Relative permittivity of organic liquids as a function of pressure and temperature

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Abstract. Precision measurements of the relative permittivity of n heptane at pressures up to 3334 bar and over a temperature range from 0 to 100 °C are reported. Similar data for carbon tetrachloride up to 1118 bar and at temperatures from 25 to 54 °C have also been obtained. The data have been fitted to various empirical and theoretical expressions involving relative permittivity, making use, where necessary, of densities determined by other workers.

1. Introduction

Theories describing the equilibrium behaviour of dielectric materials can be best tested experimentally if relative permittivity and density can be varied isothermally as well as isobarically. The first such measurements on liquids subjected to hydrostatic pressure were made by Röntgen (1894) and Ratz (1895). Other workers followed this lead but experimental techniques did not permit sufficient precision for critical appraisal of alternative theories until comparatively recently. The use of three-terminal test cells together with transformer ratio-arm bridges such as were developed by Blumlein (Clark and Vanderlyn 1949) and Cole (Cole and Gross 1949) has helped minimize spurious effects arising from changes in the shunt capacitance of test leads to earth. If the test cell itself is constructed with proper guard electrodes, for example Mopsik (1967), and Scaife and Lyons (1970), reliable determinations of relative permittivity are possible. Ideally measurements of density and permittivity should be made simultaneously on the same sample, and the work of Mopsik (1967, 1969) was carried out in this manner. However, to obtain precision in either measurement is a considerable undertaking and more commonly separate determinations are made. This approach leads to stringent demands on measurement of temperature, pressure and also on the purity of sample. Work is reported here on two liquids, n heptane and carbon tetrachloride, which were chosen because very precise information on density as a function of pressure and temperature was available for them.

2. Equipment

The design of the three-terminal, guarded electrode test cell and its encapsulation has been described elsewhere (Scaife and Lyons 1970). The General Radio transformer ratio bridge type 1615-A was used, which permitted a sensitivity of balance in the region of one or two parts per million using a sample with a capacitance of between 1 pF and 2 pF. The quoted accuracy of the bridge under the conditions which existed was $\pm 0.01\%$ in capacitance and $\pm (0.1\% + 0.00001)$ in loss tangent. The cell assembly was housed in a pressure vessel with a bore of 23 mm and having a 110 mm working length. Pressure fluid was supplied by an intensifier operated by a hand pump. A T-junction connected the pressure line to a Budenberg pressure balance. This had a certified accuracy of $\pm 0.03\%$. The upper limit of the pressure balance was 3500 kgf cm^{-2}. The pressure vessel was immersed in a double-compartment

temperature bath. In one compartment were located heater coils, refrigeration coils and a circulating pump; the pressure vessel was located in the other compartment. The entire bath was thermally insulated. For temperatures below 50 °C, kerosene was used as bath liquid, and above this a heavier mineral oil intended for use in electric power transformers. Temperature was controlled by a controller operating in the proportional mode which used a resistance thermometer probe to sense the temperature of the bath liquid. Bath temperature was measured by a Digitec model 5015 thermistor probe instrument which had a digital read out. The precision of ± 0.25 °C claimed in the range 0–100 °C was verified against melting-point standards. In addition, a Thermocoax chromel–alumel thermocouple was located inside the pressure vessel between the cell and the top closure plug. The thermocouple, like the two leads to the test cell, was mineral insulated and steel sheathed and was brazed into the closure plug. The thermocouple was calibrated against the Digitec instrument. The thermocouple voltage was measured on a Keithley digital differential voltmeter type 662 which has a resolution of 1 μV; it was also fed through a Keithley type 150B microvolt ammeter amplifier to a pen recorder. In this way the temperature transients accompanying compression and decompression could be readily followed. For measurements above room temperature, a commercial hydraulic mineral oil was used as pressure-transmitting fluid. At lower temperatures kerosene was used in the pressure vessel. Below room temperature cooling was provided by a standard refrigeration unit, the coils of which were passed into one of the compartments of the bath.

It is inherent in the operation of the pressure balance that oil should leak slowly but continuously past the loading piston. This required continual fine adjustments to maintain the pressure of the system at the desired value. For this purpose the small intensifier fitted to the pressure balance was employed.

3. Results

3.1. *n heptane*

The cell and its enclosure were subjected to a rough vacuum and the test liquid was then allowed to be drawn in by this vacuum. No purification or further degassing of the sample was attempted. The sample was Messrs Fluka's purissimus grade, better than 99·92% pure, catalogue A54362, with a stated relative density of 0.6838 g cm^{-3} at 20 °C. The results of measurements at various temperatures are given in table 1. In most cases two readings were taken, one during rising and one during falling pressure. A frequency of 1 kHz was used at a field strength of 20 kV m^{-1}. Conductivity as measured by the tangent of the loss angle was very small, of the order of 10^{-12} S m^{-1} or less. It was reduced by pressure and increased by temperature.

The choice of *n* heptane for study was determined by the very extensive density data which are available from the work of Simon *et al.* (1960) as well as from the earlier work of Eduljee *et al.* (1951). All these data were collated by Doolittle and Doolittle (1960) who used the Hudleston (1937) equation† which can be written as follows:

$$\ln\left(\frac{(v_T{}^p)^{2/3}p}{(v_T{}^0)^{1/3} - (v_T{}^p)^{1/3}}\right) - A_T - B\{(v_T{}^0)^{1/3} - (v_T{}^p)^{1/3}\} = 0. \qquad (3.1.1)$$

† This equation is readily solved for $v_T{}^p$ at a given pressure by using a Newton–Raphson iteration method. Particularly if a computer program is used for this purpose, the initial guess for $v_T{}^p$ should be a good one; a value of $0.9999\,v_T{}^0$ is satisfactory.

Table 1. Measured relative permittivity and density (g cm⁻³), calculated from equation (3.1.1), of *n* heptane as function of temperature and pressure

p(bar)	0(°C) ε	ρ	10(°C) ε	ρ	20(°C) ε	ρ	30(°C) ε	ρ
1·0	1·9493 1·9495	0·7005	1·9353 1·9352	0·6920	1·9209 1·9210	0·6836	1·9070 1·9062	0·6751
539·4	2·0081 2·0083	0·7360	1·9969 1·9971	0·7291	1·9859 1·9862	0·7226	1·9754 1·9749	0·7162
1127·8	2·0536 2·0537	0·7631	2·0437 2·0440	0·7568	2·0344 2·0346	0·7512	2·0252 2·0251	0·7457
1716·2	2·0895 2·0897	0·7843	2·0804 2·0808	0·7783	2·0720 2·0724	0·7732	2·0641 2·0635	0·7682
2304·6	2·1196 2·1201	0·8020	2·1104 2·1117	0·7961	2·1033 2·1039	0·7913	2·0960 2·0954	0·7868
2893·1	2·1449 2·1460	0·8173	2·1372 2·1383	0·8114	2·1298 2·1310	0·8069	2·1236 2·1222	0·8026
3334·4	2·1628	0·8276	2·1555	0·8217	2·1485	0·8174	2·1411	0·8133

p(bar)	49(°C) ε	ρ	60(°C) ε	ρ	80(°C) ε	ρ	100(°C) ε	ρ
1·0	1·8794 1·8789	0·6588	1·8633 1·8644	0·6491	1·8337 1·8339	0·6312	1·8031 1·8024	0·6123
539·4	1·9549 1·9548	0·7044	1·9440 1·9445	0·6977	1·9229 1·9237	0·6860	1·92026	0·6735
1127·8	2·0080 2·0079	0·7359	1·9992 1·9994	0·7307	1·9808 1·9816	0·7210	1·9649 1·9640	0·7106
1716·2	2·0484 2·0483	0·7595	2·0405 2·0406	0·7554	2·0244 2·0248	0·7466	2·0072	0·7373
2304·6	2·0818 2·0813	0·7788	2·0743 2·0746	0·7755	2·0587 2·0600	0·7672	2·0461 2·0434	0·7586
2893·1	2·1102 2·1097	0·7952	2·1029 2·1034	0·7926	2·0898 2·0885	0·7846	2·0767 2·0741	0·7766
3334·4	2·1283	0·8062	2·1219	0·8040	2·1089	0·7962	2·0957	0·7885

It relates the specific volume $v_T{}^p$ at a temperature T °C to the pressure p (bars) using the three parameters $v_T{}^0$, A_T and B. Doolittle and Doolittle fitted the data of Simon *et al.* and Eduljee *et al.* to this equation and have listed appropriate values for the parameters. They went further and evolved empirical formulae to permit calculation of these parameters for many members of the *n* alkane family over a range of temperatures. This allows density data to be calculated with reasonable precision even at temperatures at which density measurements have not been reported. The Hudleston equation is very sensitive (at low pressures) to the value of $v_T{}^0$ and so the equation was used to calculate compression ratios. These were then multiplied by the value of the density ρ g cm⁻³ at atmospheric pressure and T °C as calculated from the International Critical Table formula:

$$\rho = 0 \cdot 70048 - 8 \cdot 476 \times 10^{-4} T + 1 \cdot 88 \times 10^{-7} T^2 - 5 \cdot 23 \times 10^{-9} T^3. \quad (3.1.2)$$

The constants A_T, B and $v_T{}^0$ used with equation (3.1.1) are summarized in table 3.

3.2. *Carbon tetrachloride*

The sample used in this case was Messrs Fluka's IR spectroscopic grade, catalogue 87030. Measured values are shown in table 2.

Table 2. Measured relative permittivity and density (g cm^{-3}), calculated from equation (3.2.1), of carbon tetrachloride as a function of pressure and temperature

p(bar)	25(°C) ϵ	ρ	p(bar)	35·7(°C) ϵ	ρ	p(bar)	53·9(°C) ϵ	ρ
1	2·2320	1·5845	1	2·2209	1·5636	1	2·1820	1·5276
	2·2322			2·2209			2·1825	
274·6	2·2737	1·6257	255·0	2·6240	1·6047	245·2	2·2260	1·5719
	2·2742			2·6270			2·2263	
519·8	2·3049	1·6563	480·5	2·9300	1·6349	451·1	2·2563	1·6025
	2·3050			2·9360			2·2571	
794·4	2·3356	1·6857	755·1	2·3253	1·6662	755·1	2·2947	1·6402
	2·3356			2·3257			2·2950	
1118·0	2·3667	1·7158	1118·0	2·3619	1·7015	1059·2	2·3277	1·6720

Table 3. Constants used with equation (3.1.1) to evaluate density of n heptane as a function of temperature and pressure

Temperature (°C)	A_T	B	$(v_T{}^0)^{1/3}$
0[1]	10·25	12·900	1·1259
10[3]	10·1774	13·186	1·13024
20[3]	10·1015	13·186	1·13481
30[2]	10·023	13·180	1·13980
49[3]	9·8609	13·187	1·14877
60[1]	9·770	12·800	1·15480
80[3]	9·5607	13·186	1·16503
100[2]	9·365	13·180	1·17760

[1] Calculated by Doolittle and Doolittle (1960) to fit data of Eduljee *et al.* (1951).

[2] Calculated by Doolittle and Doolittle (1960) to fit data of Simon *et al.* (1960).

[3] Calculated from formulae quoted by Doolittle and Doolittle (1960).

Carbon tetrachloride was chosen because very precise data on density are available for a range of temperatures from the work of Gibson *et al.* (1941). There is the further incentive that precise data on refractive index have also been obtained by Waxler and Weir (1963). Recently, density and permittivity data have been published by Mopsik (1969) which makes possible a direct comparison of measurement precision.

Values of density were computed using the Tait equation

$$v_T{}^p = v_T{}^1 \left\{ 1 - c \ln \left(\frac{B+p}{B+1} \right) \right\} \tag{3.2.1}$$

and by means of the following polynomial fit to ICT data:

$$v_T{}^1 = \alpha + \beta\theta + \gamma\theta^2 + \delta\theta^3. \tag{3.2.2}$$

The appropriate values of $v_T{}^1$, c and B were calculated from the polynomials which Gibson and Loeffler (1941) had fitted to their data (see table 4) and $\theta = (T-45)$.

Table 4. Coefficients used with Tait equation 3.2.1 to calculate density of carbon tetrachloride

T (°C)	$v_T{}^1$	c	B (bar)
25·0	0·6311	0·09246	866·9
35·7	0·6395	0·09246	796·0
53·9	0·6546	0·09246	684·4

3.3. *Accuracy of results*

The absolute accuracy of the permittivity determinations is limited to twice the bridge precision, that is to ± 2 parts in 10^4, since two separate capacitance determinations are involved. At the highest pressure the geometric capacitance change is calculated to be one part in 10^3, while the effect of temperature variation between 0 and 100 °C is 1·67 parts in 10^3. The latter figure was confirmed by measurements at atmospheric pressure. Uncertainty about temperature arose because of the tendency for a small long-term drift in the oil-bath temperature to occur. This effect, when added to the accuracy limitations of the digital thermometer, could account for deviations of up to 0·5 °C from the nominal temperature of a test run. In the case of n heptane this could affect permittivity by up to 4 parts in 10^4, and density by around 6 parts in 10^4. Uncertainties of pressure measurements were less important and would account for errors of considerably less than 0·01% in either permittivity or density. To summarize, it seems that a precision of at least 0·1% was maintained, with temperature the chief cause of errors.

The consistency of data can be judged by fitting data to polynomial expressions (see table 5) using the least-squares method. It was found that by expressing isothermal data by polynomials in pressure, of the form

$$\epsilon_T(p) = a^*(T) + b^*(T)p + c^*(T)p^2 + d^*(T)p^3 \tag{3.3.1}$$

no improvement accrued from adding terms in pressure beyond the third. Even so, this is the least satisfactory way of representing data. Isobaric data were found to be well represented by expressions of the form

$$\epsilon_p(T) = \epsilon'(p) - a'(p)(T-20) \tag{3.3.2}$$

relating permittivity at T °C to that at 20 °C. A second-order equation gives a rather better fit and indicates perhaps the maximum experimental uncertainty in the determination of $\epsilon_p(T)$—one part in 10^3. Other expressions of theoretical interest are

Table 5. *n* heptane: parameters for equation (3.3.1) for $\epsilon_T(p)$

Temperature (°C)	a^*	$b^* \times 10^4$ (bar)$^{-1}$	$c^* \times 10^8$ (bar)$^{-2}$	$d^* \times 10^{12}$ (bar)$^{-3}$	SE†
0	1·9499	1·189	−2·694	3·153	0·0014
10	1·9360	1·255	−2·990	3·636	0·0018
20	· 1·9216	1·324	−3·242	3·967	0·0019
30	1·9073	1·394	−3·514	4·342	0·0020
49	1·8801	1·538	−4·079	5·143	0·0022
60	1·8650	1·638	−4·511	5·782	0·0026
80	1·8352	1·824	−5·332	7·039	0·0033
100	1·8034	2·023	−6·103	8·059	0·0035

† Standard error based on least-squares analysis.

considered later, and these are all compared in table 10 in which standard errors of the functions of ϵ and ρ have been related to the uncertainties in ϵ, with the assumption that ϵ alone is subject to error. It should be noted that the quantity whose deviations have been minimized was the function fitted by least squares, and this was not always ϵ. It is clear from table 10 that there is little to choose between the various expressions containing two or more constants as ways of expressing the data. The only exception is the polynomial in pressure which, even with four constants, is inferior in this respect.

3.4. *Comparison with other data*

The NBS circular 514 gives for n heptane values of 1·924 for $\epsilon'(p)$ and $1·40 \times 10^{-3}$ for $a'(p)$, compared with 1·921 from table 6 and $1·46 \times 10^{-3}$ for $a'(p)$, at atmospheric pressure.

Table 6. *n* heptane parameters for equation (3.3.2) for $\epsilon(T, p)$

Pressure (bar)	$\epsilon'(p)$	$10^4 \times a'(p)$	SE†
1	1·9211	14·6	·0012
539	1·9863	10·6	·0006
1128	2·0348	9·01	·0006
1716	2·0725	8·08	·0006
2304	2·1039	7·48	·0008
2893	2·1307	7·00	·0008
3334	2·1487	6·67	·0006

† Standard error based on least-squares analysis.

The value of $a'(p)$ quoted in circular 514 was determined between -50 and $+50$ °C. If $a'(p)$ is calculated from measurements between 0 and 50 °C only, a value equal to $1·40 \times 10^{-3}$ is found. The only previously reported pressure measurements were those due to Francke (1925).

Data for carbon tetrachloride are best compared with the work of Mopsik (1969). At 25 °C there is quite close agreement: $\epsilon'(p) = 2·2321$ compared with 2·2286 quoted by Mopsik; but at higher temperatures the discrepancy is greater, reaching 0·5% at 53·9 °C. This is reflected in $a'(p)$ which, at $1·78 \times 10^{-3}$, is less than the figure $2·0 \times 10^{-3}$ obtained by Mopsik. This sample was less pure than was the n heptane, which may account for the greater discrepancies.

4. Discussion

4.1. *n heptane*

The simple Clausius–Mossotti relation between density and permittivity of a nonpolar liquid is not obeyed in practice, as was shown by Kyropoulos (1926), Chang (1934), Danforth (1931) and Mopsik (1967, 1969). Yvon (1936) and
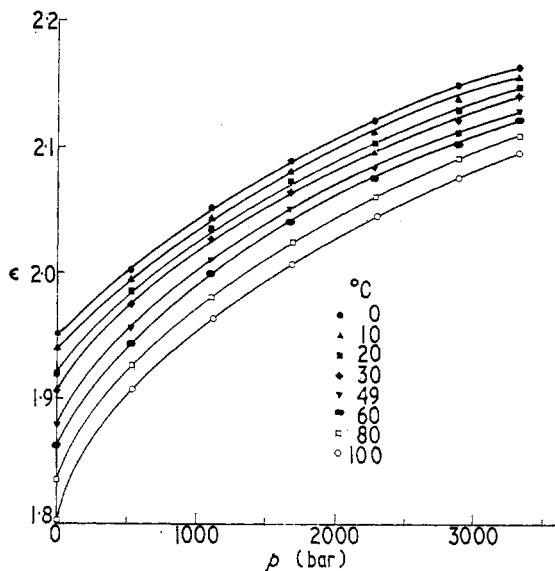

Figure 1. Relative permittivity of *n* heptane as a function of pressure p (bar) at temperatures between 0 and 100 °C.

Kirkwood (1936) considered the effect of translational fluctuations on the permittivity of a fluid composed of simple, spherical electrically symmetric molecules. This analysis has been continued by Brown (1950) who has also related other theories, for example that of Böttcher (1942), to the expression which Brown has derived. This expression takes the form of a polynomial

$$\frac{\epsilon+2}{\epsilon+1} = \frac{d_0}{\rho} - c_0 + \left(\frac{c_1}{d_0}\right)\rho - c_2\left(\frac{\rho}{d_0}\right)^2 + \dots. \tag{4.1.1}$$

For a simple model of hard nonattracting spheres, Kirkwood's model, the constants are expected to have the values

$$c_0 = \frac{2}{3}\ln\left(\frac{1+\alpha/c^3}{1-2\alpha/c^3}\right) \tag{4.1.2}$$

and

$$c_1 = 0\cdot9375 + 1\cdot553\,\frac{\alpha}{c^3} \tag{4.1.3}$$

where α is the polarizability and c is the radius of a molecule. We can use experimental data at $\rho = 0\cdot73$ g cm^{-3} to obtain an estimate of the ratio α/c^3, on the assumption that the simple Clausius–Mossotti relation holds. Then the comparison between predicted and measured parameters can be judged from table 7. Clearly the

Table 7. n heptane: comparison of measured with calculated values of parameters for equation (4.1.1)

Temperature		0 °C	10 °C	20 °C	30 °C	49 °C	60 °C	80 °C	100 °C
c_0	(calc.)	0·964	0·964	0·964	0·964	0·963	0·963	0·962	0·961
	(meas.)	0·464	0·205	0·431	0·571	0·508	0·974	0·400	0·590
c_1	(calc.)	1·47	1·47	1·47	1·47	1·47	1·47	1·47	1·47
($cm^3\ g^{-1}$)	(meas.)	1·47	1·02	1·48	1·62	1·62	2·82	1·43	1·86

signs of the constants are correct. There is a discrepancy amounting to a factor of two in c_0, while c_1 is reasonably well predicted. The scatter in the values of both c_0 and c_1 is not excessive bearing in mind that these are the second and the third coefficients of a polynomial expansion. The model used by Kirkwood and Yvon differs from real molecules which are neither spherical nor isotropic, and moreover possess quadrupole and higher moments. But an analysis of data for other members of the n alkane family, which is currently in progress, may serve to throw light on areas where the theory could be improved.

Brown favoured the form of equation (4.1.1) because it is readily related to theory. He has shown that Böttcher's equation

$$12\pi\rho\,\frac{N_A}{M}\,\frac{\epsilon}{(\epsilon-1)(2\epsilon+1)} = \frac{1}{\alpha} - \frac{2(\epsilon-1)}{c^3(2\epsilon+1)} = \varphi_B(\rho,\epsilon) \qquad (4.1.4)$$

can be written in the form of a series expansion like equation (4.1.1), where N_A is Avogadro's number, and M is the weight of one mole. It may be expected to be no more successful in representing data than any similar series with a similar number of constants. Table 8 lists values of α and c obtained by a least-squares fit of

Table 8. n heptane: parameters derived from Böttcher's equation (4.1.4)

$T\,°C$	$\alpha(Å)^3$	$c(Å)$
0	13·36	3·60
10	13·19	3·47
20	13·13	3·43
30	13·10	3·41
49	13·06	3·39
60	13·24	3·51
80	13·15	3·46
100	13·10	3·43

equation (4.1.4). The estimates of α and c are far less precise than those of $\varphi_B(\rho, \epsilon)$. They do not appear to vary systematically with temperature. Certainly on the basis of these measurements there is no evidence to reject the Böttcher model, which conflicts with Mopsik's (1969) rejection of the theory for carbon disulphide.

The measurements by Mopsik (1967, 1969) on non-dipolar liquids, which are the most precise available to date, have been analysed in terms of a series expansion of the Clausius–Mossotti function $\varphi_{CM}(\rho, \epsilon)$:

$$\varphi_{CM}(\rho, \epsilon) = \frac{M(\epsilon-1)}{(\epsilon+2)\rho} = a + b\rho + c\rho^2 + \dots . \qquad (4.1.5)$$

A three-term series is little improvement in terms of the standard error of $\varphi_{CM}(\rho, \epsilon)$ over Mopsik's two-term version, but it does have the merit of predicting more accurately the behaviour at lower densities. As can be seen in table 9, a two-term

Table 9. n heptane: least-squares fit to equation (4.1.5) using two terms only

Temperature (°C)	a (cm^3 mole^{-1})	b (cm^6(g mole)$^{-1}$)	CM($\rho = 0.73$) (cm^3 mole^{-1})
0	37.476 ± 0.062†	-4.391 ± 0.081	34.270 ± 0.012
10	37.101 ± 0.053	-3.870 ± 0.070	34.276 ± 0.011
20	36.939 ± 0.058	-3.649 ± 0.077	34.275 ± 0.012
30	36.846 ± 0.074	-3.530 ± 0.098	34.269 ± 0.016
49	36.654 ± 0.064	-3.287 ± 0.085	34.254 ± 0.015
60	36.976 ± 0.106	-3.744 ± 0.144	34.243 ± 0.026
80	36.675 ± 0.072	-3.373 ± 0.099	34.213 ± 0.019
100	36.439 ± 0.108	-3.060 ± 0.152	34.205 ± 0.034

† Standard error calculated by least-squares analysis.

expression predicts a limiting molar polarizability in the range 36·5 to 37·5 cm^3 mole^{-1}. In fact the value reported by Smyth and McAlpine (1934) for the gas is 34·9 cm^3 mole^{-1}. By contrast the three-term fit to the data for 0 °C, for example, predicts a value of 34·1 cm^3 mole^{-1}. Thus while the precision of the estimate of the three constants in equation (4.1.5) is poor, they have the correct order of magnitude and sign to conform to what is known of low-density behaviour.
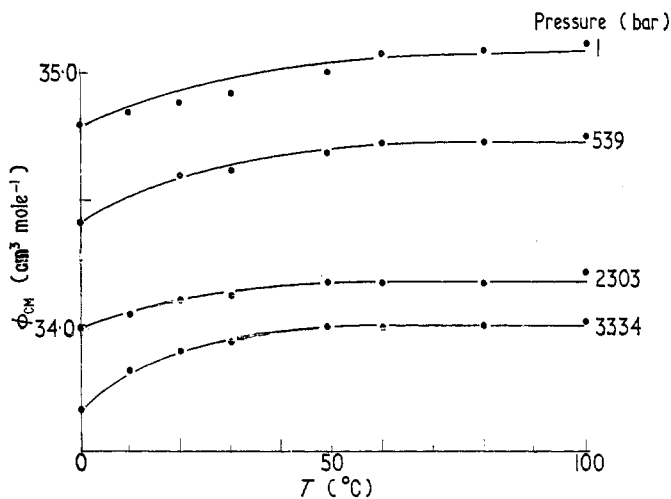

Figure 2. Clausius–Mossotti function φ_{CM} (cm^3 mole^{-1}) for n heptane as a function of temperature for pressures between atmospheric and 3334 bar.

Isobaric plots of φ_{CM} against temperature (figure 2) show a tendency at all pressures to increase with temperature. Isothermal plots of φ_{CM} against density show a tendency for the slope to become less negative with increasing temperature (figure 3). The precision of the estimate of φ_{CM} given by the two-constant form of

equation (4.1.5) is greatest when ρ has a value equal to the mean value for a given series of measurements. For convenience $\rho = 0.73$ g cm^{-3} has been used throughout to plot isochoric data. Table 9 and figure 4 display these values, and show a tendency for φ_{CM} to decline at first slowly but then increasingly rapidly with temperature. Mopsik (1967) reports a similar effect with n hexane, and work in progress (Scaife 1970) has confirmed this trend for other members of the n alkane family.
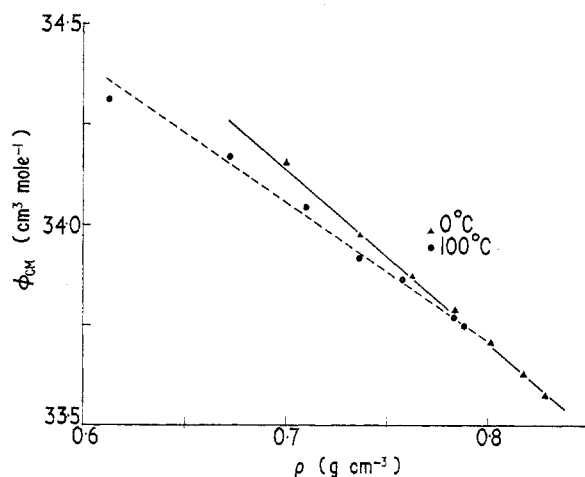

Figure 3. Clausius–Mossotti function φ_{CM} (cm^3 mole^{-1}) for n heptane as a function of density ρ (g cm^{-3}) at temperatures of 0 and 100 °C.
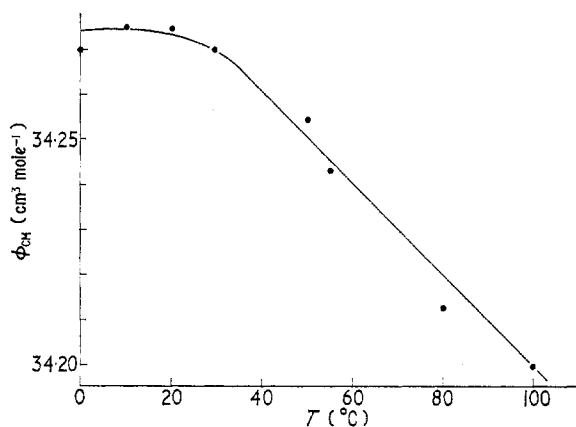

Figure 4. Clausius–Mossotti function φ_{CM} (cm^3 mole^{-1}) for n heptane at a density of 0.73 g cm^{-3} plotted as a function of temperature T (°C).

Mopsik tentatively proposed that a dipole moment sufficiently large to explain the effect would not be impossible. In the case of n heptane if we write

$$\varphi_{CM}(\rho, \epsilon) = \frac{4\pi N_A M}{3\rho}\left(\alpha + \frac{\mu^2}{3kT}\right)$$

the appropriate value of dipole moment μ varies from 0.1 D to 0.27 D over the range

of measurements at a density of 0.73 g cm^{-3}. Overall, the straight n heptane molecule has no net dipole moment. However, if it bends, the moments of the end CH$_3$ groups cease to cancel each other. It would be reasonable to suppose that as the temperature is raised an increasing proportion of molecules would assume increasingly bent configurations and so the average dipole moment would increase. It must be noted, however, that Mopsik's (1967) data were derived at lower temperatures and showed no variation in the slope b with temperature. With n heptane, on the other hand, as can be seen in table 9, both a and b are temperature-sensitive. From figure 3 it can

Table 10. n heptane: standard errors in ϵ deduced from least-squares analysis of various equations

Function	Equation	SE $\times 10^3$
$\epsilon_T(p)$ 3rd order	(3.3.1)	1·4 −2·2
$\epsilon_p(T)$ 1st order	(3.3.2)	0·55–1·6
2nd order		0·37–0·73
$(\epsilon+2)/(\epsilon-1)$ 1st order	(4.1.1)	0·5 −1·5
2nd order	(4.1.1)	0·3 −1·2
$\varphi_{\mathrm{B}}(\rho, \epsilon)$	(4.1.4)	0·34–1·4
$\varphi_{\mathrm{CM}}(\rho, \epsilon)$ 1st order	(4.1.5)	0·40–1·3

be seen that at a density of 0.779 g cm^{-3}, the value of φ_{CM} is the same at 0 and 100 °C. While it is not unreasonable that a dipole moment caused by a bent configuration should be reduced with density increases, the situation is clearly more complicated. This can be seen by considering values of φ_{CM} at a density above 0.779 g cm^{-3}. Between 0 and 100 °C φ_{CM} actually *increases*.

There are other possible temperature-dependent mechanisms which could explain the fall in polarizability with temperature. Garg *et al.* (1968) for example have considered the effect of dipole moments induced in molecules by the permanent quadrupole moments of their neighbours. The theory of such effects was developed by Buckingham and Pople (1955) and by Zwanzig (1956) and Jansen (1958). Garg *et al.* made measurements at far-infrared frequencies on non-dipolar liquids which included n heptane together with benzene, cyclohexane, carbon disulphide and carbon tetrachloride. It is interesting to note that a relaxation mechanism was observed which was attributed to multipole induced dipoles in all the liquids except n heptane.

The parameters which fit the various expressions for ϵ and ρ are sensitive to the adequacy of the equations used to relate density to pressure and temperature. To illustrate this, consider the parameters fitting equation (4.1.5) calculated by using the data of Eduljee *et al.* (1951) firstly with the Tait equation (3.2.1), using constants given by Eduljee, and secondly taking the Hudleston equation (3.1.1), using constants computed by Doolittle and Doolittle (1960). At 0 °C we find the Tait equation predicts a value for a which is 0.76% greater, and, for b, 8.5% greater, than that given by the Hudleston equation. But the isochoric polarizability (at $\rho = 0.73$ g cm^{-3}) is only 0.03% less than the Hudleston value. These discrepancies arise from a difference in the computed value of density which is, for example, 0.24% at 3334 bars. Clearly the real uncertainty about the values of the parameters a and b is much greater than their standard error suggests.

4.2. *Carbon tetrachloride*

The purpose of making measurements on carbon tetrachloride was to try to assess whether the equipment was producing systematic errors which were not foreseen,

such as Brown's (1950) analysis had revealed in Danforth's (1931) and Chang's (1934) measurements on carbon disulphide. The availability of measurements of refractive index by Waxler and Weir (1963), which were of high precision, offered some guidance. Recently Mopsik (1969) has reported permittivity and density data.

Because of the smaller range of pressures involved, the most appropriate way of presenting data is a two-term fit to equation (4.1.5)—see table 11. The appropriate

Table 11. Carbon tetrachloride: least-squares fit to equation (4.1.5)

Temperature ($^\circ$C)	a (cm^3 mole^{-1})	b (cm^6 (g mole)$^{-1}$)	CM ($\rho_3 = 1 \cdot 65$) cm^3 mole^{-1}
$25 \cdot 0$[1]	$30 \cdot 701 \pm \cdot 043$*	$-1 \cdot 538 \pm \cdot 026$*	$28 \cdot 163 \pm \cdot 0034$*
$35 \cdot 7$[1]	$31 \cdot 020 \pm \cdot 052$	$-1 \cdot 639 \pm \cdot 032$	$28 \cdot 316 \pm \cdot 0042$
$53 \cdot 9$[1]	$31 \cdot 021 \pm \cdot 053$	$-1 \cdot 674 \pm \cdot 033$	$28 \cdot 259 \pm \cdot 0047$
$24 \cdot 80$[2]	$28 \cdot 684 \pm \cdot 095$	$-1 \cdot 389 \pm \cdot 057$	$26 \cdot 392 \pm \cdot 0058$
$34 \cdot 50$[2]	$28 \cdot 625 \pm \cdot 184$	$-1 \cdot 353 \pm \cdot 112$	$26 \cdot 392 \pm \cdot 012$
$54 \cdot 34$[2]	$28 \cdot 235 \pm \cdot 086$	$-1 \cdot 077 \pm \cdot 054$	$26 \cdot 459 \pm \cdot 006$
0[3]	$30 \cdot 476 \pm \cdot 293$	$-1 \cdot 435 \pm \cdot 176$	$28 \cdot 109 \pm \cdot 009$
$25 \cdot 0$[3]	$30 \cdot 602 \pm \cdot 091$	$-1 \cdot 516 \pm \cdot 055$	$28 \cdot 100 \pm \cdot 003$
$50 \cdot 0$[3]	$30 \cdot 582 \pm \cdot 065$	$-1 \cdot 507 \pm \cdot 039$	$28 \cdot 095 \pm \cdot 003$

[1] Permittivity data from table 2.
[2] Refractive index data from Waxler and Weir (1963).
[3] Taken from Mopsik (1969).
* Standard error.

refractive index data have been fitted to the Lorentz–Lorenz analogue, writing n^2 (n being the refractive index) for ϵ in equation (4.1.5) to give $\varphi_{LL}(\rho, n^2)$. The tendency for measured ϵ to be greater than corresponding values reported by Mopsik is reflected in somewhat higher isochoric molar polarizabilities. None of the three sets of measurements show any systematic temperature trend for isochoric polarizability such as was encountered with n heptane.

On the whole it is concluded that differences in b determined by permittivity measurements do not exceed 10%, and in the case of a are less than $0 \cdot 7\%$. All the discrepancy between the reported values of isochoric polarizability and those of Mopsik, namely $0 \cdot 5\%$, can be accounted for by the differences in ϵ.

The smaller values of a determined by Waxler and Weir reflect the existence of the dispersion found to exist by Garg *et al.* (1968) in the far-infrared frequency region. As in the case of n heptane, the two-term versions of equation (4.1.5) predict gas phase polarizabilities well in excess of those quoted in the NBS circular 537. For example, the molar dielectric polarizability of the gas is quoted as $28 \cdot 14$ cm^3 mole^{-1} which compares with $30 \cdot 7$–$31 \cdot 0$ cm^3 mole^{-1} in this series of measurements. A similar situation exists in regard to refractive index measurements. The range of pressures for which data are available for carbon tetrachloride precludes any attempt to obtain a three-term fit to data.

Acknowledgments

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