INVESTIGATION OF THE TEMPERATURE DEPENDENCE OF DIELECTRIC CONSTANT AND ITS FIRST DERIVATIVE FOR LIQUIDS AND SOLUTIONS

Part 1.—Some Preliminary Measurements on Benzene

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As an extension of previous investigations of the first temperature derivatives of viscosity, density, and refractive index of various liquids and solutions, some preliminary measurements are reported here for the first derivative of *dielectric constant*, ε, of benzene from 28°C. to 41°C. The measurements are made by filling benzene in a coaxial cylindrical capacitance cell, constructed specially for the purpose, and the quantity $\frac{1}{\varepsilon}\Delta\varepsilon/\Delta T$ is obtained for intervals ΔT of 2°C. The results show an approximately sinusoidal variation, having a period of about 6°C., and an amplitude of about ± 30 percent about the mean value. Other liquids are being studied.

Introduction

Over the last decade, a considerable amount of experimental work has been carried out by Qurashi and coworkers on determining the temperature variation of the activation energy, E_η, for viscous flow of various liquids and solutions. The results have led, on the one hand, to the finding of periodic oscillations in this energy for ethyl alcohol,[1] benzene[2] and certain other hydrocarbons,[3] and to the discovery of a step-like energy-level structure for the activation energy for water,[4] ethylene glycol,[5] dilute aqueous alcohol[6] and some aliphatic hydrocarbons.[7]

In an effort to elucidate these phenomena, a programme was initiated for making similar measurements of the coefficient of dilatation β and refractive index n, as well as their first derivatives with temperature, i.e. $\delta\beta/\delta T$ and $\delta n/\delta T$. Some experiments along these lines have so far been carried out on $\delta\beta/\delta T$ and $\delta n/\delta T$ for water,[8,9] and on β for ethylene glycol,[10] and currently benzene is being studied. These investigations have so far indicated that periodicities exist in these properties as well, and are moreover definitely correlated with the steps and the cyclic oscillations previously observed in E_η. The refractive index proved especially interesting, and it was therefore considered worthwhile to undertake a similar study of the temperature variation of the dielectric constant, ε, and its first derivative i.e. $\delta\varepsilon/\delta T$. Such a study is expected to be of great value in view of the ideas put forward at the 1962 Conference on Liquids[11] that a correlation probably exists between the anomalies found in the viscous behaviour and the dielectric relaxation phenomena measured at radio-frequencies in several liquids.

Accordingly, the present communication gives a brief account of some of the preliminary experiments carried out on benzene, using a measuring interval of 2° to 3°C. in the narrow range of 30°C. to 45°C.

Experimental Technique

The basic idea is to measure the small changes $\Delta\varepsilon$ in the dielectric constant from measurements taken at small intervals of temperature ΔT, and calculate $\frac{1}{\varepsilon}\Delta\varepsilon/\Delta T$. Now if the fixed (parallel-plate or cylindrical) capacitor is filled with the liquid under test, and the capacity C measured at two temperatures T, and $T+\Delta T$, then we have

$$C = \varepsilon \times C_{vac}. \quad (1)$$

whence

$$\Delta C = C_{T+\Delta T} - C = C_{vac} \times \{\varepsilon_{T+\Delta T} - \varepsilon_T\} = C_{vac} \times \Delta\varepsilon$$

and

$$\Delta \ln \varepsilon = \frac{\Delta\varepsilon}{\varepsilon} = \frac{\Delta C}{C}, \quad (2)$$

so that

$$\frac{\Delta \ln\varepsilon}{\Delta T} = \frac{\Delta\varepsilon}{\varepsilon\Delta T} = \frac{1}{C} \cdot \frac{\Delta C}{\Delta T} \quad (3)$$

It is seen that the constant C_{vac} disappears from (3), which provides the basic equation for our measurements, and is comparable with the equation previously used for obtaining E_η from the viscosity measurements. Care must of course be taken to note that C has to be corrected for stray capacitance of the leads, etc., from the capacitor to the measuring set-up, while ΔC is independent of this effect. Two types of capacitors were made for this experiment: first a parallel-plate type with two plates of 75 sq. cm. area and variable distance, mounted between two thick glass plates held apart by spacers; and then a cylindrical condenser having an outer metal cylinder of 6.47 cm. diameter and 18 cm. height, with an inner coaxial cylinder of 14 cm. height and 5.71 cm. diameter suspended from an ebonite disc fitted in the outer cylinder, thus leaving an annular space of nearly 4 mm. between the two cylinders and a gap of 1 cm. between the bottom of the outer and inner cylinders (Fig. 1). The parallel-plate capacitor was tried in a few preliminary experiments, but was later rejected in favour of the cylindrical coaxial design.

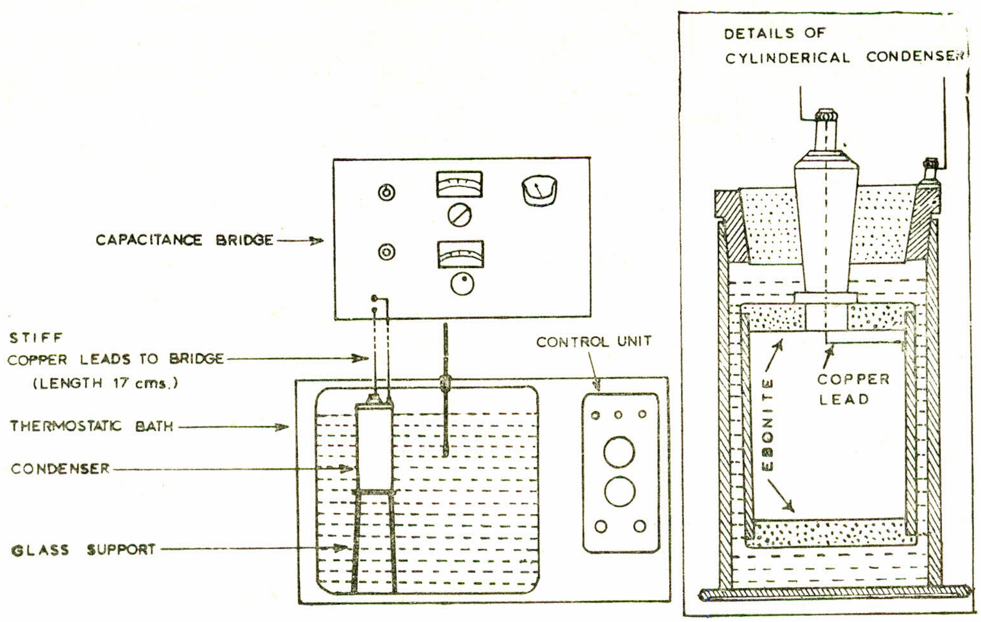

Fig. 1.—Diagrammatic sketch of the coaxial cylindrical condenser constructed for liquids, placed inside the thermostatic water bath. The constructional details of the condenser are shown alongside.

The cylindrical capacitor of about 70 $\mu\mu F$ capacity in air was filled, to a mark about 1 cm. above the top of the inner cylinder, with liquid, and the outer cylinder was itself immersed (up to well above the liquid level) in a thermostatically controlled water bath, as shown in Fig. 1. For measuring the capacitance, various bridges were tried for stability and precision, and finally a Boonton Model 75A-S8 bridge working at one Megacycle/Sec. was adopted. This bridge has one decade-reading dial and a vernier dial subdivided into 250 equal divisions, and it will give a precision of 2 parts in 10,000 under favourable circumstances.

Results and Discussion

In the first set of measurements with benzene, the range from 31°C. to 41°C. was covered in eight steps, and five readings were taken at each temperature, the zero setting of the bridge being reset each time. The results are shown in Table 1(a), together with the r.m.s. scatter of the mean capacitance at each temperature and values of $\Delta C/\Delta T$ for intervals of 2° to 3°C. It is seen that the values of $\Delta C/\Delta T$ are reliable to within 25 percent, and have been plotted in Fig. 2(a) as solid circles with the short vertical lines through them representing the r.m.s. experimental errors.

Since this limited data shows a regular smooth variation in $\Delta C/\Delta T$, the experiment was repeated (with more careful zero resetting) from 32°C. to 42°C., and these results are given in Table 1(b) and plotted as hollow circles in Fig. 2(a). This plot resembles the earlier one, but displaced sideways a little, and the bottom curve in Fig. 2(b) is a combined plot of both sets of data. The second scale for the ordinates shows the quantity

TABLE I (a).—MEASUREMENT OF CAPACITANCE OF THE CYLINDRICAL CONDENSER CONTAINING BENZENE AT DIFFERENT TEMPERATURES AND DEDUCEED VALUES OF $\Delta C/\Delta T$.

Temp. (°C.)	Capacitance C (in $\mu\mu$ Farads) Actual readings	Mean	ΔC for alternate readings (in $\mu\mu$ Farads)	$\frac{\Delta C}{\Delta T}$
31.00	147.00 146.65 146.64 146.25 146.45	146.60±0.12		
31.99	146.10 146.60 146.30 146.70 146.10	146.36±0.12	+0.06±0.16	+0.03±0.08
32.99	146.95 147.20 147.10 146.10 145.95	146.66±0.26	+0.30±0.16	+0.12±0.06
34.53	146.55 146.65 146.80 146.60 146.70	146.66±0.10	−0.20±0.16	−0.07±0.05
36.02	146.75 146.45 146.90 146.05 146.15	146.46±0.16	−0.82±0.16	−0.31±0.06
37.18	146.35 145.88 145.70 145.70 145.70 145.68	145.84±0.11	−0.54±0.16	−0.27±0.08
38.00	145.93 145.91 145.92 145.90 145.93	145.92±0.01	+0.14±0.16	+0.07±0.08
39.15	146.00 145.95 145.99 145.93 145.99 145.96 145.99 145.99	145.98±0.01	+0.08±0.16	+0.04±0.08
39.81	146.00 145.95 146.00 146.05 146.00	146.00±0.02	+0.04±0.16	+0.02±0.08
40.91	146.00 145.95 146.10 146.10 146.00 146.00 146.00 146.00	146.02±0.02		

R.M.S. deviation of ten readings=±0.12.

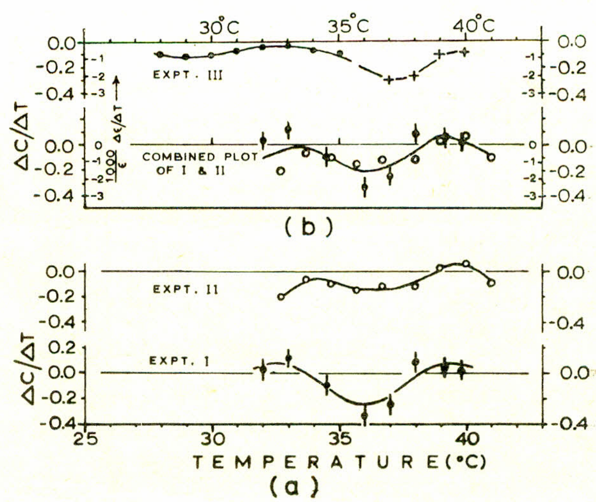

Fig. 2(a).—Graphs showing experimental measurements of $\Delta C/\Delta T$ in the range of 32° to 41°C. It is seen that there is a general correspondence between the results of Experiment I and Experiment II.

Fig. 2(b).—The lower graph shows a combined plot of the data of Experiment I and Experiment II providing evidence for the existence of a sinusoidal variation with a period of about 6°C. The upper graph shows the results obtained from a more refined experiment in which the zero adjustment of the capacitance bridge was made once for all and the residual drift was corrected by taking the mean of measurements during heating and cooling. The graph shows the improved accuracy obtained and confirms the previously noted sinusoidal variations. The inner scale for this ordinates denotes $\frac{1000}{\varepsilon}\Delta\varepsilon/\Delta T$.

$\frac{1000}{\varepsilon}\Delta\varepsilon/\Delta T$. While this combined graph does show a definite undulatory behaviour with a period of 5° to 6°C., it is clear that an increase in the precision of $\Delta C/\Delta T$ is called for, because the r.m.s. scatter of the points about the mean graph is ±0.1 and ±0.05 for the data of Expt. I and II, respectively.

TABLE 1(b).—REPEAT MEASUREMENTS OF CAPACITANCE AND $\Delta C/\Delta T$ FOR THE CYLINDRICAL CONDENSER CONTAINING BENZENE.

Temp. (°C.)	Capacitance C (in $\mu\mu$ Farads) Actual readings	Mean	ΔC (in $\mu\mu F$) for alternate readings	$\frac{\Delta C}{\Delta T}$
32.10	144.10 144.15 144.15 144.10 144.10	144.12±0.01		
32.69	143.92 143.92 143.90 143.88 143.82 143.82 143.83	143.87±0.02	−0.32±0.02	−0.198±0.01
33.72	143.80 143.80 143.80 143.80 143.79	143.80±0.00	−0.12±0.02	−0.060±0.01
34.68	143.70 143.70 143.78 143.79 143.79	143.75±0.02	−0.19±0.02	−0.097±0.01
35.68	143.60 143.64 143.60 143.62 143.60 143.62	143.61±0.01	−0.29±0.02	−0.143±0.01
36.70	143.45 143.48 143.45 143.48 143.46 143.46	143.46±0.01	−0.26±0.02	−0.112±0.01
38.00	143.34 143.34 143.36 143.36 143.36	143.35±0.01	−0.27±0.02	−0.118±0.01
39.01	143.18 143.16 143.18 143.20 143.25	143.19±0.03	+0.06±0.02	+0.027±0.01
40.21	143.42 143.42 143.40 143.40 143.41	143.41±0.01	+0.13±0.02	+0.064±0.01
41.06	143.32 143.30 143.32 143.34 143.32	143.32±0.01	−0.16±0.02	−0.093±0.01
41.93	143.24 143.22 143.25 143.28 143.28 143.26	143.25±.01		

R.M.S. deviation = ±0.015.

As a first step in this direction, it was decided to dispense with the adjustment of the zero-setting knob for each reading, and instead to wait for one to two hours before commencing the experiment, so as to allow this setting to achieve sufficient stability. Also, in order to cancel the effect of any remaining slow drift of the zero, the readings were first taken during the heating of the thermostatic bath and then while cooling the bath. The mean of the two values of $\Delta C/\Delta T$ thus obtained at each temperature will now be substantially independent of error due to this cause, as well as any similar systematically varying error. Table 2 shows the results obtained from two such experiments, one from 27° to 36°C., and the other from 36°C. to 41°C. The stability is seen to be of the order of $\pm 0.01 \mu\mu F$, which is excellent, and the fluctuation in differences between the values of $\Delta C/\Delta T$ for heating and cooling is about 0.05 $\mu\mu$ F/°C. The mean values of $\Delta C/\Delta T$ are plotted as solid circles and crosses in the top of Fig. 2(b), and a smooth curve is drawn through them, the r.m.s. scatter of the points about this curve being of the order of ± 0.02. The inside scale for the ordinates represents $\frac{1000}{\varepsilon} \Delta\varepsilon/\Delta T$, as obtained from equation(3).

This curve confirms the lower graph of Fig.2(a) based on the earlier approximate measurements, and the two pairs of maxima correspond to within 1°C. It can now be concluded that the values of $\frac{1}{\varepsilon}\Delta\varepsilon/\Delta T$ for benzene show evidence of a roughly sinusoidal variation, having a period of the order of 6°C. and an amplitude of nearly ±30 percent of the mean value, which is about -1×10^{-3}. These findings bear comparison with our reported measurements of $E\eta$ for benzene,[7] and with similar experiments already being carried out to investigate the behaviour of the coefficient of dilatation and refractive index of benzene, which will be reported separately. In the meantime, the dielectric measurements of $\frac{1}{\varepsilon}\Delta\varepsilon/\Delta T$ are

TABLE 2.—REFINED MEASUREMENTS OF CAPACITANCE AND ΔC/ΔT FOR CYLINDRICAL CONDENSER CONTAINING BENZENE.

Measurements with rising temperature				Measurements with falling temperatures				
Temp. °C.	Mean value of capacity in μμ Farads	ΔC for alternate readings	ΔC/ΔT	Temp. °C.	Mean value of capacity in μμ Farads.	ΔC for alternate readings	ΔC/ΔT	Mean value of ΔC/ΔT
27.00	143.64±0.005			27.00	143.41±0.002			
28.00	143.58±0.002	−0.18±0.003	−0.09±0.002	27.95	143.35±0.002	−0.20±0.005	−0.10±0.002	−0.095±0.02
29.00	143.46±0.004	−0.23±0.003	−0.115±0.002	28.95	143.21±0.003	−0.24±0.005	−0.12±0.002	−0.12±0.02
30.01	143.35±0.003	−0.20±0.003	−0.10 ±0.002	29.96	143.11±0.010	−0.20±0.005	−0.10±0.002	−0.10±0.02
30.98	143.26±0.003	−0.18±0.003	−0.09 ±0.002	30.94	143.01±0.001	−0.12±0.005	−0.06±0.002	−0.08±0.02
31.99	143.17±0.003	−0.17±0.003	−0.085±0.002	31.96	142.99±0.003	−0.02±0.005	−0.01±0.002	−0.05±0.02
33.03	143.09±0.004	−0.16±0.003	−0.08 ±0.002	32.92	142.99±0.004	−0.01±0.005	−0.005±0.002	−0.04±0.02
33.98	143.01±0.003	−0.21±0.003	−0.105±0.002	34.00	142.98±0.004	−0.07±0.005	−0.035±0.002	−0.07±0.02
35.24	142.88±0.003	−0.20±0.003	−0.10 ±0.002	35.00	142.92±0.005	−0.17±0.005	−0.085±0.002	−0.09±0.02
35.99	142.81±0.004			39.99	142.81±0.004			
	R.M.S. deviation =±0.003				R.M.S. deviation =±0.005			
36.00	142.77±0.003			36.00	140.64±0.002			
37.01	142.39±0.001	−1.16±0.004	−0.58±0.002	37.00	140.67±0.007	−0.01±0.004	−0.005±0.002	−0.29±0.05
38.01	141.61±0.003	−1.10±0.004	−0.55±0.002	38.00	140.63±0.003	−0.05±0.004	−0.025±0.002	−0.28±0.05
39.02	141.29±0.001	−0.41±0.004	−0.205±0.002	39.00	140.62±0.002	−0.03±0.004	−0.015±0.002	−0.11±0.05
40.02	141.20±0.002	−0.38±0.004	−0.19±0.002	39.98	140.60±0.003	−0.01±0.004	−0.005±0.002	−0.10±0.05
41.02	140.91±0.006			41.00	140.61±0.004			
	R.M.S. deviation =±0.004							

being extended to (1) cover a larger range of temperatures for benzene and (2) examine other liquids.

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