187. *The Association of Water and Deuterium Oxide in Dioxan Solution.*

By R. P. Bell and J. H. Wolfenden.

In comparing the physical properties of pure water and deuterium oxide, some of the differences observed (such as the change in the temperature of maximum density) can be attributed to a difference in the " degree of association " of these two liquids. It was thought of interest to investigate whether this difference persists in moderately dilute solutions of the two kinds of water. Dioxan (diethylene dioxide) is a non-polar solvent of convenient freezing point which is miscible with water in all proportions, and is thus a suitable solvent for detecting any such differences by means of freezing-point measurements. Chlorobenzene was used as a normal solute for comparison.

The dioxan was a pure product dried over calcium chloride and sodium, and froze at 11·8°. The specimen of D_2O was kindly supplied by Professor H. S. Taylor, and contained not less than 99·8% D_2O. The chlorobenzene was dried over phosphoric oxide and fractionally distilled; the middle fraction boiling within 0·1° was used.

The measurements were carried out by means of the usual Beckmann technique,* about 10 g. of dioxan being used in each experiment. The freezing-point depressions in the following table represent the mean of 2—4 readings. The data for water were obtained in five independent series of measurements. In the tables, *m* is the concentration in molality (g.-mols. per 1000 g. of solvent), and ΔT the freezing-point depression.

TABLE I.

Solutions of H_2O *in dioxan.*

m.	ΔT.	$\Delta T/m$.	Deviation.	*m.*	ΔT.	$\Delta T/m$.	Deviation.	*m.*	ΔT.	$\Delta T/m$.	Deviation.
0·0955	$0{\cdot}42_0$°	4·39°	$-0{\cdot}00_5$°	0·456-	$1{\cdot}78_0$°	3·90°	$-0{\cdot}05_0$°	1·042	$3{\cdot}35_0$°	3·21°	$0{\cdot}00_0$°
0·121	$0{\cdot}52_0$	4·31	$-0{\cdot}01_5$	0·575	$2{\cdot}19_0$	3·82	$-0{\cdot}01_0$	1·142	$3{\cdot}54_5$	3·02	$-0{\cdot}01_0$
0·161	$0{\cdot}72_0$	4·43	$0{\cdot}00_0$	0·626	$2{\cdot}41_5$	3·86	$+0{\cdot}05_5$	1·204	$3{\cdot}60_5$	2·99	$-0{\cdot}05_5$
0·244	$1{\cdot}06_5$	4·37	$+0{\cdot}00_5$	0·719	$2{\cdot}61_0$	3·63	$0{\cdot}00_0$	1·390	$3{\cdot}96_5$	2·85	$0{\cdot}00_0$
0·246	$1{\cdot}05_5$	4·29	$-0{\cdot}00_5$	0·830	$2{\cdot}92_0$	3·52	$+0{\cdot}01_5$	1·517	$4{\cdot}18_5$	2·76	$0{\cdot}00_0$
0·321	$1{\cdot}33_0$	4·15	$-0{\cdot}01_5$	0·840	$2{\cdot}90_5$	3·46	$-0{\cdot}02_5$	1·572	$4{\cdot}32_0$	2·74	$+0{\cdot}05_5$
0·335	$1{\cdot}39_5$	4·16	$0{\cdot}00_0$	0·886	$2{\cdot}98_5$	3·33	$-0{\cdot}05_0$	1·652	$4{\cdot}39_0$	2·66	$+0{\cdot}00_5$
0·336	$1{\cdot}48_0$	4·40	$+0{\cdot}02_0$	1·003	$3{\cdot}33_0$	3·32	$+0{\cdot}04_0$	1·747	$4{\cdot}49_0$	2·57	$-0{\cdot}04_0$

TABLE II.

Solutions of D_2O *in dioxan.*

0·204	$0{\cdot}88_0$	4·30	$-0{\cdot}02_0$	1·126	$3{\cdot}43_5$	3·05	$-0{\cdot}09_5$	1·594	$4{\cdot}21_5$	2·64	$-0{\cdot}09_0$
0·617	$2{\cdot}26_0$	3·66	$-0{\cdot}07_5$	1·350	$3{\cdot}81_0$	2·82	$-0{\cdot}09_5$	1·819	$4{\cdot}49_0$	2·47	$-0{\cdot}14_5$
0·954	$3{\cdot}09_5$	3·24	$-0{\cdot}09_5$								

TABLE III.

Solutions of chlorobenzene in dioxan.

m.	ΔT.	$\Delta T/m$.	*m.*	ΔT.	$\Delta T/m$.	*m.*	ΔT.	$\Delta T/m$.
0·087	$0{\cdot}39_0$°	4·47°	0·508	$2{\cdot}32_0$°	4·56°	0·842	$3{\cdot}76_0$	4·47°
0·193	$0{\cdot}91_0$	4·72	0·609	$2{\cdot}77_0$	4·55	0·916	$4{\cdot}05_5$	4·43
0·399	$1{\cdot}82_5$	4·56	0·761	$3{\cdot}42_5$	4·51	1·040	$4{\cdot}54_5$	4·37

The freezing points of the H_2O solutions were plotted against their concentrations, and a smooth curve drawn to fit the points as closely as possible. Col. 4 of Table I gives the deviations (in temperature) of the individual points from this curve, the average deviation being $\pm 0{\cdot}020$°. On plotting the points for D_2O on the same graph, it was found that they all lay slightly below the curve (see Table II, col. 4). With the exception of the most dilute solution of D_2O (where the association is very small), the negative deviations for D_2O range from 3 to 7 times the mean deviation for H_2O, and they are individually all greater than the greatest deviation observed for H_2O. It must thus be concluded that D_2O is slightly but unmistakably more associated than H_2O in dioxan solutions of the same molar concentration.

The figures for chlorobenzene serve to establish the molecular freezing-point depression for dioxan. [The slight decrease of the values of $\Delta T/m$ with increasing concentration is no more than would be expected for an ideal solute, owing to the fact that we are plotting against *m* instead of log $(1 - x)$, where x is the mole-fraction of solute.] The value 4·65 being taken for $\Delta T/m$ at infinite dilution, this gives 0·75 and 0·58 for the osmotic coefficients of H_2O at 1*M* and 2*M* respectively. The corresponding coefficients for D_2O appear to be about 3% less.

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* Although the Beckmann method is not suitable for accurate absolute measurements, yet under constant conditions it gives very reproducible results, and therefore lends itself to comparative measurements such as those described.

It is interesting to speculate as to the cause of this difference. The abnormal behaviour of pure hydroxyl compounds has been explained by assuming the formation of a "hydrogen bond" between two molecules (Sidgwick, *Ann. Reports*, 1934, **31**, 41). If this factor is also operative in dilute solutions, then our results indicate that the "deuterium bond" is formed more readily than the "hydrogen bond." It is noteworthy, however, that an explanation is possible on the basis of a purely electrostatic interaction between the water dipoles. Fuoss (*J. Amer. Chem. Soc.*, 1934, **56**, 1027) has derived a limiting expression for the osmotic coefficient g (in a medium of dielectric constant D) of ellipsoidal molecules with axes a and b having dipoles of moment μ at their centres. His expression is

$$1 - g = n\left(\frac{\pi}{3}\right)^{3/2}\frac{\mu^2}{2DkT}\left(\frac{2b^2}{a^2 - 2b^2}\right)^{1/2}\left(\frac{\mu^2}{b^3DkT}\right)^{7/2}e^{\mu^2/b^3DkT}$$

where n is the number of solute molecules per c.c. With $D = 2{\cdot}20$ and $\mu = 1{\cdot}84 \times 10^{-18}$, this expression leads to our experimental value of g in molar solution if we assume the plausible values $a = 3 \times 10^{-8}$, $b = 1{\cdot}5 \times 10^{-8}$ for the dimensions of the water molecule. The observed difference of 3% between the values of g for H_2O and D_2O could be accounted for by a change of about 1% in the factor μ^2/b^3. In the lowest state of the molecules, H_2O and D_2O, the different zero-point energies will give to the former an amplitude of vibration about 2×10^{-10} cm. greater than the latter. This is unlikely to lead to any appreciable difference in dipole moment, but it is reasonable to expect that a difference of the same order of magnitude will occur in the distance of closest approach of two molecules (b in the above equation). The D_2O molecule would thus have an effective radius 1 or 2% greater than the H_2O molecule, which would be sufficient to account for the differences in osmotic behaviour.*

SUMMARY.

(1) The freezing points of solutions of H_2O and D_2O in dioxan have been determined up to a concentration of about $2M$, and compared with the results of similar measurements with the normal solute chlorobenzene.

(2) Both H_2O and D_2O show considerable departures from the laws of ideal solution. The association factor for D_2O is about 3% greater than for H_2O at the same molar concentration.

(2) The values of the osmotic coefficients are consistent with Fuoss's quantitative treatment of dipole interaction. The difference between H_2O and D_2O can be accounted for by the assumption of a small difference in effective radius due to the difference in zero-point energy.

PHYSICAL CHEMICAL LABORATORY, BALLIOL COLLEGE AND
TRINITY COLLEGE, OXFORD.

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