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Verdet constant of liquids; measurements with a pulsed magnetic field

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The dispersion of the Verdet constant of several inorganic and organic liquids was measured at room temperature with a pulsed magnetic field in the spectral range from 0.3471 μm up to 0.6943 μm. We also measured the Verdet constant, at the wavelength of 0.4579 μm and at room temperature, of the three binary systems methanol–water, ethanol–water, and acetic acid–water. We found that the Verdet constant of mixtures is not additive. The deviation from additivity is positive for the three systems.

I. INTRODUCTION

The dispersion of the Verdet constant of several pure liquids was measured by using laser sources from the ultraviolet up to the red. The liquids were selected in order to cover a wide range of Faraday rotation strength, starting from the weakest (nitromethane) up to the strongest (carbon disulfide). We also calculated for each liquid the magneto-optic anomaly factor γ; so it was possible to compare our data with the one previously reported for some other wavelengths. The values of γ range between 0.79 for water to 0.26 for nitrobenzene.

In addition to the pure liquids, we also measured the magneto-optical rotation of three binary mixtures of water with acetic acid, ethanol, and methanol as a function of the volume concentration, at the wavelength of 0.4579 μm. We found that the Verdet constant of every mixture is not a linear function of the volume concentration. The deviation from additivity is positive for all the three cases.

II. DISPERSION OF THE VERDET CONSTANT OF PURE LIQUIDS

We used a pulsed magnetic field for the Faraday rotation measurements, with a pulse duration of 10 msec. The system characteristics, as well as the calibration procedure, are described elsewhere.[1] A teflon cell with glass windows of inner length of 50.6 mm was used to contain the liquids under investigation. The cell was also mounted mechanically isolated in order to avoid interferences due to vibrations of the magnet during the pulse discharge. Our measurements were carried out at room temperature and to prevent the heating of the sample, the system was operated at a slow rate and refrigerated by forced air.

The Verdet constant was calculated by measuring the magnetic field needed to rotate the plane of polarization of the light by a preset angle, which was different for each sample. The angle was always chosen as large as it was possible in order to minimize the experimental errors. We used magnetic fields with a maximum peak intensity of 35 kG. In every case, the contribution of the glass windows to the total magnetic rotation was taken into account. Measurements were carried out for nine different laser lines, covering the whole visible spectrum, from the near ultraviolet (0.3471 μm line from the second harmonic of a ruby laser) up to the red

(0.6943 μm from the ruby laser line). The other lines were supplied by argon, He–Ne, and rodamine 6G tunable dye lasers.

In all, 11 liquids were investigated, ranging from nitromethane, with the lowest value of the Verdet constant, up to carbon disulfide, with the highest one. Four out of the 11 liquids (nitromethane, nitrobenzene, benzene, and carbon disulfide) are strong absorbers in the near ultraviolet; because of that, no measurements of the magneto-optical rotation were undertaken for those liquids, at the wavelength of 0.3471 μm. Table I summarizes the values obtained for the Verdet constant as a function of the wavelength for each liquid tested. The experimental errors are estimated to be of the order of ± 2% in the ultraviolet, where the rotated angles are bigger and about ± 4% in the red region.

It was found that a fitting curve given by

$$V = A + B\lambda^{-2} + C\lambda^{-4} \tag{1}$$

is appropriate for our data for interpolation purposes, where V is the Verdet constant in min$\,$G^{-1}cm^{-1}, λ is the wavelength in μm, and A, B, and C are constants, but different for each liquid. The values of the three constants A, B, and C are given in Table II.

The Verdet constant of the water as a function of the wavelength is shown in Fig. 1, where the solid line corresponds to a fitting curve with $A = -8.36 \times 10^{-4}$, $B = 4.78 \times 10^{-3}$, and $C = 5.5 \times 10^{-5}$. The dispersion of the Verdet constant is quite similar for all the other liquids, despite the fact that it increases by a factor of 5 from nitromethane to carbon disulfide. Ethanol and acetone present the same value in the ultraviolet–blue region; but it decreases towards the red more sharply for acetone than for ethanol, this difference reaching about 5% at the 0.6943 μm laser line. This is due to the fact that the absorption bands start at longer wavelengths for acetone than for ethanol. On the other hand, toluene shows a peculiar behavior with its Verdet constant increasing in the ultraviolet more than any other liquid.

For diamagnetic materials, like the liquids under investigation here, the Verdet constant can be related to the optical dispersion through the Becquerel relation

$$V = (e/2mc^2)\gamma\lambda(dn/d\lambda) = 1.01\ \gamma\lambda(dn/d\lambda)\ , \tag{2}$$

where V is the Verdet constant in min$\,$G^{-1}cm^{-1}, λ is the wavelength in μm, $(dn/d\lambda)$ is the optical dispersion in

TABLE I. Wavelength dependence of the Verdet constant of pure liquids.

Wavelength (μm)	Verdet constant ($\min G^{-1} cm^{-1}$)					
	Nitromethane	Methanol	Acetic acid	Ethanol	Acetone	Water
0.3471	•••	0.0291	0.0335	0.0361	0.0361	0.0426
0.4579	0.0140	0.0161	0.0182	0.0193	0.0194	0.0233
0.4765	0.0130	0.0149	0.0169	0.0178	0.0178	0.0210
0.4880	0.0123	0.0143	0.0160	0.0170	0.0170	0.0201
0.5017	0.0118	0.0135	0.0150	0.0161	0.0161	0.0191
0.5145	0.0112	0.0127	0.0142	0.0153	0.0153	0.0180
0.5800	0.00895	0.0103	0.0113	0.0120	0.0119	0.0141
0.6328	0.00740	0.00824	0.00930	0.00997	0.00978	0.0115
0.6943	0.00574	0.00647	0.00718	0.00790	0.00960	0.00913

Wavelength (μm)	Verdet constant ($\min G^{-1} cm^{-1}$)				
	Carbon tetrachloride	Nitrobenzene	Toluene	Benzene	Carbon disulfide
0.3471	0.0528	•••	0.108	•••	•••
0.4579	0.0276	0.0369	0.0490	0.0551	0.0762
0.4765	0.0258	0.0343	0.0444	0.0501	0.0694
0.4880	0.0242	0.0330	0.0421	0.0468	0.0659
0.5017	0.0229	0.0306	0.0391	0.0439	0.0616
0.5145	0.0217	0.0289	0.0367	0.0415	0.0579
0.5800	0.0170	0.0229	0.0278	0.0314	0.0442
0.6328	0.0139	0.0186	0.0227	0.0254	0.0356
0.6943	0.0111	0.0149	0.0180	0.0204	0.0284

μm^{-1}, and γ is the called magneto-optic anomaly factor. The optical dispersion for each liquid was calculated by using the tabulated values of the index of refraction[2] and by assuming that a Sellmeir relation holds in the visible:

$$n^2(\lambda) = 1 + [A \lambda^2/(\lambda^2 - \lambda_0^2)] , \qquad (3)$$

where A and λ_0 are empirical parameters. λ_0 expresses the average position of the absorption bands of the liquids in the ultraviolet. The obtained values of λ_0 range from 0.0995 μm for ethanol up to 0.1800 μm for carbon disulfide.

With the experimental values of the Verdet constant and the calculated optical dispersions, it was possible to find the magneto-optic anomaly factor for each liquid.
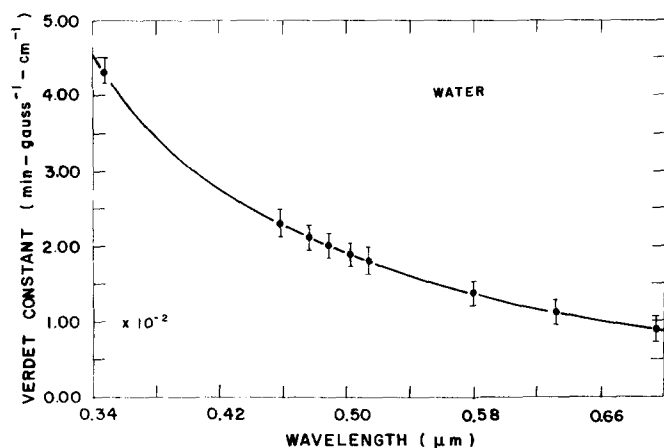
In Table III, the average value of γ for every liquid is compared (between the wavelengths of 0.4579 and 0.5800 μm) with the mean values of γ calculated from the data reported by Darwin et al.,[3] for approximately the same spectral region and by using cw, low intensity magnetic fields. The maximum discrepancy between both sets of data is of the order of 10% and in some cases they agree within the experimental errors.

Measurements of the Verdet constant for some of the liquids studied by us were already reported by George et al.[4] and by Dismukes et al.,[5] at the wavelength of 0.6328 μm and by using strong pulsed magnetic fields. In Table IV, we make a comparison between our data and those previously reported. It can be seen that there is fair agreement with the data given by Dismukes whereas there is a significant discrepancy with George's data. This may be due to the fact that this last author used in

FIG. 1. Verdet constant of the water as a function of wavelength at room temperature.

TABLE II. Coefficients of the dispersion curve of the Verdet constant of pure liquids.

Liquid	A ($\times 10^{-3}$)	B ($\times 10^{-3}$)	C ($\times 10^{-4}$)
Nitromethane	-2.23	4.29	-1.89
Methanol	-0.529	3.47	0.11
Acetic acid	-0.540	3.77	0.39
Ethanol	0.169	3.68	0.77
Acetone	-0.612	3.98	0.53
Water	-0.836	4.78	0.55
Carbon tetrachloride	-0.580	5.22	1.38
Nitrobenzene	-4.25	9.72	-2.24
Toluene	2.60	5.93	8.14
Benzene	-1.11	9.36	5.06
Carbon disulfide	-5.72	15.9	2.59

TABLE III. The magneto-optic anomaly of pure liquids.

Liquid	γ Factor after	
	This work	Darwin
Nitromethane	0.31_9	$\cdots$
Methanol	0.56_4	0.59_6
Acetic acid	0.56_4	0.51_5
Ethanol	0.61_3	0.63_9
Acetone	0.57_0	0.57_0
Water	0.78_6	0.72_7
Carbon tetrachloride	0.56_5	0.51_9
Nitrobenzene	0.26_5	0.26_2
Toluene	0.55_8	0.52_5
Benzene	0.60_2	0.55_2
Carbon disulfide	0.39_3	0.39_9

his experiment a very fast magnetic field (with a semi-period of 58 μsec): In his case, the hysteresis effect on the Faraday rotation is very strong and the Verdet constant was calculated by averaging the values obtained at the ascending and the descending portions of the magnetic field pulse.

III. VERDET CONSTANT OF BINARY SYSTEMS OF LIQUIDS

Three different binary mixtures of water with methanol, ethanol, and acetic acid were investigated by measuring its Verdet constant as a function of the concentration, for the wavelength of 0.4579 μm, and at room temperature. The experimental setup was the same as in the case of pure liquids. The errors in this case were
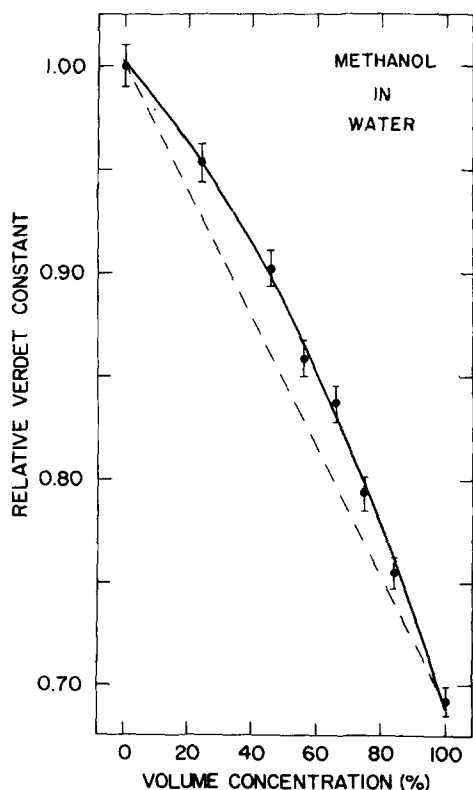

FIG. 2. Relative Verdet constant of methanol in water as a function of the concentration in volume fractions of methanol.
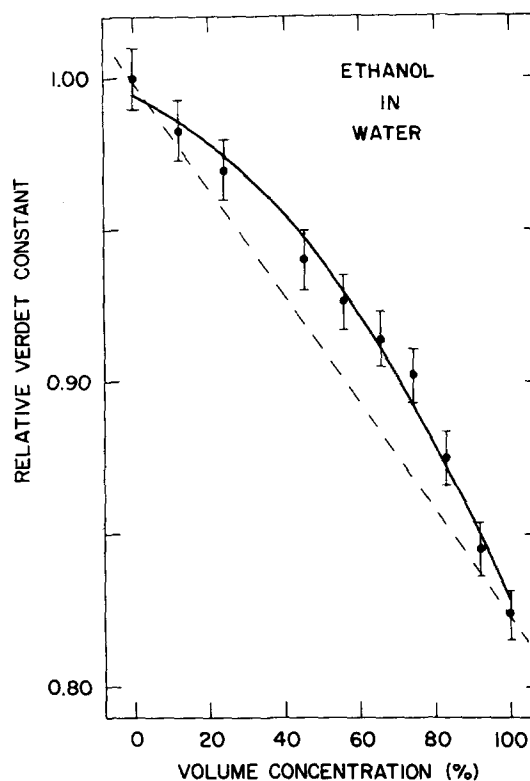

FIG. 3. Relative Verdet constant of ethanol in water as a function of the concentration in volume fractions of ethanol.

estimated to be only of the order of ± 1%, because the angle between the polarizer and the analizer was kept fixed at 45° through the entire set of measurements while the strength of the magnetic field was changed in every case.

Ioffe[6] has shown that for binary systems the correct form to study the deviations from additivity of the component refractive indices is by expressing the system index of refraction as a function of the concentration in volume fractions, rather than the weight of molar fractions, and since this is also true for the case of the magneto-optical rotation of a binary system, we plotted in Figs. 2–4 the Verdet constant, relative to pure water, of the three binary mixtures methanol in water, ethanol in water, and acetic acid in water, respectively, as a function of the volume concentration. It can be seen that the Verdet constant is not additive in the mixture components for any of the three systems we studied. In our case, the deviations are always positive, i. e., the curves are concave towards the composition axis. The deviation from additivity reaches a maximum of the

TABLE IV. The Verdet constant of some pure liquids at 0.6328 μm.

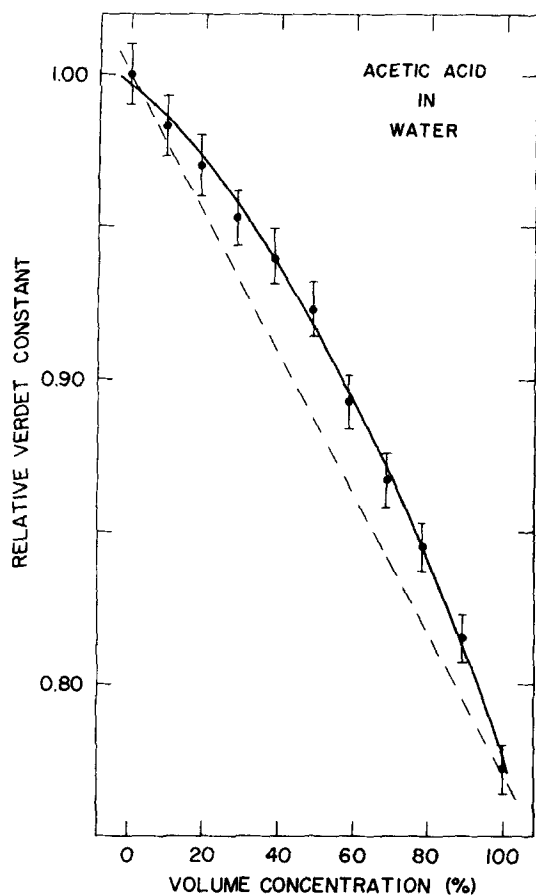| Liquid	Verdet constant ($\min G^{-1} cm^{-1}$)		
	This work	George	Dismukes
Carbon disulfide	0.0356	0.0347	0.0354
Benzene	0.0254	0.0263	0.0260
Carbon tetrachloride	0.0139	$\cdots$	0.0136
Water	0.0115	0.0129	0.0117
Acetone	0.00978	0.0107	$\cdots$

FIG. 4. Relative Verdet constant of acetic acid in water as a function of the concentration in volume fractions of acetic acid.

order of 5%, in every mixture, which is much bigger than the assumed experimental errors.

For the sake of interpolation only, we found that the following parabolic curves fit the data within the experimental errors:

methanol–water:

$$V_r = 1.000 - 0.155\ C_v - 0.157\ C_v^2\ ;$$

ethanol–water:

$$V_r = 0.994 - 0.053\ C_v - 0.112\ C_v^2\ ;$$

acetic acid–water

$$V_r = 0.996 - 0.102\ C_v - 0.117\ C_v^2\ ;$$

where V_r is the relative Verdet constant of the mixture and C_v is the concentration in volume fractions of methanol, ethanol, and acetic acid. These fitting curves are represented by solid lines in the Figs. 2 thru 4 whereas the dashed lines in the same figures give the linear relation that should exist if additivity were present.

The deviation from additivity may be due to density changes when the mixture is formed (just because of purely physical or even geometrical effects) as well as to chemical interaction such as formation of new products or dissociation of the components. In particular, for the three binary systems under study, we found that, within the accuracy of ± 1% of our experiment, the deivation from additivity can be attributed entirely to changes in the mixture density with concentration. In view of our results, it looks promising to use the deviation from additivity (in sign and in absolute value) of the Verdet constant of a binary system as a tool to investigate the type of interaction that takes place between the components of the mixture, in the same way that the measurements of the refractive index of a binary mixture are being used to study the interactions between the components of the system. A more complete characterization of binary systems, by using its magneto-optical rotation properties, is under way in our laboratory.

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