Some Electrolyte Solution Refractive Indices at 5893 and 6328 A.

R. N. O'BRIEN[1]
Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada

The refractive index of various electrolyte solutions of interest to electrochemists and others are given. The effects of concentration, temperature, and pH are shown. Data are given at either 5893 or 6328 A. and, in some cases, at both.

THE use of refractive index as the variant property in following chemical and physical processes is growing. Recently, it has been used as the control variable in chemical process industries, and it has always been used in the sugar refining industry as an assay of sugar content of solutions. In research, organic chemists have used it, and recently schlieren patterns have been used intensively in ultracentrifuge, electrophoresis, and diffusion studies. Refractive index data are needed to interpret schlieren results quantitatively. Interferometry has also been enjoying an upsurge in popularity. In most interferometric work, the refractive index is known (it is 1 in air) or it is not the variable being measured. This laboratory has published results obtained by interferometry in the field of electrochemistry but has not published the refractive index data amassed in the process.

With the advent of a truly monochromatic collimated uniphase output source, the gas laser, the use of refractive index and interferometry in chemical research and industrial process control should rapidly increase. What few refractive index data are available are almost all taken at the sodium D line wavelength (5893 A.). These data have limited usefulness, since refractive index changes with wavelength, and sodium light has neither sufficient temporal nor spatial coherence to be useful in longpath interferometry of condensed phases. The most common wavelength in the future would appear to be that of the gas laser. For this reason, data in this field and especially at the common gas laser frequency (6328 A.) are presented.

DATA

All refractive indices were obtained with a Pulfrich, manufacturer's rated accuracy ±0.00002, or a thermostatically controlled Precision Bausch and Lomb refractometer, manufacturer's rated accuracy ±0.00005, using either a sodium vapor lamp (5893 A.) or Spectra-Physics

Table I. Refractive Index of Pure Water[a] at Various Temperatures

Temp., °C.	Refractive Index 5893 A.	5893 A. (*1*)	6328 A.
0	1.33377		
5	1.33371		
10	1.33364		1.33412
15	1.33346	1.33339	1.33393
20	1.33294	1.33299	1.33367
25	1.33248	1.33250	1.33315
30	1.33183	1.33194	1.33258
35			1.33199
40			1.33130
45			1.33060
50			1.32993

[a] 4x Distilled.

[1] Present address: University of Victoria, Victoria, British Columbia, Canada

Table II. Effect of pH on the Refractive Index of Various $CuSO_4$ Solutions at 25° C. (5893 A.)

pH	Concn., *M*	Refractive Index
	0.7422*M* $CuSO_4$	
1.1	0.6330	1.35083
2.1	0.5938	1.34936
3.05	0.5938	1.35261
3.5	0.5938	1.34910
3.95	0.5938	1.34898
4.4, ppt.	0.4430	1.34131
4.9, ppt.	0.3787	1.33862
5.6, ppt.	0.3549	1.33790
5.95, ppt.	0.3586	1.33790
6.4, ppt.	0.3528	1.33790
pH of 0.7422*M* $CuSO_4$ = 3.25		
	0.500*M* $CuSO_4$	
1.1	0.400	1.34470
2.1	0.400	1.34387
3.0	0.400	1.34393
3.48	0.400	1.34374
3.95, ppt.	0.400	1.34387
4.45, ppt.	0.3411	1.33926
5.0, ppt.	0.2992	1.33713
5.4, ppt.	0.2942	1.33700
5.95, ppt.	0.2889	1.33693
6.4, ppt.	0.2889	1.33674
pH of 0.400*M* $CuSO_4$ = 3.48		
	0.200*M* $CuSO_4$	
1.1	0.1600	1.33803
2.1	0.1600	1.33752
3.0	0.1600	1.33713
3.45	0.1600	1.33707
4.05, ppt.	0.1600	1.33707
4.40, ppt.	0.1600	1.33707
5.0, ppt.	0.1584	1.33500
5.6, ppt.	0.1543	1.33480
6.1, ppt.	0.1556	1.33480
6.6, ppt.	0.1550	1.33480
pH of 0.200*M* $CuSO_4$ = 3.80		
	0.1*M* $CuSO_4$	
1.1	0.08	1.33558
2.0	0.08	1.33500
2.9	0.08	1.33487
3.41	0.08	1.33487
4.0	0.08	1.33480
4.4, ppt.	0.08	1.33467
5.0, ppt.	0.0889	1.33390
5.5, ppt.	0.0877	1.33371
5.9, ppt.	0.0871	1.33371
6.5, ppt.	0.0858	1.33384
pH of 0.1*M* $CuSO_4$ = 4		

Table III. Effect of pH on the Refractive Index of Various $ZnSO_4$ Solutions at 25° C. (5893 A.)

pH	Concn., N	Refractive Index
	$0.3N$ $ZnSO_4$	
1.2	0.26	1.33661
2.1	0.29	1.33616
3.15	0.30	1.33609
3.9	0.30	1.33609
5.1	0.30	1.33616
6.1, ppt.	0.30	1.33609
7.2, ppt.	0.25	1.33410
8.2, ppt.	0.25	1.33416
9.2, ppt.	0.26	1.33416
9.95,, ppt.	0.24	1.33403
10.95, ppt.	0.24	1.33403
11.85, ppt.	0.24	1.33448
pH of $0.3N$ $ZnSO_4$ = 5.65		
	$0.2N$ $ZnSO_4$	
1.2	0.18	1.33519
2.1	0.20	1.33474
3.15	0.20	1.33467
4.2	0.20	1.33467
5.15	0.20	1.33467
5.85	0.26	1.33467
7.0, ppt.	0.18	1.33338
7.95, ppt.	0.18	1.33332
8.8, ppt.	0.18	1.33338
9.95, ppt.	0.18	1.33338
11.2, ppt.	0.17	1.33364
11.85, ppt.	0.17	1.33397
pH of $0.2N$ $ZnSO_4$ = 5.85		

pH	Concn., N	Refractive Index
	$0.138N$ $ZnSO_4$	
1.1	0.129	1.33467
2.0	0.137	1.33390
2.75	0.138	1.33390
3.95	0.136	1.33397
4.7	0.137	1.33390
6.2, ppt.	0.137	1.33390
6.9, ppt.	0.127	1.33313
8.0, ppt.	0.125	1.33306
8.9, ppt.	0.125	1.33306
10.0, ppt.	0.124	1.33313
11.2, ppt.	0.123	1.33319
11.8, ppt.	0.118	1.33351
pH of $0.138N$ $ZnSO_4$ = 2.75		
	$0.1N$ $ZnSO_4$	
1.1	0.092	1.33435
2.1	0.099	1.33364
2.9	0.10	1.33351
4.15	0.10	1.33351
4.8	0.098	1.33351
6.05, ppt.	0.099	1.33351
6.8, ppt.	0.095	1.33306
7.8, ppt.	0.093	1.33294
8.95, ppt.	0.093	1.33294
10.1, ppt.	0.092	1.33294
11.1, ppt.	0.092	1.33306
11.7, ppt.	0.090	1.33319
pH of $0.1N$ $ZnSO_4$ = 2.9		
	$0.01N$ $ZnSO_4$	
1.1	0.0095	1.33019
1.9	0.0099	1.33242
2.9	0.01	1.33222
4.15	0.0097	1.33229
5.30	0.0096	1.33229
6.2, ppt.	0.01	1.33222
6.9, ppt.	0.01	1.33222
7.85, ppt.	0.0089	1.33281
8.8, ppt.	0.0098	1.33222
10.05, ppt.	0.0099	1.33216
11.1, ppt.	0.0099	1.33222
11.8, ppt.	0.0098	1.33229
pH of $0.01N$ $ZnSO_4$ = 3.72		

Model 130 gas laser (6328 A.). The two refractometers agreed within the manufacturer's stated accuracies. All solutions were made up from water initially double distilled (once from permanganate solution), then in a duplex quartz still, and finally freshly boiled and cooled out of contact with air. Solutions were then made by adding the required part of a molecular weight of solute to give the required molarity or normality to a volumetric flask, and the distilled water was then added to the mark with as little exposure to air as possible. No correction was made for the buoyancy of air in weighings.

M indicates molarity defined as the number of moles of solute (the weight in grams of Avogadro's number of molecules) in 1 liter of solution at 25° C. N indicates the normality defined as the number of equivalents of solute (the weight in grams required to react with or replace the weight in grams of Avogadro's number of hydrogen atoms) in 1 liter of solution at 25° C.

Table I gives the refractive index of quadruple-distilled water at various temperatures at 5893 and 6328 A. One of the distillations was from $KMnO_4$ and two from a quartz still. The data of Tilton and Taylor (*1*) are given for comparison.

Table II shows the effect of adjusting the pH of various

Table IV. Effect of Temperature on the Refractive Index of $CuSO_4$ and $ZnSO_4$ Solutions at Various Concentrations (5893 A.)

1.0 to 0.10N $CuSO_4$

Temp., °C.	1.0N	0.80N	0.60N	0.40N	0.20N	0.10N
40	1.34605	1.34322	1.34007	1.33707	1.33397	1.33248
35	1.34665	1.34373	1.34072	1.33777	1.33468	1.33300
30	1.34779	1.34467	1.34156	1.33842	1.33538	1.33371
25	1.34810	1.34520	1.34221	1.33881	1.33596	1.33429
20	1.34872	1.34584	1.34266	1.33944	1.33643	1.33468
15	1.34930	1.34623	1.34311	1.33996	1.33681	1.33513
10	1.34977	1.34668	1.34355	1.34035	1.33720	1.33545
5		1.34702	1.34375	1.34067	1.33734	1.33564
0	1.35045	1.34727	1.34413	1.34092	1.33752	1.33585

0.080 to 0.010N $CuSO_4$

Temp., °C.	0.080N	0.060N	0.040N	0.020N	0.010N
35	1.33275	1.33247			
30	1.33337	1.33307			
25	1.33402	1.33370	1.33345	1.33293	1.33281
20	1.33435	1.33403	1.33390	1.33337	1.33320
15	1.33476	1.33436	1.33411	1.33364	1.33346
10	1.33513	1.33474	1.33448	1.33402	1.33384
5	1.33534	1.33483	1.33474	1.33429	1.33410
0	1.33545	1.33512	1.33492	1.33492	1.33422

1.0 to 0.07N $ZnSO_4$

Temp., °C.	1.0N	0.40N	0.30N	0.20N	0.10N	0.07N
40	1.34329	1.33577	1.33435	1.33306	1.33183	...
35	1.34393	1.33642	1.33500	1.33377	1.33255	1.33209
30	1.34470	1.33713	1.33578	1.33455	1.33326	1.33287
25	1.34560	1.33810	1.33674	1.33545	1.33416	1.33371
20	1.34623	1.33862	1.33726	1.33603	1.33468	1.33429
15	1.34662	1.33894	1.33758	1.33629	1.33500	1.33455
10	1.34662	1.33901	1.33758	1.33642	1.33500	1.33455
5	1.34643	1.33919	1.33778	1.33648	1.33506	1.33467
0	1.34732	1.33939	1.33790	1.33655	1.33519	1.33480

0.05 to 0.001N $ZnSO_4$

Temp., °C.	0.05N	0.02N	0.01N	0.007N	0.005N	0.002N	0.001N
30	1.33261	1.33216	1.33203	1.33203	1.33203	1.33196	1.33190
25	1.33346	1.33307	1.33294	1.33287	1.33287	1.33287	1.33287
20	1.33410	1.33364	1.33345	1.33338	1.33338	1.33338	1.33332
15	1.33429	1.33390	1.33384	1.33377	1.33371	1.33364	1.33364
10	1.33436	1.33390	1.33377	1.33371	1.33371	1.33364	1.33364
5	1.33435	1.33397	1.33384	1.33377	1.33377	1.33377	1.33371
0	1.33448	1.33403	1.33390	1.33384	1.33384	1.33377	1.33377

concentrations of cupric sulfate with H_2SO_4 or NaOH. Wherever the notation ppt. occurs, a solid has precipitated out and the refractive index refers to the clear solution only, which will not, therefore, be identical with the concentration shown. The concentration shown was obtained from dilution calculations but not using solubility product or hydrolysis data. All cupric ion concentrations were made with quadruple-distilled water and Analar grade $CuSO_4$. The concentration was determined by EDTA titration. The EDTA solution was standardized in the usual way against $CaCO_3$. The NaOH was standardized against potassium acid phthalate and the H_2SO_4 was standardized against the NaOH. No solution was kept for more than 5 days without being restandardized.

Table V. Refractive Indices of Some Common Electrolyte Solutions at 25° C. and 6328 A.

Concn., M	Refractive Index NaCl	KCl	$CaCl_2$
1	1.34329	1.34253	1.35783
0.5	1.33817	1.33786	1.34572
0.2	1.33502	1.33496	1.33799
0.1	1.33405	1.33399	1.33554
0.05	1.33361	1.33340	1.33425
0.03	1.33340	1.33321	1.33367
0.02	1.33329	1.33302	1.33341
0.01	1.33315	1.33296	1.33315

Table VI. Refractive Indices of Various Salt Solutions at 25° C. and 6328 A.

Concn. N	Refractive Index
Cupric Nitrate	
1.1670	1.34917
0.9331	1.34591
0.7124	1.34290
0.4672	1.33932
0.2543	1.33609
0.1171	1.33429
0.0919	1.33402
0.0737	1.33370
0.0439	1.33332
0.0224	1.33300
1.0545	1.34738
0.8192	1.34412
Cupric Perchlorate	
0.8920	1.34476
0.7136	1.34233
0.5352	1.33990
0.4460	1.33874
0.3568	1.33752
0.2676	1.33625
0.1784	1.33496
0.0713	1.33345
0.0357	1.33300
0.0176	1.33270
Zinc Perchlorate	
0.7584	1.34380
0.7669	1.34150
0.5750	1.33932
0.4792	1.33822
0.3833	1.33706
0.2875	1.33596
0.1916	1.33487
0.0950	1.33370
0.0383	1.33303
Silver Nitrate	
1.0728	1.35115
0.8593	1.34674
0.6722	1.34425
0.4234	1.33996
0.2218	1.33642
0.1034	1.33435
0.0897	1.33416
0.0630	1.33364
0.0408	1.33332
0.0257	1.33306
Ferrous Perchlorate	
1.4537	1.34591
1.1630	1.34329
Ferrous Perchlorate	
0.5815	1.33790
0.8722	1.34073
0.4361	1.33673
0.2567	1.33525
0.1253	1.33325
0.0581	1.33313
Ferric Nitrate	
3.0161	1.35293
2.6951	1.35128
2.4116	1.34991
2.0907	1.34668
1.4537	1.34259
1.8265	1.34502
0.8891	1.33874
0.6020	1.33680
0.3004	1.33461
0.1230	1.33325
Ferric Chloride	
1.3822	1.35261
1.1057	1.34872
0.8293	1.34476
0.5528	1.34079
Ferric Chloride	
0.4146	1.33887
0.2764	1.33680
0.1387	1.33468
0.0553	1.33351
0.0276	1.33325
0.7198	1.35083
0.6405	1.34923
0.5180	1.34623
0.4364	1.34406
0.2904	1.34028
0.2007	1.33797
0.1492	1.33648
0.0660	1.33319
0.0285	1.33280
Ferrous Sulfate	
0.9271	1.35325
0.7417	1.34910
0.3708	1.34124
0.2781	1.33919
0.1854	1.33700
0.1112	1.35532
0.0742	1.33429
0.0371	1.33351

The analogous data for $ZnSO_4$ is given in Table III. The $ZnSO_4$ was prepared and the concentration determined in the same way. Table IV shows the effect of temperature over the range 0° to 40° C. and concentrations from 1.0 to 0.1N at 5893 A. for $CuSO_4$ and $ZnSO_4$. The thermostat supplied water at ±0.1° C. of the temperature shown. No readings were taken until the effluent coolant was within 0.5° C. of the thermostat.

Table V gives the refractive indices of several electrolyte solutions at varying concentrations, 25° C. and 6328A. Table VI gives the refractive indices of various concentrations of electrolyte solutions important in electrochemistry at 6328 A.

In the use of the data, it is suggested that the user keep in mind that no correction has been made for weighing in air, so that accuracy is limited by this factor but not precision. Also, in Table I where literature data are available, the agreement at 25° C. is within less than half of the manufacturer's rated accuracy (0.00002 *vs.* ±0.00005) but, at temperatures above and below, discrepancies develop. The author felt this was due to dissolved gases in the literature data solutions since these cause refractive index changes of the order of 0.0001 at room temperature and 1 atm. A large scale plot of the data and values obtained from a smooth curve through them is to be recommended.

ACKNOWLEDGMENT

The author thanks K. Kinoshita, P. Seto, H. L. Sawhney, M. Tessman, and W. F. Yakymyshyn, who did the experimental work. A table of corrections for the Bausch and Lomb Precision Refractometer for 6328 A. was kindly supplied by the manufacturer of the instrument, using a computer program. This service, the author believes, is readily available.

LITERATURE CITED

(1) Tilton, L.W., Taylor, J.K., *J. Res. Natl. Bur. Std.* **20**, 419 (1938).

RECEIVED for review February 1, 1966. Accepted October 16, 1967. Work partially supported by the National Research Council and the Defense Research Board of Canada.