tion of composition, without accompanying disturbances in the intramolecular electronic groupings. Under these conditions, no deviation of molecular Verdet constants with composition is to be expected, but such properties as density and viscosity may show maxima or minima in their composition curves. These latter deviations may be interpreted as solely due to loose dipole attractions.

In the case of the acetic acid-water system, magneto-optic rotation measurements indicate that, if intramolecular changes do, in fact, occur, they are too feeble to affect the electronics of the system appreciably. Certainly, they are not of the same order of magnitude, at least, as the changes produced in the H_2SO_4–H_2O mixtures. Consequently, corresponding differences should then be expected in the type of solvation or complex formation in the two systems.

It must be admitted that it is not readily possible to determine whether or not this difference is one of degree or of kind. It is interesting, nevertheless, that two methods of observing the influence of external fields on the internal electronic configurations lead to the same results.

Summary

The magneto-optic rotations of the acetic, monochloroacetic, dichloroacetic and trichloroacetic acids in aqueous solutions were determined. The mole per cent., density, Verdet constant, molecular Verdet constant, refractive index and molecular refractivity were determined and tabulated for each aqueous solution. For comparison, non-polar solvents such as carbon tetrachloride and carbon disulfide have been included in the tabulation.

Curves were plotted for the mole per cent. against the molecular Verdet constant. An explanation of the resulting straight line graph obtained was given as being due to the absence of change in the intramolecular electronic configuration. The association and other dipole effect exhibited by the acetic acid does not alter this structure. The possible application of this effect to the study of solvate formation is suggested.

BROOKLYN, N. Y. RECEIVED JULY 30, 1942

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Magneto-optic Rotation. V. Selenium Oxychloride in Aqueous Solutions

BY CHAS. E. WARING, SAMUEL STEINGISER AND HERBERT H. HYMAN[1]

From a study of the viscosity and molar volume changes of selenium oxychloride in water, Smith and Jackson[2] have given evidence for the formation of a dihydrate, $SeOCl_2 \cdot 2H_2O$. In order to account for this solvated complex they proposed that certain structural changes occurred in solution. Since it has been established that the magneto-optic method is useful in detecting changes in intramolecular structure, it was thought that an investigation of the $SeOCl_2$–H_2O system by this method might tend to confirm the type of structural changes proposed by Smith and his coworkers. It was with this purpose, then, that the present study was undertaken.

Experimental

Materials and Apparatus.—The selenium oxychloride was carefully prepared by G. B. L. Smith, *et al.*, and is the best available to date. The solutions were made up by weight and used immediately, eliminating any possibility of decomposition. An important improvement has been made in the apparatus as described in a previous paper.[3] The densities were measured with extreme precision by Smith, *et al.*

Measurements.—The primary standard and the technique of measurements were the same as before.[3] The improved apparatus has resulted in some improved precision, but not enough to permit an additional significant figure. Table I is a summary of the experimental measurements. The molecular Verdet constants as given in the

TABLE I

Mole % $SeOCl_2$	Molecular weight, M	Density, d_{25}	Verdet constant V_{25}	Molecular Verdet constant $V = VM/D$
0.00	18.02	0.9969	0.01305	0.2359
8.45	30.51	1.4770	.02755	0.5691
14.76	39.84	1.7015	.03532	0.8270
28.50	60.16	2.0120	.04575	1.3680
34.05	68.36	2.0900	.04879	1.596
42.40	80.71	2.1775	.05003	1.854
57.09	102.43	2.2785	.05267	2.368
67.75	118.20	2.3354	.05417	2.741
100.00	165.87	2.4208	.05270	3.611

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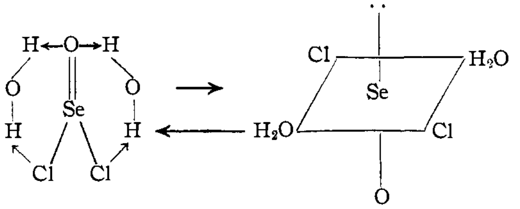
(1) Present address: C. W. S., Huntsville Arsenal, Huntsville, Ala

(2) G. B. L. Smith and J. Jackson, private communication.

(3) Waring, Steingiser and Hyman, THIS JOURNAL, **65**, 1066 (1943).

table are plotted against mole per cent. composition in Fig. 1. Due to experimental difficulties, the upper portion of the $SeOCl_2$ curve cannot be measured with the precision we wished and therefore no attempt has been made to draw the curve at these higher concentrations.

Discussion.—Examination of Fig. 1, where mole per cent. $SeOCl_2$ is plotted against the molecular Verdet constant, reveals that a definite discontinuity occurs at 33.3 mole per cent. $SeOCl_2$. This corresponds perfectly to the formation of the solvate $SeOCl_2 \cdot 2H_2O$, and at the same time indicates an accompanying alteration of the internal bond configuration. Not only does this confirm the work of Smith and Jackson but it also lends positive support to their hypothesis advanced for the structure of the dihydrate. For the structure of $SeOCl_2 \cdot 2H_2O$, they propose two forms



I II

If one considers the possibility of a resonance existing between the above two forms in solution, then a plausible explanation can be offered to account for the observed discontinuity at 33.3% $SeOCl_2$ in Fig. 1. At this concentration, a great predominance of structure I over structure II would be expected. It is evident that the former completely inhibits the free movement of the water molecules in response to a magnetic field and provides a new set of internal bond configurations. These, in turn, would markedly affect the rotation. Structure II, on the other hand, is similar to a simple association through residual valences and no new bonds are involved. Such an association would not be expected to produce an effect upon the rotation on the basis of our previous theory.[3]

This shift from one resonating form to another in solution due to concentration changes has been established previously by the magneto-optic method. A similar state of affairs was found to exist for carbon disulfide in various substituted benzene solutions.[4] In this latter case, no other physical evidence such as density, viscosity, refractive index, etc., indicated the existence either of compound formation or solvation. As a result,

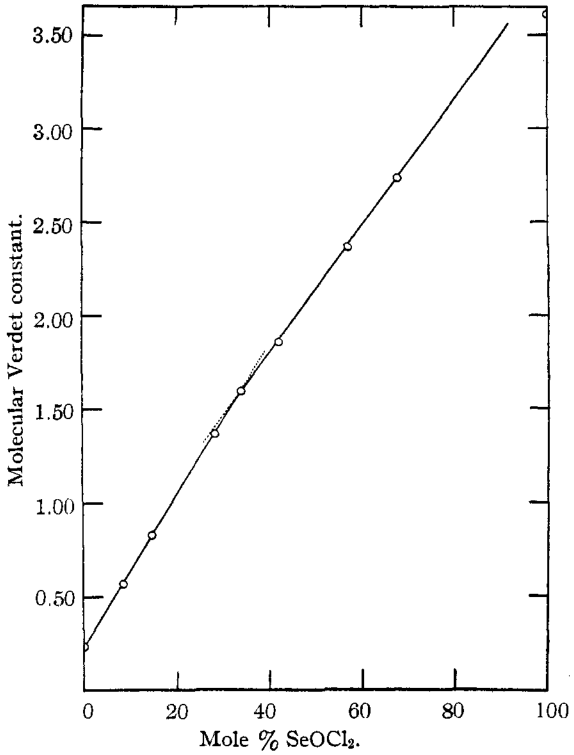


Fig. 1.

the discontinuities in the molecular Verdet constant–composition curves for carbon disulfide were attributed simply to shifts from one resonating form of this molecule to another, without any accompanying solvate formation.

As we have previously pointed out, systems exist where such properties as density, viscosity, etc., *vs.* composition exhibit the type of curves to which solvation is normally attributed. The corresponding molecular Verdet constant plots, however, indicate no such abnormalities. In these systems we believe that if actual compounds are indeed formed, they are merely loose association complexes resulting from residual valence forces. On the other hand, when both the ordinary physical properties and the molecular rotation indicate solvation in solution, it may be taken as evidence that these structures are the result of a definite change in the internal bond configurations. We feel, therefore, that our present results offer a good physical confirmation for a structure of $SeOCl_2 \cdot 2H_2O$ similar to I, namely, a structure which is the result of an intra-molecular change.

A further proof of the presence of hydrogen bonding in inorganic oxychlorides has been advanced by Audrieth and Steinman.[5] These au-

(4) Waring, Hyman and Steingiser, THIS JOURNAL, **63**, 1985 (1941).

(5) Audrieth and Steinman, *ibid.*, **63**, 2115 (1941).

thors showed definite hydrogen bonding characteristics in oxychloride and chloroform solutions by a determination of heats of mixing.

Finally, we wish to emphasize that the type of solvation that exists in the $SeOCl_2$–H_2O system must, in view of the facts, be necessarily different from that observed in CH_3COOH–H_2O[3] mixtures. Both may be considered as undergoing solvate formation but only one system has an accompanying alteration in its electronic configuration. The authors feel that some such explanation could plausibly account for the phenomena observed by the magneto-optic method.

Summary

The magneto-optic rotations of aqueous solutions of $SeOCl_2$ were determined. The mole per cent., density, Verdet constant and molecular Verdet constant were determined and tabulated for each solution.

The curve of mole per cent. against molecular Verdet constant was plotted. A definite discontinuity was noted at 33.3 mole per cent. corresponding to the solvate $SeOCl_2 \cdot 2H_2O$ with accompanying alteration in the internal bond configuration. The probable structure is shown.

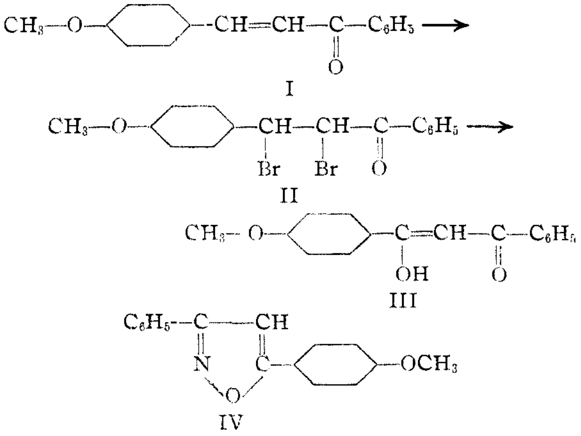
Brooklyn, N. Y. Received July 30, 1942

[Contribution from the Chemistry Department, Howard University]

The Properties of *p*-Methoxydibenzoylmethane

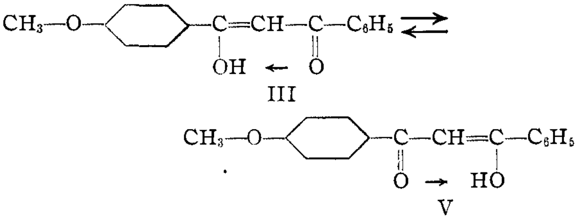
By R. Percy Barnes and Alfred Brandon[1]

In 1900, Pond and Shoffstall[2] investigated the action of sodium alcoholate upon anisylidene acetophenone dibromide (II), which was obtained by brominating anisylidene acetophenone (I), obtained by condensing anisaldehyde with acetophenone. These investigators obtained several intermediates between anisylidene acetophenone dibromide and the final product which they characterized as α-oxyanisylidene acetophenone (III), and state that α-oxyanisylideneacetophenone (III) yields the isoxazole (IV) upon treatment with hydroxylamine, whereas anisylideneacetophenone dibromide (II) yields an isomeric isoxazole.



In the light of the behavior of dibromochalcones and the enolic modifications of 1,3-diketones, one would expect (II) and (III) to give rise to one and the same isoxazole (IV).

Because of the well-established mechanism for the formation of enolic modifications of 1,3-diketones,[3] and because of the *p*-methoxyl effect,[4,5,6,7] we set out to make the isomer of α-oxyanisylidene acetophenone (V), with the prediction that the chemical reactions of these extreme forms of the resonance hybrid would be those of (V)



Thus we condensed *p*-methoxyacetophenone with benzaldehyde to produce benzal-*p*-methoxyacetophenone (VI). This substance was brominated to give dibromobenzal-*p*-methoxyacetophenone (VII). The dibromide was treated with freshly fused potassium acetate in glacial acetic acid solution, yielding the α-bromobenzal-*p*-methoxyacetophenone (VIII) which is a viscous yellow oil. This α-bromo unsaturated ketone was converted to the methyl ether (IX), which was in

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(1) In partial fulfillment of the requirements for the Master's Degree.

(2) Pond and Shoffstall, This Journal, **22**, 658 (1900).

(3) E. P. Kohler and R. Johnston, *Am. Chem. J.*, **33**, 35 (1905).

(4) R. P. Barnes and V. J. Tulane, This Journal, **63**, 867 (1941).

(5) R. P. Barnes and Wendell M. Lucas, *ibid.*, **64**, 2258 (1942).

(6) R. P. Barnes and Wendell M. Lucas, *ibid.*, **64**, 2260 (1942).

(7) R. P. Barnes, S. R. Cooper, Victor J. Tulane and Harold Delaney, "The Acetylation of Some Desoxybenzoins," accepted for publication by *J. Org. Chem.*, Jan., 1943.