benzene and *o*-, *m*- and *p*-dichlorobenzene in benzene and in hexane are given.

The polarization and electric moments calculated indicate that, as might be expected, the molecules affect one another more strongly, the greater their moments, the greater their concentrations and the lower the temperature.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY]

THE DIELECTRIC POLARIZATION OF LIQUIDS.
II. THE TEMPERATURE DEPENDENCE OF THE POLARIZATION IN CERTAIN LIQUID MIXTURES[1]

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As the results reported in Part I showed that the effect of polar molecules upon one another in dilute solution varied greatly with concentration and with temperature, it was evident that accurate determinations of dielectric constant and density over a wide range of temperature were needed.

Apparatus

The apparatus described in Part I was modified, although the same capacity bridge with the same wave length of 600 meters was used. The Western Electric 216-A tube in the oscillator was replaced by a 5-watt 104-DW power tube, upon the plate of which 250 volts were applied by means of a high speed motor generator. This increased the accuracy of the bridge balance by supplying more current. The measuring cell used in the earlier work was replaced by a condenser of approximately 200 $\mu\mu$f. capacity, which greatly reduced the relative error of a capacity measurement. Since the capacity of this cell when filled with a liquid of high dielectric constant was greater than that of the precision condenser which was used to measure it, a 1000 $\mu\mu$f. variable air condenser of the same type as that used in the balancing arm of the bridge was so arranged that, by means of interchangeable brass rods dipping into cups filled with mercury, it could be connected in series with the cell or in parallel with the precision condenser or could be totally disconnected. When the capacity of the cell was too great to be measured by direct substitution on the precision condenser, this variable air condenser was set at a convenient value, measured on the precision condenser, and then connected in series with the cell. The capacity of the cell and condenser, thus reduced by the series connection, was measured on the precision condenser and the capacity of the cell alone then calculated.

The measuring cell (Fig. 1) was designed in such a way as to have large electrical capacity, small internal volume and small temperature lag. It was made up of three concentric platinum cylinders (A), with diameters 1.95, 1.80 and 1.64 cm., respectively, open at the ends. The outer and inner cylinders, which were 9.2 cm. long, were con-

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[1] A paper based upon the results of the present contribution was presented before the Physical and Inorganic Division of the American Chemical Society in Richmond, April, 1927.

[2] DuPont Fellow in Chemistry, 1926–27.

nected together and to ground while the middle cylinder, which was 8 cm. long, was centered between them and held at a distance of 0.05 cm. from them by small blocks of mica placed at the top and bottom. The entire condenser was enclosed in a vessel consisting of two concentric glass tubes sealed together at top and bottom, the outer tube being but slightly larger than the outer platinum cylinder and the inner tube fitting inside the innermost platinum cylinder. The leads, which were platinum wires welded to the cylinders, were brought out through heavy capillary tubes (B, B′), spread to a distance of 8 cm. from one another to reduce the mutual inductance and capacity of the leads, the ends of which were sealed into the bottoms of mercury filled cups (C, C′) to make connections with the bridge.

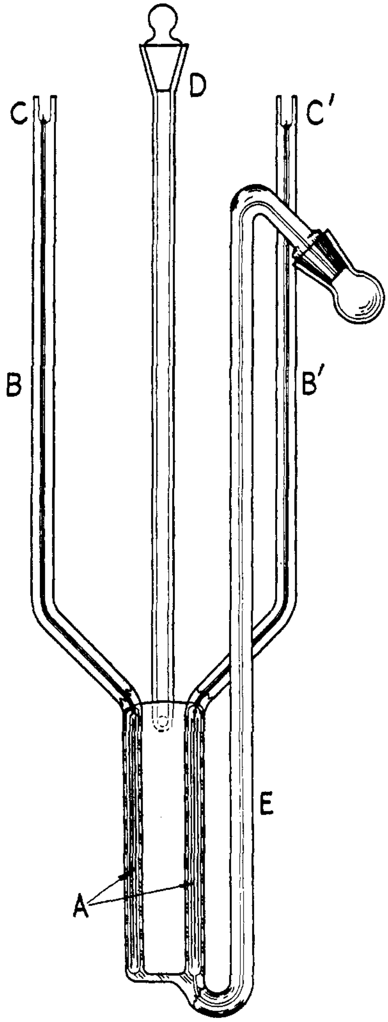

Fig. 1.—Measuring condenser.

These tubes (B, B′), as well as the inlet and outlet tubes (D and E), extended 22 cm. above the cell, which could, therefore, be immersed well below the surface of a constant temperature bath. The cell, which held only 18 cc., was filled through the inlet tube D, which was provided with a ground glass stopper, and was emptied by applying air pressure to D and forcing the liquid through the capillary outlet tube E, which could be closed with a ground glass cap over the end. The cell was normally kept in a vertical position and, if necessary, could be filled and emptied without removal from the constant temperature bath. It was dried by means of a current of filtered, dry air. As the cross section of the cell was a ring, it was in contact with the bath liquid both inside and out. The grounded outer and inner cylinders of the condenser served as shielding for the shorter cylinder between them. Stray, fixed and lead capacities were so reduced that the capacity which depended upon the substance in the cell was 96% of the total when the cell contained air. The variation of the air capacity of the condenser over the temperature range −90 to +60° was no greater than the error of the measurement. The cell was standardized as in the earlier work by determining its capacity when filled with air and with benzene (ϵ = 2.273 at 25°), the standardization being checked from time to time.

The constant temperature bath[3] was a Pyrex Dewar tube, 18″ tall by 4″ inside diameter, which, for temperatures below −90°, was filled with petroleum ether, between −90 and +90°, with toluene, and, above +90°, with kerosene. Immersed in the bath was a small copper cylinder into which liquid air could drip through a small,

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[3] Compare Walters and Loomis, This Journal, **47**, 2302 (1925).

straight tube and out of which the evaporated air could escape through a spiral tube. A vacuum jacketed siphon carried the liquid air to this cooling device from a stoppered 2-liter Pyrex Dewar flask, pressure being developed by the evaporation of liquid in the flask and regulated by attachment to a tube passing through the stopper of capillary tubes of varying bore and length. The copper cylinder was surrounded by a small heating coil which was used to raise the temperature of the bath when desired.

The temperatures were measured with a Leeds and Northrup platinum resistance thermometer fitted with compensating leads, the resistances being determined with a Callendar bridge. The thermometer was calibrated at +100, 0 and −95.5°, the melting point of toluene, and was later checked against the freezing point of a pure sample of normal heptane which had been previously determined with a calibrated thermocouple. The end of the thermometer was placed inside the hollow ring of the cell and, in every case, the temperature was held constant to within 0.1° for ten or fifteen minutes before making a measurement. At least two capacity readings differing from one another by less than 0.03% were made at each temperature in order to eliminate any possibility of error due to temperature variation. Densities were measured with a pycnometer (Fig. 2) somewhat similar in form to that used by Isnardi.[4] The bulb, A, which had a volume of about 25 cc., was connected to the stoppered overflow bulb B by the carefully ground joint C. The vessel was filled and hung with the bulb A immersed in the bath. When the liquid in the pycnometer had had time to attain the temperature of the bath, the bulb B was removed and the level of the liquid adjusted to a definite height in the capillary D. The bulb B was then replaced and the pycnometer removed from the bath, allowed to come to room temperature and weighed. Deposition of frost on the cold pycnometer was prevented by immersion in ether while it was warming up. The usual corrections were made in weighing and calibration was effected at different temperatures with toluene and with water. By proper design and grinding of the joints pycnometers were obtained which, when filled with hexane at −90°, tightly stoppered and allowed to come to room temperature, lost only 5 to 10 milligrams in weight on standing for fifteen hours. The probable error in the low temperature density determinations was 0.1% but in the measurements carried out at ordinary temperatures it was not more than 0.03%. The probable error in the dielectric constant measurements was 0.2%, although the relative accuracy within a given series of measurements was usually greater than this.

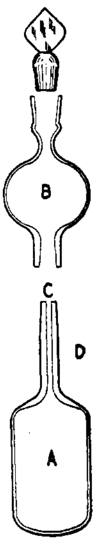

Fig. 2.—Pycnometer.

Preparation of Materials

Chlorobenzene was prepared in the manner described in the first paper. Pure normal hexane was obtained from the Eastman Kodak Company and treated just as was the petroleum hexane in the earlier investigation. Its refractive index at 20° for sodium light was found to be 1.37527, agreeing within the experimental error with the value 1.37536 given in Landolt-Börnstein "Tabellen" (5th ed.).

Ethyl bromide was freshly prepared from alcohol and potassium bromide, shaken once with concentrated sulfuric acid, then several times with water, dried over fused calcium chloride and distilled. Its density, d_4^{20} = 1.452, differed from the values found in the literature. It was

[4] Isnardi, *Z. Physik*, 9, 153 (1922).

washed again three times with small quantities of concentrated sulfuric acid, seven times with ice water and dried over fused calcium chloride. It all distilled at 38.5° and had a density, d_4^{20} = 1.4586. This value agrees with those given in Landolt-Börnstein "Tabellen," 1.4555 and 1.4569, but differs greatly from the value d_4^{20} = 1.430 given in "International Critical Tables." The density measurement has been repeated on other samples of ethyl bromide and the value d_4^{20} = 1.458 is believed to be correct.

Chloroform was shaken several times with concentrated sulfuric acid, with dilute sodium hydroxide and with water. It was dried over anhydrous potassium carbonate and fractionated.

Results

The dielectric constants and densities of hexane, ethyl bromide, chloroform, chlorobenzene and solutions of the substances in hexane were measured over the entire range of temperatures at which the materials were liquid under atmospheric pressure. The data were plotted against temperature on a very large scale and the values at 10° temperature intervals read off. The values for different mixtures at the same temperature were then plotted against c_2, the mole fraction of the polar substance, ethyl bromide, chloroform or chlorobenzene, as the case might be, and the

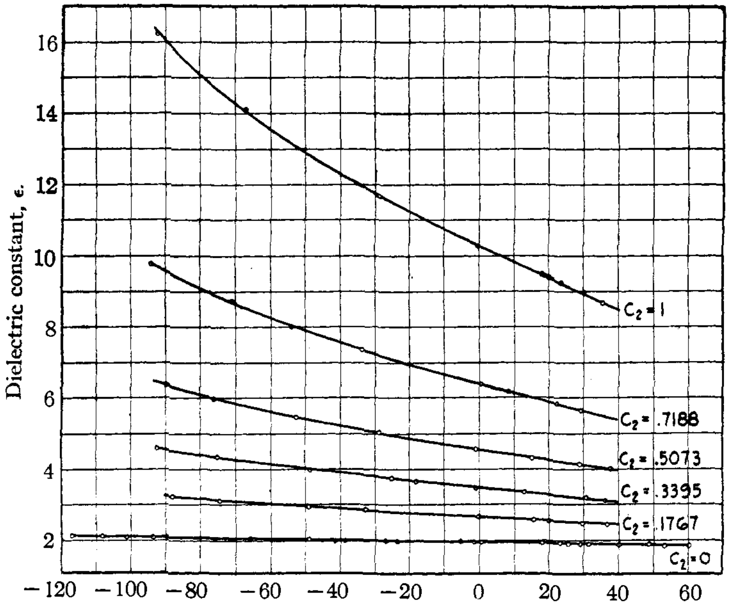

Fig. 3.—Temperature variation of dielectric constants of hexane–ethyl bromide mixtures.

values for c_2 = 0.05, 0.1, 0.2, 0.3, etc., were read off. By means of the equations $P_{12} = (\epsilon - 1)/(\epsilon + 2)\ (c_1M_1 + c_2M_2)/d$, and $P_2 = [(P_{12} - P_1)/c_2] + P_1$, in which ϵ = the dielectric constant, d = the density, c_1 and c_2 = the mole fractions and M_1 and M_2 = the molecular weights, the molar polarization, P_{12}, of the mixtures, and P_2, the polarization of the polar substance, were obtained at the different concentrations and temperatures. The values of P_2 at one temperature were plotted against c_2 and the curve was extrapolated to $c_2 = 0$ to obtain P_∞, the polarization at infinite dilution, where the molecules should be oriented at random when no external field is applied. A series of curves at different temperatures gave P_∞ over the entire temperature range within which the mixtures were liquid.

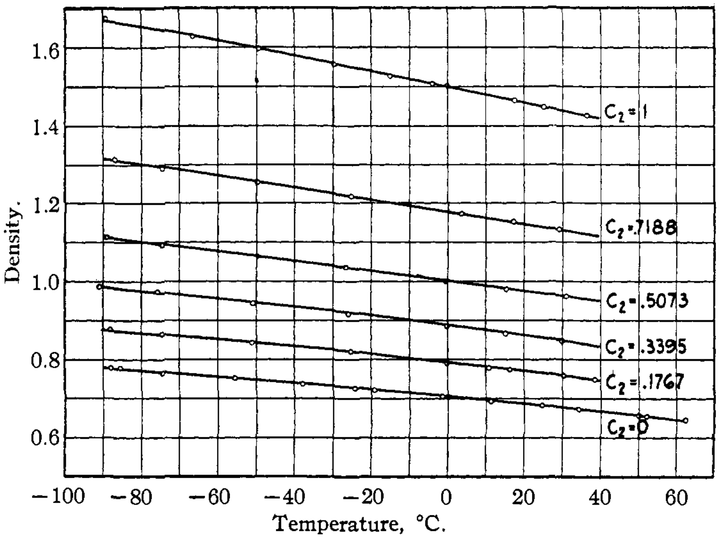

Fig. 4.—Temperature variation of densities of hexane–ethyl bromide mixtures.

Table I contains the values of the dielectric constant, ϵ, and the density, d, at the actual temperatures of measurement, for the pure liquids, but, for the sake of brevity, omits the measurements on the mixtures. Table II gives for each combination of substances the values of ϵ and d interpolated at 10° intervals for each mixture studied, but omits the data interpolated for c_2 = 0.05, 0.1, 0.2, etc. The results shown under c_2 = 0 in the hexane–ethyl bromide combination are for petroleum hexane which, as in the earlier work, was used in the mixtures. The constants of this mixture of isomers were, of course, somewhat different from those for the pure normal hexane given in Table I. In Table III, the polarization of both the pure normal hexane and the petroleum hexane are designated as P_1, which is assumed to be independent of concentration. For each of the other substances the polarization of the pure liquid, P_2, is shown beside P_∞, the polarization extrapolated to infinite dilution.

Fig. 3 shows the temperature variation of the dielectric constant of each mixture of petroleum hexane and ethyl bromide, each curve being designated by the value of c_2, the mole fraction of ethyl bromide, and Fig. 4 shows in similar fashion the temperature variation of the densities.

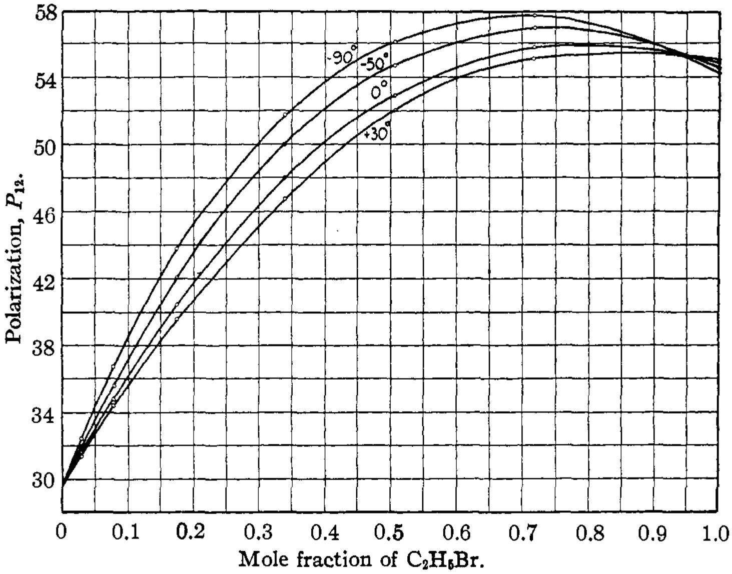

Fig. 5.—Molar polarizations of hexane–ethyl bromide mixtures.

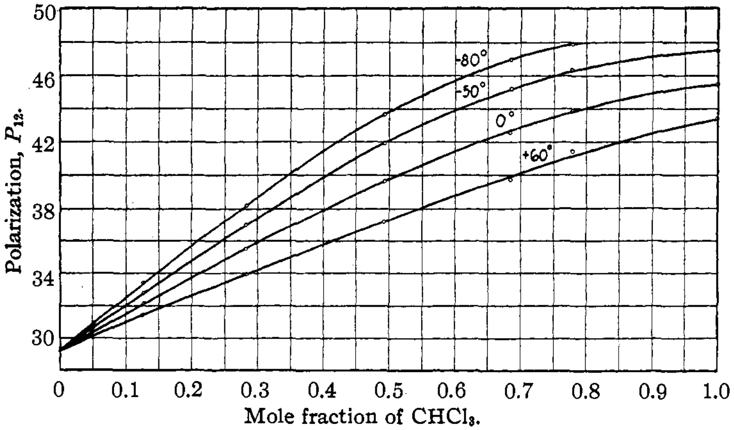

Fig. 6.—Molar polarizations of hexane–chloroform mixtures.

The curves for the mixtures of the other substances which are not shown are similar to these in form. Figs. 5, 6 and 7 show the variation with concentration of the molar polarization of the mixture, P_{12}, at a given temperature. For each set of mixtures curves are given at convenient intervals over the entire temperature range. It is hoped that the variation of P_2 with temperature and concentration may be treated in a later paper.

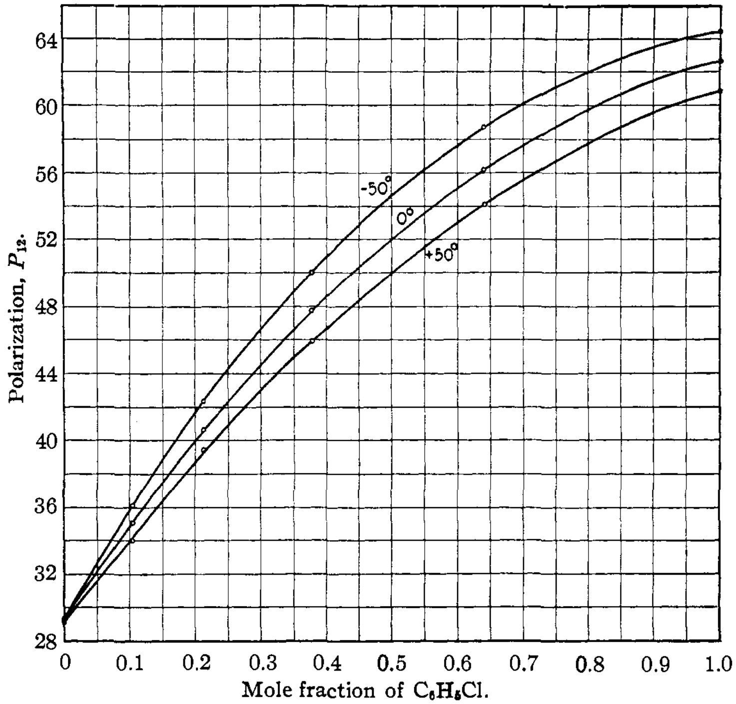

Fig. 7.—Molar polarizations of hexane–chlorobenzene mixtures.

TABLE I

DIELECTRIC CONSTANTS AND DENSITIES OF PURE LIQUIDS

n-Hexane				Ethyl Bromide			
t, °C.	ε	*t*, °C.	*d*	*t*, °C.	ε	*t*, °C.	*d*
−91.3	2.051	−89.5	0.7540	−92.3	16.22	−89.2	1.6737
−89.4	2.050	−77.6	.7442	−66.7	14.10	−66.4	1.6283
−71.6	2.023	−63.6	.7324	−28.6	11.67	−49.0	1.5950
−61.3	2.006	−47.0	.7185	0	10.28	−29.5	1.5572
−57.8	2.003	−29.5	.7035	+18.3	9.49	−14.6	1.5274
−37.0	1.976	−12.7	.6886	+18.5	9.48	− 3.3	1.5050
−19.3	1.948	− 1.3	.6787	+18.7	9.45	0	1.4996
− 0.1	1.918	+10.4	.6686	+20.0	9.40	+17.7	1.4634
+ 9.1	1.907	+15.8	.6664	+23.8	9.25	+25.2	1.4479
+15.0	1.898	+27.5	.6555	+30.3	8.99	+36.6	1.4245
+28.2	1.879	+38.3	.6458	+35.5	8.67		
+39.4	1.863	+50.1	.6325				
+47.1	1.848	+61.2	.6219				
+57.0	1.824	+67.0	.6158				

TABLE I (*Concluded*)

Chloroform				Chlorobenzene			
t, °C.	ϵ	t, °C.	d	t, °C.	ϵ	t, °C.	d
−62.6	6.810	−61.3	1.6397	−49.0	7.240	−42.7	1.1742
−61.0	6.748	−54.6	1.6271	−45.5	7.150	−24.5	1.1561
−59.7	6.707	−48.7	1.6161	−25.8	6.684	− 3.3	1.1314
−55.6	6.576	−25.0	1.5725	+ 0.1	6.013	0	1.1277
−51.8	6.428	−23.4	1.5696	+18.3	5.662	+18.7	1.1080
−49.6	6.387	− 1.1	1.5282	+22.0	5.593	+46.3	1.0777
−40.5	6.120	0	1.5265	+23.2	5.580	+73.5	1.0475
−22.4	5.703	+24.2	1.4814	+29.2	5.475	+97.2	1.0206
−18.8	5.552	+50.1	1.4308	+47.8	5.174	+103.3	1.0319
−15.0	5.466	+59.8	1.4116	+75.1	4.822	+124.5	0.9914
− 2.2	5.195			+100.0	4.516	+126.0	.9906
+ 4.5	5.078			+100.5	4.460		
+17.2	4.825			+115.5	4.346		
+18.7	4.802			+126.0	4.174		
+35.5	4.520						
+45.8	4.351						
+54.0	4.231						
+58.6	4.163						

TABLE II

INTERPOLATED VALUES OF DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS

HEXANE–ETHYL BROMIDE

Mole fraction of C_2H_5Br =	0	0.0309	0.0783	0.1767	0.3395	0.5073	0.7188	1.000
t, °C.	Dielectric Constant							
−90	2.078	2.270	2.568	3.240	4.573	6.360	9.60	16.05
−80	2.063	2.245	2.520	3.152	4.416	6.095	9.12	15.15
−70	2.048	2.219	2.476	3.075	4.270	5.856	8.68	14.35
−60	2.033	2.194	2.437	3.002	4.135	5.634	8.28	13.62
−50	2.017	2.170	2.400	2.934	4.006	5.418	7.91	12.95
−40	2.002	2.147	2.365	2.870	3.887	5.217	7.56	12.32
−30	1.987	2.123	2.331	2.808	3.776	5.027	7.23	11.75
−20	1.972	2.101	2.300	2.752	3.667	4.852	6.93	11.22
−10	1.957	2.080	2.270	2.700	3.570	4.690	6.65	10.73
0	1.942	2.059	2.240	2.648	3.476	4.544	6.38	10.27
+10	1.927	2.038	2.211	2.599	3.385	4.407	6.14	9.82
+20	1.912	2.018	2.181	2.552	3.294	4.275	5.91	9.41
+30	1.896	1.997	2.153	2.500	3.200	4.146	5.65	8.98
+40	1.880	1.975	2.124	2.444	3.112	3.985	5.40	8.44
+50	1.862	1.953	2.093					
+60	1.843	1.929						
	Density							
−90	0.7813	0.7973	0.8235	0.8804	0.9880	1.1155	1.3176	1.6752
−80	.7734	.7887	.8140	.8704	.9767	1.1026	1.3020	1.6555
−70	.7650	.7800	.8048	.8605	.9653	1.0897	1.2867	1.6358
−60	.7564	.7710	.7956	.8505	.9540	1.0768	1.2717	1.6162
−50	.7478	.7622	.7862	.8405	.9423	1.0640	1.2560	1.5966
−40	.7390	.7533	.7770	.8305	.9306	1.0512	1.2405	1.5776

Table II (*Continued*)

Mole fraction of C_2H_5Br =	0	0.0309	0.0783	0.1767	0.3395	0.5073	0.7188	1.000
t, °C.	Density							
−30	.7300	.7443	.7677	.8206	.9193	1.0383	1.2255	1.5580
−20	.7210	.7356	.7585	.8106	.9078	1.0256	1.2100	1.5384
−10	.7120	.7266	.7493	.8005	.8963	1.0126	1.1947	1.5188
0	.7032	.7174	.7400	.7906	.8848	1.0000	1.1797	1.4993
+10	.6940	.7082	.7302	.7800	.8735	0.9872	1.1640	1.4790
+20	.6854	.6990	.7204	.7693	.8615	.9743	1.1480	1.4586
+30	.6760	.6897	.7103	.7588	.8495	.9616	1.1313	1.4380
+40	.6668	.6800	.7003	.7480	.8374	.9486	1.1144	1.4164
+50	.6574	.6702	.6900					
+60	.6473	.6600						

Hexane–Chloroform

Mole fraction of $CHCl_3$ =	0.0517	0.1277	0.2862	0.4953	0.6856	0.7803	1.000
t, °C.	Dielectric Constant						
−90	2.201	2.409	....	....	....	....	....
−80	2.177	2.371	2.848	3.710	4.785	5.465	....
−70	2.155	2.335	2.786	3.584	4.582	5.210	....
−60	2.133	2.302	2.726	3.469	4.400	4.984	6.720
−50	2.113	2.271	2.668	3.363	4.234	4.778	6.402
−40	2.092	2.241	2.612	3.265	4.076	4.586	6.100
−30	2.072	2.212	2.560	3.174	3.934	4.406	5.825
−20	2.053	2.186	2.512	3.090	3.802	4.256	5.580
−10	2.033	2.159	2.466	3.010	3.680	4.108	5.356
0	2.014	2.134	2.426	2.937	3.568	3.972	5.150
+10	1.995	2.109	2.387	2.867	3.462	3.843	4.960
+20	1.976	2.086	2.348	2.800	3.360	3.720	4.783
+30	1.957	2.062	2.310	2.736	3.266	3.606	4.614
+40	1.938	2.038	2.270	2.670	3.173	3.496	4.450
+50	1.919	2.012	2.230	2.606	3.076	3.394	4.292
+60	1.900	1.984	2.189	2.544	2.974	3.295	4.140
	Density						
−90	0.8122	0.8580	....	....	....	....	....
−80	.8032	.8484	0.9547	1.1175	1.2955	1.3967	....
−70	.7942	.8388	.9440	1.1053	1.2810	1.3813	1.6560
−60	.7853	.8295	.9333	1.0933	1.2668	1.3660	1.6374
−50	.7763	.8198	.9225	1.0804	1.2525	1.3500	1.6188
−40	.7673	.8102	.9120	1.0685	1.2380	1.3342	1.6000
−30	.7582	.8008	.9008	1.0560	1.2234	1.3188	1.5814
−20	.7488	.7914	.8900	1.0435	1.2087	1.3034	1.5633
−10	.7392	.7818	.8790	1.0303	1.1963	1.2875	1.5445
0	.7304	.7722	.8682	1.0173	1.1800	1.2706	1.5262
+10	.7210	.7623	.8576	1.0042	1.1648	1.2557	1.5080
+20	.7116	.7522	.8462	0.9914	1.1498	1.2398	1.4895
+30	.7013	.7420	.8353	.9784	1.1342	1.2236	1.4704
+40	.6922	.7317	.8236	.9652	1.1188	1.2073	1.4516
+50	.6823	.7214	.8116	.9517	1.1038	1.1905	1.4315
+60	.6721	.7115	.7998	.9380	1.0888	1.1737	1.4105

TABLE II (*Concluded*)

HEXANE–CHLOROBENZENE

Mole fraction of C_6H_5Cl = t, °C.	0.1068	0.2132	0.3798	0.6458	1.000
	Dielectric Constant				
−80	2.532	3.053	....	....	....
−70	2.490	2.977	3.848	5.484	....
−60	2.448	2.908	3.730	5.268	....
−50	2.409	2.844	3.620	5.086	7.28
−40	2.371	2.784	3.518	4.882	7.01
−30	2.336	2.728	3.424	4.717	6.758
−20	2.304	2.677	3.336	4.560	6.502
−10	2.273	2.629	3.257	4.415	6.260
0	2.244	2.584	3.180	4.280	6.027
+10	2.214	2.540	3.108	4.156	5.818
+20	2.184	2.497	3.040	4.038	5.633
+30	2.153	2.456	2.977	3.928	5.460
+40	2.120	2.416	2.913	3.827	5.300
+50	2.084	2.377	2.846	3.723	5.150
+60	2.050	2.347	2.777	3.627	5.016
+70		2.300	2.706	3.538	4.888
+80				3.443	
	Density				
−80	0.8140	0.8548	....	....	....
−70	.8050	.8460	0.9166	1.0325	....
−60	.7960	.8368	.9067	1.0225	....
−50	.7868	.8278	.8967	1.0120	1.1838
−40	.7777	.8188	.8868	1.0015	1.1726
−30	.7687	.8096	.8774	0.9914	1.1614
−20	.7597	.8005	.8677	.9810	1.1502
−10	.7505	.7912	.8578	.9704	1.1394
0	.7414	.7815	.8480	.9603	1.1280
+10	.7323	.7723	.8384	.9500	1.1172
+20	.7232	.7632	.8285	.9398	1.1060
+30	.7138	.7532	.8185	.9296	1.0953
+40	.7044	.7434	.8086	.9192	1.0840
+50	.695	.7333	.7983	.9087	1.0732
+60	.685	.7228	.7878	.8980	1.0620
+70		.7124	.7770	.8872	1.0513
+80				.8760	

TABLE III

POLARIZATIONS

	C_6H_{14}		C_2H_5Br		$CHCl_3$		C_6H_5Cl	
	Petroleum	normal						
t, °C.	P_1	P_1	P_2	P_∞	P_2	P_∞	P_2	P_∞
−90	29.15	29.57	54.24	143.5	...	..	...	...
−80	29.15	29.63	54.32	138.5	...	62.1	...	106.5
−70	29.15	29.65	54.38	135.0	...	60.2	...	103.0
−60	29.16	29.66	54.47	131.0	47.85	58.9	...	100.0
−50	29.16	29.69	54.54	127.0	47.42	57.5	64.33	97.0
−40	29.16	29.72	54.60	123.5	46.97	56.0	64.00	94.0
−30	29.20	29.72	54.67	118.5	46.53	54.6	63.70	91.0

Table III (*Concluded*)

	C_6H_{14} Petroleum	C_6H_{14} normal	C_2H_5Br		$CHCl_3$		C_6H_5Cl	
t, °C.	P_1	P_1	P_2	P_∞	P_2	P_∞	P_2	P_∞
−20	29.23	29.76	54.74	114.3	46.14	53.1	63.30	89.3
−10	29.23	29.79	54.84	111.0	45.76	52.3	62.88	87.5
0	29.26	29.81	54.92	107.9	45.42	51.1	62.47	85.5
+10	29.28	29.87	54.98	105.5	45.04	50.0	62.06	83.5
+20	29.29	29.92	55.07	103.3	44.70	49.7	61.74	81.5
+30	29.30	29.91	55.07	100.2	44.35	48.8	61.40	79.0
+40	29.28	29.90	54.82	97.6	44.02	48.3	61.12	77.8
+50	29.23	29.85		95.4	43.63	47.5	60.82	76.8
+60	29.16	29.74			43.30	47.3	60.65	76.0
+70							60.40	

Discussion of Results

The values for petroleum hexane are slightly different from those for the pure normal hexane, but their polarizations are so nearly equal and show such similarity of behavior that the use of the petroleum hexane as an indifferent solvent is justified. In Fig. 3 the almost horizontal curve for $c_2 = 0$ shows the small temperature variation of the dielectric constant of petroleum hexane, but a rapid increase of slope accompanies increase in the ethyl bromide content of the mixture. The density curves, on the other hand, are nearly parallel.

As was observed in the earlier work, the curves in which the values of P_{12}, the polarizations of the mixtures, are plotted against the concentration of the polar substances, show strong deviation from the theoretical linearity, the deviation, as before, being larger, the larger the moment of the polar molecule, the greater the concentration of the polar molecules and the lower the temperature. Thus, the P_{12} curves for chloroform, which has the smallest moment of the three polar substances studied, are nearly straight lines in the dilute region, and the curve for 60° shows only a small departure from linearity throughout its course, but this departure from linearity increases as the temperature is lowered. Chlorobenzene, which has a larger moment, shows a noticeable curvature throughout all the curves, but the curvature increases with decreasing temperature and increasing concentration. The effect upon one another of the dipoles in the ethyl bromide molecules, which have the largest moments of the three considered, is so great that the curves pass through a maximum. As this effect diminishes rapidly with rising temperature, the curves intersect almost at one point, the polarization of the mixture containing 0.95 mole fraction of ethyl bromide being practically independent of temperature. In pure ethyl bromide increasing thermal agitation by increasing the freedom of the molecules from one another's fields does more to facilitate the orientation of the molecule in an externally applied field than it does to destroy this orientation by the increasing violence of the motion. Thus, the polarization actually increases with rising temperature instead of decreasing as required by the Debye equation, $P = a + b/T$, which should apply when the molecules are free to assume a random orientation. In terms of the quantities discussed in the earlier work, the constant

$a = P_E + P_A$, $b/_T = P_M$, and the constant $b = 4\pi N\mu^2/9k$, where
P_E = the polarization due to electronic shifts induced in the molecules
P_A = the polarization due to shifts of atoms or radicals induced in the molecules
P_M = the polarization due to orientation of the dipoles
μ = the electric moment of a single molecule
N = the number of molecules in a gram molecule = 6.061×10^{23}, and
k = the molecular gas constant = 1.372×10^{-16}

As it is apparent that the polarization should be a linear function of $1/T$, the values of both P_2 and P_∞ are plotted against $1/T$ in Fig. 8. All the curves are linear, but the P_2 curve for ethyl bromide gives a negative value of b and the P_2 curves for the other two substances give values of b much lower than those which determine the slopes of the P_∞ curves. The low values of b are due to the orienting effects of the dipoles upon one another, which cause the deviation from linearity of the $P_{1,2} - c_2$ curves. The values of P_∞, to which the Debye equation should apply, vary so much with temperature that the linearity of these curves affords strong evidence in support of the Debye theory.

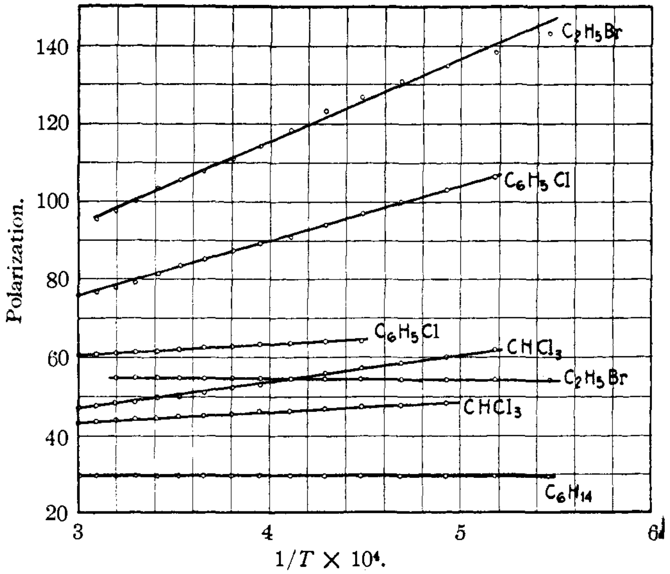

Fig. 8.—Variation of P_2 and P_∞ with $1/T$. (The higher curve for each substance represents P_∞.)

If the equation is written in the form $PT = a\,T + b$ and the values of PT are plotted as ordinates against T, as abscissas, we should obtain a straight line of which the slope is a and the ordinate at $T = 0$ is b. In

Fig. 9, $P_\infty T$ is plotted for the three polar substances and P_1T for hexane. The values obtained from these curves for a, b and μ, calculated from b, are given in Table IV, together with the values of $MR_\infty = P_E$, calculated

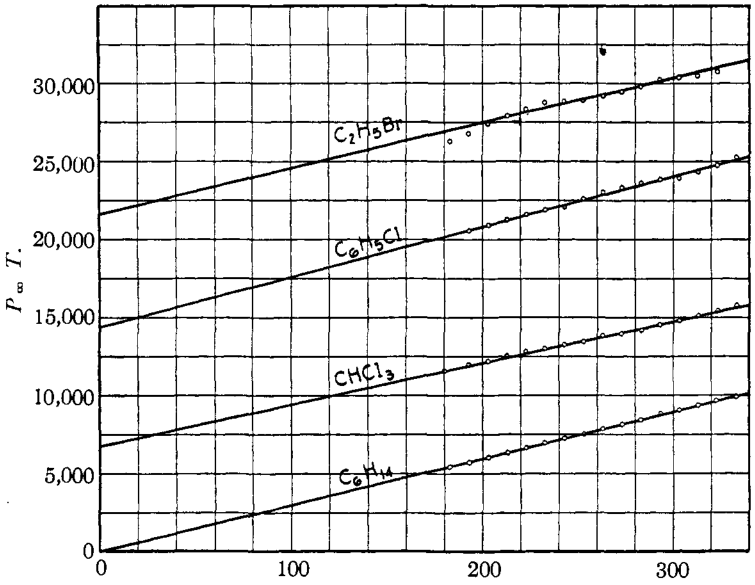

Fig. 9.—Variation of $P_\infty T$ with T.

by extrapolation of refractive index data from the visible region, and values of P_A, calculated from the relation $P_E + P_A = a$.

Table IV

Values of Fundamental Constants

	a	P_E	P_A	b	$\mu \times 10^{18}$
C_6H_{14}	29.8	29.20	0.6	0	0
$CHCl_3$	26.6	20.84	5.8	6800	1.05
C_6H_5Cl	33.2	29.93	3.3	14150	1.52
C_2H_5Br	29.5	18.55	(11)	21420	1.86

The very small difference between a and P_E for hexane confirms the value of 0 obtained from the fact that $b = 0$. The value of $\mu = 1.05 \times 10^{-18}$ for chloroform differs from the value 0.95×10^{-18} obtained by Sänger[5] from measurements on the vapor by an amount no greater than that which might arise from the probable errors of the two determinations. This agreement between results in the liquid and in the gaseous states provides further confirmation of the Debye theory. The values for ethyl bromide are less satisfactory than those for the other substances, as the great variation of P_2 with c_2 in the dilute region makes difficult the extrapolation to $c_2 = 0$

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[5] Sänger, *Physik. Z.*, **27**, 556 (1926).

thereby causing some inaccuracy in P_∞ and in the results derived from the P_∞ curves. As a very small variation in the drawing of the $P_\infty T-T$ curves causes a considerable variation in the values of a, the values obtained for P_A cannot be regarded as exact although the value 5.8 for chloroform agrees with the difference, 6.0, between P_E and the polarization of the solid in the tabulation of Ebert.[6] a and P_A for ethyl bromide are probably too high as a result of the difficulties which have been discussed. The values of the moments agree roughly with those calculated by one of the authors[7] by a very approximate method from data on the pure liquids: $\mu \times 10^{18}$ for C_6H_{14}, 0; $CHCl_3$, 1.25; C_6H_5Cl, 1.42; C_2H_5Br, 1.56. In view of the necessary disregard of P_A and the impossibility of taking accurate account of the orienting effects of the molecules upon one another in these old calculations, the agreement of their results with the accurate values of the present work is better than would be expected.

In conclusion, it may be stated that a new, though somewhat inaccurate, method has been employed to obtain the value of P_A, the polarization due to the shifts of atoms and groups of atoms within the molecule, that accurate values have been obtained for the electric moments of molecules by measuring not merely the concentration variation but also the temperature variation of the dielectric constants and densities of liquid mixtures, and that the validity of the Debye equation as applied to liquids at infinite dilution has been established.

Summary

The dielectric constants of solutions of ethyl bromide, chloroform and chlorobenzene in hexane have been measured with a capacity bridge over the entire range of temperature and concentration within which the mixtures are liquid and the densities have been determined with a special form of pycnometer.

The polarizations calculated from these data have been used to estimate approximate values for the polarization due to the shifts of atoms and groups of atoms within the molecule, to obtain accurate values for the electric moments of the molecules and to establish the validity of the Debye equation as applied to infinitely dilute liquids.

As in earlier work, it is found that the molecules affect one another more strongly, the greater their moments, the greater their concentrations and the lower the temperature.

PRINCETON, NEW JERSEY

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[6] Ebert, *Z. physik. Chem.*, **113**, 1 (1924).

[7] Smyth, THIS JOURNAL, **46**, 2151 (1924).