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that is, as prepared in the apparatus as shown in Fig. 1 and prepared by vacuum sublimation, gave identical powder patterns. The observed d -spacings and visually observed intensities were reported recently.⁸

A single crystal of the pentabromide was hermetically sealed in a 0.5 mm. Lindemann capillary. Precession photographs were obtained by precession of the crystal about the b and c axis and Weissenberg photographs obtained of the 0, 1 and 2 levels by translation about the a axis; copper radiation was used.

The elementary orthorhombic cell dimensions were found to be $a_0 = 6.125$ Å., $b_0 = 12.92$ Å., and $c_0 = 18.60$ Å. This results, with eight formula weights per unit cell, in an X-ray density of 4.44 g. cc.⁻¹ which is in excellent agreement with the pycnometric density of 4.36 g. cc.⁻¹ The tentative space group is D_{2h}^2 -P2₁/b2₁/a2/m.

Acknowledgment.—I am grateful to Mr. Albert F. Biddle and Mr. Keith R. Babcock for their assistance on the powder diffraction and single crystal work, respectively.

(8) Deposited with Library of Congress, ADI Auxiliary Publication Project, Washington 25, D. C., Document number 5365.

THE DIELECTRIC CONSTANTS OF ETHYLENE CARBONATE AND OF SOLUTIONS OF ETHYLENE CARBONATE IN WATER, METHANOL, BENZENE AND PROPYLENE CARBONATE

BY RALPH P. SEWARD AND ERNEST C. VIEIRA¹

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania

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The measurements reported here were made to provide information which might be useful in investigations of the properties of electrolytes. Ethylene carbonate was chosen because it was reported to have a high dielectric constant and to be completely miscible with both water and benzene. Non-aqueous solvents having dielectric constants comparable to that of water may be useful where it is desired to eliminate the reactivity or solvation effects peculiar to water, or to study organic electrolytes which are not sufficiently soluble in water. Ethylene carbonate does have the disadvantage of melting above room temperature. When ethylene carbonate is mixed with other liquids, however, solvents melting below room temperature and having a variety of solvent powers are obtained.

Experimental

Materials.—Ethylene carbonate and propylene carbonate from the Jefferson Chemical Company were distilled several times at about 5 mm. Their specific conductances were 10^{-7} ohm⁻¹ cm.⁻¹ or less. The freezing point of the ethylene carbonate was 36.4° . Benzene, methyl alcohol and dioxane were taken from a 4-foot packed distilling column after treatment with phosphorus pentoxide, magnesium and sodium, respectively. The water was a triple still product, having a conductance of about 1×10^{-6} ohm⁻¹ cm.⁻¹.

Bridge.—Two arms of the bridge were the two equal resistances of the Leeds and Northrup Campbell-Shakelton ratio box. A third arm consisted of a fixed 10,000 ohm resistor and, in parallel with it, a capacitor set at a fixed value of about 900 μ mf. The fourth arm consisted of an 11,000 ohm variable resistor, a General Radio Company precision capacitor, and the cell containing the liquid to be investigated. In this arm the resistor, precision capacitor and cell were connected in parallel. The bridge was energized

by a Hewlett-Packard variable frequency oscillator and a cathode ray oscillograph served as the null detector. The bridge was balanced with the cell empty and again after filling the cell. The change in cell capacitance is then the difference in the two readings on the precision capacitor. In none of the measurements was there any significant variation of recorded capacitance with change of frequency in the range 10–20 kilocycles.

Two cells were employed. For liquids having dielectric constants below 15 the larger cell, with a capacitance of about 60 μ mf. when empty, was used. For larger dielectric constants a cell of about 7 μ mf. capacitance was used. Both cells were of simple concentric cylinder type with Teflon separators between cylinders. In the larger cell the cylinders were stainless steel, in the small brass. The cylinders were sealed into a glass container in both cells. When measurements were taken the cells were immersed in a 5-gallon oil-bath with temperature control to 0.03° .

The change in capacitance between the empty cell and the liquid-filled cell, ΔC , is

$$\Delta C = DC_v - C_v = C_v(D - 1)$$

where D is the dielectric constant of the liquid, the dielectric constant of air being taken as unity, and C_v is a constant characteristic of the cell. Having evaluated C_v by means of liquids of known dielectric constants the above relationship was used to obtain the desired dielectric constants of other liquids from the observed ΔC values.

The constant C_v for the larger cell was determined, with benzene at 25° , taking its dielectric constant as 2.276.² As a check, measurements were made on four solutions of acetonitrile in benzene, the dielectric constants of which had been reported by Smyth,² with dioxane, and on four solutions of dioxane in water for which dielectric constants had been measured by Critchfield, Gibson and Hall.³ Using the cell constant obtained from pure benzene, dielectric constants were obtained which deviated by a maximum of 0.3% from the values reported by these investigators.

For the smaller cell, measurements were made on dioxane-water mixtures up to pure water and the cell constant evaluated using the data of Critchfield, Gibson and Hall.³ With this cell the values of C_v decreased by about 1% with a change in dielectric constant from 15 to 78. In subsequent measurements the value of C_v employed was taken from a plot of C_v against condenser reading. With this procedure measurements were made on several methanol-water mixtures, and dielectric constants obtained which agreed, with a maximum deviation of 0.16%, with the data of Albright and Gosting.⁴ The dielectric constants reported by Critchfield, Gibson and Hall,³ those by Albright and Gosting, and hence those of the present report, are based on the value of 78.48 for water at 25° . According to the more recent work of Malmberg and Maryott⁵ the dielectric constant of water at 25° is 78.30. The effect of temperature on the cell constant was investigated by measuring the capacitance of the water-filled cell at several temperatures. Up to 70° a maximum correction of 0.4% in the cell constant was required to bring the measurements to agreement with the Wyman⁶ dielectric constant-temperature equation for water.

Results

For rounded weight percentages (w) of ethylene carbonate, dielectric constants obtained for the various liquid mixtures are given in Table I which also includes, separately, values for small mole fraction of ethylene carbonate in dilute benzene solutions. These values were read from dielectric constant-composition curves of the original data.

Dielectric constants obtained for ethylene carbonate at various temperatures are given in Table II.

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TABLE I
DIELECTRIC CONSTANTS OF ETHYLENE CARBONATE SOLUTIONS

w	0	20	40	60	80	100
Ethylene carbonate-benzene solutions						
D , 25°	2.27	9.47	21.2	38.6	62.8	...
D , 40°	2.24	9.03	20.0	36.1	58.5	89.1
Ethylene carbonate-methanol solutions						
D , 25°	32.6	39.1	47.4	58.6	74.0	...
D , 40°	29.8	35.9	43.7	54.0	68.5	89.1
Ethylene carbonate-water solutions						
D , 25°	78.5	80.5	81.6	83.3	86.4	...
Ethylene carbonate-propylene carbonate solutions						
D , 25°	64.6	69.1	74.6	80.5	87.2	...
dilute benzene solution; N_2 = mole % ethylene carbonate, d = density						
N_2	0.50	1.00	1.50	2.00	2.50	3.00
d , 25°	0.8754	0.8770	0.8790	0.8803	0.8829	0.8848
D , 25°	2.41	2.60	2.80	2.93	3.09	3.25

TABLE II
THE DIELECTRIC CONSTANT OF ETHYLENE CARBONATE AT VARIOUS TEMPERATURES

t °C.	25	36	40	50	60	70
D	95.3 (extrap.)	90.8	89.1	85.1	81.0	77.3

From the molar polarization of the dilute benzene solutions and the molar polarization of benzene (26.67), the molar polarizations of ethylene carbonate in the various solutions were calculated. From extrapolation of these values graphically to infinite dilution, a limiting value was obtained from which after subtracting the molar refraction, 16.8, the dipole moment of ethylene carbonate was calculated to be 4.87 Debye unit. Use of the Halverstadt and Kumler⁷ extrapolation method gave 4.86 for the dipole moment. Arbuzov and Shavsha,⁸ also working with benzene solutions, have found the dipole moment of ethylene carbonate to be 4.80.

The dielectric constant of ethylene carbonate is linearly related to temperature. Dielectric constant values from $D = 85.1 - 0.408(t - 50)$ where t is degrees centigrade, agree with the observed values within 0.2%, except at 70° where the calcu-

lated value is 0.5% low. Comparison of the value 64.6, found for propylene carbonate at 25° with 65.1 from the measurements of Watanabe and Fuoss⁹ suggests that in absolute accuracy there may be errors in the present measurements of the order of 1%.

As with most liquids of high dielectric constant, the Onsager¹⁰ equation does not successfully relate the dielectric constant of the liquid to the dipole moment of ethylene carbonate. Failure of the Onsager equation is commonly attributed to some type of association in the liquid state. A Trouton constant of 23 suggests association in ethylene carbonate. The correlation parameter, g , of the Kirkwood¹¹ equation, is 1.6 for ethylene carbonate, while alcohols, considered strongly associated, show values approaching three.

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