

Influence of metal ions on the response of solvatochromic Reichardt indicators: NMR spectroscopic study

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Association of Mg^{2+} and La^{3+} ions with Reichardt betaine dyes in deuterated DMSO has been studied using 1H -NMR method. Basing on chemical shifts of the betaine protons in the presence of metal ions as well as on the chemical shifts of the protonated betaine protons, the Mg^{2+} and La^{3+} ions interaction with the dye molecule has been concluded to be of acid-base nature. The data obtained suggest the inadmissibility of the betaine acid-base sensors in the presence of multicharged metal ions.

Ассоциация ионов Mg^{2+} и La^{3+} с бетаиновым красителем Райхардта в дейтерированном DMSO изучена с использованием метода ПМР. На основании значений химических сдвигов протонов бетаина в присутствии ионов металлов, а также химических сдвигов протонов протонированного бетаина сделан вывод о кислотно-основном характере взаимодействия ионов Mg^{2+} и La^{3+} с молекулой красителя. Полученные данные позволяют сделать вывод о недопустимости применения кислотно-основных сенсоров на основе бетаинов в присутствии многозарядных ионов металлов.

The Reichardt betaine dyes are used widely due to solvatochromic properties thereof [1, 2]. The betaine solution color change depending on the molecule micro-environment is often the only characteristic indicating some properties of the liquid medium, for example, its polarity ($E_T(30)$ empirical parameter [3]). These dyes make it possible to study various properties of mixed solvents, the surface structure of modified and unmodified silicon and aluminum oxides, zeolites, and polymers. Moreover, the solvatochromic effect has been found to be useful for estimating the activity of surfaces in chromatographic supports [4]. Due to high sensitivity of betaines to moisture and acids, the corresponding film or micro-porous sensors can be prepared [5]. The thermochromism of the substances of-

fers some prospects to use thereof as temperature sensors [6]. The betaine indicators have been found to be useful for investigation of the phase properties in the complex systems such as micellar solutions and micro-emulsions [7–9]. The experimental techniques being rather simple, the data obtained (taking into account the dye specific properties) are quite sufficient to explain some effects. It is just the 2,4,6-triphenyl-*N*-(3,5-diphenyl-4-hydroxyphenyl)pyridinium presented in Fig. 1 (from here on, betaine) that is used widely due to its optimum physicochemical properties (good solubility in many solvents, the highest observable solvatochromic effect).

While the Reichardt betaine dyes are rather long ago in use, some physicochemical properties thereof remain studied insufficiently to date, e.g., their behavior fea-

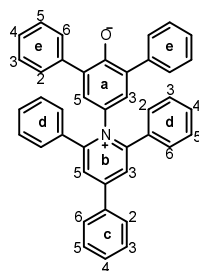


Fig. 1. Betaine. The letters denote the corresponding aromatic rings; the numerals, the proton numbers.

tures in the presence of metal ions in organic media. Some investigation in this field were carried out using acetonitrile [10–13], acetone, *N,N*-dimethyl acetamide, dimethyl sulfoxide, a series of aliphatic alcohols [8], diethyl ether, tetrahydrofuran [14]. Binary mixtures methanol/water, *t*-butanol/dimethyl sulfoxide and *t*-butanol/acetonitrile were used, too [15]. In the presence of metal ions, the dye absorption maximum in the visible spectral region was found to shift towards shorter wavelengths. This effect is more pronounced for ions of small radii and large positive charge. So Li^+ ions cause a hypsochromic shift of the dye absorption maximum in acetonitrile from 620 nm to 525 nm while Na^+ ions, to 560 nm. Mg^{2+} ions render the betaine essentially colorless. The association of metal ions occurs at oxygen atom of the phenolate molecular fragment where a considerable electron density is localized (dipole moment about 14 D). The association constant of the betaine with Li^+ ions in acetonitrile, as determined from the absorption spectra, is $K_{ass} = 5.47 \cdot 10^4 \text{ M}^{-1}$ [13]. Moreover, it is to note that these effects are most pronounced in aprotic media having low or moderate dielectric constants (diethyl ether, tetrahydrofuran, acetone, acetonitrile). Lower alcohols forming strong hydrogen bonds with the betaine molecule as well as the solvents having a high solvability (DMSO) hinder the metal ion association with the dye. Using NMR method, we have identified more precisely the interaction character of Mg^{2+} and La^{3+} ions with the betaine in d_6 -DMSO.

Lanthanum and magnesium perchlorates were obtained by neutralizing the corresponding carbonates with 30 % perchloric acid. After filtration, the solutions were evaporated using a water bath and the crystals obtained were recrystallized thrice from distilled water. Magnesium perchlorate was dried for 20 h at 200°C and 0.5 mm Hg, lan-

Table 1. Composition and concentration of the components in the A, B, C, D systems.

System		C, mol/L
A	Betaine	$3.4 \cdot 10^{-3}$
B	Betaine	$3.4 \cdot 10^{-3}$
	$\text{Mg}(\text{ClO}_4)_2$	0.5
C	Betaine	$3.4 \cdot 10^{-3}$
	$\text{La}(\text{ClO}_4)_3$	$1.4 \cdot 10^{-2}$

thanum perchlorate, for 10 h at 150°C and 0.5 mm Hg. The betaine (dihydrate) was kindly offered by Prof. Christian Reichardt. The protonated dye was obtained by treating its alcoholic solution with 10 % perchloric acid. The colorless solution so obtained was diluted with a little distilled water and concentrated by evaporation. The precipitated fine crystals were recrystallized twice from aqueous ethanol and dried for 5 h at 90°C. The proton spectra were measured using a Mercury Varian VX-200 NMR spectrometer at 200 MHz. The measurements were done in 5 mm ampoules containing 0.6 mL of the solutions at 25°C. The initial substances were weighed directly in the ampoule and then solvent (0.6 mL) was added. The d_6 -DMSO with 99.9 % deuterium content was used. TMS was used as the external standard. The spectra were recorded for four systems (see Table 1).

Table 2 presents the chemical shifts of the betaine protons (systems A, B, C, D). In the weak field region lie the signals from $3^b, 5^b$ protons (singlet) as well as those from $2^c, 6^c$ and $3^c, 4^c, 5^c$ ones as a doublet of multiplets. The proton signal splitting into two components untypical of phenyl substituent evidences a considerable polarizability of the molecule along the axis connecting nitrogen and oxygen atoms. The multiplet signals from protons of the phenyl substituents being in the ortho positions of the pyridinium and phenolate molecular fragments are within 7.00 to 7.55 ppm region. The multiplets are slightly split also into two components having the integral intensities 2 and 3 for each phenyl substituent. In the presence of metal ions as well in the protonated betaine, the largest shift is observed for signals of the phenolate protons. So, the signal from $3^a, 5^a$ protons is shifted towards weak field from 6.734 to 7.274 ppm. Fig. 2 shows the changes of the chemical shifts for the betaine protons when passing from the A system to the D one. The Mg^{2+} and La^{3+} ions are seen to cause the shift of all proton signals (except for $2^e, 3^e$

Table 2. The chemical shifts and spin-spin constants of the betaine protons (Fig. 1) in the A, B, C, D systems.

System	δ_H , ppm					
	$3^a, 5^a$	$3^b, 5^b$	$2^c, 6^c$	$3^c, 4^c, 5^c$	$3^d, 4^d, 5^d$ $2^d, 6^d$	$3^e, 4^e, 5^e,$ $2^e, 6^e$
A	6.734 (s)	8.491 (s)	8.278 (m)	7.618 (m)	7.435 (m, 6H) 7.557 (m, 4H)	7.061 (m, 6H) 7.345 (m, 4H)
B	7.160	8.515 (s)	8.224 (dm, J 7.0 Hz)	7.602 (dm, J 7.0 Hz)	7.394 (m, 6H) 7.493 (m, 4H)	7.268 (m, 6H) 7.105 (m, 4H)
C	7.242 (s)	8.662 (s)	8.338 (dm, J 7.3 Hz)	7.648 (dm, J 7.3 Hz)	7.445 (m, 6H) 7.523 (m, 4H)	7.316 (m, 6H) 7.127 (m, 4H)
D	7.274 (s)	8.680 (s)	8.348 (dm, J 7.3 Hz)	7.655 (dm, J 7.3 Hz)	7.456 (m, 6H) 7.521 (m, 4H)	7.333 (m, 6H) 7.117 (m, 4H)

ones) towards weak field. The signal positions tend to those for protonated molecule.

Thus, the similarity between the spectra of protonated betaine and of that associated with Mg^{2+} and La^{3+} ions suggests a parallelism between the usual acid-base interaction and that of the betaine with Lewis acids, the metal ions being the latter. In this connection, it is to note that the use of betaine dyes as acid-base sensors or metal ion ones is associated with some difficulties, mainly with that these interactions are of the same type.

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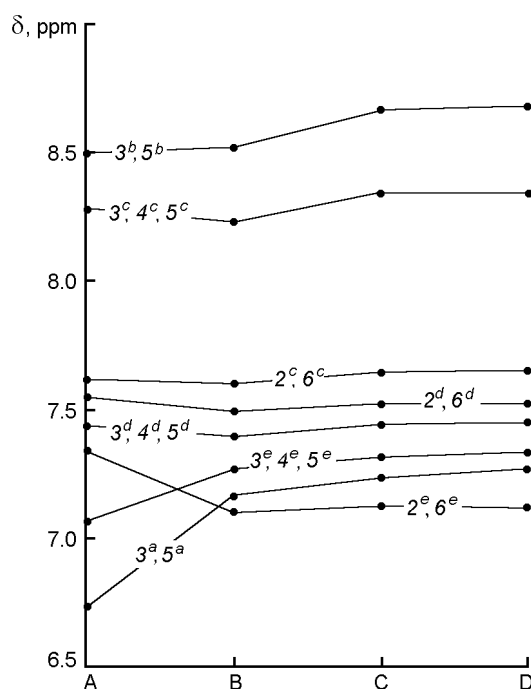


Fig. 2. Changes in chemical shifts of the betaine molecule protons when passing from A to D systems.

**Вплив іонів металів на відгук
сольватохромних індикаторів Райхардта:
ЯМР-спектроскопічне дослідження**

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Асоціацію іонів Mg^{2+} і La^{3+} з бетаїновими барвниками Райхардта у дейтерированому DMSO досліджена з застосуванням метода ПМР. На підставі значень хімічних зсувів протонів бетаїну у присутності іонів металів, а також хімічних зсувів протонів протонаного бетаїну зроблено висновок щодо кислотно-основного характеру взаємодії іонів Mg^{2+} і La^{3+} з молекулою барвника. Отримані дані дозволяють зробити висновок про неприпустимість застосування кислотно-основних сенсорів на основі бетаїнів у присутності багатозарядних іонів металів.