The Dielectric Constant of Dioxane–Water Mixtures between 0 and 80°

BY GÖSTA ÅKERLÖF AND OLIVER A. SHORT

Dioxane is in many respects a remarkable substance. In accordance with its symmetrical structure dioxane has a very small dipole moment, which possibly even may be equal to zero. Yet dioxane is completely miscible in all proportions with such a highly polar compound as water and quite large quantities of strong electrolytes are needed to salt it out. However, this particular property, combined with a very low dielectric constant, makes dioxane–water mixtures highly suitable as solvents for the study of the behavior of electrolytes in media of continuously and rapidly varying dielectric constant. This has been pointed out and made use of already by Kraus and Fuoss,[1] who studied the conductance of certain strong electrolytes in dioxane–water mixtures. The values they used for the dielectric constants of these mixtures were obtained by G. S. Hooper and our results to be presented below are in good agreement with his, but since the measurements were carried out only at a single temperature and principally confined to mixtures containing small quantities of water, a more complete study was deemed desirable.
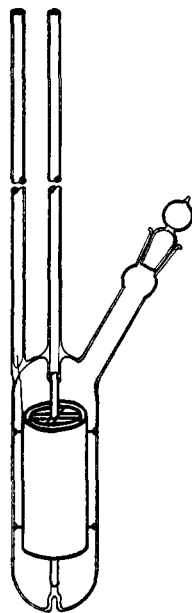
Apparatus and Materials.—The experimental method employed was practically identical with the procedure previously given[2] and therefore a repetition is unnecessary. The wave length used was, also as before, 150 meters. Due to the relatively great length of the leads to the test cell in the present case they were twisted together and the readings of the resonance circuit were calibrated at a large number of points against a continuously variable precision condenser calibrated by the Naval Research Laboratory and kindly loaned to us by Professor Norman I. Adams of the Sloane Physics Laboratory. The design of the test cells is given by Fig. 1. The electrodes were made of platinum and firmly held in place, the outer grounded one by a number of short wires, one end of which was welded to the electrode and the other end

Fig. 1.—Cell.

fused into the wall of the glass vessel. The inner electrode was held by an upper and a lower cross welded to a center tube, also of platinum. Two cells were employed, one with a capacity of about 13.70 and the other of 55.0 $\mu\mu$F. For the calibration of the smaller cell water was used employing the value obtained by Wyman[3] for its dielectric constant at
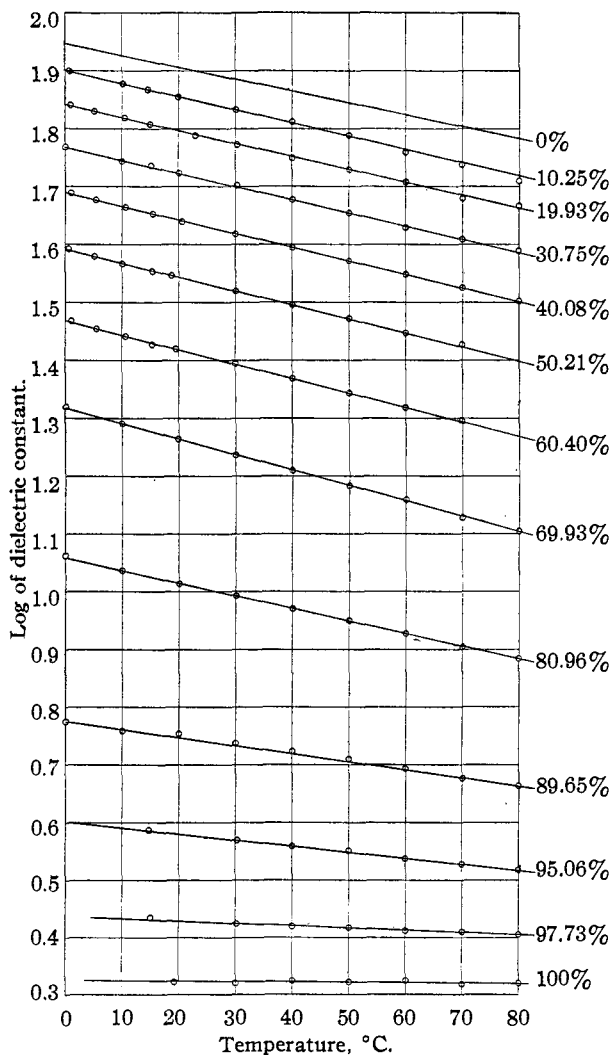

Fig. 2.—Curves for the logarithm of the dielectric constant of dioxane–water mixtures of constant composition and varying temperature.

20°. The large cell was calibrated by readings at several temperatures with a 70 wt. % dioxane–water mixture, the dielectric constant of which previously had been measured at the same temperatures with the small cell. The use of platinum electrodes was resorted to after a futile attempt

(1) Kraus and Fuoss, THIS JOURNAL, **55**, 21 (1933).

(2) G. Åkerlöf, *ibid.*, **54**, 4125 (1932).

(3) Wyman, *Phys. Rev.*, **35**, 623 (1930); *cf.* Drake, Pierce and Dow, *ibid.*, **35**, 613 (1930).

TABLE I

INTERPOLATED VALUES FOR THE DIELECTRIC CONSTANT OF A SERIES OF DIOXANE–WATER MIXTURES AT VARIOUS ROUND TEMPERATURES

Dioxane, wt. %	0	10	20	30	40	50	60	70	80	90	95	98	100
0	88.31	78.86	69.16	59.34	49.37	39.50	29.84	20.37	12.19	6.16	3.91	2.73	2.109
10	84.25	75.06	65.68	56.24	46.71	37.31	28.17	19.25	11.58	5.93	3.82	2.70	2.104
20	80.37	71.43	62.38	53.30	44.19	35.25	26.60	18.20	10.99	5.71	3.74	2.68	2.102
30	76.73	67.98	59.24	50.52	41.80	33.30	25.12	17.20	10.44	5.50	3.65	2.65	2.100
40	73.12	64.70	56.26	47.88	39.54	31.46	23.72	16.26	9.91	5.30	3.57	2.62	2.098
50	69.85	61.57	53.43	45.38	37.41	29.72	22.40	15.37	9.41	5.10	3.49	2.60	2.096
60	66.62	58.60	50.75	43.01	35.39	28.08	21.15	14.52	8.93	4.91	3.41	2.57	2.094
70	63.50	55.77	48.20	40.76	33.48	26.52	19.97	13.73	8.48	4.73	3.33	2.55	2.092
80	60.58	53.07	45.77	38.63	31.67	25.05	18.86	12.97	8.05	4.56	3.25	2.52	2.090

to use cells with silver films for the same purpose.[4] The results obtained with the silver films were erroneous but the closest approach to the true values for the dielectric constant was found in the case of mixtures containing a high percentage of dioxane.

The raw material for the dioxane employed was a commercial varnish remover from the Carbide and Carbon Chemicals Corporation and it consisted apparently of practically pure dioxane. The raw dioxane was first refluxed in an all-glass apparatus with sodium metal for several hours. The distilled product was then subjected to a fractional crystallization in an apparatus with a mercury-sealed stirrer. After four recrystallizations the freezing point had gone up to 11.78°, which value did not show any further visible changes upon repeating the freezing process. Water was obtained from a Barnstead still for conductivity water.

Experimental Results.—The dielectric constant data obtained have been plotted in Fig. 2 using the equation employed by Åkerlöf

$$\log D = \log a - bt \qquad (1)$$

where D is the observed dielectric constant of the solvent mixture, a and b are empirical constants and t is the temperature. As previously had been found in numerous other cases this equation was also in the case of dioxane–water mixtures able to express the experimental data well within their estimated accuracy. Using equation (1) the original measurements have been interpolated to round temperatures and weight per cent. of dioxane and a summary of the result is given in Table I. For interpolation to odd temperatures the following table may be used:
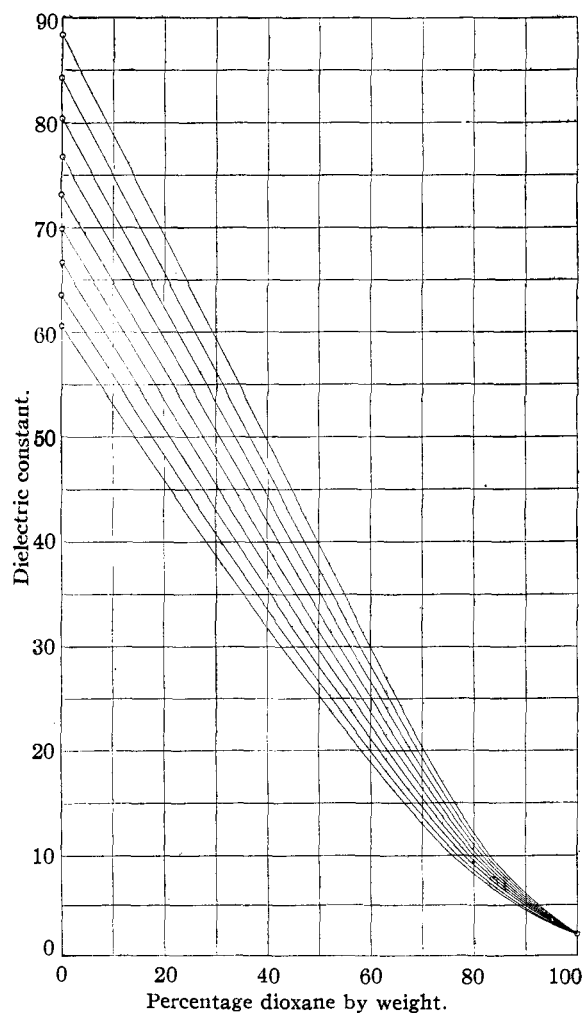

Fig. 3.—Curves for the isotherms of the dielectric constant of dioxane–water mixtures of varying composition: top curve 0° isotherm, then follow in order those for 10, 20, 30, 40, 50, 60, 70 and 80°.

Dioxane, wt. %	Log a	b
0	1.9461	0.00205
10	1.8969	.00215
20	1.8398	.00224
30	1.7734	.00233
40	1.6935	.00241
50	1.5965	.00247
60	1.4747	.00249
70	1.3090	.00245
80	1.0860	.00225
90	0.7896	.00164
95	.5923	.00100
100	.3234	.00004

(4) The design of the cells was practically identical with that of the cells used by Sugden, J. Chem. Soc., 768 (1933); cf. Sayce and Briscoe, ibid., 315 (1925); Ball, ibid., 570 (1930).

A graphical representation of the isotherms for the variation of the dielectric constant of the dioxane–water mixtures with changing composition is shown in Fig. 3.
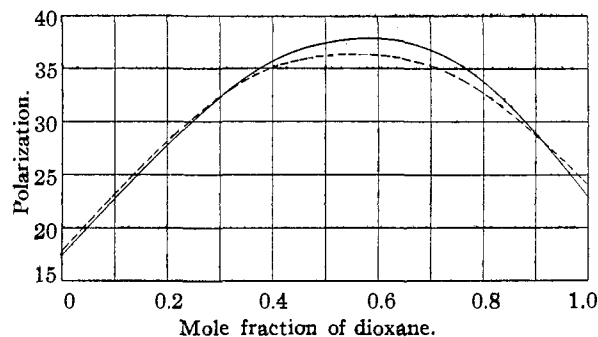

Fig. 4.—Curves for the dielectric polarization of dioxane–water mixtures at 20 and 70°; dotted curve 70° isotherm.

The curve for the molar dielectric polarization of dioxane–water mixtures is considerably different from that of a number of other organic solvent–water mixtures. In the case of methyl and ethyl alcohol–, ethylene glycol– and glycerol–water mixtures, a practically linear variation of the polarization over the entire mixture range is obtained when it is plotted against the mole fraction of one of the components. The polarization of a mixture P_{12} is given by the equation

$$P_{12} = f_1 P_1 + f_2 P_2 = \frac{D-1}{D+2} \frac{f_1 M_1 + f_2 M_2}{d} \quad (2)$$

where f_1 and f_2 denote mole fractions, M_1 and M_2 molecular weights and d is the density of the mixture. In Table II is given the calculated values for 20 and 70° and the corresponding curves are shown in Fig. 4. Data used for the density of dioxane–water mixtures were those of Herz and Lorenz.[5]

According to present theory, if a substance is non-polar its polarization is constant and independent of the concentration. Thus since dioxane as already mentioned probably is non-polar we might calculate the variations of the polarization of water in dioxane–water mixtures. The calcu-

(5) Herz and Lorenz, Z. physik. Chem., **A140**, 406 (1929).

Table II
The Dielectric Polarization of Dioxane–Water Mixtures at 20 and 70°

Dioxane, wt. %	Dioxane mole fr.	P_{12} at 20°	P_{12} at 70°
0	0	17.39	17.59
10	0.0222	18.66	18.82
20	.0487	20.10	20.31
30	.0806	21.83	22.11
40	.1200	23.94	24.26
50	.1699	26.54	26.84
60	.2349	29.69	29.83
70	.3232	33.21	33.00
80	.4501	36.65	35.78
90	.6481	37.47	35.78
95	.7954	34.06	32.92
98	.9093	28.35	28.40
100	1.0000	22.90	24.06

lated values vary approximately linearly when plotted against the dioxane mole fraction as shown in Fig. 5 for the 20° isotherm, but the theoretical significance of this result is difficult to
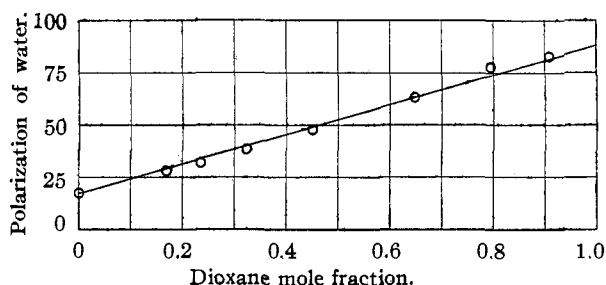

Fig. 5.—Curve for the dielectric polarization of water in dioxane–water mixtures at 20°.

understand. The polarization of water in pure dioxane at 20° extrapolates to 88.0, while the corresponding value in pure water is only 17.4.

The authors wish to express their appreciation of the help given them by Professor Norman I. Adams.

Summary

The dielectric constant of a series of dioxane–water mixtures has been measured over the temperature range 0 to 80° for a wave length of 150 meters and using a resonance method.