Refractive Indices of Aqueous Solutions of $CuSO_4$, $ZnSO_4$, $AgNO_3$, KCl, and H_2SO_4 for He-Ne Laser Light at $\theta = 25°C$

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Relative to air, refractive indices of some dilute aqueous solutions of strong electrolytes were measured with a Pulfrich refractometer illuminated with a He-Ne laser at 25°C. Several corrections were applied to determine these indices with this instrument, which was not calibrated for the laser light (λ = 6328 Å). Refractive index variations were proportional to molarity in the low concentration ranges only (<0.1*M*).

Today, the He-Ne laser is widely used in classical or holographic interferometry. However, refractive indices of liquids for this red line (λ = 6328 Å) are scarce because classical refractometers of the Abbe or Pulfrich type are not calibrated for this wavelength. The few published results (*1*) involve many obvious errors (e.g., refractive index of pure water would be greater for λ = 6328 Å than for λ_D = 5893 Å). Corrections are given in another paper (2). We made some measurements with a Pulfrich refractometer (Zeiss), which gives refractive indices relative to air.

Experimental

Materials. Solutions were made from Merck Titrisol concentrated solution, Prolabo R.P., and Merck p.a. solid pure anhydrous salts and double-distilled water. For copper sulfate, a double analysis (of Cu^{2+} by electrogravimetry and of SO_4^{2-} by $BaSO_4$ precipitation) indicated that the "Titrisol" solution concentration was exact within 0.1%.

Apparatus and procedure. The condenser of the original refractometer was suppressed. A continuous wave He-Ne laser (Spectra Physics Model 120, 5 mW) illuminates a moving diffuser (ground glass) set as close to the prism as possible. The speckle effect, owing to the great coherence of the laser beam, can be washed out. The dark-to-light dividing line is still sharper than with the conventional sources (e.g., sodium lamp).

The angle read from the graduated circle must be corrected to take into account the deviation between the graduated circle zero and the perpendicular to the vertical prism surface (zero-point correction) (*4*).

The manufacturer gave detailed tables for the direct determination of indices relative to the yellow light of sodium (λ_D = 5893 Å) at the temperature θ = 20°C. These tables include corrections $\Delta(\lambda)$ for using the refractometer with several spectral lines (λ_C = 6563 Å; λ = 5461 Å; λ_F = 4861 Å; λ = 4358 Å; $\lambda_{G'}$ = 4361 Å). By nonlinear interpolation, corrections corresponding to the He-Ne laser light for several refractive index ranges were obtained. For example, near the refractive index of pure water, one must substract the quantity (402 ± 1) · 10^{-5} from the value for λ_D. The temperature correction was calculated from the equation given by the manufacturer:

$$\Delta(t) = +0.34\ (t - 20) \cdot 10^{-5}$$

where $\Delta(t)$ is the correction in the pure water refractive index range, and t the working temperature. At 25°C this correction amounts to 1.7 10^{-5}. The total correction for λ = 6328 Å and θ = 25°C is

$$\Delta(6328\ \text{Å};\ 25°\text{C}) = -(400 \pm 1)\ 10^{-5}\ \text{RI unit}$$

Accuracy. Absolute values obtained with the Pulfrich refractometer involve errors which can be divided in two parts:

1°, experimental errors, mainly visual uncertainties
2°, systematic errors owing to mechanical faults of the apparatus

The first errors can be minimized by careful experimentation and can be evaluated by repeating the same experiment. We believe these errors are lower than 3 · 10^{-5} RI unit. On the other hand, the second class of errors can be eliminated by convenient standardization of the apparatus. Consequently, absolute results obtained with the Pulfrich refractometer reach the same accuracy as differential measurements—3 · 10^{-5} in our determinations.

The following value of the refractive index of double-distilled water was obtained:

$$n_{\text{water/air}}\ (6328\ \text{Å};\ 25°\text{C}) = 1.33131 \pm 3 \cdot 10^{-5}$$

This result must be compared to the one calculated from the Tilton and Taylor tables (*3*):

$$n^{TT}_{\text{water/air}}\ (6328\ \text{Å};\ 25°\text{C}) = 1.331263$$

which can be taken as a standard datum. The difference, $\delta = -5 \cdot 10^{-5}$, between these two values was added to the correction term Δ previously calculated to obtain the final correction term:

$$\Delta' = \Delta + \delta$$

Table I gives the values of Δ' corresponding to the critical angles of emergence (angles read on the graduated circle corrected for zero point) in the dilute aqueous solutions range.

Results

Table II gives relative refractive indices for copper sulfate, zinc sulfate, silver nitrate, and potassium chloride aqueous solutions. Table III gives similar results for sulfuric acid solutions. These tables indicate the products used to make each solution.

From these results, refractive index variations are linear only for a small range of concentration—in the 0; 0.1 mol/l. range. In this narrow interval,

$$n = n_{\text{water/air}} + kC$$

Table I. Corrections for Pulfrich Refractometer for λ = 6328 Å and θ = 25°C

Critical angle of emergence,°	Correction Δ'
63	−400
64	−402
65	−404
66	−405

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Table II. Refractive Indices (Relative to Air) of Aqueous Solutions for $\lambda = 6328$ Å and $\theta = 25°C$

Molarity	Refractive indices			
	$CuSO_4$[a]	$ZnSO_4$[b]	$AgNO_3$[b]	KCl[c]
0.000	1.33126	1.33126	1.33126	1.33126
0.010	1.33156			1.33134
0.025	1.33198			
0.050	1.33276	1.33269		1.33174
0.100	1.33421	1.33403	1.33298	1.33227
0.125	1.33486			
0.250	1.33840	1.33817	1.33560	
0.400	1.34250			
0.500	1.34518	1.34464	1.33992	
0.750			1.34421	
1.000			1.34843	

[a] Solution prepared from Titrisol Merck. [b] Solution prepared from anhydrous Prolabo R.P. salt. [c] Solution prepared from anhydrous Merck p.a. salt.

Table III. Refractive Indices (Relative to Air) of Sulfuric Acid Solutions for $\lambda = 6328$ Å and $\theta = 25°C$

Normality	H_2SO_4[a]
0.000	1.33126
0.100	1.33186
0.250	1.33275
0.500	1.33411
0.750	1.33543
1.000	1.33671

[a] Solution prepared from Titrisol Merck.

where n is the relative refractive index of the dilute aqueous solution, the molarity of which is C (in mol/l.), and k is a constant for a given solute. Table IV gives values of k corresponding to the four salt solutions investigated and also the values of the regression coefficients R calculated by means of an Olivetti desk computer.

Table IV. Values of Coefficient k in (0; 0.100 mol/l.) Range and Corresponding Values of Regression Coefficient R

Solute	k, mol^{-1}/l.	R
$CuSO_4$	2.96 10^{-2}	0.9999
$ZnSO_4$	2.77 10^{-2}	0.9998
$AgNO_3$	1.74 10^{-2}	0.9999
KCl	1.02 10^{-2}	0.9996

Discussion

During solution diffusion studies, the difference between the refractive index of pure water and the refractive index of potassium chloride at 0.100 mol/l. was measured directly by holographic interferometry. Accuracy in this case is $1 \cdot 10^{-5}$ RI unit.

$$n(\text{KCl; 0.1 mol/l.}) - n(\text{water}) = (101 \pm 1) \cdot 10^{-5}$$

for $\lambda = 6328$ Å and $\theta = 25°C$, a result which agrees well with that obtained by Pulfrich refractometer measurements. However, interferometry cannot directly give the refractive index, only the refractive index variations. To obtain the absolute value of the refractive index of dilute aqueous solution with the same precision (10^{-5}), one can measure the difference in refractive index Δn between this solution and pure water, which gives

$$n_{\text{solution/air}} = n^{TT}{}_{\text{water/air}} + \Delta n$$

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Solubility of Water in Benzene

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The solubility of water in benzene was measured over the temperature range 15–35°C by use of a coulometric method for the determination of water. The accuracy of the solubility determinations was about ±0.3% over the whole range. Some thermodynamic functions of solutions were also calculated.

The low solubility of water in many nonpolar organic liquids is difficult to determine, especially that of water in benzene, which is apparently the most widely investigated system. The methods published are either based on those directly worked out for the solubility determinations of water in nonpolar solvents or on conventional methods for the determination of water. There are, however, large variations among the results published. In most of the cases, this depends on too low an accuracy of the method for water determination and, in some cases, on too short a time for ensuring complete equilibrium between the two phases, water and benzene.

The method presented here for the determination of the solubility of water in benzene in the range 15–35°C is based on an accurate method for the determination of small amounts of water by use of coulometrically generated iodine at controlled potential in a Karl Fischer reagent previously described (*6, 7*).

Experimental

Two 100-ml Erlenmeyer flasks, each containing 10 ml of water (twice distilled) and 40 ml of benzene (Fisher Scientific Co., thiophene-free and twice recrystallized), were placed in a specially built temperature bath containing about 8 liters of water, with a low heat exchange with the surroundings. The solutions were agitated in the bath for 2 hr and then left another 3 hr in the bath to allow the liquid layers to separate completely. Solutions agitated more than 2 hr and left overnight in the bath showed no observable difference from the former. The minimum time for the solutions to stand after agitation is about 1 hr in the actual temperature range with the technique used.