ions are not sufficiently numerous to form more than about one-eighth of a monomolecular layer. This is of the same order as that found in our measurements of specific surface conductivity of an insoluble fatty acid on conductivity water.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY]

THE DIELECTRIC POLARIZATION OF LIQUIDS. VI. ETHYL IODIDE, ETHANOL, NORMAL-BUTANOL AND NORMAL-OCTANOL

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The extreme complexity of the dielectric behavior of the alcohols as observed by various investigators over a limited range of temperature or of concentration, together with the importance of the electric moments of this group of substances, has made it desirable to measure several alcohols from the pure liquid to the most dilute solutions in non-polar solvents over the entire range of temperature within which they are liquid. The methods of measurement and calculation used in the present work have been described in the first two papers of the series on dielectric polarization.[1] In these earlier measurements, benzene and hexane were employed as non-polar solvents, the latter being particularly useful because of the wide range of temperature within which it is liquid. Since pure normal heptane can now be obtained much more readily than hexane of a comparable purity and, at the same time, is liquid over a wider temperature range, it has replaced hexane in the present determinations. Although it had been found that none of the isomers of heptane had detectable electric moments and the similarity of heptane to hexane[2] indicated that it would give identical results as a non-polar solvent, three solutions of ethyl bromide in heptane were measured for comparison with those in hexane previously studied. The results showed the expected agreement and are, therefore, omitted from this paper. However, measurements upon the similar substance, ethyl iodide, are reported and ethyl alcohol has been studied in both hexane and heptane with results that show similar behavior in the two solvents.

Method of Measurement

The densities were determined with the same type of pycnometer used in the earlier work and the dielectric constants were measured with the

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[1] Smyth, Morgan and Boyce, THIS JOURNAL, 50, 1536 (1928); Smyth and Morgan, *ibid.*, 50, 1547 (1928).

[2] Smyth and Stoops, *ibid.*, 50, 1883 (1928).

capacity bridge previously described, a frequency of 5 × 10^5 cycles, corresponding to a wave length of 600 meters, being used as before. The constancy of the wave length was checked by means of a wave meter, and the platinum resistance thermometer was calibrated at −95.1°, the freezing point of toluene, at 0°, and at 100° and checked occasionally at the ice point to make sure that there was no change. In addition to the condenser cell with platinum cylinders used in the earlier work, a cell, similar in form but consisting of three concentric brass cylinders, heavily gold plated, was employed. This differed further from the platinum cell in that the cylinders had separate leads and could thus be connected together in different combinations having capacities of 66, 40, 27 and 17$\mu\mu$f., as compared to the 200$\mu\mu$f. of the platinum cell, the outer cylinder always being grounded as in the latter.

The errors involved are not very different from those in the earlier work. The probable error in the densities measured at low temperatures was 0.07% and in those above 0° not more than 0.03%. The dielectric constants of mixtures whose maximum value did not exceed five were measured in the platinum cell by direct substitution on the precision condenser. The probable error here was 0.2%, although the error within a given series of measurements was less. For other mixtures, measured either with the platinum cell in series with another variable air condenser or with the gold-plated cell, the accuracy was less, the probable error being 0.5%. Again the accuracy within a given series of measurements was greater. When considerable resistance was required in the balancing arm to compensate for conductance or absorption in the cell, the dielectric constants are probably not accurate to more than 2%. These large resistances were necessary only in the case of the pure alcohols and their most concentrated solutions at low temperatures. The effect of the resistance was to cause the apparent values of the dielectric constants to be too large. The change in concentration due to evaporation of the more volatile component at the highest temperatures was troublesome in the dilute mixtures, but error from this source was corrected by comparison of measurements made at room temperature before and after the high temperature determinations.

Preparation of Materials

Heptane.—Pure normal heptane was obtained from the Ethyl Gasoline Corporation. A portion of it was washed with sulfuric acid, then with dilute sodium carbonate solution and with water. It was dried over calcium chloride, and finally distilled over sodium. As the boiling point, refractive index and dielectric constant were not appreciably different after this treatment, the heptane was normally used without purification.

Ethyl Iodide.—C. P. ethyl iodide was washed repeatedly with water, dried over fused calcium chloride and fractionally distilled; b. p. 72.4–72.5° at 773.7 mm.

Benzene.—Merck's C. P. benzene was washed three times with sulfuric acid, then with dilute sodium carbonate solution and with water, dried over calcium oxide and twice fractionally crystallized. It was then dried over sodium and fractionally distilled; b. p. 80.1°; n_D^{20} 1.50139.

Cyclohexane.—Eastman's purified grade cyclohexane was fractionally crystallized. The fractions melting at 6.2 and 6.0° were mixed, dried over sodium and fractionally distilled; b. p. 80.90–80.95°.

Ethyl Alcohol.—Ninety-five per cent. ethyl alcohol was refluxed over freshly ignited calcium oxide for twenty-four hours, the lime being changed once during this time, and fractionally distilled; b. p. 78.4°; n_D^{20} 1.36139.

Butyl Alcohol.—Normal butyl alcohol from the Commercial Solvents Corporation, b. p. 114–117°, was refluxed over freshly ignited lime and fractionally distilled; b. p. 117.2–117.4°; n_D^{20} 1.39922. A sample prepared by Dr. H. B. Glass at Johns Hopkins University was used in some of the work; b. p. 117.2–117.3°; n_D^{20} 1.39920.

Octyl Alcohol.—*n*-Octyl alcohol was obtained from the Eastman Kodak Company and fractionated by Dr. H. B. Glass and Dr. G. B. Malone working with Professor E. Emmet Reid of Johns Hopkins University.

Experimental Results

The densities, which showed only a small departure from a linear dependence upon temperature, were determined at 20–25° intervals and the dielectric constants at approximately 15° intervals, except when the temperature variation of the latter was so great as to necessitate 5–10° intervals. The densities, *d*, and dielectric constants, ϵ, in Table II were obtained at 10° intervals by graphical interpolation and the polarizations, P_2, of the polar components were calculated from them by means of the equations

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2} \times \frac{c_1M_1 + c_2M_2}{d} \text{ and}$$

$$P_2 = \frac{P_{12} - P_1}{c_2} + P_1$$

in which P_{12} is the polarization of the mixture, and c_1 and c_2, M_1 and M_2, and P_1 and P_2 are, respectively, the mole fractions, molecular weights

Table I

Dielectric Constants and Compensating Resistances for Ethanol and *n*-Butanol

t, °C.	ϵ	*R*	*t*, °C.	ϵ	*R*	*t*, °C.	ϵ	*R*
	C_2H_5OH		41.7	20.9	14.4	−67.4	30.8	29.7
−110.4	56.6	34.2	55.4	18.8	18.7	−62.3	30.2	20.3
−104.7	54.3	20.5	73.5	17.5	25.0	−58.3	29.5	15.5
−93.0	50.3	9.5		*n*-C_4H_9OH		−49.7	27.8	8.5
−88.8	48.9	7.5	−96.9	2.60	1.5	−39.9	26.2	4.9
−75.9	44.7	4.2	−92.9	2.79	2.3	−30.8	24.8	3.3
−67.1	42.0	3.3	−91.3	3.02	4.0	−19.9	22.9	2.5
−54.2	38.5	3.0	−88.7	20.3	85.0	−7.3	21.0	2.4
−43.4	35.7	3.1	−86.3	24.0	90.0	5.5	19.2	2.8
−31.6	33.0	3.6	−84.6	26.2	88.2	17.2	17.7	3.6
−19.5	30.5	4.3	−80.8	29.5	76.7	29.4	16.2	4.6
−7.5	28.3	5.2	−77.6	30.9	63.4	44.0	14.4	5.9
4.7	26.2	6.6	−76.4	31.1	58.4	56.8	13.1	7.3
17.0	24.2	8.4	−74.0	31.3	49.0	71.7	11.6	9.2
29.3	22.5	11.4	−71.7	31.4	41.4			

and polarizations of the individual components. The values of P_2 for ethyl iodide are omitted as they vary regularly with concentration. In Table I the dielectric constant values for pure ethyl alcohol and butyl alcohol are given, together with the compensating series resistances, R, in ohms which had to be used to balance out the effects of conductance or absorption in the measuring cell. This resistance gives an indication of the magnitude of the conductance and of the absorption of the liquid for a wave length of 600 meters.

TABLE II

INTERPOLATED VALUES OF DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS AND POLARIZATIONS OF POLAR COMPONENTS

Heptane–Ethyl Iodide

Mole fr., C_2H_5I =	0.0328	0.0365	0.0843	0.1889	0.4130	0.6155	0.8035	1.000
t, °C.				ϵ				
−100	2.258	2.266	2.522	3.053	4.541	6.52		
−90	2.234	2.244	2.484	2.991	4.408	6.25	8.96	12.27
−80	2.211	2.220	2.447	2.932	4.277	6.02	8.55	11.64
−70	2.188	2.198	2.412	2.875	4.158	5.79	8.19	11.11
−60	2.168	2.177	2.376	2.820	4.040	5.59	7.87	10.60
−50	2.147	2.157	2.346	2.766	3.927	5.405	7.58	10.16
−40	2.128	2.137	2.316	2.719	3.824	5.235	7.30	9.74
−30	2.109	2.117	2.287	2.673	3.723	5.075	7.03	9.36
−20	2.089	2.098	2.257	2.628	3.630	4.920	6.78	9.01
−10	2.070	2.078	2.230	2.584	3.539	4.774	6.54	8.67
0	2.051	2.059	2.203	2.541	3.456	4.630	6.31	8.38
10	2.032	2.039	2.177	2.501	3.372	4.493	6.09	8.10
20	2.014	2.022	2.154	2.462	3.296	4.360	5.88	7.82
30	1.995	2.003	2.134	2.422	3.220	4.240	5.66	7.56
40	1.977	1.984	2.113	2.383	3.149	4.122	5.46	7.29
50	1.959	1.964	2.093	2.349	3.078	4.017	5.27	7.03
60	1.940	1.944	2.074	2.314	3.010	3.909	5.08	6.80
70	1.920	1.922	2.057	2.280	2.940	3.809	4.89	6.59
t, °C.				d				
−100	0.8075	0.8106	0.8495	0.9382	1.1734	1.4413		
−90	.7990	.8018	.8407	.9287	1.1615	1.4265	1.7408	2.1777
−80	.7906	.7936	.8317	.9188	1.1491	1.4117	1.7226	2.1548
−70	.7822	.7852	.8228	.9089	1.1370	1.3966	1.7044	2.1321
−60	.7737	.7766	.8138	.8993	1.1248	1.3820	1.6862	2.1094
−50	.7652	.7682	.8049	.8898	1.1126	1.3671	1.6682	2.0867
−40	.7570	.7596	.7960	.8802	1.1003	1.3523	1.6503	2.0640
−30	.7484	.7514	.7872	.8705	1.0882	1.3377	1.6324	2.0411
−20	.7398	.7430	.7781	.8607	1.0761	1.3228	1.6140	2.0187
−10	.7313	.7342	.7692	.8510	1.0637	1.3078	1.5961	1.9967
0	.7231	.7252	.7604	.8411	1.0515	1.2927	1.5778	1.9740
10	.7142	.7168	.7513	.8315	1.0394	1.2775	1.5593	1.9514
20	.7058	.7082	.7422	.8215	1.0271	1.2622	1.5410	1.9288
30	.6971	.6995	.7333	.8112	1.0140	1.2471	1.5226	1.9062
40	.6881	.6905	.7238	.8005	1.0010	1.2315	1.5038	1.8831

TABLE II (*Continued*)

Mole fr., C_2H_5I =	0.0328	0.0365	0.0843	0.1889	0.4130	0.6155	0.8035	1.000
t, °C.	*d*							
50	0.6791	0.6815	0.7144	0.7897	0.9879	1.2155	1.4844	1.8600
60	.6702	.6726	.7047	.7789	.9747	1.1998	1.4648	1.8368
70	.6609	.6635	.6950	.7684	.9610	1.1836	1.4460	1.8133

Hexane–Ethyl Alcohol

Mole fr., C_2H_5OH =	0.0153	0.0578	0.0962	0.2076	0.0153	0.0578	0.0962	0.2076
t, °C.	ε				*d*			
−90	2.093	2.160	2.259	3.418	0.7820	0.7842	0.7844	0.7945
−80	2.077	2.144	2.248	3.360	.7742	.7755	.7763	.7857
−70	2.060	2.129	2.232	3.295	.7660	.7670	.7682	.7771
−60	2.045	2.114	2.214	3.225	.7574	.7582	.7599	.7703
−50	2.030	2.098	2.197	3.150	.7483	.7495	.7525	.7611
−40	2.016	2.083	2.179	3.075	.7397	.7408	.7430	.7518
−30	2.002	2.068	3.162	2.996	.7310	.7321	.7344	.7423
−20	1.989	2.054	2.145	2.913	.7220	.7235	.7256	.7330
−10	1.976	2.040	2.128	2.830	.7130	.7148	.7169	.7240
0	1.964	2.026	2.111	2.755	.7040	.7060	.7076	.7143
10	1.952	2.014	2.096	2.687	.6950	.6965	.6983	.7051
20	1.940	2.002	2.082	2.622	.6859	.6874	.6890	.6960
30	1.928	1.990	2.069	2.563	.6766	.6782	.6797	.6864
40	1.914	1.978	2.054	2.507	.6671	.6690	.6700	.6770
50	1.898	1.968	2.039	2.453	.6577	.6589	.6601	.6670
60	1.882	1.958	2.025	2.403	.6476	.6480	.6501	.6571
t, °C.	$P_2(C_2H_5OH)$							
−90	33.1	40.4	48.4	99.3				
−80	31.1	40.7	49.9	98.7				
−70	28.5	41.9	50.2	97.8				
−60	30.5	42.0	50.3	95.8				
−50	31.8	43.1	50.4	94.4				
−40	35.7	43.8	50.8	92.5				
−30	35.1	43.6	50.8	90.3				
−20	37.7	44.4	51.1	87.4				
−10	42.3	45.5	51.6	84.5				
0	46.2	46.7	51.9	81.9				
10	50.8	48.5	52.6	79.6				
20	58.7	50.8	53.8	77.0				
30	64.5	52.5	55.4	75.1				
40	70.4	55.4	56.6	73.3				
50	77.5	60.2	58.6	71.7				
60	83.4	66.2	60.9	70.4				

Heptane–Ethyl Alcohol

Mole fr., C_2H_5OH =	0.0256	0.4252	0.6142	0.8300	0.9260	1.000
t, °C.	ε					
−110						56.4
−100	2.129					52.9

TABLE II (*Continued*)

Mole fr., C_2H_5OH =	0.0256	0.4252	0.6142	0.8300	0.9260	1.000
t, °C.			ε			
−90	2.113				40.8	49.3
−80	2.099			29.8	38.1	46.1
−70	2.084			28.0	35.6	43.0
−60	2.069			26.3	33.2	40.1
−50	2.053			24.7	31.0	37.4
−40	2.040			23.1	29.0	35.0
−30	2.027	5.80	11.02	21.7	27.2	32.7
−20	2.015	5.55	10.49	20.3	25.5	30.7
−10	2.003	5.31	9.96	19.0	24.0	28.7
0	1.991	5.06	9.43	17.8	22.5	27.0
10	1.980	4.82	8.92	16.6	21.1	25.3
20	1.968	4.59	8.40	15.5	19.8	23.8
30	1.956	4.36	7.87	14.5	18.6	22.4
40	1.944	4.14	7.39	13.6	17.4	21.0
50	1.931	3.95	6.92	12.7	16.3	19.8
60	1.915	3.76	6.48	11.8	15.2	18.7
70	1.900	3.59	6.05	11.0	14.2	17.6
t, °C.			*d*			
−110						0.9031
−100	0.7830					.8941
−90	.7749				0.8649	.8852
−80	.7669			0.8369	.8562	.8762
−70	.7586			.8281	.8476	.8674
−60	.7503			.8193	.8390	.8586
−50	.7422			.8108	.8303	.8498
−40	.7340			.8022	.8216	.8412
−30	.7259	0.7487	0.7657	.7938	.8132	.8327
−20	.7177	.7400	.7572	.7851	.8048	.8242
−10	.7092	.7317	.7488	.7766	.7962	.8158
0	.7010	.7232	.7401	.7678	.7876	.8073
10	.6927	.7146	.7314	.7590	.7790	.7988
20	.6843	.7058	.7226	.7500	.7702	.7901
30	.6760	.6968	.7139	.7411	.7617	.7816
40	.6671	.6876	.7048	.7322	.7528	.7727
50	.6582	.6782	.6953	.7233	.7436	.7638
60	.6494	.6688	.6858	.7143	.7344	.7547
70	.6404	.6592	.6760	.7053	.7251	.7456
t, °C.			$P_2(C_2H_5OH)$			
−110						48.5
−100	44.4					48.7
−90	43.3				55.4	49.0
−80	43.3			65.0	55.7	49.3
−70	42.9			65.3	55.9	49.6
−60	42.6			65.6	56.2	49.8
−50	41.1			65.8	56.4	50.1
−40	41.8			66.0	56.7	50.3

TABLE II (*Continued*)

Mole fr., C_2H_5OH =	0.0256	0.4252	0.6142	0.8300	0.9260	1.000
t, °C.	$P_2(C_2H_5OH)$					
−30	42.7	102.6	87.8	66.2	56.9	50.5
−20	44.7	101.2	87.7	66.3	57.1	50.7
−10	47.8	99.8	87.3	66.4	57.3	50.9
0	49.9	97.6	86.8	66.5	57.5	51.1
10	53.0	95.4	86.2	66.4	57.6	51.3
20	55.9	93.2	85.5	66.5	57.8	51.5
30	58.0	90.7	84.4	66.4	57.9	51.7
40	61.7	88.0	83.3	66.3	57.9	51.8
50	64.2	85.5	82.2	66.1	58.0	52.0
60	63.4	82.9	80.8	65.8	58.0	52.2
70	63.8	80.5	79.2	65.3	58.0	52.3

Heptane–*n*-Butyl Alcohol

Mole fr., C_4H_9OH =	0.0312	0.0525	0.0805	0.1042	0.1383	0.2655	0.4451	0.6152	0.8042	1.000
t, °C.	ϵ									
−90	2.113	2.131	2.196	2.223		4.790	9.27		16.3	
−80	2.098	2.118	2.168	2.208	2.360	4.703	10.32	16.85	24.0	30.0
−70	2.082	2.105	2.148	2.194	2.333	4.502	10.31	16.20	24.4	31.3
−60	2.068	2.092	2.134	2.179	2.308	4.177	9.61	15.40	23.0	29.8
−50	2.052	2.080	2.122	2.164	2.285	3.889	8.89	14.44	21.6	27.9
−40	2.041	2.066	2.109	2.149	2.263	3.628	8.18	13.40	20.0	26.2
−30	2.028	2.054	2.096	2.136	2.241	3.401	7.48	12.40	18.6	24.6
−20	2.016	2.042	2.084	2.123	2.221	3.200	6.80	11.44	17.3	22.9
−10	2.004	2.032	2.073	2.111	2.203	3.040	6.13	10.49	16.0	21.4
0	1.993	2.021	2.063	2.100	2.186	2.910	5.55	9.57	14.9	20.0
10	1.982	2.011	2.053	2.088	2.167	2.798	5.16	8.78	13.8	18.6
20	1.972	2.001	2.044	2.077	2.153	2.696	4.82	8.00	12.6	17.4
30	1.961	1.991	2.034	2.068	2.141	2.608	4.48	7.30	11.6	16.1
40	1.950	1.980	2.024	2.058	2.132	2.547	4.19	6.64	10.6	14.9
50	1.936	1.969	2.013	2.046	2.118	2.500	3.92	6.07	9.71	13.8
60	1.921	1.955	2.001	2.034	2.105	2.454	3.70	5.54	8.72	12.8
70	1.907	1.939	1.986	2.019	2.089	2.416	3.53	5.11	8.01	11.8
80	1.890	1.921	1.968	2.003	2.070	2.384	3.39	4.80	7.30	10.8
90	1.872	1.902	1.949	1.985	2.042	2.348	3.26	4.46	6.69	9.9
t, °C.	*d*									
−90	0.7760	0.7775	0.7798	0.7812		0.7948	0.8134	0.8261	0.8604	
−80	.7679	.7692	.7718	.7732	0.7762	.7868	.8054	.8182	.8526	0.8872
−70	.7598	.7612	.7636	.7651	.7680	.7789	.7974	.8101	.8448	.8793
−60	.7514	.7530	.7552	.7570	.7600	.7709	.7895	.8022	.8369	.8713
−50	.7432	.7450	.7473	.7489	.7518	.7630	.7815	.7942	.8289	.8634
−40	.7352	.7369	.7391	.7409	.7437	.7552	.7736	.7862	.8211	.8556
−30	.7272	.7289	.7311	.7329	.7355	.7470	.7657	.7782	.8132	.8479
−20	.7192	.7208	.7231	.7249	.7267	.7388	.7577	.7701	.8053	.8402
−10	.7108	.7126	.7148	.7164	.7184	.7305	.7494	.7621	.7974	.8328
0	.7024	.7040	.7062	.7081	.7101	.7222	.7414	.7540	.7897	.8250
10	.6940	.6958	.6980	.6997	.7017	.7139	.7331	.7458	.7820	.8173

Table II (*Continued*)

Mole fr., C_4H_9OH =	0.0312	0.0525	0.0805	0.1042	0.1383	0.2655	0.4451	0.6152	0.8042	1.000
t, °C.	*d*									
20	0.6854	0.6872	0.6895	0.6911	0.6936	0.7053	0.7247	0.7376	0.7737	0.8098
30	.6769	.6788	.6810	.6826	.6855	.6970	.7160	.7289	.7657	.8022
40	.6681	.6700	.6722	.6739	.6767	.6882	.7072	.7201	.7574	.7945
50	.6591	.6610	.6631	.6650	.6682	.6796	.6987	.7115	.7491	.7867
60	.6502	.6520	.6539	.6559	.6597	.6709	.6898	.7022	.7410	.7787
70	.6412	.6428	.6447	.6467	.6512	.6616	.6803	.6930	.7320	.7703
80	.6320	.6333	.6350	.6372	.6424	.6525	.6710	.6839	.7231	.7616
90	.6239	.6240	.6257		.6334	.6431	.6616		.7140	.7527
t, °C.	$P_2(C_4H_9OH)$									
−90	46.7	44.3	53.7	52.2		151.8	136.8		87.4	
−80	45.2	45.0	50.3	52.2	66.8	151.6	144.1	117.8	93.9	75.7
−70	43.9	45.8	48.1	52.4	65.6	147.8	145.8	119.1	94.9	76.7
−60	45.6	46.5	49.6	52.9	64.7	139.2	144.0	119.2	95.2	77.0
−50	44.0	47.7	50.4	53.3	63.9	130.6	141.5	117.8	95.4	77.2
−40	46.3	48.9	51.2	53.6	63.6	121.8	138.4	117.1	95.4	77.4
−30	47.3	48.8	51.9	54.2	62.8	113.5	134.7	116.1	95.2	77.5
−20	48.3	50.5	52.6	54.9	62.7	105.6	130.0	114.9	94.9	77.6
−10	49.0	52.3	54.0	56.8	62.8	98.9	124.6	113.3	94.6	77.6
0	51.2	53.8	55.8	56.9	62.9	93.4	118.7	111.3	94.2	77.6
10	55.4	56.3	57.4	57.9	62.8	88.5	114.4	109.3	93.6	77.6
20	59.3	59.2	60.0	59.2	63.4	84.0	111.6	106.7	92.8	77.3
30	62.9	61.4	61.9	60.4	64.3	79.8	106.0	103.9	91.9	77.0
40	66.4	64.1	64.0	62.1	66.0	77.4	101.6	100.7	90.8	76.6
50	68.1	66.6	66.3	63.7	67.0	76.0	97.1	97.6	89.3	76.3
60	68.4	68.0	68.3	65.6	67.9	74.5	93.1	93.9	87.3	76.0
70	69.7	68.5	69.5	66.9	68.5	73.5	90.3	90.8	85.8	75.4
80	70.7	69.1	70.1	68.4	68.6	73.5	87.9	88.5	83.9	74.5
90	67.8	68.9	70.2		67.0	73.0	85.9	85.3	81.8	73.7

Cyclohexane–*n*-Butyl Alcohol

Mole fr., C_4H_9OH =	0	0.0391	0.1102	0.2002	0	0.0391	0.1102	0.2002
t, °C.	ϵ				*d*			
10	2.041	2.108	2.272	2.743	0.7877	0.7878	0.7889	0.7905
20	2.027	2.099	2.260	2.674	.7784	.7783	.7795	.7813
30	2.013	2.088	2.248	2.623	.7690	.7690	.7701	.7721
40	1.998	2.076	2.236	2.579	.7594	.7593	.7605	.7625
50	1.981	2.061	2.224	2.537	.7498	.7494	.7508	.7528
60	1.963	2.045	2.210	2.497	.7398	.7387	.7407	.7428
70	1.944	2.028	2.192	2.458	.7299	.7282	.7308	.7326

t, °C.	$P_1(C_6H_{12})$	$P_2(C_4H_9OH)$		
10	27.50	57.2	62.3	80.8
20	27.55	60.5	63.3	77.9
30	27.61	62.4	64.4	76.2
40	27.65	64.7	65.6	74.9
50	27.64	67.0	67.4	74.1
60	27.62	70.1	69.3	73.4
70	27.58	72.7	70.3	72.9

TABLE II (*Continued*)

Benzene–*n*-Butyl Alcohol

Mole fr., C_4H_9OH =	0	0.0211	0.0578	0.0798	0.1117	0.2525	0.4899	0.7385
t, °C.	ϵ							
10	2.315	2.400	2.548	2.655	2.835	4.066	8.29	14.03
20	2.294	2.378	2.526	2.631	2.797	3.899	7.58	12.84
30	2.274	2.354	2.502	2.600	2.756	3.747	6.94	11.72
40	2.253	2.330	2.473	2.565	2.713	3.604	6.37	10.68
50	2.231	2.304	2.438	2.525	2.665	3.472	5.96	9.74
60	2.209	2.274	2.401	2.480	2.612	3.350	5.43	8.91
70	2.186	2.243	2.358	2.435	2.555	3.238	5.03	8.11
t, °C.	*d*							
10	0.8899	0.8875	0.8843	0.8824	0.8801	0.8693	0.8523	0.8354
20	.8791	.8768	.8738	.8719	.8695	.8591	.8430	.8269
30	.8682	.8661	.8632	.8615	.8591	.8489	.8334	.8182
40	.8574	.8553	.8528	.8512	.8489	.8388	.8240	.8095
50	.8466	.8447	.8421	.8403	.8378	.8284	.8142	.8007
60	.8358	.8338	.8311	.8296	.8270	.8180	.8048	.7917
70	.8250	.8231	.8203	.8188	.8162	.8076	.7948	.7826
t, °C.	$P_1(C_6H_6)$	$P_2(C_4H_9OH)$						
10	26.73	84.6	82.4	84.3	86.9	98.3	101.3	89.5
20	26.75	85.2	83.4	85.0	86.5	95.3	98.7	88.7
30	26.80	83.8	83.7	84.4	85.6	92.6	96.0	87.7
40	26.82	82.9	82.7	83.1	84.4	89.6	93.0	86.4
50	26.82	81.0	80.8	81.3	82.7	87.0	91.0	85.0
60	26.82	76.7	78.5	78.5	80.3	84.4	87.1	83.6
70	26.80	71.9	74.5	75.9	77.5	82.0	84.1	81.8

Heptane–*n*-Octyl Alcohol

Mole fr., $C_8H_{17}OH$ =	0.0447	0.0671	0.1260	0.2347	0.4374	0.7360	1.000
t, °C.	ϵ						
−30	2.046	2.070	2.162	2.489	4.928	11.22	
−20	2.033	2.059	2.152	2.457	4.456	10.21	
−10	2.021	2.049	2.141	2.426	4.045	9.25	13.31
0	2.010	2.039	2.131	2.399	3.770	8.36	12.26
10	2.000	2.029	2.122	2.376	3.554	7.52	11.26
20	1.991	2.020	2.114	2.357	3.384	6.78	10.34
30	1.981	2.012	2.107	2.341	3.233	6.14	9.45
40	1.971	2.004	2.100	2.326	3.130	5.60	8.62
50	1.960	1.994	2.091	2.311	3.030	5.14	7.84
60	1.948	1.982	2.082	2.295	2.943	4.75	7.09
t, °C.	*d*						
−30	0.7318	0.7364	0.7438	0.7591	0.7881	0.8278	
−20	.7236	.7280	.7358	.7512	.7805	.8202	
−10	.7151	.7194	.7277	.7432	.7730	.8131	0.8461
0	.7068	.7109	.7193	.7351	.7650	.8058	.8391
10	.6987	.7023	.7111	.7272	.7573	.7985	.8322
20	.6904	.6940	.7028	.7192	.7498	.7912	.8253

TABLE II (*Concluded*)

Mole fr., $C_8H_{17}OH$ =	0.0447	0.0671	0.1260	0.2347	0.4374	0.7360	1.000
t, °C.	*d*						
30	0.6820	0.6853	0.6943	0.7113	0.7418	0.7838	0.8186
40	.6738	.6766	.6857	.7031	.7338	.7763	.8115
50	.6647	.6679	.6770	.6945	.7258	.7690	.8042
60	.6557	.6591	.6688	.6858	.7176	.7615	.7970
t, °C.	$P_2(C_8H_{17}OH)$						
−30	65.1	64.1	70.4	87.1	141.8	142.7	
−20	65.6	65.5	71.5	86.2	135.4	140.3	
−10	67.7	67.8	72.5	85.2	124.4	137.3	123.7
0	69.8	70.1	73.9	84.7	118.0	134.0	122.5
10	72.2	72.1	75.4	84.5	112.8	130.1	121.0
20	75.9	74.7	77.4	84.8	108.3	125.8	119.3
30	78.5	77.8	79.5	85.1	104.3	121.3	117.3
40	81.2	81.1	81.7	85.7	101.8	117.1	115.1
50	84.7	83.7	83.7	86.6	99.7	113.1	112.5
60	87.4	85.5	85.4	87.2	97.1	108.8	109.4

Benzene-*n*-Octyl Alcohol

Mole fr., $C_8H_{17}OH$ =	0.0280	0.0406	0.0492	0.0666	0.0860	0.0280	0.0406	0.0492	0.0666	0.0860
t, °C.	ε					*d*				
10	2.420	2.464	2.490	2.556	2.619	0.8864	0.8852	0.8840	0.8822	0.8802
20	2.398	2.442	2.468	2.535	2.599	.8759	.8748	.8737	.8720	.8699
30	2.374	2.418	2.444	2.510	2.576	.8654	.8643	.8634	.8618	.8597
40	2.348	2.391	2.417	2.482	2.549	.8549	.8539	.8531	.8514	.8494
50	2.321	2.361	2.387	2.450	2.516	.8443	.8433	.8426	.8409	.8391
60	2.292	2.331	2.355	2.414	2.479	.8334	.8326	.8317	.8301	.8286
70	2.263	2.300	2.323	2.376	2.438	.8226	.8219	.8210	.8195	.8182
t, °C.	$P_2(C_8H_{17}OH)$									
10	101.3	99.9	98.5	99.2	98.0					
20	101.4	100.4	98.9	100.1	99.2					
30	100.7	100.1	98.9	100.1	99.7					
40	98.6	98.7	97.7	99.6	99.6					
50	97.2	96.9	96.5	98.4	98.9					
60	94.7	95.0	94.7	96.5	97.4					
70	92.5	93.1	92.9	94.1	95.1					

Discussion of Results

In Table I the high compensating resistance for ethyl alcohol (freezing point −117.3°) at low temperatures shows a considerable absorption although the dielectric constant has not begun to fall off even at −110.4°. For butyl alcohol, with its larger molecules, the absorption is noticeable at higher temperatures and the dielectric constant begins to fall off nearly 20° above the freezing point, −89.8°. On solidification the dielectric constant shows a tremendous decrease as the dipole contribution drops out and the absorption becomes negligible. The measurements on the heptane solutions of ethyl alcohol do not extend down to temperatures at which absorption is considerable, but the concentrated butyl alcohol solutions show an increasing absorption at low temperature and a decrease in the dielectric constant as −90° is approached. The effect is negligible in the concentrations measured below mole fraction 0.4451 of butyl alcohol. *n*-Octyl alcohol (freezing point −16.3°) was not measured at temperatures low enough to cause strong absorption, but the slight absorption observed in the pure alcohol diminished in the 0.7360 solution and was negligible in the 0.4374 solution at the same temperatures.

With rising temperature the compensating resistance decreases as the absorption decreases, then passes through a minimum and increases up to the highest temperatures measured, presumably because of electrolytic conductance which increases with rising temperature. The increase is not apparent in *n*-octyl, is considerable in butyl, large in ethyl and so large in methyl alcohol that the apparatus is inadequate for the measurements at higher temperatures. The minimum occurs at a lower temperature, the smaller the alcohol molecule. In the heptane solutions the effect decreases with decreasing concentration and is not evident in the concentrations measured below $c_2 = 0.6$.

When P_{12} at different temperatures is plotted against c_2, the mole fraction of ethyl iodide in the heptane–ethyl iodide mixtures, the curves obtained resemble those for ethyl bromide, passing through a maximum, which, however, is less pronounced than in the ethyl bromide curves. The P_2–c_2 curves also resemble those for ethyl bromide but possess a slightly smaller curvature. The polarization of the pure substance decreases slightly with rising temperature instead of increasing as does that of ethyl bromide. These facts indicate that the effect of orientation is less in ethyl iodide than in ethyl bromide, as would be expected from the slightly smaller electric moment, 1.66×10^{-18}, as compared to 1.86×10^{-18}, and the screening effect of the iodine atom, which should be greater than that of the bromine. When the P_2–c_2 curves are extrapolated to $c_2 = 0$, the values of P obtained give a straight line when plotted against $1/T$, as required by the Debye equation: $P = a + b/T$. The values of the constants a and b are obtained graphically from the values of P_∞ in Table III and in order to show the linearity of the variation of P_∞ with $1/T$, the values of $(P_\infty - a)\ T = b$ are shown. There is evidently no departure from the linearity demanded by theory, the maximum deviation from the value $b = 17{,}000$ being less than 1%. The electric moment μ is calculated from b; the value of P_E, the electronic contribution to the polarization, is obtained by extrapolation to infinite wave length of the molar refraction for visible light, and the somewhat doubtful atomic contribution is obtained as $P_A = a - P_E$. The dipole contribution P is, of course, $P_\infty - a$. The value of the electric moment, 1.66 ×

10^{-18}, agrees well with that obtained by Williams, 1.7 × 10^{-18}, from measurements at one temperature, and with the value 1.62 × 10^{-18} of Mahanti and Sen Gupta from measurements on the vapor.[3]

Table III

Polarization Contributions of Ethyl Iodide

T, °A.	P_∞	$(P_\infty - a)T$	T, °A.	P_∞	$(P_\infty - a)T$	T, °A.	P_∞	$(P_\infty - a)T$
173	134.7	17150	233	108.9	17080	293	93.7	17020
183	128.3	16920	243	106.0	17100	303	91.9	17050
193	123.3	16930	253	102.6	16950	313	89.6	16900
203	119.6	17050	263	99.7	16850	323	88.1	16950
213	116.1	17150	273	97.5	16900	333	86.6	16970
223	112.6	17160	283	95.8	17040	343	85.0	16950

$a = 35.6$; $b = 17000$; $P_E = 23.3$; $P_A = 12.3$; $\mu = 1.66 \times 10^{-18}$.

An attempt to apply the Debye equation to solutions of ethyl alcohol in heptane meets with serious difficulties. The values of P_{12} and P_2 for dilute alcohol solutions increase with rising temperature instead of decreasing as the theory requires (Figs. 1 and 2). In these and the subsequent diagrams, one circle sometimes represents several almost coincident points on different curves. At slightly higher concentrations (c_2 = 0.12–0.20) of alcohol the P_{12}–c_2 and the P_2–c_2 curves at different temperatures intersect, the polarization becoming practically independent of tempera-

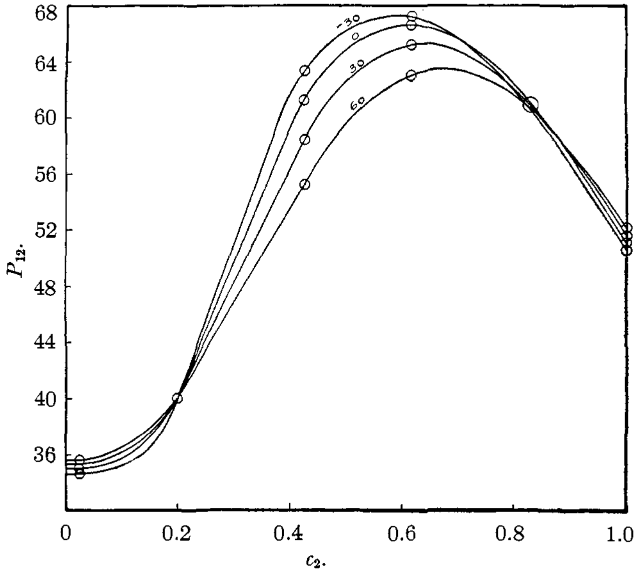

Fig. 1.—Molar polarizations (P_{12}) of heptane–ethyl alcohol mixtures.

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[3] Williams, *Z. physik. Chem.*, **138A**, 75 (1928); Mahanti and Sen Gupta, *Indian J. Phys.*, [II] **12**, 181 (1928).

ture. Just beyond this point they rise sharply, go through a maximum and finally decrease to the values for the pure alcohol. Thus, in very dilute solutions and in the pure alcohol, the polarization increases with the temperature. At intermediate concentrations the polarization decreases with rising temperature, with the result that the P_2–c_2 curves intersect both in the dilute and concentrated regions. The values of P obtained by extrapolating the P_2 curves to zero concentration of alcohol obviously

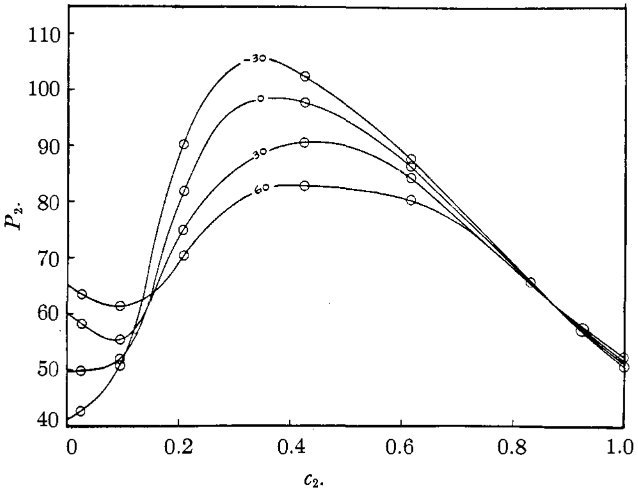

Fig. 2.—Polarizations (P_2) of ethyl alcohol in solution in hexane and in heptane.

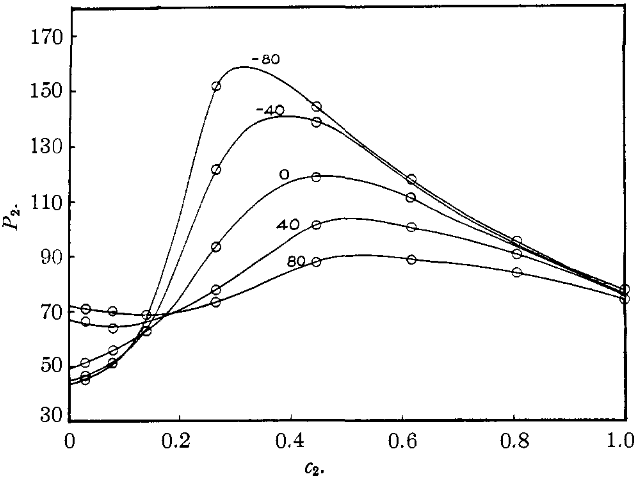

Fig. 3.—Polarizations (P_2) of butyl alcohol in solution in heptane.

do not correspond to the unassociated state, since they increase with rising temperature instead of decreasing.

The P_{12}–c_2 and the P_2–c_2 curves (Fig. 3) for butyl alcohol in heptane show a less sharply defined maximum and a greater dependence of polarization upon temperature in the concentrated solutions. For octyl alcohol in heptane, the maximum has disappeared in the P_{12}–c_2 curves (Fig. 4) and is less pronounced in the P_2–c_2 curves (Fig. 5). This decrease in the effect of orientation is also evident in the variation with temperature of the polarization in the pure alcohols. Whereas the polarization of ethyl alcohol increases with temperature over the entire range, that of butyl alcohol at first increases, then becomes practically constant and finally decreases with rising temperature. The polarization of the normal octyl alcohol, however, decreases with rising temperature over the entire temperature range within which it is measured. Another indication of this effect is given by the variation in P_M for these alcohols. The values of $P_M = P - MR_D$ at 20° for ethyl, butyl and octyl alcohols are, respectively, 38.8, 55.1 and 78.6. In dilute solution this progressive variation of the effect of orientation does not occur, the curves for the three alcohols all being quite similar.

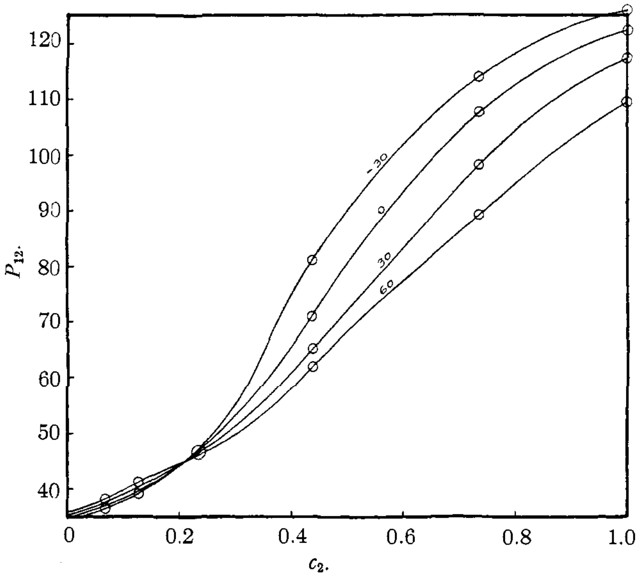

Fig. 4.—Molar polarizations (P_{12}) of heptane-*n*-octyl alcohol mixtures.

It should be explained at this point that, in the absence of a value of a determined from the temperature variation of P_∞, the small quantity P_A is neglected and a is set equal to MR_D, the molar refraction for the sodium D line. The error thus introduced is negligible in comparison to the uncertainties caused by molecular orientation.

These P_{12}–c_2 and P_2–c_2 curves resemble those calculated by Debye[4] from the data of Philip at 16° for solutions of ethyl alcohol in benzene in that they possess a maximum, but differ from those of Debye in that the P_2–c_2 curves generally show a minimum. The P_2–c_2 curve for butyl alcohol in benzene (Fig. 6) at 70° resembles that of Debye for ethyl alcohol, but at 50° a slight minimum appears in the region of low alcohol concentration, and at 16° it is more pronounced, showing that the same orientating influences are at work in these solutions as in those in heptane, although the intensity of the influences is somewhat less. The difference in behavior is shown by the fact that the increase in dielectric constant over that of the pure solvent is very much greater for a solution in benzene than in heptane. For example, a solution of butyl alcohol in benzene, mole fraction alcohol = 0.0525, has a dielectric constant of 2.505 at 20°. The dielectric constant of the sample of benzene used in the solution is 2.294 at 20°, and the increase in dielectric constant due to the alcohol is 2.505 − 2.294 = 0.311. The increase caused by alcohol in heptane at the same concentration and temperature is 2.001 − 1.930 = 0.071, less than one-fourth that in benzene.

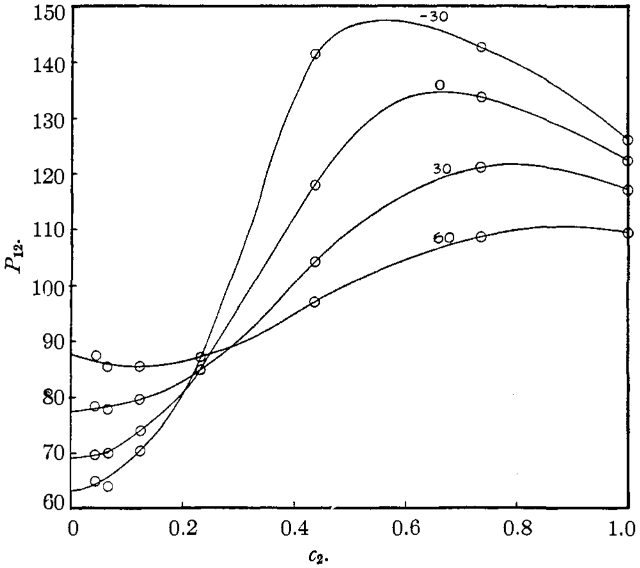

Fig. 5.—Polarizations (P_2) of *n*-octyl alcohol in solution in heptane.

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[4] Debye, "Polar Molecules," The Chemical Catalog Company, New York, **1929**, p. 47.

The results of Lange show maxima in the curves for propyl, *n*-butyl and *iso*butyl alcohols in benzene with some irregularities or points of inflection in the dilute solutions, and a curve for dimethylethylcarbinol resembling in form the P_2–c_2 curves for ethyl iodide, while the two maxima appearing in the curve for *iso*-amyl alcohol may be attributed to the presence of two isomers in the material used for the measurements. The values of P_2 given by Krchma and Williams[5] for methyl and ethyl alcohol in solution in carbon tetrachloride at 25° indicate the presence of a minimum as well as a maximum in the curves. The course of the P_2–c_2 curves for dilute solutions of methyl alcohol in carbon tetrachloride at different temperatures determined by Stranathan[6] shows a slight minimum between 20 and 50° and a probability of intersection in a somewhat more concentrated region, the apparent value of P increasing with rising temperature. Similar curves for ethyl, propyl and *iso*-amyl alcohols in benzene show no minimum, but indicate the possibility of one if the measurement could be extended below 0°. They also show the usual rise toward a maximum. These results of other investigators are evidently consistent with those of the present paper.

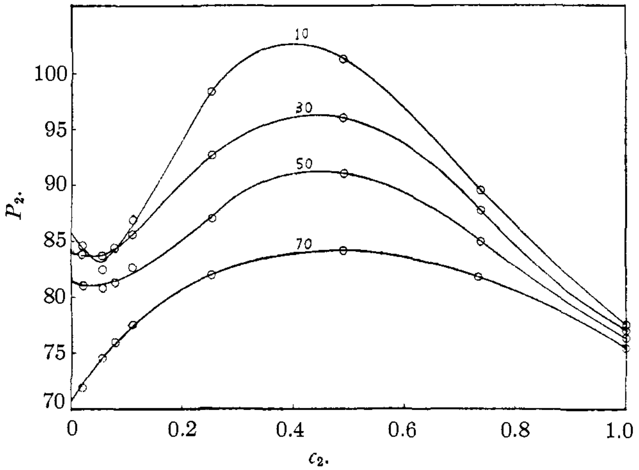

Fig. 6.—Polarizations (P_2) of butyl alcohol in solution in benzene.

In order to study further the effect of the solvent upon the variation of polarization with concentration and temperature, solutions of butyl alcohol in cyclohexane were measured. The values of P_2 check very closely with those obtained in heptane solution, showing that the effect of orientation is the same in these two solvents and somewhat different from that in benzene. It appears that in very dilute solution in heptane,

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[5] Krchma and Williams, This Journal, **49**, 2408 (1927).

[6] Stranathan, *Phys. Rev.*, **31**, 653 (1928).

hexane, cyclohexane and carbon tetrachloride, and at lower temperatures in benzene, there is a tendency toward an orientation which decreases the polarization. With increasing concentration this tendency is soon obscured by an orientation which increases the polarization until, in the more concentrated solutions, a maximum is reached. In the most concentrated solutions the effect of orientation is to decrease the polarization once more. In the benzene, which has a slightly higher dielectric constant to weaken the forces of attraction between the solute molecules, the orientation which diminishes the polarization in the most dilute solutions is too weak at higher temperatures to be detected. It is apparent only in benzene at lower temperatures and in the other solvents at higher temperatures, being obscured or superseded in the latter at lower temperatures by the stronger tendency toward the orientation which increases the polarization. The possible mechanism of these orientations of primary alcohols will be discussed in the next paper of this series in connection with the isomers of the octyl alcohols.

The results on the solutions in benzene may be extrapolated to obtain P_∞, from which the moment may be calculated. The small temperature range obtainable in benzene prevents an accurate determination of the moment by plotting $P_\infty T$ against T, as was done for ethyl iodide, but b may be obtained with sufficient accuracy as $(P_\infty - MR_D)T$ and used to calculate the values of μ shown in Table IV, which gives the results obtained at different temperatures. The values at 10° are omitted because they are more seriously affected by orientation, as in the heptane solutions.

TABLE IV

ELECTRIC MOMENTS OF ALCOHOLS CALCULATED AT DIFFERENT TEMPERATURES IN BENZENE SOLUTION

	n-C_4H_9OH (MR_D = 22.2)			n-$C_8H_{17}OH$ (MR_D = 40.7)		
T, °A.	P_∞	$(P_\infty - MR_D)T$	$\mu \times 10^{18}$	P_∞	$(P_\infty - MR_D)T$	$\mu \times 10^{18}$
293	86.3	18800	1.75	102.3	18000	1.71
303	84.1	18750	1.74	100.7	18200	1.72
313	83.2	19100	1.76	98.0	17900	1.70
323	81.0	19000	1.76	95.7	17800	1.70
333	75.5	17700	1.70	93.3	17500	1.69
343	71.0	16750	1.65	91.4	17400	1.68
		Mean,	1.74		Mean,	1.70

The approximate constancy of the values of $(P_\infty - MR_D)T$ and μ indicate that molecular orientation is slight in the very dilute solutions in benzene. In heptane solution the polarization curves indicate that marked orientation occurs even in the most dilute solutions which can be measured. However, the values of P_2 at the highest temperatures approach closely those observed in benzene solution at the same temperatures, indicating that the effects of orientation are becoming less at high temperature. If the orientation is decreasing with rising temperature, the values of $(P_\infty - MR_D)T$ plotted aginst T should approach a constant value. Actually the values for butyl alcohol are found to approach 17,800 asymptotically, from which the moment 1.70×10^{-18} is calculated, in good agreement with that obtained from the solutions in benzene. The P_∞ values for ethyl alcohol in hexane and heptane are not as accurate as those of butyl alcohol, but the $(P_\infty - MR_D)T$ values show an approach to constancy at high temperatures, the value of the moment calculated at 60° being 1.68×10^{-18}, in excellent agreement with the values 1.74×10^{-18} obtained by Stranathan for the liquid and 1.69×10^{-18} by Miles[7] from measurements upon the vapor. The close agreement of these and other values for the moment of ethyl alcohol in the liquid state with that of Miles for the vapor shows the incorrectness of Sänger's[8] value 1.1×10^{-18} for the vapor. These results taken in conjunction with those of the other investigators to whom reference has been made indicate that the moments of the primary alcohols differ from a value of 1.68×10^{-18} by no more than the experimental error. It may, therefore, be concluded that the electric moment of the molecule of a primary alcohol is independent of the length of the carbon chain.

Summary

The dielectric constants and densities of solutions of ethyl iodide in heptane and of ethanol, *n*-butanol and *n*-octanol in a number of nonpolar liquids have been measured over a wide range of temperature and concentration. A qualitative indication of the anomalous dispersion and absorption for a wave length of 600 meters has been obtained for the pure alcohols and their solutions.

The dielectric polarizations of ethyl iodide give further evidence of the applicability of the Debye equation to liquids in very dilute solution. The polarizations of the alcohols are greatly affected by molecular orientation, being increased in some regions of temperature and concentration and decreased in others. These complicated effects of orientation interfere with the exact application of the Debye equation, but do not prevent the calculation of the electric moments of the molecules.

It is concluded that the electric moment of the molecule of a primary alcohol is independent of the length of the carbon chain.

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[7] Miles, private communication to the authors.

[8] Sänger, *Physik. Z.*, **28**, 455 (1927).