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.

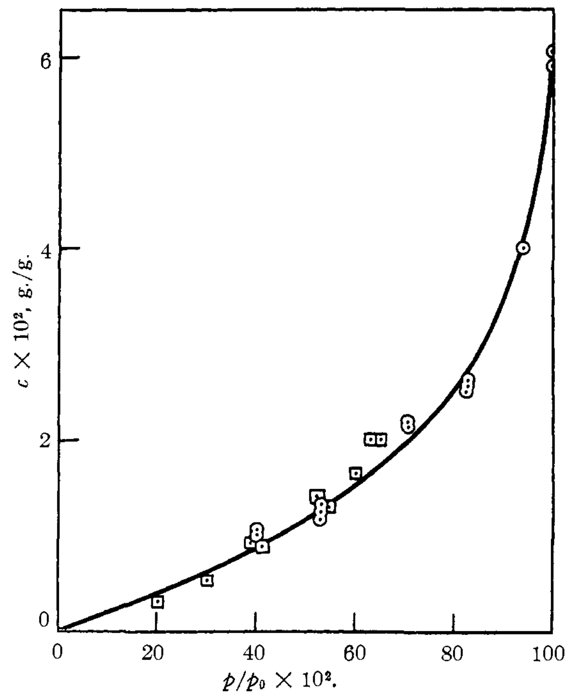

Fig. 1.—Isotherm for water–PVAc at 40°. Circles are results from present studies; squares are results from experiments with thin films.

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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Determination of Thermodynamic Equilibrium Constants in Mixed Solvents

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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 expressed as molality quotients (often called concentration constants). Such quotients would be much more useful if they could be expressed as true (activity) constants.

It has been demonstrated[1] that by calibrating the cell

glass electrode; H^+, Cl^-: satd. calomel electrode

as a concentration probe and by employing the dilute solution activity coefficient data for hydrogen chloride in water–dioxane solutions determined by Harned, *et al.*,[2] approximate thermodynamic values (±0.05 in the log) for the acid dissociation constants (pK_D values) of the organic materials can be determined.[3] Further, the pK_D values together with concentration data for the formation of coördination compounds of metals in which the acid anion functions as a ligand (chelate group) permit the determination of formation (or stability) constants for the various coördinated species.[4] Because the calculation procedures as presented[1] are somewhat complex, requests have been received that simplified correction data be made available. For this purpose, the accompanying graph and tables of data at 30° from which the graph may be calculated are provided. (For any temperature other than 30° a different graph must be prepared.)

The procedure to employ the graph is as follows.

(A) Determination of pK_D Values.—(1) Choose the water–dioxane ratio to be employed and calculate N_2, the mole fraction of dioxane present.

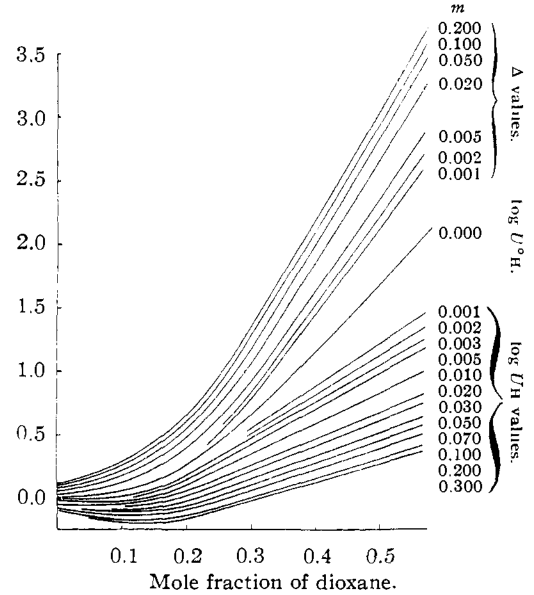

Fig. 1.—pH meter reading corrections for 30° to obtain thermodynamic approximations: for lines above log $U_H°$. $\Delta = \log U_H° + \log 1/\gamma$: for lines below log $U_H°$. $\log U_H = \log U_H° - \log 1/\gamma$.

(2) Add the organic material to be investigated and neutralize with standard tetramethylammonium hydroxide. All readings on the pH meter should be made while the solution is rapidly stirred. Locate the point of half neutralization on the titration curve. Work in dilute solution so that the molality of strong electrolyte (m) in the solution is in the range 0.10 to 0.01 m. It is undesirable to add an inert electrolyte.

(3) Standardize the pH meter in an aqueous buffer solution using a Beckman type (1170) saturated calomel electrode or its equivalent.

(4) Record (B) the pH meter reading at half neutralization.

(5) From the known values of N_2 and m determine $\Delta = \log U^{\circ}_{H} + \log 1/\gamma^1$ from the graph. (Log U°_{H} is a conversion factor independent of ionic concentration.)

(6) $pK_D = B + \Delta$ where pK_D is the negative log of the acid dissociation constant of the organic material.

(B) Determination of Stability Constants of Chelate Compounds.—The indicated log U_H values are to be added to the pH meter reading (B) to determine the stoichiometric concentrations of hydrogen ion in solution in accordance with the procedures previously outlined.[1]

$$-\log [H^+] = B + \log U_H$$

$$\log K_{f_1} = pK_D + \log ([H^+]_{\bar{n}-1/2}/[HCh]_{\bar{n}-1/2}), \text{ etc.}$$

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TABLE I

pH METER CORRECTIONS AT INFINITE DILUTION

N_2	log U°_{H}	N_2	log U°_{H}
0.00	0.00	0.30	0.67
.05	.02	.35	0.90
.10	.07	.40	1.15
.15	.13	.45	1.41
.20	.27	.50	1.67
.25	.44	.55	1.94

TABLE II

LOG $1/\gamma$ VALUES IN THE WATER–DIOXANE SYSTEM

Calculated from data of Harned, *et al.*: $\Delta = \log U^{\circ}_{H} + \log 1/\gamma$: $\log U_H = \log U^{\circ}_{H} - \log 1/\gamma$.

	N_2 values				
m	0.00	0.0486	0.143	0.323	0.482
0.001				0.1574	0.4108
.002				.2125	.5129
.003			0.0762	.2495	.5784
.005	0.0327	0.0482	.0953	.3019	.640
.010	.0441	.0650	.1267	.385	.799
.020	.0585	.0862	.1647	.474	.928
.030		.0996	.1878	.527	1.000
.050	.0818	.1181	.2219	.597	1.097
.070		.1308	.2441	.640	1.161
.100	.1001	.1452	.2676	.648	1.215
.200	.1175	.1720	.3116	.757	1.301
.300		.1818	.3316	.788	1.333

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