

Dissociation Constant of Acetic Acid in (N,N-Dimethylformamide + Water) Mixtures at the Temperature 298.15 K

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Received: 16 June 2010 / Accepted: 17 November 2010 / Published online: 24 May 2011
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Abstract In the present work the thermodynamic dissociation constants of acetic acid were determined in (N,N-dimethylformamide (DMF) + water) mixtures over the DMF mole fraction range from 0 to 0.65 at the temperature 298.15 K by the potentiometric titration method. The dissociation constant in pure DMF was obtained by extrapolation and comparative calculation methods. The dependence of the acetic acid dissociation constant on the mixed solvent composition was fitted with linear multiple regression of the solvatochromic parameters of (DMF + water) mixtures at every studied composition.

Keywords Dissociation constant · Acetic acid · N,N-Dimethylformamide · Potentiometric titration

1 Introduction

The transfer of protons from Brønsted acids to bases is one of the most important and general reactions in chemistry. Acid dissociation constants are significant parameters for quantifying the extent of ionization of molecules in a certain media. Solvent mixtures, both organic and aqueous–organic, are interesting because two solvents mixed together produce a solvent with quite different properties, both physical (permittivity, density, viscosity) and chemical (acid–base and acceptor–donor properties).

The realization of various physico-chemical properties of liquid systems and the understanding of their influence on acid–base processes are of interest from various points of view,

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e.g. in capillary electrophoresis [1] and in liquid chromatography [2], where the solvent determines both the actual mobility and pK_d value of the solute; for development of buffers solutions for acid–base titration in non-aqueous media, where the knowledge of dissociative properties of the solutes in a certain media is necessary, etc. A serious problem may arise when pH and pK_d values are measured in pure organic solvents. Normally the glass electrode, used as a H^+ sensitive electrode, is calibrated with buffers with pH values defined for pure aqueous solutions. Furthermore, the liquid junction potentials are almost unknown in such systems consisting of interfaces between aqueous and organic phases. Therefore, rather operational mixed-mode pK_d values are usually measured rather than thermodynamic ones.

Acetic acid (CH_3COOH) is one of the most important chemical intermediates and frequently used aliphatic carboxylic acids. The knowledge of its acid properties is of great interest as it is the principal acidic constituent of vinegar and wines. Acetic and some others acids and their alkali-metal salts are components of buffers for pH measurements in mixed solvents [3]. DMF as a solvent with moderately high permittivity and aprotic nature is useful for acid–base studies and for a wide range of organic reactions [4]. It appears to be a suitable co-solvent since it is aprotic and fully miscible with water. These solvent mixtures have been widely used as solubilizing agents for drugs and water-insoluble reagents [5].

Earlier we determined the first two dissociation constants of phosphoric acid in (DMF + water) mixtures by the potentiometric titration method [6]. Using these measured data, the dissociation constants in pure DMF were evaluated by different indirect methods. The same approach is now applied for determination of the dissociation constant of the acetic acid in DMF and its mixtures with water.

The dissociation constant of acetic acid, determined by different methods, is available both in organic [1, 7–11] and (water + organic solvent) mixtures [3, 12–17]. The dissociation constant of acetic acid in pure DMF was determined potentiometrically at 298.15 K and zero ionic strength [8] ($pK_d = 13.5$) and one other value was presented in [1] ($pK_d = 13.3$). The dissociation constants of some organic acids including acetic acid in (DMF + water) mixtures were determined by potentiometric titration [3, 18] over the range from 0 to 0.45 DMF mole fractions and ionic strengths $I \neq 0$.

Therefore, the purpose of the work is to determine the acetic acid dissociation constant in (DMF + water) mixtures of various compositions and evaluate this constant in pure DMF. The main distinctions of the investigation reported here are, firstly, the extended range of (DMF + water) mixture compositions and, secondly, the extrapolation of a $pK = f(\sqrt{I})$ function to $I = 0$ to determine thermodynamic dissociation constants. The results are more reasonable, in our opinion, compared with activity coefficients calculations made by using the Debye–Hückel equation.

2 Experimental

2.1 Preparation of Reagents

N,N-dimethylformamide (PRS, 99% of assay, Panreac) and glacial acetic acid (chemical pure, ChimMed) were used for solution preparations. The water content in both DMF and CH_3COOH was determined by amperometric titration with Karl Fisher reagent. No further DMF purification or drying were applied. The water content of the DMF was taken into account in preparing (DMF + water) mixtures. Glacial acetic acid was dried by freezing until its water content was less than 0.03%. Mixtures of (DMF + water) and its solutions with acetic acid were prepared gravimetrically with an accuracy of ± 0.00005 g.

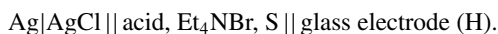
The background electrolytes were crystalline tetraethylammonium bromide (Et_4NBr , analytical grade, Aldrich) and KCl ("pure for analysis" grade, ChimMed). The procedure for purifying this Et_4NBr included recrystallization from (ethanol + doubly distilled water) mixtures three times, and finally drying it in a vacuum box at $T = 363.15 \text{ K}$ for 48 h. The purified salt was stored in a box over P_2O_5 . It was shown by additional potentiometric titration that these compounds did not contain acidic or basic impurities.

Tetraethylammonium hydroxide (Et_4NOH) (20 wt.-% in water, analytical grade, Aldrich) was used without additional purification.

2.2 Potentiometric Studies

Potentiometric titrations of solutions of acetic acid, with concentrations of 0.0021 to 0.0133 $\text{mol}\cdot\text{kg}^{-1}$ in ($\text{DMF}(1) + \text{water}(2)$) mixtures with $x_1 = (0 \text{ to } 0.65)$, were performed using a solution of Et_4NOH at the same mixed solvent composition. The concentration of Et_4NOH was an order of magnitude higher than the concentration of the acid solution being titrated. In order to be able to calculate the thermodynamic dissociation constants, the titrations were carried out at various ionic strengths. The selection of the background electrolyte and the highest ionic strength were determined by considering the solubility of the relevant salts at each given mixed solvent composition. Thus KCl was used as a background electrolyte in binary solvent mixtures with DMF mole fractions of (0.05 to 0.25), and Et_4NBr for $x_1 \geq 0.3$, and the ionic strength was varied from 0.0134 to 1.3835 $\text{mol}\cdot\text{kg}^{-1}$.

Electromotive force (emf) measurements were performed using an OP-300 analyzer (Radelkis) in a temperature-controlled electrochemical cell composed of the acid solution under investigation along with background electrolyte and a combined electrode consisting of silver chloride and glass electrodes (Radelkis):



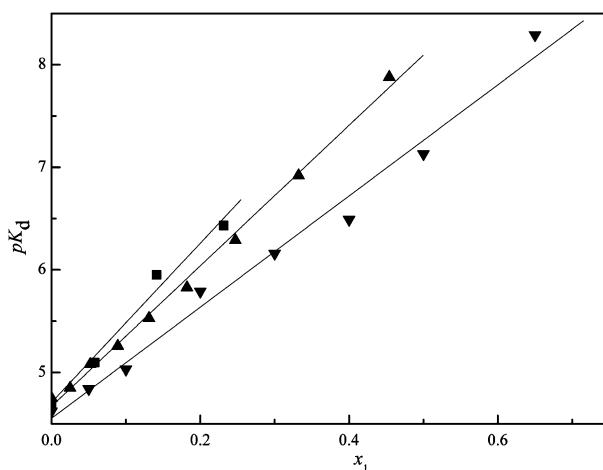
The accuracy of emf measurements determined with the OP-300 was $\pm 0.1 \text{ mV}$. For all solutions, the potential was considered established if it did not change by more than 0.1 mV over a 5 min interval. The time for establishment of equilibrium in all solutions did not exceed 10 min. The temperature in the electrochemical cell was maintained at $298.15 \pm 0.05 \text{ K}$ using a Termex VT-8-02 thermostat. The procedure for cell calibration with buffer solutions, (salicylic acid + sodium salicylate), (benzoic acid + potassium benzoate), and HClO_4 solutions in ($\text{DMF} + \text{water}$) mixtures, was described in [6]. It was shown that both the buffer solutions and solutions of HClO_4 in appropriate mixed solvents could be used for determination of combined electrode parameters for titration in ($\text{DMF} + \text{water}$) mixtures. The electrode parameters (or coefficients θ in the Nernst equation: $E = E^0 + \theta \ln a_1$) were determined for each ($\text{DMF} + \text{water}$) mixture, and θ varied from 57.49 to 58.41 depending on mixture composition.

3 Results and Discussion

The potentiometric titration curves of acetic acid solutions in mixed ($\text{DMF} + \text{water}$) solvents show a jump at all mixed solution compositions studied. As the content of DMF increases, the intensity of the titration jump sharply decreases, which is evidence for a decrease in the degree of dissociation of the acid. Using the information from these potentiometric titrations the concentration dissociation constant at every ionic strength and

Table 1 Thermodynamic dissociation constants (pK_d) of acetic acid in (DMF(1) + water(2)) mixtures at different compositions

x_1	w_1	$100/\varepsilon$	pK_{ap}	pK_d
0	0	1.270	14.00	4.62
0.05	17.60	1.332	13.82	4.84
0.1	31.08	1.397	14.22	5.03
0.2	50.36	1.541	14.90	5.79
0.3	63.48	1.701	15.81	6.16
0.4	73.01	1.867	16.62	6.49
0.5	80.23	2.029	17.43	7.13
0.65	88.28	2.242	18.64	8.29
1	100	2.724	29.6	

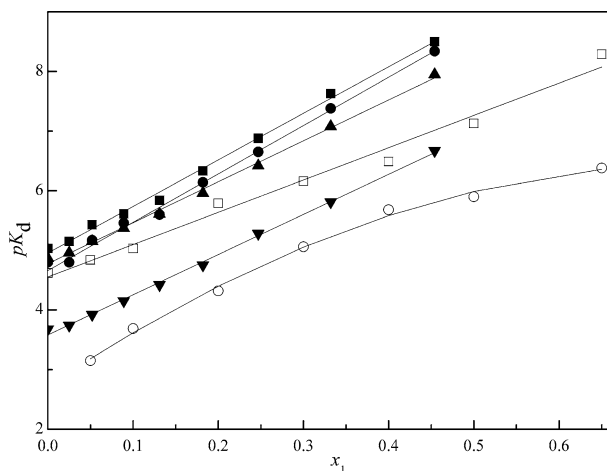
Fig. 1 Dependences of the pK_d values of acetic acid on the DMF content (x_1) in (DMF + water) mixtures: ■, data from [3]; ▲, data from [18]; ▼, this study; the lines correspond to linear fits for each data set

mixed solvent composition was calculated with the “pH-metr” program [19]. Within this program, $\text{pH} = -\log_{10} c_{\text{H}^+}$ values were calculated at every titration step from the electrode calibration results and basic species concentrations. For the equilibrium constant calculations the solvent autoprotolysis and the acid dissociation reactions were taken into account. The autoprotolysis constants (pK_{ap}) of (DMF + water) mixtures were taken from [18]. The uncertainty of pK calculations did not exceed of 0.2 pK units.

The dependence of concentration constants for acetic acid dissociation on the square root of the ionic strength was linear for all mixed solvent compositions ($R^2 \geq 0.97$). By extrapolation of these dependences to zero ionic strength, the thermodynamic dissociation constants (pK_d) were calculated at every mixed solvent composition (Table 1). Solvent properties such as the reciprocal permittivity ($100/\varepsilon$) and pK_{ap} , as well as solvent composition expressed in terms of mole fraction (x_1) and weight percents (w_1) of DMF, are presented in the Table 1. In general the dissociation constants values decrease with increasing of DMF content in the mixed solvent.

A comparison of literature data with our results is presented in Fig. 1. The differences do not exceed 1.07 pK_d units. These differences can be explained by the following considerations. First of all, the dissociation constants taken from the literature either are “con-

Fig. 2 Dependences of some acid dissociation constants on the DMF content (x_1) in (DMF + water) mixtures: ■, trimethylacetic acid [18]; ●, 2-methylbutyric acid [18]; ▲, propionic acid [18]; □, acetic acid, present work; ▼, formic acid [18]; ○, phosphoric acid [6]; and lines correspond to linear fits of literature pK_d values of the first five acids and to a second-order polynomial fit of pK_d values of phosphoric acid



centration” (not thermodynamic) values ($I = 0.1 \text{ mol} \cdot \text{L}^{-1} \text{ KNO}_3$ [3]) or were measured at an ionic strength ($0.01 \text{ mol} \cdot \text{L}^{-1} \text{ KCl}$ [18]) and recalculated to its corresponding thermodynamic value on the basis of the Debye-Hückel theory. Moreover, standard aqueous buffers were used [3, 18] for the electrode calibration. We obtained our values by extrapolation of concentration constants to zero ionic strength and used the glass electrode parameters determined for every of (DMF + water) mixture composition. This probably explains the difference in the observed data.

In Fig. 2 the dissociation constants of different acids in (DMF + water) mixtures are presented, including acetic and phosphoric [6] acid constants determined by us.

The similar shapes and close slopes of the $pK_d = f(x_1)$ functions for different acids in (DMF + water) mixtures suggest the possibility, that the main contribution to the change of the dissociation constant, with variation of the mixture composition, comes from proton solvation.

As we could not carry out the potentiometric titration in pure DMF because the low solubility of the components and lack of glass electrode reversibility, we estimated the dissociation constant of acetic acid in N,N-dimethylformamide using several different approaches. Thus the $pK_d = f(100/\varepsilon)$, $pK_d = f(x_1)$ and $pK_d = f(pK_{ap})$ functions were extrapolated to yield the appropriate parameters for pure DMF. The pK_d values thus obtained and correlation coefficients of all dependences are listed in the Table 2.

Evaluation of the dissociation constant by the comparative method was made using literature values of the dissociation constants of different carboxylic acids in DMF (pK_d^{DMF}) and in water (pK_d^{w}), presented in Table 3, and was based on the linear correlation:

$$pK_d^{\text{DMF}} = a + b(pK_d^{\text{w}}), \quad (1)$$

where a and b are empirical coefficients being equal to 4.3985 and 1.9655, respectively.

The results of the comparative calculation method are also given in Table 2. For comparison, in the table pK_d^{DMF} values obtained by the same method but with the other acids set [6] are also presented. It is obvious that the correlation coefficient is higher when using the set of acids with similar natures.

Comparison of the results in Table 2 shows that the best coincidence with literature data is observed for the acetic acid dissociation constant estimated by the comparative calculation method using the set of acids from the same homologous series. It should be noted that

Table 2 Dissociation constants of CH_3COOH in pure DMF ($\text{p}K_{\text{d}}^{\text{DMF}}$) estimated by extrapolation of different functions and by a comparative method

	R^{2a}	$\text{p}K_{\text{d}}^{\text{DMF}}$
$\text{p}K_{\text{d}} = f(x_1)$	0.9508	~ 12
$\text{p}K_{\text{d}} = f(100/\varepsilon)$	0.9332	~ 12
$\text{p}K_{\text{d}} = f(\text{p}K_{\text{ap}})$	0.9563	~ 12
Comparative calculation	0.9943 ^b	13.48 ^b
	0.9222 ^c	13.24 ^c
Literature data		13.3 [1], 13.5 [8]

^a Correlation coefficient of a linear fit to the considered function^b Values obtained with Eq. 1 and $\text{p}K_{\text{d}}$ values in water and DMF for acids with similar nature from Table 3^c Values obtained with Eq. 1 and $\text{p}K_{\text{d}}$ values in water and DMF for acids of different nature [6]**Table 3** The $\text{p}K_{\text{d}}^{\text{w}}$ and $\text{p}K_{\text{d}}^{\text{DMF}}$ values of different acids in water and in DMF, respectively

Acid	$\text{p}K_{\text{d}}^{\text{w}}$	$\text{p}K_{\text{d}}^{\text{DMF}}$
Dichloroacetic [1]	1.48	7.21
Chloroacetic [1]	2.81	10.1
Citric [20]	3.1	10.6
Formic [20]	3.75	11.55
Phenylacetic [20]	4.31	12.9

there are no clear linear dependences between the dissociation constant of acetic acid and x_{DMF} , $100/\varepsilon$ or $\text{p}K_{\text{ap}}$ over the whole concentration range, causing larger difference between extrapolated results and literature data.

Situations where the solvent influence on the equilibrium processes is solely the result of only one medium property occur only occasionally. To illustrate this situation, the dependences of the acetic acid dissociation constant in different (water + organic solvent) mixtures are shown in Fig. 3. For example, the permittivities of water mixtures with tetrahydrofuran and acetone differ substantially, e.g., for equimolar mixtures they are of 17.84 and 33.89, respectively, whereas the dissociation constants of acetic acid in these mixtures are almost equal over the whole range of organic co-solvent content.

For clearer insight into the influence of solvent properties on the acid dissociation constants, multiparameter methods are more reasonable. The linear correlation between acid dissociation constants and solvatochromic parameters of (DMF + water) mixtures (Kamlet-Taft equation [22]) was used:

$$\text{p}K_{\text{d}} = a_0 + a_1\pi + a_2\alpha + a_3\beta, \quad (2)$$

where the a_i are empirical coefficients; and π^* , α , and β are Kamlet-Taft solvatochromic parameters of (DMF + water) mixtures, namely dipolarity–polarizability, hydrogen bond donor acidity and hydrogen bond donor acceptor basicity, respectively. Polarity parameters for the mixtures taken from [22] and [23] are listed in Table 4.

As one can see from Table 4 there are some differences in literature values of solvatochromic parameters for (DMF + water) mixtures, but they do not seem to be so significant

Fig. 3 Dependences of the acetic acid pK_d values on the organic solvent content (x_S) in different (organic + water) mixtures: ■, in (acetone + water) mixtures [16]; ▲, in (tetrahydrofuran (THF) + water) mixtures [12]; ●, in (DMF + water) mixtures, present work; ▼, in (ethanol + water) mixtures [21]; the lines correspond to linear fits for each data set

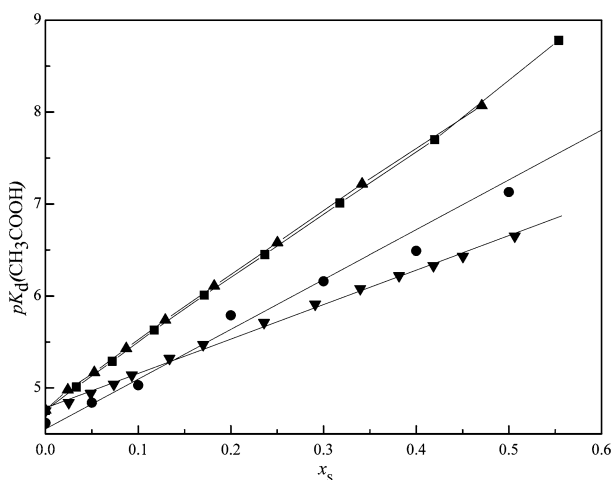


Table 4 Solvent parameters used for calculations with Eq. 2

X_{DMF}	π^* [22] ^a	π^* [23] ^a	α [22] ^a	α [23] ^a	β [22] ^a	β [23] ^a
0.05	1.16	1.11	0.91	0.95	0.54	0.52
0.1	1.13	1.12	0.82	0.79	0.59	0.56
0.2	1.09	1.12	0.65	0.57	0.69	0.62
0.3	1.04	1.08	0.53	0.46	0.78	0.66
0.4	1	1.04	0.44	0.40	0.87	0.69
0.5	0.95	1.00	0.38	0.36	0.97	0.71
0.65	0.88	0.95	0.37	0.30	1.11	0.74

^a All parameter values were calculated by interpolation of data in the cited literature for the required (DMF + water) mixture compositions

Table 5 Empirical coefficients (a_i) and standard deviation (σ) of Eq. 2 for pK_d values of acetic and phosphoric acids in (DMF + water) mixtures using solvent parameters taken from different references

Acid	a_0	a_1	a_2	a_3	σ^a	Reference
Acetic	−20.45	14.08	1.506	14.16	0.03	[22]
	152.5	−45.59	−35.18	−122.4	0.004	[23]
Phosphoric	29.18	−16.77	−3.65	−6.05	0.001	[22]
	−59.88	12.49	14.80	67.55	0.010	[23]

^a $\sigma = \sqrt{(pK_d^{\text{exp}} - pK_d^{\text{calc}})/(n - m)}$ where n is the number of direct experimental values (dissociation constants) and m is the number of solvent parameters

at first sight. Nevertheless, we carried out the calculations with Eq. 2 for acetic and phosphoric acid in (DMF + water) mixtures using solvent parameters from both literature sources [22] and [23] separately. The empirical coefficients of Eq. 2 and standard deviation obtained with these different sets of solvent parameters are listed in the Table 5.

As Table 5 indicates, differences in the solvatochromic parameter values influence substantially the quality of description of pK_d values (decreasing or increasing the σ value). But in general, using the Kamlet-Taft solvatochromic parameters provides a rather satisfactory description of the dependences of the dissociation constants of acetic and phosphoric acid (first stage) on the (DMF + water) solvent mixture composition.

4 Conclusions

Dissociation constants of acetic acid in (DMF + water) mixtures containing (0 to 0.65) DMF mole fraction were determined by the potentiometric titration method at $T = 298.15$ K. The CH_3COOH dissociation constant in pure DMF was evaluated using different methods. The best agreement with literature values was obtained by the comparative calculation method on the basis of a linear correlation between carboxylic acids dissociation constants in water and DMF.

Analyzing the pK_d values for acetic acid and some other acids taken from literature for various (DMF + water) mixture compositions demonstrated a similarity of all functions. It was assumed that the main contribution to the change of acid dissociation constants with solvent composition probably comes from proton solvation.

The $pK_d = f(x_1)$ functions of acetic and phosphoric acids were fitted satisfactorily by multiple linear regressions using polarity solvent parameters (π^* , α , and β). It was shown that the choice of solvent parameter values significantly influenced the quality of the fits.

Acknowledgements This work was financially supported by the Russian Foundation for Basic Research (project No. 08-03-00288).

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