[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CONNECTICUT]

The Faraday Effect of Some Molecules Chelated or Associated by Hydrogen Bonding

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It is the purpose of this paper to present absolute Verdet constants of benzene solutions of *o*- and *p*-nitrophenol and of *o*- and *p*-nitrochlorobenzene in an effort to detect differences in their solute molecular interactions. Apparent molecular Verdet constants, temperature coefficients of molecular Verdet constants and magnetic rotatory dispersions are calculated from the data. Three magneto-optic methods provide additional magnetochemical evidence that the hydrogen bond occurs as ordinary electrostatic attraction.

Introduction

Recent work on the application of the Faraday effect to problems of chemical structure[2] has shown that where certain solute molecular interactions occurred, these would be indicated by definite discontinuities in the plot of molecular Verdet constant for the system against the mole fraction of solute. In extending this work, Waring and co-workers have studied the system acetone–chloroform.[3] The results of this research indicated the necessity for systematic studies of other systems of molecules whose structural characteristics were well known in order to test more fully the ability of the Faraday effect to detect changes in structure.

The results obtained in a study of the Faraday effect of water[4] indicated that the temperature dependence of the Faraday effect might be an additional means of detecting modifications in electronic structure. Thus, in a system where solute molecular interactions were sufficient to modify the electronic configuration of the molecule to the point where the Faraday effect was able to detect it, a difference in the aspect of the temperature dependence for the system might be expected.

Conditioned by an investigation by Rumpf and Seguin[5] of the magnetic susceptibility of similar molecules, the *ortho* and *para* isomers of nitrophenol and of nitrochlorobenzene were selected for a study of the Faraday effect of their solutions in an inert solvent in the concentration range where solute molecular interactions would be expected to become important.

It is the purpose, therefore, of this paper to present absolute Verdet constants for benzene solutions of *o*- and *p*-nitrophenol and of *o*- and *p*-nitrochlorobenzene in an effort to detect differences in their solute molecular interactions.

Experimental

The samples of *o*-nitrophenol and *p*-nitrophenol used in making up the solutions were EK P-191 and EK 192, respectively. The former was purified by recrystallizing twice from benzene and then twice from a water–methanol mixture, after which the crystals were dried in a vacuum desiccator. The *p*-nitrophenol was recrystallized once from a water–methanol solution and dried in a vacuum desiccator over NaOH. The *o*-nitrochlorobenzene and *p*-nitrochlorobenzene were Matheson grades No. 5278 and No. 2796, respectively, which were employed without further purification. A comparison between the melting points of these four compounds with those given in the literature is:

	M.p., °C. Exptl.	M.p., °C. Lit.
o-Nitrophenol	44.3	45[6]
p-Nitrophenol	112.1	114[6]
o-Nitrochlorobenzene	32.7	32.5[7]
p-Nitrochlorobenzene	82.0	83.5[7]

The benzene used to prepare the solutions was reagent grade, thiophene-free and dried over P_2O_5. This was distilled in a 30-plate Oldershaw column and only those fractions having a refractive index greater than 1.4974,[8] were collected and stored in glass-stoppered Pyrex bottles until used.

The solutions were prepared by weight using ground-glass stoppered Pyrex bottles and a Christian Becker large capacity balance. Corrections for buoyancy and for differences in vapor density in the tare and in the gas space above the material in the solution bottle were made to all weights. The solute mole fractions of the solutions so prepared[9] had values of 1, 2, 4, 8 and 16 $\times 10^{-3}$ for the four compounds which were calculated with uncertainties of $\pm 0.05\%$.

Magnetic rotation constants, k, were measured in the manner previously described[3,4] over temperature ranges from 10° to 50° for each of the wave lengths 589, 578 and 546 mμ. The experimental rotation constants for the solutions were plotted against temperature on large laboratory graphs. From these curves, smoothed data at arbitrary temperatures were obtained. These data, together with experimental densities for the solutions[9] and the experimentally determined magnetic field strength of the solenoid employed,[9] were used to calculate specific Verdet constants for the solutions. Molecular Verdet constants were next calculated on the bases of molecular weights for the solutions which were computed from the data on weighings.

Results

Apparent molecular Verdet constants for the solute compounds, V_2, were calculated from the relation

$$\bar{V}_2 = \frac{V - N_1V_1}{N_2} \qquad (1)$$

where V is the molecular Verdet constant for the solution, V_1 is the molecular Verdet constant for the solvent, benzene,[10] and N_1 and N_2 are the mole fractions for the solvent and solute, respectively. Results of calculations of apparent molecular Verdet constants are given in Table I.

Temperature coefficients, $(1/V_{25})(\Delta V/\Delta t)$, where ΔV is $V_{10} - V_{60}$ and Δt is equal to 50°, of the mo-

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[1] The data presented were submitted in partial fulfillment of the requirements of the Ph.D. degree at the University of Connecticut.

[2] Chas. E. Waring, *et al.*, THIS JOURNAL, **62**, 2028 (1940); **63**, 1985 (1941); **65**, 1066 (1943); **65**, 1068 (1943).

[3] Chas. E. Waring, *et al.*, *Rev. Sci. Instruments*, **21**, 109 (1950); S. Steingiser, Ph.D. Thesis, University of Connecticut, 1949.

[4] Chas. E. Waring and R. L. Custer, THIS JOURNAL, **74**, 2506 (1952); ONR N6 orl 216 T.O. No. 1 Technical Report No. 5 (1950); Robert L. Custer, Ph.D. Thesis, University of Connecticut, 1952.

[5] P. Rumpf and M. Seguin, *Bull. soc. chim. France*, D366 (1949).

[6] "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., 31st Edition, 1949, p. 678.

[7] *Ibid.*, p. 1002.

[8] N.B.S. Circular, C-461, p. 67 (1947).

[9] Robert L. Custer, Ph.D. Thesis, University of Connecticut, 1952.

[10] R. L. Custer and C. E. Waring, THIS JOURNAL, **74**, 5726 (1952).

TABLE I

APPARENT MOLECULAR VERDET CONSTANTS FOR THE SOLUTE COMPOUNDS AT 25°

Material	$N_2 \times 10^3$	$\bar{V}_2$ 589	578	546
o-$NO_2C_6H_5OH$	2.1	2.6	2.7	2.4
	3.8	2.0	2.4	2.4
	7.6	2.1	2.5	2.3
	15.4	2.2	2.4	2.5
p-$NO_2C_6H_5OH$	0.9	...	2.9	0.9
	2.0	1.8	3.3	2.6
	3.9	2.0	2.8	2.7
	7.5	2.5	3.0	3.1
o-$NO_2C_6H_5Cl$	1.9	3.9	3.9	4.1
	3.7	3.0	3.5	3.6
	7.5	2.8	3.2	3.4
	15.1	2.8	3.0	3.3
p-$NO_2C_6H_5Cl$	2.5	0.7	1.1	0.5
	4.3	2.0	2.4	2.1
	7.8	2.0	2.3	2.6
	15.1	2.3	2.5	2.8

lecular Verdet constants were calculated for the solutions and are summarized in Table II.

TABLE II

TEMPERATURE COEFFICIENTS OF MOLECULAR VERDET CONSTANTS FOR THE SOLUTIONS STUDIED

Material	$N_2 \times 10^3$	589	$1/V_{25} \times \Delta V/\Delta t$ 578	546
o-$NO_2C_6H_5OH$	2.1	3.2	3.5	3.5
	3.8	3.3	3.6	3.5
	7.6	3.3	3.6	3.6
	15.4	3.4	3.7	3.6
p-$NO_2C_6H_5OH$	0.9	3.5	3.3	3.4
	2.0	3.4	3.3	3.4
	3.9	3.4	3.3	3.4
	7.5	3.5	3.3	3.4
o-$NO_2C_6H_5Cl$	1.9	3.3	3.4	3.3
	3.7	3.4	3.5	3.4
	7.5	3.4	3.5	3.4
	15.1	3.5	3.6	3.5
p-$NO_2C_6H_5Cl$	2.5	3.7	3.8	3.7
	4.3	3.7	3.8	3.8
	7.8	3.8	4.0	4.0
	15.1	4.1	4.2	4.2
Benzene		3.7	3.8	3.8

The dispersions at 25°, obtained by dividing molecular Verdet constants at two wave lengths by those at 589 mμ, were found to remain constant to just outside their experimental uncertainties.

Discussion

The experimental magnetic rotation constants were calculated with uncertainties of ±0.02–0.03%. These were plotted on such a scale that values of the rotation constants could be read from the curves with the same uncertainty. The Verdet constants had an uncertainty of ±0.04%, since the uncertainty in the value of the magnetic field strength of the solenoid was ±0.03%. The uncertainty in the densities of the solutions obtained at arbitrary temperatures from curves of the experimental values was ±0.03%, making the uncertainty in the specific Verdet constants equal to ±0.05%. The uncertainty in the molecular Verdet constants, then, was also ±0.05%. The uncertainty in the apparent molecular Verdet constants for the solute compounds, on this basis, was ±10%. The uncertainty in the values of ΔV was ±4%. Thus the uncertainty in the temperature coefficients was ±4%. The uncertainty in the values of the dispersions was found to be ±0.04%.

As was pointed out in the Introduction, recent work of Waring and co-workers had shown that in certain cases molecular interactions are detected by deviations from additivity in the molecular Verdet constants. In the present case, since the molecular Verdet constants of the solute compounds are not known, such interactions should be shown by systematic variation in the value of apparent molecular Verdet constant as a function of concentration. Differences in the degree or kind of solute molecular interaction among molecules would be detected by differences in the magnitude or direction of these variations. It is seen from the results in Table I that no significant variation with concentration occurs in these constants for any of the compounds. These results indicate that of the various types of solute molecular interactions that might be expected to occur, none were detected by this particular magneto-optic method.

The similarity between the temperature coefficients of the magnetic susceptibility and of the molecular Verdet constants for water was pointed out previously.[4] In view of the possible applicability of a relation of the Van Vleck type, this would seem to indicate that in systems where associations of the kind present in water occurred, similar effects on the molecular Verdet constant might be expected. Thus the possibility exists that significant differences between the temperature coefficients of molecules interacting through hydrogen bonds and of those undergoing dipole interactions might occur. It is seen from the results in Table II that the molecular Verdet constants for the solutions generally increase significantly with solute mole fraction, and inversely with wave length in about the same way. These results indicate that the different types of solute molecular interactions which might be expected to occur in these systems do not cause significant differences in the aspects of temperature dependency of their molecular Verdet constants. In this respect, the results are consistent with those found from the standpoint of deviations from additivity. Rabinovitch[11] has evolved a method of appraising binary systems on the basis of their magnetic rotatory dispersions. In terms of the systematics of Rabinovitch, in certain cases solute molecular interactions can be shown by systematic variation of the values of dispersions as a function of concentration. Results obtained for the dispersions of the solutions studied do not show such variation but are an additional indication that no significant differences occur in the kind or degree of solute molecular interactions among the compounds investigated.

With respect to the question as to whether the Faraday effect might show essential differences among the types of solute molecular interactions

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(11) J. Rabinovitch, *Ann. Phys.*, **13**, 176 (1940).

which would be expected to occur in the systems studied, the results of the three methods of attack are consistently negative. The results serve as additional magnetochemical evidence that the hydrogen bond occurs as simple electrostatic attraction.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

The Partition of Electrolytes between Aqueous and Organic Phases. I. The Partition of the Alkali Reineckates and Perrhenates between Water and Nitromethane[1,2]

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An experimental approach to the thermodynamics of electrolytic solutions in organic solvents is provided by the study of the partition of electrolytes between aqueous and organic phases. An investigation of the distribution equilibria of the alkali reineckates [$MCr(NH_3)_2(SCN)_4$] and perrhenates ($MReO_4$) shows that these salts are strong electrolytes in the nitromethane phase as well as the aqueous phase in the concentration range investigated. For the reaction, $M^+(aq) + ReO_4^-(aq) = M^+(MeNO_2) + ReO_4^-(MeNO_2)$, with hyp. 1 molar std. states, ΔF^0_{298} is: Li, 6.23; Na, 5.83; K, 4.08; Rb, 3.43; Cs, 2.71; H, 5.32 kcal./mole. For the reaction, $ReO_4^-(aq) + Cr(NH_3)_2(SCN)_4^-(MeNO_2) = ReO_4^-(MeNO_2) + Cr(NH_3)_2(SCN)_4^-(aq)$, $\Delta F^0_{298} = 5.0$ kcal./mole. In simple cases both electrostatic and non-electrostatic contributions to the free energy of transfer of an ion from water to an organic phase tend to make this free energy more negative for larger ions, as observed.

The study of the partition of electrolytes between aqueous and organic phases provides a method of investigating the thermodynamic properties of the organic solutions. The direct results of such an investigation are limited to organic solvents in equilibrium with water, but it appears that partition experiments will be of value to supplement measurements on solutions in anhydrous solvents for the following reasons: First, the partition experiments are relatively easy and may be used to select the systems for which a complete investigation will yield the most information. Second, the partition experiments relate the state of the electrolyte in the organic solvent directly to its state in water, which is relatively well understood, rather than to its state in the solid electrolyte, possibly solvated, in equilibrium with the organic solvent. Finally, a recent theoretical development by McKay[3] leads to a method of calculating the free energy of transfer of an electrolyte from pure water to pure organic solvent from partition experiments combined with measurements of partial derivatives which are directly related to salting out constants. Thus the combined measurements can lead to knowledge of the thermodynamics of the anhydrous organic solutions relative to those of the pure aqueous solutions.

The experiments described here were undertaken to provide information about the effect of ion size upon the free energy of transfer of ions from an aqueous phase to an organic phase. Nitromethane was chosen as the organic medium in these experiments because it is incompletely miscible with water and has a dielectric constant high enough to avoid complications due to ion-pair formation at the concentrations employed here.

Experimental

Materials.—Redistilled water was used throughout. Nitromethane was distilled from phosphoric anhydride. The fraction boiling between 100.4 and 100.6° was taken. For the perrhenate studies, an acid impurity in the purified nitromethane was removed by washing with sodium bicarbonate solution. Commercial ammonium reineckate (C.P.) was recrystallized from water. The product was metathesized by CsCl, KCO_2CH_3 or $NaClO_4$ to produce the respective reineckate. This was recrystallized once from water for final purification in each case. The reineckate ion decomposes slowly (1% per day in 0.01 *M* solutions) at room temperature in the dark, and decomposes more rapidly at elevated temperatures or in diffuse sunlight. All recrystallizations were carried out from aqueous solution between 30 and 0°. The solutions were handled only in artificial light and were stored in an ice-box. C.P. potassium perrhenate was recrystallized twice from water and fused in a platinum crucible in air at 750° to constant weight. The stock perrhenate solution was made up from this known weight of $KReO_4$. $CsReO_4$ was prepared by the reaction in water of resublimed Re_2O_7 with recrystallized (from alcohol) Cs_2CO_3, and the product was recrystallized from water.

Partition of the reineckates was studied by equilibrating aqueous reineckate solutions with nitromethane at 25 ± 2°, and analyzing each phase by measuring the light absorption due to the reineckate ion near 5220 Å. (decadic molar extinction coefficient = 116). The extinction maximum was shifted slightly toward longer wave lengths in nitromethane, but the extinction coefficient at the peak remained unchanged. The results are presented in Fig. 1.

Partition of the perrhenates was studied by equilibrating accurately known amounts of $KReO_4$, an alkali metal chloride, water and nitromethane at 25.2°, and then analyzing each phase for rhenium by an application of the spectrophotometric Re(VI) thiocyanate method of Hurd and Babler.[4] A sample of each phase was evaporated to dryness with a drop of concd. HNO_3, taken up in 5–6 drops of concd. HNO_3, and evaporated again. The evaporation was carried out below 100° to avoid loss of Re_2O_7. The residue was dissolved in known volumes of KSCN and $SnCl_2$–HCl solutions and the resulting solution examined spectrophotometrically 15 min. after mixing. The molar decadic extinction coefficient depends upon the details of the procedure but is about 10^4, calculated on the basis of known ReO_4^- concentrations in standardizing experiments. Beer's law is obeyed up to optical densities of 1.5 (1 cm. light path) and the results seem reproducible to within ±2% in concentra-

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[1] Presented in part at the meeting of the American Chemical Society, Los Angeles, California, March, 1953.

[2] This work was supported by the U. S. Atomic Energy Commission.

[3] H. A. C. McKay, *Trans. Faraday Soc.*, **49**, 237 (1953).

[4] L. C. Hurd and B. J. Babler, *Anal. Chem.*, **8**, 112 (1936).