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Pressure and Temperature Dependence of the Electrical Permittivities of Formamide and Water

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The electrical permittivities of formamide and water have been measured over the temperature range 5-65°C and at pressures up to 2000 bar, using a transformer bridge technique in the frequency-range 10-520 kHz. Densities of formamide at 1 bar and temperatures 5-65°C are also reported, and a confirmatory value for the compressibility at 25°C.

The theoretical evaluation of the limiting slope of the curves of apparent molar volumes of strong electrolytes against the square root of concentration requires a knowledge of the pressure dependence of the electrical permittivity of the solvent.¹ This quantity is also of interest in connection with theories of electrostriction.² While precise values are available for water,³ the most accurate work is confined to the region up to 1 000 bar. For formamide, an important solvent for electrolytes because of its small molecular size and high permittivity, no high-pressure values have been available and even the data at atmospheric pressure* are sparse. The present work, though its primary purpose is the study of formamide, includes data for water up to 2 000 bar in the range 10-65°C.

EXPERIMENTAL

PURIFICATION OF MATERIALS

Water was distilled and de-ionized, and when first put in the cell usually had a conductance of $\sim 8 \times 10^{-7}$ ohm⁻¹ cm⁻¹. This increased several-fold during the pressure-runs, without effect on the extrapolated capacitance readings.

Formamide (analytical reagent grade) was fractionally frozen three times (final f.p., 2.38°C). The product was neutralized to bromothymol blue with a few drops of dilute sodium hydroxide solution and heated to $\sim 40^\circ\text{C}$ under reduced pressure. Further acidity developed during the process, and the neutralization was repeated until the liquid remained neutral on heating. It was then distilled at ~ 0.1 torr and 32-35°C. A conductance cell in the condensate was used to monitor the quality. After four such distillations the product had the following physical properties (literature values¹⁰ in parenthesis):

f.p.	2.50°C	(2.55°C)
conductance	2.8×10^{-6} ohm ⁻¹ cm ⁻¹	(1.445 91)
n_D^{25}	1.446 51	(1.129 18 g cm ⁻³)
$d(25^\circ\text{C})$	1.129 15 g cm ⁻³	(1.129 18 g cm ⁻³)
est. water content	0.025 %	

The density of formamide was measured over the range 5-65°C with the results in table 1.

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TABLE I.—DENSITY OF FORMAMIDE

$t/^\circ\text{C}$	$d/\text{g cm}^{-3}$	$10^4 \alpha / (^\circ\text{C})^{-1}$
5.79	1.145 31 ₁	7.33
15.00	1.137 59 ₀	7.41
25.00	1.129 14 ₇	7.49
35.00	1.120 61 ₈	7.58
45.00	1.112 13 ₀	7.67
55.00	1.103 61 ₆	7.76
65.00	1.095 02 ₃	7.85

$$d/\text{g cm}^{-3} = 1.150 172 - 8.372 5 \times 10^{-4} t - 1.740 5 \times 10^{-7} t^2; \alpha = -(\partial \ln d / \partial t)_p.$$

The compressibility of formamide was measured in a preliminary model piezometer, giving $\beta(25^\circ\text{C}) = 4.11 \times 10^{-5}$ bar⁻¹ in good agreement with the value of 4.119×10^{-5} bar⁻¹ obtained from the adiabatic compressibility (ultrasonic method) reported by Mikhailov, Rozina and Shutilov⁵ combined with the heat capacity given by Egan and Luff.⁶

HIGH-PRESSURE CELL

The dielectric cell (fig. 1) consisted of two concentric platinum cylinders, the inner one A 2 cm long and 1.1 cm ext. diam., and the outer one B 4.5 cm long and 1.5 cm int. diam. One end of the outer cylinder was closed with a platinum disc C perforated with 4 small holes to permit the free passage of liquid, and a central hole to serve as a support for a solid glass cone D which was attached to the inside of the inner cylinder, thus locating that end rigidly with respect to the outer cylinder. Heavy platinum wires E were welded to the closed end of the outer cylinder and the other end of the inner cylinder, and were then sealed through the Pyrex glass cell with tungsten seals F. The outer cylinder, at its open end, was rigidly located by four indentations G in the glass cell wall. The outer cylinder projected about 1 cm beyond the ends of the inner one to minimize end effects. The platinum surfaces were coated with platinum black, as for conductance cells; this vastly improved the constancy of the bridge readings at different frequencies. Though three-terminal cell designs are usually preferred for precise capacitance measurements, these were not possible with the pressure-bomb available to us, as this had only a single insulated electrical connection to the inside. Nevertheless, we believe that our cell design shows no significant disadvantages.

The cell was filled with the liquid under study and a thin P.V.C. bulb full of the liquid was attached to the filling-tube H to take up volume changes. The inner electrode was connected to the insulated pressure-sealed lead of the bomb, and the outer one to the earthed bomb casing. The pressure-vessel was filled with transformer oil. Pressure was developed by a small-stroke hand-operated piston pump, and measured on a large Bourdon gauge readable within ~ 1.5 bar, which had been calibrated against a dead-weight gauge by the Defence Standards Laboratory. The vessel was immersed in an oil thermostat controlled to better than 0.01°C. Temperatures were measured with a Dymec quartz oscillator thermometer calibrated against a platinum resistance thermometer.

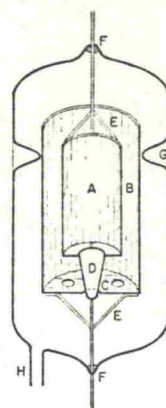


FIG. 1.—High pressure capacitance cell.

CALIBRATION OF THE CAPACITANCE-CELL

The cell was calibrated by two independent methods: (a) the capacitance at 25°C was measured with air and then deionized distilled water at 1 atm in the cell. Using the value of 78.30₄ given by Malmberg and Maryott⁷ for the relative permittivity of water at 25°C, and