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# THE DIELECTRIC CONSTANTS OF BINARY MIXTURES. XI. THE USE OF DIOXAN AS A SOLVENT FOR ELECTRIC MOMENT STUDIES

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There are at present two methods by which the electric moment of a molecule may be determined, as follows: (1) from the temperature coefficient of the dielectric constant of a gas or vapor;[1] (2) from dielectric constant and density data for suitable binary mixtures.

The previous articles of this series have utilized the second of these methods, for while it is perhaps not as sound theoretically as the first one, it is easier from an experimental viewpoint and does give a result which is in good (though not exact) agreement with that of the first method. The latter statement has now been amply verified. It has been the purpose of these articles to show the application of a new physical method to the study of the structure of molecules—an important chemical problem.

Both methods have difficulties inherent in them. For example, the electric moments of a number of organic molecules may never be determined by the first method because these substances are unstable in the vapor state. The second method is not as yet a general one because for it there are required "suitable" binary mixtures. A suitable binary mixture is defined as one in which one of the components, the solvent, is non-polar, that is, its electric moment is zero. Benzene, carbon tetrachloride, carbon bisulfide and hexane are liquids having no moment and considered to be suitable solvents for electric moment determinations of this sort. Unless other solvents can be found the second method will then be applicable only to those substances which can be dissolved in these solvents to the extent of something like 1%, using the best apparatus now available for the dielectric constant and density determinations. Measurements have been made for substances having lower solubilities, but the results cannot be considered to be entirely dependable. Thus the electric moment of the water molecule has been calculated from dielectric constant and density data for a saturated solution of water in benzene,[2] but it can only be claimed that the result is of the right order of magnitude.

Several recent articles have discussed the solvent properties of 1,4-dioxan.[3,4] It is found to be an excellent solvent for a large number of

[1] Dielectric constant measurements on gases and vapors at a single temperature have also been utilized for this purpose.

[2] Williams, *Physik. Z.*, **29**, 204 (1928).

[3] Anschütz and Broeker, *Ber.*, **59B**, 2844 (1926).

[4] Reid and Hofmann, *Ind. Eng. Chem.*, **21**, 695 (1929).

substances, inorganic as well as organic. Its electric moment, reported in the previous article of this series,[5] is not greater than $\mu = 0.4 \times 10^{-18}$ e. s. u. This value is so small that it is indistinguishable from zero by the method used; therefore it seemed possible that dioxan might act as a non-polar solvent, in spite of the fact that it is a molecule containing two very active groups. Dielectric constant and density data at 25° were obtained for dilute solutions of chlorobenzene, water, chlorocyclohexane and *o*-diethyl phthalate in 1,4-dioxan, and the molar polarizations of the respective solute molecules were calculated, making the assumption that the polarization due to the solvent dioxan was always exactly proportional to its mole fraction in the solution. The electric moments were calculated from the molar polarizations in the usual manner. These four substances were chosen at random to represent different types of molecules. In the interest of a saving of space the dielectric constant and density data for the four mixtures have not been included. The results of the calculations of the electric moments of the solute molecules are presented in Table I. The symbols used have been defined completely in the previous article.[5]

Table I

Electric Moment Data for Solute Molecules

| Molecule | $P_2$ | $P_2''$ | $P_2'$ | $\mu \times 10^{18}$ e. s. u. |
|---|---|---|---|---|
| Chlorobenzene | 80 | 31 | 49 | 1.5 |
| Water | 82 | 4 | 78 | 1.9 |
| Chlorocyclohexane | 146 | 33 | 113 | 2.3 |
| *o*-Diethyl phthalate | 226 | 60 | 166 | 2.8 |

Electric moment data for chlorobenzene, water and chlorocyclohexane are available in the literature. The electric moment of *o*-diethyl phthalate was determined from dielectric constant and density data (Table II) for this substance in dilute benzene solution.

Table II

Dielectric Constant and Density Data for Binary Mixture Benzene–*o*-Diethyl Phthalate

| $f_1$ (Benzene) | $\epsilon$ | $d_4^{25}$ | $P_{1,2}$ | $P_2$ |
|---|---|---|---|---|
| 100.00 | 2.280 | 0.8731 | 26.77 | 205 |
| 99.64 | 2.316 | .8756 | 27.37 | 202 |
| 99.29 | 2.360 | .8782 | 28.10 | 209 |

Finally, there is given in Table III the comparison of the polarization and electric moment data for the four solute molecules obtained from benzene solution and from dioxan solution.

The only conclusion to be drawn from this table is that dioxan is just as good a solvent as benzene for determinations of the electric moments of these particular molecules. For chlorobenzene and chlorocyclohexane

[5] Williams, This Journal, **52**, 1831 (1930).

TABLE III

COMPARISON OF DATA USING DIOXAN AND BENZENE AS SOLVENTS

| Molecule | Solvent | $P_2$ | $P_2'$ | $\mu \times 10^{18}$ |
|---|---|---|---|---|
| 1 Chlorobenzene | $C_6H_6$ | 82 | 51 | 1.5 |
| | $C_4H_8O_2$ | 80 | 49 | 1.5 |
| 2 Water | $C_6H_6$ | 64 | 60 | 1.7[2] |
| | $C_4H_8O_2$ | 82 | 78 | 1.9 |

Electric moment of water, calculated from temperature coefficient of dielectric constant of water vapor = 1.85–1.87.[6]

| Molecule | Solvent | $P_2$ | $P_2'$ | $\mu \times 10^{18}$ |
|---|---|---|---|---|
| 3 Chlorocyclohexane | $C_6H_6$ | 143 | 110 | 2.3 |
| | $C_4H_8O_2$ | 146 | 113 | 2.3 |
| 4 *o*-Diethyl phthalate | $C_6H_6$ | 205 | 145 | 2.7 |
| | $C_4H_8O_2$ | 226 | 166 | 2.8 |

the results are identical, within the limits of experimental error. Dioxan would appear to be the more desirable solvent for the determination of the electric moment of the water molecule, since the value obtained using it, $\mu = 1.9 \times 10^{-18}$ e. s. u., is identical, to two significant figures, with the commonly accepted value obtained from the temperature coefficient of the dielectric constant of the vapor. The molar polarization value for *o*-diethyl phthalate obtained from the dioxan solution is somewhat higher than the corresponding value obtained from the measurements in benzene solution. Indeed, there is good reason to believe that in a number of cases the resulting molar polarization obtained in dioxan solution will be somewhat higher than they should be. Since dioxan contains two very active groups in the molecule, one might expect segregation and orientation effects upon solute molecules which happen to be within a certain distance of these more active centers.[7] These orientation effects would result in an additional polarization contributing to the total polarization. In this case the assumption could hardly be made that the polarization due to the dioxan (as solvent) is always exactly proportional to its mole fraction in solution.

Furthermore, in spite of the fact that it is a stable substance it does form addition compounds with both organic and inorganic substances in solution. It is evident in the event of a compound formation between solvent and solute that the dielectric constant and density measurements would be of little significance.

[6] Jona, *Physik. Z.*, **20**, 14 (1919); Sänger, in Debye, "Leipzig Lectures," S. Hirzel, Leipzig, **1929**.

[7] These segregation and orientation effects are important not only in connection with measurements of molar polarization but also in connection with numerous chemical phenomena. For example, they will undoubtedly have to be considered in the study of solubility relationships and in the study of reactions in solution. These effects, now the subject of further investigation by us, have been defined by Langmuir [*Chem. Rev.*, **6**, 451 (1929)].

It is not claimed as a result of this table that dioxan is a suitable solvent for the determination of the electric moment of any dissolved molecule in the same sense that either benzene or carbon tetrachloride is. However, it does appear possible that dioxan may be used to determine at least the correct order of magnitude of the electric moment of molecules which are difficultly soluble in the recognized non-polar solvents. For example, if the electric moment of the water molecule could not have been determined by studying the temperature coefficient of the dielectric constant of its vapor, the value obtained from the dioxan solution would have indicated that the value obtained from the single solution of water in benzene could not be greatly in error. Indeed, it would be desirable to make comparison measurements in some solvent like dioxan in every case where the solute molecules are so difficultly soluble that measurements for only one (very dilute) solution can be made.

Another use of dioxan suggests itself. In a practical way it should be a suitable solvent in which to study the electrical properties of cellulose derivatives, gums, resins and other more complicated organic compounds, the idea being that certain information concerning the sizes and shapes of the various substances could be made available.

## Summary

1. Dielectric constant and density data have been obtained for dioxan solutions of chlorobenzene, water, chlorocyclohexane and *o*-diethyl phthalate and for benzene solutions of *o*-diethyl phthalate.

2. The electric moments of the solute molecules calculated from the data in dioxan solution are compared with those obtained using the usual non-polar solvents, and found to be in good agreement.

3. It is suggested that while dioxan is probably not a suitable solvent for the determination of the electric moment of any dissolved molecule, it does offer interesting and important possibilities in cases where the usual solvents cannot be used.

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