this system was found to have a composition 48.5 mole per cent. dioxane with a boiling point at 87.59°.

2. Refractive index and density data for the analysis of the ternary system: dioxane–ethanol–water have been obtained. An analy-

sis diagram for the system is included.

3. Some vapor–liquid equilibria data at one atmosphere for the ternary system are presented, which permit the estimation of a ternary minimum azeotrope.

Magneto-optic Rotation. IV. Acetic and Chloroacetic Acids in Polar and Non-polar Solvents

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

In the last two papers of this series, the molecular Verdet constants were determined for solutions of carbon disulfide in various organic liquids and an interpretation proposed for the irregularity of the function plotted against mole per cent. concentration.[2,3] In order to establish the abnormality of this observed behavior and to demonstrate the possible causes for its presence or its absence, several other systems were studied. It was suspected, although not previously definitely established, that ordinary dipole association, simple hydrogen bonding and addition type complex formation without intramolecular rearrangement would not produce any effect. That is, the rotation per individual molecular group would remain constant if there were no internal bond rearrangements, regardless of how the density and direct Faraday rotation were altered by intermolecular combinations.

As a result of our present investigations, we now believe that when any alterations in intramolecular structure are produced in solution, whether by virtue of solvation, resonance or disturbed resonance effects, this method will reveal that change. On the other hand, the magneto-optic method will also show the absence of any such changes in the internal bond configuration even in cases where other physical methods, such as density, viscosity, molar volume, etc., indicate the probability of solvate formation.

Experimental

Materials and Apparatus.—The acids were the best grades of c. p. material available. The acetic acid was

purified with a single distillation and fractional crystallization to reduce the water content, but no attempt to obtain really anhydrous material was thought necessary. The carbon disulfide was the same as previously described.[3] An important improvement has been made in the apparatus over that described in a previous paper.[2] Instead of measuring the current directly with an ammeter, the *IR* drop in a fixed resistance in the circuit is balanced against an e. m. f. in an auxiliary circuit and the small deflections of a galvanometer in that circuit used to measure the current.

Since the error in measuring the current is now solely the error in measuring impressed voltage with the potentiometer and the galvanometer deflection, it is considerably smaller than that of the direct ammeter method.

Densities and refractive indices were measured with conventional instruments as previously described.[3] The solutions were made up to approximately the concentrations desired and titrated against standard alkali. Potassium acid phthalate was used as the primary standard. The procedure was to neutralize weighed portions of the acid with weighed excess of standard alkali, back titrate with known hydrochloric acid, and finally titrate to the end-point with dilute alkali using phenol red as indicator. All concentrations are the result of, at least, two analyses with a deviation of less than 0.1% by weight.

Measurements.—The primary standard and the technique of measurements were the same as before.[3] Table I is a summary of all the experimental measurements. Included in this tabulation are the recalculated results taken from Schwers[4] for the acetic acid–carbon tetrachloride systems. The molecular Verdet constants as given in the table are plotted against mole per cent. composition in Fig. 1.

Discussion.—Studies of viscosity and density on acetic acid-water mixtures show wide deviations from linearity at 50 mole per cent., which indicate interaction between the acetic acid and water molecules. Studies of infrared and Raman spectra[5] in this system also indicate interactions of a type readily interpreted as due to hydrogen bonding.

(1) Submitted in partial fulfillment for the Master of Science degree.

(2) Waring, Hyman and Steingiser, THIS JOURNAL, **62**, 2028 (1940).

(3) *Ibid.*, **63**, 1985 (1941).

(4) Schwers, *Bull. class. Sci. Acad. Roy. Belg.*, 648 (1912).

(5) Krishnamurthi, *Nature*, **128**, 639 (1931).

TABLE I

Mole% B	Density, d_{25}	Verdet constant, V_{25}	Molecular Verdet constant $V = VM/D$	Refractive index $n^{25}D$	Molecular refractivity $n^{25}D$
		Water–Acetic Acid			
0.0	0.9971	0.01302	0.2351	1.3325	3.711
10.75	1.0271	.01263	.2772	1.3522	4.749
19.19	1.0477	.01223	.3042	1.3635	5.538
26.21	1.0538	.01214	.3353	1.3655	6.165
33.37	1.0596	.01184	.3585	1.3700	6.850
45.15	1.0627	.01152	.4020	1.3734	7.940
59.08	1.0645	.01103	.4440	1.3764	9.242
83.05	1.0538	.01063	.5337	1.3754	11.509
99.08	1.0441	.01039	.5934	1.3700	12.930
		Water–Monochloroacetic Acid			
1.90	1.0316	.01305	.2462	1.3435	3.993
4.19	1.0770	.01309	.2579	1.3550	4.294
13.00	1.1580	.01316	.3180	1.3775	5.800
		Water–Dichloroacetic Acid			
2.99	1.0869	.01320	.2591	1.3533	4.258
6.92	1.1555	.01334	.2963	1.3734	5.066
23.30	1.3470	.01393	.4526	1.4215	8.251
58.40	1.4921	.01462	.8006	1.4530	15.474
80.95	1.5339	.01500	1.0543	1.4611	19.293
		Water–Trichloroacetic Acid			
1.72	1.0610	.01321	0.2554	1.3494	4.155
3.73	1.1375	.01367	.2818	1.3760	4.730
5.22	1.1685	.01387	.3042	1.3767	5.041

	d_{15}	V_{15}			
	Acetic Acid–Carbon Tetrachloride (Schwers 1912)				
0.00	1.6040	0.01603	1.5375		
58.576	1.3419	.01322	.9745		
78.158	1.2205	.01200	.7920		
90.436	1.1324	.01111	.6776		
100.000	1.0554	.01035	.5887		
	Acetic Acid–CS$_2$ (Schwers 1912)				
14.84	1.226	0.03312	1.992		
56.26	1.125	.02239	1.334		
66.18	1.105	.01942	1.149		
81.81	1.078	.01535	0.901		
100.00	1.0554	.01035	0.5887		

Magneto-optic rotation studies, on the other hand, give a linear relationship between the molecular Verdet constant and the mole fraction of acetic acid, as seen in Fig. 1. Thus, the hydrogen bonding, which markedly affects other physical properties of the acetic acid-water system, does not perturb, to any measurable extent, those intramolecular electronic groupings which are responsible for magneto-optic rotation. Magnetic susceptibility[6] and molecular refractivity measurements give a similar linear relation.

The partial molar Verdet constant for acetic acid in non-polar solvents, such as carbon disulfide

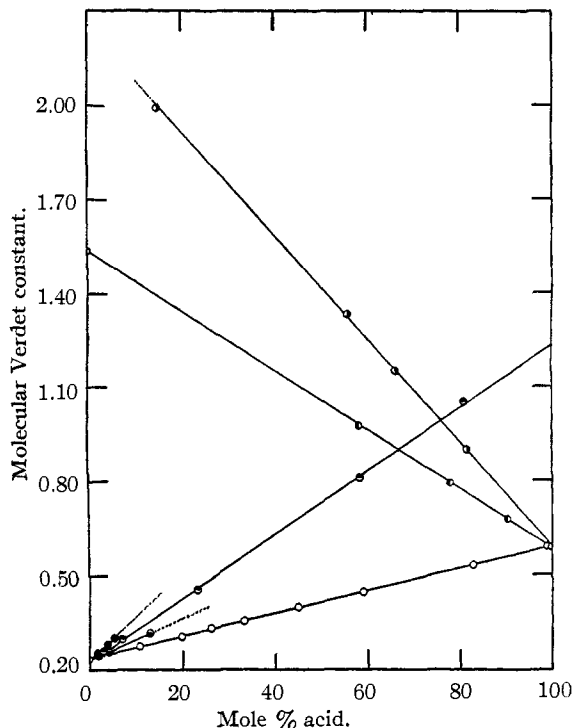(6) Varadachari, *Proc. Ind. Acad. Sci. 2A,* **161,** 75 (1935).

Fig. 1.—O, Acetic acid–water; ◖, monochloroacetic acid–water; ◑, dichloroacetic acid–water; ●, trichloroacetic acid–water; ◐, acetic acid–carbon disulfide; ◔, acetic acid–carbon tetrachloride.

and carbon tetrachloride, is identical with that in water, indicating that the nature of the solvent has no effect.

In the sulfuric acid-water system, on the other hand, intermolecular interaction is far more intense. Both magneto-optic rotation and magnetic susceptibility measurements show marked deviations from linearity—as, of course, do other physical properties. Our measurements on mixtures of chloroacetic acids with water, however, resemble the acetic acid–water rather than the sulfuric acid–water system.

This difference in the behavior of sulfuric and acetic acids in water may be logically attributed to the differences in magnitude of the changes which are produced in their electronic configurations upon solution. Intramolecular changes result from a rearrangement of the electrons within the molecules, and hence are detectable by magneto-optic measurements. When such strong electronic interactions occur, they may be considered as indicative of definite solvation, or, in some cases, of compound formation in solution.

On the other hand, changes may occur in the intermolecular distributions of molecules, as a func-

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.

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

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

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

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 % SeOCl₂	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

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