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

By L. A. DUNN* AND R. H. STOKES

Department of Physical Chemistry, University of New England, Armidale, N.S.W. 2351, Australia.

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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.

* present address: Chem. Dept., University of Tasmania, Hobart, Australia.

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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

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

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.

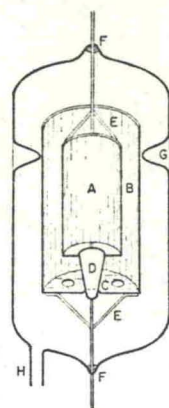


FIG. 1.—High pressure capacitance cell.

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

taking that of air from standard tables, lead capacitances were eliminated giving a vacuum capacitance $C_0 = 4.356$ pF. (b) The cell was filled with a dilute solution of tetra-ethyl ammonium iodide in ethanol, and the resistance R of this solution was measured at 25° with a Leeds and Northrup Jones-Dike conductance bridge. The conductance κ of the solution was also measured in normal calibrated conductance cells. The cell-constant J of the capacitance-cell was then calculated as $J = R\kappa$. Since the electric field distribution is the same whether the cell is used for conductance or capacitance, the corresponding cell constants are related by

$$JC_0 = 8.854 \times 10^{-16} \text{ farad m}^{-1}.$$

This method also yielded $C_0 = 4.356$ pF. For other temperatures and pressures, values of $C_0 = 4.356$ pF. For other temperatures and pressures, values of C_0 were calculated from the thermal expansion coefficients and compressibilities of platinum and Pyrex and the geometry of the cell.

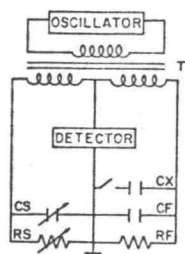


FIG. 2.—Transformer bridge.

TRANSFORMER BRIDGE

A balanced, screened equal-arm transformer T (fig. 2) was specially built for bridge use. It was energized by an oscillator providing several volts at 10-520 kHz. The out-of-balance signal from the bridge was displayed on an oscilloscope. The standard arm of the bridge consisted of a calibrated General Radio 722 D precision capacitor CS , in parallel with a resistance-balance element RS which was specially designed to show a negligible capacitance-change with change of resistance setting. CF and RF were fixed capacitance and resistance elements used to bring the standard arm readings to a suitable point on the scale. CX represents the dielectric cell, which could be switched in or out by unplugging a coaxial cable. An alternative substitution mode of the bridge was also available and was used for some of the measurements; the extrapolated capacitances in this mode agreed with the direct-reading ones within the reading uncertainty. A parallel $R-C$ network with set values can match the impedance of the capacitance-cell at all frequencies only if the equivalent circuit of the cell is also a parallel $R-C$ network. This is an oversimplification for any real cell containing a conducting liquid, because of the unusual frequency dependence of the Warburg impedance W of the solution-electrode interface (fig. 3). However, the coating

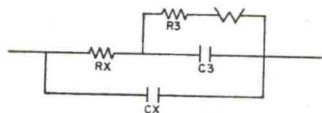


FIG. 3.—Network electrically equivalent to capacitance cell.

of the electrodes with platinum black has the effect of shunting this awkward component of the impedance by a large simple capacitance $C3$, greatly reducing its influence on the apparent values of CX and RX . Graphs of the capacitance in the substitution network against f^{-1} (f = frequency) were linear within 0.02% over the range 10-520 kHz and the total change in capacitance over this range was only 0.15%. Values extrapolated to infinite frequency on such graphs (fig. 4) were used in calculating all permittivities reported here.

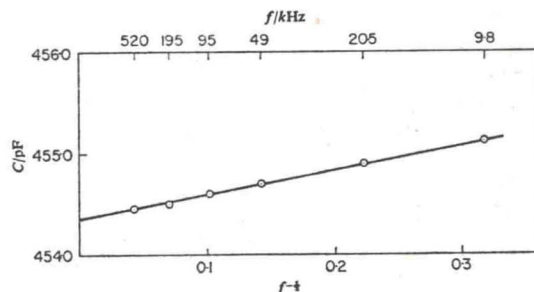


FIG. 4.—Frequency dependence of capacitance; formamide at 45°C, 1 bar.

Since there is no dispersion in the frequency-range used, the permittivities so obtained are static values. The validity of the extrapolations is indicated by the fact that for most of the samples used the resistive component RX of the cell impedance decreased with time (owing to ionic contamination) without affecting the constancy of the extrapolated capacitance. In tests with water, the same results were obtained for highly purified water of conductance $8 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$, and a relatively contaminated sample of conductance $\sim 1 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$. The resistance of the cell contents could drop to a few hundred ohms without affecting the extrapolated capacitance readings.

TABLE 2.—DIELECTRIC CONSTANTS OF WATER AT 1 BAR IN THE TEMPERATURE RANGE 5-65°C

$t/^\circ\text{C}$	ϵ	$\delta\epsilon$	$-10^4 (\partial \ln \epsilon / \partial t)_p = 1 \text{ bar}$
5	85.75 ₂	0.005	4.54 ₂
10	83.82 ₂	0.003	4.54 ₂
15	81.97 ₂	-0.025	4.54 ₇
20	80.10 ₀	0.005	4.54 ₈
25	78.30 ₀ *	0.000	4.54 ₈
30	76.54 ₁	0.003	4.54 ₈
35	74.81 ₀	0.005	4.54 ₆
40	73.15 ₀	-0.008	4.54 ₄
45	71.50 ₃	-0.004	4.54 ₁
50	69.89 ₃	0.002	4.53 ₇
55	68.33 ₆	-0.008	4.53 ₂
60	66.80 ₂	-0.004	4.52 ₆
65	65.30 ₃	0.002	4.51 ₉

ϵ (1 bar) = $87.727 - 0.398 t + 8.699 \times 10^{-4} t^2 - 7.948 \times 10^{-7} t^3$ (1). $\delta\epsilon = \epsilon$ (eqn (1)) - ϵ .

* calibration point.

RESULTS

WATER.—Measurements at 1 bar were made at 5 deg intervals from 5 to 65°C (table 2). The pressure-dependence was measured at 10, 25, 45 and 65°C (table 3).

FORMAMIDE.—Table 4 gives results at 1 bar in the range 5-60°C. Pressure runs were made at 10, 25 and 45°C (table 5). The pressure range at 10°C is restricted by the need to avoid solidification. At the foot of each table are eqn (1)-(4) fitted to the data by least-squares methods. Eqn (2) and (4), analogues of the Tait equation, gave much more satisfactory representations of the data than did simple polynomials in *P*.

TABLE 3.—DIELECTRIC CONSTANTS OF WATER AT VARIOUS TEMPERATURES AND PRESSURES

<i>P</i> /bar	10°C	25°C	45°C	65°C
1	83.82 ₈	78.30 ₄	71.50 ₃	65.30 ₃
163	84.42 ₁	78.85 ₂	72.05 ₁	65.87 ₉
339	85.08 ₁	79.47 ₈	72.62 ₇	66.45 ₁
517	85.75 ₇	80.10 ₂	73.25 ₁	67.03 ₁
689	86.37 ₄	80.67 ₆	73.82 ₃	67.54 ₆
862	86.99 ₈	81.30 ₃	74.35 ₂	68.01 ₈
1034	87.60 ₃	81.83 ₁	74.89 ₉	68.54 ₆
1207	88.23 ₇	82.40 ₁	75.45 ₂	69.03 ₃
1379	88.81 ₆	82.99 ₈	75.95 ₁	69.50 ₂
1551	89.38 ₁	83.49 ₈	76.41 ₃	69.90 ₅
1724	89.94 ₈	84.02 ₃	76.92 ₄	70.38 ₃
1896	90.52 ₈	84.54 ₆	77.42 ₃	70.84 ₉
2068	91.10 ₀	85.09 ₃	77.90 ₀	71.27 ₄

At fixed temperatures,

$$\epsilon(P) = A + [BP/(1 + CP)], \quad (2)$$

where *A*, *B*, *C* have the following values:

<i>t</i> /°C	<i>A</i>	10 ³ <i>B</i> /bar	10 ³ <i>C</i> /bar	<i>P</i> _{max} /bar	s.d. of ϵ
10	83.810	3.840 9	4.394 5	2 100	0.012
25	78.281	3.618 1	4.840 0	2 100	0.018
45	71.486	3.529 4	6.730 0	2 100	0.016
65	65.324	3.403 0	9.0345	2 100	0.021

TABLE 4.—DIELECTRIC CONSTANTS OF FORMAMIDE AT 1 BAR IN THE TEMPERATURE RANGE 5-60°C

<i>t</i> /°C	ϵ	$\delta\epsilon$	$-10^3 (\partial \ln \epsilon / \partial t)_P = 1 \text{ bar}$
5	117.19	-0.02	3.50
10	115.07	0.04	3.57
15	113.04	0.01	3.64
20	111.00	-0.01	3.70
25	109.03	-0.08	3.75
30	106.85	0.05	3.80
35	104.89	0.00	3.84
40	102.87	0.01	3.88
45	100.89	0.00	3.90
50	98.92	0.03	3.92
55	97.09	-0.06	3.93
60	95.11	0.03	3.92

$$\epsilon(1 \text{ bar}) = 119.208 - 0.408 3 t - 2.311 \times 10^{-4} t^2 + 5.833 \times 10^{-6} t^3, \quad (3)$$

$$\delta\epsilon = \epsilon(\text{eqn (3)}) - \epsilon$$

TABLE 5.—DIELECTRIC CONSTANTS OF FORMAMIDE AT VARIOUS TEMPERATURES AND PRESSURES

<i>P</i> /bar	10°C	25°C	45°C
1	115.06 ₆	109.02 ₇	100.89 ₃
20	115.17 ₂	109.14 ₆	101.01 ₂
50	115.30 ₈	109.30 ₀	101.15 ₁
120	115.64 ₉	109.64 ₂	101.51 ₄
156	115.81 ₀	109.80 ₃	101.73 ₁
195	115.99 ₀	109.98 ₅	101.90 ₇
339	116.69 ₀	110.64 ₁	102.60 ₇
414	117.00 ₃	110.96 ₆	102.98 ₇
517	117.47 ₀	111.38 ₃	103.45 ₃
689	118.14 ₆	112.08 ₃	104.15 ₃
862	118.78 ₃	112.75 ₁	104.85 ₃
1034		113.32 ₃	105.55 ₃
1207		114.01 ₀	106.17 ₆
1379		114.59 ₃	106.75 ₄
1551		115.11 ₃	107.28 ₁
1724		115.64 ₇	107.81 ₃
1896		116.15 ₃	108.31 ₁
2068		116.64 ₇	108.76 ₃

At fixed temperatures,

$$\epsilon(P) = A + [BP/(1 + CP)], \quad (4)$$

where *A*, *B*, *C* have the following values:

<i>t</i> /°C	<i>A</i>	10 ³ <i>B</i> /bar	10 ³ <i>C</i> /bar	<i>P</i> _{max} /bar	s.d. of ϵ
10	115.054	5.133 5	2.116 9	900	0.014
25	109.055	4.880 1	1.598 2	2 100	0.020
45	100.888	5.474 8	2.105 1	2 100	0.015

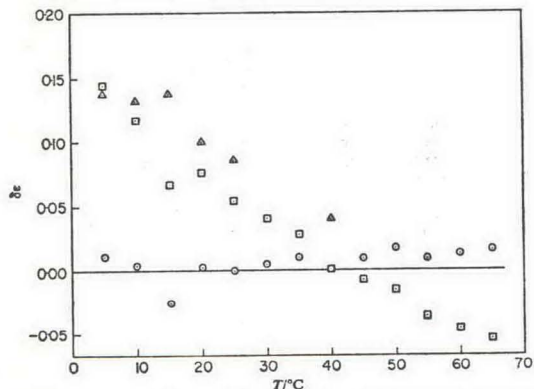


FIG. 5.—Dielectric constants of water at 1 bar—comparison with earlier work. $\delta\epsilon = \epsilon(\text{lit.}) - \epsilon$ (this work): \circ , ref. (7); \square , ref. (3); \triangle , ref. (9).

ELECTRICAL PERMITTIVITIES

COMPARISONS WITH OTHER DATA

WATER.—Fig. 5 compares our results at 1 bar (solid line) with those of three recent high-precision studies. Our results agree well with those of Malmberg and Maryott⁷ at all temperatures. Those of Owen *et al.*³ and of Vidulich and Kay⁹ are up to 0.14 higher at low temperatures, and cross ours at 40°C. Owen *et al.*³ used a radio-frequency technique. We cannot explain this difference, especially as our measurements of the pressure-dependence at constant temperature agree well with those of Owen *et al.*³ as shown in table 6 where values of $(\partial \ln \epsilon / \partial P)^*$ calculated from eqn (2) are compared with the corresponding values given by the equation of Owen *et al.*³

TABLE 6.—PRESSURE-DEPENDENCE OF THE DIELECTRIC CONSTANT OF WATER

P/bar	10°C		25°C		45°C		65°C	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
1	45.82	45.84	46.21	47.10	49.36	49.18	52.08	51.72
200	44.63	44.68	44.93	45.67	47.61	47.47	49.75	49.83
400	43.48	43.53	43.69	44.24	45.93	45.76	47.57	47.93
600	42.37	42.37	42.50	42.81	44.35	44.05	45.52	46.03
800	41.31	41.21	41.37	41.38	42.85	42.34	43.61	44.13
1000	40.28	40.05	40.27	39.95	41.43	40.63	41.82	42.23

FORMAMIDE.—The only other data at 1 bar are those of Leader⁴ at temperatures of 15–35°C. His cell was calibrated with water using an older value. On adjusting to the basis $\epsilon_{H_2O}(25^\circ\text{C}, 1\text{ bar}) = 78.30$ his results agree with ours within 0.1%. No other results at high pressures have been reported. Values of $(\partial \ln \epsilon / \partial P)$ for formamide calculated from eqn (4) are given in table 7.

TABLE 7.—PRESSURE-DEPENDENCE OF THE DIELECTRIC CONSTANT OF FORMAMIDE AT 1 BAR

t/°C	$10^4(\partial \ln \epsilon / \partial P)^*/\text{bar}^{-1}$
10	44.59
25	44.73
45	54.24

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Heat Conductivity of the Slowly Dissociating System
 $2\text{NO}_2 \rightleftharpoons 2\text{NO} + \text{O}_2$ from 200 to 400°C

By T. K. RAI DASTIDAR, P. K. BHATTACHARYYA AND A. K. BARUA,
Indian Association for the Cultivation of Science, Calcutta-32, India

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The thermal conductivity of the slowly dissociating system $2\text{NO}_2 \rightleftharpoons 2\text{NO} + \text{O}_2$ has been measured from above 200 to 400°C by the hot wire technique. On comparison of the experimental data with the theories of heat transfer in reacting gases, it is found that the effect of chemical reaction upon the heat conductivity is apparent at 350°C and higher temperatures, while at 300°C and below it is negligibly small. However, the present theories of heat conductivity in reacting gas mixtures are found to be inadequate to account for the effects quantitatively.

The problem of heat transfer in dissociating and chemically reacting gas mixtures has been treated theoretically by Hirschfelder¹ and Butler and Brokaw² by assuming local chemical equilibrium. Subsequently, Secret and Hirschfelder³ considered the effect of relaxation of chemical energy on the heat conductivity. A more rigorous treatment of relaxation effects was given by Brokaw⁴ when the departure from the local chemical equilibrium is slight. It has been suggested by Rai Dastidar and Barua⁵ that, owing to the effect of chemical reaction on diffusion, the heat transport due to chemical enthalpy will be less than that obtained by using the diffusion coefficient calculated on the Chapman-Enskog theory.⁶ This effect, which should be present even when the condition of local chemical equilibrium is satisfied, has been confirmed by experiment.⁷

For the $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ system the reaction rate is fast but that for $2\text{NO}_2 \rightleftharpoons 2\text{NO} + \text{O}_2$ is slow at ordinary temperatures and the effect of chemical reaction on heat conductivity is almost negligible. However, this rate increases with the increase of temperature.⁸ Consequently at higher temperatures transport of chemical enthalpy should play a significant role. Experiments on the system $2\text{NO}_2 \rightleftharpoons 2\text{NO} + \text{O}_2$ have been previously confined to the range below 200°C. A study of the heat conductivity of this system at higher temperatures would enable a more critical test of the range of validity of Brokaw's theory to be made. In this paper we report the heat conductivity of $2\text{NO}_2 \rightleftharpoons 2\text{NO} + \text{O}_2$ in the temperature range 200–400°C and at various pressures.

EXPERIMENTAL

For the heat conductivity measurements, the thick-wire-variant of the hot-wire method was used. The conductivity cell used was similar to that of Rai Dastidar and Barua.⁷ The electrical leads were insulated from the bath liquid by porcelain insulators enclosed in stainless steel tubes. The cell was immersed in a high-temperature bath prepared by melting a mixture of sodium and potassium nitrates taken in equal proportions. The insulation between the electrical leads and the body of the cell prevents any electrolytic action in the bath liquid. The temperature was controlled by an electronic controller; the control at the highest temperature was $\pm 0.2^\circ\text{C}$ and better than this at the lower temperatures.

To provide a steady state in the cell, a large cube made of stainless steel (volume 500 ml)