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Abstract. Precision measurements of the relative permittivity of the n alkanes from n pentane to n decane have been made over a range of pressures and temperatures. All the data for each alkane have been fitted by a polynomial to within better than 0·1 %. Results are compared where possible with those of other workers.

1. Introduction

The techniques and equipment used were the same as those described already (Scaife 1971) in connection with a similar study of n heptane. The data points for all the alkanes studied, including n heptane, are very numerous and total almost nine hundred in all. Since individual data points are too numerous to list, they have been fitted to a polynomial expression in temperature and pressure, and the details of the relevant coefficients have been tabulated. This polynomial representation facilitates comparison with the work of others.

2. Samples

All the samples were supplied by Messrs Fluka and were purissimus grade with one exception. In the case of n hexane purum grade was used for temperatures above 25 °C. No difference could be detected in the relative permittivity of the two grades at either 0° or 25 °C. Particulars are summarized in table 1.

3. Equipment

The only variant on the equipment described earlier (Scaife 1971, Scaife and Lyons 1971) relates to the thermocouple which senses temperature inside the pressure vessel just above the cell encapsulation. Previously difficulty with the plug and socket connection between thermocouple and compensating cable had prevented accurate measurements of temperature, so that only transients following compression and decompression could be followed. In the present series a factory-made junction obviated this weakness. At temperatures above 0 °C the thermocouple was calibrated against a Digitec instrument as before. Below 0 °C calibration was against a platinum resistance thermometer using a Rosemount Engineering VLF51A bridge.

Table 1. Particulars of samples used in measurements (quoted by supplier)

Material	Grade	Mol %	d_4^{20}†	n_D^{20}‡	T_s§
n pentane	puriss.	99·98	0·6262	1·3588	‖
n hexane	puriss.	>99·96	0·659	1·375	69
n hexane	purum	>99	0·660	1·375	68·8–69
n heptane	puriss.	99·92	0·6838	‖	98·4
n octane	puriss.	99·81	0·7026	‖	‖
n nonane	puriss.	99·68	0·7177	‖	‖
n decane	puriss.	99·49	‖	‖	‖

† Density at 20 °C determined by Westphal scale.
‡ Refractive index at 20 °C.
§ Boiling point (°C).
‖ Not quoted.

4. Representation of data

A polynomial in both pressure and temperature has several advantages. Firstly relatively few isotherms have in themselves sufficiently numerous data points and, in consequence, polynomials in pressure only have relatively low statistical certainty. Secondly a combined polynomial permits the fullest use to be made of the improved precision in temperature measurement. Finally such a representation facilitates comparison with other results. A similar approach was used by Owen et al (1961) to represent values of lg ϵ for water.

A study of the data suggested that an adequate representation could be achieved by the following equation:

$$\epsilon(p, T) = a_1 + a_2 T + a_3 T^2 + (a_4 + a_5 T)p + (a_6 + a_7 T)p^2$$
$$+ (a_8 + a_9 T)p^3 + (a_{10} + a_{11} T)p^4. \tag{4.1}$$

In this, pressure is quoted in kilobars (absolute) and temperature in degrees centigrade. The coefficients were determined by a least squares regression analysis. As part of this analysis, the 'residuals' were listed, that is the deviations of measured points from the polynomial curve. It is worth reporting that analysis of the data using numbers with seven significant digits led to appreciable errors. For example, the standard error of estimate was overestimated by a factor of three. These anomalies were removed by using numbers with sixteen significant digits for the calculations. In table 2, details are given of the coefficients for equation (4.1), their standard errors in the form of the 't' statistic, and the fraction of residuals which exceed one and two standard errors of estimate (SEE) in magnitude.

In general it can be said that less than 5 % of measured values deviate by more than 0·1 % from the polynomial value. In each series of measurements one or more temperature runs were duplicated, and systematic divergencies could be found in some sets of data. However, the largest systematic discrepancies in the corresponding sets of residuals did not exceed 0·1 %. The ranges of pressures and temperatures over which data were acquired are given in table 3. Extrapolation beyond this area carries considerable probability of error. It was found that the largest residuals most frequently occurred at the edges of the region of pressure and temperature which was covered on these measurements.

Table 2. Coefficients for equation (4.1), expressing ϵ in terms of pressure p (kbar) and temperature T (°C)

Coefficient	n pentane	n hexane	n heptane	n octane	n nonane	n decane	Term
a_1	1.87336	1.91638	1.95051	1.97624	1.9966	2.01535	
$-a_2 \times 10^2$	0.16406 (-309)†	0.14955 (-201)†	0.14853 (-124)†	0.14097 (-171)†	0.13482 (-133)†	0.13232 (-147)†	T
$a_3 \times 10^6$	0.63627 (15)	0.41157 (7.0)	0.20919 (2.1)	0.34915 (5.0)	0.24779 (2.8)	0.50128 (6.3)	T^2
a_4	0.16659 (131)	0.14396 (99)	0.12320 (62)	0.11521 (85)	0.11361 (63)	0.10886 (67)	p
$a_5 \times 10^2$	0.11205 (47)	0.089966 (27)	0.10674 (29)	0.09337 (35)	0.077789 (23)	0.074319 (26)	pT
$-a_6 \times 10$	0.82341 (-34)	0.57088 (-23)	0.37199 (-13)	0.31564 (-16)	0.36002 (-12)	0.32331 (-12)	p^2
$-a_7 \times 10^3$	0.67890 (-18)	0.50471 (-11)	0.71175 (-13)	0.65938 (-16)	0.45813 (-8.7)	0.45185 (-9.7)	$p^2 T$
$a_8 \times 10$	0.18460 (8.7)	0.17654 (12)	0.087416 (6.7)	0.062916 (5.9)	0.09462 (5.9)	0.083042 (5.5)	p^3
$a_9 \times 10^3$	0.31920 (19)	0.13147 (6.0)	0.22736 (9.1)	0.23607 (11)	0.13808 (5.0)	0.14253 (5.6)	$p^3 T$
$-a_{10} \times 10^2$	0.52088 (-14)	0.22871 (-8.7)	0.088781 (-4.5)	0.046713 (-2.6)	0.10556 (-3.9)	0.095119 (-3.5)	p^4
$-a_{11} \times 10^4$	0.14332 (-3.4)	0.11461 (-3.2)	0.26546 (-7.0)	0.31596 (-8.3)	0.15609 (-3.4)	0.16885 (-3.9)	$p^4 T$
SEE(ϵ)	0.00063	0.00101	0.00092	0.00073	0.00072	0.00077	
N‡	188	158	103	175	103	166	
$R\%>$ 1SEE§	24%	32%	29%	22%	25%	26%	
$R\%>$ 2SEE‖	3.7%	3.2%	3.0%	4.0%	5.0%	4.8%	

† 't' statistic (regression coefficient divided by standard error of the coefficient).
‡ Number of data points.
§ Percentage of data points with residuals in excess of 1SEE.
‖ Percentage of data points with residuals in excess of 2SEE.

Table 3. Range of temperatures and pressures covered by measurements which have been fitted to equation (4.1)

n pentane p (bar)	T (°C)	n hexane p (bar)	T (°C)	n heptane p (bar)	T (°C)	n octane p (bar)	T (°C)	n nonane p (bar)	T (°C)	n decane p (bar)	T (°C)
1–1716	−20	1–1962	−25	1–3334	0–100	1–1962	0	1–981	0	1–735	0
1–1863	−10	1–2453	0			1–2453	10–20	1–1962	20–30	1–1912	10
1–2010	0	1–2943	25			1–3433	30–50	1–3335	40–80	1–2500	20
1–2207	10	1–1864	41			1–2943	60–100	1–2452	100	1–2893	30–40
1–2304	20	1–2455	50							1–3089	50–100
1–1912	30	1–2943	75								
148–2109	40–60	1–3483	100								
148–2501	70–90										
148–2883	100										

5. Results

5.1. Atmospheric pressure data

The National Bureau of Standards circular 514 (1951) lists the best available values of relative permittivity at 20 °C, $\epsilon(1, 20)$. It also gives the best available value for the temperature coefficient as defined in the following equation:

$$\epsilon(1, t') = \epsilon(1, t) - a(t' - t). \tag{5.1}$$

In this t and t' are temperatures in degrees centigrade. The NBS values are summarized in table 4 together with values taken from this work. Since $\epsilon(1, t')$ is not a linear function of temperature, comparison of values of a is only valid when they have been calculated over the same span of temperature.

Table 4. Coefficients for equation (5.1)

	$\epsilon(1, 20)$†	$\epsilon(1, 20)$‡	$a \times 10^2$†	$a \times 10^2$‡
n pentane	1·844	1·841	1·60(−50, 30)§	1·63(−·25, 30)§
n hexane	1·890	1·887	1·55(−10, 50)	1·45(−10, 50)
n heptane	1·924	1·921	1·40(−50, 50)	1·47(0, 50)
n octane	1·948	1·948	1·30(−50, 50)	1·39 (0, 50)
n nonane	1·972	1·970	1·35(−10, 90)	1·33 (0, 90)
n decane	1·991	1·989	1·30(10, 110)	1·27(10, 100)

† Values taken from NBS circular 514.
‡ Present work.
§ Range of temperatures for which equation (5.1) is valid.

With the exception of n octane, the values of $\epsilon(1, 20)$ are all lower by about 0·15% than those reported in the NBS circular. Two explanations may account for this. The samples used in this work were of very high purity. In general contamination tends to raise ϵ. Secondly, these measurements used a three terminal guarded electrode cell, (Scaife and Lyons 1971) which, like that of Mopsik (1967) allows absolute measurements to be made.

5.2. n pentane

Previous measurements were reported by Danforth (1931) and Chang (1934) working in Bridgman's laboratory. A comparison of values calculated from equation (4.1) with Chang's data, shows the latter to be $+0.4\pm0.18\%$ larger at 30 °C and $+1.06\pm0.16\%$ at 75 °C. More recently Brazier and Freeman (1969) have published some data collected at 30 °C. These are given as ratios of the permittivity at elevated pressures to that at atmospheric pressure. Brazier's ratios run from $+0.23\%$ at 500 bar to $+0.64\%$ at 2500 bar, greater than the corresponding ratios calculated from equation (4.1).

5.3. n hexane

Earlier work has been reported by Chang (1934) to 10 kbar, by Hartmann *et al* (1965) and by Mopsik (1967) to 2 kbar, and by Brazier and Freeman (1969) to 4 kbar. Mopsik alone used a three terminal cell with guarded electrodes. A comparison of Chang's values at 30 °C with values calculated by equation (4.1) showed systematic differences of about $+0.8\%$ up to 3 kbar. At 75 °C his values were roughly $+1.1\%$ different up to 3 kbar. If equation (4.1) is used to extrapolate beyond this pressure, the discrepancies become rapidly greater (eg $+1.94\%$ at 4 kbar, $+8.8\%$ at 5 kbar). This serves to under-line the danger of using equation (4.1) beyond its limits of applicability. The data of Hartmann *et al* at 20 °C diverge from the values calculated by equation (4.1) by $+0.1\%$ at 1 bar, $+0.24\%$ at 300 bar, reaching exact agreement at 1.8 kbar. At 35 °C the trend is from $+0.06\%$, to $+0.29\%$ at 300 bar, to $+0.06\%$ at 1.8 kbar. At 50 °C Hartmann's values are -0.1% at 1 bar, $+0.21\%$ at 300 bar and -0.02% at 1.8 kbar different to those predicted by equation (4.1).

Mopsik's values were determined at pressures up to 2 kbar. At 25 °C the discrepancies ranged from $+0.03$ to $+0.13\%$, at 0 °C from $+0.07$ to $+0.11\%$ and at -25 °C from -0.01 to $+0.16\%$. Using equation (4.1) to extrapolate down to -50 °C we find Mopsik's measurements differ by -0.02% at 1 bar to $+0.21\%$ at 1.751 kbar.

The permittivity ratios of Brazier and Freeman (1969) differ by from -0.08% at 500 bar to -0.46% at 3 kbar from the ratios calculated by equation (4.1).

5.4. n octane

The only data available for comparison are the ratios of permittivity quoted by Brazier and Freeman at 30 °C. These differ by from -0.45% at 500 bar to -1.2% at 3 kbar from the ratios predicted by equation (4.1).

5.5. n heptane, n nonane and n decane

No other comparable experimental data appears to be available.

6. Discussion

6.1. Precision

In discussing the deviations of measured values of ϵ from those calculated from equation (4.1), we must consider the absolute precision of measurements, the probable random

errors and the systematic deviations arising from deficiencies in equation (4.1). The absolute precision with which capacity can be measured is 0·01 %, so that provided the cell constant does not change, ϵ can be known to within 0·02 %. Pressure is known to within 0·03 %. Temperature is estimated to be known within $\pm 0·25 \,°C$. However, in transient conditions some temperature gradient is likely between the sample in the cell and the thermocouple in the surrounding hydraulic fluid. Its magnitude is impossible to assess. A study of the residuals associated with pairs of readings taken at the same nominal temperature and pressure suggests that the random errors of observation are in the region of a quarter of the overall SEE and seem likely to be associated with errors in the determination of temperature. A study of replicate measurements at a given temperature show, in the case of n pentane and n octane, no systematic trend, but in the case of n decane there is a small tendency for the later measurements to yield larger residuals, though these do not exceed 0·1 %. This, it is believed, is possibly due to slight contamination of the sample with hydraulic oil. In all cases care was taken not to have a succession of runs at ever increasing temperatures, but rather to intersperse high and low temperature runs. Consequently the overall SEE reflects the contribution due to any gradual contamination of the sample as well as that due to the deficiencies in equation (4.1) for representing measured values.

    An examination of the incidence of residuals ranging in size from 1 to 2 SEE disclosed no obvious tendency for them to appear in one area of the pressure–temperature region rather than another. Table 2 shows that appreciably less than 5 % of all measurements depart by more than 0·1 % from the value predicted by equation (4.1).

6.2. Empirical expression for ϵ

In a discussion of the n heptane data (Scaife 1971) it was noted that in terms of the SEE, isobaric data were easier to fit than isothermal data using polynomials; the ratio of SEE being about one to three. The combined polynomial in pressure and temperature (equation (4.1)) comes quite close in performance to polynomials in pressure only. Thus for equation (4.1) the SEE is 0·00092, which compares with 0·00060 to 0·00120 for isobars and 0·00140 to 0·00350 for isotherms. This improvement results from the availability of a greater number of data points on which to base an estimate of the polynomial coefficients.

7. Conclusion

Measurements have been made of relative permittivity of members of the alkane family with a precision of at least 0·1 % over a wide range of temperatures and at pressures up to 2 to 3 kbar. Comparison with recent work, particularly that of Mopsik (1967) shows excellent agreement. It has been possible to relate previously reported data to these measurements.

    The polynomial in pressure and temperature exemplified by equation (4.1) has been shown to be a satisfactory and advantageous way of representing data.

    By making use of the work of Doolittle and Doolittle (1960) who have derived equations for the density of these members of the alkane family as a function of temperature and pressure, it is proposed to continue the analysis of permittivity data. This work is in progress and has been reported on briefly (Scaife 1970).

Acknowledgments

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