

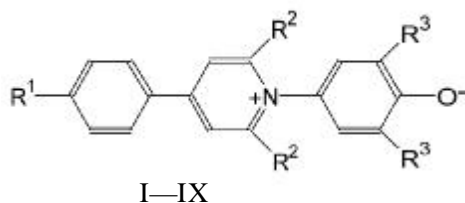
УДК 541.13

N.O. Mchedlov-Petrossyan, Yu.V. Isaenko, S.T. Goga, L.N. Vilkova, V.I. Borodenko, S.V. Shekhovtsov, C. Reichardt

ACID/BASE PROPERTIES OF SOLVATOCHROMIC PYRIDINIUM-*N*-PHENOLATE BETAINE DYES IN PURE AND MIXED SOLVENTS

The protonation constants of a set of solvatochromic pyridinium-*N*-phenolate betaine dyes I–XI (D^{\pm}) were determined in methanol, water, and the ternary solvent mixture benzene – ethanol – water (with mass ratio 47:47:6) using the vis spectroscopic method. Both, medium effects on transferring from water to organic solvents and salt effects in aqueous media are in agreement with the zwitterionic nature of the betaines, which possess a high dipole moment in the electronic ground state. The character of solvation of dyes D^{\pm} in the ternary solvent mixture is discussed basing on the position of the charge-transfer (CT) absorption band in the visible region. The association of the betaine dyes with metal ions (Na^+ , Mg^{2+} , La^{3+}) in 1-butanol manifests itself in a disappearance of the long-wavelength CT band as result of a complex formation with the cationic Lewis acids.

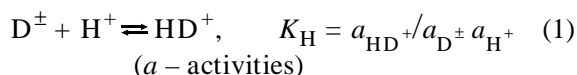
Pyridinium *N*-phenolate betaine dyes exhibit the largest range of solvatochromism among up-to-now known organic dyes. Therefore, they are often used for creating polarity scales of solvents [1] as well as for the polarity estimation of interfaces in various micro- and ultramicroheterogeneous systems, such as micellar solutions of colloidal surfactants, microemulsions, suspensions of liposomes, etc. [1–5]. Furthermore, they can be used as pH-indicators for simultaneous checking of the interfacial acidity in the aforesaid colloidal systems [3–5]. The structural formulas of some typical solvatochromic betaine dyes D^{\pm} are presented below:



I: $R^1=R^3=H$, $R^2=C_6H_5$; II: $R^1=H$, $R^2=R^3=C_6H_5$; III: $R^1=C(CH_3)_3$, $R^2=R^3=4-C(CH_3)_3-C_6H_4$; IV: $R^1=H$, $R^2=C_6H_5$, $R^3=C(CH_3)_3$; V: $R^1=CO_2^-Na^+$, $R^2=R^3=C_6H_5$; VI: $R^1=CF_3$, $R^2=R^3=4-CF_3-C_6H_4$; VII: $R^1=C_6F_{13}$, $R^2=C_6F_{13}-C_6H_4$, $R^3=C_6H_5$; VIII: $R^1=H$, $R^2=C_6H_5$, $R^3=Cl$; IX: $R^1=H$, $R^2=R^3=3$ -pyridyl. (In the case of dye V, the colored species exists in solutions as an anion D^{\mp}).

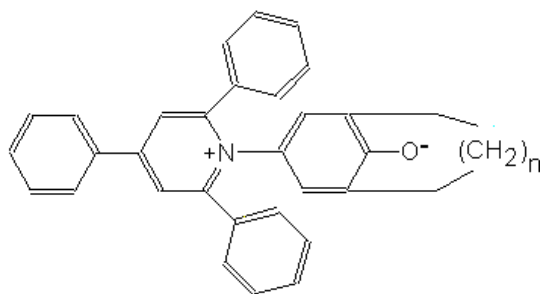
Whereas the vis absorption spectra of these dyes in their highly dipolar zwitterionic form, D^{\pm} , especially their polarity-sensitive charge-transfer (CT) band, are well documented, the information

concerning their acid/base properties is relatively sparse. Protonation of the phenolate oxygen leads to decolorization of the dye solutions. The protonation constants in lyophilic colloidal systems are traditionally compared with those in non-aqueous solvents, including water-organic mixtures. At present, solvatochromic betaine dyes serve as useful tools for the versatile examination of the properties of surfactant micelles, vesicles, droplets of microemulsions, etc. Using a set of dyes instead of the single standard betaine dye II allows to obtain manifold informations. Therefore, it seemed to be pertinent to determine the protonation constants K_H :



of a whole set of the betaine dyes I–XI in two kinds of solvents: in pure methyl alcohol as a standard organic solvent ($\epsilon_r=32.7$), where preferential solvation is impossible, and in a ternary benzene–ethanol–water mixture, with mass ratio 47:47:6 ($\epsilon_r=12.8$), designated as BEW. In the latter solvent mixture, marked differences in the solvation character of hydrophobic and relatively hydrophilic (at least, water-soluble) betaine dyes can be expected. Besides, dissociation constants of some organic acids, e.g., of salicylic and benzoic acids, measured in methanol, are close to those obtained in the BEW solvent mixture, which is convenient for a comparison of the values of the betaine dyes. The betaine dyes X and XI with a polymethylene chain surrounding the phenolate moiety were studied as well.

© N.O. Mchedlov-Petrossyan, Yu.V. Isaenko, S.T. Goga, L.N. Vilkova, V.I. Borodenko, S.V. Shekhovtsov, C. Reichardt, 2007



X: $n=9$; XI: $n=12$.

Some of betaine dyes are only sparingly soluble in water. In methanol, ion association, homocoupling, and some other effects hindering the exact determination of K_H values, are expected to be less expressed as compared with other organic solvents. On the other hand, the ternary solvent mixture can be considered as a model of water/micelle or water/microdroplet interfaces, owing to its complicated character. The mole fractions of the components in the BEW mixture are equal to 0.31, 0.52, and 0.17, respectively.

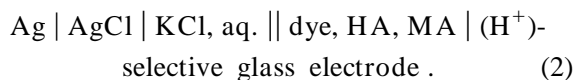
The K_H values were determined vis-spectroscopically, using the pH scale of acidity in water. In non-aqueous solvents, the $pa_{H^+}^*$ scales were used, standardized to a hypothetical state with H^+ activity equal to unity and with some properties of an infinitely diluted solution in the given solvent.

The origin and main properties of betaine dyes I—XI were described earlier [1—4, 6, 7]. All the substances used for preparation of buffer mixtures, salts, and solvents were purified using conventional procedures. The water content in methanol was 0.01—0.02 % mas., as estimated by potentiometric titration according to Fischer's method. Initial solutions of sodium methylate were prepared dissolving sodium in the proper amount of methanol; its concentration was determined by titration after proper dilution with water. The vis spectra were run using a SF-46 apparatus, at dye concentrations of about $c \approx 5 \cdot 10^{-5}$ mol/L. All solutions were prepared and the measurements were performed at 298 ± 0.2 K.

The determination of K_H in methanol was performed using benzoate, diethylbarbiturate, and ethylphenylbarbiturate buffer mixtures, which were created by varying the acid concentration. The ionic strength was equated to the total concentration of CH_3ONa , which was maintained constant ($c=0.01$ mol/L). The $pa_{H^+}^*$ values were calculated using the following $\log K_H (=pK_a)$ values for buffer acids, HA, in methanol: 7.90 (salicylic) [5], 9.40 (benzoic) [5], 12.70 (diethylbarbituric) [5], and 12.35 (ethylphenyl-

barbituric). The last value (± 0.11) was determined by us using thymol blue as an indicator. During the $\log K_H$ determinations, approximately ten working solutions with different $pa_{H^+}^*$ values were prepared. Several wavelengths near the λ_{max} value of the CT band were used as analytical positions. Some vis spectra were registered in methanol solutions, in HA solutions, or in diluted solutions of HCl in methanol. The activity coefficients f of all ionic species were calculated using the Debye-Huckel equation (second approach).

In the BEW solvent system, the procedure was the same, with two exceptions: (i) the incomplete dissociation of MA salts of the buffers ($M^+ = Na^+$, Li^+) was taken into account, $\log K_{ass}(M^+ + A^-) = 3.46$ — 3.48 [5], and (ii) the $pa_{H^+}^*$ values were additionally checked using a glass electrode in a cell with liquid junction:



The buffer mixtures were prepared with a constant initial concentration of NaOH (0.01 mol/L) and concentrations of HA varying from $1.5 \cdot 10^{-3}$ to $7.5 \cdot 10^{-3}$ mol/L. The cell (2) was standardized using buffer solutions with $pa_{H^+}^* = 6.83$ ($8.4 \cdot 10^{-3}$ mol/L salicylic acid + $8.4 \cdot 10^{-3}$ mol/L lithium salicylate) and $pa_{H^+}^* = 8.48$ ($8.4 \cdot 10^{-3}$ mol/L benzoic acid + $8.4 \cdot 10^{-3}$ mol/L lithium benzoate). For parallel $pa_{H^+}^*$ calculations, the iterative procedure was used. The degree of MA dissociation appeared to be 34 to 39 %. The $\log K_H (=pK_a)$ values for buffer acids, HA, are as follows: 7.60 (salicylic acid), 9.26 (benzoic acid), and 11.97 (5,5-diethylbarbituric acid).

For the determination of the K_H values of betaine dyes D^\pm in water, K_H^w , a common vis-spectroscopic procedure was used, accompanied by pH checking with a glass electrode.

Thermodynamic values of $\log K_H$ are compiled in table 1. All the constants are expressed in the mol/L scale. At this stage, the possibility of HD^+ association with anions X^- of the buffer acids (see below) was not taken into account.

The vis spectra of some typical dyes measured in methanol are shown in fig. 1, the λ_{max} values are given in table 2. Generally, the results obtained are in agreement with literature data [1, 5, 6]. In the case of dye IV, the deviation is 5 nm (the most significant difference). It must be taken into account that the λ_{max} values of a given dye measured in pure methanol and in corresponding buffer systems differ sometimes from each other. The largest diffe-

Table 1

Logarithms of the thermodynamic protonation constants, $\log K_H$, of betaine dyes I—XI, determined in water, methanol, and the ternary solvent mixture BEW ($C_6H_6-C_2H_5OH-H_2O$ with mass ratio 47:47:6) at 298 K

Dye	$\log K_H$			$\Delta \log K_H$	
	in H_2O	in CH_3OH	in BEW	$H_2O \rightarrow CH_3OH$	BEW $\rightarrow CH_3OH$
I	8.55 ± 0.02	11.72 ± 0.15	10.27 ± 0.05	3.17	1.45
II	8.64 [2,5]	11.59 ± 0.06	9.52 ± 0.03	2.95	2.07
III	—	11.80 ± 0.03	9.90 ± 0.05	—	1.90
IV	—	13.30 ± 0.06	11.29 ± 0.01	—	2.01
V	8.77 ± 0.02	12.06 ± 0.10	—	3.29	—
VI	—	9.73 ± 0.05	—	—	—
VII	—	10.99 ± 0.04	—	—	—
VIII	4.76 ± 0.03 [5]	8.44 ± 0.01	6.99 ± 0.01	3.68	1.45
IX	6.66 [3]	9.25 ± 0.15	—	2.59	—
X	—	13.42 ± 0.10	—	—	—
XI	—	13.69 ± 0.07	—	—	—

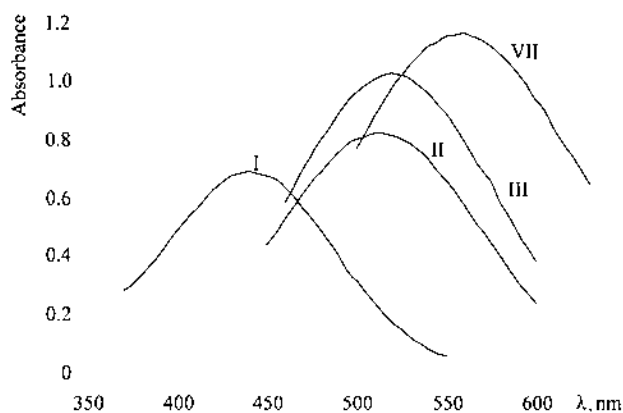


Fig. 1. Vis absorption spectra of betaine dyes I, II, III, and VII, dissolved in methanol. Dye concentration $c = 8 \cdot 10^{-5}$ mol/L, optical path length 3 cm.

rences were observed for dye IX ($\lambda_{max} = 492$ nm in pure methanol, 490—491 nm in benzoate, and 487 nm in 5,5-diethylbarbiturate buffer solutions) and for dye VI ($\lambda_{max} = 522$ nm in pure methanol and 513 nm in 5,5-diethylbarbiturate buffers). This can be regarded as indication of some weak interactions of secondary character (see below).

The λ_{max} values of the betaine dyes D^\pm measured in the BEW solvent mixture are essentially higher than those in methanol. The difference $\Delta \lambda_{max}$ varies from 42 to 84 nm (table 2). For all these solvatochromic betaine dyes, except X and XI, linear correlations are known between their molar transi-

tion energies (E_T) and those of the standard betaine II in a set of individual solvents [1, 2, 6, 7]. Hence, the expected λ_{max} values in the ternary solvent mixture can be easily calculated. Inspection of table 2 reveals that the 'predicted' λ_{max} values are generally higher than those obtained experimentally in the BEW solvent mixture. The difference $\Delta \lambda_{max}$ is markedly expressed for the most hydrophilic dyes, I and IX. However, even for the betaine dyes having large hydrophobic sites, namely, dyes III, IV, VI, and VII, the experimental values do not exceed the calculated ones. Hence, neglecting the high content of benzene (mole fraction $x_1 = 0.31$), a complete solvation of the hydrophobic (and benzene-soluble!) dyes with benzene solvent molecules does not occur. Probably, not only ethanol, but also water molecules (mole fractions $x_2 = 0.52$ and $x_3 = 0.17$, respectively) take part in solvation of

the negative part of the D^\pm dipoles. For example, the expressed negativity of the difference [λ_{max} (experimental) — λ_{max} (calculated)] probably indicates the strong preferable hydration of the phenolate group. Besides, for such large molecules dissolved in mixed solvents, a selective solvation of different sites by different solvent molecules seems to be very probable.

The $\log K_H^w$ values presented in table 1 are thermodynamic ones. We also determined the 'mixed' $\log K_H^{w*}$ values at ionic strengths of $I = 0.025, 0.03, 0.0375, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3,$ and 0.5 mol/L. The required I values were maintained with additions of NaCl to acetate, phosphate, and borate buffer mixtures. These data are depicted in fig. 2, in form of traditional dependences on $I^{1/2}$.

The character of the curves in fig. 2 indicates that the colored betaine species behave themselves not as usual neutral molecules. For charge types of acid/base couples such as A^+B^0 and A^0B^- , in terms of Kolthoff and Bates [5, 8], the $\log K_H^{w*}$ values must correspondingly increase and decrease along with an increase in $I^{1/2}$, at least up to medium ionic strengths. However, the protonation constants of dyes I and VIII stay practically unchanged (fig. 2). Hence, the situation is typical for such indicators as methyl orange and thymol blue (acid region), acids of charge type $A^\pm B^-$ [8]. Zwitterions are known to behave themselves as two separate charges only in dilute solutions; maybe, this is the case with betaine dye VIII at low I (fig. 2). Betaine dye V possesses

Table 2

Vis absorption maxima, λ_{\max}/nm , of the betaine dyes I—XI, measured in methanol and in the ternary solvent mixture BEW ($\text{C}_6\text{H}_6\text{—C}_2\text{H}_5\text{OH—H}_2\text{O}$ with mass ratio 47:47:6) and related wavelength differences, $\Delta\lambda_{\max}/\text{nm}$

Dye	λ_{\max}		$\Delta\lambda_{\max} = \lambda_{\max}$ (in BEW) – λ_{\max} (in CH_3OH)	$\Delta\lambda_{\max}$ (BEW) = λ_{\max} (exp.) – λ_{\max} (calc.)
	in CH_3OH	in BEW		
I	440	484	44	–(30–20)
II	514	575	61	0
III	520	586	66	0
IV	558	642	84	–11
V	521	570	49	–6
VI	522	565	43	–17
VII	560*	625	65	–9
VIII	441	486	45	–4
IX	492	529	37	–23
X	533	603	70	—
XI	530	596	66	—

* $\lambda_{\max} = 600 \text{ nm}$ in the binary solvent mixture methanol—benzene (1:1 v/v).

an additional CO_2^- group; the charge type can be represented as $\text{A}^{\pm}\text{B}^{\pm}$, and the ($\log K_{\text{H}}^{w*}$ vs. $I^{1/2}$) dependence is more close to that for acids of A^0B^- type [5, 8]. Therefore, the thermodynamic K_{H}^w value for betaine dye I was equated to K_{H}^{w*} , and for an estimate of the $\log K_{\text{H}}^w$ values of betaine dyes V and VIII, a quantity of 0.06 (calculated by the Debye–Huckel equation, second approach) was added to their $\log K_{\text{H}}^{w*}$ values at $I=0.025 \text{ mol/L}$.

Simultaneously, the influence of salt additives on the spectra of D^{\pm} in water was checked. Even at

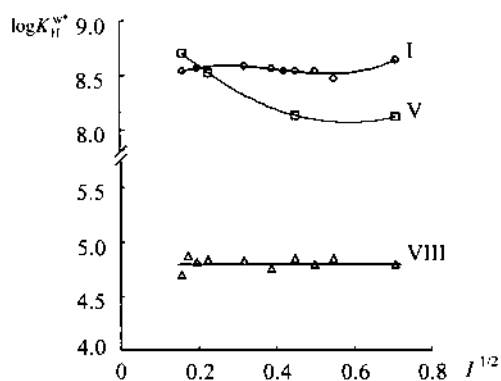


Fig. 2. The dependence of $\log K_{\text{H}}^{w*}$ on $I^{1/2}$ ($\text{NaCl} + \text{buffer}$) for the betaine dyes I, V, and VIII.

$c(\text{NaCl})=0.5 \text{ mol/L}$, the alterations of CT bands were very modest.

The $\log K_{\text{H}}$ values in methanol (table 1) were determined following the standard procedure. As the length of the $\text{pa}_{\text{H}^+}^*$ scale in methanol is 16.7–17.2, the solution of CH_3ONa with $c=0.01 \text{ mol/L}$ corresponds to $\text{pa}_{\text{H}^+}^* \approx 15$ and hence is suitable for measurements of D^{\pm} spectra. The slopes of the graphs $\log\{[\text{HD}^+]/[\text{D}^{\pm}]\}$ vs. $\text{pa}_{\text{H}^+}^*$ are close to unity. For instance, for dye VIII in benzoate buffer solutions, the following dependence is valid:

$$\begin{aligned} \log\{[\text{HD}^+]/[\text{D}^{\pm}]\} &= \\ &= (9.03 \pm 0.02) - (1.036 \pm 0.002) \cdot \text{pa}_{\text{H}^+}^* \quad (3) \\ (r = 0.996, n = 11) \end{aligned}$$

In the case of dye V, the carboxylic group is ionized in the solutions used for the $\log K_{\text{H}}$ determination, hence the protonated species is a zwitterion with a CO_2^- group. For dye IX, the second equilibrium (protonation of N-atom) is also to be taken into account.

Let us consider the $\log K_{\text{H}}$ values determined in methanol. The $\log K_{\text{H}}$ value of dye I is with 11.72 markedly lower than that of the phenolate ion in methanol (14.46) [9], thus reflecting the electron-acceptor properties of the 4-phenyl-pyridinium moiety. The protonation constants for dyes I, II, and III differ but only slightly. Such finding agrees with the fact that for the groups C_6H_5 and 4- $\text{C}(\text{CH}_3)\text{-C}_6\text{H}_4$ the Hammett σ constants are close to zero [10]. Replacement of the phenyl groups by electron-withdrawing 3-pyridyl rings (Hammett's $\sigma_a = +0.72$ for 3-pyridyl [10]) reduces the basicity of the phenolate moiety of IX and increases the acidity of the corresponding *N*-(4-hydroxyphenyl)pyridinium ion [3]. This explains the difference between $\log K_{\text{H}}$ values of betaine dyes II (11.59) and IX (9.25). The $\log K_{\text{H}}$ value of dye V is by 0.47 units higher than that of dye II. The effective positive charge at the carbon atom can cause electron-acceptor properties of the CO_2^- group. However, the inductive and mesomeric effects are probably low in the given case, and the CO_2^- group favors protonation of the phenolate oxygen owing to the additional negative charge in V as compared with that of II. In water, the effect is less expressed (table 1), but a decrease in the ϵ_r value of the solvent is known to strengthen such effects [5].

The $\log K_{\text{H}}$ values of betaine dyes IV, X, and XI are by 1.6–2.0 units higher than that of the unsubstituted dye I. This agrees with the well-known effects [3, 4, 9, 10]: the influence of two strong elec-

tron-withdrawing chlorine substituents in 2,6-positions results in a decrease in $\log K_H$ value by 3.3 units on going from betaine I to betaine VIII. This is in line with the data for unsubstituted phenol-sulfonephthalein and its 3,3',5,5'-tetrabromoderivative in methanol ($\log K_H=12.8$ and 8.9, respectively) [5, 8], as well as with the data for halogen-substituted phenols [3].

Hammett constants of $\sigma_m=0.46$ and $\sigma_p=0.53$ [9] reflect the influence of the CF_3 group. The similarity of σ values for the groups CF_3 , C_2F_5 , and C_4F_9 [9] allows to expect that the electron influence of CF_3 and C_6F_{13} groups is also similar. The effect of one 2- C_6H_4 -4- CF_3 group, as obtained by comparison of the $\log K_H$ values for dyes VII and VI, is 0.63. This approximately agrees with the electron-acceptor properties of the trifluoromethyl group.

The character of medium effects in the given solvent S (here $S = CH_3OH$), i.e., $\Delta \log K_H = \log K_H^S - \log K_H^w$, gives some information about the structure of the acid/base couple [1, 8, 10]. The $\Delta \log K_H$ value can be expressed through activity coefficients of transfer, $\gamma(i)$, of the reactants from water to S :

$$\Delta \log K_H = \log {}^w\gamma^s(H^+) + \log {}^w\gamma^s(D^\pm) - \log {}^w\gamma^s(HD^+) \quad (4)$$

Naturally, the ${}^w\gamma^s(H^+)$ value is the same for all the acid/base couples for the given H_2O-S pair. If S is CH_3OH , $\log {}^w\gamma^s(H^+) = 1.52$ (molar scale of concentrations), as obtained by the tetraphenylborate assumption [5]. For betaine dyes, $\Delta \log K_H$ values are within the range of 2.6–3.7 units (table 1), whereas for common neutral bases, such as *ortho*-chloroaniline, *meta*-nitroaniline, and methyl yellow, the $\Delta \log K_H$ values do not exceed unity [8]. For such acid/base couples the charge type is A^-B^0 [5, 8]. At the same time, for anionic bases (hydrosalicylate, benzoate, etc.) the $\Delta \log K_H$ values are ≈ 5 [5, 8]; for phenolate, this value equals to 4.5. Here, the charge type of the acid/base couple is A^0B^- [10]. Hence, the medium effects for betaine dyes are markedly higher than for acid/base systems of the A^+B^0 charge type and somewhat lower than that for A^0B^- couples. This is typical for acid/base couples of the A^+B^\pm charge type [5, 8]; e.g., for the rhodamine B zwitterion in methanol, $\Delta \log K_H = 4.3$ [5]. Hence, the $\Delta \log K_H$ values of the betaine dyes are in accord with the zwitterionic character of the dye species D^\pm .

In contrast to the λ_{max} values, the K_H constants are much higher in methanol than in the BEW solvent mixture, notwithstanding the much lower ϵ_r value of the last solvent system. The difference is

1.45 to 2.07 logarithmic units (table 1). Such a result is obviously caused by the presence of a macroamount of water, which inevitably leads to hydration of the proton. Hence, the lyonium ion stays mainly as H_3O^+ (or $H_5O_2^+$, etc.), while in methanol the proton is methanolated, and the $\log {}^w\gamma^s(H^+)$ quantity ($S = CH_3OH$) makes a much higher contribution to the $\Delta \log K_H$ value.

The protonation constants of the D^\pm species in the BEW solvent mixture presented in table 1 are calculated without taking into account the (probable) association of HD^+ cations with anions A^- of the buffer acids. If such association is expressed well enough, the formulas used for the calculation of the thermodynamic $\log K_H$ values must include an additional logarithmic term containing K_{ass} :

$$\log K_H = pa_{H^+}^* + \log \{ [HD^+] / [D^\pm] \} + \log f_{HD^+} - \log \{ 1 + [A^-] f_{HD^+} f_{A^-} K_{ass} \}, \quad (5)$$

with $[A^-] = 3.6 \cdot 10^{-3}$ mol/L and $\log f = -0.374$. If we assume that the K_{ass} value for the $HD^+ + A^-$ interaction is analogous to that for association of Na^+ (Li^+) with A^- , i.e., $K_{ass} = 2.95 \cdot 10^3$ L/mol (average

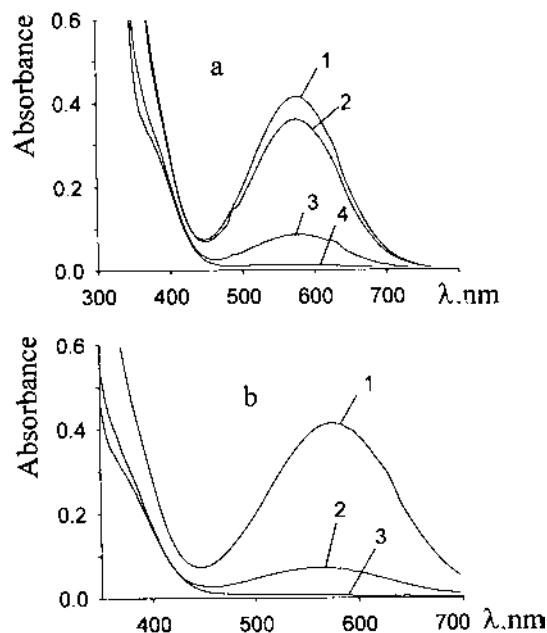


Fig. 3. Vis-absorption spectra of betaine II, dissolved in 1-butanol and measured at 298 K, with initial dye concentration of $c = 1.00 \cdot 10^{-4}$ mol/L: *a* — without any additives (1); with $1.00 \cdot 10^{-4}$ mol/L $NaClO_4$ (2); $0.5 \cdot 10^{-4}$ mol/L $Mg(ClO_4)_2$ (3); $0.333 \cdot 10^{-4}$ mol/L $La(ClO_4)_3$ added (4); *b* — without any additives (1); with 0.01 mol/L $NaClO_4$ (2); $5.0 \cdot 10^{-3}$ mol/L $Mg(ClO_4)_2$ added (3).

value), see above, then the $\log K_H$ values given in table 1 must be reduced by 0.4—0.5 logarithmic units. On the other hand, the phenolate oxygen of the D^\pm species is known to associate with metal cations in anhydrous, mainly aprotic solvents. This phenomenon leads to rather distinct spectral changes.

Indeed, while the λ_{\max} value of dye IX in methanol equals to 490—491 nm (in diluted benzoate buffers), progressive addition of NaCl results in band shifts to $\lambda_{\max} = 486—488$ nm (0.01 mol/L NaCl) and 470—474 nm (0.3 mol/L NaCl). For dye X in diluted CH_3ONa solutions in methanol, addition of 0.3 mol/L NaClO_4 leads to a band shift from $\lambda_{\max} = 442$ to 428—429 nm. However, the aforesaid effects manifest themselves more distinct in 1-butanol, a solvent with much lower dielectric constant ($\epsilon_r = 17.5$; compared with 32.7 for methanol).

In 1-butanol, the association of the betaine dyes with metal ions (Na^+ , Mg^{2+} , La^{3+}) manifests itself in a disappearance of the long-wavelength CT bands as a result of complex formation with these cationic Lewis acids. Typical vis spectra are shown in fig. 3. A detailed study of such interactions in different organic solvents will be published elsewhere.

РЕЗЮМЕ. Константи протонізації серії сольватохромних піридиній-*N*-фенолятичних бетаїнових барвників (D^\pm) визначено у метанолі, воді та у тернарному розчиннику бензол—етанол—вода (з масовим співвідношенням 47:47:6) за допомогою спектрофотометричного методу. Як ефекти середовища, що спостерігаються при переході від води до метанолу, так і сольові ефекти у водних розчинах узгоджуються з цвіттерійною будовою бетаїнів, молекули яких мають великий дипольний момент в основному стані. Характер сольватації барвників D^\pm у тернарній суміші розглянуто з урахуванням положення смуги переносу заряду. Асоціація бетаїнів з йонами Na^+ , Mg^{2+} та La^{3+} в 1-бутанолі приводить до зникнення цієї смуги внаслідок створення комплексів з цими кислотами Льюїса.

V.N. Karazin Kharkov National University
Philipps University, Marburg, Germany

РЕЗЮМЕ. Константы протонизации серии сольватохромных пиридиний-*N*-фенолятичных бетаиновых красителей (D^\pm) определены в метаноле, воде и в тернарном растворителе бензол—этанол—вода (с массовым соотношением 47:47:6) спектрофотометрическим методом. Как эффекты среды, которые наблюдаются при переходе от воды к метанолу, так и солевые эффекты в водных растворах согласуются с цвиттерийонным строением бетаинов, молекулы которых имеют большой дипольный момент в основном состоянии. Характер сольватации красителей D^\pm в тернарной смеси рассмотрен с учетом положения полосы переноса заряда. Ассоциация бетаинов с ионами Na^+ , Mg^{2+} и La^{3+} в 1-бутаноле приводит к исчезновению этой полосы вследствие образования комплексов с этими кислотами Льюиса.

1. Reichardt C. Solvents and Solvent Effects in Organic Chemistry. 3rd, updated and enlarged ed. -Weinheim, Germany: Wiley-VCH, 2003; and references cited therein.
2. Kessler M.A., Wolfbeis O.S. // Chem. Phys. Lipids. -1989. -**50**. -P. 51—56.
3. Vodolazkaya N.A., Mchedlov-Petrosyan N.O., Heckenkemper G., Reichardt C. // J. Mol. Liquids. -2003. -**107**, № 1—3. -P. 221—234.
4. Mchedlov-Petrosyan N.O., Isaenko Yu.V., Goga S.T. // Russ. J. Gen. Chem. -2004. -**74**, № 11. -P. 1741—1747, and references cited therein.
5. Mchedlov-Petrosyan N.O. Differentiation of the Strength of Organic Acids in True and Organized Solutions (in Russian). -Kharkov: Kharkov University Press., 2004.
6. Reichardt C., Eschner M., Schafer G. // J. Phys. Org. Chem. -2001. -**14**. -P. 737—751.
7. Stadnicka K., Milart P., Olech A., Olszewski P.K. // J. Mol. Struct. -2002. -**604**. -P. 9—18.
8. Bates R.G. Determination of pH (Russian translation). -Leningrad: Khimiya, 1972.
9. Exner O. // Correlation Analysis in Chemistry-Recent Advances / Eds.: N.B. Chapman, J. Shorter. -New York; London: Plenum Press, 1978. -Ch. 10. -P. 439—540.
10. Ershov V.V., Nikiforov G.A., Volodkin A.A. Sterically hindered phenols (in Russian). -Moscow: Khimiya, 1972.

Received 01.11.2006