DIELECTRIC CONSTANT AND DENSITY OF CYCLOHEXANE-BENZENE MIXTURES UNDER HIGH PRESSURE

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New experimental data on the dielectric constant and the density of cyclohexane-benzene mixtures are presented as functions of temperature, pressure and composition.

The dielectric constant has been measured by a frequency counting method with the uncertainty of 0.04% at temperatures from 25°C to 75°C and pressures up to 190 MPa. The density measurements have been performed at the same temperature range under pressures up to 100 MPa with an estimated uncertainty of 0.06%, using a new high pressure burette.

The isotherms of the dielectric constant and the density increase with increasing pressure and their behavior are represented by some empirical equations. The effect of temperature and pressure on the dielectric constant is found to be expressed by a simple linear function of the density. The molar polarization is discussed as functions of density, tempertaure and composition. An analogy between the Owen-Brinkley equation and the Tait equation is also discussed.

Introduction

The dielectric constant of fluids is one of the important physical properties representing the behavior of molecules in an electrostatic field. The effect of pressure on the dielectric constant is also of chemical importance because it relates to the volume change of reacting species which determines the effect on the equilibrium or the rate of a reaction. The study on the pressure and temperature dependence of the dielectric constant provided some valuable information on the molecular interaction[1], and the measurements were applied to determined the density of fluids under the particucar conditions, such as in a critical region[2] or for multiple mixtures at low temperatures[3~6]. So far, however, the investigations on the density dependence of the dielectric constant are quite limited, especially for binary liquid mixtures.

This paper provides the new experimental data of the dielectric constant and the density of cyclohexane-benzene mixtures under high pressures. The measurements have been carried out at

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(*Received November 13, 1979*)

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2) L. A. Weber, *Phys. Rev. A*, **2**, 2379 (1970).
3) D. W. Burfield, H. P. Richardson and R. A. Guereca, *AIChE J.* **16**,, 97 (1970)
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temperatures, 25°C, 50°C and 75°C and under pressures up to 190 MPa for the dielectric constant and 100 MPa for the density. From the experimental results, the behavior of dielectric constant with temperature, pressure, density and composition is described empirically and theoretically. The molar polarization defined by the Clausius-Mossotti equation is also discussed as functions of density, temperature and composition.

Experimentals

Dielectric constant

The dielectric constant of a fluid, ε, is defined by the ratio of the capacitance between two plates filled with the fluid, C, to that in vacuum, C_o,

$$\varepsilon=C/C_o \tag{1}$$

Therefore the measurement of the dielectric constant is reduced to that of the capacitance of a condenser. The bridge method and the heterodyne-beat method are commonly known as accurate techniques to measure the dielectric constant. However these need the tedious and time-consuming procedures to adjust the precision variable condenser. The present method employed is a "frequency counting method" developed recently[7], based on counting the resonant frequency of a L–C oscillating circuit including a high pressure capacitance cell filled with a sample fluid. The resonant frequency of the circuit, f, is expressed by

$$f=1/(2\pi\sqrt{L\cdot(C+C_s)}) \tag{2}$$

where L and C_s are the inductance of a coil and the whole stray capacitance in the circuit, respectively. Substitution of Eq. (1) into Eq. (2) and rearrangement yield

$$\varepsilon=\frac{1}{4\pi^2LC_o}\,\frac{1}{f^2}-\frac{LC_s}{LC_o} \tag{3}$$

Assuming that L, C_o and C_s are independent of temperature and pressure, the equation is reduced to

$$\varepsilon=A'\cdot f^{-2}+B' \tag{4}$$

The dielectric constant of the fluid can be calculated by the measured frequency when the instrument constants, A' and B', have been determined by use of vacuum and a reference liquid, whose dielectric constant was known accurately. Benzene is selected as the reference in the present work and its dielectric constant is 2.2740 at 25°C and atmospheric pressure[8].

The schematic diagram of the apparatus is given in Fig. 1. The left part of this figure is the high pressure system and the right one the electronics measuring system. The latter consists of a frequency counter, a stabilized power supply and the L–C oscillating circuit which is set in an air bath controlled at 40±0.1°C and is covered with a wire gauze for electric shielding. The Hartley-

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[7] T. Makita, H. Kubota, Y. Tanaka and H. Kashiwagi, *Refrigeration*, **52**, 543 (1977)

[8] A. A. Maryott and E. R. Smith, "Table of Dielectric Constants of Pure Liquids", NBS Circ. 514, National Bureau of Standards (1951)

type oscillating circuit is composed of a fixed coil L, a variable condenser C_v and a high pressure capacitance cell filled with a sample liquid. The standard condenser (100.0 pF) C_{SD} could be connected with the circuit by a coaxial switch, in order to confirm the stability of the circuit. The variable condenser is used for a fine adjustment of the resonant frequency. The frequency used ranges between 3.7 and 4.4 MHz with the precision of 1 Hz. The fluctuation of the frequency during one measurement at an experimental condition was less than 10 Hz.

The high pressure capacitance cell is a concentric cylindrical capacitor of two-terminal type as shown in Fig. 2. The outer diameter of inner electrode F is 8 mm and the inner diameter of outer electrode G is 10 mm. The effective length is about 100 mm. The geometrical capacitance of this cell is nearly 25 pF in vacuum. The electrodes are provided with two holes at each end so as to be filled with a fluid. The spacers, H and I, made of glass-fiber reinforced PTFE (Teflon), are employed to insulate between the electrodes and to support them coaxially. The high pressure vessel is made of Ni-Cr-Mo steel, SNCM-5, and is immersed in a thermostat controlled within±0.01°C. The temperature of the sample liquid is determined with a standard thermometer calibrated by the National Research Laboratory of Metrology. The accuracy in temperature measurement is estimated to be better than 0.05°C.

Pressure is generated by an oil pump and, if necessary, is raised by an intensifier, as shown in Fig. 1. The pressure is transmitted to the sample liquid from the oil by bellows, whose displacement

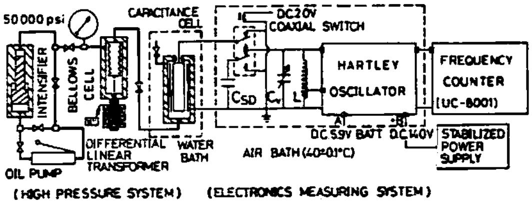

Fig. 1 Schematic diagram of apparatus for dielectric constant measuremants

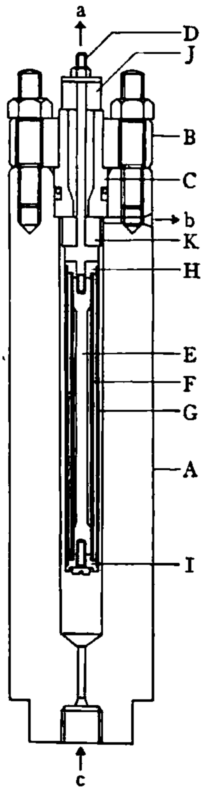

Fig. 2 Cross section of high presssure capacitance cell

A, High Pressure Vessel;
B, Flange;
C, O-ring Closure;
D, Electrode Connector;
E, Support Rod;
F, Inner Electrode;
G, Outer Electrode;
H, I, Teflon Spacers;
J, K, Pyrex Glass Spacers;
a, to Electronic Measuring System;
b, Sample Outlet;
c, Sample Inlet;

is detected by a differential linear transformer so as to prevent an excess compression. Pressure is measured with a Bourdon gauge calibrated against a standard pressure balance with an accuracy of 0.1 percent.

The measurements have been performed isothermally with increasing pressure up to the maximum pressure and then with decreasing pressure down to atmospheric pressure. No hysteresis was observed between the results at increasing and decreasing pressures. With the values of the instrument constants determined, the dielectric constants of cyclohexane and benzene were measured at temperatures up to 75°C under atmospheric pressure. It was found that they agree well with literature values[8] within the uncertainty of the present work and there is no trend of deviation with temperature. The pressure dependence of the capacitance cell was examined by calculating the compression of the cell[9]. This evaluation proved that the effect of pressure on the geometric dimensions of the electrodes was sufficiently small in comparison with the reproducibility of the present measurement. It was also confirmed that the difference between the instrument constants determined before and after a pressure-temperature cycle is insignificant.

Taking account of the uncertainties due to the instruments, the reproducibility of the measurement, the accuracy of the reference dielectric constant values cited, the comparison with literatures and so on, the total uncertainty of the dielectric constant obtained is estimated to be less than 0.04%.

Density

The density has been measured by a new "high pressure burette" method, whose details were described elsewhere[10]. Its principle is similar to that developed by Doolittle et al.[11] When high pressure is applied to the system measured, the compression of the sample liquid of a known weight in a high pressure vessel causes the displacement of mercury level in a high pressure burette. The position of a magnetic float on the surface of mercury is detected outside the burette by a differential linear transformer, whose height is measured with a cathetometer.

The density of the liquid under high pressure, ρ, is calculated by

$$\rho=\frac{W}{(W/\rho_0)-\Delta V} \tag{5}$$

where W is the whole weight of the liquid filled in the vessel, ρ_0 is the density of the liquid at atmospheric pressure and ΔV is the volume change of the liquid in the vessel. ΔV is obtained by the difference between the position of the mercury surface at atmospheric presssure and that at a high pressure, compensated with the volume change of the burette, the vessel, mercury and tubing. The density of cyclohexane-benzene mixtures at atmospheric pressure was cited from the results of Wood *et al.*[12] The density of mercury under high pressure was obtained from the values by Grindley *et al.*[13] The measurement and controll of pressure and temperature were performed in the same

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[9] B. A. Younglove and G. C. Straty, *Rev. Sci. Instrum.*, **41**, 1087 (1970)

[10] H. Kubota, Y. Tanaka and T. Makita, *Kagakukogaku Ronbunshu*, **1**, 176 (1975)

[11] A. K. Doolittle, I. Simon and R. M. Cornish, *AIChE J.*, **6**, 150 (1960)

[12] S. E. Wood and A. E. Austin, *J. Am. Chem. Soc.*, **67**, 480 (1945)

[13] T. Grindley and J. E. Lind, Jr., *J. Chem. Phys.*, **54**, 3983 (1971)

way as those in the dielectric constant measurements. The uncertainty of the density obtained is estimated to be less than 0.06%.

Meterials

Pure cyclohexane and benzene used were "super-special grades" supplied by Wako Pure Chemical Industries, Ltd. and their reported purities are more than 99.8% in volume. They were purified twice by the fractional crystallization.

The mixtures were prepared by the weighing method. The uncertainty of the composition is estimated within 0.03 mole percent.

Results

Dielectric Constant

The raw data obtained for pure components and three mixtures at 25°C, 50°C and 75°C are listed in Table 1, where X_b, P and ε denote the mole fraction of benzene, the pressure in MPa and the dielectric constant, respectively. Although the data at 20°C, 30°C, 40°C and 60°C are not included in Table 1, they are also used in the analysis described below. The data at 75°C and 0.101 MPa are determined by the extrapolation from both the pressure dependence at higher pressures and the temperature dependence at 0.101 MPa.

Fig. 3 exhibits typical curves for a mixture of X_b=0.50, as an instance to show the relationship between the dielectric constant and the pressure. Every isotherm for each mixture increases monotonously with increasing pressure and is represented by the following polynomials:

$$\varepsilon=a+bP+cP^2+dP^3+eP^4 \qquad (6)$$

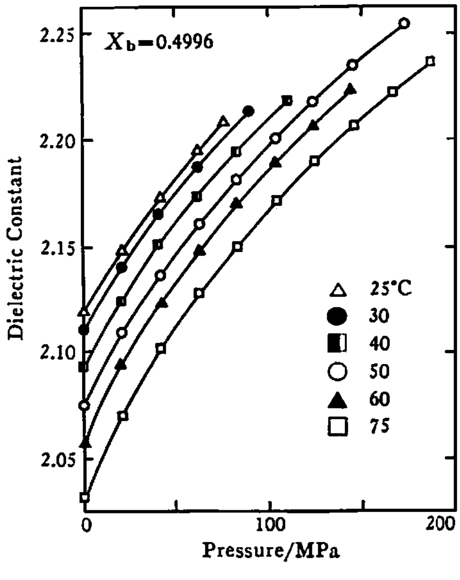

Fig. 3 Pressure dependence of dielectric constant of cyclohexane-benzene mixture of X_b=0.4996

Table 1 Dielectric Constant of Cyclohexane-Benzene Mixtures

(X_b: mole fraction of benzene, P: pressure in MPa)

Temp.	X_b = 0.0000		X_b = 0.2500		X_b = 0.4996		X_b = 0.7462		X_b = 1.0000	
°C	P	ε	P	ε	P	ε	P	ε	P	ε
25	0.10	2.0150	0.10	2.0589	0.10	2.1189	0.10	2.1906	0.10	2.2740
	6.96	2.0241	6.96	2.0689	7.52	2.1302	7.24	2.2017	6.96	2.2832
	13.86	2.0335	14.00	2.0782	14.20	2.1396	13.93	2.2111	14.07	2.2931
	20.72	2.0419	20.89	2.0868	21.03	2.1486	20.99	2.2205	20.68	2.3020
	27.27	2.0497	27.79	2.0950	27.92	2.1572	27.89	2.2290	27.58	2.3102
	33.85	2.0570	34.47	2.1027	34.34	2.1647	34.75	2.2370	34.47	2.3182
			41.44	2.1099	41.37	2.1725	41.30	2.2452	41.54	2.3270
			48.34	2.1172	48.40	2.1801	48.88	2.2534	48.47	2.3350
			55.30	2.1239	55.30	2.1874	55.43	2.2601	55.37	2.3424
			62.19	2.1309	62.19	2.1945	62.05	2.2677	62.26	2.3499
			69.29	2.1372	69.22	2.2010	69.36	2.2754	69.50	2.3579
					76.19	2.2077	76.05	2.2818		
							83.29	2.2888		
							89.63	2.2946		
50	0.10	1.9757	0.10	2.0172	0.10	2.0754	0.10	2.1467	0.10	2.2240
	7.24	1.9876	7.24	2.0303	7.10	2.0871	7.31	2.1603	7.17	2.2350
	14.27	1.9985	14.13	2.0411	13.58	2.0983	13.82	2.1703	13.86	2.2465
	21.00	2.0088	20.82	2.0506	20.75	2.1084	21.03	2.1809	20.75	2.2570
	28.06	2.0168	27.89	2.0601	27.65	2.1190	27.86	2.1904	27.86	2.2672
	35.09	2.0254	34.20	2.0689	34.68	2.1275	34.47	2.1989	34.75	2.2762
	42.06	2.0337	41.71	2.0784	41.71	2.1365	41.85	2.2078	48.47	2.2934
	48.54	2.0416	48.61	2.0863	48.61	2.1450	48.88	2.2159	55.23	2.3020
	55.99	2.0495	55.37	2.0938	55.50	2.1530	55.64	2.2237	62.19	2.3097
	62.26	2.0560	62.40	2.1017	62.54	2.1608	62.95	2.2318	69.22	2.3178
	69.36	2.0629	69.26	2.1086	70.05	2.1687	69.64	2.2392	76.15	2.3250
	76.26	2.0693	76.05	2.1147	76.26	2.1753	76.05	2.2460	83.12	2.3324
	82.81	2.0751	83.01	2.1215	82.77	2.1813	83.12	2.2535	89.98	2.3396
			89.91	2.1273	89.80	2.1882	89.98	2.2602	96.53	2.3467
			96.80	2.1334	96.70	2.1947	96.46	2.2667	103.42	2.3531
			103.77	2.1394	103.42	2.2008	103.77	2.2735	110.87	2.3603
			110.32	2.1452	110.25	2.2070	110.66	2.2797	117.52	2.3657
			117.35	2.1510	117.14	2.2119	117.56	2.2856	124.11	2.3717
			124.24	2.1566	123.62	2.2175	124.11	2.2914	131.00	2.3776
			131.35	2.1621	131.00	2.2236	131.00	2.2972	145.10	2.3888
					137.90	2.2285	138.24	2.3028	151.41	2.3941
					144.79	2.2341	144.79	2.3068	159.06	2.3979
					151.82	2.2390				
					158.65	2.2438				
					165.54	2.2484				
					172.71	2.2536				
75	0.10	1.9370	0.10	1.9776	0.10	2.0317	0.10	2.0994	0.10	2.1744
	7.10	1.9502	7.27	1.9912	7.58	2.0459	7.38	2.1137	7.58	2.1891
	14.62	1.9630	13.79	2.0032	13.93	2.0579	14.00	2.1262	14.00	2.2013
	21.31	1.9739	20.68	2.0149	20.96	2.0702	20.75	2.1376	20.51	2.2127
	27.86	1.9838	27.72	2.0260	27.58	2.0810	27.58	2.1485	27.92	2.2253
	34.68	1.9929	34.51	2.0357	34.82	2.0914	34.47	2.1592	34.47	2.2353
	41.71	2.0021	41.37	2.0447	41.85	2.1014	41.51	2.1696	41.47	2.2450
	48.68	2.0110	48.54	2.0530	48.68	2.1105	48.61	2.1795	48.61	2.2551
	55.43	2.0195	55.30	2.0615	55.61	2.1188	55.30	2.1881	55.16	2.2636
	62.54	2.0274	62.40	2.0696	62.43	2.1270	62.40	2.1970	62.05	2.2725
	69.64	2.0349	69.29	2.0768	69.36	2.1361	68.95	2.2052	69.09	2.2811
	76.19	2.0420	76.12	2.0844	76.12	2.1424	75.84	2.2130	75.84	2.2884
	83.01	2.0492	83.01	2.0910	83.01	2.1495	82.74	2.2201	82.74	2.2962
	90.05	2.0550	89.94	2.0984	89.91	2.1566	89.63	2.2277	89.84	2.3042
	96.60	2.0615	97.22	2.1051	96.87	2.1639	96.80	2.2340	96.66	2.3112
	103.84	2.0677	117.56	2.1241	104.11	2.1719	103.49	2.2406	110.59	2.3258
	110.11	2.0731	124.38	2.1293	110.45	2.1778	110.59	2.2477	131.21	2.3452
	117.35	2.0784	131.62	2.1357	117.59	2.1829	117.21	2.2539	138.24	2.3520
			138.10	2.1409	124.45	2.1896	124.52	2.2605	151.68	2.3635
			144.93	2.1463	131.07	2.1950	131.35	2.2660	158.58	2.3683
			152.37	2.1524	137.85	2.2008	138.52	2.2721	165.47	2.3740
					145.13	2.2065	145.34	2.2789	172.44	2.3801
					152.03	2.2125	152.10	2.2845	179.26	2.3857
					158.72	2.2173	158.65	2.2904	185.40	2.3906
					166.16	2.2228	164.51	2.2961		
					172.37	2.2274	172.92	2.3022		
					179.26	2.2323	179.26	2.3071		
					184.43	2.2357				
					186.09	2.2367				

where P is the pressure in MPa. The coefficients of Eq. (6), determined by means of the least squares method, are given in Table 2 with the average and the maximum deviations.

Fig. 4 shows the temperature effect on the dielectric constant for a mixture of $X_b=0.50$. It is obvious that every isobar of the dielectric constant for each mixture decreases with an increase of

Table 2 Coefficients of Polynomial (6) for the Dielectric Constant of Cyclohexane-Benzene Mixtures

Mole fraction of benzene	Temp. °C	a	$b\times10^3$	$c\times10^5$	$d\times10^8$	$e\times10^{10}$	Ave.Dev* %	Max.Dev.* %
X_b = 0.000	25	2,01476	1.4075	-0.4683	—	—	0,005	0.01
	50	1,97544	1.8213	-1.6367	18,471	-9,343	0,01	0,04
	75	1,93709	1,9264	-1,0975	6,415	-1,964	0.009	0.02
X_b = 0.2500	25	2,05883	1,4740	-0,6952	2,925	—	0,005	0,01
	50	2,01756	1,7378	-0,7641	2,135	—	0.01	0.03
	75	1,97696	2,0788	-1.3600	7.6916	-1.818	0.01	0.03
X_b = 0,4996	25	2,11883	1.5566	-0,7433	3,047		0,004	0.01
	50	2,07539	1,7437	-0,7711	3,0583	-0,5706	0,01	0,03
	75	2,03109	2,0714	-1,1358	5,2511	-1,0425	0,01	0.04
X_b = 0,7462	25	2,19078	1,5160	-0.5693	1.933		0,01	0.02
	50	2,14704	1,8147	-1,1499	8.0425	-2,413	0.01	0.03
	75	2,09913	2,0363	-0.9376	3,2926	-0,4346	0,01	0,04
X_b = 1,000	25	2,27373	1,4343	-0.4486	1.816		0,007	0,02
	50	2,22350	1,7577	-0.8320	4,5882	-1,233	0,01	0,03
	75	2,17446	2,0446	-0.9722	4,0477	-0,7374	0,01	0,03

* The deviation percent is calculated by $|100(\varepsilon_{exp}-\varepsilon_{cal})/\varepsilon_{cal}|$

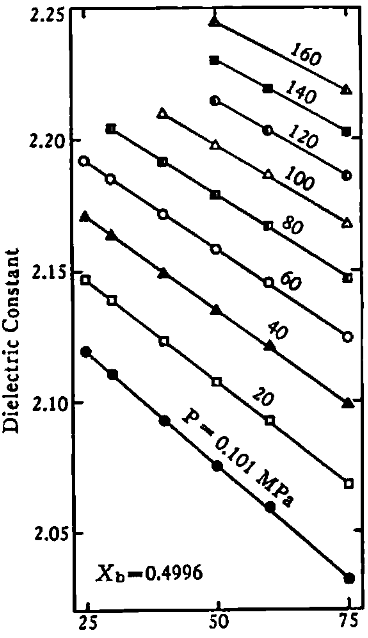

Fig. 4 Temperature dependence of dielectric constant of cyclohexane-benzene mixture of X_b=0.4996

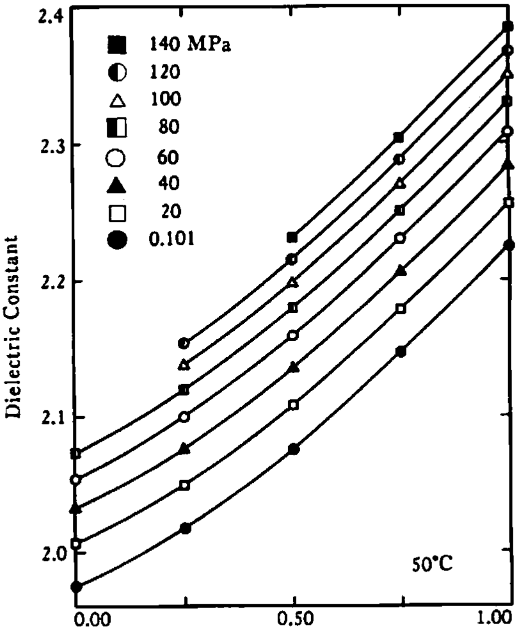

Fig. 5 Dependence of dielectric constant of cyclohexane-benzene mixtures on mole fraction of benzene at 50°C

temperature and its slope is linear over the whole temperature range in this work like other liquids[14~16]. The composition dependence of the dielectric constant at 50°C is shown along isobars in Fig. 5. All the isobars at each temperature behave as slightly concave curves, but they have no anomalous minima.

The dielectric constant obtained for pure benzene are compared with the values in the recent literatures. At 50°C the present results are in good agreement with those by Hartmann et al[17]. under pressures up to 180 MPa with the average deviation of 0.04%. On the other hand, most of the smoothed values by Vij et al.[16] are higher than those of this work over the whole range of temperature and pressure. So far there exist no data on the pressure dependence of the dielectric constant for cyclohexane-benzene mixtures in the literature.

Density

Table 3 lists the raw data obtained at temperatures 25°C, 50°C and 75°C under pressures up to 100 MPa. As an example, Fig. 6 shows the pressure dependence of the density for a mixture of X_b $=0.50$. All the isotherms of the density increase with increasing pressure like those of the dielectric constant and are fitted to the polynomials:

$$\rho=a'+b'P+c'P^2+d'P^3+e'P^4 \tag{7}$$

where ρ is the density in $10^3\mathrm{kg/m^3}$ and P is the pressure in MPa. The above equations are found to reproduce the experimental data satisfactorily at each temperature and composition. However, they are often unsuitable to derive the thermodynamic properties, such as the isothermal compressibility. Therefore, the data are also expressed by the Tait equation:

$$\frac{\rho-\rho_0}{\rho}=C\log\left(\frac{B+P}{B+P_0}\right) \tag{8}$$

where ρ_0 is the density in $10^3\mathrm{kg/m^3}$ at P_0, which is taken as 0.101 MPa in the present work. It was

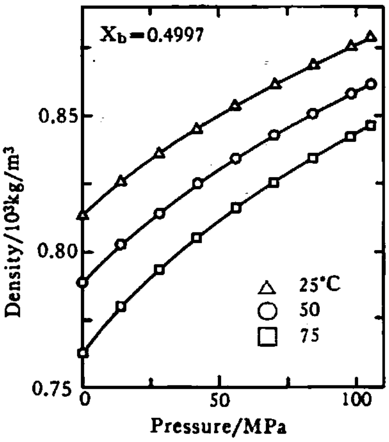

Fig. 6 Pressure dependence of density of cyclohexane-benzene mixture of $X_b=0.4997$

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14) R. G. Bennett, G. H. Hall and J. H. Calderwood, *J. Phys., D*, **6**, 781 (1973)

15) W. G. S. Scaife, *J. Phys., A*, **4**, 413 (1971)

16) J. K. Vij and W. G. S. Scaife, *J. Chem. Phys.*, **64**, 2226 (1976)

17) H. Hartmann, A. Neumann and G. Rinck, *Z. Phys. Chem. (Frankfurt)*, **44**, 204 (1965)

Table 3 Density of Cyclohexane-Benzene Mixtures

(X_b : mole fraction of benzene, P: pressure in MPa, ρ : density in 10^3kg/m^3)

Temp.	X_b = 0.0000		X_b = 0.2504		X_b = 0.4997		X_b = 0.7497		X_b = 1.0000	
°C	P	ρ	P	ρ	P	ρ	P	ρ	P	ρ
25	0.10	0.77378	0.10	0.79154	0.10	0.81352	0.10	0.84063	0.10	0.87380
	6.87	0.7794	6.80	0.7976	6.89	0.8197	6.95	0.8470	7.49	0.8802
	13.86	0.7848	13.83	0.8032	14.12	0.8255	14.11	0.8527	13.95	0.8852
	21.10	0.7901	21.21	0.8086	21.50	0.8311	21.18	0.8581	21.06	0.8903
	27.93	0.7947	29.09	0.8141	28.34	0.8358	28.05	0.8630	27.89	0.8950
	35.10	0.7993	35.23	0.8181	34.79	0.8402	35.10	0.8677	35.01	0.8997
			41.87	0.8223	41.96	0.8449	41.78	0.8721	42.11	0.9042
			49.30	0.8267	48.97	0.8492	49.44	0.8768	48.98	0.9085
			56.03	0.8306	56.01	0.8534	55.89	0.8807	55.88	0.9125
			62.84	0.8344	62.62	0.8573	63.30	0.8850	62.94	0.9165
			70.09	0.8382	70.46	0.8616	70.51	0.8889	70.01	0.9203
			77.13	0.8419	77.19	0.8651	77.31	0.8925		
			84.15	0.8452	84.34	0.8687	84.36	0.8961		
			91.17	0.8486	91.55	0.8723	91.35	0.9000		
			98.28	0.8518	98.41	0.8756	98.39	0.9036		
			105.12	0.8547	105.42	0.8789	105.62	0.9071		
50	0.10	0.74984	0.10	0.76711	0.10	0.78846	0.10	0.81476	0.10	0.84689
	7.22	0.7573	7.32	0.7746	7.32	0.7963	7.06	0.8222	6.94	0.8538
	14.21	0.7636	14.13	0.7808	14.06	0.8026	14.25	0.8289	14.07	0.8601
	21.10	0.7694	21.16	0.7869	21.06	0.8086	21.29	0.8349	20.75	0.8657
	27.96	0.7748	27.99	0.7922	27.99	0.8142	28.05	0.8403	27.83	0.8713
	35.15	0.7800	35.18	0.7976	35.19	0.8196	35.13	0.8457	35.02	0.8766
	42.01	0.7851	42.17	0.8025	42.28	0.8248	42.26	0.8509	42.26	0.8817
	49.43	0.7899	48.86	0.8070	49.25	0.8296	48.92	0.8555	49.09	0.8864
	56.27	0.7942	56.05	0.8115	56.20	0.8341	55.82	0.8600	56.03	0.8908
	63.15	0.7983	63.07	0.8158	63.25	0.8385	62.91	0.8648	63.05	0.8953
	70.32	0.8024	70.21	0.8199	70.32	0.8427	70.51	0.8693	70.23	0.8995
	77.15	0.8062	77.43	0.8241	78.25	0.8472	77.30	0.8733	77.16	0.9034
	84.03	0.8100	84.20	0.8277	84.35	0.8506	84.60	0.8774	84.11	0.9073
			91.26	0.8313	91.16	0.8541	91.35	0.8811	91.21	0.9111
			98.26	0.8347	98.31	0.8579	98.07	0.8848	98.60	0.9149
			105.13	0.8381	105.28	0.8615	105.15	0.8888	105.12	0.9186
75	0.10	0.72484	0.10	0.74189	0.10	0.76267	0.10	0.78814	0.10	0.81938
	7.15	0.7337	7.02	0.7504	6.99	0.7722	6.99	0.7968	6.86	0.8275
	13.98	0.7409	14.18	0.7582	13.94	0.7800	13.94	0.8043	13.98	0.8349
	21.01	0.7478	20.79	0.7648	20.93	0.7868	20.80	0.8111	21.09	0.8417
	27.98	0.7540	27.87	0.7712	28.04	0.7936	28.04	0.8178	28.20	0.8481
	35.10	0.7599	35.02	0.7772	34.99	0.7996	35.02	0.8238	35.25	0.8540
	41.95	0.7653	42.08	0.7828	41.98	0.8053	41.87	0.8294	42.21	0.8595
	49.17	0.7705	49.19	0.7880	48.95	0.8106	49.23	0.8349	49.73	0.8652
	56.11	0.7753	56.03	0.7927	55.24	0.8160	55.78	0.8401	56.19	0.8697
	62.92	0.7798	63.05	0.7975	63.09	0.8208	62.91	0.8451	63.03	0.8744
	69.95	0.7845	69.94	0.8019	70.13	0.8254	70.33	0.8500	70.35	0.8792
	77.41	0.7891	76.98	0.8063	77.13	0.8299	77.40	0.8545	77.50	0.8836
	84.04	0.7930	84.32	0.8104	84.22	0.8341	84.42	0.8588	84.41	0.8878
	91.42	0.7970	91.06	0.8142	91.17	0.8382	91.16	0.8629	91.61	0.8919
	98.17	0.8007	97.99	0.8178	98.03	0.8421	98.09	0.8670	98.47	0.8958
	105.33	0.8044	104.93	0.8214	105.40	0.8463	105.10	0.8712	105.13	0.8991

known that the coefficient *C* is independent of temperature for many organic liquids[18]. In the present analysis, the coefficients, B and C, are first determined for each composition and temperature by the least squares method. For each composition C is found to vary scarcely with temperature. Therefore, on the assumption that C is a constant independent of temperature over the whole experimental range, B and C are redetermined and listed in Table 4. The Tait equation represents the present results as well as or slightly worse than the polynomial expression. As mentioned above, however, the Tait equation can be applied to calculate the isothermal compressibility and is a simple closed equation of state with only two parameters. So the Tait equation is preferable to the poly-

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[18] R. E. Gibson and J. F. Kincaid, *J. Am. Chem. Soc.*, **60**, 511 (1938)

nomial for representing the PVT relations of the present mixtures. The density values at 50°C smoothed by Eq. (8) are plotted against the composition of the mixtures in Fig. 7. Every isobar exhibits the similar behavior to that of the dielectric constant.

There are many reports on the pressure dependence of the density of pure benzene. The measurement by Gibson et al.[18] is considered as an accurate and representative one of them at temperatures 25°C to 65°C under pressures up to 100 MPa. They fitted their data to the Tait equation and concluded that C was independent of temperature and that ρ_0 and B were expressed by the polynomials of temperature. As they did not measure the density at 50°C and 75°C, the density has been calculated with the coefficients interpolated to 50°C and extrapolated to 75°C. Their values agree well with the present results at only 25°C. The pressure coefficient of the density, $(\partial\rho/\partial P)_T$, of Gibson et al. is larger than the present one. The discrepancy increases with increasing pressure up to 0.2% at 75°C

Table 4 Coefficients of the Tait Equation (8) for Cyclohexane-Benzese Mixtures

Mole fraction of benzene	Temp. °C	ρ_0 10^3 kg/m^3	B MPa	C —	Ave. Dev. %	Max. Dev. %
X_b = 0.000	25	0.77378	77.9	0.1988	0.01	0.01
	50	0.74984	61.5		0.01	0.05
	75	0.72484	49.3		0.03	0.06
X_b = 0.2504	25	0.79154	74.9	0.1947	0.01	0.03
	50	0.76711	61.1		0.01	0.03
	75	0.74189	48.9		0.01	0.03
X_b = 0.4997	25	0.81352	76.7	0.1976	0.02	0.04
	50	0.78846	62.6		0.02	0.06
	75	0.76267	48.9		0.03	0.11
X_b = 0.7497	25	0.84063	85.2	0.2087	0.02	0.05
	50	0.81476	70.2		0.02	0.06
	75	0.78814	56.8		0.02	0.06
X_b = 1.000	25	0.87380	88.5	0.2000	0.01	0.03
	50	0.84689	72.7		0.01	0.05
	75	0.81938	58.9		0.01	0.04

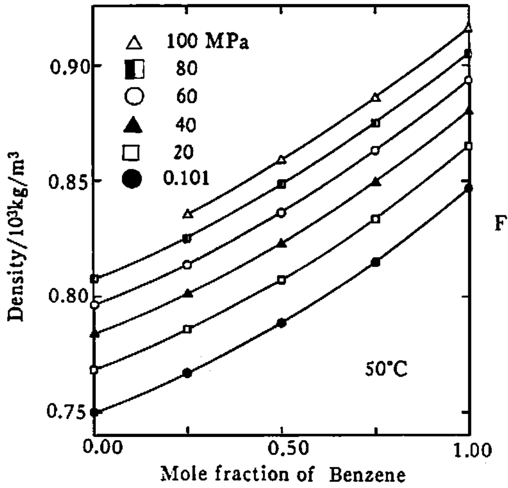

Fig. 7 Dependence of density of cyclohxane-benzene mixtures on mole fraction of benzene at 50°C

and 100 MPa. It seems that this inconsistency would come partly from the inadequacy of extrapolating their data to 75°C.

There are a few available papers[19~22] on the density for pure cyclohexane under high pressure. The values of Kerimov et al.[21] are only ones that can be compared with the present results at 50°C under pressures up to 70 MPa. Most of their data are found to be higher than those of this work. Holder et al.[22, 23] carried out the measurement for cyclohexane-benzene mixtures under pressures up to 10 MPa. Their data agree well with the present results within the experimental error.

Since the present results can not be sufficiently compared with the literature values, it is attempted to represent the data by the Hudleston equation[24] which is often used to verify the reliability of the PVT data of liquids. The equation is found to represent the data very well except the low pressure region below 20 MPa, where it would be sensitive to the uncertainty in the measurements. The reproducibility of the Hudleston equation is also found to be better than that of the Tait equation. It is, however, not easy to solve the Hudleston equation for the density at a given pressure.

Discussion

The compositions of the mixtures prepared for density measurements slightly differ from those for dielectric constant measurements. In order to correlate the dielectric constant with the density, the density of mixtures of the same compositions used in the dielectric constant measurements is calculated using the Tait equation.

It was found in our previous work[7] that a simple relation exists between the dielectric constant and the density of a fluid. In Fig. 8, a part of the dielectric constant obtained is plotted against the density in the limited range. It is found that the difference between the isotherms of the same compositions almost disappears and that the linear relations exist over the whole range of the present work. This fact suggests that the pressure and temperature effect on the dielectric constant is reduced to the effect of the density only. In each composition, the dielectric constant is found to be represented by a linear function of density within the average deviation of 0.06%.

A few equations have been proposed to express the pressure dependence of the dielectric constant of liquids. Representative one of them is the Owen-Brinkley equation[25, 26], which was derived from the Tait equation and the electrostatic theory.

$$\frac{\varepsilon-\varepsilon_0}{\varepsilon}=A\log\frac{D+P}{D+P_0} \qquad (9)$$

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[19] H. H. Reamer and B. H. Sage, *Chem. Eng. Data Ser.*, 2, 9 (1957)

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[22] G. A. Holder and E. Whalley, *Trans. Faraday Soc.*, 58, 2095 (1962)

[23] G. A. Holder and E. Whalley, *ibid.*, 58, 2108 (1962)

[24] L. J. Hudleston, *Trans. Faraday Soc.*, 33, 97 (1937)

[25] B. B. Owen and S. R. Brinkley, Jr., *Phys. Rev.*, 64, 32 (1943)

[26] B. B. Owen, *J. Chem. Educ.*, 21, 59 (1944)

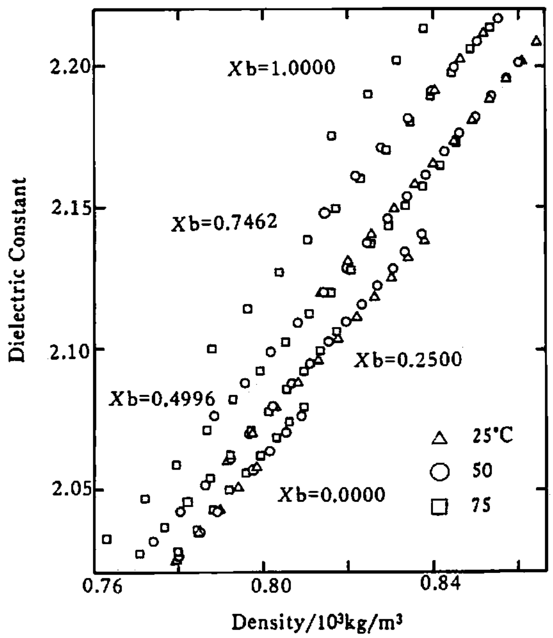

Fig. 8 Density dependence of dielectric constant of cyclohexane-benzene mixtures

where ε_0 is the dielectric constant at P_0, which is taken as 0.101 MPa in the present work. Owen et al. pointed out that the coefficient D was identical with B in the Tait equation and A was practically independent of temperature. However the data used for their analysis are now out of date and inaccurate. Although there are several reports on the equation[27~29], the validity of the equation was not discussed sufficiently. Therefore, using the present data, the coefficients of the equation have been determined on the following assumptions:

1) Both coefficients, A and D, are determined without restriction, that is, D is not identical with B in the Tait equation, and A is dependent on temperature, T. ($D \neq B$, $A(T_1) \neq A(T_2)$)
2) D is not identical with B and A is independent of T. ($D \neq B$, $A(T_1) = A(T_2)$)
3) D is identical with B and A is dependent on T. ($D = B$, $A(T_1) \neq A(T_2)$)
4) D is identical with B and A is independent of T. ($D = B$, $A(T_1) = A(T_2)$)

As representatives of the mixtures, the coefficients obtained for cyclohexane, mixture of $X_b = 0.50$ and benzene are listed in Table 5. There is a good agreement between the present raw data and the dielectric constants calculated with the assumption (1). It is concluded that the Owen-Brinkley equation without restriction represents the dielectric constants of liquids under high pressure satisfactorily, as described by Hartmann et al.[28] and Srinivasan et al.[30] With the assumption (2), it is found that Eq. (9) can also reproduce the data well. On the other hand, Eq. (9) with the assumption (4) expresses the data worst because of the rigorous restriction. The ability with the assumption (3)

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27) E. Hückel and E. Ganssauge, *Z. Phys. Chem.* (*Frankfurt*), **12**, 110 (1957)
28) H. Hartmann, A. Neumann and G. Rinck., *ibid.*, **44**, 218 (1965)
29) M. Nakahara, *Rev. Phys. Chem. Japan*, **44**, 57 (1974)
30) K. R. Srinivasan and R. L. Kay, *J. Chem. Phys.*, **60**, 3645 (1974)

Table 5 Coefficients of the Owen-Brinkley Equation (9) for Cyclohexane- Benzene Mixtures

mole fraction of benzene	Temp. °C	Assumption	ε_0	B MPa	C	Ave.Dev. %	Max.Dev. %
X_b = 0.000	25	(1)	2.0150	105.8	0.1703	0.01	0,02
	50		1.9757	71.4	0.1435	0.01	0,05
	75		1.9370	65.7	0.1538	0.01	0,03
	25	(2)		92.9	0.1517	0.01	0,02
	50			76.8		0,02	0.07
	75			64.4		0,01	0.03
	25	(3)		77.9	0.1301	0.01	0.03
	50			61.6	0.1287	0.03	0.06
	75			49.3	0.1271	0.08	0.13
	25	(4)		77.9	0.1275	0.03	0.05
	50			61.6		0.04	0.09
	75			49.3		0.08	0.14
X_b = 0.4996	25	(1)	2.1189	87.3	0.1475	0.01	0,01
	50		2.0754	81.0	0.1595	0.01	0.03
	75		2.0317	70.6	0.1637	0.02	0.04
	25	(2)		96.7	0.1601	0.01	0.02
	50			81.4		0.01	0.03
	75			68.1		0.02	0.05
	25	(3)		76.7	0.1334	0.02	0.04
	50			62.6	0.1353	0.08	0.15
	75			48.9	0.1316	0.15	0.23
	25	(4)		76.7	0.1330	0.02	0,05
	50			62.6		0.11	0.29
	75			48.9		0.16	0.28
X_b = 1.000	25	(1)	2.2740	153.8	0.2196	0.01	0.02
	50		2.2240	97.9	0.1749	0.02	0.08
	75		2.1744	79.5	0.1726	0.02	0.04
	25	(2)		117.5	0.1745	0.02	0.05
	50			97.6		0.02	0.07
	75			80.9		0.02	0.05
	25	(3)		88.5	0.1384	0.04	0.09
	50			72.7	0.1428	0.08	0.14
	75			58.9	0.1432	0.12	0.23
	25	(4)		88.5	0.1428	0.08	0.13
	50			72.7		0.08	0.14
	75			58.9		0.13	0.26

to represent the data is also not good. This fact does not necessarily mean the inadequacy of assumption (3), because not only the dielectric constant data but also the density data are subject to the errors of measurements. If one used the values of B given by Gibson et al., the reproducibility of the equation is improved but still not good for the present work.

By combining the Tait equation (8) and the Owen-Brinkley equation (9) with assumption (3), a simple relation is deduced as follows:

$$\frac{1}{\varepsilon}=\left(\frac{1}{\varepsilon_0}-\frac{A}{C}\cdot\frac{1}{\rho_0}\right)+\frac{A}{C}\cdot\frac{1}{\rho}=f'+(g'/\rho) \qquad (10)$$

that is, a linear relationship between the reciprocals of the dielectric constant and the density exists. However, the least squares reduction of the data shows slightly worse fit for equation (10) than for the simple ε vs. ρ linear relations as shown in Fig. 8. This fact implies that D is not identical with B for the present mixtures.

The Clausius-Mossotti equation is theoretically derived for nonpolar liquids in an electrostatic field as follows:

$$P_M=\frac{\varepsilon-1}{\varepsilon+2}\,\frac{M}{\rho}=\frac{4}{3}\pi N\alpha \tag{11}$$

where P_M is the molar polarization, M the molecular weight, N the Avogadro's number and α the molecular polarizability. According to the theory, the temperature and pressure dependence of the molar polarization is very small, and an additive law

$$P_M=\sum_i X_i P_{Mi} \tag{12}$$

is held for a mixture of nonpolar liquids as an ideal solution. Since cyclohexane and benzene are nonpolar liquids, it is expected that the present mixtures exhibit such a behavior. The density dependence of the molar polarization is shown in Fig. 9, where the molecular weights of the mixtures were calculated by the mole fraction average of the pure component values. Then, the molar polarization of the mixtures was obtained by

$$P_M=\frac{\varepsilon-1}{\varepsilon+2}\,\frac{1}{\rho}\{(1-X_b)M_1+X_bM_2\} \tag{13}$$

where M_1 and M_2 are the molecular weights of cyclohexane and benzene, respectively. It is found that the variation of the molar polarization with density is very small and that the molar polarization is sensitive to the inaccuracies in the dielectric constant and the density measurements. The molar polarization shows an approximately linear decrease with increasing density and is slightly dependent on temperature. The same linear relationship has been reported for other liquids[15,31,32], and for a polar liquid the temperature effect is distinct due to a dipole moment[32]. In the present results, the temperature coefficients of the molar polarization, $(\partial P_M/\partial T)_\rho$, are negative for mixtures of $X_b=0.50$, 0.75 and pure benzene. However they are too small to confirm the presence of a dipole moment. On

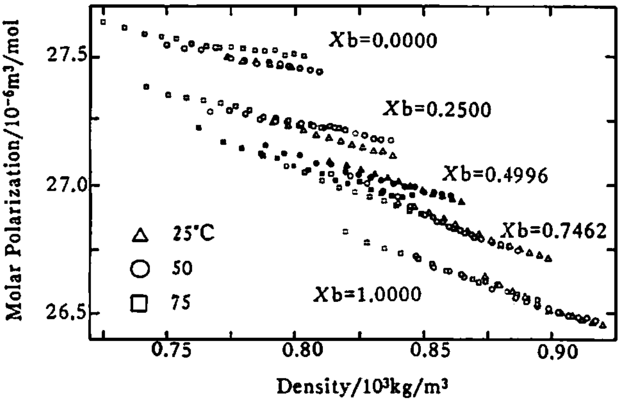

Fig. 9 Density dependence of molar polarization of cyclohexane-benzene mixtures

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31) F. I. Mopsik, *J. Res. Nat. Bur. Stand.*, **71A**, 287 (1967)
32) F. I. Mopsik, *J. Chem. Phys.*, **50**, 2559 (1969)

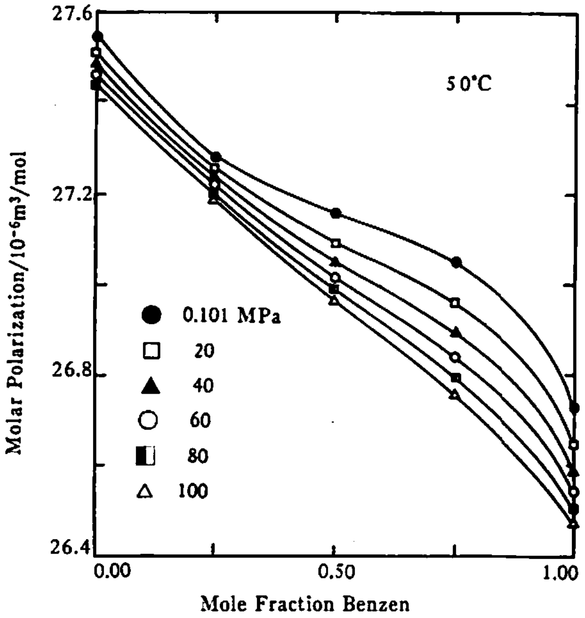

Fig. 10 Dependence of molar polarization of cyclohexane-benzene mixtures on mole fraction of benzene at 50°C

the other hand, those for cyclohexane and mixture of X_b=0.25 are positive contrary to the theory. The similar temperature dependence was observed for carbon disulfide[32]. The isotherms of 0.50 mixture are close to those of 0.75 mixture, while those of other mixtures depart from each other.

For the mixture composed of simple fluids it was verified[3~6] that an additive law of the molar polarization was held at a given pressure and temperature. In the present results, however, as shown in Fig. 10, every isobar deviates from the behavior of an ideal mixture and an inflexion is observed at the composition between X_b=0.50 and X_b=0.75. This deviation reveals that the particular molecular interaction between unlike molecules exists. Since the Clausius-Mossotti relation was ideally derived, it is not suitable to assume that the molecular polarizability does not change even in the dense state. Other formulas derived for the compressed fluid should be necessary to discuss the present results.

The authors wish to express their appreciation to Mr. Toshiharu Takagi, Kyoto Technical University, for his advice and assistance in constructing the apparatus for the dielectric constant measurements and are also indebted to Mr. Junzo Kobo and Miss Ryoko Tanaka for their careful measurements of the density.

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