proved difficult, whereas complete sublimation under an atmosphere of ammonia may be realized more rapidly and at lower temperatures.[9] This suggests that the halogen was not present as the ammonium salt but rather as a constituent of the silicon compound. The absence of X-ray diffraction lines in the intermediate products referred to above indicates that ammonium chloride was not present in concentrations sufficient to account for the observed chloride contents (11–15%). Furthermore, the sudden evolution of ammonium chloride when intermediate products were treated with ammonia suggests the occurrence of a reaction.

The amorphous nature of the compounds when heated to 1300–1350° indicates that they are essentially oxynitrides of silicon. The absence of X-ray diffraction lines for any crystallographic modifications of SiO_2 even in compounds heated to higher temperatures indicates that silica is not present as such. Decomposition of these compounds with the formation of Si_3N_4 in the temperature range of 1500–1600° is to be expected in view of the fact that the decomposition pressure of Si_3N_4 becomes appreciable, approaching 15 mm. at the latter temperature.[10]

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(9) E. Lay, "Über Silicium-Stickstoff-Wasserstoff Verbindungen," Leopold-Buchdruckerei, München, 1910.

(10) W. Hincke and L. Brantley, THIS JOURNAL, **52**, 48 (1930).

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The Refractive Indices of Aqueous Solutions of H_2O^{18} and CO_2

BY H. E. WATSON

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As the generally accepted value for the refractive index of H_2O^{18} could not be reconciled with the results obtained when examining light water, a redetermination of this quantity has been undertaken. About 80 deuterium-free samples from 200 p.p.m. light to 800 p.p.m. heavy and of varying degrees of purity have been examined in a Rayleigh interferometer, the purity being checked by conductivity measurements. The change in refractive index at 18°, with white light, for a molecular proportion y of H_2O^{18}, was found to be $0.00008y$, the factor being only one-tenth of the accepted value.

Measurements were greatly facilitated by the use of an interferometer cell machined from solid copper and silver-plated, temperature equilibrium being reached in about three minutes.

Observations on water containing CO_2 kept in contact with silica and metals have been made in order to determine the effect of possible impurities. For dilute CO_2 solutions, the relation $\kappa^2 = -4.6\ \delta n$ held good with an error of about 10%, κ being the conductivity in reciprocal megohms at 18° and δn the difference between the refractive index of the solution and that of pure water, multiplied by 10^7.

Introduction

Lewis and Luten[1] measured the effect of H_2O^{18} on the refractive index of water, using a Rayleigh-Zeiss interferometer and a sample said to contain 0.5% of H_2O^{18}. No details of the preparation or purification of this sample were given. It was deduced that if y was the molecular proportion of H_2O^{18} in a sample of water, the difference in the refractive indices of this sample and water containing the same amount of D_2O but no H_2O^{18}, was $0.0008y$. A formula was given for determining the amounts of H_2O^{18} and D_2O in water from measurements of the density and refractive index. On attempting, a few years later, to use this formula for estimating the H_2O^{18} content of deuterium-free water, the author could find no change in the refractive index with density and it appeared that refractive index measurements were useless for analytical purposes. In 1939, Brodsky and Scarre[2] made further interferometer measurements with 3 samples heavier than water by 200 p.p.m. or less, which gave discordant results. They deduced that Lewis and Luten's factor should be 0.00069 ± 0.0001, but do not appear to have tested the purity of their samples or to have taken adequate steps to ensure the normality of the D_2O in them.

As measurement of the refractive index is a convenient method of estimating the concentration of D_2O in water if the correction for H_2O^{18} is known, it was decided to make further determinations of the latter quantity. As expected, these proved to be by no means easy, since the effect of traces of impurity in the solutions was much greater than that of the H_2O^{18}. The nature of the impurities was not obvious, but as CO_2 was always present and no data could be found for the refractive index of its solutions, a number of these were examined. The results indicated that in some cases the containing vessel was attacked, and further measurements were made to estimate the magnitude of this effect.

Experimental

All refractive index differences δn are for white light and are expressed in units of 1×10^{-7}. All conductivities κ are in reciprocal megohms at 18°.

A Rayleigh interferometer was used for the refractive index measurements, a consistency of 1 scale division or $^1/_{58}$ of a band, being obtained. With a 10-cm. cell, this corresponded with a change of 1.0×10^{-7} in refractive index. It was consequently necessary that the temperature of the two solutions should be the same within 0.001°. This was achieved by using as the interferometer cell a solid bar of copper 1.5″ square. A length of 10 cm. was cut off and two parallel holes $^5/_{16}$″ in diameter drilled through it, the centers being 0.5″ apart to correspond with the separation of the two light beams. A slot was milled out underneath the holes for the lower beams. The ends were ground parallel, polished, and closed with two optically flat glass plates. The joints were watertight, but to avoid possible displacement they were cemented with a trace of cellulose varnish. The effective length was 100.00 ± 0.01 mm., and the difference between the lengths of the cells less than one wave length. The capacity was 5 cc. and filling was effected through 0.25″ holes drilled through the top of the block near one end. These were closed with loosely fitting flanged plugs of polythene. The internal tubes were at first silver plated and later gilt. The whole block was cased in insulating material and equilibrium was reached in about three minutes. For some of the experiments with CO_2, a con-

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(1) G. N. Lewis and D. B. Luten, THIS JOURNAL, **55**, 2616 (1933).

(2) A. E. Brodsky and O. S. Scarre, *Acta Phys. Chim. URSS*, **10**, 729 (1939).

ventional cell of fused silica was used with a heavy metal cover. It was closed with a glass lid, and to prevent the water wetting this, the corners of the cell were coated with a thin layer of polystyrene. When filled with liquids not differing in temperature by more than a few tenths of a degree, equilibrium was reached in about 10 minutes, but the values were not as reliable as those with the copper block, and the time required was much greater.

It was found that water left in the copper cell overnight increased in refractive index by about 10 units, and consequently when making measurements, the cell was refilled with standard water whenever a new sample was introduced. In the silica cell, the reference liquid was very stable unless the liquid in the other compartment was giving off CO_2.

The electrical conductivity of the solutions was found to be a valuable guide to their purity and was measured at frequent intervals. A Mullard universal bridge was used and two dipping electrodes, the first consisting of two concentric platinum cylinders and the second of two parallel platinum wires 1.5 mm. in diameter, 10 mm. long and 4 mm. apart, fused into Pyrex. The latter, although giving slightly different readings in different vessels, was very convenient and could be used in the silica interferometer cell, measurements occupying only a few seconds.

The preparation of samples with high and low H_2O^{18} content, and of standard water, and the separation of D_2O and H_2O^{18} by electrolysis, have been described previously by Hayter[3] and by Watson.[4] Equilibrium water with conductivity 1.0 was normally used as a standard for comparison, the refractive index of different preparations agreeing within the limits of measurement. The purification of samples was difficult. All of them when taken from the still in which they were prepared decolorized permanganate on boiling, although the original feed water did not, and the only non-metallic parts of the still were two small rubber packings. The methods used varied with the sample, but generally speaking, they consisted in repeated fractionation from a silica flask with a silver-gilt condenser until the refractive index became constant, very small additions of potassium bisulfate and of sodium being made in alternate distillations. Potassium permanganate was also added until no longer decomposed. The same procedure was followed with standard water. Vacuum distillation was not employed as it was found that evacuation increased the refractive index by as much as 10 units at 14°, an effect previously noted by Demidenko[5] who stated however that degassing *decreased* the refractive index by 8 units. This is unlikely, since degassing increases the density and it may be a mistranslation. Assuming that $(n - 1)/d$ is constant, and taking Marek's[6] value of 25×10^{-7} for the decrease in density of water on saturating with air at 14°, the calculated change in refractive index is 8 units, agreeing as closely as can be expected with the observed value.

Results

(i) **H_2O^{18}**.—About 80 deuterium-free preparations both lighter and heavier than normal water were examined. Some were small fractions collected from the still in platinum vessels, but the majority were larger samples stored in silica flasks. In all cases the partially purified samples had a refractive index greater than that of normal water, the difference being sometimes as much as 30 units. On purification, this figure was usually reduced and so was the conductivity. Table I shows the lowest values obtained for 10 samples, d being the density difference of the sample from normal water in p.p.m. due to excess or deficiency of H_2O^{18}.

Sample 1 was examined in an early series of experiments before the technique of purification was fully developed. No. 2, 3 and 4 were obtained by distillation and more than 600 cc. of each was available, so that ample heads and tails could be discarded on redistillation. No. 5 was obtained by combining the oxygen from a sample containing much deuterium with the hydrogen from a deuterium-free distillate; it was calculated to contain sufficient deuterium to decrease the refractive index by two units. It was re-electrolyzed and the oxygen combined with hydrogen from sample 4, giving 6 and 7. The hydrogen was combined with the oxygen from no. 4 to give 8 and 9. These samples were only 50 and 70 cc. in volume and, unexpectedly, by no means pure; 6 and 7 were then mixed to give 10 and the values in the table were obtained after three fractionations. After two more fractionations the same values for κ and δn were found, measurements being made in the silica cell.

TABLE I

DENSITY, CONDUCTIVITY AND REFRACTIVE INDEX DIFFERENCE OF H_2O^{18} SOLUTIONS

Sample	d	κ	δn
1	−209	2.8	17
2	−200	1.4	6
3	−199	1.4	7
4	− 91	1.1	5
5	817	1.3	12
6	793	2.3	13
7	794	2.5	20
8	− 81	2.7	12
9	− 81	3.2	10
10	794	1.4	12

Taking Taylor and Selwood's[7] value for the difference between the refractive indices of D_2O and H_2O at 20°, 0.00462, the effect of removing D_2O from normal water would be an increase of 6.9 units in the refractive index; this number must consequently be subtracted from the values of δn in Table I. In the case of sample 5, the correction is only 5 units. The value of δn may thus be taken as -1 for $d = -200$, and 6 for $d \simeq 800$, so that the increase in refractive index for a molecular fraction y of H_2O^{18} is $0.00008y$ using Watson's[4] figure 1.113 for the specific gravity of H_2O^{18}. This result is only one tenth of that of Lewis and Luten[1] and may still be too large, as the heavy samples were not as pure as desirable.

(ii) **Carbon Dioxide Solutions**.—Preliminary measurements in the metal cell indicated that the relation between the refractive index and the conductivity was complex. A freshly made CO_2 solution had a lower refractive index than water, but after a few minutes an increase occurred and after standing overnight, a value considerably greater than that of water was reached. This effect was found to result from attack of the material of the cell and, by using the silica cell, it was eliminated. CO_2 was bubbled into water in the cell itself and the solution allowed to stand until the refractive index became constant. The conductivity was measured immediately afterwards without disturbing the liquid, and the relation $\kappa^2 = -4.6\ \delta n$ found to hold good to about 10%, the units being the same as before. By calculation from Wilke's[8] and Shedlovsky and MacInnes'[9] results for the conductivity of CO_2 solutions, it was found that $\kappa^2 = 5.1 \times$

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(3) A. J. Hayter, Ph.D. thesis, London University, 1950.

(4) H. E. Watson, *J. Appl. Chem. London*, **3**, 556 (1953).

(5) S. Demidenko, *Acta Phys. Chim. URSS*, **13**, 305 (1940).

(6) W. Marek, *Ann. Phys.*, **44**, 171 (1891).

(7) H. S. Taylor and P. W. Selwood, THIS JOURNAL, **56**, 998 (1934).

(8) E. Wilke, *Z. anorg. Chem.*, **119**, 365 (1921).

(9) T. Shedlovsky and D. A. MacInnes, THIS JOURNAL, **57**, 1705 (1935).

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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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).