## ФИЗИКОХИМИЯ РАСТВОРОВ

УДК 541.13

IONIC EQUILIBRIA OF TETRAMETHYLAMMONIUM 2,4-DINITROPHENOLATE, TETRAETHYLAMMONIUM PICRATE, AND SODIUM SALICYLATE IN ACETONE-DMSO MIXED SOLVENT (MOL. RATIO 95:5). CONDUCTANCE AND ION ASSOCIATION

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The association constants, K_A, of three salts in acetone containing 5 mol. % DMSO were determined using conductivity method. The $\log K_A$ values for tetramethylammonium 2,4-dinitrophenolate, tetraethylammonium picrate, and sodium salicylate ($NaC_6H_4OHCO_2$) are found to be equal to 2.09±0.07, 2.27±0.05, and 4.32±0.04, respectively.

Acetone is widely used in analytical, physical, and organic chemistry, as well as in technology as a useful medium for many reactions, including acid-base ones [1, 2]. However, the state of protolytic equilibria in this solvent is strongly influenced by traces of moisture, because of extremely low basicity of acetone [1, 3]. Even if very small amounts of water are present in acetone, the lyonium ion in various buffer mixtures can exist as H_3O^+, $H_5O_2^+$, etc. This phenomenon hinders quantitative studies of properties of a lot of organic acids in acetone. This also makes somewhat doubtful the data on acid-base ionization constants reported in a set of early studies.

Therefore we decided to introduce a kind of mixed acetone-based solvent, namely, acetone + dimethyl sulfoxide (DMSO), with molar fraction of the latter equal to 0.05. Taking into account the high basicity of DMSO [1–3], even in the presence of moisture the state of the proton-exchange equilibrium, given below in a somewhat simplified manner,

$$H_3O^+ + (CH_3)_2SO \rightleftharpoons H_2O + [(CH_3)_2SOH]^+ \tag{1}$$
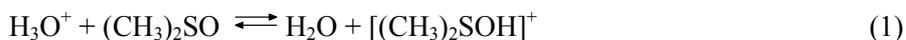
is expected to be strongly shifted toward the right. Therefore, lyonium ion in such a system must be the protonated DMSO molecule. Some authors assume more complicated character of proton solvation with DMSO [4]. Such DMSO-containing acetone is expected to possess, like pure acetone, strong differentiating influence on acidic strength of solutes of various nature and can serve as a medium for reproducible determination of the constants of acid-base equilibria. The density, viscosity, and relative permittivity of this solvent at 25.0 °C, determined by us, are 800.7 kg m^{-3}, 3.28×10^{-4} Pa s, and 22.19, respectively.

In this mixed solvent system, we studied a set of acid-base indicators vis-spectroscopically in picrate, 2,4-dinitrophenolate, and salicylate buffer solutions. The latter were prepared by mixing tetraethylammonium picrate with picric acid, tetramethylammonium 2,4-dinitrophenolate with 2,4-dinitrophenole, and sodium salicylate with salicylic acid, respectively.

For calculation of acid-base equilibrium constants, including the so-called homoconjugation constants [1, 5], rationalization of the equilibrium state in corresponding buffer solutions is necessary.

As a first step, we determined the constants of ion association

$$Ct^+ + An^- \rightleftharpoons Ct^+An^-, \qquad K_A \tag{2}$$

in solutions of the above-mentioned salts.

Experimental

Synthesis of salts. The salts were prepared according to Kolthoff and Chantooni [6]. Tetraethylammonium picrate was prepared by neutralizing the picric acid with 0.73 M aqueous tetraethylammo-

nium hydroxide solution after dissolving the acid in a minimum volume of water. The resulting solution was taken to dryness, and the residues were re-crystallized from methanol and dried *in vacuo* at 50-70 $^{\circ}$C. Tetramethylammonium 2,4-dinitrophenolate was prepared by neutralizing the 2,4-dinitrophenole with 0.1 M aqueous tetramethylammonium hydroxide solution after dissolving the 2,4-dinitrophenole in a minimum volume of acetone-water mixture. The resulting solution was taken to dryness, and the residues were re-crystallized from methanol and dried *in vacuo* at   50-70 $^{\circ}$C. Sodium salicylate was re-crystallized from 95.6 % ethanol and dried *in vacuo* at 50-70 $^{\circ}$C.

Purification of solvents. Commercial acetone was distilled, and the middle fraction was used for further work. It was stored over potassium permanganate and then distilled; the fraction boiling at 56.2 $^{\circ}$C was collected and stored (with periodical stirring) two weeks over tempered magnesium sulfate, and finally distilled. Commercial DMSO was stored over sodium hydroxide within a week. Then the solvent was passed through a column filled with tempered Al_2O_3 and distilled under low pressure. The middle fraction was passed again through the column and distilled at 5 to 7 Torr, collecting the middle fraction boiling at 80 $^{\circ}$C.

The water content in the solvents was 0.02 mass % as determined by Karl Fischer potentiometric titration.

Procedure. The solutions were prepared gravimetrically [7]. Conductance measurements were carried out using platinized platin electrodes in molybdenum-glass cells with an R 5083 ac bridge operating at a frequency of 1 kHz. The cells were calibrated using twelve standard aqueous solutions of potassium chloride, within concentration range 1×10^{-4} to 0.01 mol dm^{-3}. All the measurements were done at 25.00 ± 0.05 $^{\circ}$C. The numerical results are compiled in Table 1; the phoreograms are depicted in Figure 1.
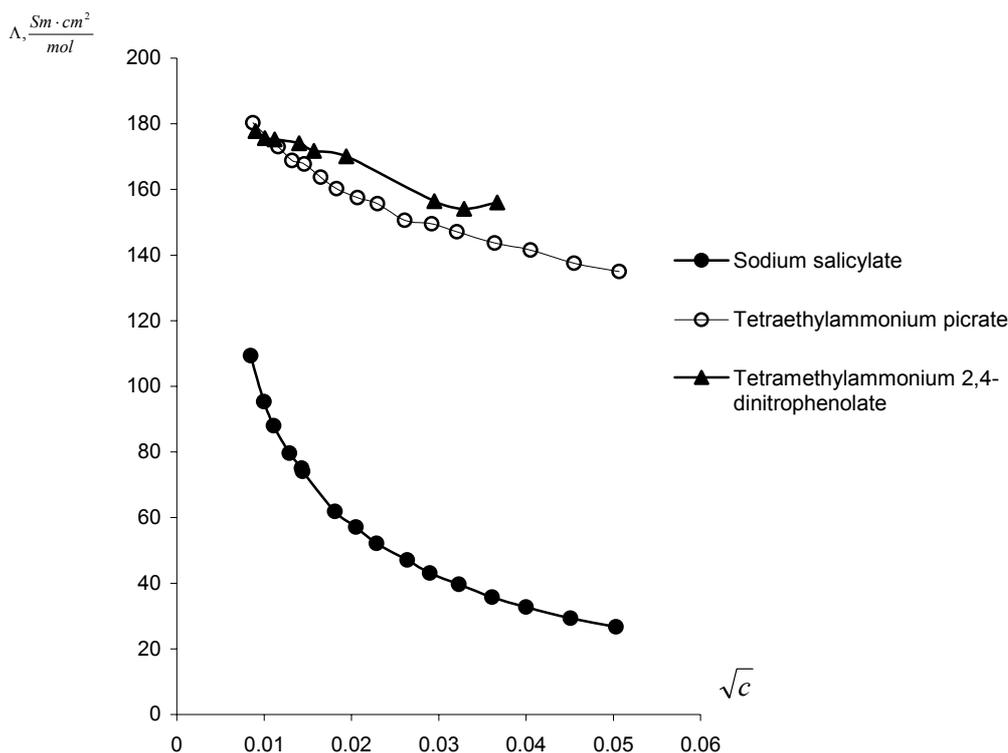

Fig. 1. Molar conductivities of salts in acetone – DMSO (mol. ratio 95 : 5) mixture as a function of the square root of the concentration.

Results and Discussion

The limiting molar electrical conductivities and association constants were calculated using the method of joint treatment of experimental data [8, 9] and LOPT program, created by O. N. Kalugin and V. F. Platukhin. The extended Lee–Wheaton equation for symmetrical electrolytes [10] and the second approximation of the Debye–Hückel theory were used to describe the concentration dependence of the molar conductivity. The parameter of closest approach was equated to the Bjerrum length (a = 1.262 nm). The results of limiting molar conductivities, Λ_O, and K_A calculations are presented in Table 2.

Table 2. Limiting molar conductivities and (cation + anion) association constants in acetone containing 5 mol. % DMSO, 25.0 $^{\circ}$C

Electrolyte	Λ_0 / Sm mol^{-1} cm^2	$K_A \times 10^{-2}$ / M^{-1}	$\log K_A$
N(CH$_3$)$_4$ (NO$_2$)$_2$C$_6$H$_3$O	184.3 $\pm$ 1.2	1.23 $\pm$ 0.20	2.09
N(C$_2$H$_5$)$_4$ (NO$_2$)$_3$C$_6$H$_2$O	180.3 $\pm$ 1.7	1.86 $\pm$ 0.21	2.27
NaC$_6$H$_4$OHCO$_2$	192 $\pm$ 6	209 $\pm$ 19	4.32

The influence of the a value on the calculated values of K_A and Λ_O was also examined using the data for tetraethylammonium picrate. Calculations were made with the value a = 0.531 nm, used by Fuoss et al. for ion pair in water-methanol mixtures [11]. We also utilized the sums of crystal radii of tetraethylammonium and picrate, reported by different authors and compiled by Karapetyan and Eychis [12]: 0.641, 0.700, and 0.761 nm. However, in all these cases the calculated $\log K_A$ equals 2.27 $\pm$ 0.05, while the Λ_O value was within the range 180.7 to 181.03 ($\pm$ 1.6) Sm mol^{-1} cm^2.

The results can be compared with the available literature data for pure acetone (relative permittivity 20.7). For example, in 1948 Reynolds and Kraus reported the values Λ_0 = 176.5 and $\log K_A$ = 1.76 for tetraethylammonium picrate [13]. By processing their experimental data with the Lee–Wheaton equation, values 176.5 and 1.93 were obtained in this Laboratory by Dr. Alexander Lebed. Thus, this salt is strongly dissociated in acetone; even for HClO$_4$ the $\log K_A$ value in acetone (2.64) [14] is higher. For sodium salicylate, the $\log K_A$ value of 4.56 determined by Dippy et al. [15] is also markedly higher than that for (tetraethylammonium + picrate) association. These authors [15] used the Λ_0 value of 170, estimated from Walden's rule. Using the Lee–Wheaton equation, we obtained the values Λ_0 = 156.1 and $\log K_A$ = 4.44.

Hence, sodium salicylate is a markedly weaker electrolyte than tetraethylammonium picrate both in acetone and acetone with 5 mol. % DMSO. The $\log K_A$ values in these two solvents coincide within 0.1–0.3 units.

In acetonitrile, a solvent with relative permittivity 35.9, Kolthoff and co-workers [16] obtained the following $\log K_A$ values of cation-anion association: 2.00 (tetraethylammonium 3,5-dinitrophenolate), 2.51 (sodium 4-nitrophenolate), and 2.54 (potassium 2,4-dinitrophenolate). Again, in the case of sodium salicylate the corresponding value is markedly higher: 3.62 [17]. This is natural, taking into account much stronger interaction between small alkali metal cation and localized carboxylate anion in the ion pair, as compared with that between relatively large tetraalkylammonium cation and nitrophenolate with strongly delocalized negative charge.

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Kharkov University Bulletin. 2007. №770. Chemical Series. Issue 15(38). Д.Ю. Филатов, С.Т. Гога, В.Г. Панченко, Н.О. Мчедлов-Петросян. Ионные равновесия 2,4-динитрофенолята тетраметиламмония, пикрата тетраэтиламмония и салицилата натрия в смеси ацетона с диметилсульфоксидом (мольное отношение 95 : 5). Электропроводимость и ионная ассоциация.

При помощи кондуктометрического метода определены константы катион-анионной ассоциации, K_A, в растворах 2,4-динитрофенолята тетраметиламмония, пикрата тетраэтиламмония и салицилата натрия в ацетоне, содержащем 5 мольных процентов диметилсульфоксида. Значения K_A при 25°С найдены равными (1.23±0.20) $\times10^2$, (1.86±0.21) $\times10^2$ и (2.09±0.19) $\times10^4$, соответственно. Значения предельной молярной электрической проводимости солей равны: 184.3±1.2, 180.3±1.7 и 192±6 См моль$^{-1}$ см^2, соответственно.

Table 1. Molar conductivities of three salts in acetone containing 5 mol. % DMSO, 25.0 °C

Sodium salicylate, $C \times 10^4$ / M	Λ / Sm mol^{-1} cm^2	Tetraethylammonium picrate, $C \times 10^4$ / M	Λ / Sm mol^{-1} cm^2	Tetramethylammonium 2,4-dinitrophenolate, $C \times 10^4$ / M	Λ / Sm mol^{-1} cm^2
0.714	109.39	0.761	180.30	0.810	177.74
0.990	95.30	1.346	173.04	1.019	175.63
1.232	87.97	1.730	168.76	1.263	175.29
1.652	79.63	2.124	167.70	1.955	174.11
2.049	75.05	2.731	163.72	2.480	171.74
2.079	74.05	3.342	160.27	3.764	170.10
3.284	61.89	4.268	157.49	8.722	156.40
4.186	57.08	5.285	155.65	10.808	154.07
5.253	52.11	6.812	150.63	13.469	156.07
6.970	47.07	8.519	149.47		
8.395	43.07	10.323	147.08		
10.443	39.64	13.280	143.70		
13.059	35.76	16.403	141.49		
16.039	32.75	20.703	137.53		
20.333	29.30	25.705	134.96		
25.262	26.74				