Use of He-Ne Laser with Abbé Refractometer to Obtain Some Electrolyte Refractive Indices

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The difficulties encountered in using laser light for refractive index measurements in an Abbé refractometer have been overcome by the use of a rotating diffuser disc. Refractive indices of some simple and complex electrolyte solutions are listed. Accuracy is believed to exceed the manufacturer's specifications.

Refractive index data of electrolyte systems at the common He-Ne laser frequency (6328Å) has previously been published *(3, 4)*. Considerable difficulty in obtaining a sharp division between the dark and light fields in the viewing telescope of a Bausch & Lomb Precision Abbé refractometer had been encountered. Laser light, because of its coherency, is passed through a diffusing plate to fully illuminate the prism. However, associated with this diffuse light source is a well-defined speckle pattern consisting of light and dark spots caused by the granularity of the diffusing surface, and readily observable in the viewing field of the refractometer. The problem can be solved by insertion of a rotating, light-diffusing disc which, as shown in Figure 1, consists of a perspex disc lightly scratched with emery paper and set as close to the refractometer as possible. The apparent visibility of the speckle pattern is markedly reduced and the net result is the formation of light and dark fields of constant intensity. Correct speeds for good light diffusing are easily discovered as the dark-to-light dividing line in the field of view changes abruptly from that shown as *A* in Figure 1 to *B*. The need for diffuse light is explained by the finite thickness of the liquid layer between the two prisms and is detailed in Bauer and Lewis *(1)*. The temperature was controlled at 25° ± 0.02°C.

All reagents were analar grade, and solutions were made up gravimetrically with water distilled four times, then diluted as needed. Five decimal places were carried in all cases. The manufacturer suggests an accuracy and reproducibility of ±0.00005. Our experience indicates that with the laser light source and a properly rotated and positioned scattering disc estimation between marks on the vernier scale is the limiting factor and that the fifth decimal place digit is significant. A modification to the vernier has been designed and will be reported on when in use. The refractometer scale readings could be converted to refractive index values of 6328Å through a computer printout supplied by the manufacturer.

The refractive index value for pure water at 25°C and 6328Å from Table I is 1.33126. This value is in good agreement with that obtained by interpolating the refractive index values between 6350 and 6300Å from the standard work of Tilton and Taylor *(5)* (1.331263). The accuracy of measurement was checked with an API standard sample of toluene. The modified Hartmann equation *(2)* was used to interpolate between the certi-

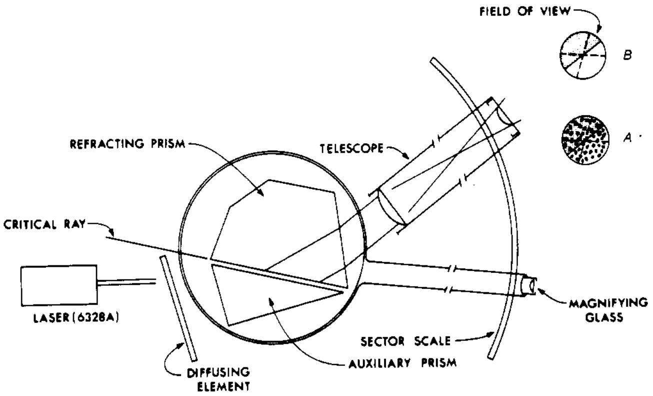

Figure 1. Schematic of Abbé precision refractometer showing field of view without rotating diffuser disc *(lower)* and with it *(upper)*

Table I. Refractive Index of KCl–HCl Water Solutions at 25°C

KCl (*M*)	HCl concn (*M*) 0	0.00001	0.0001	0.001	0.01	0.1	1.0
0	1.33126				1.33136	1.33214	
0.0001	1.33127	1.33127	1.33127	1.33128	1.33133		
0.0005	1.33127	1.33126	1.33122		1.33134		
0.001	1.33127	1.33126	1.33127	1.33127			1.33940
0.002	1.33127	1.33129	1.33127	1.33127			
0.005	1.33128		1.33132		1.33138		
0.01	1.33133		1.33135			1.33221	1.33959
0.02	1.33140			1.33145			
0.05	1.33172			1.33172	1.33179		1.33995
0.1	1.33218			1.33221	1.33225	1.33304	1.34155
0.2	1.33327			1.33328	1.33336	1.33408	1.34263
0.3	1.33425						
0.5	1.33580						
1.0	1.34088						

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fied refractive index values to obtain a refractive index value of 1.49105 corresponding to 6328Å at 25°C. The determined value was 1.49107 which is within the uncertainty in refractive index of the API standard estimated at ±0.00003.

Data

All data reported in Tables I–VI were plotted. All simple solutions in which only one solute was present displayed a straight-line dependence of refractive index vs. concentration over the ranges reported. In Table I various concentrations of KCl in increasing concentrations of HCl were found to behave like simple solutions yielding straight-line refractive index vs. concentration plots as did the Cd$(NO_3)_2$ solutions in 1.0*M* $NaClO_4$.

Among the chelated solutions, however, changes in slope occurred. Plots of the data in Table IV show breaks at 0.2*M* ethylenediamine (en) for 0.1*M* $CuSO_4$, 0.4*M* en for 0.2*M* $CuSO_4$, 0.6*M* en for 0.3*M* $CuSO_4$, and 0.8*M* en for 0.4*M* $CuSO_4$ as closely as can be determined with the experimental accuracy quoted. This is what is expected for a bidentate chelation agent forming a square planar complex. Similarly for glycine-$CuSO_4$ solutions (Table V), where glycine is also bidentate, a slope change occurs at about 0.02*M* glycine for 0.01*M* $CuSO_4$ solutions, at 0.04*M* glycine for 0.02*M* $CuSO_4$, 0.06*M* glycine for 0.03*M* $CuSO_4$, 0.08*M* glycine for 0.04*M* $CuSO_4$, and 0.1*M* glycine for 0.05*M* $CuSO_4$, again because the square-planar complex is formed. A similar effect is evident in the EDTA-$CuSO_4$ solutions (Table VI) and at about the correct concentration to indicate the EDTA is quadradentate, but there are insufficient data to establish the region of the slope changes with any certainty.

Table II. Refractive Index of $CoSO_4$ in H_2O at 25°C

$CoSO_4$ (*M*)	Refractive index
0.005	1.33140
0.0071	1.33147
0.00955	1.33155
0.0200	1.33187
0.0264	1.33206
0.03585	1.33235
0.0400	1.33248
0.0488	1.33275

Table III. Refractive Index of Cadmium Solutions in Water at 25°C

$CdCl_2$ in H_2O	
$CdCl_2$ (*M*)	Refractive index
0.00565	1.33141
0.01130	1.33153
0.01201	1.33157
0.01504	1.33165
0.02371	1.33184
0.03278	1.33212
0.05273	1.33261
0.07362	1.33324
0.1106	1.33425

Cd$(NO_3)_2$ in H_2O	
Cd$(NO_3)_2$ (*M*)	Refractive index
0.004	1.33136
0.00575	1.33139
0.010	1.33152
0.01314	1.33161
0.020	1.33179
0.0249	1.33193
0.03424	1.33218
0.0452	1.33249
0.0655	1.33305

Cd$(NO_3)_2$ in 1.0 *M* $NaClO_4$ water solution	
Cd$(NO_3)_2$ (*M*)	Refractive index
0.0	1.33998
0.002	1.34003
0.004	1.34011
0.010	1.34025
0.016	1.34042
0.020	1.34052
0.030	1.34080
0.0337	1.34089
0.0380	1.34101

Table IV. Refractive Index of Copper Sulfate Solutions Chelated with Ethylenediamine ($CH_2NH_2CH_2NH_2$) in H_2O at 25°C

	$CuSO_4$ Concn (*M*)				
en (*M*)	0	0.01	0.02	0.03	0.04
0	1.33126	1.33159	1.33191	1.33220	1.33243
0.01	1.33136	1.33166	1.33193	1.33222	1.33248
0.02		1.33171	1.33196	1.33223	
0.025			1.33201	1.33225	1.33254
0.030					
0.040		1.33193	1.33210	1.33236	1.33262
0.050				1.33243	1.33267
0.080		1.33225	1.33251	1.33268	1.33297
0.10	1.33223		1.33267	1.33289	1.33314
0.15		1.33294	1.33317	1.33340	1.33363
0.20	1.33314			1.33382	1.33406
0.30	1.33409				
0.40	1.33508				
0.50	1.33793				

Table V. Refractive Index of Copper Sulfate Solutions Chelated with Glycine (CH_2NH_2COOH) in H_2O at 25°C

	$CuSO_4$ Concn (*M*)					
Glycine (*M*)	0	0.01	0.02	0.03	0.04	0.05
0	1.33126	1.33161	1.33189	1.33224	1.33249	1.33275
0.01		1.33174	1.33205	1.33228	1.33255	1.33285
0.02		1.33186	1.33218	1.33242	1.33271	1.33293
0.03		1.33195	1.33225	1.33253	1.33281	1.33309
0.04		1.33206	1.33239	1.33264	1.33293	1.33329
0.05		1.33216	1.33249		1.33305	1.33340
0.06				1.33287	1.33314	
0.08		1.33257	1.33287	1.33310	1.33338	
0.10	1.33254	1.33325	1.33309	1.33335	1.33360	1.33386
0.15		1.33351	1.33372	1.33400	1.33423	1.33443
0.20	1.33395	1.33415	1.33436	1.33456	1.33482	1.33500
0.25	1.33465					
0.30	1.33533					
0.40	1.33666					
0.50	1.33799					

Table VI. Refractive Index of Copper Sulfate Solutions Chelated with Disodium EDTA $[(CNH_2)_2(CH_2COOH)_2(CH_2COONa)_2]$ in H_2O at 25°C

	$CuSO_4$ concn (*M*)			
EDTA (*M*)	0	0.01	0.02	0.03
0	1.33126	1.33162	1.33193	1.33224
0.01		1.33204	1.33231	1.33263
0.02	1.33250	1.33262	1.33275	1.33303
0.03		1.33314	1.33326	1.33345
0.04		1.33372	1.33386	1.33397
0.05	1.33424	1.33428	1.33443	1.33450
0.10	1.33708			
0.15	1.33993			
0.20	1.34274			

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Correction

In the article, "Refractive Index of Some Alcohols and Saturated Hydrocarbons at 6328Å," by R. N. O'Brien and D. Quon [*J. Chem. Eng. Data*, **13** (4), 517 (1968)], a calibration error in the precision Abbé refractometer used in this work has caused the quoted refractive index to be greater than the correct value by 0.00189, which should be subtracted from all values. To obtain this correction, the values of Tilton and Taylor *(2)* for pure water at 25°C were converted to 632.8 nm by interpolation of their values at 630.0 and 635.0 nm. The O'Brien and Quon instrument values using the Cauchy formula were then converted to Tilton and Taylor's at 589.3 nm and found to agree. The instrument was also calibrated with a standard A.P.I. toluene sample.

To test that the subtraction of 0.00189 would give the correct value, some of the substances' refractive indices were redetermined at 25°C. It can be seen from Table I the average difference is between 0.00184 and 0.00185 or about 0.00004 below the calculated correction. This difference is less than the guaranteed accuracy of the instrument (0.00006). The new values were determined using the new background scattering technique *(1)* and would be expected to give more accurate values than those obtained earlier.

The samples used were not the original ones. Some had purities as good as the samples used in the publication, others did not. The alcohols are hygroscopic and the new values would be expected to be low or the difference to be generally above 0.00189. The alkanes were 99% pure and would be expected to have more heavier fractions (with higher refractive indices) than the original samples which were specially prepared. This is consistent with the lower difference shown. The average difference of the set would be expected to be close to the calculated correction as it was.

Table I. Refractive Indices at 632.8 nm and 25°C Relative to Air

Substance	Publ refractive index	Redetermined refractive index	Diff, $n_P - n_R$
1-Propanol	1.38382	1.38181	+0.00201
1-Butanol	1.39748	1.39559	+0.00189
1-Pentanal	1.40822	1.40632	+0.00190
1-Hexanal	1.41704	1.41493	+0.00211
Pentane	1.35575	1.35404	+0.00171
Heptane	1.38581	1.38405	+0.00176
Octane	1.39574	1.39405	+0.00169
Nonane	1.40373	1.40206	+0.00167
Av		+0.00184 → +0.00185	

Plots of the refractive index vs. number of carbons in the alkane series lead the authors to suspect that the original sample labeled *n*-hexane was not normal hexane.

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