THE REFRACTIVE INDICES OF NON-AQUEOUS SOLUTIONS OF METALLIC CHLORIDES

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The refractive indices of solutions have been only slightly considered during the last few years, and information in this direction concerning non-aqueous solutions is especially rare. The authors have collected the following data on the subject and believe that they are worthy of consideration and an attempt at interpretation. We have been concerned primarily with the effect of salts of different types upon the refractive properties of closely related, yet distinctly different, solvents. Ethyl alcohol, methyl alcohol, and water were used as solvents. The salts were of two kinds: (1) Di-univalent salts, such as cupric chloride; and (2) tri- and quadri-univalent salts, aluminum, ferric, and stannic chlorides. Because of limited solubilities and of reactions with the solvent, it was not possible to study each salt in each solvent.

All measurements were made on a Zeiss-Pulfrich refractometer. The value of N, the refractive index, $\triangle N$, the refractive index increment, and R, the specific refraction, were calculated in the usual manner for a temperature of 25° C. Our measurements were made by using the D-line of the sodium spectrum.

Experimental

Materials. Absolute ethyl alcohol was prepared by treating one liter of 95 per cent grain alcohol first with 5 ml. of concentrated sulphuric acid, and then three times with 300 gms. of freshly prepared quicklime, 25 gms. of lead acetate being added with the third portion of lime. A distillation was made between each of the above steps, and the final product was redistilled through an efficient fractionating column. The first and last 100 ml. of distillate were discarded. Absolute methyl alcohol was prepared in essentially the same manner. Absolute ethyl acetate was distilled once from fused calcium chloride to remove any moisture present. Pure acetic acid was prepared from a good grade of glacial acetic acid by fractional crystallization.

Pure stannic chloride was made by distillation from a mixture of its hydrate, $SnCl_4 \cdot 5H_2O$, and concentrated sulphuric acid. Ferric chloride was prepared by passing chlorine over heated iron filings. Aluminum chloride was purified by sublimation. The remainder of the salts were prepared by dehydrating the purest salts obtainable. The usual precautions were taken to protect all of these materials from atmospheric moisture during storage.

Results. The refractive indices, the rates of increase of the index with increasing concentration of salt, and the specific refractions for the solutions studied are given in the accompanying tables (Tables I-V).

TABLE I

Solutions in Ethyl Alcohol

Concentration—Weight Fraction	$n_d^{25°}$	$\triangle n_d^{25°}$	r
Cupric Chloride—			
0.00000	1.358320	0.000000	....
0.00526	1.359032	0.000712	0.1297
0.01050	1.359744	0.001424	0.1772
0.02028	1.362068	0.003748	0.1514
0.04134	1.365126	0.006806	0.1590
0.07957	1.371798	0.013478	0.1416
Mercuric Chloride—			
0.00000	1.359437	0.000000	....
0.01008	1.359614	0.000177	0.0294
0.01996	1.360622	0.001186	0.0563
0.04164	1.362056	0.002620	0.0753
0.08035	1.365236	0.005800	0.0806
0.15020	1.370958	0.011522	0.0818
Nickel Chloride—			
0.00000	1.359820	0.000000	....
0.00192	1.360710	0.000890	0.0183
0.00382	1.361427	0.001607	0.0000
0.00757	1.362860	0.003040	−0.0385
0.01492	1.365841	0.006021	−0.0226
Cadmium Chloride—			
0.00000	1.359823	0.000000	....
0.00393	1.360357	0.000534	0.1193
0.00784	1.360713	0.000890	0.1172
0.01557	1.361250	0.001427	0.0952
0.03072	1.363220	0.003397	0.1075
Ferric Chloride—			
0.00000	1.358577	0.000000	....
0.00424	1.359645	0.001068	0.2274
0.00845	1.360713	0.002136	0.2189
0.01679	1.362414	0.003837	0.2166
0.03313	1.365753	0.007176	0.2044
0.06454	1.372345	0.013868	0.1969
Aluminum Chloride—			
0.00000	1.359378	0.000000	....
0.00380	1.360357	0.000979	0.1504
0.00757	1.361070	0.001692	0.1414
0.01501	1.363040	0.003662	0.1515
0.02955	1.366845	0.007467	0.1534
0.05734	1.374195	0.014817	0.1549
Stannic Chloride—			
0.00000	1.358666	0.000000	....
0.00550	1.359601	0.000935	0.1620
0.01095	1.360491	0.001825	0.1703
0.02172	1.361745	0.003079	0.1586
0.04266	1.364075	0.005409	0.1385
0.08242	1.369534	0.010868	0.1368

TABLE II

SOLUTIONS IN METHYL ALCOHOL

Concentration—Weight Fraction	$n_d^{25°}$	$\triangle n_d^{25°}$	r
MERCURIC CHLORIDE—			
0.00000	1.326935	0.000000	....
0.01070	1.328214	0.001279	0.0975
0.02110	1.329270	0.002335	0.0933
0.04150	1.331027	0.004092	0.0883
0.08010	1.334445	0.007510	0.0876
0.14970	1.341260	0.014325	0.0883
CUPRIC CHLORIDE—			
0.00000	1.327095	0.000000	....
0.00530	1.327695	0.000600	0.0367
0.01060	1.328376	0.001281	0.0679
0.02100	1.330344	0.003249	0.1068
0.04100	1.334613	0.007518	0.1296
0.07900	1.342510	0.015415	0.1377
NICKEL CHLORIDE—			
0.00000	1.328207	0.000000	....
0.00940	1.330404	0.002197	0.1193
0.01870	1.332873	0.004666	0.1189
0.03650	1.337933	0.009726	0.1182
0.06990	1.347498	0.019291	0.1230
STANNIC CHLORIDE—			
0.00000	1.327385	0.000000	....
0.00500	1.327760	0.000375	0.0903
0.01000	1.328670	0.001285	0.1381
0.01980	1.329648	0.002263	0.1329
0.03890	1.332490	0.005105	0.1324
0.07550	1.337380	0.009995	0.1333
FERRIC CHLORIDE—			
0.00000	1.327460	0.000000	....
0.00710	1.329195	0.001735	0.1976
0.01440	1.330642	0.003182	0.1573
0.02780	1.333660	0.006200	0.1893
0.05440	1.339630	0.012170	0.1913
0.10430	1.351082	0.023622	0.1937

Discussion of Results

The refractive indices of all the solutions studied were found to be linear functions of the concentration, except for slight abnormalities at low concentrations in the solutions of ferric chloride and stannic chloride in ethyl alcohol and mercuric chloride in methyl alcohol. Similar deviations for ethyl and methyl alcohol solutions of cadmium iodide have been reported by Getman and Gibbons,[1] who attributed them to experimental error. Our ability to reproduce the results that show these abnormalities leads us to believe, however, that they are probably caused by association between solute and solvent or are dependent upon some abnormal

[1]Getman and Gibbons, 1915. J. Am. Chem. Soc. 57:1990.

TABLE III

SOLUTIONS IN WATER

Concentration—Weight Fraction	$n_d^{25°}$	$\triangle n_d^{25°}$	r
CADMIUM CHLORIDE—			
0.00000	1.332594	0.000000	....
0.00190	1.332958	0.000364	0.1250
0.00378	1.333270	0.000676	0.1185
0.00760	1.333816	0.001222	0.1392
0.01500	1.334998	0.002404	0.1109
0.02960	1.337180	0.004586	0.1136
NICKEL CHLORIDE—			
0.00000	1.332607	0.000000	....
0.00290	1.333309	0.000702	0.1396
0.00570	1.333894	0.001287	0.1280
0.01140	1.335235	0.002628	0.1463
0.02250	1.337780	0.005173	0.1397
0.04410	1.342910	0.010303	0.1397
ALUMINUM CHLORIDE—			
0.00000	1.332646	0.000000	....
0.00230	1.333270	0.000624	0.1489
0.00470	1.333833	0.001187	0.1484
0.00930	1.335314	0.002668	0.1708
0.01840	1.338100	0.005454	0.1678
0.03610	1.345699	0.011053	0.1731

TABLE IVa

ETHYL ALCOHOL AND WATER

Concentration—Weight Fraction EtOH	$n_d^{25°}$	r EtOH	r H_2O
0.0000	1.332413	....	0.2060
0.1637	1.343657	0.2743	0.2048
0.3436	1.354094	0.2781	0.2048
0.5400	1.360090	0.2784	0.2037
0.7580	1.362681	0.2793	0.2027
0.8757	1.362058	0.2797	0.2046
0.9494	1.360535	0.2801	0.2012
1.0000	1.358933	0.2803	....

effect that involves the ionization of the salt and the independence of its ions.

The belief has been generally held that the members of a series of salts increase the index of refraction in the inverse order of their molecular weights. Our results show, however, that this is not strictly true. Ferric, aluminum, and stannic chlorides are the only salts of those investigated that do not conform to this rule. The abnormalities in the solutions of these salts are always in the direction of a greater increase in the index than that predicted on the basis of molecular weight.

TABLE IVb

ALUMINUM CHLORIDE IN ETHYL ALCOHOL AND WATER

Solvent Composition—mol-fraction H_2O	$AlCl_3$ Concentration mols per liter	$n_d^{25°}$
0.147	0.0000	1.360900
	0.1874	1.368210
	0.3748	1.375036
0.302	0.0000	1.362300
	0.1874	1.369212
	0.3748	1.375318
0.449	0.0000	1.362681
	0.0937	1.366845
	0.1874	1.369948
	0.3748	1.376065
0.685	0.0000	1.360090
	0.0937	1.364030
	0.1874	1.367118
	0.3748	1.373270
0.830	0.0000	1.354094
	0.0937	1.358399
	0.1874	1.361610
	0.3748	1.367846
0.929	0.0000	1.343657
	0.0937	1.345908
	0.1874	1.349205
	0.3748	1.355670

TABLE V

STANNIC CHLORIDE IN ETHYL ACETATE

Concentration—Weight Fraction	$n_d^{25°}$	$\triangle n_d^{25°}$	r
0.00000	1.363040	0.000000	....
0.00390	1.369396	0.006356	0.3894
0.00770	1.371512	0.008470	0.2782
0.01500	1.374009	0.010969	0.2013
0.03070	1.380300	0.017260	0.1687
0.06080	1.391964	0.028924	0.1552

A comparison of the refractive indices of the same salt in different solvents shows that, in general, the order of the rate of increase of the refractive index is greater in water than in methyl alcohol, and greater in methyl than in ethyl alcohol. We are led, therefore, to the conclusion that the refractive index of a solution is increased in proportion to the independence exhibited by the ions of the salt in the solution, since the order of increasing dielectric constants is ethyl alcohol, methyl alcohol, and water. The solutions of mercuric chloride, a salt that ionizes but slightly in any solvent, show the least refractive power of all the solutions studied. The molecular weight of mercuric chloride is probably responsible in part, however, for these results.

The specific refractions of all the salts show only slight abnormalities, and these usually occur in the solutions of the lowest concentrations. They may be due, in whole or in part, to slight experimental errors, which are greatly magnified for dilute solutions in the calculation of specific refractions, because of the small differences in the indices of refraction for these solutions. The following significant fact is to be noted in the majority of the cases: The specific refraction of any one salt approaches a constant value as the concentration is increased, and this constant is approximately the same for the same salt in all the solvents. The extremely small specific refraction in the ethyl alcohol solution of nickel chloride amounts to anomalous behavior of this salt in this solvent. It indicates that a compound is probably formed between these two substances, since the same solutions show similar anomalous results in densities. In this connection, however, it is interesting to note the refractive indices and specific refractions of solutions of stannic chloride in ethyl acetate (Table 5). The solute and solvent undoubtedly combine in these solutions. No values of r differing as widely as those for the stannic chloride-ethyl acetate solutions are found for any salt in alcoholic or aqueous solutions. Hence, chemical combination, or whatever factor is responsible for the effects observed in the ethyl acetate medium, is not a very prominent factor, at any rate, in the solutions with which the major interest of this investigation is concerned.

The specific refractions of water and ethyl alcohol in different mixtures of the two liquids are shown in Table IVa. These are seen to be almost constant throughout the entire range of concentrations but show a definite, although slight, decrease as the concentration of the component decreases. These results confirm, in general, those of Andrews[2] and show a maximum index for the mixture containing 0.42 mole-fraction of water.

The indices of refraction for solutions of aluminum chloride in different mixtures of ethyl alcohol and water are shown in Table IVb. The salt has a much greater effect in increasing the index of the solutions containing large mole-fractions of ethyl alcohol than it has upon those containing the largest mole-fraction of water. The rate of increase in refractive power with increasing concentration of aluminum chlorides is less for all the mixtures than for the single solvent. These results may be interpreted as the effect of the salt in increasing the association between the two solvents.

[2]Andrews, 1908. J. Amer. Chem. Soc. 30:358.