[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PRINCETON UNIVERSITY]

THE DIELECTRIC POLARIZATION OF LIQUIDS. IV. THE DEPENDENCE OF MOLAR REFRACTION UPON CONCENTRATION IN MIXTURES

BY C. P. SMYTH, E. W. ENGEL AND E. BRIGHT WILSON, JR.

RECEIVED FEBRUARY 23, 1929 PUBLISHED JUNE 5, 1929

In considering the dependence of the polarization of a binary mixture upon composition, it has been customary to attribute all deviations from a linear relation to variation in the polarization due to orientation of the dipoles. The molar polarization, P_{12}, of a mixture of two liquids 1 and 2 is represented by the expression

$$P_{12} = c_1P_1 + c_2P_2 = P_1 + c_2(P_2 - P_1)$$

in which P_1 and P_2 are the polarizations and c_1 and c_2 the mole fractions of Components 1 and 2, respectively. From this it follows that P_{12} is a linear function of c_2 if P_1 and P_2 are constant. The polarization of a pure substance is regarded as the sum of three quantities, the polarization P_E caused by electronic shifts induced in the molecules, the small polarization P_A attributed mainly to shifts of atoms or radicals induced in the molecules, and P_M caused by orientation of the molecular dipoles. P_A is difficult to determine accurately, but is usually small in comparison with P_E and sometimes very small in comparison with P_M. The possible variation with concentration of P_A for a substance in solution need not, therefore, be considered as a serious factor in our present methods of obtaining polarization. The assumption of the independence of P_E of concentration has appeared warranted by the approximate constancy found in a number of mixtures for the Lorentz–Lorenz expression for the molar refraction,[1] which is equivalent to P_E, that is, $P_E = (n^2 - 1)/(n^2 + 2)M/d$, in which n is the refractive index, M is the molecular weight and d is the density. The electronic polarization of a mixture of two components 1 and 2 is

$$P_{E,1,2} = \frac{n^2 - 1}{n^2 + 2} \times \frac{c_1M_1 + c_2M_2}{d} = P_{E,1} + c_2(P_{E,2} - P_{E,1})$$

in which M_1 and M_2 are the molecular weights of 1 and 2 and $P_{E,1}$ and $P_{E,2}$ are the electronic polarizations or molar refractions of the two components.[2] Not only the approximate constancy found for the molar refractions in a number of mixtures but also the additivity of the refractions of radicals give ground for the belief that $P_{E,1}$ and $P_{E,2}$ are usually approximately independent of c_2. However, the refraction calculated

---

[1] See Smiles, "The Relations between Chemical Constitution and Some Physical Properties," Longmans, Green and Co., London, **1910**, p. 244.

[2] *Cf.* Debye, "Handbuch der Radiologie" (Marx), Akademische Verlagsgesellschaft m. b. H., Leipzig, Germany, **1925**, Vol. VI, p. 619.

for an isolated ion has been found to be different from that possessed by the ion when attached to other ions because the forces acting on the outer electrons are different.[3] It would appear possible, therefore, that the occurrence of pronounced molecular association in a liquid might affect the forces acting on the outer electrons of the molecules. Change in the degree of association of the molecules brought about by change of temperature or change in the concentration of a mixture might alter the forces acting upon some of the outer electrons and thus alter the polarization. It has been shown for a number of substances that the molar refraction does not change much with temperature or even with change of state, but it has seemed desirable to use a series of refractive index measurements carried out upon fifteen pairs of liquids to examine further the constancy of $P_{E,1}$ and $P_{E,2}$. Unfortunately, the densities are not available for a number of these mixtures, but all the refractive indices are, nevertheless, reported. The liquids used were carefully purified but, as the same materials were used for vapor pressure measurements, the methods of purification and the criteria of purity are given elsewhere.[4] The excellent agreement of the indices of the pure components with the values contained in the literature is evidence of their purity.

The indices of refraction for the sodium D line were measured with a Pulfrich refractometer, a temperature of 20° constant within 0.01° being obtained by a flow of water from carefully adjusted thermostats. The probable error in a value of the index was 0.00007. The results are given in Table I, in which the first column under each pair of substances gives the mole fraction of one component and the second the refractive index. In order to show the deviation of the refractive indices from a linear dependence upon composition, the third column gives the composition calculated from the observed refractive index on the assumption that the latter is a linear function of composition. For example, a refractive index half way between the values for the pure components of a mixture would give a calculated mole fraction of 0.5000. The difference between the known value of the mole fraction and that calculated in this manner is given in the fourth column as a measure of the departure from a linear relation between refractive index and composition.

The densities of the mixtures of several of these pairs of substances have been determined by Mr. W. N. Stoops and Mr. H. E. Rogers and will be published in another connection. The values of the refractive indices for the concentrations at which the densities were determined were obtained by interpolation. Additional refractive indices for the sodium D line and densities were selected from the measurements of Williams and Krchma, who determined these quantities at 25° for a few mixtures of a

---

[3] Fajans and Joos, *Z. Physik*, **23**, 1 (1924); Smyth, *Phil. Mag.*, **50**, 361 (1925).

[4] Smyth and Engel, THIS JOURNAL, **51** (1929).

TABLE I

REFRACTIVE INDICES (n_D) OF BINARY MIXTURES AT 20°

Carbon Tetrachloride–Heptane

M. f., C_7H_{16}	n_D	M. f., calcd.	Diff.
0	1.46026	...	...
0.0335	1.45643	0.0528	0.0187
.0705	1.45221	.1109	.0404
.1422	1.44484	.2124	.0702
.2181	1.43759	.3123	.0942
.2989	1.43056	.4091	.1102
.3430	1.42700	.4582	.1152
.3825	1.42382	.5020	.1195
.4383	1.41962	.5598	.1215
.4811	1.41656	.6027	.1216
.5883	1.40945	.7000	.1117
.7071	1.40243	.7967	.0896
.8348	1.39553	.8916	.0568
.9072	1.39201	.9402	.0330
1.0000	1.38767	...	...

Heptane–Ethyl Bromide

M. f., C_2H_5Br			
0	1.38770	...	...
0.1251	1.38940	0.0469	0.0782
.2227	1.39095	.0898	.1329
.3019	1.39258	.1345	.1674
.3162	1.39289	.1430	.1732
.4724	1.39680	.2508	.2216
.5136	1.39807	.2858	.2278
.5724	1.40004	.3401	.2323
.6121	1.40142	.3782	.2339
.6526	1.40310	.4245	.2281
.6886	1.40454	.4642	.2244
.7308	1.40646	.5171	.2137
.7740	1.40854	.5744	.1996
.7998	1.41004	.6158	.1840
.8453	1.41262	.6869	.1584
.8646	1.41377	.7186	.1460
.9064	1.41662	.7971	.1093
.9439	1.41932	.8716	.0723
1.0000	1.42398	...	...

Heptane–Butyl Bromide

M. f., C_7H_{16}	n_D	M. f., calcd.	Diff.
0	1.43984	...	...
0.0496	1.43612	0.0713	0.0217
.1020	1.43251	.1405	.0385
.1471	1.42950	.1982	.0511
.2299	1.42410	.3017	.0718
.3222	1.41870	.4052	.0830
.3667	1.41600	.4570	.0903
.4167	1.41321	.5104	.0937
0.5095	1.40836	0.6034	0.0939
.6136	1.40333	.6998	.0862
.7235	1.39834	.7955	.0720
.7884	1.39570	.8461	.0577
.8427	1.39347	.8888	.0461
.9038	1.39114	.9335	.0297
1.0000	1.38767	...	...

Heptane–Ethyl Iodide

M. f., C_7H_{16}			
0	1.51330	...	...
0.0596	1.49882	0.1153	0.0557
.1297	1.48358	.2366	.1069
.2018	1.47007	.3442	.1424
.2795	1.45716	.4470	.1675
.3219	1.45076	.4979	.1760
.3632	1.44494	.5443	.1811
.4138	1.43821	.5978	.1840
.4612	1.43247	.6435	.1823
.5723	1.42042	.7395	.1672
.6903	1.40934	.8277	.1374
.8407	1.39768	.9205	.0798
1.0000	1.38770	...	...

Heptane–Ethyl Alcohol

M. f., C_7H_{16}			
0	1.36130	...	...
0.0207	1.36221	0.0345	0.0138
.0506	1.36355	.00853	.0347
.0723	1.36448	.1206	.0483
.0985	1.36566	.1653	.0668
.1554	1.36805	.2560	.1006
.2184	1.37044	.3466	.1282
.2537	1.37161	.3910	.1373
.2945	1.37292	.4407	.1462
.3369	1.37426	.4915	.1546
.3816	1.37540	.5347	.1531
.4946	1.37830	.6447	.1501
.6150	1.38091	.7437	.1287
.6964	1.38246	.8024	.1060
.7901	1.38409	.8636	.0735
.8878	1.38573	.9264	.0386
1.0000	1.38767	...	...

Hexane–Heptane

M. f., C_7H_{16}			
0	1.37508	...	...
0.1743	1.37748	0.1902	0.0159

TABLE I (*Continued*)

Hexane–Heptane

M. f., C_7H_{16}	n_D	M. f., calcd.	Diff.
0.2216	1.37814	0.2425	0.0209
.4029	1.38051	.4303	.0274
.4708	1.38137	.4984	.0276
.5705	1.38261	.5967	.0261
.6103	1.38309	.6340	.0237
.6709	1.38376	.6878	.0169
.7176	1.38434	.7337	.0161
.7706	1.38492	.7797	.0091
.8748	1.38616	.8780	.0033
1.0000	1.38770	...	...

Heptane–Butyl Chloride

M. f., C_7H_{16}			
0	1.40173	...	...
0.0449	1.40059	0.0811	0.0362
.0669	1.40012	.1145	.0476
.1468	1.39842	.2354	.0886
.2276	1.39678	.3521	.1245
.3198	1.39522	.4630	.1432
.3598	1.39456	.5100	.1502
.4066	1.39383	.5619	.1553
.4540	1.39314	.6109	.1569
.5008	1.39252	.6550	.1542
.6159	1.39105	.7596	.1437
.7202	1.38992	.8400	.1198
.9134	1.38823	.9602	.0468
1.0000	1.38767	...	...

Heptane–Heptyl Bromide

M. f., $C_7H_{15}Br$			
0	1.38770	...	...
0.1022	1.39455	0.1094	0.0072
.1919	1.40043	.2033	.0114
.2715	1.40558	.2856	.0141
.3674	1.41183	.3854	.0180
.4194	1.41522	.4395	.0201
.4725	1.41862	.4939	.0214
.5151	1.42122	.5354	.0203
.6702	1.43087	.6895	.0193
.7713	1.43700	.7874	.0161
.8840	1.44354	.8919	.0079
1.0000	1.45031	...	...

Heptane–Butyl Alcohol

M. f., C_7H_{16}	n_D	M. f., calcd.	Diff.
0	1.39942	...	...
0.0327	1.39883	0.0502	0.0175
.1336	1.39707	.2000	.0664
.2104	1.39579	.3089	.0985
0.2867	1.39448	0.4204	0.1337
.3321	1.39377	.4809	.1488
.3767	1.39313	.5353	.1586
.4249	1.39252	.5872	.1623
.5795	1.39069	.7430	.1635
.6989	1.38945	.8485	.1496
.8327	1.38833	.9438	.1111
.9097	1.38788	.9821	.0724
1.0000	1.38767	...	...

Ethyl Bromide–Ethyl Iodide

M. f., C_2H_5I			
0	1.42408	...	...
0.1937	1.44143	0.1945	0.0008
.2901	1.45016	.2923	.0022
.3151	1.45247	.3182	.0031
.3824	1.45866	.3876	.0052
.4280	1.46264	.4322	.0042
.4732	1.46671	.4778	.0046
.5148	1.47036	.5187	.0039
.5741	1.47567	.5782	.0041
.6114	1.47899	.6154	.0040
.6750	1.48471	.6796	.0046
.7640	1.49258	.7678	.0038
.8817	1.50302	.8848	.0031
1.0000	1.51330	...	...

Butyl Chloride–Butyl Bromide

M. f., C_4H_9Br			
0	1.40173	...	...
0.0444	1.40353	0.0472	0.0028
.0832	1.40518	.0905	.0073
.1903	1.40935	.1999	.0096
.2878	1.41309	.2981	.0103
.3888	1.41703	.4015	.0127
.4333	1.41874	.4463	.0130
.4842	1.42062	.4957	.0115
.5307	1.42233	.5405	.0098
.5791	1.42430	.5922	.0131
.6816	1.42826	.6962	.0146
.7798	1.43187	.7909	.0111
.8844	1.43585	.8953	.0109
.9397	1.43792	.9496	.0099
1.0000	1.43984	...	...

Carbon Tetrachloride–Butyl Alcohol

M. f., C_4H_9OH			
0	1.46026	...	...
0.0555	1.45677	0.0574	0.0019

TABLE I (*Concluded*)

Carbon Tetrachloride–Butyl Alcohol

M. f., C_4H_9OH	n_D	M. f., calcd.	Diff.
0.1196	1.45307	0.1182	0.0014
.1686	1.45017	.1659	.0027
.2255	1.44687	.2201	.0054
.3240	1.44125	.3125	.0115
.4243	1.43532	.4099	.0144
.4742	1.43251	.4561	.0181
.5214	1.42980	.5007	.0207
.5707	1.42690	.5483	.0224
.6197	1.42390	.5976	.0221
.7154	1.41830	.6897	.0257
.8095	1.41212	.7913	.0182
.8598	1.40886	.8448	.0150
.9117	1.40540	.9017	.0100
.9505	1.40280	.9445	.0060
1.0000	1.39942	...	...

Butyl Bromide–Butyl Alcohol

M. f., C_4H_9Br			
0	1.39942	...	...
0.0506	1.40177	0.0580	0.0072
.1394	1.40570	.1550	.0156
.1711	1.40698	.1866	.0155
.2673	1.41124	.2917	.0244
.3580	1.41500	.3845	.0265
.4155	1.41690	.4314	.0259
.4520	1.41870	.4758	.0238
.4780	1.41970	.5005	.0225
.5484	1.42240	.5671	.0187
.7622	1.43065	.7707	.0085
.8188	1.43291	.8265	.0077
1.0000	1.43994	...	...

Ethyl Bromide–Ethyl Alcohol

M. f., C_2H_5OH	n_D	M. f., calc.	Diff.
0	1.42403	...	...
0.0729	1.41992	0.0657	0.0072
.1220	1.41717	.1097	.0123
.1646	1.41477	.1481	.0165
.2427	1.41027	.2201	.0226
.2749	1.40830	.2516	.0233
.3765	1.40256	.3435	.0330
.4100	1.40058	.3751	.0349
.4780	1.39646	.4407	.0373
.5337	1.39312	.4945	.0392
.5949	1.38935	.5548	.0401
.6538	1.38559	.6149	.0389
.7218	1.38118	.6850	.0368
.7767	1.37748	.7447	.0320
.8166	1.37475	.7884	.0282
.8930	1.36934	.8749	.0181
.9382	1.36603	.9279	.0103
1.0000	1.36152	...	...

Ethyl Iodide–Ethyl Alcohol

M. f., C_2H_5OH			
0	1.51330	...	...
0.1393	1.49552	0.1171	0.0222
.2594	1.47967	.2216	.0378
.3681	1.46472	.3201	.0480
.4759	1.44906	.4232	.0527
.5156	1.44314	.4622	.0534
.5268	1.44153	.4729	.0539
.5744	1.43408	.5219	.0525
.6248	1.42614	.5743	.0505
.6636	1.41992	.6152	.0484
.7517	1.40528	.7116	.0401
.8439	1.38950	.8157	.0282
.9345	1.37329	.9225	.0120
1.0000	1.36152	...	...

considerable number of pairs of substances.[5] Some of the latter data were eliminated because of apparent small discrepancies, while a few pairs were omitted as being of less interest than the others. Table II gives the results of the calculations from the data in Table I combined with the densities mentioned. The first column gives the mole fraction of one of the two components, the second column gives the value of $(n^2 - 1)/(n^2 + 2)(c_1M_1 + c_2M_2)/d$, which is the observed $P_{E,1,2}$, the third column gives the value of $c_1P_{E,1} + c_2P_{E,2} = P_{E,1} + c_2(P_{E,2} - P_{E,1})$, where $P_{E,1}$ and $P_{E,2}$ are taken as the values of the pure components, and the fourth column gives the difference between the observed and calculated. As the

[5] Williams and Krchma, THIS JOURNAL, **49**, 1678, 2408 (1927).

probable error in the density determinations was 0.0002 and in the refractive indices 0.00007, the probable error in the observed value of $P_{E,1,2}$ should usually be about 0.014. The results calculated from the data of Williams and Krchma are shown in Table III, in which the error is probably somewhat greater than in Table II, although the less certain results have been eliminated.

TABLE II

MOLAR REFRACTIONS (D LINE) AT 20°

Heptane–Butyl Chloride

M. f., C_4H_9Cl	$P_{E,1,2}$ (obs.)	$P_{E,1,2}$ (calcd.)	Diff.
0	34.530	(34.530)	...
0.0242	34.363	34.310	0.053
.0653	33.943	33.938	.005
.0889	33.737	33.724	.013
.1562	33.116	33.113	.003
.2617	32.190	32.157	.033
.5619	29.463	29.434	.029
.8623	26.743	26.710	.033
1.0000	25.461	(25.461)	...

Heptane–Butyl Bromide

M. f., C_4H_9Br	$P_{E,1,2}$ (obs.)	$P_{E,1,2}$ (calcd.)	Diff.
0	34.527	(34.527)	.....
0.0456	34.235	34.244	−0.009
.0930	33.939	33.951	− .012
.1409	33.643	33.654	− .011
.2579	32.924	32.929	− .005
.4154	31.923	31.953	− .030
.5958	30.816	30.835	− .019
.8413	29.299	29.313	− .014
1.0000	28.330	(28.330)	.....

Heptane–Ethyl Iodide

M. f., C_2H_5I			
0	34.530	(34.530)	.....
0.0328	34.191	34.195	−0.004
.0843	33.664	33.669	− .005
.1889	32.617	32.600	+ .017
.4130	30.271	30.310	− .039
.6155	28.181	28.241	− .060
.8035	26.291	26.320	− .029
1.0000	24.312	(24.312)	.....

Heptane–Heptyl Bromide

M. f., C_4H_9Br			
0	34.530	(34.530)	.....
.0488	34.901	34.907	−0.006
.0889	35.212	35.216	− .004
.1626	35.806	35.785	.021
.3330	37.124	37.100	.024
.5327	38.644	38.642	.002
1.0000	42.249	(42.249)	.....

Heptane–Ethyl Alcohol

M. f., C_2H_5OH			
0	34.527	(34.527)	..
0.0312	34.167	34.141	0.026
.0525	33.892	33.877	.015
.0805	33.544	33.530	.014
.1043	33.256	33.237	.019
.1383	32.848	32.815	.033
.2655	31.263	31.240	.023
.4451	29.025	29.017	.008
.6152	26.917	26.912	.005
.8042	24.591	24.572	.019
1.0000	22.148	(22.148)	..

Heptane–Butyl Alcohol

M. f., C_4H_9OH			
0	34.527	(34.527)	.....
0.0256	33.991	33.974	0.017
.4252	25.322	25.333	− .011
.6142	21.222	21.246	− .024
.8300	16.604	16.581	.023
.9260	14.504	14.505	− .001
1.0000	12.905	(12.905)	.....

The average deviation of the individual differences in Table **II** from their arithmetical mean is of the same order of magnitude as the mean itself and as the probable error estimated for the individual values of $P_{E,1,2}$ (obs.). Consequently, it may be concluded that the difference,

TABLE III

MOLAR REFRACTIONS (D LINE) AT 25°

Carbon Tetrachloride–Benzene

M. f., CCl_4	$P_{E,1,2}$ (obs.)	$P_{E,1,2}$ (calcd.)	Diff.
0	26.194	(26.194)	..
0.25	26.290	26.263	0.027
.50	26.380	26.332	.048
.75	26.456	26.401	.055
1.00	26.469	(26.469)	..

Carbon Tetrachloride–Ethyl Ether

M. f., CCl_4	$P_{E,1,2}$ (obs.)	$P_{E,1,2}$ (calcd.)	Diff.
0	22.513	(22.513)	..
0.25	23.558	23.502	0.056
.50	24.526	24.491	.035
.75	25.529	25.480	.049
1.00	26.469	(26.469)	..

Carbon Tetrachloride–Methyl Acetate

M. f., CCl_4			
0	17.598	(17.598)	..
0.25	19.826	19.815	0.011
.50	22.049	22.033	.016
.75	24.241	24.250	− .009
.90	25.680	25.582	.098
1.00	26.469	(26.469)	..

Carbon Tetrachloride–Acetone

M. f., CCl_4			
0	16.186	(16.186)	..
0.60	22.371	22.356	0.015
.70	23.416	23.384	.032
.75	23.901	23.898	.003
.90	25.496	25.441	.055
1.00	26.469	(26.469)	..

Carbon Tetrachloride–Ethyl Alcohol

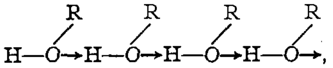
M. f., CCl_4			
0	12.893	(12.893)	..
0.50	19.725	19.681	0.044
.60	21.092	21.039	.053
.75	23.114	23.075	.039
.90	25.137	25.111	.026
1.00	26.469	(26.469)	..

Carbon Tetrachloride–*Iso*-amyl Alcohol

M. f., CCl_4			
0	26.754	(26.754)	..
0.75	26.574	26.540	0.034
.90	26.498	26.497	.001
1.00	26.469	(26.469)	..

less than 0.1%, between the observed and calculated values of $P_{E,1,2}$ is no larger than the experimental error. In other words, $P_{E,1}$ and $P_{E,2}$ are constant as far as can be measured throughout the mixtures, which means that in these liquids the contribution to the polarization of the electronic shifts induced in a molecule is practically independent of the surrounding molecules. The differences are about one-tenth as large as those found by Falk[6] between the molar refractions of several substances at 20 and at 80°.

These results have an interesting bearing upon the problem of molecular association. Sidgwick[7] states that "the great majority of associated substances contain a hydroxyl group," polymerization arising through the hydroxyl "hydrogen acting as acceptor and the oxygen as donor," that is, the hydrogen of one hydroxyl group becomes attached to the oxygen of the hydroxyl of another molecule and, as a result, shares electrons with both oxygens. Alcohol molecules would associate thus



$$\mathrm{H{-}\overset{R}{O}{\rightarrow}H{-}\overset{R}{O}{\rightarrow}H{-}\overset{R}{O}{\rightarrow}H{-}\overset{R}{O}{\rightarrow}}$$, etc.

---

[6] Falk, THIS JOURNAL, **31**, 86, 807 (1909); *Z. physik. Chem.*, **82**, 504 (1913).

[7] Sidgwick, "The Electronic Theory of Valency," Oxford University Press, Oxford, England, 1927, p. 134.

It has been shown that an oxygen atom with a completed octet of electrons to which two hydrogen nuclei are attached to form a water molecule has a refraction of 3.76. When one of the linkages to hydrogen is replaced by a linkage to carbon, the refraction is reduced to 3.23, and when both hydrogen linkages are replaced by carbon linkages the refraction is reduced to 2.85.[3] Fajans and Joos[3] have calculated the following refractions: O^{--}, 7; OH^-, 5.10; OH_2, 3.75; OH_3^+, 3.04. Evidently, the attachment of a hydrogen nucleus to oxygen brings about a considerable reduction in the refraction. A somewhat smaller reduction would probably be effected by attaching a hydrogen to an hydroxyl already linked to carbon, since the electrons are here more tightly bound, as evidenced by the lower refraction 3.23. Also, if the hydrogen were already attached to another oxygen, as pictured by Sidgwick for the alcohols, the forces which it exerted on the electrons of this oxygen would probably be weakened by its sharing with a second oxygen. This weakening would raise the refraction and thus tend to compensate for the reduction in the refraction of the other oxygen. An exact compensation, however, would be a very improbable coincidence. There is good reason then to believe that an association like that supposed by Sidgwick would bring about a reduction of 0.2 to 0.5 in the molar refraction of the alcohols. As the degree of association would be altered by mixing with another liquid and would vary with the concentration of the mixtures, the refraction of the alcohol should vary to an extent readily detectible in the results in Table II. The absence of such a variation provides evidence against the hypothesis of Sidgwick. If, however, the association is merely an orientation brought about by the powerful forces between the dipoles in the alcohol molecules, as discussed by two of the authors[4] in another connection, the forces of the electrons may not be sufficiently affected by change of concentration in the mixtures to alter the refraction by a detectible amount.

It has been found that the molar refraction of a pure substance in the vapor state at 100° is often from 1 to 3% higher than the refraction of the liquid at room temperature,[8] although for some liquids a decrease of about the same magnitude accompanies the rise in temperature and vaporization. The changes observed are of the same order of magnitude as the increases found by Falk to result from raising the temperature from 20 to 80°. Moreover, these changes are no greater for substances containing an hydroxyl group than for those supposed to be unassociated. For example, water vapor at 100° has a refraction 0.4 to 1.3% higher than the liquid at 10°, the values of different investigators varying; ethyl alcohol vapor at 100° is 0.7% higher than the liquid at 10°, the

---

[8] Lorenz, *Ann. Physik*, **11**, 70 (1880); Prytz, *ibid.*, **11**, 109 (1880); Brühl, *Z. physik. Chem.*, **7**, 4 (1891).

supposedly unassociated ethyl ether is 1.4% higher in the vapor state at 100° and ethyl iodide is 0.9% higher, while methyl alcohol vapor at 100° is 0.3% lower than the liquid at 10°. The refraction of liquid *n*-heptyl alcohol increases 0.7% between 10 and 80° and that of the hydrocarbon, di-*iso*-amyl, increases by a similar amount. It is interesting to note that these increases are, in proportion to the temperature rise of 70°, of the same size as the increases, 1.6 to 1.9%, found by Smyth and Stoops[9] in the total polarizations of three isomers of heptane and an octane for a temperature increase of 180°. As these substances have no electric moments, the total polarization is $P_E + P_A$ and P_A is found to have a value only about 3% of that of P_E for these isomers. It is evident that the alcohols fail to show a change of refraction greater than that shown by supposedly unassociated substances when not only the temperature but even the state is changed, although the association must decrease with rise of temperature and, for most of the substances, become negligible on vaporization. Just as the change in the degree of association almost certain to accompany change in the concentration of mixtures leaves the refraction unaffected within the limit of accuracy of the measurements, so the change produced by change of temperature has no distinguishable effect. Further evidence is thus brought to bear against the hypothesis of an actual sharing of electrons between molecules when association occurs in the alcohols and water.

Summary

The refractive indices for the sodium D line at 20° are measured for a large number of mixtures of fifteen different pairs of liquids.

The data are used to calculate the molar refractions of the liquids. It is found that the molar refractions of the components of the mixtures are independent of the concentration to within 0.07%. This proves that the contribution of induced electronic shifts to the polarization of a molecule of one of these substances is practically unaffected by the surrounding molecules.

The independence of composition shown by the molar refraction of the alcohols is used as evidence against the sharing of electrons between their molecules to bring about molecular association.

PRINCETON, NEW JERSEY

---

[9] Smyth and Stoops, THIS JOURNAL, 50, 1883 (1928).