 1$ and the CO_2 correction is negligible; moreover, since removal of CO_2 should raise the refractive index, the high values found in impure specimens are not due to this substance.

The increase in refractive index in the metal cell was found to be due to imperfections in the plating. A comparatively soluble copper hydroxy–carbonate is probably formed in the first instance; on exposure to air, this slowly loses CO_2 and deposits a skin of the less soluble hydroxide on the surface. Increases in refractive index up to 140 units were recorded both in the cell, and in water containing CO_2 in which silver-plated copper was immersed for 3 days, the conductivity rising to 12. After standing for several days in a closed vessel containing sodium hydroxide, the lowest value found for the change in refractive index was 11 units, the conductivity having fallen to 3.7.

Measurements on water containing CO_2 standing in vessels of silica, platinum and silver during several days in an atmosphere of CO_2 and then evacuated or exposed to air, showed that there was no action on silica, but in several cases the metals appeared to dissolve, silver giving the most marked results. These were less than one tenth of the values found for copper and were very irregular. It seems probable that they were due to the solution of adsorbed impurities. In this connection it may be noted that Wilke[8] found an increase in conductivity of 20% in a CO_2 solution in which gold electrodes were immersed for three hours.

Conclusions

The refractive index of H_2O^{18} is much smaller than has been believed, the change in the refractive index of water resulting from the addition of a molecular proportion y being $0.00008y$, with an estimated error of +10 and −25%. This is only 1.7% of the figure for an equal proportion of D_2O, and thus the H_2O^{18} correction when determining D_2O by the refractive index method is frequently negligible.

The refractive index of dilute CO_2 solutions is given by the equation $-4.6\,\delta n = \kappa^2 = 5.1 \times 10^4\,C$, with an error of about 10%. These solutions sometimes gave irregular values after being in contact with metals, but the high values of conductivity and refractive index found in impure solutions of H_2O^{18} cannot be ascribed to metallic corrosion or to the presence of CO_2, and their origin is still obscure.

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Molar Volumes, Isotherm and Interaction Parameter for Water in Polyvinyl Acetate[1]

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RECEIVED JULY 1, 1954

Measurements have been made on the equilibrium sorption isotherm for water in polyvinyl acetate at 40° and also on the apparent molar volume of water in the polymer. Although these measurements were made in connection with studies of the diffusion of water in polyvinyl acetate[2] they have bearing on the more general problem of interactions between polymers and solvents or swelling agents.

Experimental

Transparent beads of polyvinyl acetate (grade AYAT from Union Carbide and Carbon Corporation) were cut into small pieces and leached in water for some weeks at elevated temperatures to remove any volatile solvent and unreacted monomer. After drying, the polymer was molded into blocks with a thickness of about 0.60 cm. and with areas varying from 3.5 to 9 cm.[2] The blocks were thoroughly redried, weighed and then suspended in sealed containers above aqueous salt solutions of known relative humidity.[3] (For 100% relative humidity the polymer blocks were suspended in pure water.) The containers were then immersed in a water-bath held at 40 ± 0.2°. After equilibration for periods varying from 17 to 60 days, the blocks were rapidly weighed first in air (wrapped in tared metal foil) and then in hexane at 40 ± 0.3°. From these weights and the density of the pure polymer, which was found by similar buoyancy experiments with the dried polymer blocks to be 1.176 g./ml. at 40°, it is possible to calculate weight fractions and volume of the water in the polymer and the apparent molar volume of the polymer.

Data for the equilibrium sorption of water in polyvinyl acetate are also available from earlier studies with the thin polymer films used in the diffusion experiments.[2]

Results

Table I gives the data obtained. The first two columns give the relative pressure of water vapor for the experiments and days of equilibration of the polymer. The symbols W_o, W_A and W_H refer, respectively, to weights of the dried polymer in air, the equilibrated polymer–water sample in air and the same sample in hexane (density, 0.6410 g./ml. at 40°). The column ρ_0 is the density of the dry polymer blocks, determined by weighing in hexane. The last two columns, V_e and V_i, give, respectively, the equilibrium volume of the polymer–water sample as calculated from the weighing in hexane and the "ideal" volume of the same sample assuming simple additivity of the volumes of polymer and water.

TABLE I

DENSITIES AND VOLUMES OF POLYVINYL ACETATE–WATER MIXTURES AT 40°

p/p_0	Equil., days	W_o, g.	ρ_0, g./ml.	W_A, g.	W_H, g.	V_e, ml.	V_i, ml.
0.40	21	6.9520	1.176_3	7.025_8	3.188_5	5.986	5.984
.40	30	6.9520	....	7.022_0	3.186_4	5.984	5.981
.53	30	4.6945	1.177_2	4.753_9	2.158_1	4.050	4.048
.53	48	4.6945	....	4.749_7	2.158_8	4.044	4.044
.53	59	4.6945	....	4.757_1	2.159_4	4.053	4.051
.705	22	7.0056	1.175_6	7.160_2	3.240_9	6.114	6.114
.705	31	7.0056	....	7.157_6	....	...	...
.824	21	6.7467	1.175_1	6.925_6	3.134_3	5.915	5.922
.824	46	6.7467	....	6.917_6	3.134_6	5.902	5.913
.824	59	6.7467	....	6.921_4	3.131_1	5.913	5.917
.824	17	4.6945	1.177_2	4.816_0	....	...	...
.824	29	4.6945	....	4.814_7	....	...	...
.936	28	6.9520	1.176_3	7.230_1	3.260_6	6.193	6.190
.936	35	6.9520	....	7.233_5	3.266_7	6.188	6.194
1.00	22	2.2255	1.176_1	2.357_5	1.058_1	2.027	2.025
1.00	31	2.2255	....	2.360_2	1.058_7	2.031	2.028
1.00	17	7.0056	1.175_6	7.415_7	3.331_0	6.372	6.372
1.00	27	7.0056	....	7.419_7	3.331_1	6.378	6.376

From these data, straightforward calculation gives the apparent molar volumes of the water in

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(1) Sponsored in part by the Office of Ordnance Research, U. S. Army.

(2) F. A. Long and L. J. Thompson, *J. Polymer Sci.*, to be published.

(3) F. E. M. O'Brien, *J. Sci. Instruments*, **25**, 73 (1948).

the polyvinyl acetate. The average values are given in column four of Table II. The unexpected result is that over the entire concentration range studied the apparent molar volume of water appears to be constant and equal within experimental error to the molar volume of pure water (18.16 ml./mole at 40°). Comparatively few data are available on the molar volumes of liquids in polymers and almost none for water. However, Bueche[4] has recently studied densities of water–polymethyl methacrylate mixtures and reports that for this system also, the molar volume of the water is close to that for the pure liquid. In contrast Hermans[5] reports for water in cellulose a marked decrease in the molar volume of water at water concentrations below about 0.05 g./g.

Table II also lists the values of the weight ratio of water in the various samples in grams per gram and of v_1, the volume fraction of water in the samples. Both this table and Fig. 1, which gives the sorption isotherm for water in polyvinylacetate at 40°, include data from the diffusion studies with thin films[2] and indicate the character of the agreement between the two studies. The isotherm of Fig. 1 shows slightly greater water sorption than reported by Katchman and McLaren[6] at 25° but, considering that the polymer sources were different, the agreement is satisfactory. The present value of $v_1 = 0.066$ for water in polyvinyl acetate at saturation vapor pressure is in marked disagreement with the result of Irany[7] who reports a volume fraction of 0.42 at 40°. A possible explanation is that Irany's sample may have been a polyvinyl acetate–alcohol copolymer.

TABLE II

VALUES OF MOLAR VOLUMES OF WATER AND INTERACTION PARAMETER FOR WATER–POLYVINYL ACETATE AT 40°

p/p_0	10^2c, g./g.	10^2v_1	v_{H_2O} ml./mole	χ_1
0.20[a]	0.31[a]	0.365[b]	..	3.0[a]
.30[a]	0.53[a]	0.624[b]	..	2.9[a]
.40	1.02	1.23	18.8	2.6
.53	1.30	1.54	18.4	2.6
.705	2.21	2.54	18.1	2.5
.824	2.59	2.91	17.4	2.5
.926	4.03	4.52	18.1	2.3
1.00	5.95	6.58	18.3	2.0

[a] Equilibrium in sorption apparatus using thin films. [b] Calculated assuming additivity of volumes.

From the data of Table II one can calculate values of the interaction parameter, χ_1, using the well known Flory–Huggins equation

$$\ln p/p_0 = \ln v_1 + (1 - v_1) + \chi_1(1 - v_1)^2$$

The values which result are given in the last column of Table II. A legitimate question is whether this equation can properly be applied to a system involving such polar species as water and polyvinyl acetate. However as Guggenheim[8] has shown even when a correction for non-random arrangements is indicated, it is small for dilute solutions.

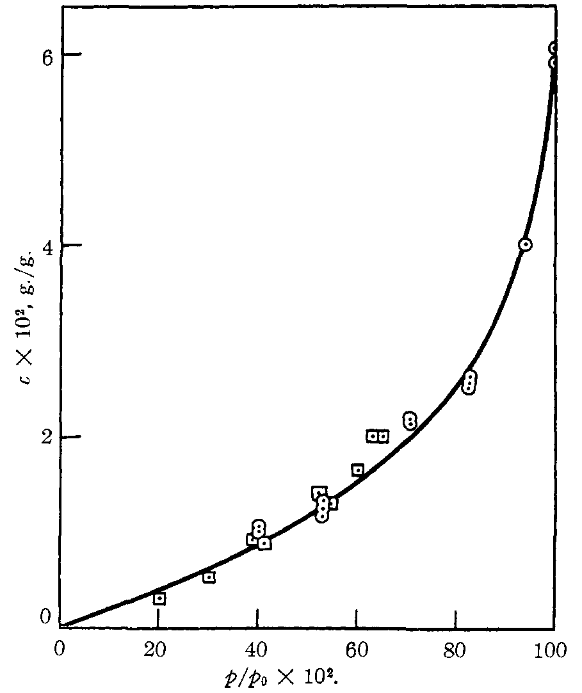

Fig. 1.—Isotherm for water–PVAc at 40°. Circles are results from present studies; squares are results from experiments with thin films.

The average value of 2.5 ± 0.5 for χ_1 for water and polyvinyl acetate is large and is, in fact, one of the largest values of χ_1 so far reported. (For values of χ_1 for other water–polymer systems see Rowen and Simha.[9]) However, in view of the limited swelling of water with the polymer such a large value is perhaps to be expected. Incidentally the decrease in χ_1 to 2.0 at the highest concentration of water is probably real since the change is well outside the experimental error; in contrast the χ_1 value of 3 at the lowest concentration is from studies with thin films and may well be in error by 15%.

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[7] E. P. Irany, *Ind. Eng. Chem.*, **33**, 1551 (1941).

[8] E. A. Guggenheim, *Proc. Roy. Soc.* (*London*), **A183**, 213 (1944).

(9) J. W. Rowen and R. Simha, *J. Phys. Colloid Chem.*, **53**, 921 (1949).

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Determination of Thermodynamic Equilibrium Constants in Mixed Solvents

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RECEIVED MAY 3, 1954

Considerable interest exists today in the determination of the proton dissociation or association properties of water-insoluble compounds. This information is useful in itself as a measure of the acid–base characteristics of such compounds or, in conjunction with similar measurements in the presence of metal ions, as a measure of the relative stabilities (formation constants) of coördination entities of metals. Such data are obtained by potentiometric titrations in mixed solvents (to increase solubility) and the relationships, for the most part have been