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Protolytic Equilibria of Picric Acid in a Mixture of Protophobic and Protophilic Polar Solvents Non-Donors of H-bonds

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Abstract—A new differentiating medium for the study of prototropic equilibria is proposed: acetonitrile with a small addition of DMSO. From the dependence of the picric acid pK_a on the content of DMSO in this medium the optimum composition of the mixture was found ensuring the stability of the pK_a values with minimal addition of DSMO: 4 wt %. It was experimentally confirmed that the addition of water in an amount up to 0.1 wt % has virtually no effect on the measured pK_a value in a mixture with the optimum composition.

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Organic solvents belonging to *dipolar aprotic* or *polar, non-donor of hydrogen bond* (NDHB) are a suitable medium for many chemical processes [1]. The polar NDHB solvents are classified by their chemical properties as weakly basic *protophobic* (e.g., propylene carbonate, acetonitrile, acetone, and particularly nitromethane and nitrobenzene) and the more basic *protophilic* (like dimethyl sulfoxide, dimethylformamide, and hexamethylphosphoramide) ones [2, 3].

The nature of the proton solvation is the main factor determining the pK_a^S value of an acid (HA ↔ $H^+ + A^-$) in a polar NDHB solvent S**.** Another factor is the medium effect in going from water to the solvent S:

$$\Delta pK_a = pK_a^S - pK_a\,(\text{in water})$$
$$= \log {}^{w}\gamma_H^S + \log {}^{w}\gamma_A^S - \log {}^{w}\gamma_{HA}^S, \tag{1}$$

where ${}^{w}\gamma_H^S$, ${}^{w}\gamma_A^S$, and ${}^{w}\gamma_{HA}^S$ are the activity coefficients of the transfer of ion (molecule) from water into the solvent. For example, the difference between the values of pK_a^S in acetonitrile and dimethyl sulfoxide (DMSO) for a large series of neutral and anionic acids is ranged from 10.0 to 11.5 [4]. As a rough approximation, this corresponds to the logarithm of activity coefficient of proton transfer from DMSO to acetonitrile, $\log {}^{MeCN}_{tr}\gamma_{H^+}^{DMSO}$ or, equivalently, the difference $\log {}^{w}_{tr}\gamma_{H^+}^{MeCN} - \log {}^{w}_{tr}\gamma_{H^+}^{DMSO} = 7.85 - (-3.4) = 11.25$.

For the same reason, in the weakly basic *protophobic* solvents, unlike *protophilic* ones, even traces of water may distort the nature of the acid–base equilibrium in any part of the pa_H* scale.

Dipolar aprotic solvents show a pronounced differentiating effect, changing differently the strength of the acids of different nature. The length of the pH scale of both protophobic and protophilic NDHB solvents is usually about 30 logarithmic units [1, 2]. However, the large difference in the basicity of the solvents of two main types suggests that even at a small additive of a protophilic NDHB solvent to a protophobic one, one can expect that in such a mixture the proton will be solvated totally by the protophilic solvent only.

Another important feature of the polar NDHB solvents is rather pronounced formation in them of the associates between an acid and its conjugate anion or between a base and the conjugate cation ($A^- + HA \leftrightarrow A^-\cdots HA$; $BH^+ + B \leftrightarrow BH^+\cdots B$). This phenomenon is known as *homoassociation*. The occurrence of these processes, along with the processes of *heteroas-*

Table 1. Characteristics of the most widely used solvents at 25°C[a]

Solvent	ε_r	μ, D[2]	*DN*	*AN*	PA, kJ mol^{-1}	pK_S	E_T^N	$\log^{H_2O}\gamma_H^{S+}$ [b]
Water	78.5	1.85	18.0	54.8	691.0	14.0	1.000	0
Dimethylsulfoxide	46.4	3.96	29.8	19.3	884.4	33.3	0.444	–3.40
N,N-Dimethylformamide	36.7	3.86	26.6	16.0	887.0	29.4	0.404	–2.52
N, N'-dimethylacetamide	37.8	3.79	27.8	13.6	908.0	23.9	0.401	–
Acetonitrile	35.9	3.92	14.1	18.9	779.2	33.3	0.460	+7.85
Acetone	20.6	2.88	17.0	12.5	812.0	32.5	0.355	≈7.0
Propylene carbonate	65.0	4.98	15.1	18.3	814.2	–	0.472	+6.5[c]
Nitromethane	2.7	3.17	2.7	20.5	754.6	–	0.481	+15[d]

[a] ε_r is a relative dielectric permeability, μ is a dipole moment, D; *DN* is Gutmann donor numbers, *AN* is an acceptor number determined by ^{31}P NMR spectroscopy, *PA* is protonation enthalpy in the gas phase, pK_a^S is the index of the autoprotolysis rate constant, E_T^N is normalized Reihardt parameter. [b] The values of $\log^{H_2O}{}_{tr}\gamma_H^{S+}$ were calculated according to the tetraphenylborate hypothesis. [c] Data from [9]. [d] Data from [10].

sociation ($BH^+ + A^- \leftrightarrow BH^+\cdots A^-$; $HX + A^- \leftrightarrow XH\cdots A^-$), is due to the lack of hydrogen bonds in the NDHB solvents.

Acetonitrile is one of the most common solvents. The strongly pronounced differentiating effect of this solvent toward the dissociation of dissolved electrolytes is well known [5, 11]. However, high hygroscopic ability of the water absorption combined with the low basicity of acetonitrile leads to the fact that even in a very carefully dehydrated solvent there is a danger of hydration of the proton, that is, the existence of a lyonium ion not as $H(MeCN)^+_m$, but as H_3O^+, $H_5O_2^+$, etc. Despite the strong complication of the experimental quantitative study of ionic equilibria in pure acetonitrile due to the great influence of the negligible amounts of water on the mechanism of the proton solvation [12], the reliability of the acidity scale in acetonitrile is well known thanks to a series of papers by Kolthoff and co-workers [13–18], and the Kaljurand's group [19–22].

By its basicity, acetonitrile is noticeably inferior compared to DMSO and slightly to acetone. As can be seen from Table 1, the Gutmann donor numbers (*DN*) for acetonitrile, acetone and DMSO are 14.1, 17.0 and 29.8, respectively [2], and the values of the proton affinity in a vacuum (*PA*) 779.2, 812.0 and 884.4 J mol^{-1}, respectively [23]. The acetonitrile relative permittivity ($\varepsilon^{25} = 36.0$), is significantly higher than that of acetone ($\varepsilon^{25} = 20.56$). Nevertheless, by analogy with the equilibrium in acetone there is a possibility of incomplete dissociation of salts in acetonitrile.

Therefore, we investigated the properties of acetonitrile with small additions of DMSO, a solvent, which is more basic than water. Thus, in acetonitrile the protonation constants of DMSO and H_2O are 6×10^5 and 3×10^2, respectively [24]. It is expectable that such a solvent will retain the general solvation properties of acetonitrile, but a proton solvated with DMSO will serve as the lyonium ion, while the influence of the water traces becomes irrelevant, if this solvent is not used for the study of the acids weaker than water. In addition, DMSO will solvate the trace amounts of water remaining after purification and/or coming into the solvent from the atmosphere, and thereby preventing to some extent the hydration of anions. These considerations have found experimental evidence in a series of studies of protolytic and ionic equilibria in analogous mixed solvent: acetone containing 5 mole percent DMSO [25–27].

Thus, acetonitrile with the addition of DMSO has a differentiating ability with respect to the acid strength typical of aprotic solvents. Furthermore, this system is insensitive to small water admixtures. The combination of these two factors makes the mixture a very promising medium for studying the prototropic ionic equilibria. For the study, we used the acetonitrile–DMSO mixture with the content of the latter less than 10 wt %. The accumulation of experimental data on the pK_a in the chosen medium will allow obtaining the values of pK_a in acetonitrile (their experimental determination is extremely difficult) by analogy with [10, 28, 29] using the linear relations of the type

$$pK_a^{AN} = a pK_a^{S} + b, \tag{2}$$

where pK_a^{S} and pK_a^{AN} are the pK_a values in the system under study and acetonitrile, respectively, a and b are empirical parameters, which are constant for the acids similar by the structure. For the construction of such correlations, one must initially obtain the pK_a values in the considered system for the reference acids (for which the values in acetonitrile are known) of different chemical classes.

Starting the study of protolytic equilibria in the proposed medium it was important to establish the optimal composition of the mixture in which the content of acetonitrile (which determines the solvation of ions, except for protons) is maximal and the DMSO content is sufficient for the stability of the pK_a values at adding small amounts of water. For this purpose we investigated a dependence of the measured pK_a value of picric acid on the content of DMSO in the mixture from 0.18 to 6 wt % (0.01 to 3.24 mol %). The choice of picric acid is defined by the fact that because of spatial constraints and the charge delocalization in the picrate anion, its homoassociation in polar NDHB solvents is minimal [3, 4, 31]. An important argument in favor of picric acid is the pos-sibility of using spectrophotometric method without buffering for determining the pK_a values. To apply the method it is necessary to study a strong enough acid (pK_a in the studied mixture not higher than 5) and the spectra of the prototropic forms should be clearly distinguishable. Based on the values of pK_a of picric acid (3.45) in a similar mixture of acetone–DMSO of the molar ratio 95:5 [25], this acid is expected to meet the requirements for the study in the medium under investigation applying the method of dilution. It is crucial that for this method the knowledge of the pa_{H}^{*} scale in the selected solvent is not required. Furthermore, the addition of DMSO (as a strong hydrogen bond acceptor) contributes to weakening the possible homoassociation of picric acid.

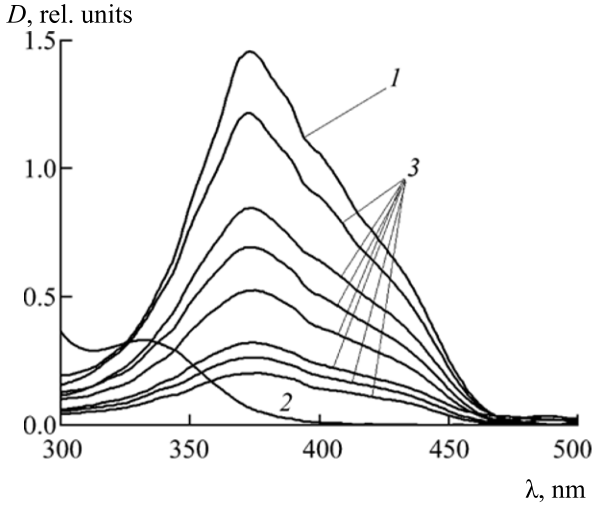

Fig. 1. Electron absorption spectra of picric acid in the boundary forms: (*1*) anion, (*2*) protonated, (*3*) in the process of dilution.

The determination n of pK_a values was performed using the spectrophotometric method in an unbuffered system, by analyzing changes in the absorption spectra of picric acid in the region 300–500 nm at the acid concentration 5×10^{-5} to 2×10^{-4} M. For saving the solvent, the dilution was performed by weight method: a weighed portion of the mother solution of picric acid in the studied mixture with the concentration about 3×10^{-4} M was diluted with a weighted sample of the mixed solvents and then the resulting concentration was calculated. The degree of dilution of working solutions ranged from 2 to 4.5. In each mixed solvent to obtain the HA spectrum shape a small amount of $HClO_4$ was added. The spectra of the A^- anion were measured from the solutions of picric acid with the addition of 1,8-diazabicyclo[5.4.0]-7-undecene (DBU); these spectra practically coincided with the spectra of tetraethylammonium picrate. As can be seen from the figure, the absorption spectra of ionic and molecular forms are well resolved.

The magnitude of the mixed dissociation constants (pK_a^{m}) was calculated from the experimental data using formulas (3), (4):

$$pK_a^{m} = \log (c_{\mathrm{HPic}} - x)/x^2, \tag{3}$$

$$x = c_{\mathrm{HPic}} \frac{E - E_{\mathrm{HPic}}}{E_{\mathrm{Pic}} - E_{\mathrm{HPic}}}, \tag{4}$$

where c_{HPic} is analytical concentration of picric acid, x is equilibrium concentration of picrate anion, E is molar extinction coefficients of the solution of picric acid with the concentration c_{HPic}, $E_{\mathrm{Pic^-}}$, and E_{HPic} are the molar extinction coefficients of the picrate ion and undissociated picric acid, respectively.

For the calculation of the thermodynamic dissociation constant corrections were introduced for the

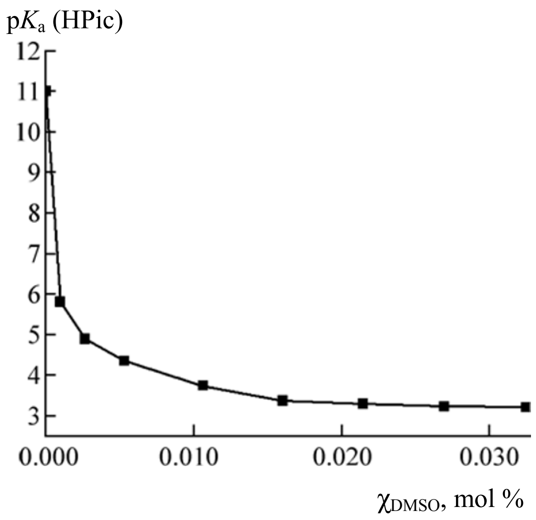

Fig. 2. The dependence of the thermodynamic ionization constants of picric acid in acetonitrile at various molar content of DMSO.

concentration activity coefficients according to the Debye–Hueckel second approximation (5):

$$pK_a = pK_a^m + (2A\sqrt{x})/(1 + Ba\sqrt{x}). \tag{5}$$

The coefficients *A* and *B* in the Debye–Hueckel equation were calculated by the expressions (6) and (7) with the *a* parameter 5 Å.

$$A = (1.82455\times10^6\sqrt{\rho})/(\varepsilon T)^{3/2}, \tag{6}$$

$$B = (50.2904\sqrt{\rho})/(\varepsilon T)^{1/2}, \tag{7}$$

where ε and ρ are the dielectric constant and the density of the mixture, respectively, *T* is absolute temperature, K.

Table 2. Thermodynamic pK_a values of picric acid in the mixtures of acetonitrile with DMSO at 25.0°C found by the spectrophotometric dilution method

ω(DMSO), wt %	χ(DMSO), mol %	pK_a (HPic)
0	0	11.0[a]
0.18	0.097	5.81
0.50	0.26	4.72
1.00	0.53	4.36
2.00	1.06	3.75
3.00	1.60	3.38
4.00	2.14	3.30
5.00	2.69	3.24
6.00	3.24	3.22

[a] Data from [32].

The dependence of the pK_a value on the mole fraction of DMSO in the mixture is shown in Table 2 and graphically in Fig. 2.

As a result of analysis of this dependence, we found that the optimum composition of acetonitrile–DMSO mixture is the weight ratio 96:4 (molar ratio 97.86: 2.14). Mass fraction of water in the purified solvents did not exceed 0.033% (determined by titration according to Fischer). The *A* and *B* coefficients for this mixture in the Debye–Hueckel relation are equal to 1.329 and 0.418 respectively.

The dependence of the picric acid pK_a value on the content of DMSO in the acetonitrile–DMSO mixture in the range 0–1 mol fractions of the latter with the increment 0.1–0.2 has also been studied in [33]. The resulting curve has a similar form with that obtained by us (Fig. 2), but is smoother. Thus, at the DMSO mole fraction equal to 0.1 the picric acid pK_a was equal to 5.98, while at 0.2 mole fraction decreased to 4.51. The most likely cause of significant differences in these results from the data of this study is the use in [33] of incorrect pK_a value of picric acid (1.0) in pure DMSO, while in the referred Kolthoff publication [4] is given an estimated value –1. The method used in [33] for calculating the values of p*K* in mixed solvents of different composition is based on the relation which includes the value of pK_a in the pure components of the mixture and the data of measurements of EMF of buffer acid/salt solutions in a 1:1 molar ratio at the current composition of the mixture. It is therefore logical to assume that with such an approach the difference in the pK_a in DMSO by 2 units to the lower values leads to a shift of values in the mixtures containing DMSO down by about the same amount. Based on this, an estimate of “corrected” value of pK_a of picric acid from the data of [33] in a mixture of acetonitrile with DMSO at the molar ratio 0.9: 0.1 is about 4, which is consistent with the results of this study.

To estimate the effect of the water additives, we carried out measurements of the ionization constant of picric acid in a acetonitrile–DMSO mixture 96: 4 in the presence of 0.1, 0.5, and 1.25 wt % (3.4–13.4 mol %) of water. In the first case, the pK_a varied within error, while in two others the found decrease was rather significant (0.5 log units and more). However, the possibility of spontaneous increase in the water content above 0.1 wt % in the working solution is excluded.

According to data of titration by Fischer, such content of water is reached by the 20 ml sample in a closed sample bottle in a week. The content of water in the mixture stored in a 2-liter bottle which was used for preparing the solutions did not exceed 0.04 wt % a month after preparation. The values of pK_a obtained in the acetonitrile–DMSO mixtures (Table 2) are significantly lower than the pK_a^{AN} in pure acetonitrile.

Thus, we proposed a new differentiating medium for the study of prototropic equilibria: acetonitrile with 4 wt % of DMSO. Addition of water in an amount up to 0.1 wt % does not affect the measured pK_a value.

EXPERIMENTAL

Acetonitrile of extra high purity, grade 0, for chromatography, from NPO Kriokhrom, St. Petersburg, was used without further purification. The purity control was performed by observing the border of transmission in the absorption spectrum [27], density, and refractive index. The water content in acetonitrile determined by coulonometric titration method of Fischer was 0.034 wt %.

Dimethylsulfoxide of chemically pure grade was purified by triple fractional freezing at 8°C. The purified fraction was kept overnight over calcined alumina and distilled in a vacuum of 10 mm Hg, the fraction boiling at 80°C was collected, the first and last 10% were discarded. Purified DMSO was stored over molecular sieves 4A.

For the measurements we used bidistilled water obtained with a bidistilling device "BS" of Khimlaborpribor. The density of the solvent at 20 or 25°C (error less than 0.0002 g cm^{-3}) was determined by a DA-500 densitometer of Kyoto Electronics with built-in thermostat. Refractive index at 20°C was measured on an IRF-454B2M refractometer. Dielectric constant was measured on an instrument OH-301 calibrated on DMSO. The purity of solids was monitored by measuring the melting point using a Köffler device RNMK 05. The absorption spectra in the visible and UV regions were recorded in 1 cm quartz cells on a SF-2000 spectrophotometer produced by OKB Spektr. The purity of the solvents was monitored by their spectra relative to air, the spectra of the mixtures were registered relative to the pure solvent. The water content in solvents was monitored by coulonometric Fisher titration according to the GOST 24614-82 with an Expert-007 titrator produced by Econix-expert.

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