

SHORT COMMUNICATIONS

ESTIMATING DIELECTRIC CONSTANTS FOR LIQUID MIXTURES AT HIGH PRESSURES*

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Electrochemical transport calculations for ions in solutions of liquid mixtures at high pressures require some knowledge of the dielectric constant of the mixture under these conditions. If no reliable experimental dielectric constants are available, a simple linear interpolation method as described here may give useful estimates of sufficient accuracy.

In the experimental work described elsewhere,¹ the dielectric constant of dioxan-water mixtures was of interest, and at an early stage of the work this had not been measured. Recently these data have become available,² and it is possible to compare the estimates with experimental values.

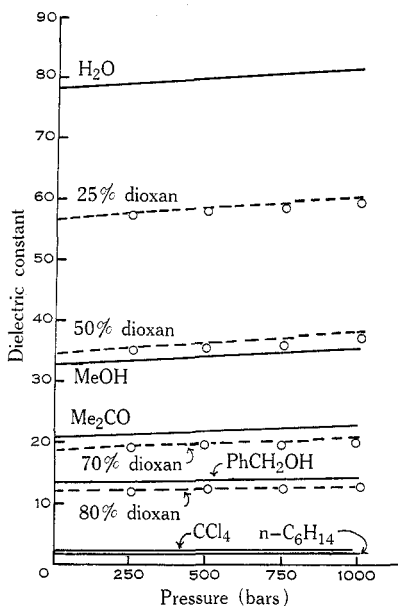


Fig. 1.—Dielectric constants at different pressures and 25°. — Various solvents; - - - estimates by linear interpolation for dioxan-water mixtures; ○ experimental dioxan-water values.

The dielectric constants of a number of liquids have been measured under pressure (at 25°) and for the present argument the values for water by Owen *et al.*,³

* Manuscript received March 8, 1968.

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¹ Pearce, P. J., and Strauss, W., unpublished data; Pearce, P. J., Ph.D. Thesis, University of Melbourne, 1968.

² Heydtmann, H., and Büttner, D., personal communication, 1967.

³ Owen, B. B., Miller, R. C., Milner, C. E., and Cogan, L., *J. phys. Chem.*, 1961, **65**, 2065.

and n-hexane, carbon tetrachloride, benzyl alcohol, acetone, and methanol by Hartmann, Neumann, and Rinck⁴ have been used. In Figure 1, the dielectric constants are plotted against pressure, and it can be seen that the pressure has little effect on the dielectric constant of liquids with very low values, but an increasing effect with higher dielectric constants, the largest being seen in the case of water.

TABLE I
DIELECTRIC CONSTANTS OF DIOXAN-WATER MIXTURE

Pressure (bar)	Experimental*	Linear Interpolation	Owen-Brinkley†
25% (w/w) Dioxan-Water			
1	56.5	56.5	56.5
250	57.3	57.4	57.23
500	57.9	58.3	57.92
750	58.6	59.3	58.67
1000	59.2	59.9	59.2‡
50% (w/w) Dioxan-Water			
1	34.5	34.5	34.5
250	35.0	35.4	34.98
500	35.5	36.2	35.45
750	36.0	36.9	35.91
1000	36.4	37.6	36.4‡
70% (w/w) Dioxan-Water			
1	18.7	18.7	18.7
250	19.1	19.3	19.00
500	19.4	19.9	19.30
750	19.6	20.3	19.60
1000	19.9	20.7	19.9‡
80% (w/w) Dioxan-Water			
1	12.0	12.0	12.00
250	12.2	12.2	12.21
500	12.4	12.3	12.41
750	12.6	12.5	12.61
1000	12.8	12.6	12.8‡

* Based on interpolation of experimental values of Owen *et al.*³ and Heydtmann and Büttner.²

† Using Owen-Brinkley equation with *B* determined from densities.

‡ Value at 1000 bars, taken from experimental work.

It is assumed that the pressure effect in the case of pure dioxan (D_1 2.21, where D_1 is the dielectric constant at 1 bar) will be the same as for n-hexane (D_1 1.88) and carbon tetrachloride (D_1 2.23); it is then possible to estimate the dielectric constant under pressure (D_p) for pure dioxan. The dielectric constants for dioxan-water mixtures (25, 50, 70, and 80%) under pressure were then estimated from the values

⁴ Hartmann, H., Neumann, E., and Rinck, G., *Z. phys. Chem. (N.F.)*, 1965, **44**, 204.

for the mixture at atmospheric pressure,^{2,3,5-10} and the assumption that the proportional change is similar under pressure to that at 1 atm using simple, linear interpolation. In other words, it has been assumed that the change in D_p for the dioxan-water mixture under pressure does not depend on the nature of the non-aqueous component, as long as some idea of the pressure dependence of the dielectric constant change in a pure non-aqueous component of similar dielectric constant is known. That this gives values of reasonable precision is seen from the plots on Figure 1, as well as the values in Table 1.

The Owen-Brinkley equation¹¹ which has been extensively used for predicting and extending dielectric constants for pure liquids is also found to be applicable to liquid mixtures.

The Owen-Brinkley equation, which is

$$1 - (D_1/D_p) = AD_1 \log[(B+P)/(B+1)]$$

contains two constants, A and B , and is similar in form to the Tait equation for compressibility of liquids. It has been shown elsewhere^{11,12} that the constant B is virtually the same for the compressibility and dielectric constant form of the equation.

If therefore, compressible data are available for determining B , then only a single dielectric constant determination under pressure for the particular system is necessary for the calculation of a range of D_p values. The dielectric constants of dioxan-water mixtures have been calculated using the present workers' compressibilities¹³ for determining B and Heydtmann and Büttner's experimental dielectric constants² at 1000 bars for calculating A . These have also been included in Table 1, and indicate the precise nature of the dielectric constants estimated by this method.

The authors wish to thank Dr Heydtmann and Dr Büttner of the University of Frankfurt am Main for making available their unpublished dielectric constant measurements for dioxan-water mixtures and Dr S. D. Hamann, Chief, Division of Applied Chemistry, CSIRO Chemical Research Laboratories, for helpful discussions.

⁵ Akerlof, G., and Short, O. A., *J. Am. chem. Soc.*, 1936, **58**, 1241.

⁶ Lind, J. E., and Fuoss, R. M., *J. phys. Chem.*, 1961, **45**, 991.

⁷ Critchfield, F. E., Gibson, J. A., and Hall, J. L., *J. Am. chem. Soc.*, 1953, **75**, 1991.

⁸ Garg, S. K., and Smyth, C. P., *J. chem. Phys.*, 1965, **43**, 2959.

⁹ Clement, C. J., Forest, E., and Smyth, C. P., *J. chem. Phys.*, 1964, **40**, 2123.

¹⁰ Harned, H. S., and Morrison, J. O., *J. Am. chem. Soc.*, 1936, **58**, 1908.

¹¹ Owen, B. B., and Brinkley, S. R., *Phys. Rev.*, 1943, **64**, 32.

¹² Hartmann, H., Neumann, E., and Rinck, G., *Z. phys. Chem. (N.F.)*, 1965, **44**, 218.

¹³ Pearce, P. J., and Strauss, W., *Aust. J. Chem.*, 1968, **21**, 1213.