substitutions of water for ammonia is related to the probability of electronic transitions within the group.

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Summary

1. The visible absorption spectra of some chromammines and cobaltammines have been measured.

2. Certain empirical generalizations have been deduced from these measurements.

3. A theory has been put forth to account for the light absorption of complex compounds.

4. As a test of the theory, a prediction of the x-ray crystal analysis of a series of chromammines has been recorded.

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THE PRECISION WITH WHICH THE CONCENTRATIONS OF SOLUTIONS OF HYDROCHLORIC ACID AND SODIUM HYDROXIDE MAY BE DETERMINED WITH THE IMMERSION REFRACTOMETER

BY E. ROGER WASHBURN AND ALLEN L. OLSEN

The refractive index of solutions varies with the concentration. A curve may be prepared showing this variation and then if the refractive index of an unknown solution is determined, the concentration may be read from the curve, or calculated from the equation of the curve. In order to make an accurate determination, it is necessary that the solution contain no measurable amount of impurity and that the temperature at which the reading is taken be the same as that for which the curve and equation were determined. Since refractive index may be easily and accurately determined, it has been suggested[1] that the refractometer be used as a means of determining the concentrations of various standard solutions used in analytical chemistry.

The results of previous work on concentration–refractive index relation-

[1] H. H. Willard, *Ind. Eng. Chem., Anal. Ed.*, **2**, 201 (1930); C. A. Clemens, *J. Ind. Eng. Chem.*, **13**, 813 (1921); B. Wagner, *Z. angew. Chem.*, **33**, 249 (1920).

ships are recorded in standard reference works.[2]   A study of the original articles from which these tables have been compiled reveals the need for further work designed to determine the limits of precision within which the concentration of solutions may be measured by a study of the refractive index and precautions which must be taken in order to attain this accuracy. The usefulness of the method will be increased by the formulation of equations by which the normality may be calculated from refractive index.

Apparatus.—A Bausch and Lomb immersion refractometer, with a range of 1.32540 to 1.36639, was used in this investigation. A rectangular tank, provided by the makers of the instrument, was used to contain the cups of liquids during the time required to take the readings.

By siphoning water from an electrically heated, hand-controlled water-bath of thirty gallon capacity, we were able to maintain the temperature of the dipping tank to within $\pm 0.05°$ of the desired temperature during the time required to make the measurements. The temperatures in the bath and in the dipping tank were measured with calibrated thermometers graduated to 0.10°. The siphoned water in the refractometer tank was stirred with air, and the field was well illuminated with artificial light.

The pipets, burets and volumetric flasks used in preparing and standardizing the solutions were calibrated at 25.0°.

Solutions.—The water that was used in all of the experimental procedures was redistilled from an alkaline permanganate solution contained in a copper boiler fitted with a block tin condenser.

Hydrochloric Acid.—The hydrochloric acid solutions used in the major part of this study were prepared from freshly distilled samples of Grasselli c. p. quality acid. Some solutions were prepared by direct dilution of different samples of commercial c. p. acid. No significant differences were noted between the refractive indices of solutions of equal normality prepared from the two sources. The actual normality of each prepared solution was established by at least one of the following methods, gravimetric determination of silver chloride, the use of constant boiling hydrochloric acid prepared according to the method of Foulk and Hollingsworth[3] as a primary standard in making up the samples, or by quantitative dilution of a solution, the normality of which had been established by one of these procedures. The method used in each case is indicated in the table of results. All normalities were determined at 25.00°.

Sodium Hydroxide.—The sodium hydroxide solutions were prepared by the dilution of a saturated aqueous solution of Mallinckrodt reagent quality sodium hydroxide. Analysis[4] indicated that these solutions contained less than 0.5% sodium carbonate in terms of the sodium hydroxide content. The concentrations of the solutions of sodium hydroxide were determined by titration with hydrochloric acid which had been standardized by means of chloride analysis. Methyl orange was used as the indicator. Some of the test solutions were prepared by dilution of standard solutions and from the proportions used the concentrations were calculated. The solutions of sodium hydroxide

[2] Landolt-Börnstein, "Phys.-chem. Tab.," J. Springer, Berlin, Vol. II, 1923, pp. 988–990; "International Critical Tables," The McGraw-Hill Book Co., Inc., New York, 1929, Vol. VII, pp. 65–76; B. Wagner, "Tabellen zum Eintauchrefraktometer," Sondershausen, 1907.

[3] Foulk and Hollingsworth, This Journal, 45, 1220–1228 (1923).

[4] Treadwell-Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, 1928, 7th ed., Vol. II, p. 486.

were kept in bottles which had been coated with a rubber preparation designed to be resistant to alkali.[5] A few tests were run on solutions prepared by simply dissolving ordinary C. P. sodium hydroxide and U. S. P. X sodium hydroxide in water. The source of the different test solutions is indicated in the tables of results.

Measurement of Refractive Index.—Immersion refractometers are graduated in arbitrary scale divisions which may be converted into refractive indices by means of an equation or by conversion tables provided with the instrument. Since not all instruments have the same arbitrary scale, it is important to be sure that the conversion tables fit the instrument which is used. Our instrument was adjusted at each temperature to give the correct value for water. The uniformity of the scale and accuracy of the instrument were checked by measurement of the refractive indices of sodium chloride solutions. The results obtained, throughout the range of the instrument, checked accepted[6] values within ±0.00003 at 25.0°.

In view of the fact that a 1° change in temperature is equivalent to about 0.3 of a scale division or 0.00012 in refractive index for water, it is evident that temperature variations must be small. The variation which we allowed (±0.05°) is equivalent to about 0.015 scale division, which is less than the usual experimental error in reading the instrument. It was found necessary to wait several minutes after the refractometer was immersed in the solution for temperature equilibrium to be reached so that a sharp field and constant readings could be obtained.

That it is necessary to guard against evaporation from the liquid in the refractometer cups and that paraffined corks will effectively cut down evaporation are shown by the data in Table I. These readings were taken at 25.00° with an approximately 4 N solution of hydrochloric acid.

TABLE I

Open cups		Stoppered with paraffined corks	
Elapsed time, min.	Scale reading	Elapsed time, min.	Scale reading
0	99.56	0	99.56
24	99.58	20	99.58
69	99.57	62	99.55
108	99.63	103	99.55
221	100.03	254	99.57
994	101.62	917	99.68
1283	102.90	1263	99.68

The holes at each end of the rack in the dipping tank were not used as it was found that unequal illumination in these positions caused variable results.

The dipping prism of the refractometer is fastened in a mounting made

[5] Goodrich Thermoprene—Acid Seal Paint No. 1023, B. A. Soule, *Ind. Eng. Chem. Anal. Ed.*, **1**, 2 (1929).

[6] "International Critical Tables." The McGraw-Hill Book Co., Inc., New York Vol. VII, p. 73.

of an acid-resisting alloy. It was found that this dissolved slowly when in contact with concentrated solutions of hydrochloric acid and resulted in variable scale readings. The mounting was coated with a thin layer of paraffin which successfully prevented the corrosion and resulted in practically constant readings over a period of several hours.

Experimental Results

The refractive indices of a number of solutions of hydrochloric acid ranging in normality from 0 to 4, and of solutions of sodium hydroxide ranging in normality from 0 to 3, were determined at 20.00, 25.00 and 30.00°. The normalities of the solutions at 20.00 and 30.00° were calculated from the values measured at 25.00° making use of the densities and compositions listed in the "International Critical Tables."

From these results equations for each of the materials at each temperature were determined by substituting normalities and the corresponding refractive indices in the following general equation for a parabola:

$$N = A + B \text{ (ref. index soln.} - \text{ref. index water)} + C \text{ (ref. index soln.} - \text{ref. index water)}^2$$

N represents the normality of the chosen solution. Since with pure water N is zero, A is also zero, so an equation for the curve may be formulated by solving two simultaneous equations for B and C. A fourth or D term to be multiplied by the cube of the difference in refractive indices was not used because it was found that for the range of concentrations studied the agreement between the results calculated without the D term and the actual normality was within the experimental error of the method. Slightly different values for these constants resulted from using different combinations of solutions. Several combinations were used and from the constants obtained those given in the equations in Tables II and III were chosen as seeming to represent closely the relation between normality and refractive index for the system studied.

Test solutions were then prepared and the normalities calculated from refractive indices were compared with those obtained by standard methods. Since the agreement in these examples is in no sense different from that found with the original solutions studied, the results are listed together in the same tables.

In the case of hydrochloric acid, the greatest difference between the calculated normalities and the actual normalities is ± 0.005. This amounts to an error of $\pm 5.0\%$ with a 0.1 N solution, but to only 0.5% for a 1.0 N solution or 0.13% for a 4 N solution. The average difference, however, is only ± 0.002, which would be a percentage error of ± 1.0, ± 0.1 and ± 0.05 for 0.1 N, 1.0 N and 4.0 N, respectively.

The greatest difference between the calculated values and those obtained by analysis for sodium hydroxide is about ± 0.003 in normality

TABLE II

HYDROCHLORIC ACID AT 20.00°

$N = 119.1$ (ref. index HCl − ref. index H_2O) + 209 (ref. index HCl = ref. index $H_2O)^2$

Actual normality	Method of detn. of N	Refractive index	Calculated normality	Difference in normality
0.0000		1.33302		
.2430	Dil.	1.33507	0.2450	+0.0020
.4859	AgCl	1.33708	.4874	+ .0015
.8901	Dil.	1.34040	.8917	+ .0016
1.2562	AgCl	1.34336	1.2559	− .0003
1.5215	AgCl	1.34549	1.5196	− .0019
2.0262	Dil.	1.34950	2.0245	− .0017
2.5129	Dil.	1.35332	2.5116	− .0013
3.0401	AgCl	1.35738	3.0363	− .0038
3.4458	Dil.	1.36050	3.4468	+ .0010
4.0582	AgCl	1.36514	4.0612	+ .0030

At 25.00°

$N = 119.0$ (ref. index HCl − ref. index H_2O) + 253 (ref. index HCl − ref. index $H_2O)^2$

Actual normality	Method of detn. of N	Refractive index	Calculated normality	Difference in normality
0.0000		1.33251		
.1216	Dil.	1.33351	0.1192	−0.0024
.2428	Dil.	1.33457	.2460	+ .0032
.3041	AgCl	1.33506	.3049	+ .0008
.4853	AgCl	1.33659	.4898	+ .0045
.8549	AgCl	1.33956	.8513	− .0036
.8890	Dil.	1.33988	.8911	+ .0021
1.2545	AgCl	1.34283	1.2558	+ .0013
1.5194	AgCl	1.34495	1.5182	− .0012
2.0233	Dil.	1.34893	2.0222	− .0011
2.5089	Dil.	1.35269	2.5051	− .0038
3.0351	AgCl	1.35675	3.0337	− .0014
3.4399	Dil.	1.35985	3.4431	+ .0032
4.0510	AgCl	1.36441	4.0541	+ .0031

At 30.00°

$N = 118.9$ (ref. index HCl − ref. index H_2O) + 267 (ref. index HCl − ref. index $H_2O)^2$

Actual normality	Method of detn. of N	Refractive index	Calculated normality	Difference in normality
0.0000		1.33196		
.1214	Dil.	1.33299	0.1226	+0.0012
.1994	Const. boil.	1.33366	.2004	+ .0010
.2425	Dil.	1.33403	.2463	+ .0038
.2497	Const. boil.	1.33406	.2484	− .0013
.4440	Const. boil.	1.33566	.4411	− .0029
.6898	AgCl	1.33769	.6900	+ .0002
.8877	Dil.	1.33932	.8895	+ .0018
1.2525	AgCl	1.34227	1.2541	+ .0016
1.5170	AgCl	1.34435	1.5142	+ .0008
2.0200	Dil.	1.34833	2.0178	− .0022
2.6375	Dil.	1.35310	2.6328	− .0047
3.0298	AgCl	1.35610	3.0258	− .0040
3.4337	Dil.	1.35918	3.4341	+ .0004
3.9858	Const. boil.	1.36328	3.9884	+ .0026
4.0435	AgCl	1.36374	4.0482	+ .0047

TABLE III

SODIUM HYDROXIDE AT 20.00°

$N = 89.2$ (ref. index NaOH − ref. index H_2O) + 595 (ref. index NaOH − ref. index $H_2O)^2$

Source	Actual normality	Method of detn. of N	Refractive index	Calculated normality	Difference in normality
Water	0.000		1.33302		
Reagent	.197	Dil.	1.33517	0.195	− .002
Reagent	.328	Titr.	1.33660	.327	− .001
Reagent	.886	Titr.	1.34236	.884	− .002
Reagent	1.378	Dil.	1.34714	1.377	− .001
Reagent	1.805	Titr.	1.35110	1.805	.000
Reagent	2.462	Titr.	1.35685	2.463	+ .001
Reagent	2.791	Dil.	1.35962	2.793	+ .002
Reagent	3.288	Titr.	3.36364	3.289	+ .001

At 25.00°

$N = 90.7$ (ref. index NaOH − ref. index H_2O) + 585 (ref. index NaOH − ref. index $H_2O)^2$

Source	Actual normality	Method of detn. of N	Refractive index	Calculated normality	Difference in normality
Water	0.000		1.33251		
Reagent	.085	Titr.	1.33346	0.086	+0.001
Reagent	.197	Titr.	1.33467	.197	.000
Reagent	.265	Titr.	1.33543	.268	+ .003
Reagent	.327	Titr.	1.33605	.328	+ .001
Reagent	.478	Titr.	1.33763	.479	+ .001
Reagent	.528	Titr.	1.33826	.540	+ .002
Reagent	.625	Titr.	1.33912	.624	− .001
Reagent	.778	Titr.	1.34068	.778	.000
Reagent	.885	Titr.	1.34174	.886	+ .001
Reagent	1.376	Dil.	1.34644	1.375	− .001
Reagent	1.802	Titr.	1 35034	1.802	.000
Reagent	2.457	Titr.	1.35603	2.455	− .002
Reagent	2.785	Dil.	1.35879	2.785	.000
Reagent	3.280	Titr.	1.36279	3.280	.000
C. P.	0.116	Titr.	1.33379	0.117	+ .001
C. P.	.707	Titr.	1.33995	.706	− .001
C. P.	.756	Titr.	1.34043	.754	− .002
U. S. P. **X**	.143	Titr.	1.33407	.141	− .002
U. S. P. **X**	.323	Dil.	1.33602	.325	+ .002
U. S. P. **X**	.647	Titr.	1.33934	.647	.000

At 30.00°

$N = 92.3$ (ref. index NaOH − ref. index H_2O) + 550 (ref. index NaOH − ref. index $H_2O)^2$

Source	Actual normality	Method of detn. of N	Refractive index	Calculated normality	Difference in normality
Water	0.000		1.33196		
Reagent	.197	Dil.	1.33411	0.200	+0.003
Reagent	.326	Titr.	1.33551	.327	+ .001
Reagent	.884	Titr.	1.34108	.885	+ .001
Reagent	1.374	Dil.	1.34572	1.374	.000
Reagent	1.799	Titr.	1.34959	1.798	− .001
Reagent	2.452	Titr.	1.35530	2.453	+ .001
Reagent	2.779	Dil.	1.35803	2.780	+ .001
Reagent	3.273	Titr.	1.36204	3.273	.000

The percentage error would be ± 3, ± 0.3 and ± 0.1 for concentrations of 0.1, 1 and 3 normal, respectively. The average difference is ± 0.001, which, when applied to the three concentrations, would be a percentage error of ± 1, ± 0.1 and ± 0.03.

The differences between the calculated and the observed normalities of hydrochloric acid and sodium hydroxide are found to fall within the limits of precision which one would calculate from the slopes of curves plotted from the values in Tables II and III and from the accuracy with which one may read the refractometer. One unit in the fifth decimal place in refractive index (0.00001) corresponds to about 0.0012 in normality for hydrochloric acid and to about 0.0009 in normality for sodium hydroxide. The makers of the instrument state that an ordinary worker is able to read scale divisions with a precision of ± 0.2 and with a little practice to a ± 0.1. One-tenth of a scale division is equivalent to 0.00004 in refractive index. Therefore

$$\pm 0.2 \text{ in scale readings} = \begin{array}{l} \pm 0.0096 \text{ in } N \text{ for HCl} \\ \pm 0.0072 \text{ in } N \text{ for NaOH} \end{array}$$

$$\pm 0.1 \text{ in scale readings} = \begin{array}{l} \pm 0.0048 \text{ in } N \text{ for HCl} \\ \pm 0.0036 \text{ in } N \text{ for NaOH} \end{array}$$

Summary

The refractive indices for hydrochloric acid solutions up to 4 N and for sodium hydroxide solutions up to 3 N have been determined at 20.00, 25.00, 30.00°.

Equations relating normalities to refractive indices for these solutions have been formulated.

Several precautions which must be taken in order to obtain precision results with the immersion refractometer have been studied.

The limits of precision with which one may expect to determine the concentrations of these solutions by this method have been determined.

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