

## THERMOCHROMISM OF CORROLE SOLUTIONS IN ETHANOL

Y. H. Ajeeb,<sup>a,b</sup> A. A. Minchenya,<sup>b</sup> P. G. Klimovich,<sup>b</sup>  
W. Maes,<sup>c</sup> and M. M. Kruk<sup>b\*</sup>

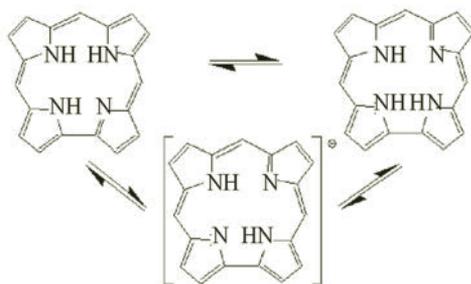
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The temperature dependence of electronic absorption spectra of a family of 5,10,15-triarylcorroles in EtOH solution was studied in the range 288–328 K. Corroles in EtOH existed as mixtures of the free base and deprotonated form, the ratio of which was determined by the donor–acceptor properties of the peripheral substituents. Free corrole bases deprotonated as the temperature rose. Deprotonation obeyed the van't-Hoff equation with activation energy  $E_a = 2.0$  kcal/mol, which was the same within measurement error limits for all studied compounds. The temperature was proposed to affect indirectly the deprotonation by changing the EtOH dielectric constant. The decreasing dielectric constant with increasing temperature shifted the acid–base equilibrium toward formation of the deprotonated form.

**Keywords:** corrole free base, acid–base equilibria, activation energy, thermochromism.

**Introduction.** Corroles form a class of contracted tetrapyrrole macrocyclic compounds because one of the bridges joining pyrrole rings is missing the C atom so that two neighboring pyrrole (pyrroline) rings are bonded to each other through a  $C_\alpha$ – $C_\alpha$  bond. The contraction of the macrocycles causes corrole free bases to differ from those of porphyrins. Corroles contain three pyrrole and one pyrroline ring whereas porphyrins have two pyrrole and two pyrroline rings. Contracted corrole tetrapyrrole macrocycles are nonplanar because the sum of van-der-Waals radii of the three protons interacting in the cavity is greater than the cavity diameter [1]. The protons cannot settle into the cavity so the pyrrole rings deviate by alternating up-down-up positions from the mean macrocycle plane. In essence, the deviations are rotations of pyrrole rings around the axis passing through the pyrrole  $C_\alpha$  atoms and pyramidal distortions of pyrrole N atoms to give partial  $sp^3$ -hybridization [2, 3]. It is noteworthy that the shorter distance between two neighboring pyrrole and pyrroline rings in the contracted corrole macrocycle favors H-bond formation that in turn helps to make the tetrapyrrole macrocycle planar. These factors even without steric interaction of peripheral substituents cause corrole tetrapyrrole macrocycles to adopt a wavy nonplanar conformation [2–4].

The acid–base properties of tetrapyrrole macrocycles change considerably if nonplanar conformers are formed. The pyrrole protons and pyrroline N atoms are exposed to the solvent and accessible for intermolecular interaction with both solvent and other molecules occurring in the solution [5–7]. The basicity and acidity decrease if the protons are shielded in the macrocycle plane and increase for nonplanar conformers [7]. Acid–base equilibria of corrole macrocycles cause the free bases to exist as two NH-tautomers in solutions:



\*To whom correspondence should be addressed.

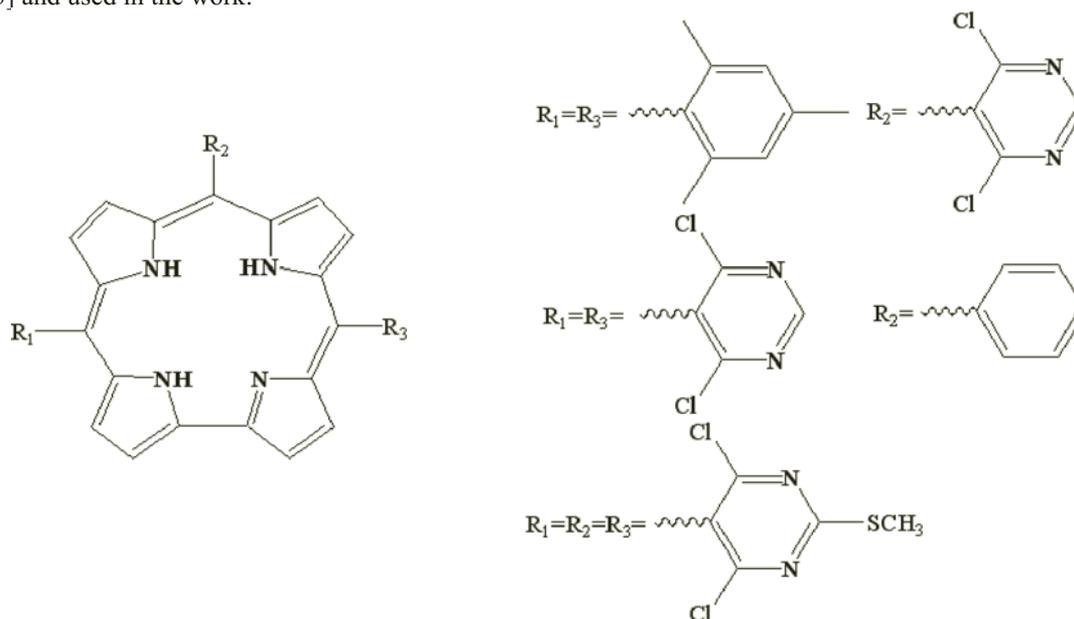
<sup>a</sup>Arts, Sciences and Technology University in Lebanon, P. O. Box 14-695, Beirut, Lebanon; email: yousef.ajeab@aul.edu.lb; <sup>b</sup>Belarusian State Technological University, 13a Sverdlov Str., Minsk, 220006, Belarus; email: m.kruk@belstu.by; krukikalai@yahoo.com; <sup>c</sup>Institute for Materials Research (IMO-IMOMEC), Hasselt University, B-3590, Diepenbeek, Belgium; email: wouter.maes@uhasselt.be. Translated from Zhurnal Prikladnoi Spektroskopii, Vol. 86, No. 5, pp. 697–704, September–October, 2019. Original article submitted May 24, 2019.

Differences in  $pK_a$  values of all macrocycle pyrroles are due to asymmetric out-of-plane distortions and different slopes of pyrrole (pyrrolenine) rings relative to the mean macrocycle plane [8]. The structure of a given NH-tautomer determines which intermolecular interactions occur during solvation by a single solvent because any solvent molecule has both basic and acidic properties. Analyzing the mechanisms of such interactions is a critical interdisciplinary problem because interactions with solvent molecules during formation of the solvation sphere affect the properties of the tetrapyrrole chromophores themselves and those of dendrimers with a tetrapyrrole core or supramolecular systems with many macrocyclic tetrapyrrole chromophores. Also, tetrapyrrole compounds can be used as molecular probes to characterize microenvironments if the processes occurring during solvation are understood.

Solvents were shown to be responsible for facile shifts of acid–base equilibria between a corrole tetrapyrrole macrocycle free base and one deprotonated in the core [8]. Attempts to establish a single-parameter correlation between the shift of acid–base equilibrium in the macrocycle core and any empirical quantity characterizing the solvent basicity or polarity were unsuccessful. A two-parameter model of acid–base equilibria was proposed by us to explain the observed transformations in various solvents [9, 10]. The model was based on multicenter intermolecular interactions in the tetrapyrrole macrocycle core during solvation of the corrole free bases in solution. Deprotonation and protonation can occur simultaneously in the macrocycle core because corrole free bases consist of three pyrrole rings ( $-NH-$  centers) and one pyrrolenine ring ( $-N=$  center). The weighting coefficients in the two-parameter function should have a 3:1 ratio because this state should be stabilized after solvation of the corrole macrocycle. The  $\alpha$ -acidity and  $\beta$ -basicity proposed by Taft and Kamlet were selected as the parameters [11, 12]. The  $\alpha$ -acidity refers to the ability of the solvent to donate a proton to a dissolved molecule to form an intermolecular H-bond. The  $\beta$ -basicity reflects the ability of the solvent to accept a proton from the dissolved molecule to form an intermolecular H-bond. Protonation of the corrole macrocycle core was proposed for  $0.75\alpha + 0.25\beta > 0.25$  because of the progressive increase of proton concentration [9, 10].

The present work studied acid–base equilibria in the core of three corrole macrocycles with different basicities. Absorption spectra in binary MeCN–EtOH solvents were measured. Temperature dependences of absorption spectra in EtOH were studied. Absorption spectra were observed to change considerably as the temperature increased because of deprotonation of corrole free bases. The activation energy of macrocycle deprotonation was determined. Mechanisms for temperature effects on acid–base equilibria in corrole macrocycle cores were discussed.

**Experimental.** Free bases 5,10-mesityl-15-(2,6-dichloropyrimidinyl)corrole (**1**), 5,10-(2,6-dichloropyrimidinyl)-15-phenylcorrole (**2**), and 5,10,15-(2,6-dichloro-4-sulfomethylpyrimidinyl)corrole (**3**) were synthesized by the literature method [13] and used in the work:



Electronic absorption spectra of the studied compounds in EtOH and binary MeCN–EtOH mixtures were recorded on an SM 2203 spectrofluorimeter (ZAO Solar, Belarus). Corrole solution concentrations ( $\leq 1 \cdot 10^{-5}$  M) were determined by spectrophotometry using known extinction coefficients [13]. Experiments used standard quartz cuvettes ( $1 \times 1$  cm) that were placed into the thermostatted compartment of the spectrofluorimeter.

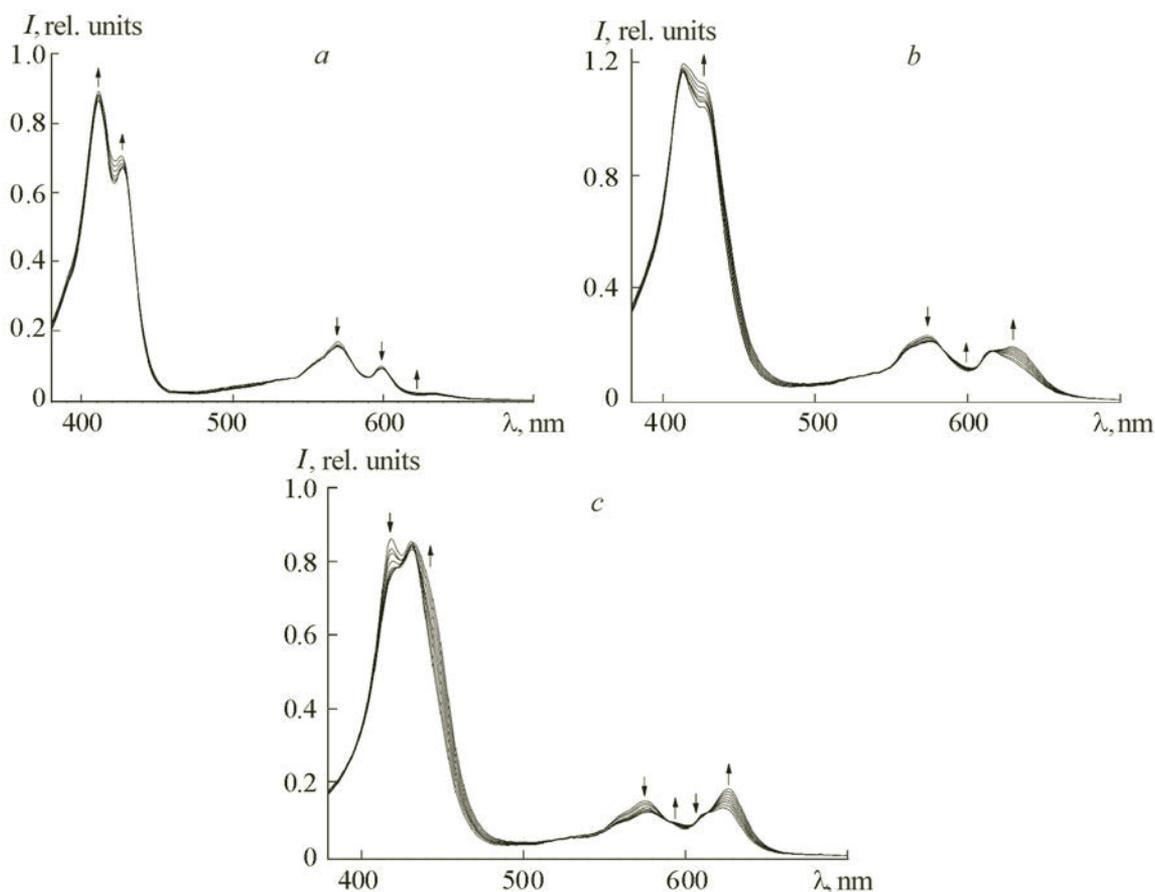


Fig. 1. Electronic absorption spectra of EtOH solutions of corroles **1** (a), **2** (b), and **3** (c) in the range 288–328 K. Arrows indicate the directions of spectral changes caused by increasing concentrations of deprotonated corrole with increasing temperature. Absorption spectra were corrected to account for solvent thermal expansion.

**Results and Discussion.** The difference in the energy barriers for T1  $\rightarrow$  T2- and T2  $\rightarrow$  T1-tautomerism in the electronic ground state of corrole **1** free base was shown before to be much less than  $kT$  [14]. Therefore, the tautomeric equilibrium at ambient temperature could not be shifted toward formation of one of them. It seemed highly interesting to determine whether the equal ground-state energies of the two NH-tautomers of corrole free bases was a common inherent property or a special case for corrole **1**. This issue was resolved by measuring temperature dependences of electronic absorption spectra in EtOH in the range 288–328 K for the three 5,10,15-triarylcorroles with a sequentially varying peripheral substitution pattern. Figure 1 shows absorption spectra that were analyzed to reach the conclusion that the temperature increase was responsible for definite structural changes of all three dissolved compounds. The thermochromic spectral changes increased in the order **1**  $\rightarrow$  **2**  $\rightarrow$  **3**. The spectral changes were fully reversible, i.e., the absorption spectra returned to the initial shape if heated solutions were cooled to the initial temperature. Absorption spectra of solutions of all three compounds exhibited isosbestic points consistent with two mutually converting forms, i.e., the concentration of one form increased at the expense of the other.

As noted above, absorption spectra of corrole **3** changed most with varying temperature. It is noteworthy that the characteristic spectral changes occurred for electronic transitions in the long-wavelength region. Significant absorption in the spectral region between the long-wavelength absorption bands of the T1- and T2-tautomers was observed for corroles **2** and **3** and increased with increasing temperature. The long-wavelength band of the deprotonated form was situated in this region and had an extinction coefficient that was characteristically greater than those of the long-wavelength transitions of the free base T1- and T2-tautomers. A bathochromically shifted absorption band developed in the Soret-band region as the temperature increased. The spectral data as a whole were previously interpreted as an increased concentration

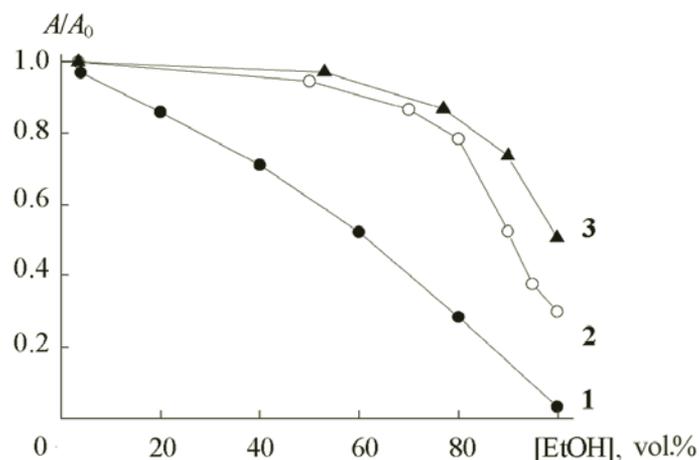


Fig. 2. Dependence of relative concentration of deprotonated corroles **1–3** on volume fraction of EtOH in binary solvent MeCN–EtOH at 295 K.

of the deprotonated corrole [8]. Corroles **2** and **3** absorbed significantly in the range 620–640 nm over the whole studied temperature range. Corrole **1** absorbed little in the range 610–630. This indicated that EtOH solutions of **2** and **3** contained significant concentrations of the deprotonated form whereas its concentration was very low in the solution of **1**.

The greatest spectral changes for **1** were observed in the Soret-band region and were interpreted as slight changes of the relative concentrations of the free base tautomers [14]. The absorption change due to the slightly increased concentration of the deprotonated form was difficult to observe in this region although its increased concentration could be detected reliably at 622 nm, which corresponded to the absorption band maximum of the deprotonated form, because the free base absorption bands were very weak. Thus, thermochromism of all studied solutions occurred because acid–base equilibria of **1–3** free bases and deprotonated forms in EtOH solutions of shifted toward formation of the deprotonated form as the temperature increased.

The significant differences in the states of the studied corroles in EtOH solutions were interesting. For example, **1** at 295 K existed 95% as the free base whereas **2** and **3** in EtOH were ~30 and 50% deprotonated. This could be explained by decreasing basicity (increasing acidity) on going from **1** to **2** to **3**. The basicity  $pK_{a3}$  of tetrapyrrole compounds was shown to be inversely proportional to the weighted sum of resonant  $\sigma_R$  and inductive  $\sigma_I$  Hammett constants of the peripheral substituents [15, 16]. The Hammett constants for the studied corroles could not be accurately calculated because the Hammett constants for pyrimidine groups were not available. However, a trend in the change of  $pK_{a3}$  could be estimated considering the sequentially increasing number of *ortho*-Cl groups in the order **1** → **2** → **3**. Cl atoms have a characteristically large positive inductive constant  $\sigma_I = 0.47$  whereas methyls have  $\sigma_I = -0.07$ . The *ortho*-Cl groups determined the trend of decreasing basicity in the order **1** > **2** > **3** because the resonance Hammett constants  $\sigma_R$  of both groups were small [17].

Absorption spectra of **1–3** were measured in binary solvents MeCN–EtOH (not shown) in order to track formation of their free bases. An analysis of these absorption spectra found that all compounds transitioned gradually from the deprotonated form to the free base as the volume fraction of EtOH increased (Fig. 2). This agreed with the previously proposed two-parameter model of acid–base equilibria in organic solvents. Practically all molecules of **1** were protonated to form the free base on going from MeCN to EtOH, i.e., a transition from the deprotonated form in MeCN to the free base in EtOH was observed. The acid–base titration spectrophotometric curves for **2** and **3** in EtOH terminated prematurely. Acid had to be added for full conversion of the deprotonated form (~30 and 50% for **2** and **3**) to the free base.

One difference between the three compounds was found. The protonation rates were different as the volume fraction of EtOH in the binary solvent MeCN–EtOH increased. The protonation rate  $dn/d[EtOH] = 0.011, 0.028, \text{ and } 0.025$  (vol.%)<sup>-1</sup> for **1**, **2**, and **3**, respectively, at the inflection point of the titration curve (at equal concentrations of free base and deprotonated form). The slow protonation rate of 0.011 for **1** was indicative of few cooperative effects, i.e., basicity constants  $pK_{a3}$  of separate pyrrole rings should noticeably differ. Conversely, the protonation rates of **2** and **3** were 2.5 times faster, indicating that they typically had higher cooperativity for proton binding so that the molecules were fully protonated rapidly after reaching the required proton concentration. This was possible if the separate pyrrole rings had similar  $pK_{a3}$  values.

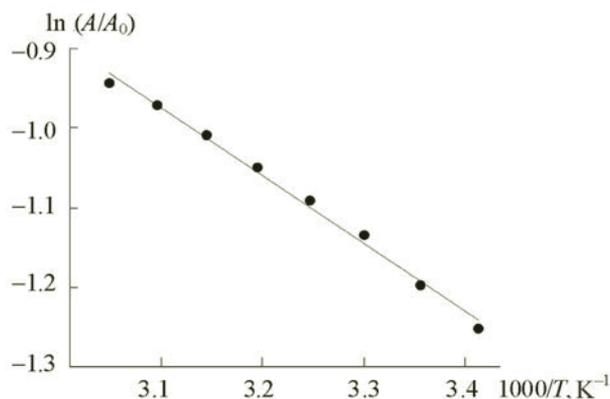


Fig. 3. Van't-Hoff function for relative concentration of deprotonated corrole **2** in the range 288–328 K.

Temperature dependences of **1–3** were analyzed using the van't-Hoff equation in order to determine the deprotonation thermodynamic characteristics (Fig. 3). The relative concentration of the deprotonated form  $A/A_0$ , which was determined as the ratio of absorption at the long-wavelength band maximum of the deprotonated form in EtOH solutions to the corresponding value for the same corrole in MeCN, where all molecules were deprotonated, was used as the analytical variable. The resulting function was linear, indicating that deprotonation was controlled by activation. The activation energies were the same within measurement error:  $E_a = 2.0$  kcal/mol ( $\sim 650\text{--}700$  cm<sup>-1</sup>). This was much less than the activation energy for NH-tautomerization in the excited singlet  $S_1$ -state (4.6 kcal/mol [18]), which excluded a deprotonation mechanism involving excited states.

Let us suppose that deprotonation of the corrole macrocycle free bases was related to specific solvation of the tetrapyrrole macrocycle core and that the solution temperature had an indirect effect on the deprotonation because of the temperature dependence of the solvent dielectric constant. The dielectric constant is known to be related to the number of solvent molecules in the first coordination sphere and; therefore, to the solvation stoichiometry [19]. According to the Born model, the free energy of solvation  $\Delta G_S$  in explicit form depends on the dielectric constant of the solvating solvent [20]:

$$\Delta G_S = -\frac{N_A z_i^2 e_0^2}{8\pi\epsilon_0 r_i} \left(1 - \frac{1}{\epsilon}\right), \quad (1)$$

where  $z_i^2 e_0^2$  and  $r_i$  are the ionic charge and radius;  $N_A$ , Avogadro's number;  $\epsilon_0$ , dielectric constant. The dielectric constant of EtOH decreased practically linearly as the temperature increased in the studied range [21]. Figure 4 shows the relative concentration of the deprotonated form of **1–3** as a function of EtOH dielectric constant  $\epsilon$ . Obviously, the spectral changes due to deprotonation of **1–3** were described well as a linear function of  $\epsilon$ . The free energies of solvation  $\Delta G_S$  changed very little in the studied temperature range. Nevertheless, they reflected correctly the nature of the solution processes. The corrole free bases were stabilized by the increased solvation of the tetrapyrrole macrocycle core as the solvent dielectric constant increased. This was consistent with the decreased (increased absolute value) of  $\Delta G_S$ . Conversely, the increased (decreased absolute value)  $\Delta G_S$  with increasing temperature promoted loosening of the solvation sphere because the acid–base equilibrium was shifted toward formation of the deprotonated form. As a result, this effect could be treated as the temperature dependence of basicity constant  $pK_{a3}$ .

Protons are solvated better by H<sub>2</sub>O than EtOH or MeCN according to the standard molar free energy  $\Delta G(W \rightarrow S)$  for transfer of ions from H<sub>2</sub>O into organic solvents,  $\Delta G = 11.1$  and 46.4 kJ/mol [22]. Therefore, MeCN can be replaced by H<sub>2</sub>O in the corrole solvation sphere if even traces of H<sub>2</sub>O are present in the MeCN. As a result, H<sub>2</sub>O solvates pyrrole protons and stabilizes the free base. This explained the previously observed "aging" of MeCN in air because of absorption of water vapor [8]. However, EtOH solvates protons better than MeCN [ $\Delta G(W \rightarrow S) = 11.1 - 46.4 = -35.3$  kJ/mol]. Therefore, deprotonation can be expected after solvation of corroles by EtOH. However, this did not happen because EtOH is a protic solvent and the acid–base equilibrium shifted toward formation of the free base because the solution acidity increased.

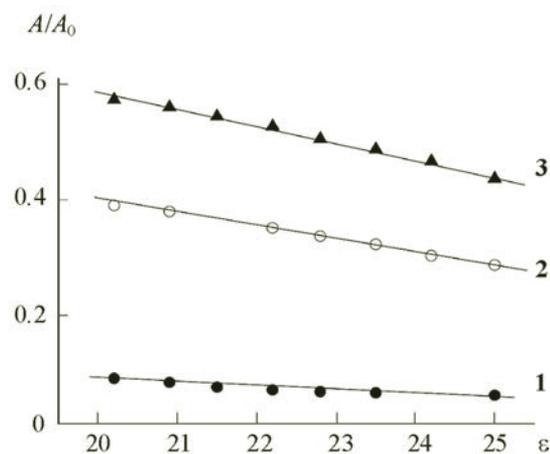


Fig. 4. Dependence of relative concentration of deprotonated corroles **1**, **2**, and **3** on EtOH dielectric constant.

MeCN molecules have large dipole moments that can polarize and cleave NH bonds in pyrrole rings so that the deprotonated form is stabilized without protons in the solution.

**Conclusions.** The influence of solvents on acid–base equilibria in corrole macrocycle cores is based on specific solvation that protonates pyrroline N atoms in the tetrapyrrole macrocycle core on going from polar aprotic solvents to protic ones. In our opinion, this transition is reflective mainly of the corrole properties, namely, the basicity  $pK_a$  of the pyrrole N atoms in the macrocycle core. The thermochromism observed for corroles in EtOH solutions is also due to specific solvation effects due to the temperature dependence of the EtOH dielectric constant. The magnitude of the thermochromic effects are determined by the basicity of the pyrrole N atoms, which depends on the macrocycle peripheral substitution pattern.

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