[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE DIELECTRIC POLARIZATION OF LIQUIDS. X. THE POLARIZATION AND REFRACTION OF THE NORMAL PARAFFINS

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This investigation was undertaken with the object of obtaining further information concerning the temperature dependence or independence of the polarization of substances possessing little or no electric moment and of studying the variation of this polarization in an homologous series. Through the kindness of the Ethyl Gasoline Corporation it has been possible to obtain samples of the straight-chain hydrocarbons from pentane to dodecane prepared by Dr. Albert L. Henne of Ohio State University, to whom the writers wish to express their indebtedness. The samples of these liquids were of a high degree of purity boiling over a range of only 0.02 to 0.03°. Although the densities and refractive indices of these substances had been measured previously, the measurements were repeated in order that all the data used should have been determined for the same materials, these materials being of exceptional purity. Moreover, the previous density measurements did not extend over the wide range of temperature which it seemed desirable to employ in the polarization investigations. Wherever the present results overlap data given in "International Critical Tables" excellent agreement is obtained.

In the first of this series of papers[1] the method of obtaining the electric moment of the molecule of a substance has been discussed. The molar polarization of a substance, $P = (\epsilon - 1)/(\epsilon + 2) \times M/d = P_E + P_A + P_M$, in which ϵ is the dielectric constant, M is the molecular weight, d is the density, $P_E + P_A$ is the polarization due to shifts of charges in the molecule inducible by an external field and P_M is the polarization due to the orientation of the permanent electric doublets of the molecules. When P_M is 0, the moment of the molecule must be 0. P_E may be calculated as the molar refraction for light of infinite wave length, $MR_\infty = (1 - \lambda_0^2/\lambda^2)$-$[(n^2 - 1)/(n^2 + 2) \times M/d]$, where n is the index of refraction for light of wave length λ and λ_0 is the wave length corresponding to a characteristic vibration frequency in the ultraviolet region. P_A, the difference between P_E, the polarization due to electronic shifts and the total induced polarization, is commonly attributed to induced shifts of atoms or radicals. The variation of P with the absolute temperature T is shown by the equation, $P = a + b/T$, in which the constant $a = P_E + P_A$, $b/t = P_M$, and the constant $b = 4\pi N\mu^2/9k$, where μ is the electric moment of a single molecule, N is the number of molecules in a gram molecule $= 6.061 \times 10^{23}$, and k is the molecular gas constant $= 1.372 \times 10^{-16}$. Evidently, if P does not

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

change with changing temperature, it is to be concluded that b is zero and that therefore the moment of the molecule is zero. If the molecule possesses a moment, P should decrease with rising temperature.

The refractive indices were measured with a Pulfrich refractometer and the molar refractions MR and dispersions calculated in the manner described in the third paper of this series.[2] The densities and dielectric constants were measured with the apparatus described in earlier papers,[1,3] the only modification being the insertion of two stages of amplification in the detector circuit of the capacity bridge. The dielectric constant of the benzene used in calibrating the condenser was taken as 2.276 at 25°. Both the dielectric constants and densities were measured at definite temperature intervals of 20° by adjusting the constant temperature bath to the exact temperatures shown in the following tables, the temperature being held constant to ±0.05° below 0° and above 90° and to ±0.02° at the intermediate temperatures. The experimental data and the polarizations and refractions calculated from them are given in Tables I and II, and in Fig. 1 the values of the polarization are plotted as ordinates against those of the temperature as abscissas. In order to keep the diagram within reasonable dimensions, the ordinates are broken several times, but the same scale is maintained throughout.

TABLE I

REFRACTIVE INDICES AND MOLAR REFRACTIONS AT 20°C.

	n_γ	n_β	n_D	n_α	MR_γ	MR_β	MR_D	MR_α
Pentane	1.36600	1.36267	1.35801	1.35663	25.79	25.57	25.28	25.19
Hexane	1.38318	1.37951	1.37490	1.37308	30.45	30.19	29.86	29.73
Heptane	1.39636	1.39251	1.38777	1.38584	35.19	34.89	34.51	34.36
Octane	1.40652	1.40238	1.39755	1.39559	39.91	39.55	39.13	38.96
Nonane	1.41458	1.41043	1.40550	1.40351	44.65	44.22	43.78	43.60
Decane	1.42119	1.41691	1.41192	1.40982	49.36	48.92	48.41	48.19
Undecane	1.42656	1.42239	1.41730	1.41519	54.10	63.53	53.06	52.83
Dodecane	1.43094	1.42685	1.42170	1.41959	58.77	58.30	57.67	57.42

TABLE II

DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS

t, °C.	C_5H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}	C_9H_{20}	$C_{10}H_{22}$	$C_{11}H_{24}$	$C_{12}H_{26}$
				Dielectric Constants				
−90	2.011	2.044	2.073	.....	.....	.....	.....	.....
−70	1.984	2.017	2.047	.....	.....	.....	.....	.....
−50	1.955	1.990	2.021	2.037	2.059	.....	.....	.....
−30	1.924	1.963	1.995	2.013	2.035	2.050	.....	.....
−10	1.892	1.936	1.968	1.987	2.010	2.027	2.039	2.047
10	1.860	1.906	1.940	1.961	1.985	2.003	2.017	2.025
30	1.828	1.875	1.912	1.935	1.959	1.979	1.994	2.002
50	.....	1.844	1.881	1.907	1.932	1.954	1.969	1.978

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

[3] Smyth and Morgan, *ibid.*, **50**, 1547 (1928).

TABLE II (*Concluded*)

t. °C.	C_5H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}	C_9H_{20}	$C_{10}H_{22}$	$C_{11}H_{24}$	$C_{12}H_{26}$
70	.....	.....	1.849	1.879	1.905	1.928	1.944	1.954
90	.....	.....	1.815	1.849	1.878	1.901	1.918	1.930
110	.....	.....	.....	1.817	1.847	1.873	1.893	1.906
130	.....	.....	.....	.....	1.818	1.844	1.866	1.881
150	.....	.....	.....	.....	1.787	1.814	1.838	1.856
170	.....	.....	.....	.....	.....	1.783	1.810	1.830
190	.....	.....	.....	.....	.....	.....	1.781	1.803
210	.....	.....	.....	.....	.....	.....	.....	1.776
				Densities				
−90	0.7257	0.7533	0.7738	.....	.....	.....	.....	.....
−70	.7083	.7370	.7580	.....	.....	.....	.....	.....
−50	.6908	.7206	.7420	0.7588	0.7726	.....	.....	.....
−30	.6728	.7037	.7256	.7432	.7573	0.7687	.....	.....
−10	.6545	.6869	.7092	.7275	.7417	.7538	0.7630	0.7715
10	.6359	.6692	.6927	.7114	.7260	.7385	.7482	.7571
30	.6163	.6507	.6755	.6945	.7105	.7230	.7333	.7424
50	.....	.6318	.6577	.6781	.6945	.7075	.7182	.7274
70	.....	.....	.6395	.6610	.6776	.6916	.7027	.7125
90	.....	.....	.6210	.6437	.6616	.6754	.6875	.6974
110	.....	.....	.....	.6257	.6445	.6583	.6720	.6820
130	.....	.....	.....	.....	.6272	.6421	.6563	.6665
150	.....	.....	.....	.....	.6096	.6257	.6398	.6509
170	.....	.....	.....	.....	.....	.6088	.6224	.6345
190	.....	.....	.....	.....	.....	.....	.6038	.6170
210	.....	.....	.....	.....	.....	.....	.....	.5986
				Polarizations				
−90	25.04	29.51	34.09	.....	.....	.....	.....	.....
−70	25.14	29.58	34.17	.....	.....	.....	.....	.....
−50	25.20	29.65	34.26	38.64	43.28	.....	.....	.....
−30	25.23	29.74	34.37	38.77	43.41	47.95	.....	.....
−10	25.25	29.81	34.44	38.84	43.53	48.10	52.66	57.07
10	25.26	29.85	34.48	38.93	43.63	48.24	52.85	57.25
30	25.30	29.88	34.55	39.05	43.69	48.38	53.01	57.40
50	.....	29.92	34.56	39.08	43.74	48.48	53.09	57.53
70	.....	.....	34.53	39.13	43.83	48.57	53.20	57.64
90	.....	.....	34.44	39.11	43.85	48.62	53.23	57.75
110	.....	.....	.....	39.05	43.78	48.68	53.31	57.89
130	.....	.....	.....	.....	43.77	48.62	53.31	57.97
150	.....	.....	.....	.....	43.69	48.49	53.30	58.05
170	.....	.....	.....	.....	.....	48.33	53.35	58.13
190	.....	.....	.....	.....	.....	.....	53.43	58.25
210	.....	.....	.....	.....	.....	.....	.....	58.43

In Fig. 1 the scale on which the polarization is plotted is so large that several of the points appear to lie at some distance from the straight lines drawn to represent them. The values for heptane, octane, nonane and decane show an increasing tendency to fall below the straight lines as the boiling point is approached. This deviation from linearity is regular and greater than the probable experimental error, but, as it is not apparent in the pentane, hexane, undecane and dodecane values, for which the same experimental technique was used and to which the same theoretical considerations should apply, its cause must be regarded as obscure and, possibly, accidental. The results indicate, however, that, as in the case of the isomers of heptane[2] previously investigated, the polarization varies but little with temperature, the variation being an approximately linear increase with rising temperature instead of the hyperbolic decrease required by the equation for the temperature variation of the polarization of substances possessing a moment. Cases have been found[3,4] in which pure substances possessing large moments show a rise in polarization with rising temperature instead of the expected fall because the rising temperature decreases the intermolecular action or association which is reducing the

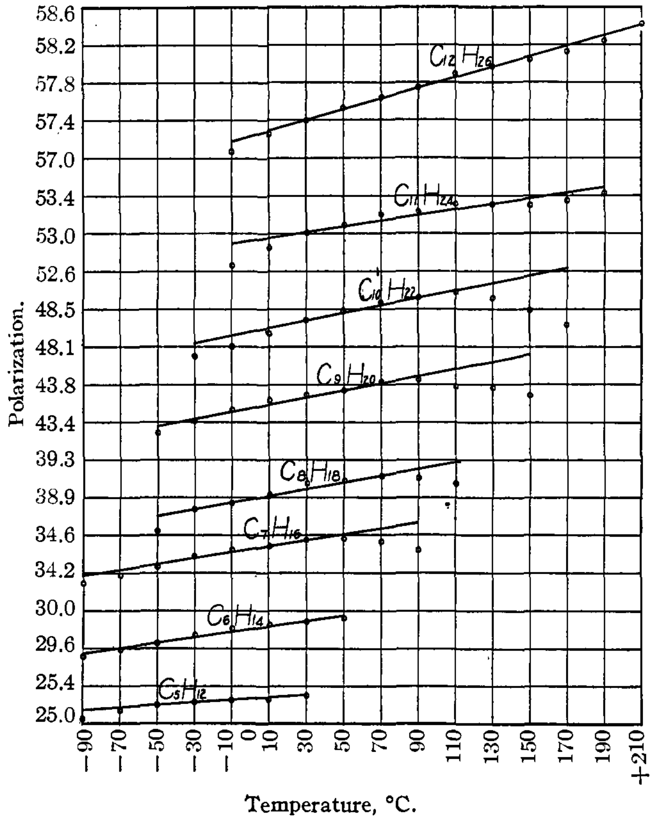

Fig. 1.—Variation of polarization with temperature.

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[4] Smyth and Stoops, This Journal, 51, 3312, 3330 (1929).

polarization. In these cases, the polarization, in spite of its reduction by intermolecular action, has been found to be considerably larger than the molar refraction, but the polarizations of these hydrocarbons at 20° are almost identical with the refractions for the sodium D line at this temperature. Only when the refraction is extrapolated to infinite wave length to obtain the values shown under P_E in Table III is the difference between P and P_E appreciable. The difference $P - P_E$ is smaller than the values commonly found for P_A,[5] which indicates a very small, if not zero, value for P_M as $P - P_E = P_A + P_M$. Moreover, the increase in $P - P_E$ in going up the series from pentane to dodecane is less than that commonly observed for P_A with increase in molecular weight, which indicates a negligible variation in any possibly existing moment. As the temperature variation of P also points to a small, if not zero, value for P_M, it may be concluded that the values of P_M and, hence, of the electric moments of the molecules, are indistinguishable from zero by the experimental method which has been employed. The difference $P - P_E$ is, therefore, set equal to P_A to obtain the values listed in Table III along with the dispersions and the values at 20° of the other constants which have been discussed.

TABLE III

PHYSICAL CONSTANTS AT 20°C.

	ϵ	d	P	P_E	P_A	$MR_\gamma - MR_\alpha$	$n_\gamma - n_\alpha$
Pentane	1.845	0.6263	25.30	24.69	0.61	0.60	0.00937
Hexane	1.890	.6600	29.85	29.18	.67	.72	.01010
Heptane	1.926	.6842	34.51	33.74	.77	.87	.01052
Octane	1.950	.7033	39.03	38.25	.78	.95	.01093
Nonane	1.972	.7182	43.66	42.88	.78	1.05	.01107
Decane	1.991	.7306	48.32	47.36	.96	1.17	.01127
Undecane	2.005	.7406	52.92	51.89	1.03	1.27	.01137
Dodecane	2.017	.7495	57.49	56.38	1.11	1.35	.01135

The value of P_A for heptane in Table III is smaller than that found by Smyth and Stoops by 0.11, which, in view of the lower value, 2.276, instead of 2.279, assigned to the dielectric constant of benzene used as standard in the calibration of the apparatus, may be regarded as excellent agreement. The values increase with increasing molecular weight in a manner to be expected from the increase in P and P_E. In view of the absence of moment, it is interesting to see whether the polarization resembles the refraction in being an additive property, as might be expected. For this purpose, the differences between the refractions and also the polarizations of successive members of the series are shown in Table IV, the difference in each case being the contribution of a CH_2 group.

The mean values of the refractions for the CH_2 group at different wave lengths agree well with those given in Landolt–Börnstein (5th ed.), which

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[5] Smyth, THIS JOURNAL, 51, 2051 (1929).

TABLE IV

REFRACTION AND POLARIZATION OF CH_2 GROUP

	MR_γ	MR_β	MR_D	MR_α	P_E	P
C_6H_{14}–C_5H_{12}	4.66	4.62	4.58	4.54	4.49	4.55
C_7H_{16}–C_6H_{14}	4.74	4.70	4.65	4.63	4.56	4.66
C_8H_{18}–C_7H_{16}	4.72	4.66	4.62	4.60	4.51	4.52
C_9H_{20}–C_8H_{18}	4.74	4.67	4.65	4.64	4.63	4.63
$C_{10}H_{22}$–C_9H_{20}	4.71	4.70	4.63	4.59	4.48	4.66
$C_{11}H_{24}$–$C_{10}H_{22}$	4.74	4.71	4.65	4.64	4.53	4.60
$C_{12}H_{26}$–$C_{11}H_{24}$	4.67	4.67	4.61	4.59	4.49	4.57
Mean value	4.711	4.676	4.627	4.604	4.527	4.60
Landolt–Börnstein	4.710	4.668	4.618	4.598		

are shown at the bottom of the table. In going down the columns of both the refractions and the polarizations there is a slight alternation in the values for the CH_2 group, which suggests the possibility that the refraction and polarization of a molecule with an even number of carbon atoms in an unbranched chain may be proportionately a little lower than those of a molecule with an odd number of carbons in the chain. The range within which the values of P vary is slightly greater than that within which those for the more accurately measurable MR_γ, MR_β, MR_D and MR_α vary but no greater than the range of the value of P_E, in which the errors of measurement accumulate. As the values of P vary about the figure 4.60 without any trend upward or downward it is evident that the polarization of these hydrocarbons is an additive property, although a glance at the values of the dielectric constants in Table III shows that this quantity is decidedly not an additive property. The difference of the mean values of P and P_E for the CH_2 group gives a value 0.07 for P_A for this group, which cannot, however, be regarded as of general significance.

The increase of polarization with temperature, about 1% per 100° in the absence of the depression noted for some substances as the boiling point is approached, is of the same magnitude as that found previously for *n*-heptane and two of its isomers. It was suggested in this work[4] that the force fields of adjacent molecules might reduce the mobilities of the bound electrons to a small extent, thereby reducing the polarization and refraction and that, as the molecular separation and motion increased with rising temperature, the effect of the force fields upon the electrons was decreased, the polarization and refraction thus being increased. However, subsequent investigations of the refractions of mixtures of heptane with strongly polar molecules,[6] including ethyl and butyl alcohol, have shown that the refraction of the mixture is a linear function of composition, deviations from linearity being of the magnitude of the experimental error, about 0.02 units. The very different force field around the heptane molecule when it is surrounded with alcohol molecules instead of with other heptane molecules

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[6] Smyth, Engel and Wilson, THIS JOURNAL, **51**, 1736 (1929).

might be expected to bring about a considerable change in the refraction and polarization if the change of polarization with temperature observed in the present work were due to change in the effect of the molecular force fields. The absence of any such considerable change of refraction with concentration would, therefore, seem to argue strongly against the attribution of the increase of polarization with temperature to decreasing effect of the force fields. It was also suggested that a more important factor might be the increase in the number of degrees of freedom with increasing temperature, which should facilitate the displacement of charges in the molecule and, hence, increase the polarization. It must, however, be borne in mind that, in the derivation of the expression for refraction and polarization, factors have, of necessity, been neglected, the effects of which may be negligible in comparison to that of a large dipole moment, but which, in the absence of a moment, may easily become evident in the results of careful measurements.

The zero or exceedingly small moments of the molecules of these hydrocarbons, as in the case of the isomers of heptane, show the absence of any polarity in the bonds of alkyl radicals which may be detected through the electric moments arising from them, and, consequently, give no evidence of a difference in the electronegativities of the radicals.

Summary

The dielectric constants and densities of the normal paraffins from pentane to dodecane have been measured over almost the entire temperature range within which these substances are liquid at atmospheric pressure and the refractive indices and dispersions have been determined at 20°.

The polarizations calculated from the dielectric constants and densities increase about 1% per 100° rise in temperature. The molar refractions at different wave lengths obtained for the CH_2 group agree well with those in the literature and the constancy of the polarization of the CH_2 groups show that, in the absence of an electric moment, the polarization is an additive property, as would be expected.

The absence of any decrease of polarization with rising temperature and the small difference between the polarizations and the refractions show that the values of the electric moments of the molecules are indistinguishable from zero. The moments are, therefore, regarded as approximately zero and the conclusion is drawn that the bonds of alkyl radicals possess no polarity detectable through electric moments arising from them.

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