

Verdet constant polarimetric measurement in aqueous solutions of salts*

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Verdet constant
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Abstract

The presented static method for measurement of an angle of polarization was used to determination of molar rotation and Verdet constants of the salts, components of synthetic seawater, the synthetic seawater and the sample of natural seawater collected from Gulf of Gdańsk, *vs.* the wavelength. It was shown that the total angle of polarization is an additive value.

1. Introduction

Circular dichroism spectroscopy is an extremely useful tool in investigation of the electronic properties of active molecules, determining the configuration of biological polymers and in more detailed studies on absorption spectra of polyatomic molecules in the UV region. In addition, circular dichroism is particularly sensitive to the interference between two kinds of radiation in mixed multipole lines.

The polarimeters used in those measurements have a Glan-Thompson or Wollaston prism as the analyzer of the light beam passing a circularly dichroitic sample. In the first case the light beam passes through a polarizer, a modulator and the Faraday cell (or the system under investigation) before it incides on the analyzer. Such a polarimeter was used in studies on the reflecting surfaces [6], in studies of the chemical reaction kinetics [3], in measurements of the circular dichroism of the

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spectral lines showing the mixed character *i.e.* having magnetic dipole and electric quadrupole radiation [8]. In the second case, the two light beams leaving the Wollaston prism are detected by two photomultipliers or two pin silicon photodiodes. The electric signal from them, amplified by a differential amplifier, is a quantity characterizing the Faraday rotation or the circular dichroism. In such a way was determined the ratio of the p and s complex amplitude reflection coefficients of a surface [5], the Verdet constants of polyatomic molecules [4]. The parity-mixing effects, which are due to the weak-current interaction observed optically in atomic bismuth vapours were studied experimentally using polarimeter of this type [2]. Different types of polarimeters are described in [1] and [10]. This paper describes an optical arrangement particularly useful at the low intensity signals and small rotation angles. This static measuring arrangement because of great sensitivity and simplicity of operation was applied to determination of Verdet constant of the synthetic seawater and the binary solutions of salts, components of the synthetic seawater. The constant characterizes the opto-magnetic properties of solutions. Till now its values for the solutions of this type were unknown.

2. The polarimetric arrangement

The C. Zeiss-Jena argon ion laser was in this polarimeter the light source (Fig. 1). The laser beam goes through a polarizer P1 (Glan-Thompson prism), the measuring and compensation Faraday cells, the polarization modulator (Faraday cell filled with water) and the Nicol polarizer. The beam reflected from the front surface of the Nicol prism is detected by the photomultiplier PM1 as the reference signal for the lock in amplifier. This signal is also the reference signal for the electric-divider circuit. The beam passing the Nicol polarizer is converted in electric current by the photomultiplier PM2. Its signal is preamplified and after dividing through the reference signal is registered by the millivoltmeter.

The polarization modulator consists of the 15 cm long circular cuvette which is placed in the solenoid producing magnetic field up to 500 Gauss of contrary

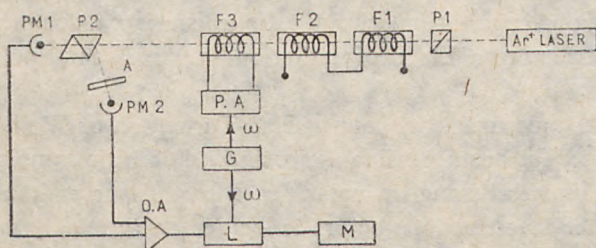


Fig. 1. The scheme of the system for measurement of the angle of polarization. P1 — polarizer (Glan); P2 — analyzer (Nicol); F1 — solenoid filled with water; F2 — solenoid filled with tested solution; F3 — Faraday cell filled with water; Ph1, Ph2 — photomultipliers; A — attenuator; OA — operation amplifier; PA — power amplifier; G — generator; L — lock in amplifier; M — millivoltmeter

direction. Application of two solenoids allows to compensate the angle of polarization of the solvent (water). The angle of polarization of the laser beam caused by the dissolved salts is determined from the amplitude of the alternating current with the frequency of the polarization modulator (ω). The amplitude of the ω frequency alternating current, as will be shown later, is proportional to $\sin 2\varphi$, where φ is the angle of polarization. This polarimeter may be considered as the conventional polarization-modulated system under measurement and linear analyzer arrangement — the PMSA system — in which all the optical elements remain immovable. The state of polarization of the incident beam is phase modulated. The relative phase shift δ_M is sinusoidally modulated at a frequency ω and is described by the equation:

$$\delta_M = A_0 \sin \omega t, \quad (1)$$

where the amplitude A_0 is a function of the modulator driving voltage and wavelength of the light. The intensity of the light incident on the detector is then given with relationship:

$$J_D = |E_x|^2 + |E_y|^2, \quad (2)$$

where the electric field components E_x and E_y are given as the result of the combined matrix and the field amplitude leaving the polarizer:

$$\begin{bmatrix} E_x \\ E_y \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} \cos \delta_M & -\sin \delta_M \\ \sin \delta_M & \cos \delta_M \end{bmatrix} \begin{bmatrix} \cos \varphi & -\sin \varphi \\ \sin \varphi & \cos \varphi \end{bmatrix} \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} 0 \\ E_0 \end{bmatrix}. \quad (3)$$

The combined matrix, expressed in terms of the Jones calculus, describes only samples which can rotate the polarization plane and is given for crossed plane of polarization of the polarizer and analyzer. In the case, of small angles in equation (3) φ indicates the angle of polarization of the sample. This angle is measured. Transformation of equation (3) and its combining with equation (2) gives:

$$J_D = E_0^2 \sin^2(\varphi + A_0 \sin \omega t) = E^2 \left\{ \frac{1}{2} - \frac{1}{2} [\cos 2\delta_M \cos 2\varphi - \sin 2\delta_M \sin 2\varphi] \right\}. \quad (4)$$

Recalling the time dependence of the phase shift δ_M , the functions $\cos \delta_M$ and $\sin \delta_M$ can be expanded in their Bessel function series and for the detected signal we obtain:

$$J_D = J_0 \left\{ \frac{1}{2} - \frac{1}{2} \cos 2\varphi J_0(2A_0) - \cos 2\varphi \sum_{k=1}^{\infty} J_{2k}(2A_0) \cos 2k\omega t + \right. \\ \left. + \sin 2\varphi \sum_{k=1}^{\infty} J_{2k-1}(2A_0) \sin(2k-1)\omega t \right\}, \quad (5)$$

where the Bessel functions depend on the phase shift amplitude. In the detected irradiance the higher harmonics participate in small degree, so they may be neglected; the intensity then is equal:

$$J_D = J_0 \left[\frac{1}{2} - \frac{1}{2} \cos 2\varphi J_0(2A_0) + \sin 2\varphi J_1(2A_0) \sin \omega t + \cos 2\varphi J_2(2A_0) \cos \omega t + \dots \right]. \quad (6)$$

Using the phase-sensitive detection we measured the ratio J_D/J_0 proportional to $\sin 2\varphi \approx 2\varphi$

3. Experimental

3.1 Reagents and solutions

All the chemicals used in this work were of reagent grade purity (POCh, Gliwice), additionally recrystallized from redistilled water. The stock solution of the ionic medium simulating seawater (synthetic seawater) of molality corresponding to

Table 1. Composition of the stock solution of the synthetic seawater

Constituent	Molality [mol(kgH ₂ O) ⁻¹]
Na ⁺	0.48516
Mg ²⁺	0.05518
Ca ²⁺	0.01077
K ⁺	0.01058
Cl ⁻	0.56912
So ₄ ²⁻	0.02926

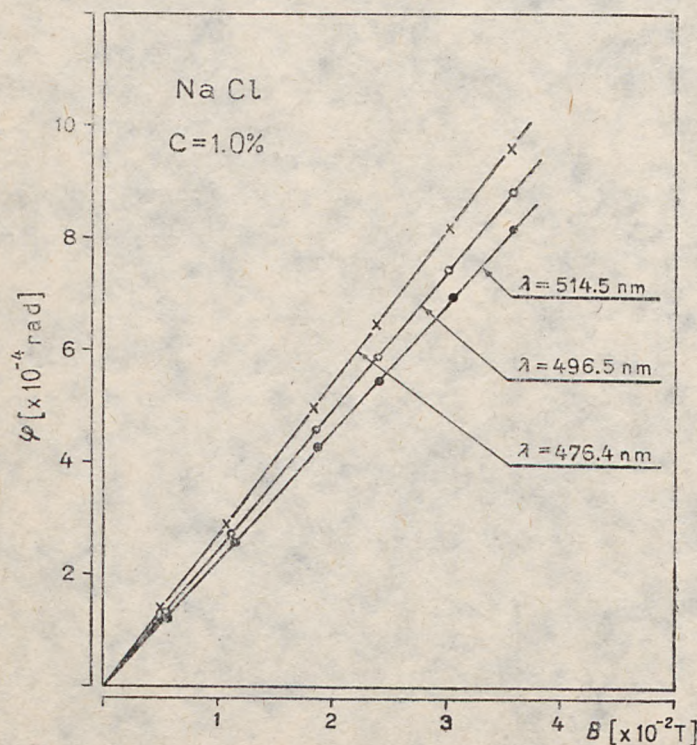


Fig. 2. Dependence of polarization angle φ on magnetic field induction B for the NaCl solution at concentration $c=1\%$ (w/v); $T=291$ K

$S=35\text{‰}$ was prepared according to recipe [7] (Table 1). The natural seawater sample of $S=7.34\text{‰}$ collected from Gulf of Gdańsk was filtered before measurement through $0.45\text{ }\mu\text{m}$ filter.

3.2. Results

The measuring system shown in Figure 1 was applied to determine the polarization angle φ of:

- (i) binary solutions of salts, components of the synthetic seawater,
- (ii) the synthetic seawater,
- (iii) natural seawater.

The obtained dependence of the polarization angle φ on magnetic field induction B and wavelength λ for the aqueous solutions of salts, components of the synthetic seawater, illustrates the example of 1‰ (w/v) NaCl solution (Fig. 2). Figure 3 shows the values φ of the NaCl solutions at two chosen wavelengths depending on concentrations. Measurements were carried on at the constant magnetic field induction $B=1.87 \cdot 10^{-2}\text{ T}$, the length of the cell was $l=0.397\text{ m}$ (F2, see Fig. 1).

The results of measurements of the angle φ vs. wavelength λ for the synthetic seawater $S=10\text{‰}$ and the natural seawater of $S=7.34\text{‰}$ presents the plot in Figure 4.

On the basis of the values of the polarization angle φ , obtained for the binary

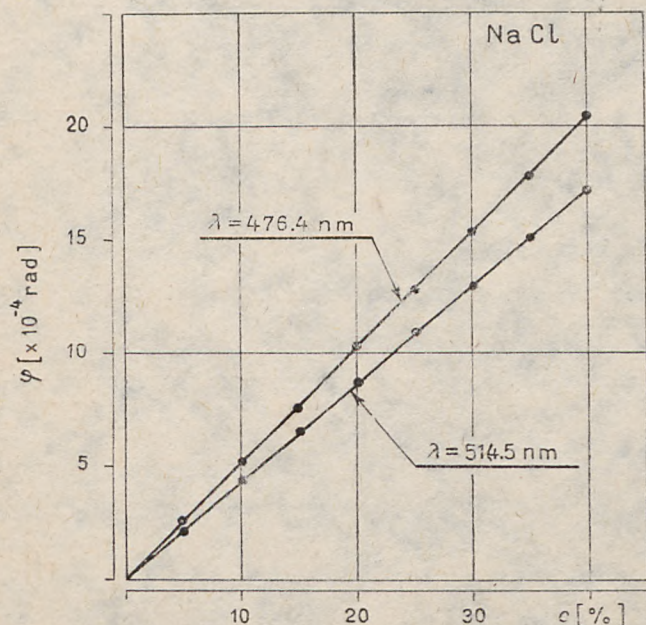


Fig. 3. Dependence of polarization angle φ for the NaCl solutions vs. concentration c and wavelength λ ; $B=1.87 \cdot 10^{-2}\text{ T}$, $l=0.397\text{ m}$; $T=291\text{ K}$

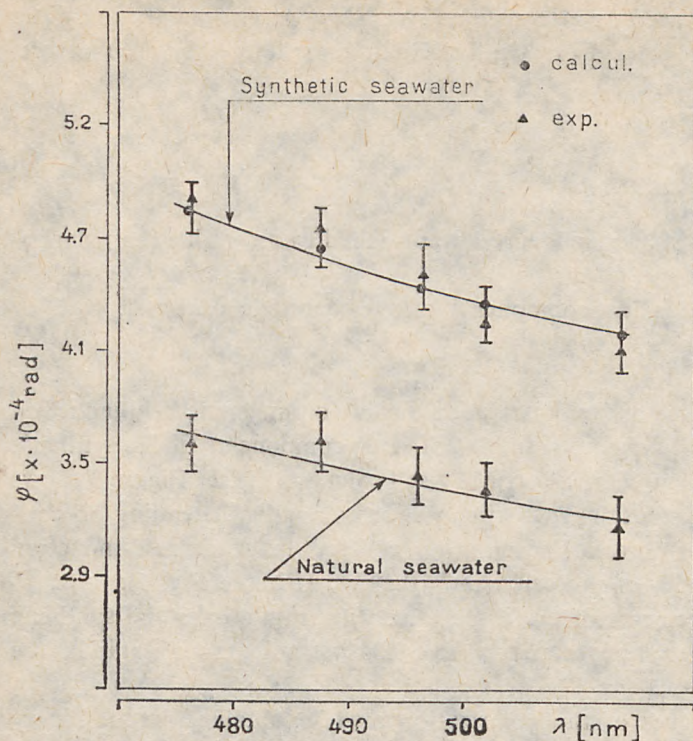


Fig. 4. Dependence of polarization angle φ vs. wavelength λ for synthetic seawater of $S=10\text{‰}$ and natural seawater from Gulf of Gdańsk, $T=291\text{ K}$

solutions of salts the molecular rotation $\Omega \left[\frac{\text{rad m}^2}{\text{T mol}} \cdot 10^{-4} \right]$ was calculated from the relationship:

$$\Omega(\lambda) = \frac{\varphi(\lambda)}{\rho B l}, \quad (7)$$

where ρ – molecular concentrations of the tested solutions in $[\text{mol} \cdot \text{m}^{-3}]$. The results are plotted in Figure 5.

The Verdet constants $V \left[\frac{\text{rad}}{\text{T} \cdot \text{m}} \right]$ for these salts were determined from the following relationship:

$$V(\lambda) = \Omega(\lambda) \frac{d}{\mu} = \Omega(\lambda) \rho_{\mu}, \quad (8)$$

where:

- d – density of the dry salt $[\text{kg} \cdot \text{m}^{-3}]$,
- ρ_{μ} – density of the dry salt $[\text{mol} \cdot \text{m}^{-3}]$,
- μ – molecular weight of the salt $[\text{kg} \cdot \text{mol}^{-1}]$.

The calculated values of Verdet constant and molecular rotation Ω are given

in Table 2. This Table contains also values of two other constants $A' \left[\frac{\text{rad} \cdot \text{nm}^2}{\text{T} \cdot \text{m}} \right]$ and $B' \left[\frac{\text{rad} \cdot \text{nm}^4}{\text{T} \cdot \text{m}} \right]$ arising from approximation of the experimental points with the curve described by the formula

$$V(\lambda) = \frac{A'}{\lambda^2} + \frac{B'}{\lambda^4} \quad (9)$$

Table 2. Experimental values of Verdet constant V [$\text{rad} \cdot \text{T}^{-1} \cdot \text{m}^{-1}$] and molar rotation Ω [$\text{rad} \cdot \text{m}^2 \cdot \text{T}^{-1} \cdot \text{mol}^{-1} \cdot 10^{-4}$] vs. wavelength for the solution of the synthetic seawater of $S=10\%$

λ [nm]	NaCl		KCl		CaCl ₂		MgCl ₂		MgSO ₄	
	A' B' V	Ω	A' B' V	Ω	A' B' V	Ω	A' B' V	Ω	A' B' V	Ω
514.5	12.59	3.403	7.080	2.880	12.42	6.370	10.297	6.254	3.345	1.512
501.7	13.23	3.578	8.086	3.025	12.68	6.516	10.850	6.574	3.462	1.570
496.5	13.44	3.636	8.319	3.112	13.09	6.719	11.141	6.748	3.470	1.575
488.0	14.19	3.839	8.784	3.287	13.73	7.039	11.548	7.010	3.665	1.658
476.4	14.83	4.014	9.250	3.461	14.69	7.534	12.130	7.359	3.723	1.687

Dependence of polarization angle φ_{exp} on the wavelength for the synthetic seawater of $S=10\%$ presents Table 3, which contains also the values of polariza-

Table 3. The values of polarization angle vs. wavelength determined experimentally and on the basis of known molar concentration ρ of salts in the synthetic seawater and the values of molar rotation given in Table 2

λ [nm]	φ [$\text{rad} \times 10^{-4}$]					φ_{cal} [$\text{rad} \times 10^{-4}$]	φ_{exp} [$\text{rad} \times 10^{-4}$]	$\frac{\varphi_{\text{c}} - \varphi_{\text{e}}}{\varphi_{\text{e}}}$
	NaCl $\rho = 138.5$	KCl $\rho = 3.0$	CaCl ₂ $\rho = 3.1$	MgCl ₂ $\rho = 7.6$	MgSO ₄ $\rho = 8.3$			
514.5	3.4906	0.06108	0.1425	0.349	0.0930	4.1364	4.072	0.0158
501.7	3.6681	0.0669	0.1599	0.3694	0.0959	4.3458	4.276	0.0163
496.5	3.7233	0.0698	0.1512	0.3781	0.0961	4.4186	4.4797	0.0136
488.0	3.9270	0.0727	0.157	0.3927	0.1018	4.6251	4.7705	0.03
476.4	4.0957	0.0756	0.1658	0.4043	0.1047	4.8462	4.8578	0.002

Table 4. The values of molar rotation (Ω) and Verdet constant (V) vs. wavelength for the synthetic seawater, determined on the basis of data in Table 3

λ [nm]	Ω_{cal}	V_{cal}	Ω_{exp}	V_{exp}
	$\left[\frac{\text{rad} \cdot \text{m}^2}{\text{T} \cdot \text{mol}} \cdot 10^{-4} \right]$	$\left[\frac{\text{rad}}{\text{T} \cdot \text{m}} \right]$	$\left[\frac{\text{rad} \cdot \text{m}^2}{\text{T} \cdot \text{mol}} \cdot 10^{-4} \right]$	$\left[\frac{\text{rad}}{\text{T} \cdot \text{m}} \right]$
514.5	3.4165	11.4137	3.47	11.592
501.7	3.5873	11.9843	3.64	12.179
496.5	3.7581	12.5549	3.70	12.383
488.0	4.002	13.3697	3.88	12.962
476.4	4.0753	13.6146	4.06	13.582

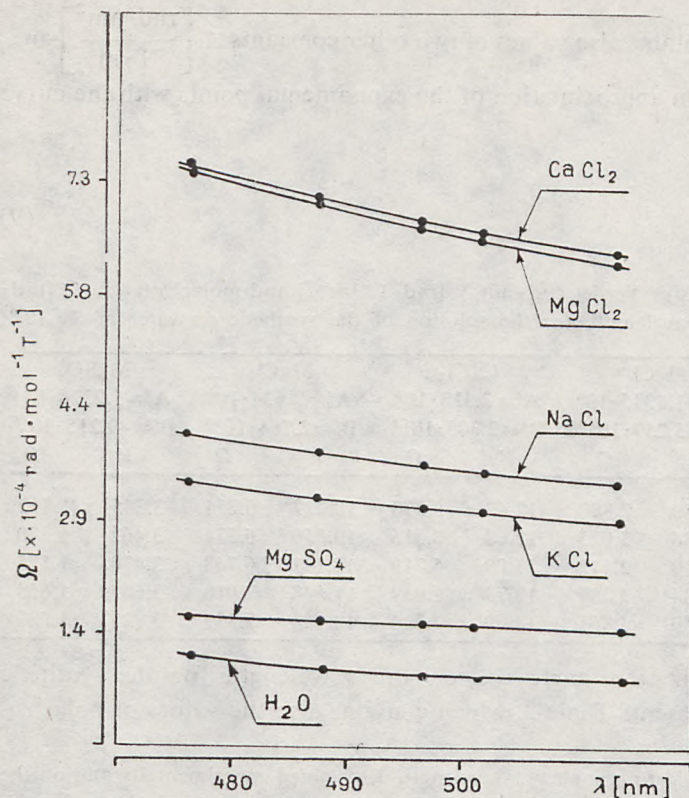


Fig. 5. Dependence of molar rotation Ω for the components of synthetic seawater vs. wavelength λ .

tion angles φ_{cal} , calculated on the basis of known molar rotations Ω (Table 2) and molar concentrations in the synthetic seawater. Basing on these data and the equations (7), (8), the values of molar rotation Ω and Verdet constant at various wavelength for the synthetic seawater (Table 4) were calculated. In these calculations $\mu=0.064689 \text{ kg}\cdot\text{mol}^{-1}$, $d=2.1611\cdot 10^3 \text{ kg}\cdot\text{m}^{-3}$ what results from the composition of the synthetic seawater. The respective values of approximation constants are: $A'=2.94085\cdot 10^6 \text{ rad}\cdot\text{nm}^2$; $B'=3.2154\cdot 10^{10} \frac{\text{rad}\cdot\text{nm}^4}{\text{T}\cdot\text{m}}$. Basing on the data of Ω_{exp} from the Table 4, the angle of polarization vs. salinity at the two chosen wavelengths was calculated (magnetic field induction $B=1.87\cdot 10^{-2} \text{ T}$, $l=0.397 \text{ m}$). The results are plotted in Figure 6.

The maximum error of all the measurements did not exceed $\pm 0.5\%$ and arised mainly from the losses of the light on the optical parts of the measuring system and from the sensitivity of the used recording devices. The error caused by absorption and scattering by water in cells F1 and F2 was small, because the values of total attenuation coefficient for this solvent at the wavelengths generated by the Ar^+ laser are less than 0.04 m^{-1} [9].

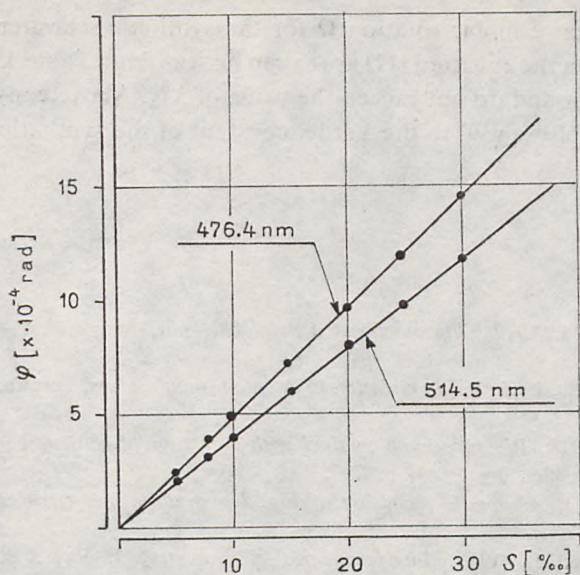


Fig. 6. Dependence of polarization angle φ for the synthetic seawater *vs.* salinity S and wavelength λ ; $B = 1.87 \cdot 10^{-2} \text{ T}$, $l = 0.397 \text{ m}$

4. Discussion

The run of the variability $\varphi = \varphi(\lambda, B)$ for all the tested binary solutions of salts is identical as for solution of NaCl (Fig. 2) and is in agreement with the theoretical predictions. The characteristic feature of the changes of $\varphi(\lambda, B)$ is the slope of these curves, which is different for various salts and wavelengths. In general case, the angle of inclination may be determined from equation (7) and the relationship given below:

$$\alpha = \arctan [\rho \Omega(\lambda) l]. \quad (10)$$

As can be seen from the equations (7) and (10), the value of angle φ determined at the fixed conditions ($l, \lambda, B = \text{const}$) depends on molar concentration of tested solution.

The experimental value of angle φ for the synthetic seawater of $S = 10\text{‰}$ is in good agreement (in the limit of error) with the values of this angle calculated as the sum of the angle φ_i of all the components (see Table 3). The result allows to state that the total angle of polarization φ for the synthetic seawater is additive. This fact makes it possible to determine also (according to equation 7) the values of molar rotation Ω of synthetic seawater, knowing the values of molar concentration and molar rotation Ω (see Table 2) of the components, from the following relationship:

$$\Omega(\lambda) = \sum x_i \Omega_i(\lambda), \quad (11)$$

where $x_i = \rho_i / \rho_\mu$.

The differences between the values of molar rotation Ω for the synthetic seawater determined experimentally and from the equation (11) are as can be seen from Table 4, smaller than the measurement error and do not exceed the value of 3%. Above conclusions (concerning additivity) apply as well to the Verdet constant of the synthetic seawater (see equations 7, 8).

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