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UV/Vis Spectroscopic Behaviour of Some New Hydroxy Azocoumarin Derivatives

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Summary. The UV/Vis spectroscopic behaviour of six new hydroxy azocoumarin compounds in solution has been investigated. The observed bands are assigned to electronic transitions. Azocoumarin compounds exist mainly in the azo form, whereas 6-(2-hydroxy-6-aminonaphthyl-1-azo)-coumarin exhibits an azo-hydrazone tautomeric equilibrium. The solvatochromic behaviour of the azo compounds is investigated by studying their spectra in pure and mixed organic solvents of different characteristics. The longer wavelength band of the azocoumarins in *DMF* solution is assigned to an intermolecular CT transition.

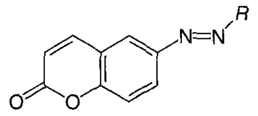
Keywords: UV/Vis spectra; Azocoumarin; Medium effect.

UV/Vis-spektroskopisches Verhalten einiger neuer Hydroxyazocumarinderivate

Zusammenfassung. Das UV/Vis-spektroskopische Verhalten von sechs neuen Hydroxyazocumarinen in Lösung wurde untersucht. Die beobachteten Banden werden elektronischen Übergängen zugeordnet. Azocumarine liegen hauptsächlich in der Azoform vor, während 6-(2-Hydroxy-6-aminonaphthyl-1-azo)-cumarin eine Azo-Hydrazon-Tautomerie zeigt. Das solvatochrome Verhalten der Azoverbindungen wird durch Messung ihrer Spektren in reinen und gemischten organischen Lösungsmitteln mit unterschiedlichen Eigenschaften studiert. Die bei in *DMF* gelösten Azocumarinen auftretende langwellige Bande wird einem intermolekularen CT-Übergang zugeordnet.

Introduction

The structure of azo compounds, especially those containing phenol or naphthol moieties, has invoked many investigations. This is due to their widespread applications as dyes, as acid-base, metallochrome, and redox indicators, and as histological stains. Careful examination of the literature reveals that considerable work has been reported on the spectroscopic and acid-base properties of heterocyclic azo compounds [1–3]. In view of these findings, this article presents an investigations of the electronic spectra of some new hydroxy azocoumarin compounds in pure and in mixed organic solvents of different polarities. The structures of the azocoumarin derivatives **1**–**6** are given below:



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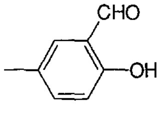

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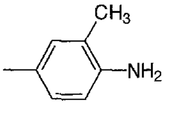

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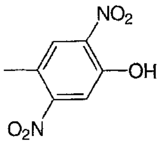

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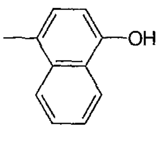

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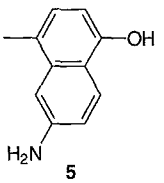

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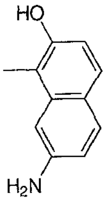

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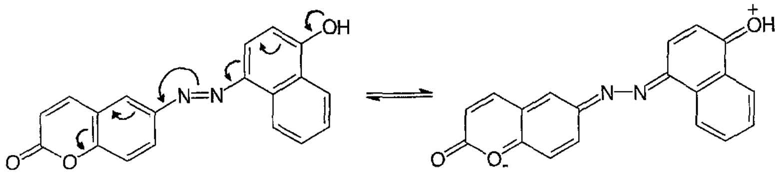
Results and Discussion

The UV/Vis characteristics (λ_{max}, ε_{max}) of compounds **1**–**6** in organic solvents of different polarities (ethanol, acetone, acetonitrile, and dimethylformamide) in the wavelength range of 250–600 nm are collected in Table 1. Generally, the spectra of compounds **1**–**3** and **6** in ethanol consist mainly of three bands, whereas those of compounds **4** and **5** exhibit two bands. The shortest wavelength bands located within the range of 262–285 nm in the spectra of all compounds is assignable to a π–π^* transition of the benzenoid system. This assignment is quite reasonable since λ_{max} of this band is slightly altered on transfer from one derivative to another, indicating the local nature of such a transition. Except in the case of compound **6**, a main broad band observed in the region from 338 to 470 nm can be assigned to a π–π^* transition involving the whole electronic system of the compounds with a considerable charge transfer character originating mainly from the phenolic or naphtholic moiety and pointing towards the hetero coumarin ring which is characterized by a high electron accepting character. This charge transfer can be represented as follows:



The charge transfer nature of this band is deduced from its broadness [4] as well as from the sensitivity of its λ_{max} to the type of substituent attached to the azo coupler. This band acquires an appreciable shift towards lower energy (red shift)

Table 1. UV/Vis spectroscopic data of hydroxy azocoumarin derivatives in various organic solvents at 25°C

	Ethanol		Acetone		Acetonitrile		*DMF*	
	λ(nm)	$\varepsilon \times 10^{-3}(\mathrm{cm}^2 \cdot \mathrm{mol}^{-1})$	λ(nm)	$\varepsilon \times 10^{-3}(\mathrm{cm}^2 \cdot \mathrm{mol}^{-1})$	λ(nm)	$\varepsilon \times 10^{-3}(\mathrm{cm}^2 \cdot \mathrm{mol}^{-1})$	λ(nm)	$\varepsilon \times 10^{-3}(\mathrm{cm}^2 \cdot \mathrm{mol}^{-1})$
1	270	24			270	24.1	270	18.3
	345	21.7	242	28.4	340	28.4	380	12.5
	430	6.7	425	1.2	425	1.1	472	16.2
2	262	19					270	15.3
	365	22.7	362	24.7	358	22.3	370	15.7
	440 (sh)	2.4	430 (sh)	4.0	420	1.1	510	14.3
3	275	17.6			270	19.5	270	19.0
	338	6.0	350	6.8	350	6.7	355	6.3
	442	2.0	340 (sh)	1.25	425 (sh)	1.2	490	6.0
4	285 (sh)	10.7			290	9.0	268	14.1
	400	17.7	400	15.6	400	13.5	410	12.1
							450	10.8
5	265	23.3			270 (sh)	22.5	260	10.7
	470	14.0	470	12.75	460	13.0	470	64.4
6	275	18.1	260	24.0	265 (sh)	20.0	270	20.3
	425	11.3	425	10.6	420	11.2	425	11.6
	470	11.7	470	11.0	462	11.0	475	11.9

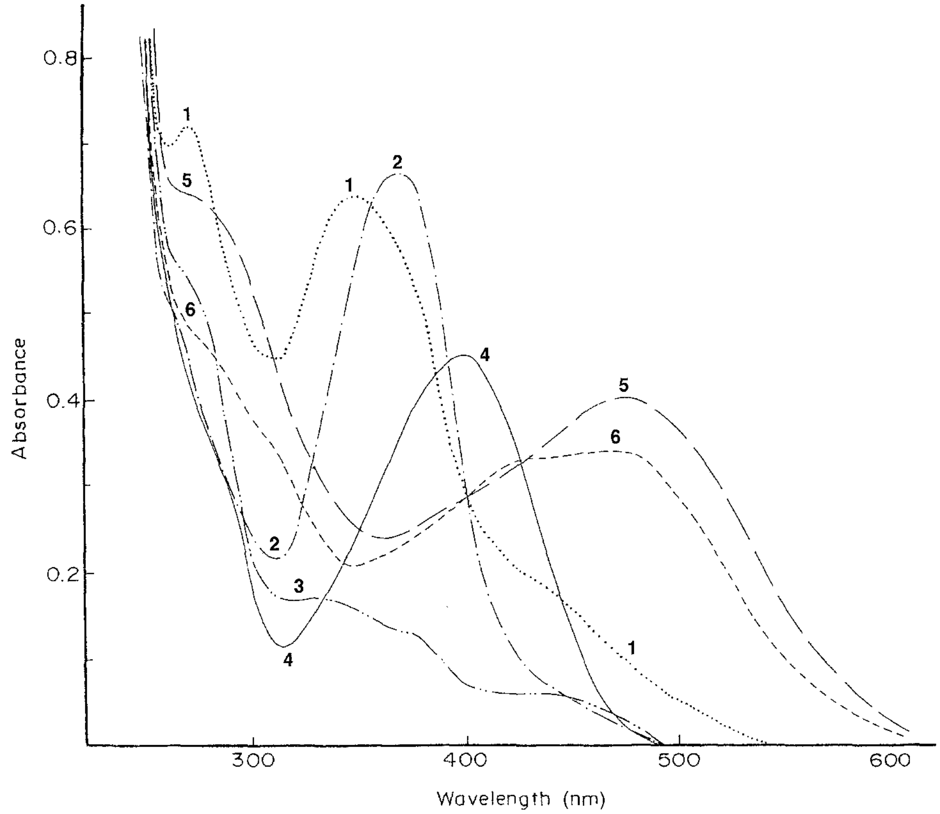
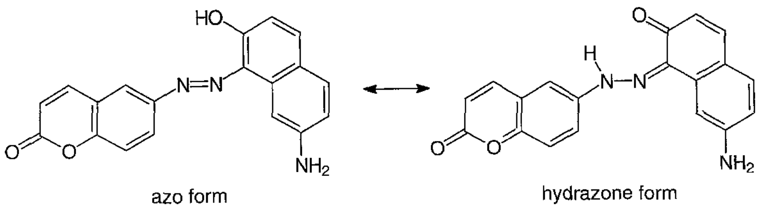


Fig. 1. Electronic absorption spectra of ethanolic solutions of the hydroxyazocoumarin derivatives **1–6** ($3.0 \times 10^{-5} M$)

when the coupler contains an additional electron donating group (**2**, **5**) compared to compounds with a hydroxy group only or with couplers containing an additional electron accepting group (**1**, **3**, **4**). This trend can be considered as good evidence for the CT character of this band.

The visible spectrum of compound **6** in ethanol is different from those discussed above, the intramolecular CT band being broad and exhibiting two maxima. This behaviour can be attributed to the existence of an azo-hydrazone tautomeric equilibrium originating from the OH group [5–7].



Accordingly, the shorter wavelength band at 425 nm corresponds to an intermolecular CT within the azo form, whereas that at 475 nm is due to the CT transition within the hydrazone form. The low excitation energy of this transition in the case of the hydrazo species relative to the corresponding one in the azo compound is presumably due to the quinonoid structure of the former isomer which is expected to facilitate such a type of transition.

The third band appearing at longer wavelength in the spectra of compounds **1**–**3** (430, 440 (sh), and 442 nm, respectively) can be ascribed to an n–π^* transition involving the lone pairs of electrons localized at the azo group nitrogen [1, 8]. A support for the intramolecular electronic transition character of this band is achieved from its disappearance in the spectra of HCl solutions of compounds **1**–**3** where excitation of the n-electrons is expected to be hindered by protonation. A further convincing evidence for the n–π^* nature of this band is attained from the linearity of the absorbance *vs.* concentration plot. The disappearance of this transition in the case of compound **6** is quite reasonable, taking into account the existence of a tautomeric equilibrium between the azo and hydrazone forms. Such a tautomerization involves the lone pair of electrons localized at the azo group nitrogen atom. The missing of the n-π^* band in the spectra of compounds **4** and **5** can presumably be ascribed to its position under the envelope of the strong and broad CT band.

Solvatochromic behaviour

The electronic absorption spectra of the investigated dyes have been studied in organic solvents of different polarities, (acetonitrile, acetone, EtOH, and *DMF*). The UV π–π^* bands suffer small solvent shifts, a behaviour which is characteristic of this type of electronic transition (cf. Table 1 and Fig. 2). The data in Table 1 reveal that the intramolecular CT band appearing in the range of 338–470 nm exhibits a red shift on changing the solvent in the series acetonitrile → acetone → ethanol → *DMF*. This trend is in harmony with the increasing polarity of the solvents and can be explained by the principle that the excited state of such a type of transition is polar and consequently it is expected to be more stabilized in highly polar solvent. Therefore, lower excitation energy is required for this band in the former solvent relative to the latter one.

On the other hand, the n-π^* band observed in the spectra of compounds **1**–**3** exhibits a blue shift in ethanol relative to *DMF*. This can be ascribed to the expected difficult excitation of the n-electrons of the azo group in ethanol due to its blocking by ethanol molecules *via* hydrogen bonds, thus confirming the n-π^* assignment of this band.

Furthermore, the visible spectra of compounds **1**–**3** in *DMF* comprise a new band appearing at longer wavelengths (495–512 nm, Fig. 2, curve d), exceeding the usual solvent shift by far. This behaviour can be interpreted on the basis that the solute molecules are liable to form a solvated complex with *DMF* molecules through an intermolecular H-bonding [1, 7]. Since charge transfer forces play an important role in H-bonding [12], this additional band is presumably due to an intermolecular CT transition [2, 13]. This involves an electron transfer from the lone pair of electrons at the oxygen atom of the *DMF* molecule (ψ_{01}) to the antibonding orbital of the OH bond of the phenolic moiety (compounds **1**, **3**) or to that of NH bond of the NH_2 group of compound **2**. The appearance of this band only in *DMF* as a solvent can be ascribed to its high basicity as well as its

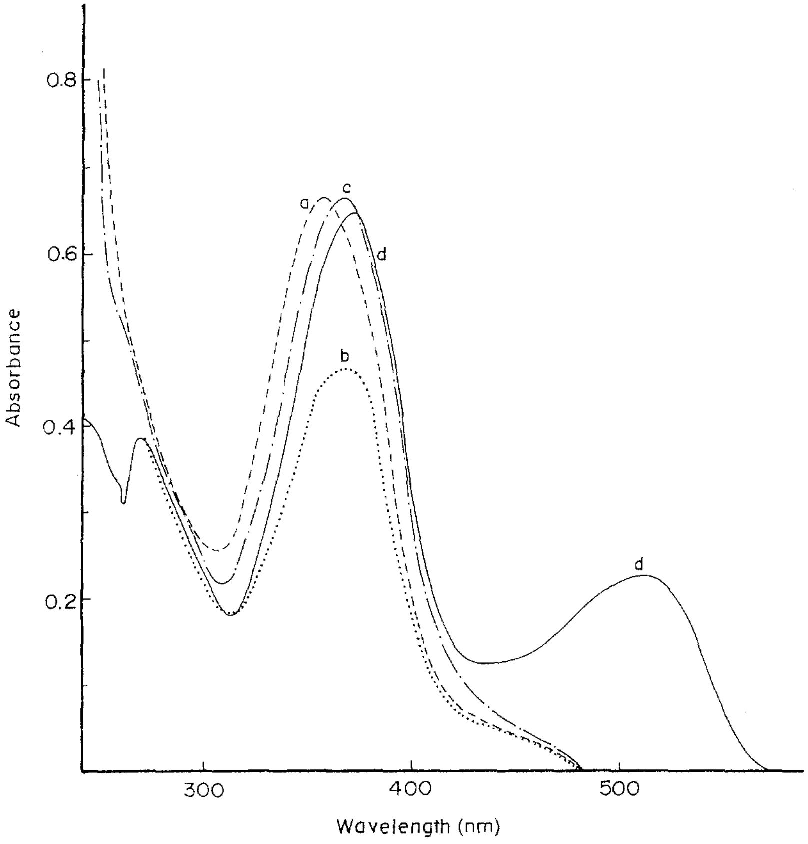


Fig. 2. Electronic absorption spectra of 4 × $10^{-5}M$ solutions of compound **2** in organic solvents; a: acetonitrile, b: acetone, c: ethanol, d: *DMF*

pronounced character as a strong proton acceptor. Good convincing evidence for the intermolecular CT nature of this band is attained from the non-linear relationship between the absorbance of this band and the molar concentration of the azo compound. Further support is achieved by studying the spectroscopic behaviour of these compounds in *DMF* containing increasing amounts of ethanol, acetone, CCl_4, or acetonitrile. It is evident that with increasing *DMF* concentration the absorbance of the intramolecular CT band decreases, whereas a new band appears at a longer wavelength (Fig. 3).

Generally, the spectra recorded in the mixed solvents (EtOH-*DMF*, acetone-*DMF*, CCl_4-*DMF*, CH_3CN-*DMF*) exhibit an isosbestic point which indicates the establishment of an equilibrium between the free and H-bond solvated species of the compound. This behaviour indicates that *DMF* molecules have a greater tendency to form solvated complexes with the solute molecule than ethanol, acetone, acetonitrile, and CCl_4. This is due to the low ionization potential of *DMF* as well as to its high H-bond accepting character.

In all compounds investigated, the graphical representation of the absorbance of the intermolecular CT band against the dielectric constant of the medium is nonlinear (Fig. 4). This behaviour suggests that other factors beside the dielectric constant of the medium are responsible for the observed spectral changes. These

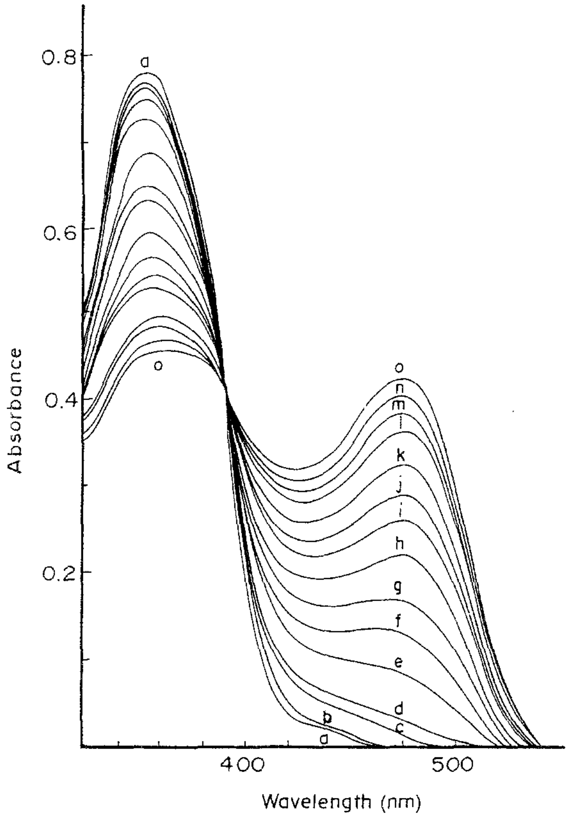


Fig. 3. Visible electronic absorption spectra of $4 \times 10^{-5} M$ solutions of compound **1** in *DMF*–CCl_4 mixtures (v/v); a: 5.16*MDMF*, b: 5.81*MDMF*, c: 6.45*MDMF*, d: 7.44*MDMF*, e: 9.03*MDMF*, f: 9.68*MDMF*, g: 10.32*MDMF*, h: 10.96*MDMF*, i: 11.61*MDMF*, j: 11.87*MDMF*, k: 12.25*MDMF*, l: 12.38*MDMF*, m: 12.51*MDMF*, n: 12.77*MDMF*, o: 1.29*MDMF*

factors include mainly a specific solute-solvent interaction (H-bond formation) which leads to the formation of molecular complexes.

The formation constants (K_f) of the different solvated molecular complexes of compound **1** (as a representative example) with *DMF* were determined from the

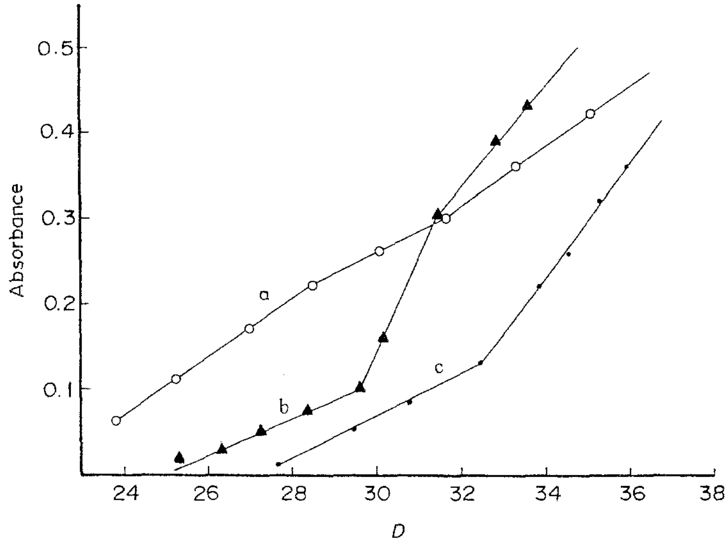


Fig. 4. Absorbance of the intermolecular CT band *vs.* dielectric constant of the medium at 25°C for compound **1**; a: acetone-*DMF*, b: ethanol-*DMF*, c: CCl_4-*DMF*

Table 2. Values of K_f and $-\Delta G$ for the H-bonding solvated complexes of **1**

System	$\log K_f$	K_f	$-\Delta G$ ($\mathrm{kJ \cdot mol^{-1}}$)
DMF–CCl_4	1.063	11.56	1.45
DMF–CH_3CN	1.06	11.48	1.45
DMF–$(CH_3)_2CO$	0.83	6.76	1.13
DMF–EtOH	0.98	9.55	1.34

variation of the absorbance of the intermolecular CT band with increasing *DMF* concentration at a given wavelength. The equation used [11] is

$$\log C_{\mathrm{DMF}} = \log K_{\mathrm{F}} + \log \frac{A - A_0}{A_1 - A}$$

where A_0 = absorbance in a low-polarity solvent, A_1 = absorbance in a high-polarity solvent, and A = absorbance in the mixed solvent. The *Gibbs* free energy (ΔG) of the solvated complexes can be obtained from $\Delta G = -RT \ln K_{\mathrm{F}}$ [10]. The values of K_{F} and ΔG of the various molecular complexed liable to exist in solution are given in Table 2.

Experimental

6-Amino coumarin [12, 13] was diazotized in the usual way by dissolving it in hydrochloric acid, cooling to 0–5°C, and adding an equivalent amount of ice-cooled sodium nitrite solution with

Table 3. Physical data of compounds **1**–**6**

	Empirical formula	m.p. (C°)	Calcd. (found)			IR ($\mathrm{cm^{-1}}$)
			C	H	N	
1	$C_{16}H_{10}N_2O_4$	270	65.31 (65.32)	3.40 (3.22)	9.52 (9.46)	3318 (OH), 3148 (NH), 1731, 1658 (2C=O), 1640 (C=N), 1451 (N=N)
2	$C_{16}H_{13}N_3O_2$	> 300	68.82 (68.81)	4.66 (4.63)	15.05 (15.01)	3322, 3212 (NH_2), 1726 (C=O), 1652 (C=N), 1451 (N=N)
3	$C_{18}H_8N_4O_7$	102	50.56 (50.51)	2.25 (2.23)	15.73 (15.70)	3267 (OH), 3112 (NH), 1710 (C=O), 1648 (C=N), 1432 (N=N)
4	$C_{19}H_{12}N_2O_3$	235	72.15 (72.11)	3.80 (3.78)	8.86 (8.82)	3450 (OH), 3271 (NH), 1722 (C=O), 1622 (C=N), 1447 (N=N)
5	$C_{19}H_{13}N_3O_3$	> 300	68.88 (68.89)	3.93 (3.90)	12.69 (12.66)	3436 (OH), 3406, 3326, 3211 (NH, HN_2), 1721 (C=O), 1631 (C=N), 1426 (N=N)
6	$C_{19}H_{13}N_3O_3$	226	68.88 (68.83)	3.93 (3.89)	12.68 (12.67)	3408 (OH), 3386, 3356, 3220 (NH, NH_2) 1710 (C=O), 1617 (C=N)

vigorous stirring. The cooled diazonium salt solution was used for coupling with the suitable agent [14]. The azo compounds were washed with water, dried, and recrystallized from a suitable solvent. The results of elemental analysis of the solid azo dyes were in accordance with their composition (Table 3).

The organic solvents used (ethanol, acetone, acetonitrile, *DMF*) were of AR grade (Merck or BDH). Solutions of compounds **1–6** ($10^{-3}M$) were prepared by dissolving the accurately weighed amount of the target compound in the required amount of the appropriate solvent. Solutions of lower concentrations as used in the spectroscopic measurements were obtained by accurate dilution.

The electronic spectra were recorded on a CECIL 599 spectrophotometer at 25°C using 1 cm matched silica cells.

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