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Spectrophotometric determination of the acidity constants of calcon in water and mixed water–organic solvents

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Abstract. The acid–base properties of calcon (1-(2-hydroxy-1-naphthylazo)-2-naphthol-4-sulfonic acid) in water and mixed water–organic solvents at 25 °C at an ionic strength of 0.10 M are studied by a multiwavelength spectrophotometric method. The organic solvents used were the amphiprotic (methanol), dipolar aprotic (dimethylsulfoxide), and low basic aprotic (acetonitrile). To evaluate the pH absorbance data, a resolution method based on the combination of soft- and hard-modeling was applied. The acidity constants of all related equilibria were estimated using the whole spectral fitting of the collected data to an established factor analysis model. The data analysis program Datan was applied for determination of the acidity constants. The corresponding pK_a values were determined in water and mixed water–organic solvents. Linear relationship between the acidity constants and the mole fraction of the different solvents in the mixtures exist. The effect of solvent properties on acid–base behavior is discussed.

Keywords: calcon; Datan; spectrophotometry; organic solvents; acidity constants.

INTRODUCTION

The accurate determination of acidity constant values is often required in various chemical and biochemical areas. These are of vital importance in understanding the distribution, transport behavior, binding to receptors and mechanism of action of certain pharmaceutical preparation.^{1,2} The acidity constants of organic reagents play a very fundamental role in many analytical procedures, such as acid–base titrations, solvent extractions and complex formation. However, in determining of acidity constants of these molecules, several drawbacks, such as low

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solubility in aqueous solutions and the low values of the acidity constants, are encountered. Therefore, in order to enhance the acidity constants on the one hand and to increase the solubility on the other, mixed solvents have to be employed.

The widespread application of anionic azo compounds as dyes, acid–bases, drugs, metallochrome indicators and histological stains have attracted many researchers to study their acid–base and complex formation properties. However, the literature lacks studies on the acid–base properties or medium effects on the acid dissociation constants of these compounds, which are thought to be of special interest owing to their biological and therapeutic importance.^{3–7} In continuation of our studies on the acid–base properties of these compounds,^{1,8} the medium effect on the ionization constants of calcon (see Scheme 1 for structure) as a good representative was studied by the study of the electronic spectra of the compound in aqueous buffer solutions containing varying proportions of organic solvents of different polarities, *i.e.*, methanol, acetonitrile and dimethylsulfoxide. The pK_a values have been determined and discussed in terms of solvent characteristics.

The solvation of a solute in a mixed solvent is much more complex than the that in a neat single solvent and the literature offers several theories and models for this process.⁹ In general, they agree in that when a solute is dissolved in a mixed solvent, specific solvation effects determine that the proportion of the solvents in the solute sphere of solvation is different from that in the bulk solvent. The solute interacts more strongly with one or more solvents of the mixture and it is preferentially solvated by these solvents. Solute properties, such as pK_a value, depend on the composition and properties of this solvation sphere and therefore they are very sensitive to preferential solvation.

The spectroscopic instrumentation employed today almost invariably has the capacity to collect data over the full spectral range. Using a single or a few wavelengths discards most of the information in the collected spectra and requires both the presence and knowledge of such suitable wavelengths. However, in many cases, the spectral responses of the components overlap and analysis is no longer straightforward.^{10,11} A predefined model, known as hard-modeling analysis, cannot be applied if crucial information is missing. Soft modeling or model free approaches are based on much more general prerequisites, such as positive molar absorbance, positive concentration of all species, unimodality of the concentration profiles and closure (concentration of all species are the same for all solutions). Naturally, if the strengths of hard- and soft-modeling methodologies are combined, a much more powerful method of data analysis can be expected.^{12–20}

Data analysis performed by the Datan package developed by the Kubista group,^{11,20} which is called a physical constraints approach, provides a unique solution by requiring that the calculated concentrations obey an assumed equilib-

rium expression. It was demonstrated by application to the determination of the acidity constants of two and four protolytic forms of fluorescein. A possible advantage of the Kubista *et al.*¹¹ method is that it mixes a soft-modeling approach with a hard-modeling approach. This might be a better and more general strategy, since it can handle different situations, with only a partial knowledge of the chemistry of the system. The physical constraints method calculates spectral profiles, concentrations, and equilibrium constants by utilizing equilibrium expressions that are related to the components. The theory and application of the physical constraints method has been discussed by Kubista *et al.* in several papers.^{21–29}

In this work, the physical constraints approach was applied to determine the acidity constants of calcon in pure water and in different binary acetonitrile and methanol–water mixtures. Data analysis was performed in the Matlab version of the Data analysis (Datan) program developed by the Kubista group.

Theory

The theory and application of the physical constraints method was discussed by Kubista *et al.* in several papers.^{20–29} Nevertheless, the general principal will be outlined briefly.

Spectra of calcon at different pH values are digitized and arranged in a data matrix A , which is decomposed into an orthonormal basis set by Nipals or any equivalent method:¹¹

$$A = Tp^T + E \approx Tp^T = \sum_{i=1}^r t_i p_i^T \quad (1)$$

T has the same dimensions as c ; its column are referred to as target vectors, and they are orthogonal linear combinations of the columns in c , where the orthogonal target vectors t_i and orthonormal projection vectors p_i are mathematical constructs that cannot be directly related to the component spectra and concentrations, r is the number of independent spectroscopic components, which corresponds to the number of light-absorbing chemical species. It is determined by visual inspection of the t and p^T vectors or by performing statistical methods, such as, the χ^2 -test.^{30–32} E is an error matrix. By assuming linear responses, the spectra in matrix A are linear combinations of the concentrations, c , and spectral responses, V , of the chemical components:

$$A = cV + E \approx cV \quad (2)$$

If the spectral profiles of the components are known, the concentration of each component can easily be calculated, for example, by least squares minimization. If standards are not available, the common belief is that the spectral responses of the components cannot be separated, which precludes their identification. This is due to ambiguity in determining the rotation matrix, R , in the

following Equations; from Eqs. (1) and (2), it follows that there is a square matrix \mathbf{R} ($r \times r$) that satisfies:

$$T = c\mathbf{R} \quad (3a)$$

$$p = \mathbf{R}^{-1}V \quad (3b)$$

Since $A = cV = c(\mathbf{R}\mathbf{R}^{-1})V = c\mathbf{R}\mathbf{R}^{-1}V = Tp^T$

If \mathbf{R} can be determined, the spectral responses V and concentrations c of the components can be calculated from the target T and the projection p^T matrices:

$$c = T\mathbf{R}^{-1} \quad (4a)$$

$$V = \mathbf{R}p^T \quad (4b)$$

The thermodynamic expression that describes the concentration of the components is the main constraint used to determine \mathbf{R} , from which the thermodynamic parameters, and the spectral responses and concentrations of the components are calculated. Therefore, the strategy for determining the rotation matrix \mathbf{R} is as follows. The concentrations of the chemical species are calculated from the equilibrium expressions for various trial values of the equilibrium constants, and are fitted to the calculated target vectors according to Eq. (3a). The accuracy of this fit depends crucially on the trial values of the equilibrium constants and the best fit determines their values and the elements of matrix \mathbf{R} .

EXPERIMENTAL

Materials

Calcon, methanol, acetonitrile, dimethylsulfoxide, hydrochloric acid, sodium hydroxide and potassium nitrate were commercial analytical grade products (Merck, Germany). These reagents were used without further purification. A standard stock solution of 7.0×10^{-4} M of calcon was prepared by dissolving the appropriate amount of calcon in water. Stock solutions of the other materials were prepared by dissolving weighed amounts of the substances in the appropriate amounts of water. All the solutions were prepared in deionized water.

Instrumentation

A Scinco S-2000 (Korea) spectrophotometer controlled by a computer and equipped with a 1 cm path length quartz cell was used for acquisition of the UV-Vis spectra. The spectra were acquired between 350 and 765 nm. The pH values were measured using a Metrohm CH-9101 pH-meter (Switzerland) furnished with combined glass-saturated calomel electrode. To precalibrate the pH meter in the various employed binary organic + water mixtures, 0.01 M solutions of oxalate and succinate buffers were employed.

Computer hardware and software

All absorption spectra were digitized at ten data points per nanometer in the wavelength range 350–765 nm and transferred to an AMD 2000 XP (256 Mb RAM) computer for subsequent analysis by Matlab software, version 6.5 (The MathWorks) or for processing using the Datan package.

Spectrophotometric titrations

For the titrations of calcon (1.5×10^{-4} M) in pure water and (2.1×10^{-4} M) in water–organic mixtures, the absorption spectra were measured with a titration set-up consisting of a com-

puter interfaced to the spectrophotometer. Control of the pH was achieved using a modified universal buffer solution. To account for differences in acidity, basicity and ion activities for the organic–water solvent mixture relative to pure water, in which the pH-meter was standardization using aqueous buffers, the pH values in the organic–water solvent mixtures were corrected using the equation $\text{pH}^* = \text{pH}(\text{R}) - \delta$, where pH^* is the corrected reading and $\text{pH}(\text{R})$ is the reading of the pH-meter obtained in a partially aqueous organic solvent, determined by Douheret.^{33,34} After each pH adjustment, the solution was transferred to a cuvette and the absorption spectra were recorded. The ionic strength was maintained at 0.10 M by adding appropriate amounts of KNO_3 (0.10 M). All measurements were performed at a temperature of 25 °C.

RESULTS AND DISCUSSION

The absorption spectra of calcon in water and mixed water–organic solvents at various pH values in the interval 350–765 nm were recorded. Sample spectra of calcon at different pH values in pure water with the pH ranging from 0.73 to 13.76 and in water containing 30 % (w/v) of an organic solvent (methanol, acetonitrile, and dimethylsulfoxide with the pH ranging from 0.52 to 13.92, from 0.48 to 13.95 and from 0.49 to 13.85, respectively) at 0.10 M KNO_3 are shown in Figs. 1 and 2, respectively. Principal component analysis of all absorption data matrices obtained at various pH shows at least four significant factors, which is also supported by the statistical indicators of Elbergali *et al.*,²⁴ which predicted four distinguishable components in the samples. These factors could be attributed to the three dissociation equilibria of a triprotic acid such as calcon. This may not be concluded by inspection of the visible spectra of calcon.

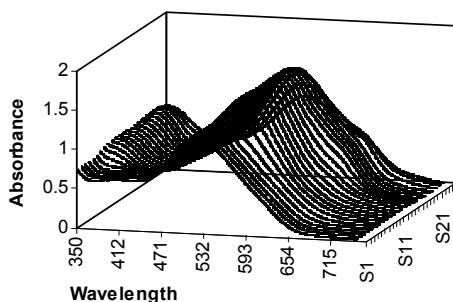


Fig. 1. Absorption spectra of calcon in pure water at 0.10 M KNO_3 at different pH values.

The pK_a values of calcon were investigated spectrophotometrically in different methanol, acetonitrile, and dimethylsulfoxide + water binary mixtures at 25 °C at an ionic strength of 0.10 M. The acidity constants of calcon in several mixtures were evaluated using the computer program Datan and the corresponding spectral absorption–pH data. From inspection of the experimental spectra, it is hard to guess even the number of protolytic species involved. The four calculated most significant projection vectors, p^T , with clear spectral features (as compared to noise) indicate the presence of three spectroscopically distinguishable components. Their profiles or shapes show some order of ambiguity, (*i.e.*, they are

clearly physically meaningless and cannot be directly related to the spectral response of the four protolytic forms). After rigorous curve resolution computational steps according to a combination of hard and soft-modeling, the outputs of the program are the pK_a values and their standard deviation (derived from the error analysis plot of the program), the number of principal components, projection vectors (loadings), concentration distribution diagrams and the pure spectrum of each assumed species.

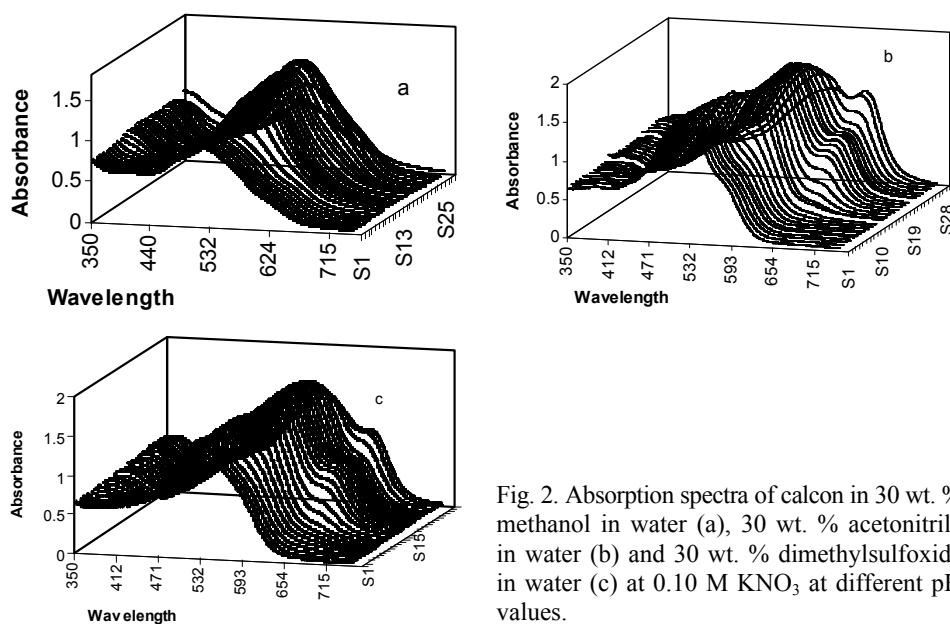


Fig. 2. Absorption spectra of calcon in 30 wt. % methanol in water (a), 30 wt. % acetonitrile in water (b) and 30 wt. % dimethylsulfoxide in water (c) at 0.10 M KNO_3 at different pH values.

The obtained pK_a values are listed in Table I. The previous reported values of the acidity constants were mainly in pure water.^{35,36} The obtained values in pure water are in good agreement with the previous values, which are also listed in Table I for comparison. The differences observed between the pK_a values are not only within the margins of experimental error but also due to the different computational strategy of the univariate methods and of newer chemometrics based methods. The manner in which noise or measurement error treatment are performed on the absorption spectra in a multivariate sense which uses the whole spectral domain, reduces considerably the level of noise and results in more precise final information. Hence, the obtained acidity constants are more reliable and precise than those obtained by previous methods. The pK_a values correspond to the pH-dependent variation of absorption spectra in all solvents mixtures. One of the very important outputs of the Datan program is the calculated spectrum of the different forms of calcon in each solvent mixture. Sample spectra of the calculated pure spectral profiles of all species in water and different organic sol-

vents/water mixtures are shown in Fig. 3. As the mole fraction of organic solvents increased, the absorption intensity changed differently for each species of calcon. It is interesting to note that the nature and the composition of the solvent have a fundamental effect on each pure spectrum. As is clear from Fig. 3, this effect is greater for H_3L and L^{3-} than for H_2L^- and HL^{2-} . The spectrum of the L^{3-} species has a larger λ_{max} than the other species which shows a splitting pattern in high weight percents of methanol, acetonitrile and dimethylsulfoxide. The splitting of the absorption peak at λ_{max} of L^{3-} is more obvious than that of the other species. This can be described using the non-electrostatic (H-bonding) property of the stabilization and/or destabilization of the ground and excited states of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. The appearance and disappearance of some shoulder and absorption peaks of each species is related to the type and mass percent of the organic solvent.

TABLE I. Acidity constants of calcon in pure water and in different percentage of MeOH, AN, DMSO (w/v) at 25 °C and at constant ionic strength (0.10 M KNO_3)

wt. %	Methanol			Acetonitrile			Dimethylsulfoxide		
	pK_1	pK_2	pK_3	pK_1	pK_2	pK_3	pK_1	pK_2	pK_3
0	1.05	7.21	13.43	—	—	—	—	—	—
0 ^a	1	7.3	13.5	—	—	—	—	—	—
10	0.96	7.38	13.55	0.93	7.45	13.58	0.91	7.12	13.45
20	0.88	7.54	13.68	0.79	7.61	13.71	0.77	7.50	13.54
30	0.69	7.76	13.76	0.62	7.90	13.83	0.61	7.68	13.61

^aRef. 35

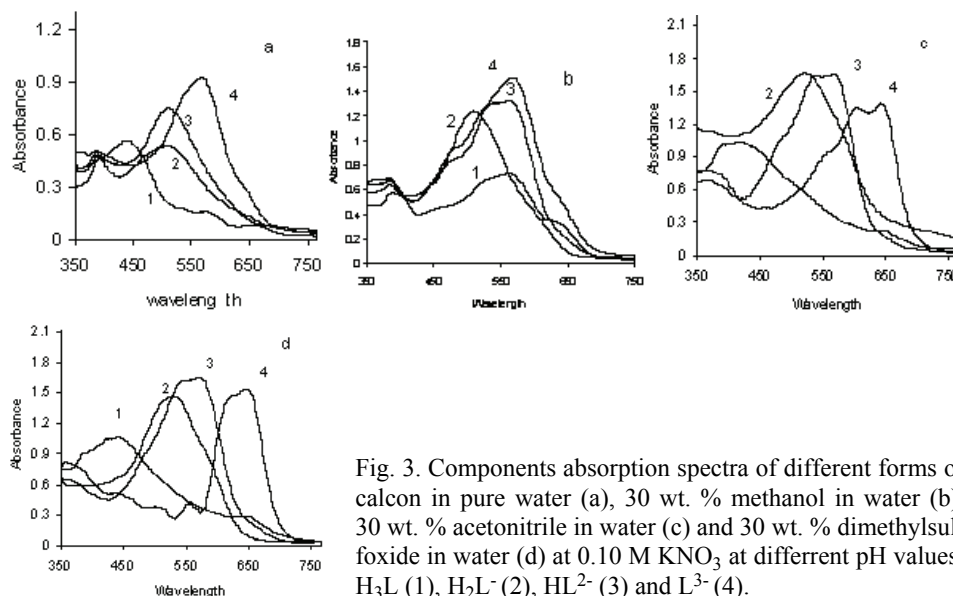


Fig. 3. Components absorption spectra of different forms of calcon in pure water (a), 30 wt. % methanol in water (b), 30 wt. % acetonitrile in water (c) and 30 wt. % dimethylsulfoxide in water (d) at 0.10 M KNO_3 at different pH values; H_3L (1), H_2L^- (2), HL^{2-} (3) and L^{3-} (4).

The most important features of the distribution diagrams are the pH limit of the evolution and disappearance of the components. Hence, according to distribution diagrams, it could be concluded that the spectra at pH lower than 1 is attributable to the H_3L form because this form is dominant in this pH range. In the pH 1.0–7.0 interval, the H_2L^- form is dominant and, hence, the spectra are mostly attributed to this form. The HL^{2-} and L^{3-} forms appeared in the pH intervals 7.0–13.5 and $pH > 13.5$, respectively. Samples of the obtained distribution diagrams are shown in Figs. 4 and 5. The data shown in Table I clearly illustrate the important influence of the nature of the solvent on the dissociation reaction. The acidity constants of the second and third dissociation steps of calcon decreased with increasing the mole fraction of methanol in the mixed solvents. It has been shown that the solvating ability³⁷ (as expressed by the Gutmann donicity scale) and dielectric constant of the solvent play a fundamental role in dissociation reactions. Water is a solvent of high solvating ability (*i.e.*, donor number $DN = 33$, dielectric constant $\epsilon = 87.3$), which can dissociate the acid and stabilize the produced anion and hydrogen ion. Thus, it is expected that addition of methanol ($DN = 19$, $\epsilon = 32.6$), acetonitrile ($DN = 14$, $\epsilon = 36$), and dimethylsulfoxide ($DN = 26.5$, $\epsilon = 46.6$) with lower donor numbers and dielectric constants relative to water decreases the extent of interaction between the acid anion and proton with the solvent, which decreases the acidity constants of calcon.

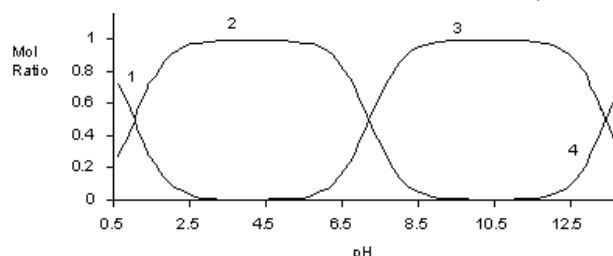


Fig.4. Distribution of major species of calcon, 1) H_3L , 2) H_2L^- , 3) HL^{2-} and 4) L^{3-} , as a function of pH for the spectral data in Fig. 1.

It is interesting to note that there is actually a linear relationship between the pK_a of the three dissociation steps (the first step decreases whereas the second and third steps increase) and the mole fraction of methanol (x_{solvent}) in the employed binary mixed solvents, as can be seen in Fig. 6.

It is clear that the dissociation of an uncharged acid in a solvent requires the separation of two ions of opposite charges. The work required to separate these charges is inversely proportional to the dielectric constant of the solvent. The energy required for dissociation is supplied by solvation of the ions and also proton transfer from the acid to the solvent molecule supplies additional energy. If the dielectric constant and the solvating ability of the solvent are decreased, more energy will be required to separate the anion and cation and, consequently, the extent of dissociation of the acid will be lowered. Therefore, the increase in first

step and the decrease in second and third steps of the dissociation constants are due to the increasing mole fraction of methanol, acetonitrile and dimethylsulfoxide in the binary mixed solvents.

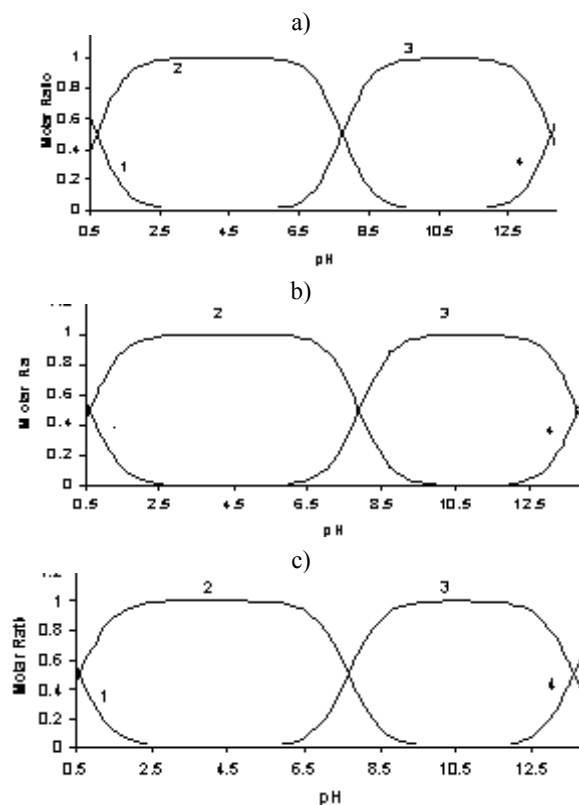


Fig. 5. Distribution of major species of calcon, 1) H_3L , 2) H_2L^- , 3) HL^{2-} and 4) L^{3-} , as a function of pH for the spectral data in Fig. 2.

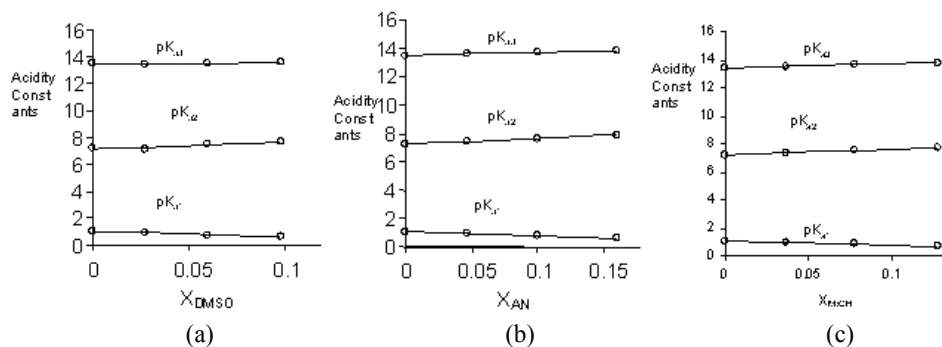


Fig.6. Variation of the values of the acidity constants of calcon with mole ratio of different organic solvents.

CONCLUSIONS

In this study, the acidity constants of calcon in different and mixed solvents were determined. The Data Analysis (Datan) program was employed to analyze correlated spectroscopic data. The pK_a values of calcon were determined in methanol, acetonitrile and dimethylsulfoxide–water mixtures. The pK_a values correspond to the pH-dependent variation of the absorption spectra in all solvent mixtures. A linear relationship was found between the pK_a values of the three dissociation steps (the first step decreases and the second and third steps increase) and the mole fraction of the organic solvents in the binary mixed solvents.

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ИЗВОД

СПЕКТРОФОТОМЕТРИЈСКО ОДРЕЂИВАЊЕ КОНСТАНТЕ КИСЕЛОСТИ КАЛКОНА У ВОДЕНИМ И ВОДА–ОРГАНСКИМ РАСТВОРАЧИМА

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Кисело–базна својства калкона (1-(2-хидрокси-1-нафтилазо)-2-нафтол-4-сулфонске киселине) у води и растворима вода–органски растварачи на 25 °С при јонској јачини 0,10 М су испитивана спектрофотометријски. Коришћени су органски растварачи метанол, диметилсулфоксид и ацетонитрил. Константе киселости у случају свих равнотежних система су одређиване у целом спектралном региону коришћењем факторске анализе применом програма Datan. Одговарајуће вредности pK_a су одређене у води и растворима вода–органски растварач. Добијена је линеарна зависност киселости и молске фракције различитих растварача. Дискутован је утицај својстава растварача на кисело–базна својства.

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