DETERMINATION OF THE ION MOBILITY IN IPA BY THE STATISTICAL METHOD OF FINDING VALUES OF THE COMPONENTS OF BINARY SUMS

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The values of limiting mobilities of 29 organic and inorganic ions in isopropyl alcohol were determined by the method of the nonlinear regression. The experimentally determined values of the molar specific limiting conductivity of salts, acids and bases obtained by the conductometric and potentiometric measurements in isopropyl alcohol.

The determination of the values of molar specific limiting conductivity of ions in non-aqueous media is a well-known issue, formulated long ago [1].

Elementary it can be divided into two parts. The first one deal with the difficulties associated with experiments in anhydrous solvents. Another one is related to the interpretation of the experiments' data.

There is no need to duplicate the analysis carried out in reliable reviews [2,3] and well-known works [4-6]. It should only be noted that the calculation results of the values of the ion mobility (for instance, hydrogen H^+ in IPA) significantly differ between researchers [7] and [8]. It can be stated that there is no procedure yet which finally eliminates any doubts in the reliability of obtained values of the ion mobility in non-aqueous media.

In the present study we suggest a fundamentally different method to determine the ion mobilities in various media. In this method the experimentally determined (by the conductometric and potentiometric measurements) values of the molar specific limiting conductivity of salts, acids and bases in a specific medium are used as a raw data.

For a symmetrical electrolyte, it can be written down as follows:

$$\Lambda_{ij}^0 = \lambda_i^0 + \lambda_j^0 = \Lambda_{ij}^0, \tag{1}$$

where Λ^0_{ij} is the values of its molar specific limiting conductivity, λ^0_i is the value of the limiting cation (anion) mobility, λ^0_j is the value of the limiting anion (cation) mobility. Hereinafter, superscripts "0" will be omitted.

This study sets a goal to determine the most reliable values of $\lambda_{i(j)}$, under known values of Λ_{ij}, which in practice are not determined for all i and j. The values of the molar specific limiting conductivity of salts, acids and bases, determined in the study [9] by the direct conductometric analysis, potentiometric and conductometric titration in IPA solutions, were selected as an experimental data base.

To solve this problem, the sum of the squares of the difference between the experimental values Λ_{ij} and the calculated ones, which represent the sum of values λ_i and λ_j, corresponding to i and j, were considered.

$$S = \sum_{i,j,i \neq j}^{N} \left(\Lambda_{ij} - \lambda_i - \lambda_j \right)^2 , \qquad (2)$$

where N is the total number of ions, forming electrolytes under the study.

Under an absolute minimum of values of the sum S, the corresponding values of λ_i and λ_j will determine the experimental data base of values of Λ_{ij} in a most reliable way. The absolute minimum S is subject to the following equality:

$$\frac{\partial S}{\partial \lambda_{i(j)}} = 0 . \qquad (3)$$

If S is a function of N variables λ_i and λ_j, then it leads to the following N equalities:

$$\frac{\partial S}{\partial \lambda_i} = -2 \sum_{j \neq i}^{N} \left(\Lambda_{ij} - \lambda_i - \lambda_j \right) = 0 , \qquad (4)$$

in the matrix formulation it is written as:

$$\mathbf{M\Lambda} = \mathbf{Y} , \qquad (5)$$

where $\mathbf{M}$ is a square matrix of order N, which can be defines as "the matrix of the existence of experimental results". The matrix form under experimental results used in this study is given in Picture 1. The elements of the matrix $\mathbf{M}$ are defined as follows:

$$m_{ij} = m_{ji} = 0,$$
(6)

if the value $\Lambda_{ij}(\Lambda_{ji})$ is absent in the experimental data base. The elements of the **M** are defined as follows:

$$m_{ij} = m_{ji} = 1,$$
(7)

if the value $\Lambda_{ij}(\Lambda_{ji})$ is present.

Elements on the main diagonal are determined by the sum:

$$m_{ii} = \sum_{j \neq i}^{N} m_{ij},$$
(8)

which corresponds to the total number of experimental values for electrolytes, including i-th cation (anion).

Λ is a column, consisting of the target values λ_i. **Y** is a column, composed of the elements Y_i, which are determined by the experimental values Λ_{ij}:

$$Y_i = \sum_{j \neq i}^{N} \Lambda_{ij}.$$
(9)

It is necessary to solve the following equation to find target values λ_i:

$$\Lambda = \mathbf{M}^{-1} \mathbf{Y},$$
(10)

where $\mathbf{M}^{-1}$ is an inverse matrix of **M**. The equation (10) was solved numerically using MATHCAD 15 software package [10].

This procedure basically repeats the method used in the study [11] to find values of the volumes of solvated solvent molecules.

In contrast to [11] here we will estimate the errors in determining the values λ_i^{th}. For that purpose, the mean-root-square deviation of target values $(\lambda_i^{th} + \lambda_j^{th})$ from the experimental Λ_{ij} was calculated

$$\Delta_i = \sum_{j \neq i}^{N} \left(\Lambda_{ij} - \lambda_i^{th} - \lambda_j^{th} \right)^2,$$
(11)

this value can be used to estimate the unbiased variance of the values λ_i^{th}

$$\sigma_i = \sqrt{\frac{\Delta_i}{m_{ii} - 1}}.$$
(12)

The experimental data base is given in Table 1. The results of calculations by formulas (10) and (12) are given in Table 2. There are also some literature values for comparison.

The discussion of results

Despite the scanty sample of the available experimental data on 29 ions in IPA (only 100 out of 812 possible values), the obtained values of λ_i show the known regularities and are agreed with the reported values. The only doubtful value ($\lambda_8 = 0$) for 4-nitrophenol is most likely associated with experimental errors. In a number of instances, errors in estimation are large ($i = 4, 6, 8, 11, 14$ relative value $\sigma_i > 100\%$), but it is due to the small content of the experimental data array.

When using this method to determine the ion mobility in water, where the sample of the experimental data is much more extensive, more stable values of λ_i under lesser errors can be expected.

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 0  0  1  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  1
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 0  1  1  1  1  1  1  1  1  1  1  1  1  1  1  1  0  0  0  0  0  0  0  0  0  0  0 15
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Pic. 1. The form of the matrix **M** for the array of available experimental values.

Table 1.

Experimental values of the molar specific limiting conductivity of electrolytes (Λ_{ij} [S·cm^2/mol]) in IPA, formed by corresponding cations and anions.

i	Anions	H^+	Na^+	Z^+_{25}	i	Cations	ClO_4^-	OH^-	A^-_8
1	OH^-		34.3		17	Pyridinium	29.1		
2	ClO_4^-	36.8	34.6		18	Quinolinium	23.6		
3	Cl^-	41.4			19	3-nitroanilinium	29.4		
4	Cl_3CCOO^-	40.0	12.9		20	NN-diethylanilium	21.9	25.0	
5	HCl_2CCOO^-	33.6	25.3		21	Triethylammonium	24.1	21.7	
6	Picrate	30.1	20.8		22	Acridinium	23.8	20.0	
7	3,5-dinitrobenzoate	39.3	18.3		23	TRIS (hydroxymeth-ylaminomethane)	27.2	32.7	
8	4-nitrobenzoate	30.8	18.3	17.3					
9	benzoate	42.9	25.5		24	diethanolammonium	23.1	20.0	
10	3-nitrophenolate	40.2	23.5		25	Morpholine	40.5	31.1	17.3
11	2- nitrophenolate	27.7	21.3		26	Tetra-butylammonium	24.1	22.2	
12	4- nitrophenolate	59.9	32.9						
13	1-Ph-5-mercapto-TZ	36.5			27	Na^+	34.6	34.3	
14	5-Ph-tetrazole	56.5	18.2		28	K^+		22.5	
15	HCO_3^-	34.3			29	H^+	36.8		
16	CO_2^{2-}	45.0							

Table 2.

Calculated values of the ion mobility (λ_i^{th}) in IPA with the variance estimate σ_i, as well as literature data.

i	Ions	$\lambda_i^{th} \pm \sigma_i$, S·cm^2/mol	λ_i^{lit}, S·cm^2/mol
1	OH$^-$	15.1 ± 2.41	
2	ClO$_4^-$	15.3 ± 3.95	15.07 [8]
3	Cl$^-$	9.66 ± *	10.38 [8]
4	Cl$_3$CCOO$^-$	2.99 ± 7.50	
5	HCl$_2$CCOO$^-$	5.99 ± 5.79	
6	Picrate	1.99 ± 5.09	12.7[7]
7	3,5- dinitrobenzoate	5.34 ± 3.18	
8	4-nitrobenzoate	0.00 ± 2.76	
9	Benzoate	10.7 ± 0.64	
10	3-nitrophenolate	8.39 ± 0.14	
11	2-nitrophenolate	1.04 ± 7.14	
12	4-nitrophenolate	22.9 ± 7.43	
13	1-Ph-5- mercapto-tetrazole	4.76 ± *	
14	5- Ph-tetrazole	13.9 ± 15.4	
15	HCO$_3^-$	2.56 ± *	
16	CO$_2^{2-}$	13.3 ± *	
17	Pyridinium	13.8 ± *	
18	Quinolinium	8.25 ± *	
19	3-nitroanilinium	14.1 ± *	
20	NN-diethylanilium	8.23 ± 2.33	
21	Triethylammonium	7.68 ± 1.56	
22	Acridinium	6.68 ± 2.55	
23	TRIS (hydroxymethylaminomethane)	14.7 ± 4.03	
24	diethanolammonium	6.33 ± 2.05	
25	Morpholine	19.5 ± 6.69	
26	Tetra-butylammonium	7.93 ± 1.02	10.1[7]
27	Na$^+$	15.2 ± 5.02	5.87[8]
28	K$^+$	7.40 ± *	7.72[8]
29	H$^+$	31.7 ± 5.28	13.4[7], 36.52[8]

± * - the variance estimate σ_i cannot be calculated using the formula (12), since the value of $m_{ii} = 1$ for this ion.

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