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

The Magnetic Rotation of Cerium Salts in Aqueous Solution

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Within recent years there have been several investigations of the magnetic rotation of cerous salts in aqueous solution. The nitrate has been investigated by Pillai,[1a] and by Chuckerbutti,[2] and an investigation of the sulfate has been made by Roberts, Wallace and Pierce.[3] Previous investigations of the magnetic rotation of the chloride have been carried out by Pernet[4] and Slack, Reeves and Peoples.[5]

In the course of our general study of the properties of the rare earth salts in aqueous solution, an attempt was made to extend the work of these authors on cerous chloride. Since preliminary work indicated a divergence between the results previously reported and those found at New Hampshire, an extensive investigation has been made of the magnetic rotation of cerous chloride in aqueous solution.

Experimental

The measurements were carried out as previously described[6] except that additional wave lengths were obtained by use of a Pointolite lamp and a carbon arc in conjunction with the monochromator.

Cerous chloride from two sources was investigated in order to eliminate any error inherent in the source. At first thought, it would seem that chemical analysis should be the first and most important proof of purity but when it is considered that the impurities would most likely be other rare earths, some means must be found to supplement the chemical analyses. First, the magnetic rotation itself should serve as a means of comparing the cerium from the two sources and, second, the Bureau of Standards kindly supplied us with a sample of cerium material whose spectroscopic analysis was known and this could be compared spectrographically with the material to be used in the investigation.

Two solutions were prepared by methods previously described,[6] and compared as outlined herein.

As one means of analysis, the two samples were compared by emission and absorption spectra against the sample procured from the Bureau of Standards. In so far as could be determined the samples prepared were spectrographically equivalent to this sample.

As a second test for purity, we analyzed stock solutions from the two sources for their cerous ion content, and by a different procedure for their chloride ion content. If our compounds were chemically pure, the concentration of the solutions calculated from these two different ion contents should check within experimental error.

The method of analysis used for the cerous ion content involved the precipitation of the cerium as the oxalate and igniting it to the oxide under conditions outlined by Sarver and Brinton[7] and Brinton and Pagel.[8]

Table I contains the results of these analyses, the concentrations being expressed in grams of cerous chloride per gram of solution. In each case the concentration cited is an average of three values. It can be seen that solution 1 gave values differing by about one part in a thousand, whereas the values for solution 2 differ by about three parts in a thousand.

TABLE I

	Concentration 1	Concentration 2
From chloride ion determination	0.4042	0.3499
From cerous ion determination	0.4037	0.3490

These values check within experimental error and therefore as far as chemical analysis is concerned the solutions seem to be chemically pure, solution 1 being more pure than 2. For this reason solution 1 was used in determining the Verdet constants which were the main object of this research.

However, a third test was at our disposal, that of magnetic rotation itself. If these two solutions were pure samples of cerous chloride, they should give the same rotation. In Table II are the results for the magnetic rotation of 2.00 molal solutions prepared from the stock solutions. The values were taken over a range of temperature and wave length in order to give a more rigorous comparison.

TABLE II

Temp., °C.	Wave length, Å.	Rotation in degrees 1	Rotation in degrees 2
20	6438	−1.74	−1.80
	5461	−2.90	−2.93
	4678	−4.84	−4.83
50	6438	−1.34	−1.36
	5461	−2.28	−2.31
	4678	−4.03	−4.04

Considering that the precision of the polarimeter alone is 0.02° for one rotation, the values in Table II stand in fairly good agreement except

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(1a) Pillai, *Indian J. Phys.*, **7**, 87 (1932).

(2) Chuckerbutti, *ibid.*, **8**, 387 (1933).

(3) Roberts, Wallace and Pierce, *Phil. Mag.*, Ser. 7, **17**, 934 (1934).

(4) Pernet, *Compt. rend.*, **195**, 376 (1932).

(5) Slack, Reeves and Peoples, *Phys. Rev.*, **46**, 724 (1934).

(6) Mason, Hickey and Wilson, THIS JOURNAL, **62**, 95 (1940).

(7) Sarver and Brinton, *ibid.*, **49**, 943 (1927).

(8) Brinton and Pagel, *ibid.*, **45**, 1460 (1923).

in the case of 20° and 6438Å. Even this discrepancy becomes less significant when one considers the difficulty of taking readings in the red end of the spectrum, due to the lack of intensity and the fact that the eye is not particularly sensitive to that region of the visible spectrum.

From these four tests of the purity of our samples, we felt warranted in making the conclusion that our samples were essentially chemically pure, solution 1 being more pure than solution 2, because the results from chemical analysis gave a better check. Therefore, we used solution 1 in all the work in refractive indices and Verdet constants that appear later in this investigation.

Results

The relationship of the magneto-optical rotation to the field strength and length of the light path is expressed by Verdet's law[9]

$$r = VHl \cos \alpha \qquad (1)$$

where r is the rotation in minutes, V is the Verdet constant, H is the field strength, l is the length of the light path in cm., and α is the angle between the path of light and the axis of the magnetic field. For the Faraday effect where the axis of the magnet and the rays of light are parallel, this law reduces to

$$r = VHl \qquad (2)$$

When an electromagnet of less than infinite length is used, this becomes

$$r = V \int H \, dl \qquad (3)$$

where $\int H \, dl$ is the average field strength over the light path used. If we choose to calibrate our cell with some pure liquid whose Verdet constant is known, such as water,[10] we find that

$$V = rV_s/r_s \qquad (4)$$

where r_s and V_s are the rotation and Verdet constants of the standard liquid used, and r and V are those for the solution being measured. The Verdet constants of the cerous chloride solutions were obtained by measuring the magnetic rotation of the various solutions and then computed by means of eq. (4). The results so obtained are given in Table III. Although the Verdet constants in the following table are in units of minutes per oersted-centimeter, they can be converted to M. K. S.[11] units of minutes per M. K. S. oersted-meter by multiplying by the proper factor.

(9) E. Verdet, *Ann. chim. phys.*, **41**, 370 (1854); **43**, 37 (1854); **52**, 129 (1858); **69**, 415 (1863).

(10) Rodger and Watson, *Z. physik. Chem.*, **19**, 356 (1896).

(11) Jauncey and Langsdorf, "M.K.S. Units and Dimensions," The Macmillan Co., New York, N. Y., 1940.

TABLE III

VERDET CONSTANTS OF CEROUS CHLORIDE SOLUTIONS

Weight molality	$V \times 10^3$ (minutes per oersted-centimeter) 4678Å.	5086Å.	5461Å.	5893Å.	6438Å.
		At 20° C.			
2.753	−43.82	−33.96	−27.16	−21.86	−17.04
2.50	−37.61	−28.87	−23.04	−18.59	−14.20
2.00	−25.93	−19.55	−15.54	−12.21	− 9.32
1.50	−14.30	−10.39	− 7.82	− 5.95	− 4.34
1.00	− 3.05	− 0.69	− 0.00	0.32	0.75
0.50	9.64	8.46	7.55	6.59	6.00
.25	15.80	13.34	11.52	9.86	8.41
.00	21.53	18.00	15.48	13.07	10.93
		At 25° C.			
2.753	−42.80	−33.05	−26.46	−21.27	−16.39
2.50	−36.59	−28.18	−22.45	−18.00	−13.82
2.00	−25.18	−18.80	−14.79	−11.73	− 8.89
1.50	−13.34	− 9.75	− 7.39	− 5.73	− 4.07
1.00	− 2.14	− 0.37	0.21	0.59	0.96
0.50	10.18	8.68	7.77	6.75	6.05
.25	15.86	13.39	11.62	9.91	8.46
.00	21.53	18.11	15.48	13.07	10.87
		At 30° C.			
2.753	−41.73	−32.14	−25.66	−20.73	−15.86
2.50	−35.57	−27.48	−21.80	−17.57	−13.55
2.00	−24.43	−18.11	−14.20	−11.30	− 8.46
1.50	−12.96	− 9.27	− 6.91	− 5.30	− 3.75
1.00	− 1.39	− 0.05	0.54	0.86	1.18
0.50	10.29	8.89	7.98	6.91	6.11
.25	15.96	13.45	11.73	9.96	8.52
.00	21.48	17.95	15.32	13.02	10.76
		At 40° C.			
2.753	−39.75	−30.64	−24.27	−19.66	−14.89
2.50	−34.02	−25.93	−20.57	−16.45	−12.59
2.00	−22.93	−16.77	−13.07	−10.45	− 7.82
1.50	−11.46	− 8.20	− 6.11	− 4.55	− 3.16
1.00	− 0.59	0.43	0.96	1.39	1.55
0.50	10.66	9.37	8.14	7.18	6.27
.25	16.18	13.61	11.95	10.07	8.57
.00	21.43	17.84	15.27	12.96	10.71
		At 50° C.			
2.753	−37.98	−28.87	−23.14	−18.64	−14.04
2.50	−31.93	−24.54	−19.50	−15.59	−11.95
2.00	−21.59	−15.64	−12.21	− 9.74	− 7.18
1.50	−10.39	− 7.39	− 5.30	− 4.07	− 2.79
1.00	0.32	1.07	1.66	1.82	1.87
0.50	11.14	9.05	8.46	7.39	6.43
.25	16.29	13.77	12.05	10.18	8.62
.00	21.32	17.73	15.16	12.86	10.66

The refractive indices which were obtained are expressed in terms of linear equations of the type $\eta = \eta_0 + am + bm^2$ where η is the refractive index, η_0 the refractive index of water, a and b are constants, and m is the molality. The values of the constants of these equations for refractive indices at 25° are given in Table IV, and the refractive indices reproduced by these equations are within the experimental error, namely ± 0.0002.

The refractive indices for temperatures from 20 to 40° can be calculated using the equation $\eta_t = \eta_{25} - (t - 25)F$ where η_t is the refractive index at temperature t, η_{25} is the refractive index at 25°, and F is the temperature coefficient, given in Table IV.

TABLE IV

CONSTANTS FOR THE EQUATIONS FOR THE REFRACTIVE INDICES OF CEROUS CHLORIDE SOLUTIONS AT 25°

Wave length, Å.	η_0	a	b
	$\eta = \eta_0 + am + bm^2$		
4678	1.33778	0.04806	−0.00300
5086	1.33564	.04757	− .00298
5461	1.33412	.04727	− .00297
5893	1.33265	.04686	− .00296
6438	1.33105	.04655	− .00294

$\eta_t = \eta_{25} - (t - 25)F$

Molality	2.753	2.50	2.00	1.50	1.00	0.50	0.25	0.00
$F \times 10^4$	1.47	1.45	1.42	1.38	1.33	1.27	1.24	1.20

It is interesting to see how the data and subsequent calculations advanced in this paper compare with values found by previous investigators.

As has already been mentioned, conflicting values for the Verdet constant of cerous chloride solutions already have been determined by Slack, Reeves and Peoples.[5] Table V will serve to show how their values compare with those of this research. The values submitted here as being taken from Slack, Reeves, and Peoples[5] are actually averages of their Verdet constants at 20° and 30°. This interpolation is entirely permissible, for they reported a linear relationship between temperature and Verdet constant, other factors being constant.

TABLE V

Molality	Wave length, Å.	Verdet constant × 10³ at 25° S. R. & P.	This paper
2.753	5893	−24.0	−21.2
	5461	−29.6	−26.4
2.077	5893	−14.0	−13.5
	5461	−17.3	−15.9
1.087	5893	− 0.58	− 0.4
	5461	− 1.15	− 1.1

Since the precision of the polarimeter is ±0.01° for any one reading, the precision of any rotation is naturally ±0.02°. Since all rotations were multiplied by a cell constant of 0.005357, the precision of all Verdet constants obtained using that cell would be of the order $\pm 0.11 \times 10^{-3}$. This precision does not take into consideration the contribution of errors due to temperature, current, and analytical discrepancies. Perhaps a reasonable estimation would place the total possible error in Verdet constants at $\pm 0.3 \times 10^{-3}$.

In view of this precision, it would seem that our results differ decidedly from the results of Slack, Reeves and Peoples. As would be expected, the difference increases with concentration of the solution, amounting to about 15% in the most concentrated solution. It hardly seems possible that this difference is due to the impurity of our samples or to error in our analyses when they were checked and rechecked so repeatedly. If our work is correct, then the deviation could only be explained by some error in the analysis of their solutions, the error probably lying in the incomplete ignition of the oxalate. They mention that their solutions had a brown color, even a precipitate in some cases. It may well have been that a reasonable concentration of reddish-brown ceric ions was present, for a pure solution of cerous chloride is water white. It might be added that the solutions used in this work were water white, and even after standing a year there had been no precipitation or discoloration.

Discussion

Okazaki[12] has published a series of papers on the Faraday effect in solutions of electrolytes. He has used the following modification of the Schönrock mixture rule

$$(w) = t_1(w_1) + t_2(w_2) \qquad (5)$$

where w, w_1, and w_2 are the specific rotations of the solution, solvent, and solute respectively, and t_1 and t_2 are the weight percentages of the solvent and the solute. The molecular rotation, $M(w)$, may easily be obtained by multiplying the specific rotation by the molecular weight. We have used this formula to compute the molecular rotation of the solute, $M(w_2)$ at 25°. The values so computed are included in Table VI. The densities used were taken from previous work.[13]

TABLE VI

MOLECULAR ROTATION OF CEROUS CHLORIDE

Weight molality	$M(w_2)$ 4678Å.	5086Å.	5461Å.	5893Å.	6438Å.
2.753	24.9	19.8	16.2	13.2	10.5
2.50	24.5	19.5	16.0	13.1	10.4
2.00	24.2	19.1	15.6	12.8	10.2
1.50	23.7	18.9	15.5	12.7	10.1
1.00	23.8	18.6	15.3	12.5	9.9
0.50	22.6	18.8	15.4	12.6	9.6
0.25	22.5	18.7	15.3	12.5	9.5

(12) A. Okazaki, *Royjun Coll. Eng., Mem.*, **6**, 181 (1933); *ibid.*, Inouye Commemoration Volume, 209 (1934); *ibid.*, **9**, 13, 101 (1936); **10**, 89, 115 (1937); **12**, 33, 45 (1939).

(13) Mason, THIS JOURNAL, **60**, 1644 (1938).

An examination of Table VI shows that the mixture rule (eq. 5) when applied to the data in Table III holds within limits of experimental error at concentrations below about 3 molal which represents about 40% anhydrous salt in the solutions. There are some discrepancies in the more dilute solutions but in this region where the rotation is small the errors of measurement are magnified in the computation of the Verdet constant and further magnified in the computations of the molecular rotation. These results in general confirm and are consistent with the results obtained by Okazaki[12] for many other electrolytes.

Roberts, Wallace and Pierce[3] have calculated for cerous sulfate solutions a quantity Δ/W which they call the "specific rotation." This is defined in the equation

$$\Delta = \frac{nV}{(n^2+2)^2 d} - \frac{n_w V_w}{(n_w^2+2)^2 d_w}\left(1 - \frac{W}{100}\right) \quad (6)$$

where n is the refractive index of the solution, n_w that for water, and W is the number of grams of salt per 100 g. of solution. V is the Verdet constant for the solution and V_w is that for water. From the theory from which this equation is developed, the quantity Δ/W should be independent of the concentration for any given wave length. This constant is independent of the concentration for cerous nitrate[6] and an examination of the data given in Table VII will show if this be true for the salts studied in this investigation.

Using the equation of Roberts, Wallace and Pierce[3] the corrected specific rotations (Δ/W) were calculated at 25° and the results are given in Table VII.

TABLE VII

CORRECTED SPECIFIC ROTATIONS

Weight molality	$-\Delta/W \times 10^3$ 4678Å.	5086Å.	5461Å.	5893Å.	6438Å.
2.753	8.93	7.12	5.84	4.79	3.81
2.50	8.86	7.07	5.81	4.74	3.79
2.00	8.87	7.02	5.76	4.73	3.77
1.50	8.81	7.05	5.79	4.77	3.79
1.00	8.98	7.02	5.81	4.75	3.78
0.50	8.65	7.20	5.90	4.84	3.69
0.25	8.68	7.24	5.93	4.86	3.71
Average	8.83	7.10	5.82	4.78	3.76

According to the theoretical background from which Δ/W was obtained, Δ/W should vary with the inverse square of the wave length. A plot (Fig. 1) shows this variation. This figure also shows the molecular rotation plotted as a function of the inverse square of the wave length. In both cases a linear plot was obtained within the experimental error. Recourse to Table VII however shows that Δ/W is not as constant as predicted by Roberts, Wallace and Pierce.

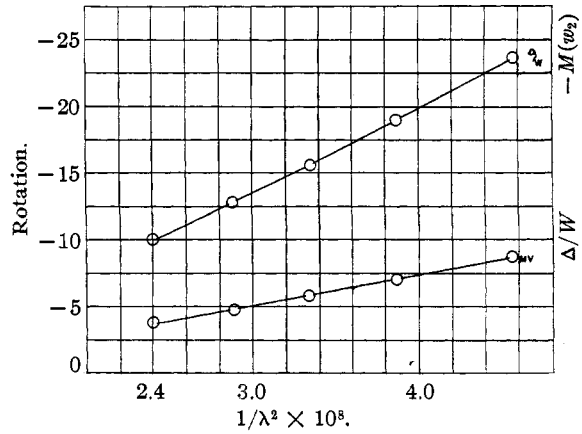

Fig. 1.—The variation of the calculated specific and molecular rotations with the reciprocal of the wave length.

Although there seems to be some tendency toward variation in the solutions, in general the constancy is pretty good. It might be noted here that although Roberts, Wallace and Pierce did find Δ/W to be constant for cerous sulfate, the solutions they investigated were less than 0.50 molal. Whether that constancy would have extended to more concentrated solutions will remain unknown, for cerous sulfate is relatively insoluble.

It is also worthy of note that the molecular rotations in Table VI show an effect somewhat the opposite to the variation in the corrected specific rotations. The values are essentially constant at low concentrations, but vary increasingly at higher concentrations. This effect might well be due to a variation from the mixture rule at higher concentrations.

Mlle. Pernet[4] has discussed the shape of the curves obtained from her work on the magnetic rotation of cerous chloride solutions, but she does not show these curves nor give sufficient data to construct them. However, she does state that for the mercury green line (5461Å.) zero rotation was obtained for a solution of 0.99 molality at 22.6°. Interpolation from a graph of our data will yield a Verdet constant of 0.40 for the same conditions at 25°. For that concentration value and wave length, the temperature coefficient for the Verdet constant is +0.50 per 10° centigrade, as interpolated from temperature variation for 1.00 molal solutions at that wave length. Such a

variation would give a Verdet constant of 0.15 for 0.99 molal solution at 22.6° and a wave length of 5461Å. This value agrees with Mlle. Pernet's within experimental error. But this agreement has no great significance, for similar agreement with Mlle. Pernet was reported by Slack, Reeves and Peoples. How workers who disagree widely elsewhere could agree with Mlle. Pernet and thus with each other is easily explained. The "Pernet Point" occurs in a concentration whose temperature coefficient is relatively small, and naturally any slight difference in concentration or temperature would be minimized there.

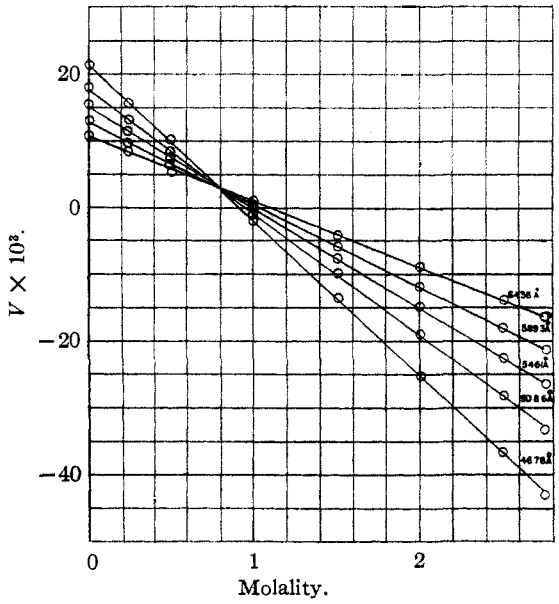

Fig. 2.—The variation of Verdet constant with concentration.

It is apparent, as shown in Fig. 2, that there is a straight line relationship between concentration and Verdet constants of cerous chloride solutions.

A straight line relationship between Verdet constant and temperature, other factors being constant was also obtained and it was apparent from these curves that the temperature coefficient (slope of curves) was greater in the more concentrated solutions.

We wish to thank Dr. William M. Meggers and the U. S. Bureau of Standards for supplying us with cerium material of known purity and Dr. Albert F. Daggett for assistance in the spectrographic analysis.

Summary and Conclusions

Two samples of cerous chloride have been prepared and found to be of a high degree of purity. The magnetic rotation of cerous chloride in aqueous solutions has been determined over a wide range of temperature and concentration. The refractive indices of cerous chloride solutions have been determined over a wide range of temperature and concentration.

It was found that the Verdet constants of cerous chloride solutions have a straight line relationship with concentration, other factors being constant. Also, there is a straight line relationship between Verdet constant and temperature.

Molecular rotations based on the Schönrock mixture rule are found to be strongly negative and show some variation with concentration, but are essentially constant at low concentrations.

Corrected specific rotations (Δ/W) based on the equation of Roberts, Wallace and Pierce[3] also show some variation with concentration but are essentially constant at high concentrations.

Furthermore, we have been unable to verify the values of Slack, Reeves and Peoples.[5] In view of the admitted discoloration of their solutions, and in view of the care taken in this work to test the purity of the cerous chloride used, it seems that a well-substantiated contradiction of their work is to be found in this report.

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