Densities, Refractive Indices, and Molar Refractions of the System Water-Dioxane at 25° C.

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DENSITIES and refractive indices of mixtures of water and 1,4-dioxane, in the course of other work, were measured at 25° C. over the entire range of composition. These data, as well as the molar refractions, are presented below.

EXPERIMENTAL

Technical dioxane was tickled through a column of activated alumina, refluxed over metallic sodium, and fractionally distilled in a nitrogen atmosphere. The purified dioxane melted at 11.8° C. and boiled at 101.4° C. (760 mm). The water was freshly distilled and free of CO_2.

The mixtures were prepared in 100-gram batches by weighing out the two liquids to the nearest milligram. Refractive indices were measured at 25 ± 0.05° C. with an Abbé refractometer; the precision of an average of several readings was ±0.00003. The refractive indices for the sodium *D* line at 25° C. are listed in Table I, with compositions expressed as mole fraction of dioxane (x_2). Densities were determined at 25 ± 0.005° C. with a Sprengel-Ostwald pycnometer of 25-ml. capacity. The values in Table I are relative to water at 4° C. Duplicate measurements were identical within ±0.00003 gram per ml. or better.

RESULTS

The plot of refractive index *vs.* weight per cent dioxane is a straight line up to 50%, represented by the least squares equation

$$n_D^{25} = 1.3325 + 0.000965 \times \text{wt. \% dioxane} \qquad (1)$$

The average error is 0.00007 unit. For mixtures richer in dioxane, the increase in refractive index with dioxane becomes increasingly less than linear.

Lynch's refractive indices *(8)* fall on the same curve as those of Table I, but are more widely scattered. The least squares equation of the linear portion, between zero and 51%, is

$$n_D^{25} = 1.3324 + 0.000973 \times \text{wt. \% dioxane} \qquad (2)$$

the average error is 0.00022.

The density and refractive index data of Hovorka, Schaefer, and Dreisbach *(6)* cover the range of composition incompletely. Only two refractive indices are listed for mixtures below 50% dioxane; their average error is 0.00035 according to Equation 1 and 0.00030 according to Equation 2. The refractive indices of the two mixtures richest in dioxane are low by about 0.00040 units compared to the data of Table I.

The density data listed in Table I are in close agreement with those of Griffiths *(4)*. Hovorka, Schaefer, and Dreisbach's density, 1.02766, for pure dioxane *(6)* is low compared to 1.02797 determined by Hammond and Stokes *(5)*, 1.02804 measured by this author, and 1.02808 determined by Griffiths *(4)*. Furthermore, the densities of their three mixtures richest in dioxane are about 0.00050 gram per ml. below those of Griffiths and of Table I.

Table I. Refractive Indices, Densities, and Molar Refractions of Water-Dioxane Mixtures

x_2	n_D^{25} obsd.	d_4^{25} obsd.	$[R]_{12\ \text{exptl.}}$
0.0000	1.3325	0.99707	3.713
0.0054	1.3351	0.99900	3.809
0.0103	1.3370	1.00073	3.893
0.0226	1.3422	1.00510	4.111
0.0354	1.3472	1.00927	4.338
0.0498	1.3522	1.01390	4.590
0.0687	1.3582	1.01850	4.925
0.0829	1.3621	1.02139	5.175
0.1228	1.3716	1.02744	5.883
0.1727	1.3813	1.03262	6.777
0.2403	1.3903	1.03617	7.980
0.2881	1.3952	1.03700	8.836
0.3301	1.3987	1.03710	9.591
0.3354	1.3991	1.03707	9.687
0.3368	1.3992	1.03703	9.712
0.4335	1.4050	1.03548	11.456
0.4563	1.4063	1.03469	11.876
0.5020	1.4081	1.03295	12.708
0.6387	1.4127	1.02966	15.194
0.6559	1.4132	1.02950	15.504
0.7500	1.4156	1.02884	17.200
0.8092	1.4168	1.02843	18.265
0.8947	1.4180	1.02827	19.783
1.0000	1.4197	1.02804	21.673

Partial molal volumes were determined graphically by the method of intercepts *(7)*, and plotted as a function of composition in Figure 1. For convenience, the molal volume of the pure component was subtracted from its partial molal volumes. Maxima in the water curve (and corresponding minima in the dioxane curve) occur at $x_2 = 0.035$ and 0.68; maxima in the dioxane curve occur at $x_2 = 0.51$ and 0.79. There is uncertainty in the location of the breaks at $x_2 = 0.83$, 0.93, and 0.98, since the density *vs.* composition curve flattens out at high dioxane concentrations, so that the intercepts of the tangents are subject to large errors. The partial molal volume-composition plots of Hovorka, Schaefer, and Dreisbach *(6)* and of Griffiths *(4)* have the same over-all shape as Figure 1. The former consists of smooth curves lacking the details of the other two plots, because it was based on insufficient data. The only significant difference between Griffiths' plot and Figure 1 is the minimum in the dioxane curve at $x_2 = 0.035$, which is missing from the former.

Additive refractive indices and densities of the mixtures were calculated by linear interpolation between the corresponding values of pure water and dioxane as a function of x_2. The differences between observed and calculated values are plotted against x_2 in Figure 2. The observed values are always higher. The maximum difference in refractive index, $\Delta n_D^{25} = 0.0375$, occurs between 29 and 30 mole % dioxane. The maximum difference in density, which amounts to 3.0%, occurs at 24 mole %.

The molar refractions of the water–dioxane mixtures were

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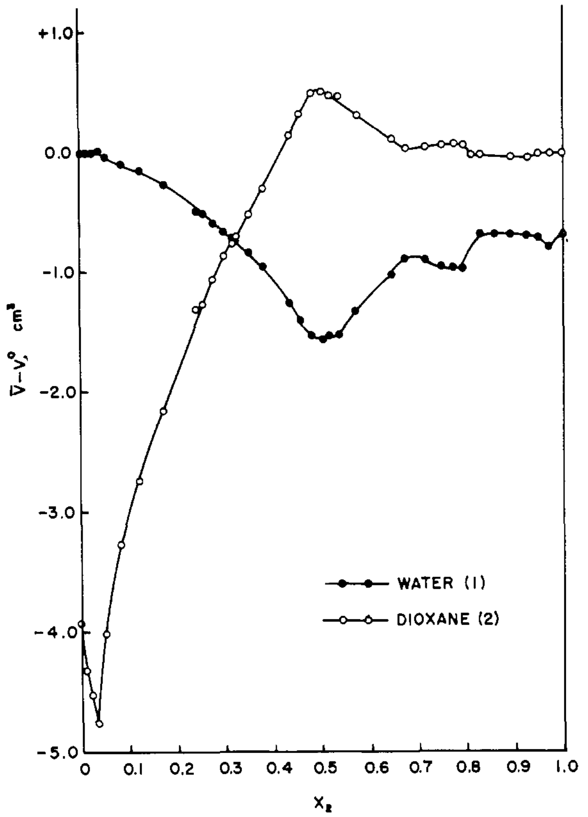

Figure 1. Partial molal volumes as a function of mole fraction of dioxane

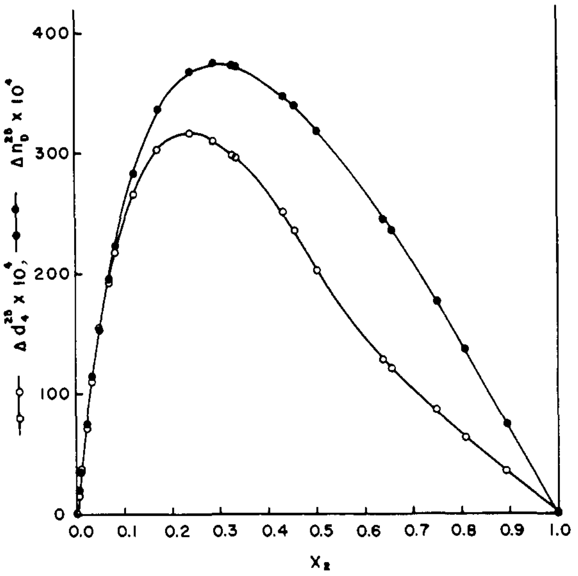

Figure 2. Deviations of observed densities and refractive indices from calculated values, as a function of mole fraction of dioxane

calculated from observed densities and refractive indices according to the equation (*1*)

$$[R]_{12\,\text{exptl}} = \left(\frac{n_{12}^2 - 1}{n_{12}^2 + 2}\right)\left(\frac{x_1M_1 + x_2M_2}{d_{12}}\right) \qquad (3)$$

These values listed in Table I are nearly linear with x_2. Molar refractions of the mixtures were also calculated from the molar refraction of pure water and of pure dioxane according to the equation (*1*)

$$[R]_{12\,\text{add}} = x_1\left(\frac{n_1^2 - 1}{n_1^2 + 2}\right)\left(\frac{M_1}{d_1}\right) + x_2\left(\frac{n_2^2 - 1}{n_2^2 + 2}\right)\left(\frac{M_2}{d_2}\right) \qquad (4)$$

The plot of $\Delta[R] = [R]_{12\text{ exptl.}} - [R]_{12\text{ add}}$ *vs.* x_2 (Figure 3) consists of a single cycle sinusoidal curve. The minimum, which occurs at about $x_2 = 0.30$, is $- 0.051$ ml. (a deviation of 0.6%). The maxiumum, which occurs around $x_2 = 0.81$, is 0.019 ml. (a deviation of 0.1%). The difference is zero near $x_2 = 0.58$. These differences between molar refractions calculated from experimental densities and refractive indices and additive molar refractions are small; above $x_2 = 0.60$ they are not more than three to ten times the probable error in determining $[R]_{12\text{ exptl.}}$ However, the trend of $\Delta[R]$ as a function of x_2 is quite consistent, indicating that the differences are real.

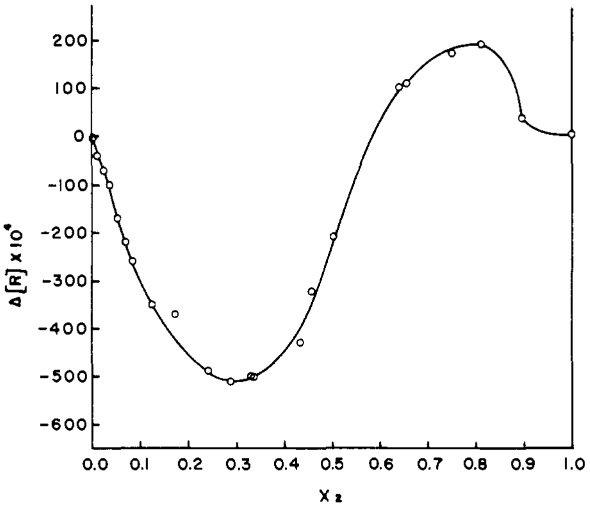

Figure 3. Differences between experimental and additive molar refractions, as a function of mole fraction of dioxane

DISCUSSION

As the dioxane content of the mixtures increases, the water-water interaction should decrease and the water-dioxane interaction should increase. The observed results are due to a combination of these effects. The minimum in $\Delta[R]$ occurs at about the same composition as the maxima in Δn and Δd. These deviations may be due to the formation of intermolecular complexes with water to dioxane ratios predominantly 3 to 1 or 2 to 1.

The heats of mixing of water and dioxane as a function of composition are reported to go through an endothermic maximum and an exothermic minimum of nearly equal magnitudes (*2, 3*). These authors attributed the minimum, at $x_2 = 0.14$ or 0.20, to the formation of 6 to 1 or 4 to 1 water to dioxane complexes. The maximum, which occurred at the same composition as the maximum in $\Delta[R]$, was ascribed to the dissociation of water aggregates on mixing with an excess dioxane.

LITERATURE CITED

(1) Bauer, N., Fajans, K. in "Physical Methods of Organic Chemistry," A. Weissberger, editor, 2nd ed., Vol. I, p. 1170, Interscience, New York, 1949.
(2) Feodos'ev, N.N., Osipov, O.A., Morozova, G.K., *Zhur. Obshchei Khim.* **24**, 1540 (1954).
(3) Goates, J.R., Sullivan, R.J., *J. Phys. Chem.* **62**, 188 (1958).
(4) Griffiths, V.S., *J. Chem. Soc.* **1952**, 1326; *Ibid.*, **1954**, 860.
(5) Hammond, B.R., Stokes, R.H., *Trans Faraday Soc.* **51**, 1641 (1955).
(6) Hovorka, F., Schaefer, R.A., Dreisbach, D., *J. Am. Chem. Soc.* **58**, 2264 (1936).
(7) Lewis, G.N., Randall, M., "Thermodynamics and the Free Energy of Chemical Substances," p. 38, McGraw-Hill, New York, 1923.
(8) Lynch, C.C., *J. Phys. Chem.* **46**, 366 (1942).

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