TABLE III

TEMPERATURE DEPENDENCE OF THE HYDRATION

	Sucrose hydration			Maltose hydration			Glucose hydration		
	$-\lim_{c \to 0} \Delta/c$	Cc./g.	Mole/OH	$-\lim_{c \to 0} \Delta/c$	Cc./g.	Mole/OH	$-\lim_{c \to 0} \Delta/c$	Cc./g.	Mole/OH
20°	0.15	0.25	0.60	0.17	0.28	0.67	0.25	0.42	0.84
25°	.12	.20	.48	.13	.22	.53	.21	.35	.70
35°	.08	.13	.31	.09	.15	.36	.17	.28	.56
45°	.05	.08	.19	.07	.12	.29	.13	.22	.44
ΔH, kcal./mole		13			12			13	

From Table III, it is found that the hydration of sucrose decreases from 0.25 to 0.08 cc./g. as the temperature rises from 20 to 45°.

Pryor and Roscoe[3] calculated the fractional volume occupied by the solute as a solvated sugar molecule, c_2, from viscosity data. Such values of c_2 were larger than the values of the fractional volume c_1 derived from that of dry sugar. The value of ratio c_2/c_1 for sucrose decreased from 1.23 to 1.06 as the temperature rises from 20 to 70°. This change corresponds to the fact that bound water decreases from 0.15 to 0.04 cc./g. as the temperatures rises from 20 to 70°. In the case of glucose, the results of Roscoe gave the values of hydration decreasing from 0.10 to 0.02 (cc./g.) with the temperature rise from 25 to 50°. Our results differ a little from these values. But considering the fact that different assumptions have been used in these methods, the agreement of the values may be satisfactory.

If we apply the theory of Langmuir's adsorption isotherm[9] in the present case, the enthalpy change of hydration could be obtained by the equation

$$\ln \frac{\theta}{1 - \theta} = \Delta H/RT + \text{const.} \qquad (2)$$

in which

θ = amount of hydration in mole number per OH radical
ΔH = enthalpy difference between the state of hydrated water and non-hydrated one

From those curves, we obtained the values of ΔH given in Table III. These values of ΔH involve several other effects than the hydration: intramolecule structural changes of solute, breaking of the hydrogen bond between water molecules, etc. Therefore, the values of Table III cannot be discussed in more detail, but it may be mentioned that these values are of the correct order of magnitude as the energy of hydrogen bonding in all saccharides examined, and it is evident that hydrogen bonding plays an important role in these changes.

The author wishes to express his thanks to Prof. I. Sano and Assist. Prof. Y. Miyahara for their kind advice and encouragement.

(9) R. H. Fowler, "Statistical Mechanics," Cambridge University Press, 1936, p. 829.

NAGOYA, JAPAN

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Determination of Atomic Polarizations and Dipole Moments for Slightly Polar Liquid Hydrocarbons[1,2]

BY ANTHONY J. PETRO[3] AND CHARLES P. SMYTH

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Dielectric constants, densities and indices of refraction at five wave lengths have been measured for the pure liquids benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, ethylbenzene, styrene and isopropylbenzene at 20, 40 and 60°. The electronic polarizations have been calculated by the Lorentz–Lorenz and Cauchy relationships and the total polarizations by the Clausius–Mosotti equation. The electronic polarizations have been found to be density dependent but a plot of the difference between total and electronic polarizations against the reciprocal of absolute temperature has been found to yield a straight line whose intercept is the atomic polarization and whose slope is proportional to the dipole moment. Values obtained by this method using the Debye equation agree well with those obtained by microwave dielectric constant measurements for all except *o*-xylene and compounds of higher moments. The liquid and vapor dipole moments have been correlated with the asymmetry of the molecules.

The determination of atomic polarization (P_A) for slightly polar compounds has, heretofore, been possible only by methods which are either indirect or difficult to apply experimentally or which give rather uncertain results.[4] Altshuller[5] recently has determined this quantity for several liquid non-polar aromatic hydrocarbons but does not give values for the slightly polar compounds used in his work. It is the purpose of this paper to describe a simple method for measuring P_A for compounds whose dipole moments are less than about 0.5×10^{-18}. Furthermore, the dipole moments may simultaneously be determined with good precision, especially for compounds whose moments are so small that they are not amenable to accurate measurement in the gaseous state or in solution.

Experimental

The aromatic compounds studied were obtained from the Brothers Chemical Company, with the exception of benzene and toluene. The benzene used was the analytical reagent grade product of Merck and Company and the toluene was obtained from the Barrett Division of the Allied Chemical and Dye Corporation. The benzene and *p*-xylene were initially purified by fractional crystallization. *o*-Xylene

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(2) This paper represents a part of the work to be submitted by Mr. A. J. Petro to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Monsanto Fellow in Chemistry, 1956–1957.

(4) A detailed summary of the various methods is given by J. W. Smith, "Electric Dipole Moments," Butterworth's Scientific Publications, London, 1955, Chapter 9.

(5) A. P. Altshuller, *J. Phys. Chem.*, **58**, 392 (1954).

was initially purified by the method of Clarke and Taylor[6] which consisted of the preparation and recrystallization of its sodium sulfonate salt followed by regeneration of the hydrocarbon by steam distillation. With the exception of vinylbenzene (styrene), which was distilled under vacuum, all the compounds were dried over and distilled from sodium hydride or calcium hydride immediately before use. The observed boiling points are listed in Table I together with literature values.

TABLE I

BOILING POINTS OF LIQUID HYDROCARBONS

	B.p., °C. Obsd.	Lit.
Benzene	79.9	80.1
Toluene	110.7–110.8	110.6
o-Xylene	144.4	144.4
m-Xylene	138.4 (747.8 mm.)	139.1
p-Xylene	138.3–138.4	138.4
Ethylbenzene	136.3	136.1
Styrene	44–45 (20 mm.)	48 (20 mm.)
Isopropylbenzene	151.2	152.4

The dielectric constants, ϵ, of the pure liquids were measured at 20, 40 and 60° with an apparatus previously described or referred to.[7] Refractive indices were measured with a Pulfrich refractometer using the sodium-D line and four lines in the mercury vapor spectrum. For measurements at 40 and 60° the index of refraction of the prism at each wave length was determined with distilled water.[8] At these temperatures some scattering of the light was observed but by careful manipulation the critical ray could be sharply defined. When good literature values were not available, densities were determined with a graduated pycnometer,[9] with an accuracy of ±0.002%. The experimental values are listed in Table II.

TABLE II

DENSITIES,[a] DIELECTRIC CONSTANTS[b] AND REFRACTIVE INDICES[c] OF LIQUID HYDROCARBONS

	t, °C.[e]	d	ϵ	n_{6234A}	n_{5893A}	n_{5791A}	n_{5461A}	n_{4359A}
Benzene	20	0.87909[f]	2.2836	1.49814	1.50126	1.50214	1.50530	1.52308
	40	.85769[f]	2.2636	1.48597	1.48871	1.48954	1.49273	1.51020
	60	.83602[f]	2.2436	1.47343	1.47586	1.47688	1.47979	1.49700
Toluene	20	.8669[g]	2.3837	1.49303	1.49575	1.49658	1.49957	1.51666
	40	.8485[g]	2.3390	1.48220	1.48496	1.48579	1.48888	1.50558
	60	.8300[g]	2.2941	1.47157	1.47394	1.47501	1.47779	1.49438
o-Xylene	20	.88001	2.5872	1.50242	1.50540	1.50614	1.50911	1.52613
	40	.86338	2.5315	1.49289	1.49553	1.49641	1.49930	1.51606
	60	.84645	2.4781	1.48297	1.48548	1.48641	1.48926	1.50566
m-Xylene	20	.86470	2.3684	1.49419	1.49717	1.49791	1.50094	1.51769
	40	.84735	2.3268	1.48452	1.48723	1.48800	1.49091	1.50735
	60	.82986	2.2860	1.47446	1.47698	1.47795	1.48073	1.49690
p-Xylene	20	.8611[g]	2.2699	1.49253	1.49537	1.49611	1.49910	1.51581
	40	.8436[g]	2.2368	1.48259	1.48529	1.48622	1.48912	1.50554
	60	.8260[g]	2.2034	1.47265	1.47483	1.47580	1.47877	1.49496
Ethylbenzene	20	.86699	2.4042	1.49286	1.49575	1.49659	1.49938	1.51553
	40	.84949	2.3587	1.48298	1.48563	1.48647	1.48932	1.50530
	60	.83171	2.3136	1.47284	1.47507	1.47604	1.47867	1.49448
Styrene	20	.9063[h]	2.4257	1.54296	1.54678	1.54803	1.55265	1.57917
	40	.8887[h]	2.3884		1.53564	1.53704	1.54141	1.56771
	60	.8721[h]	2.3510		1.52459	1.52598	1.53033	1.55603
Isopropylbenzene	20	.86192	2.3833	1.48858	1.49138	1.49202	1.49482	1.50996
	40	.84501	2.3386	1.47930	1.48166	1.48245	1.48502	1.50016
	60	.82779	2.2958	1.46930	1.47149	1.47236	1.47499	1.48981

[a] ±0.00005. [b] ±0.0002. [c] ±0.00005. [e] ±0.05°. [f] American Petroleum Institute Research Project 44, "Selected Values of Hydrocarbons and Related Compounds." [g] J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Inc. [h] R. H. Boundy and R. F. Boyer (editors), "Styrene: Its Polymers, Copolymers and Derivatives," Reinhold Publ. Corp., New York, N. Y., 1952, p. 55. Measured values: d^{25} 0.9016, d^{40} 0.8885.

The total or molar polarizations, P, were calculated from ϵ and d values by the Clausius–Mosotti equation. Electronic polarizations, P_E, were determined by extrapolating the molar refractions, as calculated from n and d values by the Lorentz–Lorenz equation, to infinite wave length according to the Cauchy dispersion formula. This extrapolation was accomplished by the method of least squares. The resulting polarization values are listed in Table III.

Discussion

It has long been known that non-polar liquids show significant deviations from the Clausius–Mosotti equation for the dependence of the low frequency dielectric constant on density.[10] Similarly, the Lorentz–Lorenz equation has been found to give a molar refraction which varies very slightly with temperature. This fact had led to the empirical equation of Eykman[11] which, however, has not found general use. This discrepancy has been interpreted to be due to fluctuations of configuration and anisotropy of the molecules caused by their translational, rotational and internal motions, which give rise to microscopic changes in molecular polarizability.[12] Consequently, equations have been derived to take this effect into account. The recent work of Brown[13] contains a detailed comparison and evaluation of the various modifications of the Clausius–Mosotti equation. As a result, it is apparent that either P_E or both P_E and P_A must be variable with density. The data listed in Table III show P_E to be temperature or density dependent.

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(6) H. T. Clarke and E. R. Taylor, THIS JOURNAL, **45**, 831 (1923).

(7) A. J. Petro, C. P. Smyth and L. G. S. Brooker, *ibid.*, **78**, 3040 (1956).

(8) "International Critical Tables," Vol. VII, McGraw–Hill Book Co., New York. N. Y., p. 13.

(9) G. R. Robertson, *Ind. Eng. Chem., Anal. Ed.*, **11**, 464 (1939).

(10) S. S. Kurtz, Jr., and A. L. Ward, *J. Franklin Inst.*, **222**, 563 (1936); **224**, 583, 697 (1937).

(11) J. F. Eykman, *Rec. trav. chim.*, **14**, 185 (1895).

(12) F. G. Keyes and J. G. Kirkwood, *Phys. Rev.*, **37**, 202 (1931).

(13) W. F. Brown, Jr., *J. Chem. Phys.*, **18**, 1193, 1200 (1950).

TABLE III

MOLAR AND ELECTRONIC POLARIZATIONS (CC.) OF AROMATIC HYDROCARBONS

	t, °C.	P (±0.01)	P_E (±0.01)	$P - P_E$
Benzene	20	26.62	25.10	1.52
	40	26.69	25.18	1.51
	60	26.75	25.24	1.51
Toluene	20	33.55	31.54	2.01
	40	33.51	31.61	1.90
	60	33.45	31.68	1.77
o-Xylene	20	41.74	34.39	7.35
	40	41.56	34.48	7.08
	60	41.40	34.56	6.84
m-Xylene	20	38.46	34.53	3.93
	40	38.42	34.62	3.80
	60	38.39	34.69	3.70
p-Xylene	20	36.66	34.56	2.10
	40	36.74	34.65	2.09
	60	36.80	34.72	2.08
Ethylbenzene	20	39.04	34.38	4.66
	40	38.96	34.46	4.50
	60	38.87	34.55	4.32
Styrene	20	37.02	34.49	2.53
	40	37.07	34.56	2.51
	60	37.12	34.63	2.49
Isopropylbenzene	20	44.00	38.93	5.07
	40	43.89	39.03	4.86
	60	43.80	39.11	4.69

Furthermore, since, for benzene and *p*-xylene, P varies by the same amount and in the same direction as P_E, it is evident that P_A is constant within the experimental error over the temperature range studied in agreement with the behavior generally observed.[14]

The fact that the molar refraction is a function of density rather than of temperature can be seen by examining the data of Gibson and Kincaid.[15] Their values of the Lorentz–Lorenz specific refraction decrease with increasing pressure and consequently decreasing specific volume at constant temperature, but, at approximately equal specific volumes at different temperatures and pressures, the specific refractions are practically equal, as illustrated below[15]

t, °C.	P (bars)	v (cc.)	Spec. refr.
25	26	1.14186	0.3478
35	154	1.14171	.3478
45	280	1.14158	.3478

In the present work, the change in density is brought about by changing the temperature, but the latter variation has no direct effect on the refraction, at least in the cases of benzene,[15] carbon dioxide and carbon disulfide.[13]

The attempt was made to utilize this effect to determine the dipole moment and atomic polarization for a pure liquid. If the Debye equation is written

$$P - P_E = P_A + \frac{4\pi N\mu^2}{9kT} \qquad (1)$$

then a plot of $(P - P_E)$ *vs.* $1/T$ might yield μ from the slope and P_A from the intercept. The values determined from equation 1 are listed in Table IV under P_{A_1} and μ_1. In order to minimize errors all calculations were made by the method of least squares. Also included in Table IV under P_{A_2} and μ_2 are those values obtained by the present authors by determining the high frequency dielectric constant from measurements at microwave frequencies, using the equation

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2}\frac{M}{d} = P_E + P_A \qquad (2)$$

to calculate P_A and the Onsager equation[16] to calculate μ. The agreement between the two methods is excellent for all except *o*-xylene. Similar measurements were carried out for a group of substituted pyridines ($\mu \cong 2 \times 10^{-18}$). The results however showed that the P *vs.* $1/T$ curve was far from linear for these compounds. It is interesting to note that, for *o*-xylene, although the plotting method fails to yield good results, when μ is calculated at each temperature using the Debye equation 1 and equation 2, the result is 0.51×10^{-18} in excellent agreement with the value calculated by the Onsager equation. The failure of the plotting method for *o*-xylene and compounds of higher moment probably is due to too high an internal field correction.

TABLE IV

DIPOLE MOMENTS[a] (× 10^{18}) AND ATOMIC POLARIZATIONS[b] (CC.) OF LIQUID HYDROCARBONS

	μ_1	μ_2	μgas	P_{A_1}	P_{A_2}
Benzene	0	..	0[c]	1.50	..
Toluene	0.31	0.31	0.37[c]	1.77	1.75
o-Xylene	.45	.52	.62[d]	3.11	1.98
m-Xylene	.30	.31	(.37)[e]	2.01	1.96
p-Xylene	.02	..	0[d]	1.95	..
Ethylbenzene	.37	.37	.58[f]	1.84	1.84
Styrene	.13	.13	<.2[g]	2.20	2.20
Isopropylbenzene	.39	.39	.65[f]	1.90	1.91

[a] ±0.01. [b] ±0.02. [c] K. B. McAlpine and C. P. Smyth, THIS JOURNAL, **55**, 453 (1933). [d] E. C. Hurdis and C. P. Smyth, *ibid.*, **64**, 2212 (1942). [e] Benzene solution; L. Tiganik, *Z. physik. Chem.*, **13B**, 425 (1931). [f] J. W. Baker and L. G. Groves, *J. Chem. Soc.*, 1144 (1939). [g] N. B. Hannay and C. P. Smyth, THIS JOURNAL, **68**, 244 (1946).

The moments listed in Table IV are in agreement with those of Altshuler[5] and are also internally consistent. The values for toluene and *m*-xylene are identical, as expected from purely geometrical considerations. From this value, the moment of *o*-xylene is calculated to be 0.54×10^{-18} in good agreement with the observed μ_2 value. The non-zero value of μ for *p*-xylene is an indication of the uncertainty of our results.

The dipole moments measured in the vapor phase are also listed in Table IV. The attempt was made to correlate the differences between μ_{liq} and μ_{gas} with the molecular asymmetry. Buckley and Maryott[17] have modified the Onsager equation to take into account the eccentricity of the molecule. These authors derived the expression

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(14) C. P. Smyth, "Dielectric Behavior and Structure, "McGraw-Hill Book Co., New York, N. Y., 1955, p. 417–422.

(15) R. E. Gibson and J. F. Kincaid, THIS JOURNAL, **60**, 511 (1938).

(16) L. Onsager, *ibid.*, **58**, 1486 (1936).

(17) F. Buckley and A. A. Maryott, *J. Research Natl. Bur. Standards*, **53**, 229 (1954).

$$\frac{(\epsilon_0 - 1)(2\epsilon_0 + 1)}{9\epsilon_0} V = \frac{4\pi N}{3}\left[\frac{\alpha k_\alpha k_c}{1 - \frac{\alpha}{v} g k_\mathrm{R}} + \frac{u_0^2 k_c}{3kT\left(1 - \frac{\alpha}{v} g k_\mathrm{R}\right)^2}\right]$$

where V is the molar volume, N the Avogadro number and k_α, k_c and k_R are functions of the dielectric constant, ϵ_0, and the eccentricity of the molecule. The terms α, the polarizability, α/v, where v is the molecular volume, and g are defined by the relationships

$$\alpha = \frac{3}{4\pi N}(P_\mathrm{E} + P_\mathrm{A})$$

$$v = \frac{V}{N}$$

$$g = \frac{4\pi}{3}\frac{(2\epsilon_0 - 2)}{(2\epsilon_0 + 1)}$$

The more accurate $(P_\mathrm{E} + P_\mathrm{A})$ has been used here instead of R_D which was used by Buckley and Maryott. The approximation that the product $k_\alpha\, k_c = 1$ has also been used in calculating μ_0. Values of eccentricity were determined from axial ratios which were measured from Stuart–Briegleb models. In Table V are listed the quantities $G = \mu_\mathrm{liq}/\mu_0$ and $G_0 = \mu_\mathrm{liq}/\mu_\mathrm{gas}$ and the axial ratios. It is seen that the Buckley–Maryott treatment yields results in fairly good agreement with the observed. It is interesting to note that the axial ratios are also in good agreement with the G_0 values. This empirical correlation is striking but undoubtedly fortuitous.

TABLE V

CORRELATION OF LIQUID AND VAPOR DIPOLE MOMENTS WITH MOLECULAR ECCENTRICITY

	Axial ratio	G	G_0
Toluene	0.79	0.74	0.84
o-Xylene	.89	.91	.84
m-Xylene	.79	(.74)	(.84)
Ethylbenzene	.66	.62	.64
Isopropylbenzene	.66	.61	.60

The dipole moment measured for styrene is identical to that of von Hippel and Wesson,[18] who used one determination of dielectric constant and loss in the microwave frequency region and assumed Debye behavior to calculate the moment. Otto and Wenzke[19] measured a value of 0.37×10^{-18} for the liquid but the styrene used appears to be impure on the basis of physical constants. Since styrene is an alternant hydrocarbon, a moment arising from a charge separation would not be expected. The value of 0.13×10^{-18} is, therefore, not an unreasonable one.

The data in Table IV also indicate that the increment in P_A for the substitution of each CH_3 group into the side chain substituted on the benzene ring is about 0.08 cc., in good agreement with Audsley and Goss[20] and with Dornte and Smyth[21] who indirectly obtained the same value for normal paraffins. Also, the increment in P_A for substitution of each CH_3 group on the benzene ring is about 0.24 cc. It appears from the P_A values of the xylenes that the dependence of P_A on the location of the methyl groups on the ring is very small. The higher value of P_A for styrene is consistent with the presence of the additional unsaturation.

The advantages of the method described above over previous methods are that the required density, dielectric constant and refractive index data are easily obtainable within a short time and with much greater precision on the liquid than on the gas. This latter fact greatly reduces the possible uncertainty involved in the long extrapolation. More important, liquids of very small dipole moment can be measured without guessing the magnitude of the induced polarization, which is a necessary procedure in solution measurements. Unfortunately, the method is limited to those compounds which exist as liquids at temperatures where the required data can be obtained.

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[18] A. von Hippel and L. G. Wesson, *Ind. Eng. Chem.*, **38**, 1121 (1946).

[19] M. M. Otto and H. H. Wenzke, THIS JOURNAL, **57**, 294 (1935).

[20] A. Audsley and F. R. Goss, *J. Chem. Soc.*, 2989 (1950).

[21] R. W. Dornte and C. P. Smyth, THIS JOURNAL, **52**, 3546 (1930).