Dielectric Constant of N-Hexane as a Function of Temperature, Pressure, and Density

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A description is given of apparatus employing a cell that is both a bellows dilatometer and a three-terminal electrode set for measuring simultaneously the density and dielectric properties of liquids as functions of temperature and pressure. Measurements are possible at temperatures from 120 °K to over 300 °K and pressures from 1 to 2000 atm with an uncertainty of 0.03 percent. The density, dielectric constant, and Clausius-Mossotti function of n-hexane have been measured for temperatures from 223 to 298 °K (− 50 to 25 °C) and at pressures from 1 to 2000 atm. There is a linear decrease in the Clausius-Mossotti function with density and a decrease with temperature corresponding to an effective dipole moment of 0.085 debye.

Key Words: Clausius-Mossotti, density, dielectric constant, dilatometer, function, high pressure, n-hexane, pressure, three-terminal electrode set.

1. Introduction

The dielectric properties of liquids have usually been measured as a function of temperature only. Any attempt to relate these properties to a molecular model requires that the density changes that accompany any temperature changes be taken into account explicitly. However, the models may not be adequate for such a purpose. Moreover, they usually use certain parameters that are assumed to be independent of the density but need not be, notably the polarizability. It would be a great aid to understanding dielectric behavior if density effects could be separated from temperature effects with good accuracy.

Since a liquid is relatively incompressible, high pressures are required to cause significant density changes apart from those due to temperature alone. While the dielectric constants of several liquids have been measured as a function of pressure [1, 2],[1] the temperature range was restricted and the accuracy not too high. This was partly because only a two-terminal capacitance cell was used.

Therefore, apparatus was assembled with the aim of making accurate dielectric measurements on liquids with a three-terminal electrode set over a wide range of pressure and temperature. At the same time, provisions were made for a means of monitoring the density simultaneously. This latter provision eliminates the reliance on previous density measurements. Furthermore, pressure gauge calibrations and sample variations are removed as sources of error when the dielectric constant is studied as a function of density.

[1] Figures in brackets indicate the literature references at the end of this paper.

2. Apparatus

2.1. Cell

The measuring cell was a bellows dilatometer in which a three-terminal electrode set was suspended. The cell, shown in figure 1, was made entirely of AISI 316 stainless steel.

a. Electrodes

The dielectric measurements were made by the electrode set, F, G, H, whose leads were brought out of the endplate, K, by alumina ceramic feedthroughs. The gold plated electrodes were self-shielded, three-terminal, coaxial cylinders. Alumina ceramic disks were used as the insulating spacers. The assembly was held together by screws in an axially symmetric manner to minimize shifts in alinement for large changes in temperature. The end alumina disks were perforated for liquid passage and the guard electrodes, G, had small oblique holes for the same purpose. The lead from the guarded central electrode, F, was shielded by a small piece of tubing at the top of the electrodes and a projecting collar on the endplate that completely shielded the feedthrough for this lead. This eliminated any measurable stray capacitance and the electrodes could be used for absolute measurements. The guard electrodes were brought out by a separate feedthrough and grounded externally. The outer electrode, H, was brought out through a third feedthrough. Electrical contact with the bellows, which was grounded, was prevented by a small ring, L, of heat-shrinkable fluorinated ethylene-propylene copolymer. This ring had a
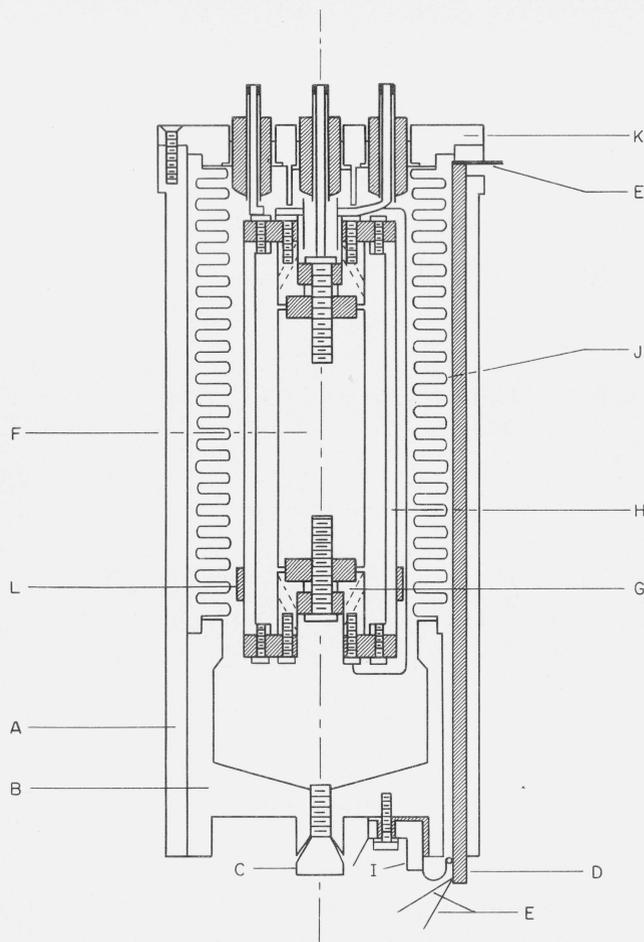
FIGURE 1. *Cross section of combined dilatometer and dielectric cell.*
A, sleeve; B, piston; C, filling plug; D, fused silica rod; E, electrical leads; F, guarded inner electrode; G, guard ring; H, outer electrode; I, sliding contact assembly; J, bellows; K, endplate; L, insulating spacer.

volume small enough so that its volume changes with temperature and pressure were negligible. The geometric capacitance of the assembly was 4.1158 ±0.0005 pF.[2]

b. Dilatometer

The dilatometer was formed with a seamless bellows, J, soldered at one end to an end plate, K, and at the other to a piston, B. The piston moved in a close fitting sleeve, A, that was attached to the endplate. Because of this constraint, the motion of the bellows assembly was purely axial. To provide access for filling, a screw plug with a tapered head, C, seated against a similar taper in the piston. A silver gasket acted as a seal that could be made or unmade with moderate torques.

The extension of the bellows was monitored by a potentiometric method. A fused silica rod, D, had a resistive stripe of Liquid Bright Platinum[3] applied to

it. The rod was mounted in a groove in the outer sleeve by a small amount of epoxy cement at the end close to the endplate. This end also was soldered to a fine copper wire, E, and to the sleeve. The other end of the rod had soldered to it two more fine copper wires, E. The piston carried a sliding contact assembly, I, consisting of a mounting block, a light beryllium copper spring and a small piece of platinum wire which served as the actual contact. By use of the cell mounting as a current return and one of the two wires at the piston end of the rod as a current source, it was then possible to use a four-terminal method for determining the voltage across the resistance stripe proper.

c. Calibration

The ratio of the voltage at the slide contact to the total voltage across the silica rod was calibrated as a function of length by deflecting the bellows and measuring the deflection on a dial gauge calibrated with gauge blocks to 1 μ. The corresponding voltage ratio was measured by means of an ordinary laboratory potentiometer. It was possible to resolve a deflection of 1 μ for a total deflection of 1.2 cm with a reproducibility of ±5 μ. A similar fused silica rod which had a very fine wire contact soldered to it showed no change in voltage ratio when placed in dry ice, so it was assumed that a given voltage ratio corresponded to the same position on the rod under all experimental conditions.

The constants needed to convert voltage ratios into density changes were obtained from calibrations using distilled water. The complete cell was weighed with and without water, the temperature and voltage ratio being taken prior to the weighing with water. Also, the filled cell was connected to a calibrated glass capillary and the bellows deflected. These data were sufficient to give both the total volume of the cell, 26.999 ±0.005 cm³ and the change in volume per unit length of bellows deflection, 4.915 ±0.004 cm³/cm.

d. Corrections

The cell constants were corrected for temperature and pressure. For the dilatometer, this was facilitated by having the inner diameter of the piston very nearly equal to the effective diameter of the bellows. Excluding the volume of the electrodes, the dilatometer will then display the temperature and pressure coefficients of fused silica in length and AISI 316 stainless steel in cross-sectional area. The electrodes consisted of 7.6 ml of steel and 1.1 ml of alumina and their change in volume was computed separately. For the electrodes, the geometric capacitance was corrected for the linear coefficients of AISI 316 stainless steel.

The thermal expansion factors for the fused silica and AISI 316 stainless steel were taken from NBS Monograph No. 29 [3]. The compressibility of the fused silica was taken as 28.09×10^{-7} atm⁻¹ [4] while that of steel was taken as 5.84×10^{-7} atm⁻¹ [5]. For alumina, the thermal expansion and compressibility were derived from data of Coors Porcelain Co. [6];

the thermal expansion was taken as 1/5 that of steel, the compressibility 7.5×10^{-7} atm^{-1}. It is believed that these factors are sufficiently accurate to introduce no appreciable systematic error.

As a check on the corrections for capacitance and on the design of the electrodes, the electrode assembly was cooled in both liquid nitrogen and dry ice and its capacitance measured. The change in capacitance agreed with that predicted from the thermal expansion factors in the Monograph and the room temperature capacitance was recovered on warming. Similarly, repeated measurements on the geometric capacitance after both pressure and temperature cycling always gave the same results within limits of measurement.

2.2. Pressure System

The cell was suspended in a cylindrical stainless steel pressure vessel, sealed on both ends by plugs with composite copper polytetrafluorethylene gaskets. The bottom plug had a standard high pressure fitting. The top plug had six electrical leads through it, two of which were coaxially shielded. The top plug also had a thermocouple well in it that extended into the working volume. The working volume was about 5 cm in diameter by 12 cm in length. The vessel was suspended from a metal plate by three thin walled stainless steel tubes to minimize thermal conduction to the vessel.

Pressures were generated by means of an air-driven differential piston pump. For the measurements reported in this paper, isopentane was used as the hydraulic fluid. A special needle valve capable of very low flow rates was placed at the output of the pump so that the pressure inside the pressure vessel could be changed slowly. Pressure was measured by an 18 in Heise pressure gauge having a full scale range of 2000 atm.[4]

2.3. Temperature Control

Temperature was maintained by immersion in a large glass Dewar filled with stirred heptane as the bath fluid. Since the leads from the pressure vessel were surrounded by the bath fluid, a hydrocarbon was chosen because of its low conductivity. An immersed heater and a large copper cooling coil were used for control. The coolant was gas from evaporating liquid nitrogen or, for rapid cooling to a desired temperature, liquid nitrogen itself.

For temperature regulation a copper-constantan thermocouple was immersed in the bath. The output was fed into a potentiometer set to the emf corresponding to the desired temperature. The error signal was detected by a chopper-stabilized D.C. amplifier (4×10^7 gain). This controlled a servo motor which in turn drove a cam-operated switch for relays supplying power from variable autotransformers to

either the heater in the bath or another heater in a Dewar containing liquid nitrogen. A vacuum-jacketed transfer tube connected the Dewar to the cooling coil of the bath. Just above the liquid nitrogen the tube had a vent plug that could be operated from outside the Dewar. In this way, either evaporating gas or liquid could be driven by the heater into the cooling coil. With this system, it was possible to stabilize the bath temperature to better than the equivalent of 1 μV of thermocouple output or approximately 0.03 °C at temperatures from 120 °K to over 300 °K.

2.4. Temperature Measurement

Temperature was measured by a copper-constantan thermocouple in the well in the top cap of the pressure vessel. The thermocouple was calibrated to ± 0.1 °C. Because of the large mass of the pressure vessel and the poor thermal conductivity of stainless steel, pressure changes of 100 to 200 atm required a wait of about $\frac{1}{2}$ hour before the temperature of the thermocouple returned to equilibrium. This final temperature was constant to 0.006 °C, the resolution of the potentiometer, with no apparent fluctuations or drift. Furthermore, there did not seem to be an appreciable thermal lag between the thermocouple and the cell as indicated by volume changes. Temperature uniformity could not be checked but it should have been excellent since the working volume was the relatively small interior of the vessel which was well immersed in the bath.

2.5. Electrical Measurements

The electrical measurements of capacitance and equivalent parallel conductance were made with a bridge of the Cole-Gross Type [7]. The bridge used a transformer from a General Radio Type 1605 Impedance Comparator (see footnote 3). A General Radio Type 1422CC variable capacitor fitted with a vernier that could be read to 0.001 pF over a range of 5 to 110 pF served as the standard capacitor. The conductance network used a Vogue Instrument 10-turn potentiometer that had very low stray and distributed impedances and was linear to 0.01 percent. The standard conductances were metal film resistors, two in series for each range. This arrangement greatly reduced their equivalent shunt capacitance; when needed, a wire connected to ground was wrapped around their junction to reduce the capacitance further. It was possible to keep the shunt capacitance below 0.05 pF quite easily. By careful shielding of the bridge to reduce capacitance to ground, balancing the capacitance to ground of the 1422CC capacitor across the transformer and carefully choosing the ground points in the wiring, the bridge was usable from 40 Hz to 400 kHz with an accuracy of 0.001 pF for parallel capacitance, at least 0.1 percent for parallel conductance over full scale ranges of 0.1 to 100 μmho, and a minimum tan δ of 0.0001 for a cell with a geometric capacitance of 4 pF.

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[4]Pressures are expressed in normal atmospheres each equivalent to 1.01325 bars, 1.01325×10^6 dyne cm^{-2}, or 1.01325×10^5 N m^{-2}.

3. Measurements

The n-hexane used in this study was reagent grade material stated to be 98+ percent pure. It was fractionally distilled through a packed 25 cm column. The initial fraction, which amounted to 10 percent of the total, was discarded and the remainder, which had a constant boiling point of 68.7 °C at 760 mm Hg, was collected. The density as measured in the dilatometer was 0.6547 ± 0.0002 g/cm^3 at 25 °C. The refractive index of a separate sample of n-hexane was measured to be 1.37407 ± 0.00005 at 22 °C for the sodium D line. Literature values [8] for the boiling point, density and refractive index are 68.74 °C, 0.65483 g/cm^3 and 1.37382 respectively.

The n-hexane was freed from dissolved air by boiling under reduced pressure produced by a mechanical vacuum pump with a trap. It was then run into the cell, which had been evacuated to about 10^{-5} torr. No air bubbles were formed inside the cell and there was never any indication of voids during the measurements. Voids would have manifested themselves by an abnormally high initial compressibility or a failure of the volume to return to its original value at atmospheric pressure after a pressure cycle.

The measurements were run at 25, 0, −25, and −50 °C for gauge pressures of 0 to 2000 atm except at −50 °C where a maximum pressure of 1500 atm was used. Measurements were taken for both increasing and decreasing pressure, and no systematic difference was found. The dielectric constant was measured at 10 kHz and no measurable loss was ever observed. The measured values of the dielectric constant and density are given in table 1. These values are averages of two measurements, one for increasing, and one for decreasing pressure. The variation of density with pressure and temperature is shown in figure 2, the variation of the dielectric constant in figure 3.

TABLE 1. *Density, dielectric constant, and CM of n-hexane*

p	25°			0°			−25°			−50°		
	ρ	ϵ	$\frac{\epsilon-1}{\epsilon+2}\frac{M}{\rho}$	ρ	ϵ	$\frac{\epsilon-1}{\epsilon+2}\frac{M}{\rho}$	ρ	ϵ	$\frac{\epsilon-1}{\epsilon+2}\frac{M}{\rho}$	ρ	ϵ	$\frac{\epsilon-1}{\epsilon+2}\frac{M}{\rho}$
(atm)	(g/cm³)		(cm³/mol)	(g/cm³)		(cm³/mol)	(g/cm³)		(cm³/mol)	(g/cm³)		(cm³/mol)
1	0.6547	1.8799	29.854	0.6769	1.9178	29.827	0.6987	1.9540	29.760	0.7193	1.9908	29.745
101	.6647	1.8972	29.846	.6856	1.9320	29.796	.7054	1.9658	29.754	.7261	2.0015	29.708
201	.6737	1.9123	29.828	.6937	1.9449	29.758	.7120	1.9778	29.751	.7320	2.0112	29.679
401	.6898	1.9379	29.759	.7067	1.9679	29.752	.7245	1.9979	29.690	.7422	2.0294	29.664
601	.7022	1.9599	29.752	.7183	1.9874	29.710	.7348	2.0158	29.667	.7513	2.0449	29.635
801	.7133	1.9789	29.723	.7286	2.0045	29.668	.7441	2.0319	29.644	.7595	2.0596	29.618
1001	.7240	1.9955	29.657	.7380	2.0204	29.636	.7523	2.0462	29.619	.7672	2.0732	29.598
1251	.7350	2.0148	29.637	.7482	2.0380	29.609	.7619	2.0626	29.587	.7761	2.0881	29.557
1501	.7450	2.0317	29.602	.7578	2.0541	29.569	.7703	2.0780	29.575	.7841	2.1021	29.530
1751	.7540	2.0478	29.592	.7660	2.0690	29.557	.7786	2.0915	29.526			
2001	.7627	2.0620	29.544	.7738	2.0828	29.537	.7858	2.1045	29.511			

4. Discussion

4.1. Treatment of Data

For a nonpolar liquid, such as n-hexane is normally assumed to be, the theory of the static dielectric constant [9] predicts that

$$\frac{\epsilon-1}{\epsilon+2}\frac{M}{\rho}=\frac{4\pi}{3}N\alpha,$$

where N is Avogadro's number, M is the molecular weight, ρ is the density, ϵ is the static dielectric constant and α is the molecular polarizability. The left-hand side of the equation, commonly called the Clausius-Mossotti function, or CM, is therefore, predicted to be a constant if α remains constant.

To check for this constancy, the CM was calculated for each measured point. The results are given in table 1 and a plot of the CM as a function of density is given in figure 4. It should be noted that the CM for a given temperature and pressure was computed for each measurement and averaged separately from the density and dielectric constant. This procedure was followed to reduce the effect of any lack of reproducibility in temperature or pressure on the CM. It can be easily seen that the CM is not a constant.

At constant temperature, the experimental CM is found to decrease linearly with density to within the experimental uncertainty, 0.03 percent. While this is at variance with the analysis of earlier data [10] which found linearity in a plot of the reciprocal of the CM, the difference between the two plots is less than experimental error. Moreover, since least squares reduction of the data showed a slightly better fit for the plot of the CM than that of its reciprocal, the simpler linear function was used here to fit the data. Similarly, the CM is seen to decrease with increasing temperature at constant density. For this case the change is much smaller so that no attempt was made to determine the functional form of the behavior.

The constants obtained by the least squares fit of the CM at each temperature as a linear function of density are given in table 2. The corresponding lines are indicated in figure 4. Also, the last column
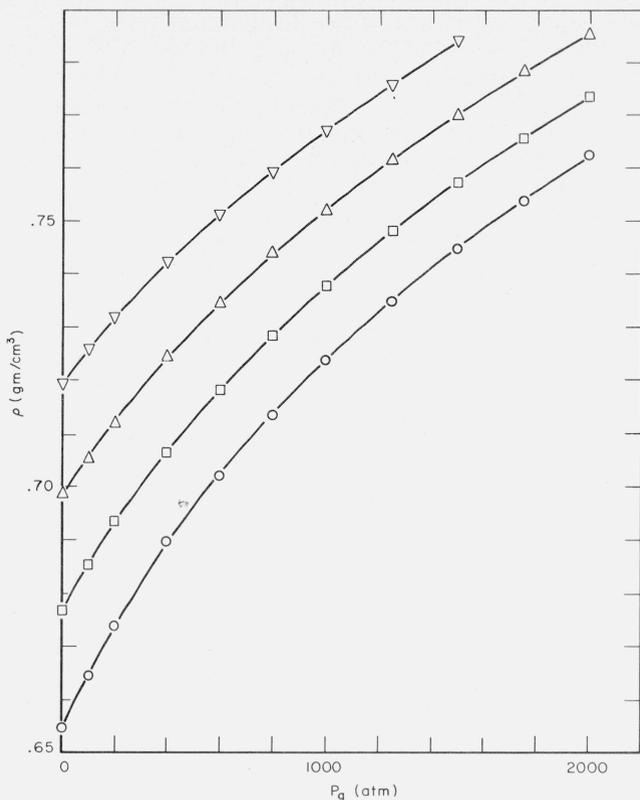
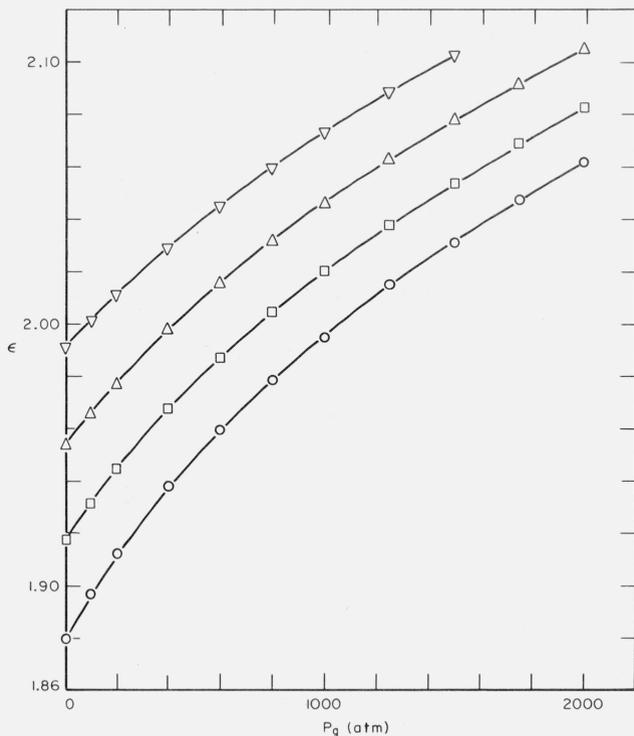FIGURE 2. *Density of* n-*hexane as a function of pressure.*
$\bigcirc$, 25 °C; $\square$, 0 °C; $\triangle$, −25 °C, $\triangledown$, −50 °C.

FIGURE 3. *Dielectric constant of* n-*hexane as a function of pressure.*
$\bigcirc$, 25 °C; $\square$, 0 °C; $\triangle$, −25 °C, $\triangledown$, −50 °C.
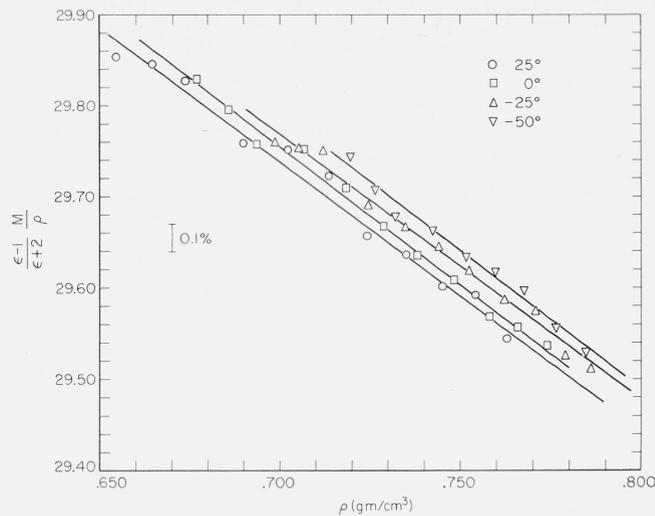
FIGURE 4. *CM of* n-*hexane as a function of density.*
$\bigcirc$, 25 °C; $\square$, 0 °C; $\triangle$, −25 °C; $\triangledown$, −50 °C.

The drawn lines are the least squares fit of the data for each temperature to a straight line of the form $CM = m\rho + b$.

TABLE 2. *Least squares fit of CM to form* $CM = m\rho + b$
(see footnote 5)

T	m $\left(\dfrac{cm^6}{g\ mol}\right)$	b (cm³/mol)	CM for $\rho = 0.7300$ (cm³/mol)
25°	−2.950 ± 0.092	31.804 ± 0.065	29.650 ± 0.004
0°	−3.028 ± .078	31.873 ± .057	29.663 ± .003
−25°	−2.903 ± .088	31.801 ± .065	29.681 ± .002
−50°	−3.019 ± .108	31.904 ± .081	29.700 ± .003

of table 2 gives the CM calculated from the fitted equation at a density of 0.7300 g/cm³, a value well within the range of values for each temperature. This is a much better indication of the variation with temperature than the intercept b, which involves a long extrapolation.

4.2. Comparison of Data

Some comparisons with published work on *n*-hexane are possible. The values of the dielectric constant and at 25 and −50°C are 1.882 and 1.990, respectively, at atmospheric pressure according to NBS Circular 514 [11]. These compare quite favorably with the values reported here of 1.8799 and 1.9908. Data as a function of pressure have also been reported [2] and the comparison given in table 3. The two sets of data are parallel to each other, but the earlier data seem to contain a significant systematic error, perhaps because the capacitance was measured using a two-terminal cell which is relatively less accurate than the three-terminal cell used in the present work.

Somewhat better comparisons can be made for the density. The density at atmospheric pressure at

TABLE 3. *Comparison of results*

p	ϵ (25 °C)		ρ (20 °C)		ρ (0 °C)	
	This work	Chang[a]	This work	Eduljee[b]	This work	Eduljee[b]
0	1.8799	1.896	0.6547	0.6550	0.6769	0.6769
101	1.8972	1.911	.6647		.6856	
501	1.9489	1.962	.6960	.6958	.7125	.7125
1001	1.9955	2.002	.7240	.7235	.7380	.7378
1501	2.0317	2.077	.7450	.7448	.7578	.7577
2001	2.0620	2.077	.7627	.7623	.7738	.7743

[a] Data of Chang [2] adjusted from pressures reported in kg/cm² and a temperature of 30 °C using coefficients derived from this work.

[b] Data of Eduljee [13] reported in volume relative to 0 °C and 1 atm pressure. The data have been made to coincide with the data reported here at 1 atm pressure and 0 °C.

25° is reported to be 0.65483 g/cm³ [8] while at 0° 0.6769 g/cm³ [12]. The measured values are 0.6547 and 0.6769 g/cm³. Some quite good density measurements have been made as a function of pressure [13] and the comparison is given in table 3. The agreement is excellent and easily within the combined experimental uncertainties. As with all comparisons that could be made, this one supports the claimed uncertainties of 0.02 percent for ϵ, 0.02 percent for ρ, and 0.03 percent for CM.

4.3. Interpretation

The observed density dependence of the CM is consistent with the results of the earlier work. Since the equations normally used for the liquid state, such as Onsager's, predict a constant CM, they are clearly inadequate and offer no guide as to the form of the density dependence. It should be noted, however, that the zero density extrapolation of the CM to 31.8 cm³/mol is considerably higher than the reported gas value of 30.0 [14]. This is possibly due to the use of an erroneous form for the density dependence. However, the use of the reciprocal of CM would lead to a still higher value.

The variation of CM with temperature at constant density is also of interest. Within experimental error, the variation seems to be independent of density. One possibility is that n-hexane in the liquid state is polar. This is reasonable since any conformation other than the straight chain could have a permanent moment. If the observed difference of 0.050 ± 0.007 cm³/mol in the CM between -50 and 25 °C is considered to result from a $\mu^2/3kT$ term [17], an effective dipole moment of 0.085 ± 0.006 D (1 debye = 10^{-12} cgs units)[5] is calculated. This is comparable to moments observed in other hydrocarbons [15]. It is doubtful that it is due to impurities, especially water,

since it is believed that the hexane used is quite dry. Even if it is assumed to be saturated with water, (0.053 mole percent [16]) the water contribution would only be 0.02 D. It is believed that the hexane used was drier than this; consequently, impurities are not a likely cause for the temperature variation observed. Also, if the dipolar contribution to the dielectric constant is subtracted out, this would lead to a dielectric constant of 1.8742 at 25 °C and 1 atm which seems too low. Therefore, the temperature dependence of the CM for n-hexane seems to be a property of the pure liquid. Caution should be exercised, however, in interpreting the temperature dependence of the CM as due to a dipole moment. In particular, since the CM is density dependent and this cannot be accounted for by a dipole moment, there could well be a temperature dependence even if there were no dipole moment. This matter will require clarification by further measurements on liquids having known dipole moments.

Much of the initial work in constructing the apparatus was done by Norman L. Brown.

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[5] The error indicated is the computed standard deviation.

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