[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

THE DIELECTRIC CONSTANTS OF BINARY MIXTURES. X. THE ELECTRIC MOMENTS OF SIMPLE DERIVATIVES OF CYCLOHEXANE AND OF DIOXAN

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In the previous papers of this series there has been discussed the relation between electric moment data and the structure of benzene and a number of its derivatives. Another article[1] has been devoted to a study of the structure of derivatives of methane and ethane. It was thought that the extension of this type of study to cyclohexane and its derivatives would lead to a number of interesting conclusions, particularly because considerable information is now available concerning the structures of the mono- and di-substitution products of benzene.

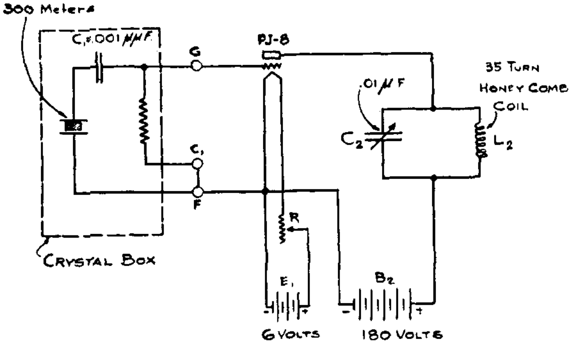

Fig. 1.—Crystal oscillator.

Experimental Method

The method of determining the electric moment of a solute molecule from dielectric constant and density data of a suitable binary mixture has been completely described in a number of places[2,3] and will not be repeated here. The measurement of the dielectric constants was made using an apparatus which was improved in several details over that previously described. A quartz crystal controlled circuit (frequency, 10^6 cycles) was used as the standard oscillator and a resistance-coupled three-tube detector and amplifier circuit replaced the transformer-coupled arrangement of the earlier investigations. The actual method of measurement of the dielectric constant of a solution was not changed from that which

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[1] Williams, *Z. physik. Chem.*, **138A**, 75 (1928).

[2] (a) Williams and Krchma, THIS JOURNAL, **49**, 1676 (1927); (b) Williams and Weissberger, *ibid.*, **50**, 2332 (1928).

[3] Debye, "Polar Molecules," The Chemical Catalog Co., New York, **1929**, *et al.*

has already been described. A diagram of the circuits used is given in Figs. 1 to 3.

Results

All chemicals used were carefully purified and their boilng points checked with those given in the "International Critical Tables." All dielectric constant and density measurements were made at 25°. The frequency 10^6 cycles was used for the dielectric constant determinations. The dielectric constant of benzene under these conditions was assumed to be 2.280.

The dielectric constant and density data for the various binary mixtures are given in Table I.

TABLE I

DIELECTRIC CONSTANT AND DENSITY DATA FOR MIXTURES

The symbols used have the following significance: f_1 is mole fraction of the solvent, in this case benzene; d_4^{25} is density of the solution; ϵ is dielectric constant of the solution; $P_{1,2}$ is molar polarization of the solution $= (\epsilon - 1)/(\epsilon + 2) \times [(f_1M_1 + f_2M_2)/d] = f_1P_1 + f_2P_2$; P_2 is molar polarization of the solute molecule.

f_1 (Benzene)	d_4^{25}	ϵ	$P_{1,2}$	P_2
		Cyclohexane		
100.00	0.8731	2.280	26.77	28
99.18	.8722	2.280	26.80	30
97.58	.8704	2.276	26.82	28
96.04	.8686	2.270	26.83	28
		Chlorocyclohexane		
100.00	0.8731	2.280	26.77	143
99.27	.8742	2.337	27.63	143
97.85	.8764	2.440	29.23	141
96.47	.8789	2.543	30.73	140
		Bromocyclohexane		
100.00	0.8731	2.280	26.77	150
98.89	.8798	2.363	28.10	149
97.48	.8884	2.489	29.96	153
96.79	.8965	2.567	30.94	156
		Cyclohexanone		
100.00	0.8731	2.280	26.77	202
99.15	.8741	2.385	28.29	205
97.40	.8761	2.605	31.27	200
		Methylcyclohexane		
100.00	0.8731	2.280	26.77	33
99.32	.8722	2.279	26.80	33
97.96	.8702	2.276	26.92	34
96.01	.8673	2.270	27.06	34
		Cyclohexanol[a]		
100.00	0.8735	2.276	26.66	105
99.64	.8737	2.292	26.93	103
99.12	.8740	2.318	27.32	101
98.25	.8745	2.357	27.93	99

[a] Data of Mr. J. M. Fogelberg.

TABLE I (*Concluded*)

f_1 (Benzene)	d_4^{25}	ϵ	$P_{1,2}$	P_2
1,4 Dioxan				
100.00	0.8731	2.280	26.77	26
97.90	.8762	2.283	26.79	28
96.00	.8793	2.290	26.84	29
94.10	.8824	2.300	26.96	30
2-Methylcyclohexanol				
100.00	0.8731	2.280	26.77	113
98.44	.8744	2.360	28.06	110
97.20	.8757	2.437	29.26	114
95.95	.8770	2.504	30.29	114
3-Methylcyclohexanol				
100.00	0.8731	2.280	26.77	108
98.50	.8743	2.356	27.99	108
97.23	.8755	2.414	28.91	106
95.95	.8768	2.496	30.19	110
4-Methylcyclohexanol				
100.00	0.8731	2.280	26.77	106
98.42	.8743	2.353	27.96	103
97.21	.8755	2.416	29.01	107
95.89	.8768	2.487	30.07	107
Cyclohexane carboxylic Acid				
100.00	0.8731	2.280	26.77	49
98.57	.8763	2.292	27.07	48
97.17	.8794	2.305	27.41	49
95.81	.8827	2.318	27.73	49

From the molar polarization of the solute molecules their electric moments have been calculated, making the assumption that that part of

TABLE II

ELECTRIC MOMENT DATA FOR SOLUTE MOLECULES

Molecule	P_2	P_2''	P_2'	$\mu \times 10^{18}$ e.s.u.
Cyclohexane	28	27.7	*ca* 0.3	0
Methylcyclohexane	33	32.7	*ca* 0.3	0
Chlorocyclohexane	143	33	110	2.3
Bromocyclohexane	150	36	114	2.3
Cyclohexanone	202	28	174	2.8
Cyclohexanol	105	30	75	1.9
1,4-Dioxan	26	22	4	0.4
2-Methylcyclohexanol	113	34	79	1.95
3-Methylcyclohexanol	108	34	74	1.9
4-Methylcyclohexanol	106	34	72	1.9
Cyclohexane carboxylic acid	49	33	16	0.9

In this table, P_2 is molar polarization of the solute molecule; P_2'' is polarization due to deformation of the molecule; P_2' is polarization due to orientation of the molecule; μ is electric moment of the molecule.

the total polarization which is due to the deformation of the molecule is given by the Lorentz–Lorenz formula, using the refractive index for the "D" line. The results of these calculations are believed to be correct to within 0.1 × 10^{-18} e. s. u., with the possible exception of dioxan, whose moment cannot be distinguished from zero by the method used. These data are presented in Table II.

Since the dielectric constants of but few of these derivatives of cyclohexane are to be found in the literature, measurements were made upon certain of the more common ones. The measurements were made in the manner described in the earlier papers of this series, using the apparatus which has just been described. It is evident that this method neglects the effect of any change in the absorption of energy in the liquid dielectric as the position of the rotor plates of the measuring condenser is changed. When substances like benzene and dilute solutions of polar molecules in benzene are studied, the absorption of energy is so low that corrections for this effect are not necessary. This is not the case, however, when appreciable and different amounts of energy are absorbed, and for precision measurements not only capacity changes but also resistance changes should be accounted for. For this reason the data, presented in Table III, are recorded to the nearest tenth of a unit only, since it was not possible to make the proper corrections. The results for the last four substances given are certainly the only ones which could be at all affected by this difficulty, and even in these cases the error introduced must be small.

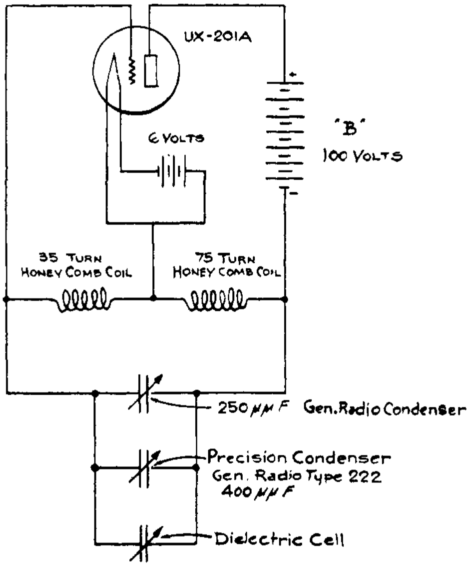

Fig. 2.—Variable oscillator.

TABLE III

DIELECTRIC CONSTANT DATA FOR CYCLOHEXANE AND ITS DERIVATIVES

Temperature, 25°. Frequency, 10^6 cycles

Molecule	Dielectric constant	Molecule	Dielectric constant
Cyclohexane	2.0	Bromocyclohexane	7.9
Methylcyclohexane	2.1	Cyclohexanol	15.0
1,4-Dioxan	2.2	Cyclohexanone	18.1
Chlorocyclohexane	7.6		

Discussion

There are now sufficient electric moment data for various mono-substitution products of cyclohexane, methane and benzene to be able to compare the effect produced by substituting a simple atom or group of atoms into these various parent substances. The data are collected in Table IV, in which those figures marked by the asterisk have been taken from other observers.[4]

Table IV

Data for Substitution Products of Simple Hydrocarbons

Atom or radical	Electric Moment × 10^{18} For $C_6H_{11}\alpha$	For $C_6H_5\alpha$	For $CH_3\alpha$	Atom or radical	Electric Moment × 10^{18} For $C_6H_{11}\alpha$	For $C_6H_5\alpha$	For $CH_3\alpha$
H	0	0	0*	OH	1.9	1.65	1.65
Cl	2.3	1.5	2.0*	NO_2		3.9	3.1*
Br	2.3	1.5	1.9*	CH_3	0	0.4	0*
I		1.3	1.6	NH_2		1.5	1.2*
CN		3.85	3.4				

As one would expect, cyclohexane itself is a symmetrical molecule. When a CH_3 group is substituted into it, an electrically symmetrical molecule is again formed, since methylcyclohexane has a zero moment as well. Thus cyclohexane behaves like methane and not like benzene on the substitution of a CH_3 group. Toluene is a slightly polar substance. Furthermore, Raman spectra for benzene and for toluene indicate distinct differences in energy levels which are not found in methane hydrocarbons and presumably will not be found in cyclohexane hydrocarbons,[5] so that

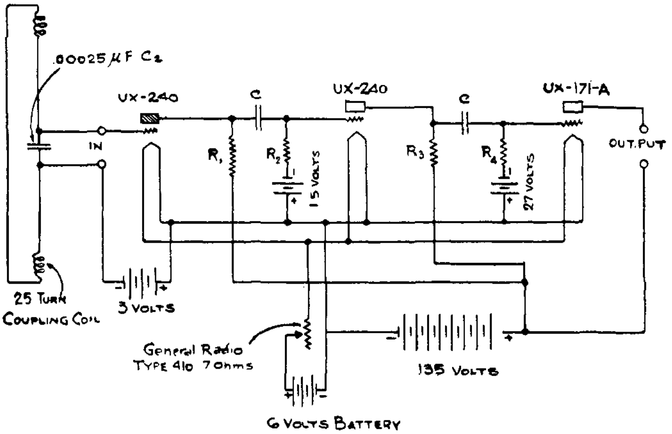

Fig. 3.—Detector-amplifier. CF 0.01μμF.; R_2F 5 megohms; R_1 = R_3F 0.25 megohms; R_4F 5 megohms.

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[4] Debye, "Polare Molekuln," Table of Dipole Moments, Hirzel, Leipzig, **1929**.

[5] Kohlrausch and Dadieu, *Physik. Z.*, **30**, 385 (1929); Reynolds and Williams, This Journal, article submitted March, 1930.

these two types of study lead to similar conclusions involving two different carbon to carbon linkages.

The electric moments for chlorocyclohexane and bromocyclohexane are practically identical. This might have been predicted since the corresponding derivatives of methane and of benzene, respectively, also have like values. The moment produced in the cyclohexane derivatives is distinctly higher than that of the other compounds in question. Also, the substitution of an hydroxyl group in cyclohexane produces a more polar molecule than the substitution of the same group into benzene or methane. This appears to be a matter of internal compensation of charges about which little is known in a quantitative way at present.

The data for cyclohexane carboxylic acid are to be compared with those previously reported[6] for benzoic acid. In each case the molar polarization of the solute molecule is constant over a considerable range of concentration. This is a surprising result, because, at least for benzoic acid and presumably for cyclohexane carboxylic acid as well, the molecular weight of the solute in benzene solution increases as its concentration is increased. In other words, the degree of association of the solute is increasing with increasing concentration and, therefore, according to the explanation given this phenomenon by Debye,[3] the molar polarization of the dissolved molecule should either increase or decrease, the latter being more probable. The same reservation must be made for the value of the electric moment reported for cyclohexane carboxylic acid as was made for benzoic acid, namely, that it is difficult to state exactly what the effect of this association will be upon the result. The moment reported is to be considered of the right order of magnitude only. It is possible that measurements over a range of temperature would be of material assistance in assigning more definite values for the electric moments of these two compounds.

The data for the methylcyclohexanols are of interest in connection with the data for the cresols.[7] For the latter it will be recalled that each had a smaller moment than phenol, and that the moments for the meta and para compounds were practically identical. The electric moments of the three methylcyclohexanols are in every case of identical magnitude with that of cyclohexanol itself and are all three practically identical. The fact that all four molecules have nearly identical moments is not surprising. The moment is characteristic of the OH group alone and is quite independent of the presence of the CH_3 group. This result was to have been expected from the zero moment found for methylcyclohexane. It is also true that these substances, bought under the names used in the tables from the Eastman Kodak Co., may be mixtures of isomers; in that event the electric moments reported are average values for equilibrium

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[6] Williams and Allgeier, THIS JOURNAL, **49**, 2416 (1927).

[7] Williams, *Physik. Z.*, **29**, 683 (1928).

mixtures. Because of the possibility of isomerism it is evident that any extension of dipole moment studies to disubstituted cyclohexanes will be considerably more difficult and involved than the corresponding study of benzene derivatives has been. Nevertheless it should be an interesting problem.

There are included in Tables I and II the results of measurements for solutions of 1,4-dioxan in benzene. Dioxan is found to have an electric moment which can differ but slightly, if at all, from zero ($\mu = 0.4 \times 10^{-18}$ e. s. u.) in spite of the fact that there must be two very active parts in the molecule. This interesting chemical, though not classed as a derivative of cyclohexane, has a ring structure and has certain properties in common with cyclohexanol and cyclohexanone. Since it is such an unusual solvent and at the same time a molecule of extremely low polarity, it was thought that it might serve as as uitable solvent for the determination of the electric moments of substances insoluble in the usual nonpolar solvents. This idea will form the basis of the next article of this series.

Summary

1. Dielectric constant and density data at 25° have been obtained for dilute benzene solutions of cyclohexane, chlorocyclohexane, bromocyclohexane, cyclohexanone, methylcyclohexane, cyclohexanol, 1,4-dioxan, 2-methylcyclohexanol, 3-methylcyclohexanol, 4-methylcyclohexanol and cyclohexane carboxylic acid. The electric moments of the solute molecules have been calculated.

2. Certain improvements, shown only by diagram, have been made in the apparatus used to measure the dielectric constants.

3. The electric moment data for the various derivatives of cyclohexane have been compared with those for the corresponding derivatives of benzene and methane.

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