

Although the molecule of *t*-butyl alcohol is not very far from spherical in shape, reasonably close packing of the molecules, such as would naturally occur in the crystal lattice, would probably cause the rotation of a molecule to be blocked by its neighbors. In the crystal of *n*-octyl alcohol, the molecules probably lie as extended zig-zag chains parallel to one another. As many cases are known in which carbon chains parallel to one another in a solid rotate about their long axes,⁹ there would seem to be a possibility of rotation of this type here, which is evidently not realized. Bernal has found by x-ray analysis¹⁰ that *n*-dodecyl alcohol shows a transition from a monoclinic to a hexagonal crystal at 289°K. with molecular rotation setting in around the axis of the carbon-chain. It is probable that the higher temperature attainable before melting gives the energy

(9) Müller, *Nature*, **129**, 436 (1932); Southard, Milner and Hendricks, *J. Chem. Phys.*, **1**, 95 (1933).

(10) Bernal, *Nature*, **129**, 870 (1932).

necessary to overcome the resistance to rotation, lacking in the *n*-octyl alcohol, which melted 32° below this transition temperature.

Summary

The dielectric constants of solid methyl, *t*-butyl and *n*-octyl alcohols have been measured from liquid air temperatures up to the melting point in order to investigate the question of dipole rotation in the solid state. The high dielectric constant of methyl alcohol just below the melting point, dropping to a low value at a transition temperature 159.9°K., gives evidence of dipole rotation in this region. The absence of dipole rotation in solid *t*-butyl and *n*-octyl alcohols and the failure of specific heat measurements to show transitions in many other alcohols, indicate that the hydroxyl group does not rotate inside the molecule, but that the entire methyl alcohol molecule rotates above the transition point.

PRINCETON, N. J.

RECEIVED JUNE 22, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW HAMPSHIRE]

The Magnetic Rotation of Lanthanum and Neodymium Chlorides in Aqueous Solution

BY CHARLES M. MASON, ROGER D. GRAY AND GRACE L. ERNST

The magnetic rotation of the plane of polarized light is particularly interesting in the case of the rare earths. The chemical properties of these substances in aqueous solutions are so nearly identical that it is only by physical measurements of this type that any differentiation of properties can be made.

In this work the Verdet constants of aqueous solutions of lanthanum and neodymium chlorides have been measured over a temperature interval of from 10 to 50°. The concentration of the solutions was varied from zero (water) to 3.7 molal for the lanthanum chloride and 0.5 molal for the neodymium chloride. For comparison the Verdet constants were determined for aluminum chloride solutions from zero to 2.8 molal over the same temperature range.

Experimental Details

The rotations were measured with a Franz Schmidt and Haensch Model 55 "Landolt" half shade polarimeter, which could be read to hundredths of a degree.

The two light sources used were a mercury "Lab-Arc" with Corning filters G-555-Q and G-35-Y to transmit λ 5460.7 Å. and a sodium "Lab-Arc." This latter was used without filters since the accuracy attained in setting

the polarimeter without any filters more than offset any error due to wave lengths other than the principal doublet λ 5893 Å.

The solution, the rotation of which was to be measured, was placed in a water-jacketed cell of Pyrex glass. This was equipped with optical windows of the same, fused on to the ends. The cell, which is shown in Fig. 1, was provided with an entrance through which a calibrated thermometer could be placed in the solution while the rotation was measured.

The magnetic field was provided by a coil of fourteen layers of No. 20 B. and S. cotton and enamel covered copper wire. The total number of turns was 2,059 and the length of the coil was 23.57 cm. The inside diameter was 2.84 cm. and the outside diameter 6.70 cm. The length of the light path through the solution was 21.74 cm. From these data the field strength, *H*, of the coil at any point along the axis is easily calculated. The product of the effective field strength times the length of the light path in the cell was determined by integration. The value of this integral was found to be 2218.2 gauss-cm. per ampere of current through the coil. This value, when used to calculate the Verdet constants for water and carbon bisulfide, checked the standard values¹ within 0.5%. This is a good check when we consider the irregularities of the coil winding as shown by an examination of Fig. 1.

(1) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, Vol. VI, 1926, p. 425.

A current of 4.000 ± 0.001 amperes was used, supplied from storage batteries. Current regulation was obtained by the use of a manually operated potential divider similar to that described by MacInnes and Longworth.²

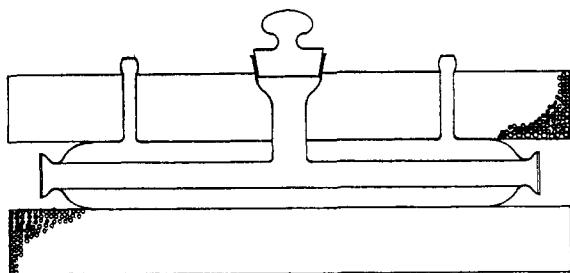


Fig. 1.—Magnetic rotation cell.

In order that the current adjustment might be made accurately, a Leeds and Northrup student type potentiometer was used to measure the potential drop across a standard 0.10 ohm resistance in series with the coil. The potential divider was operated during a reading of the rotation so that the galvanometer connected in the potentiometer circuit showed no deflection while the observation was made.

Temperature control was obtained by circulating water from a thermostat through the water jacket of the cell. The temperature could be controlled to within $\pm 0.05^\circ$ of any chosen point.

The rare earth salts had been carefully prepared by repeated recrystallization. The chlorides were prepared from the oxalates by ignition to the oxides and solution of these in redistilled hydrochloric acid. These chlorides were then twice recrystallized by concentration of the mother liquor and shaking out with hydrogen chloride gas. They were then dried at room temperature and placed for several weeks in a vacuum desiccator over potassium hydroxide. Examination of the solutions with the hand spectroscope and chemical test showed the absence of other rare earths.

The commercial c. p. grade of aluminum chloride hexahydrate was used without further purification. It was guaranteed by the manufacturer to be better than 99.85%. For the present investigation this slight percentage of impurity would not vitiate the result.

Concentrated aqueous solutions of these salts were prepared with conductivity water. These were analyzed gravimetrically for the chloride. The dilute solutions were then prepared from these by weight. The water used was of conductivity grade.

The c. p. grade of carbon bisulfide was purified by the method of McKelvey and Simpson.³

Results

The Verdet constant⁴ is given by the expression

$$V = \theta / \int Hdl \quad (1)$$

where θ is the angle of rotation in minutes and

(2) MacInnes and Longworth, *Chem. Rev.*, **11**, 189 (1932); Mason and Gray, *Rev. Scientific Instruments*, **7**, 289 (1936).

(3) McKelvey and Simpson, *THIS JOURNAL*, **44**, 108 (1922).

(4) This quantity is discussed and the literature is surveyed in Bhatnagar and Mathur, "Physical Principles and Applications of Magnetochemistry," The Macmillan Co., London, 1935.

$\int Hdl$ is the average field strength over the whole light path.

If we choose to calibrate our apparatus with some liquid whose Verdet constant is known, such as water or carbon bisulfide, we find that

$$V = \frac{\theta}{\theta_s} V_s \quad (2)$$

where θ_s and V_s are the rotation and Verdet constant of the standard liquid used and θ and V are those for the solution under investigation. In the present work equation (2) was employed to calculate the Verdet constants obtained. Water was employed as the reference liquid in these calculations. This was done because the irregularity of the coil made exact calculation of the field strength impossible.

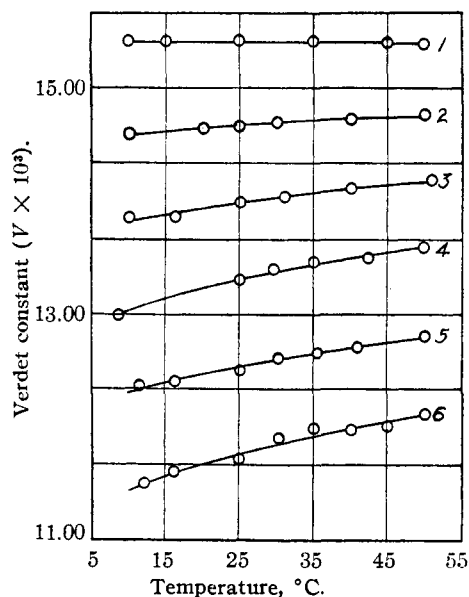


Fig. 2.—The Verdet constants of neodymium chloride solutions as a function of the temperature: 1, water; 2, 0.1 molal; 3, 0.2 molal; 4, 0.3 molal; 5, 0.4 molal; 6, 0.5 molal.

It was difficult to take readings rapidly at fixed temperature intervals due to the heating effect of the coil. The data were therefore often taken at odd temperature intervals. These data were then plotted on a large scale as shown by the plot for neodymium chloride in Fig. 2. The data taken from these plots are presented in Tables I, II and III for aluminum, lanthanum and neodymium chlorides, respectively. No data were obtained for neodymium chloride for the wave length $\lambda 5893 \text{ \AA}$. because of the strong absorption band in this region of the spectra.

TABLE I

VERDET CONSTANTS OF ALUMINUM CHLORIDE SOLUTIONS
 $\lambda = 5893 \text{ \AA}$.

Molality	10°	$V \times 10^3$ at the indicated temperature				
		20°	25° ^a	30°	40°	50°
0.00	13.19	13.12	13.07 ^a	13.10	13.10	13.10
.01	...	13.13	13.14	13.14	13.14	13.15
.05	13.22	13.25	13.27	13.29	13.32	13.36
.10	13.39	13.39	13.39	13.39	13.39	13.39
.50	14.66	14.66	14.66	14.66	14.66	14.66
1.00	15.94	15.94	15.94	15.94	15.94	15.94
1.50	17.21	17.21	17.21	17.21	17.21	17.21
2.00	18.41	18.41	18.35	18.31	18.28	18.28
2.78	20.15	20.02	20.02	19.95	19.95	19.90

 $\lambda = 5460.7 \text{ \AA}$.

0.00	15.40	15.40	15.40	15.40	15.40	15.33
.01	...	15.47	15.47	15.47	15.47	15.47
.05	...	15.83	15.78	15.73	15.62	15.51
.10	15.94	15.94	15.94	15.94	15.94	15.94
.50	17.14	17.14	17.14	17.14	17.14	17.14
1.0	18.61	18.61	18.61	18.61	18.61	18.61
1.50	20.09	20.09	20.09	20.09	20.09	20.09
2.00	21.49	21.49	21.56	21.56	21.63	21.63
2.78	23.77	23.77	23.70	23.64	23.50	23.50

^a "International Critical Tables," McGraw-Hill Book Co., Inc., New York, Vol. VI, 1926, p. 425.

TABLE II

VERDET CONSTANTS OF LANTHANUM CHLORIDE SOLUTIONS
 $\lambda = 5893 \text{ \AA}$.

Molality	10°	$V \times 10^3$ at the indicated temperature				
		20°	25° ^a	30°	40°	50°
0.00	13.19	13.12	13.07	13.10	13.10	13.10
.10	13.46	13.46	13.47	13.53	13.53	13.53
.40	14.40	14.40	14.37	14.40	14.33	14.33
.80	15.67	15.60	15.55	15.40	15.33	15.33
.9967	16.07	16.07	16.08	16.14	16.14	16.14
1.40	17.21	17.21	17.22	17.21	17.14	17.14
1.7509	...	18.08	18.21	18.15	18.01	17.94
2.20	19.08	19.15	19.14	19.10	19.10	19.10
2.50	19.89	19.86	19.83	19.69	19.69	19.69
2.80	20.56	20.56	20.35	20.30	20.29	20.15
3.10	...	20.96	20.97	20.96	20.96	20.96
3.40	21.56	21.56	21.52	21.43	21.29	21.23
3.9640	21.96	21.96	22.03	21.96	21.76	21.69

 $\lambda = 5460.7 \text{ \AA}$.

0.00	15.40	15.40	15.40	15.40	15.40	15.40
.10	15.73	15.73	15.75	15.80	15.80	15.80
.40	17.07	16.94	16.85	15.87	16.87	16.87
.80	18.35	18.35	18.17	18.40	18.41	18.41
.9967	19.15	19.08	19.03	19.02	19.02	19.02
1.40	20.42	20.35	20.35	20.29	20.22	20.22
1.7509	...	21.43	21.49	21.49	21.43	21.36
2.20	22.43	22.50	22.50	22.43	22.43	22.43
2.50	23.37	23.34	23.28	23.30	23.30	23.30
2.80	24.10	24.07	24.04	24.00	23.95	23.90
3.10	...	24.90	24.80	24.64	24.57	24.31
3.40	25.44	25.44	25.43	25.31	25.24	25.11
3.9640	26.18	25.91	25.88	25.85	25.80	25.71

^a All values of this constant at 25° are the mean of at least five measurements.

TABLE III

VERDET CONSTANT OF NEODYMIUM CHLORIDE SOLUTIONS
 $\lambda = 5460.7 \text{ \AA}$.

Molality	10°	$V \times 10^3$ at the indicated temperature				
		20°	25° ^a	30°	40°	50°
0.00	15.40	15.40	15.40	15.40	15.40	15.33
.05	15.40	15.40	15.40	15.40	15.40	15.40
.10	14.60	14.64	14.66	14.68	14.70	14.73
.20	13.84	13.95	13.99	14.06	14.10	14.16
.30	13.03	13.22	13.32	13.39	13.49	13.59
.40	12.30	12.40	12.47	12.60	12.70	12.81
.50	11.45	11.67	11.72	11.82	11.95	12.14

^a All values of this constant at 25° are the mean of at least five measurements.

In order to show more clearly the relationship between the Verdet constant and the concentration, the data obtained at 25° have been plotted in Fig. 3.

Discussion

Comparison with Other Data.—The value obtained for the Verdet constant of 0.1 molal lanthanum chloride with the green line $\lambda 5460.8 \text{ \AA}$. at 20°, 15.73×10^{-3} , may be compared with that obtained by Roberts, Wallace and Pierce⁵ for a solution of lanthanum sulfate, 0.094 molal in lanthanum ion. They obtained 15.40×10^{-3} . The maximum error of measurement in this work for the wave length $\lambda 5460.8 \text{ \AA}$. is about $\pm 0.01^\circ$ of arc which corresponds to a total possible error of 0.14×10^{-3} min. per gauss-cm. in the Verdet constant.

These authors do not state the error in their visual observations. If it is presumed to be of the same order of magnitude as in the present investigation the difference between the two values is within the experimental error. They do state, on the basis of one measurement of magnitude less than the probable error, that aqueous solutions of lanthanum sulfate have a negative rotation. In this investigation lanthanum chloride has consistently a positive rotation in solutions of all concentrations. This difference of sign is not significant however in view of the limits of error discussed above and the different negative ions present.

Direction of Rotation.—The theory of Serber⁶ for the Faraday effect in molecules points out that the Verdet constant may be expressed by an equation of three distinct terms. Two of these terms are diamagnetic and the third is paramagnetic. For diamagnetic substances the third term drops

(5) Roberts, Wallace and Pierce, *Phil. Mag.*, 17, 934 (1934).(6) Serber, *Phys. Rev.*, [2] 41, 489 (1932).

out and the theory predicts that the Verdet constant should be positive.

Lanthanum chloride and aluminum chloride are known to be weakly paramagnetic and diamagnetic, respectively. It would be expected therefore in both cases, since the third term in the equation mentioned above would either be insignificant or vanish, that these substances would have a positive effect on the Verdet constant.

Examination of the data in Tables I and II shows the experimental verification of these conclusions, as in both cases the Verdet constant of the solutions is increased positively by the added salt.

Neodymium chloride on the other hand is strongly paramagnetic and would be expected by Serber's theory to have a negative effect on the Verdet constant. Examination of the data in Table III shows the marked negative effect of neodymium chloride as predicted by the theory.

Temperature Effect.—In the equation mentioned by Serber⁶ the third or paramagnetic term contains the expression $1/T$ where T is the absolute temperature. From this the conclusion may be drawn that the Verdet constant for paramagnetic substances should vary with temperature and that diamagnetic substances should not vary with temperature. From the "International Critical Tables"¹¹ (p. 359) it is noted that the magnetic susceptibilities of aluminum chloride, lanthanum chloride and neodymium chloride (estimated) are in the ratios $-0.6:5.6:25$. From these the theoretical conclusions may be drawn that aqueous solutions of aluminum chloride should have no temperature coefficient, those of lanthanum chloride should have a slight temperature coefficient and neodymium chloride solutions a marked temperature coefficient. Examination of the data in Tables I, II and III shows that the conclusions are justified by the experimental results. No temperature coefficient was observed for the aluminum chloride solutions within the experimental error. A slight temperature coefficient was observed for the lanthanum chloride

solutions in the higher concentrations. Neodymium chloride solutions, on the other hand, showed a marked temperature coefficient, even in dilute solutions.

It was found that the Verdet constants of the neodymium chloride solutions gave a straight

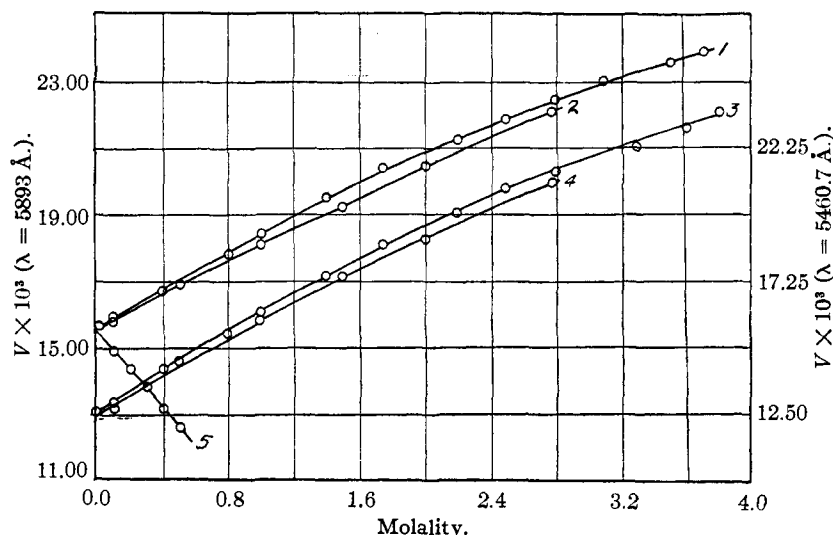


Fig. 3.—Verdet constants of the solutions as a function of concentration at 25°: 1, LaCl_3 , λ 5460.7 Å.; 2, AlCl_3 , λ 5460.7 Å.; 3, LaCl_3 , λ 5893 Å.; 4, AlCl_3 , λ 5893 Å.; 5, NdCl_3 , λ 5460.7 Å.

line when plotted against $1/T$. From these straight lines a family of equations of the type

$$V = a/T + b \quad (3)$$

were obtained, where a and b are constants. The data for these constants for equation (3) and the maximum deviation of the calculated values from the experimental values are given in Table IV.

TABLE IV
CONSTANTS FOR THE TEMPERATURE EQUATIONS (3) FOR NEODYMIUM CHLORIDE SOLUTIONS

Molality, m	a	b	Max. dev.
0.10	- 325.0	16.94	0.04
.20	- 662.5	16.60	.04
.30	-1212.5	17.37	.03
.40	-1220.0	16.21	.03
.50	-1553.6	15.75	.02

Recently several authors⁷ have shown that the Curie-Weiss law of magnetic susceptibilities may be applied to the molecular magnetic rotation. This law is usually stated

$$(T - \Delta)\chi_m = C_m \quad (4)$$

where χ_m is the gram-molecular magnetic susceptibility, T the absolute temperature, C_m a constant and Δ a constant called the Curie point.

(7) Ollivier, *Compt. rend.*, **186**, 1001 (1928); Ollivier, *ibid.*, **191**, 130 (1930); Pernet, *ibid.*, **195**, 376 (1932); Gorter, *Physik. Z.*, **34**, 238 (1933).

In order to make this application to the present data the molecular rotations for the neodymium chloride solutions have been calculated from the equation

$$D = \frac{M}{\rho d_s} (V - d_1 V_w / d_w) \quad (5)$$

where D is the molecular rotation of the solution, M is the molecular weight of the neodymium chloride, d_s is its density, ρ is the number of grams of salt per gram of solution, d_1 is the density of the solution, d_w is the density of pure water and V and V_w are the Verdet constants of the solution and pure water, respectively. The densities of the solutions at 25° were obtained from the data of Mason and Leland.⁸ The densities for the other temperatures were calculated from these on the assumption that the temperature coefficient of the density of the solutions was the same as that for pure water. The values of D obtained are listed in Table V.

TABLE V
THE MOLECULAR ROTATION OF NdCl_3 IN AQUEOUS SOLUTION

Molality, m	ρ	D at the indicated temperature					
		10°	20°	25°	30°	40°	50°
0.1	0.0245	3.07	2.96	2.91	2.85	2.80	2.67
.2	.0477	3.06	2.91	2.85	2.76	2.71	2.63
.3	.0699	3.15	2.97	2.87	2.81	2.72	2.62
.4	.0911	3.23	3.17	3.12	3.02	2.95	2.87
.5	.113	3.32	3.19	3.17	3.11	3.03	2.92
Ave.		3.16	3.04	2.98	2.93	2.82	2.72

There is some drift toward the higher concentrations but this may be due to slight error in the density calculation.

The average data in Table V were used to calculate the values of C and Δ in the equation

$$(T - \Delta)D = C \quad (6)$$

which is analogous to equation (5), the Curie-Weiss law.

(8) Mason and Leland, *THIS JOURNAL*, **57**, 1507 (1935).

The value of Δ was found to be close to 32.6° which was taken as the best value. Equation (6) was tested by calculating the values of C for the several temperatures. The values of C obtained, which checked with each other within one part in a thousand, gave an average value of -790.1. This constancy of C shows that the equation

$$(T - 32.6)D = -790.1 \quad (7)$$

is applicable to the data for neodymium chloride over the temperature range studied.

Concentration Effect.—For the wave length λ 5460.8 Å. the Verdet constants of the aluminum and neodymium chloride solutions were found to be a linear function of the concentration over the range studied. None of the other data give linear relationships, as may be seen by examination of Fig. 3.

The authors wish to express thanks to Dr. H. C. Fogg for advice regarding the purification of the rare earth salts.

Summary

The magnetic rotations of aqueous solutions of aluminum, lanthanum and neodymium chlorides have been measured from 10 to 50° at wave lengths λ 5893 and 5460.8 Å.

The Verdet constants of these solutions have been calculated and those for neodymium chloride solutions found to vary linearly with $1/T$.

The molecular rotations of the neodymium chloride solutions have been calculated and found to vary with temperature according to the equation $(T - 32.6)D = -790.1$.

The variations of the Verdet constants with temperature were found to agree qualitatively with the predictions of Serber.⁶

DURHAM, N. H.

RECEIVED MAY 28, 1936