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ION ASSOCIATION EFFECTS OF LIPOPHILIC  
QUATERNARY AMMONIUM SALTS  
IN ION-EXCHANGE AND POTENTIOMETRIC SELECTIVITY

## INTRODUCTION

Until the present time the problem of the effects exerted by ion association of lipophilic quaternary ammonium salts (QAS) on the anion-exchange and potentiometric selectivity of the anion-selective electrodes has been practically untackled, both theoretically and experimentally. Moreover, so far lipophilic QAS have been customary assumed as nonselective anion exchangers, the ion exchange constants for which are primarily determined by standard free energies of ion resolution to conform to Hofmeister's extraction series [1–5]. Indeed, this point of view has been supported by numerous experimental data bearing witness to insignificant dependence of anion exchange constants on the structural features of quaternary ammonium cations (QAC) [1, 4, 6]. However, recently we have found that this situation occurs just in the cases of QAC in which all four hydrocarbon chains are sufficiently long (no less than propyl) and in the cases when single-charged anions are exchanged for the single-charged ones. Otherwise, anion exchange constants and potentiometric selectivity coefficients of QAS-based membranes may be varying by several orders [7–10] pointing to manifestations of the factor of ion association.

It should be noted that the majority of the published reliable information concerning the ion association constants relate to solvents with medium and high dielectric permeability (acetone, methyl ethyl ketone, primary alcohols, dichloroethane, acetonitrile, nitrobenzene, etc.) [11–25], where the values of ion association constants are comparatively low and much leveled. At the same time, in solvents with low dielectric permeability, where the influence of the structural features of cation and anion on the efficiency of electrostatic interaction should be especially essential, the experimental values of the ion association constants are «hard to reach» [26]. Nevertheless, the ion exchange constants revealing the peculiarities of ion association for QAC with exchanging anions are easily accessible experimentally. Unfortunately, the direct assessment of the role played by the ion association factor in exchange selectivity on the basis of ion exchange data is impossible, since the principal part belongs to much more profound solvation effects. However, the relationship between the anion exchange constants and the QAC structure established in Refs. [7, 9, 10] unambiguously demonstrates that

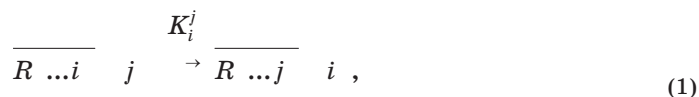
the factor of ion association may have a significant effect on the ion-exchange selectivity too.

In the present work we report some new ideas concerning the role of solvation and ion association processes in the ion-exchange and potentiometric selectivity. In our opinion, a proposed approach based on the linear Gibbs energy relations (LGER) [27–31] and ion association theory by Eigen-Denison-Ramsey-Fuoss [32–35] enables one to compare the role of hydration, solvation and ion association processes in systems involving lipophilic QAS in the ion-exchange ( $K_i^j$ ) and potentiometric ( $K_{i,j}^{Pot}$ ) selectivity and, consequently, to estimate the limits for purposefull variation of these parameters using the factor of ion association. The obtained results are of great practical importance for the development of extraction systems and ion-selective electrodes with the improved selectivity.

## 1. LGER-BASED DESCRIPTION OF ION-EXCHANGE EQUILIBRIA

### 1.1. The first approximation. Comparative estimation of the contributions made by standard free energies of anion hydration and solvation into the anion-exchange selectivity

In solvents with low and medium dielectric permeability QAS exist mainly in the form of ion associates. So the ion-exchange equilibrium in such systems is normally described by the following equation:



where  $R^+ \dots i^-$ ,  $R^+ \dots j^-$  are the ion associates of QAC with anions  $i^-$  and  $j^-$  respectively, an overcribed bar denotes the phase of organic solvent,  $K_i^j$  is the exchange constant.

It should be noted that this relationship is correct provided that ion pairs only occur without the formation of more complex aggregates (approximation of a perfectly associated solution). However, a great body of data obtained during investigations of the anion-exchange properties of trinonyloctadecylammonium (TNODA) relative to a large number of anions in a system water – toluene [6] revealed that there is no relationship between the exchange constants and concentration  $R^+ \dots i^-$  in the organic phase over the concentration range of  $10^{-3}$ – $10^{-4}$  M. This may be indicative of the absence of the aggregation processes or of their course following alike for TNODA salts with different anions (the latter seems to be highly improbable). Because of this, the ion exchange process is further described by the equation (1).

Then the exchange constant may be defined by the following equation:

$$\log K_i^j = \frac{G_h^0 \quad j \quad - \quad G_h^0 \quad i \quad - \quad G_s^0 \quad j \quad + \quad G_s^0 \quad i \quad}{2303RT} \log \frac{(k_{ass})_{jR}}{(k_{ass})_{iR}}, \quad (2)$$

where  $G_h^0$  and  $G_s^0$  are the standard free hydration and solvation energies of anions,  $k_{ass}$  are ion association constants, and  $R$  denotes a quaternary ammonium cation.

Assuming that ion association constants of anions with long-chain QAC are relatively independent of the nature of associating anions (being rather a function of the dielectric permeability of a solvent) the ion exchange constant in the first approximation will be determined solely by the difference in the standard free hydration and solvation energies of exchanging ions\*:

$$\log K_i^j = \frac{G_h^0_j - G_h^0_i - G_s^0_j + G_s^0_i}{2303RT} \quad (3)$$

Since mineral anions are solvated much more effectively by water compared to common organic solvents, the difference in free energies of hydration dominates over the difference in free energies of solvation. Because of this, the position of anions in the exchange series is determined by their hydration energies (Fig. 1).

Table 1

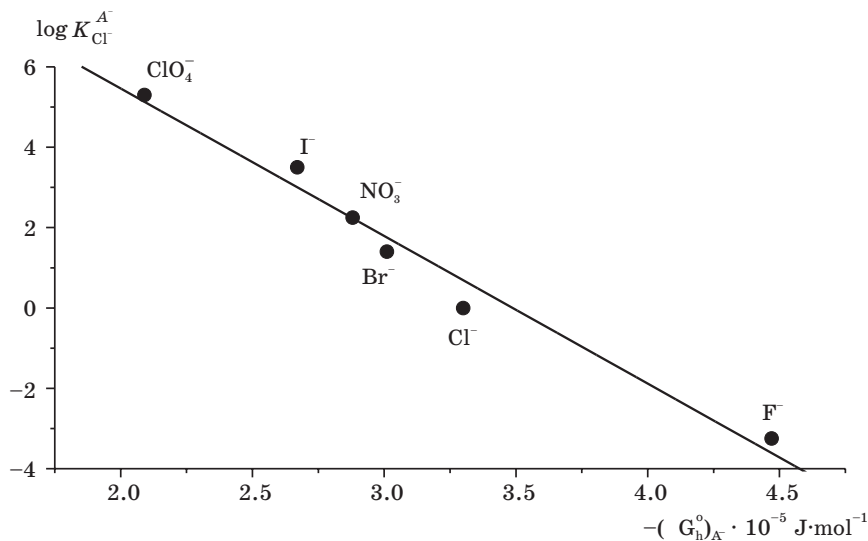


Fig. 1. The logarithms of the anion-exchange constants as a function of their standard free hydration energies. Ion exchanger – TNODA. Data taken from [6, 23].

\*Such an assumption is to some extent substantiated as in the absence of some specific interaction between cation and anion, association constant of QAS are actually little dependent on the anion nature as compared to the association constant, e.g. of amine salts exhibiting H-bonding effect, the strength of which is strongly dependent on the anion charge density. This is conclusively demonstrated by the results summarized in Table 1. However, QAS association constants also depend on the anion nature, though to a lesser degree. This aspect will be discussed at greater length in section 1.2.

The logarithmic values of the ion association constants for TNODA  
and trioctylammonium (TOA) salts in binary systems toluene – nitrobenzene.  
Data taken from [36].

Anion	log $k_{ass}$			
	TNODA		TOA	
	30 vol.% of nitrobenzene	50 vol.% of nitrobenzene	30 vol.% of nitrobenzene	50 vol.% of nitrobenzene
Cl <sup>-</sup>	5.35	3.6	>12	9.1
Br <sup>-</sup>	5.0	3.5	10.5	8.0
J <sup>-</sup>	4.88	3.3	7.8	6.2

However, the statement concerning the hydration energies of anions as a governing factor for the value of an exchange constant should not be literally understood. The hydration energies of anions determine their position in the exchange series rather than the exchange constant value. Even in the case of fairly inert organic solvents, e.g. toluene, the transport of anions from aqueous phase to the organic one is accompanied by the compensation of the greater part of free hydration energy by the free energy of solvation. For example, standard free energies of hydration for Cl<sup>-</sup> and ClO<sub>4</sub><sup>-</sup> amount respectively to  $-3.3 \cdot 10^5$  and  $-2.09 \cdot 10^5$  J · mol<sup>-1</sup> [23]. Then

$K_{Cl}^{ClO_4}$  calculated from the relationship:

$$K_{Cl}^{ClO_4} = 10^{\frac{(G_h^0)_{ClO_4} - (G_h^0)_{Cl}}{2.303RT}}, \quad (4)$$

equals to  $1 \cdot 10^{22}$ , whereas the experimental value of  $K_{Cl}^{ClO_4}$  equals to  $2 \cdot 10^5$  [6]. The last value corresponds to the difference in free standard transport energies of these ions approximately  $3 \cdot 10^4$  J · mol<sup>-1</sup>. This suggests that only about of 25 % of the difference in the standard free ions hydration energies are transformed into the ion-exchange selectivity whereas more than 75 % are compensated by the interactions in toluene phase.

The quantitative estimation of free standard energies of ion solvation by different solvents is a rather complex experimental problem. To compare the efficiencies of solvation coupling in different solvents, one can use the empirical polarity scales for solvents [27–31] based on the LGER principle. The essence this principle as applied to the anion solvation consists of the following: should anion A<sub>1</sub> be solvated by solvent S<sub>1</sub> stronger than by solvent S<sub>2</sub>, then anion A<sub>2</sub> should be solvated by this solvent S<sub>1</sub> also stronger as opposed to solvent S<sub>2</sub>. And the proportionality factor between the standard free solvation energies of one and the same ion by two different solvents is the value (constant in the first approximation) determined by the nature of these solvents and independent of the nature of solvated ions. Clearly, this principle is not and could not be rigorously substantiated theoretically. Moreover, it should be violated provided the interactions of a solvent with one of the ions is specific and distinct from interactions of the same solvent with other ions. For example, in the case of exchanging amphiphilic an-

ions, an individual estimation of the solvation effects is necessary for lipophilic and hydrophilic parts of the anion [37, 38] considering that the proportionality factors for their standard free energies of hydration and solvation differ. Nevertheless, the LGER principle shows itself rather clearly for a great body of experimental data. For example, a linear function  $\log K_{Cl}^A = G_h^0 - A$  given in Fig. 1 follows directly from this principle.

As applied to the ion-exchange equilibria under study, the LGER principle may be expressed as

$$G_0^S = K - G_h^0. \quad (5)$$

Then equation (2) can be transformed into the following form

$$\log K_i^j = \frac{G_h^0 - G_h^0 - (1 - K)}{2303RT}, \quad (6)$$

or

$$\log K_i^j = K - G_h^0 - G_h^0, \quad (7)$$

where

$$K^* = \frac{1 - K}{2303RT}. \quad (8)$$

The  $K^*$  factor defines the effect exerted by a solvent nature on the ion-exchange selectivity. Obviously, this factor should increase with the lowering of the solvation ability of a solvent as in this case the difference in the standard free hydration energies of exchanging ions is more completely transformed to selectivity of the exchange process. On the contrary, for active solvents which effectively solvate the anions, when  $K \rightarrow 1$ ,  $K^* \rightarrow 0$ , the compensation effect leading to reduced ion-exchange selectivity has to be increased.

Many attempts were undertaken to obtain quantitative correlations between the anion-exchange constants and standard free energies of anion hydration. However, the absence of trustworthy exchange constants determined over a wide range of exchange affinity and of trustworthy  $G_h^0$  values for the majority of anions put obstacles in the way of producing the reliable results [40]. The first problem has been successfully solved, primarily owing to the studies performed at the Analytical Chemistry Department of the Belarusian State University [4, 6, 41–45] as a result of which the values of exchange constants have been found for more than 100 anions in a system water – toluene. As for the standard free energies of hydration, this problem remains to be solved [40] since the values for  $G_h^0$  given in various publications are distinguished by several tens or even hundreds of  $\text{kJ} \cdot \text{mol}^{-1}$  (see also Table 2).

Table 2

The logarithmic values of the anion exchange constants in a system water–toluene (standard ion – Cl<sup>-</sup>, ion exchanger – TNODA) and the values of standard free energies of anion hydration. Data taken from the following sources: a – [6], b – [23], c – [46] (experimental values), d – [46] (calculated values).

Anion	$G_h^0 \cdot 10^{-5}, \text{J} \cdot \text{mol}^{-1}$			
	$\log K_{Cl}^A$	a	b	c
F <sup>-</sup>	-3.25	-4.47	-4.65	-3.45
OH <sup>-</sup>	-2.8	-4.64	-4.30	-3.45
H <sub>2</sub> PO <sub>4</sub>	-2.45	-	-4.65	-2.45
HCO <sub>3</sub>	-2.0	-	-3.35	-3.10
CH <sub>3</sub> COO <sup>-</sup>	-1.6	-	-3.65	-3.00
Cl <sup>-</sup>	0	-3.30	-3.40	-2.70
CN <sup>-</sup>	0.2	-	-2.95	-2.60
JO <sub>3</sub>	0.3	-	-4.00	-2.70
NO <sub>2</sub>	0.55	-	-3.30	-2.55
BrO <sub>3</sub>	1.0	-	-3.30	-2.60
Br <sup>-</sup>	1.4	-3.01	-3.15	-2.50
NO <sub>3</sub>	2.25	-2.88	-3.00	-2.75
ClO <sub>3</sub>	2.7	-	-2.80	-2.45
I <sup>-</sup>	3.5	-2.67	-2.75	-2.20
SCN <sup>-</sup>	4.15	-	-2.80	-2.30
BF <sub>4</sub>	4.35	-	-1.90	-2.05
ClO <sub>4</sub>	5.3	-2.09	-4.30	-1.80
Pic <sup>-</sup>	8.15	-	-	-
TPhB <sup>-</sup>	12.8	-	0.50	0.15

Because of this, the  $K^*$  values may vary significantly (nearly twice) depending on the  $G_h^0$  set used (Fig. 2), and associated functions  $\log K_{Cl}^A$

$G_{hA}^0$   $G_{hCl}^0$   $10^{-5}$  are characterized by low correlation coefficients.

Using a set of  $G_h^0$  values for a limited number of anions (F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, I<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>), chosen as the most likely values [23], we have derived the values of  $K$ ,  $K^*$  and coefficient  $\alpha \equiv 1-K$ , that defines the extent to which the difference in the standard free hydration energies of exchanging anions is transformed into the exchange selectivity (for a hypothetical perfectly inert solvent  $K$  and  $\alpha$  amount to 1 and 0 respectively). The obtained values of  $K$ ,  $K^*$  and  $\alpha$  are summarized in Table 3.

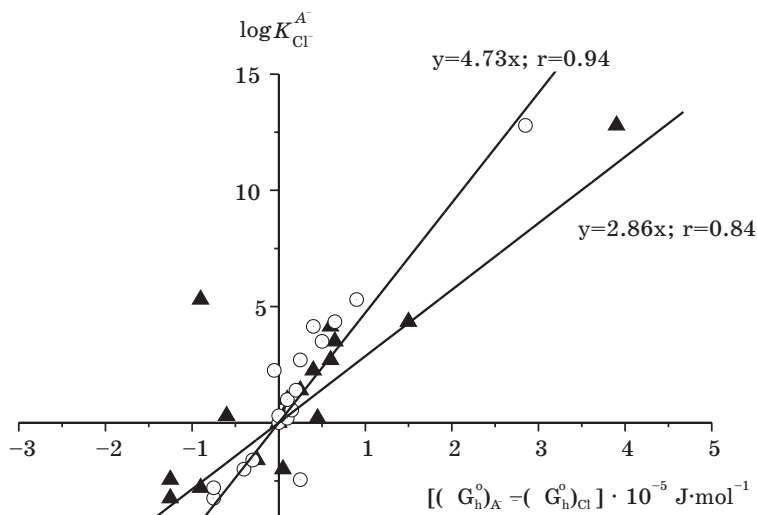


Fig. 2. Logarithms of anion-exchange constants (taken from [6]) as a function of the difference in standard free hydration energies

(taken from [46]).  $\blacktriangle$  – experimental values of  $G_h^0$ ;

Table 3

The values of  $K$ ,  $K^*$ ,  $\alpha$  coefficients characterizing the solvation ability relative to anions and derived from the anion-exchange constants and standard free hydration energies by equations (6), (7).  
Ion exchanger – TNODA

Solvent	$K$	$G_s^0 / G_h^0$	$K^* \cdot 10^5$	$\alpha = 1 - K$
n-decanol	0.94		1.1	0.06
chloroform	0.85		2.7	0.15
toluene	0.776		4.0	0.224
n-decane	0.781		3.9	0.219
toluene + nitrobenzene (1:9)	0.75		4.4	0.25

As can be seen, the values of  $K^*$  and  $\alpha$  increase with the decreasing of the solvents polarity in a sequence decanol < chloroform < toluene in accordance with the above concept. At the same time, when using n-decane instead of toluene the obtained values of  $K^*$  and  $\alpha$  were surprisingly lower than those of toluene, whereas with the use of a more polar binary mixture toluene – nitrobenzene (1:9) they were somewhat higher. The differences observed in the values of  $K^*$  and  $\alpha$  for these solvents are not large. However, these differences could not be considered as experimental errors because they are reproducible [6].

A discrepancy between the above-mentioned approach and the experimental results is still larger in the case when double-charged anions are exchanged for the single-charged ones. As applied to the case of chloride exchanged by sulphate, equation (7) takes the following form:

$$\log K_{2Cl}^{SO_4^2} = K \left( G_{h, SO_4^2}^0 - 2 G_{h, Cl}^0 \right) \quad (9)$$

Substituting the value  $K^* = 4 \cdot 10^{-5}$ , obtained for a system water – toluene on the basis of single-charged anions exchange data and  $G_{h, SO_4^2}^0 = -1.042 \cdot 10^6 \text{ J} \cdot \text{mol}^{-1}$ ,

$G_{h, Cl}^0 = -3.3 \cdot 10^5 \text{ J} \cdot \text{mol}^{-1}$  [23], into the equation (9) we obtained the  $\log K_{2Cl}^{SO_4^2}$  calc value of  $-15.3$ . The experimental value  $\log K_{2Cl}^{SO_4^2}$  exp is equal to  $-2.8$ . So, the difference between the experimental and the calculated exchange constants is huge (by 12.5 orders). It seems that the most likely explanation for these discrepancies can be the effect of the ion association processes on the ion-exchange equilibrium, which has not been taken into account in the above approach.

## 1.2. Corrected model. Inclusion of the ion association factor

### 1.2.1. General approach

On the assumption that the difference in the ion association constants of QAC with exchanging anions has really a pronounced effect on the exchange constant value, equation (2) may be transformed as follows:

$$\log K_i^j = K^{**} \left( G_{h, j}^0 - G_{h, i}^0 \right) + \log \frac{(k_{ass})_{jR}}{(k_{ass})_{iR}} \quad (10)$$

Apparently,  $K^{**}$  factor differs from the  $K^*$  factor in the equation (7).

In the first approximation the ion association constants are described by Eigen-Denison-Ramsey-Fouss equation [25] as a function of the closest approach parameter of associating ions, charge product, dielectric permeability of the medium and temperature. At  $T = 293 \text{ K}$  this equation assumes the form

$$\log(k_{ass})_{RA} = 2.6 - 3 \log a(\text{\AA}) - 247 \frac{|z_R z_A|}{D a(\text{\AA})} \quad (11)$$

where  $a(\text{\AA})$  is the closest approach parameter in Ångström units,  $D$  is the relative dielectric permeability of solvent,  $z_R, z_A$  are the cation and anion charges.

It has been found that in solvents with low solvation ability such as toluene so-called contact ion pairs [15, 16] are formed without solvent molecules between the associated cation and anion. In this case the parameter  $a(\text{\AA})$  is mainly dependent on the geometry of associating ions and primarily on their sizes. Therefore, in media with not very high dielectric permeability, when the last term in equation (11) makes the principal contribution to the association constant, small ions are stronger associated as compared to large ones.

With allowance made for the ion association factor one is enabled to explain an apparent discrepancy between the solvation ability of solvents and  $K^*$  values calculated from equation (7) for n-decane, toluene and toluene – nitrobenzene mix-



ture (see Table 3). Due to high dielectric permeability of a binary mixture toluene – nitrobenzene containing up to 90 % of nitrobenzene, an extent of ion association of QAS at concentrations of  $\leq 1 \cdot 10^{-2}$  M is never in excess of a few per cent. Because of this, the effect of ion association on ion-exchange equilibrium may be neglected. In consequence,  $K^*$  factor in this case defines «pure» solvation effects, and its fairly high value compared to other solvents ( $4.4 \cdot 10^{-5}$ ) is conditioned by the fact that nitrobenzene belongs to the solvents poorly solvating the anions, despite its high dielectric permeability, being a weak base rather than Lewis acid.

As for toluene, the solvation effects interfere with the effects of ion association. Since the strength of QAS ion associates increases as the anion size decreases, this causes the leveling of the ion-exchange constants. Because of this a formal description of the exchange equilibrium based on equation (7) that takes no account of the ion association factor gives undervalued  $K^*$ , i.e. solvation of the ions by toluene seems higher than is actually the case. In n-decane characterized by a lower dielectric permeability compared to toluene (1.99 and 2.385 respectively) [47] the leveling effect of ion association is enhanced. As seen from the calculations based on equation (11), for ion pairs characterized by the closest approach parameters of 4.0 and 4.5 Å, the ion association constants in toluene should be differing by a factor of 530, whereas in n-decane – by a factor of 2000. As a result, without due regard for ion association the value of  $K^*$  will be severely undervalued.

The effect of the ion association factor is still greater in the case of single-charged ions exchanged by the double-charged ones. In this case equation (10) takes the form

$$\log K_{2i}^j = K^{**} \left( G_h^0 \right)_j - 2 \left( G_h^0 \right)_i + \log \frac{(k_{ass})_{jR} (k_{ass})_{jRR}}{(k_{ass})_{iR}^2}, \quad (12)$$

where  $(k_{ass})_{jR}$  is the formation constant for the ion associate  $j^{2-} \dots R^+$  formed from a double-charged anion  $j^{2-}$  and cation  $R^+$ ;  $(k_{ass})_{jRR}$  is the formation constant for the ion associate  $R^+ \dots j^{2-} \dots R^+$  formed from a negatively charged associate  $j^{2-} \dots R^+$  and cation  $R^+$ ; all other designations similar to equation (10).

As seen from the calculations based on equation (11) with the assumption that the closest approach parameters for the associates formed by QAC with single- and double-charged anions are close and equal to e.g. 4.5 and 5 respectively, in toluene ( $D = 2.385$ ) the contribution of ion association (the last term in equation (12)) to  $\log K_{2i}^j$  is +16.4. Because of this, the experimental constants characterizing the exchange of double-charged ions for the single-charged ones are much larger than might be expected reasoning from their standard free hydration energies.

### 1.2.2. Semiquantitative approach to estimation of the contributions made by ion association to anion-exchange selectivity

A theory of Eigen-Dension-Ramsey-Fouss allows for semiquantitative estimation of the ion association constants in media with low dielectric permeability, where these values are experimentally inaccessible. The required values of  $a(\text{Å})$  may be iterati-

vely calculated using equation(11) from the association constants values experimentally determined in the media with rather high dielectric permeability. However, it should be taken into consideration that equation (11) has been derived on the basis of a «sphere in a continuous dielectric» model, disregarding a specific interaction of the associating ions with each other and with a solvent dictated by their structural features. Consequently, the values of  $a(\text{Å})$  calculated from equation (11) for one and the same pair of ions in different solvents may differ appreciably. At the same time, the values of  $a(\text{Å})$  calculated from the data on ion association in solvents similar in nature are, as a rule, in good agreement. All the afore-said is supported by Table 4.

As seen, for ion associates formed by tetraethyl ammonium cation with the same anion in acetone and methyl ethyl ketone the corresponding values of  $a(\text{Å})$  are very close and the maximum difference is about 0.2 Å. On the contrary, the difference of the corresponding values in these solvents and in pyridine is approximately 1.5 Å. Therefore, even though the parameter  $a(\text{Å})$  is said to be practically constant in binary mixtures of solvents with significantly different dielectric permeabilities [34] and what is more in different solvents [20], to our mind, the reliability of the predicted ion association constants directly depends on similarity of the solvation properties of the solvent for which the values of  $a(\text{Å})$  have been calculated and the solvent for which the  $k_{ass}$  values are to be predicted. Binary mixtures of toluene and nitrobenzene with as high toluene content as possible for wch reliable  $k_{ass}$  values still may be experimentally determined seem to be most suitable for predictions of  $k_{ass}$  values in toluene.

Table 4

The logarithmic values of the ion association constants for tetraethylammonium salts in acetone, methyl ethyl ketone and pyridine (data taken from [23]) and the values of the closest approach parameter calculated from equation (11) at T=298 K.

Anion	Acetone (D=19,1)		Methyl ethyl ketone (D=17,8)		Pyridine (D=12,3)	
	$\log k_{ass}$	$a(\text{Å})$	$\log k_{ass}$	$a(\text{Å})$	$\log k_{ass}$	$a(\text{Å})$
Cl <sup>-</sup>	2.59	3.62	3.02	3.39	3.51	4.88
Br <sup>-</sup>	—	—	2.90	3.55	3.41	5.07
J <sup>-</sup>	2.44	3.89	2.63	3.98	3.24	5.44
Pic <sup>-</sup>	2.1	4.78	2.36	4.59	2.9	6.42

Table 5

The logarithmic values of the ion association constants for TNODA salts with different anions in binary mixtures of toluene – nitrobenzene (data taken from [36]), the values of the closest approach parameters calculated from equation (11) and the values of radii for the corresponding anions (data taken from [46])

Anion	20 vol.% of nitrobenzene (D=7.1)		10 vol.% of nitrobenzene (D=4.7)		$\bar{a}(\text{Å})$	$r_A(\text{Å})$
	$\log k_{ass}$	$a(\text{Å})$	$\log k_{ass}$	$a(\text{Å})$		
Cl <sup>-</sup>	6.95	4.60	11.0	4.52	4.56	1.81
Br <sup>-</sup>	6.62	4.86	10.5	4.75	4.80	1.96
J <sup>-</sup>	6.48	4.98	9.7	5.17	5.08	2.20
SCN <sup>-</sup>	6.6	4.87	9.65	5.20	5.03	2.13
C <sub>8</sub> H <sub>17</sub> OSO <sub>3</sub> <sup>-</sup>	6.7	4.79	9.8	5.11	4.95	—
Pic <sup>-</sup>	5.94	5.51	9.05	5.58	5.55	—
TФБ <sup>-</sup>	4.9	7.01	7.5	6.94	6.98	4.21

Table 5 presents the values of ion association constants for TNODA salts with different anions in binary toluene–nitrobenzene mixtures containing from 80 to 90 vol.% of toluene. As is seen, for both compositions of the binary mixture, in which the values of  $k_{ass}$  differ by 3–4 order of magnitude, the calculated values of  $a(\text{Å})$  correlate well with each other.

The obtained values of  $a(\text{Å})$  enable one to estimate the  $k_{ass}$  values in toluene. Based on equation (11), the values of  $\log k_{ass}$  calculated for ion associates of  $\text{TNODA}^+ \dots \text{Cl}^-$  and  $\text{TNODA}^+ \dots \text{TPhB}^-$  equal to 22.1 and 14.8 respectively, i.e. they differ by 7.3 orders of magnitude. Compare, in binary toluene – nitrobenzene mixtures containing 50, 20 and 10 % of nitrobenzene this difference amounts to 0.7, 3.0 and 4.5 orders of magnitude [36], whereas in n-decane – to 8.9 orders of magnitude. Thus, even in the case of lipophilic quaternary ammonium salts the factor of ion association may have a profound leveling effect on the values of exchange constants, especially in media with low dielectric permeability.

#### 1.2.2.1. The relationship between the closest approach parameter and the size of associating ions

Proceeding from pure mechanistic ideas about the closest approach parameter as a center-to-center distance between anion and cation, the presence of such a relationship for contact ion pairs is absolutely obvious. However, it should be noted that for QAS the parameter  $a(\text{Å})$  is not a sum of the radii of cation and anion since anions penetrate deeply between the hydrocarbon chains of QAC. Besides, the closest approach parameter  $a(\text{Å})$  derived from  $k_{ass}$  values should not be identified with a distance between the geometrical centers of cation and anion too. This is stipulated by the fact that complex polyatomic ions may be aligned relative each other in such a way that the total efficiency of the interaction of electrostatic charges distributed in individual atoms be a maximum. Quantum-chemical calculations have demonstrated that a positive charge of QAC is predominantly centered at four  $-\text{CH}_2-$  groups nearest to the nitrogen atom [48]. For example, when QAC interacts with nitrate ion, the resultant mutual orientation may be so that three oxygen atoms of nitrate will be simultaneously interacting with three  $-\text{CH}_2-$  groups of QAC. Naturally, such an interaction is much more efficient than that of two spherical ions of the same size as above, the charges of which are uniformly distributed over the whole surface of ions. Moreover, mutual polarization of the ions also contributes the interaction efficiency. As a result, in some cases the parameter  $a(\text{Å})$  may assume the values below a possible minimum of the distance between the geometrical centers of associating ions that is calculated from the atomic sizes, bond lengths and angles (e.g. the values in Table 4). The parameter  $a(\text{Å})$  calculated from the values of  $k_{ass}$  could not be also determined as a center-to-center distance between the charges of polarized ions. We are of the opinion that  $a(\text{Å})$  is a certain theoretical variable characterizing the integral interaction efficiency of cation and anion, including a change in solvation interaction with a solvent (suggested by the differences in  $a(\text{Å})$  values calculated for contact ion pairs in different solvents), and also the effect of entropy due to reduced number of QAC conformations caused by penetration of anion between the alkyl chains, reflected as an increase in  $a(\text{Å})$  values with growing length of hydrocarbon chains in QAC (see Table 6).

Table 6

The values of the closest approach parameters for contact ion pairs  $R_4N^+ \dots Pic^-$  in 1,2-dichloroethane. Data taken from [12]

QAC	$(CH_3)_4N^+$	$(C_2H_5)_4N^+$	$(C_3H_7)_4N^+$	$(C_4H_9)_4N^+$	$(C_5H_{11})_4N^+$
a(Å)	4.65	5.80	6.00	6.16	6.25

Nevertheless, as seen from Table 5, the values of a(Å) calculated on the basis of the ion association constants correlate well with the radii of the associated anions. A  $a_{RA}(\text{Å}) - a_{RCl}(\text{Å}) - r_A(\text{Å}) - r_{Cl}(\text{Å})$  plot yields a straight line for this correlation function starting from the origin and with a slope close to unity (Fig. 3).

Consequently, the values of the closest approach parameters for ion pairs formed by TNODA cations with anions differing in nature may be estimated in the very first approximation by the following equation:

$$a_{RA}(\text{Å}) = a_{RCl}(\text{Å}) + r_A(\text{Å}) - r_{Cl}(\text{Å}) \tag{13}$$

The obtained values of  $a_{RA}(\text{Å})$  enable one to estimate reliably the ion association constants.

1.2.2.2. Estimations of the limiting values of the exchange constants

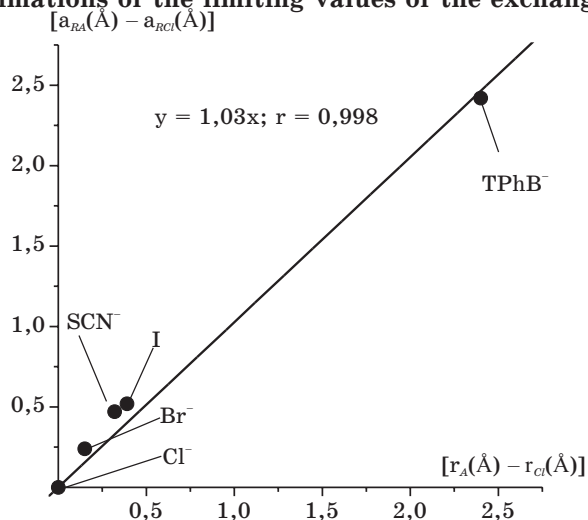


Fig. 3. The differences in the closest approach parameters for various anions and chloride ion in their ion associates with TNODA, calculated from experimental values of the association constants (taken from [36]) as a function of the difference between radii of the corresponding anions and chloride ion (taken from [46])

The experimental values of ion-exchange constants and radii for all anions simultaneously available from the Refs. [6], [46], which to the best of our knowledge are currently most adequately reflecting the actual situation, are listed in Table 7. With the use of equation (13) and the literature data for  $r_A(\text{\AA})$ , the values of  $a(\text{\AA})$  have been calculated for the corresponding ion associates, and the values of  $\log k_{ass}$  in toluene have been calculated from equation (11).

Table 7

The logarithmic values of the experimental anion exchange constants in water-toluene system  $\log(K_{Cl}^A)_{exp}$  (standard ion -  $Cl^-$ ), ion radii  $r_A(\text{\AA})$ , closest approach parameters  $a(\text{\AA})$ , ion association constants in toluene  $\log k_{ass}$  and limiting exchange constants  $\log(K_{Cl}^A)_{lim}$ . Data are taken from the following sources: a - [6], b - [46]; c, d, e - calculated from equations (13), (11) and (14) respectively.

Anion	$\log K_{Cl}^A_{exp}$	$r_A(\text{\AA})$	$a(\text{\AA})$	$\log k_{ass}$	$\log K_{Cl}^A_{lim}$
	a	b	c	d	e
$F^-$	-3.25	1.33	4.08	24.6	-5.75
$OH^-$	-2.8	1.33	4.08	24.6	-5.3
$H_2PO_4$	-2.45	2.00	4.75	21.2	-1.55
$HCO_3$	-2.0	1.69	4.44	22.7	-2.6
$CH_3COO^-$	-1.6	1.62	4.37	23.0	2.5
$Cl^-$	0	1.81	4.56	22.1	0
$CN^-$	0.2	1.91	4.66	21.6	0.7
$JO_3$	0.3	1.81	4.56	22.1	0.3
$NO_2$	0.55	1.92	4.67	21.6	1.05
$BrO_3$	1.0	1.91	4.66	21.6	1.5
$Br^-$	1.4	1.96	4.71	21.4	2.1
$NO_3^-$	2.25	1.79	4.54	22.2	2.15
$ClO_3^-$	2.7	2.00	4.75	21.2	3.6
$J^-$	3.5	2.20	4.95	20.4	5.2
$SCN^-$	4.15	2.13	4.88	20.7	5.55
$BF_4$	4.35	2.32	5.07	19.9	6.55
$ClO_4$	5.3	2.50	5.25	19.3	8.1
$Pic^-$	8.15	-	5.55*	18.3	11.95
$TPhB^-$	12.8	4.21	6.96	14.8	20.1

\* The  $a(\text{\AA})$  values for  $Cl^-$  and  $Pic^-$  ion associates with TNODA were taken from table 5.

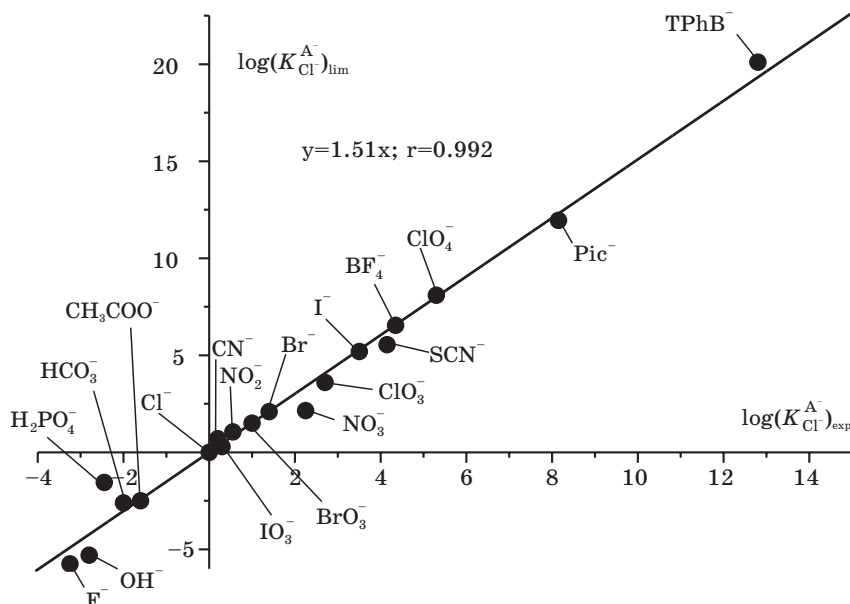


Fig. 4. The logarithms of the limiting values of anion exchange constants calculated from equation (14) in water – toluene system as a function of the logarithms of the experimental exchange constants (taken from [6]). Ion exchanger is TNODA

We have introduced the notion of a «limiting value» for the ion exchange constant  $K_i^j$ \_{lim} to characterize the net hydration and solvation effects, excluding the effects of ion association, as follows:

$$\log K_i^j \text{_{lim}} \equiv \log K_i^j \text{_{exp}} \log \frac{(k_{ass})_{jR}}{(k_{ass})_{iR}}. \quad (14)$$

The values of  $K_i^j$ \_{lim} obtained in this way represent nothing but the ratio of so-called «individual distribution coefficients» of ions by Eisenman,  $k_j / k_i$  [49]. The calculated values of  $K_i^j$ \_{lim} are present in Table 7.

As seen from Fig. 4, logarithms of the limiting values of exchange constants calculated using equation (14) correlate well with the experimental values.

The observed correlation may be described as follows:

$$\log K_i^j \text{_{lim}} = 1.51 \log K_i^j \text{_{exp}}. \quad (15)$$

Despite of the fact that the principal contribution into this correlation is made only by two ions (tetraphenylborate and picrate), their exclusion has practically no effect on the form of the correlation function, and the proportionality factor in equation (15) is varying from 1.51 to 1.45. In this case the correlation coefficient remains rather large ( $r = 0.992$  for the whole set of ions and with the exception of picrate and tetraphenylborate  $r = 0.982$ ). This is a circumstantial confirmation of the proposed approach and realistic character of  $K_i^j$ \_{lim} values.

As seen, the differences in  $\log K_i^j$   $_{lim}$  values are much larger than those for  $\log K_i^j$   $_{exp}$ . For example,  $\log K_{Cl}^A$   $_{lim}$  and  $\log K_{Cl}^A$   $_{exp}$  values for the most hydrophilic  $F^-$  and the most lipophilic  $TPhB^-$  ions amount to 26.85 and 16.05 respectively. This suggests that the selectivity of ion exchange may be improved by many orders provided the factor of ion association is excluded or at least reduced.

This may be realized by two ways: (1) using of a solvent with rather high dielectric permeability and as low solvation ability to anions as possible and (2) increasing of the closest approach parameter through the use of anion exchangers with enhanced steric hindrance of the exchange center (e.g. owing to branching hydrocarbon substituents). Unfortunately, these approaches are hardly realizable in practice. As for the solvents with high dielectric permeability, the data on anion exchange in a system water – toluene–nitrobenzene mixture [6] reveal a somewhat better exchange selectivity than in a system water – toluene. At the same time, this improvement is not so great as might be expected reasoning from the values of  $\log k_{ass}$  given in Table 7. To illustrate, with the use of TNODA solutions in toluene and binary mixture toluene – nitrobenzene (1:9) as ion exchanges the values of  $\log K_{Cl}^{ClO_4}$  were respectively 5.3 and 6.2 [6], differing by 0,9 of the order of magnitude, whereas the values of  $k_{ass}$  were differing by 2.8 orders (see Table 7). This may be explained by a somewhat better solvation ability of nitrobenzene as compared to toluene. As a consequence, the compensation effect due to ion solvation by the solvent increases, leading to a decrease in selectivity. As regards the use of steric hindered anion exchangers, all attempts of the authors aimed at synthesis of such QAS have failed all together: QAS refused to form or were thermodynamically instable decaying in storage.

### 1.2.2.3. The solvation effect on the ion-exchange selectivity. The refined estimations

From equations (7), (10), (14) it follows that

$$K^{**} = K^* \frac{\log K_i^j}{\log K_i^j} \frac{_{lim}}{_{exp}}. \quad (16)$$

Assuming for toluene that  $\log K_i^j$   $_{lim}$  amounts to  $1.5 \log K_i^j$   $_{exp}$  (see equation (15)) and  $K^* = 4.0 \cdot 10^{-5}$  (Table 3), we obtain  $K^{**} = 6.0 \cdot 10^{-5}$ . And assuming identical values of the parameter  $a(\text{\AA})$  in n-decane and toluene, with proper calculations for n-decane one obtains  $K^{**} = 1.65$ ,  $K^* = 6.4 \cdot 10^{-5}$ . Such an estimation for chloroform and n-decanol seems fairly risky, since in these solvents effectively solvating anions the values of  $a(\text{\AA})$  may vary considerably. Besides, in the case of n-decanol it is likely that the formed ion pairs will be separated by the solvent and owing to better solvation ability for small ions the above relationship between  $a(\text{\AA})$  and  $r_A(\text{\AA})$  may be changed by the reverse one [18, 21]. Because of this, the consideration is limited to toluene, n-decane and toluene–nitrobenzene mixture. With due regard for the ion association factor the parameters characterizing the efficiency of solvation interaction in these solvents assume the values given in Table 8.

Table 8

$K^{**}$ ,  $K$  and  $\alpha$  values characterizing the solvation properties of solvents relative to anions and calculated for toluene, n-decane and toluene – nitrobenzene (1:9) mixture with due regard for ion association\*

Solvent	$K^{**} \cdot 10^{-5}$	$K$	$G_s^0 / G_h^0$	$\alpha$	$1/K$
n-decane	6.4	0.64		0.36	
toluene	6.0	0.66		0.34	
toluene + nitrobenzene (1:9)	4.4	0.75		0.25	

\* The value of  $K$  was calculated by the equation :  $K' = 1 - 2.303RT \cdot K^{**}$ .

As seen from the Table 8, after inclusion of the ion association factor everything «goes into place», and the proportionality factor between the standard free energies of hydration and solvation ( $K$ ) is changing in accordance with varying solvation properties of the solvents to increase in the following sequence: n-decane < toluene < toluene – nitrobenzene mixture.

It is interesting that calculation of the exchange constant for chloride exchanged by sulphate from equation (12) with  $K^{**} = 6.0 \cdot 10^{-5}$  and of the ion association constants  $\log(k_{ass})_{SO_4R} = 41.3$ ;  $\log(k_{ass})_{SO_4RR} = 20.4$ ;  $\log(k_{ass})_{ClR} = 22.1$  from equation (11) using  $a(\text{\AA})$  values of 4.95 and 4.56 derived from the ion-association constants for TNODA with octyl sulphate and chloride ions (Table 5), results in  $\log K_{2Cl}^{SO_4^2-} = -5.4$ . This value is much closer to the experimental value of  $-2.8$  than that obtained from equation (9) disregarding the factor of ion association (see Section 1.1). Considering that the final result  $\log K_{2Cl}^{SO_4^2-}$  is an algebraic sum of two very large values (see equation (12)), it should be accepted as wholly satisfactory.

Thus, the obtained data suggest that the proposed approach on the basis of linear Gibbs energy relations, including the effect of ion association, makes it possible to perform a more adequate estimation of a relative solvation ability of the solvents based on the results for exchange of single-charged ions by single-charged ions and provides a means for better insight into the factors causing extractability of double-charged ions.

#### 1.2.2.4. The steric accessibility effect of QAC exchange center on the ion-exchange selectivity

The presence of such effect follows from the relationship between the closest approach parameter  $a(\text{\AA})$  and the length of hydrocarbon chains of QAC (see Table 6). In an effort to test the existence at this effect experimentally, we especially have synthesized QAS with different numbers of methyl substituents at the nitrogen atom  $(C_{12}H_{25}O)_3C_6H_2CH_2N^+(CH_3)_n(C_8H_{17})_{3-n}$ , where  $n$  is varying from 1 to 3, and determined the exchange constants between chloride ion and single- or double-charged ions in toluene. Table 9 gives the logarithmic values of the exchange constants for QAS containing three methyl substituents at the nitrogen atom (TMA) and those for TNODA.



Table 9

The logarithmic values of the exchange constants for the case when chloride ions are exchanged by single-charged anions and sulphate ion in a system water – toluene. Ion exchangers – TNODA and TMA: a – experimental values, b –calculated values.

Anion	$\log K_{Cl}^A, \log K_{2Cl}^{SO_4^2}$		
	TNODA	TMA	
		a	b
$SO_4^2$	-2.8	0.4	0.1
$F^-$	-3.25	-1.8	-2.6
$CH_3COO^-$	-1.6	-1.1	-1.0
$Br^-$	1.4	0.6	1.0
$NO_3^-$	2.25	0.8	2.35
$SCN^-$	4.15	2.6	3.3
$I^-$	3.5	2.2	2.6
$ClO_4^-$	5.3	3.2	3.8
$Pic^-$	8.15	6.1	6.25

The comparison of the exchange constants for the appropriate anions obtained using TNODA and TMA as ion exchangers has revealed that the presence of three methyl radicals in QAC is leading to a significant leveling of the exchange constants for single-charged anions. To illustrate, for TNODA the exchange constants  $K_{Cl}^F$  and  $K_{Cl}^{Pic}$  differ by 11.4 orders of magnitude and in case of TMA – by 7.9 orders only. The effect is very strong on exchange of chloride by double-charged sulphate ion when  $K_{2Cl}^{SO_4^2}$  increases by a factor of 1600. In general, the observed effects are not unexpected following directly from analysis of equation (11). In media with low dielectric permeability the major contribution to the value of  $\log k_{ass}$  is made by the last term in this equation. Because of this, a decrease in the closest approach parameter  $a(\text{\AA})$  due to better steric accessibility of the exchange center in QAC should result in sharply growing ion-association constants of QAC with small anions. The most profound effect should be exerted by a decreasing  $a(\text{\AA})$  on the value of the first association constant of double-charged anions with QAC. In an effort of numerical simulation for the effect on the exchange constant value, the following assumptions have been made:

1)  $a(\text{\AA})$  parameter for the ion pair of a picrate ion with TMA equals 4.65 (the value of  $a(\text{\AA})$  for tetramethylammonium picrate in dichloroethane, see Table 6);

2) decrease of  $a(\text{\AA})$  in case of TMA cation substitution for TNODA cation is independent of the anion nature and amounts to 0.9  $\text{\AA}$  corresponding to a decrease of  $a(\text{\AA})$  for picrate ion ( $5.55 - 4.65 = 0.90$ ).

3) the value of  $a(\text{\AA})$  for ion associates formed by a sulphate ion with TNODA is accepted as 4,95 obtained for the ion pair of TNODA with octyl sulphate (Table 5).

The values of  $a(\text{\AA})$  parameter for the ion pairs formed by single-charged ions with TNODA are taken from Table 7. In accordance with item 2, the values of  $a(\text{\AA})$  have been calculated with TMA as ion exchanger, and the values of  $\log k_{ass}$  were

calculated from equation (11). The calculated values of exchange constants with TMA as ion exchanger have been obtained from equation (17) as follows:

$$\log K_{Cl}^A \text{ TMA} = \log K_{Cl}^A \text{ ТНОДА} + \log \frac{(k_{ass})_{AR}}{(k_{ass})_{CIR}} \text{ TMA} - \log \frac{(k_{ass})_{AR}}{(k_{ass})_{CIR}} \text{ ТНОДА} \quad (17)$$

Changes of the contribution made by ion association into  $\log K_{2Cl}^{SO_4^2-}$  have been taken into consideration according to equation (12). The calculated values for the logarithms of exchange constants are summarized in Table 9.

The comparison between the calculated and experimental values of the logarithms of exchange constants shows that in the majority of cases the proposed calculation procedure describes adequately a real situation.

However, the exchange constant for nitrate ion falls out of the general pattern: experimental  $\log K_{Cl}^{NO_3}$  decreases when TMA replaces TNODA as ion exchanger, whereas the calculated value is increased by 0.1. This discrepancy is probably explained by the fact that a compact nitrate ion ( $r = 1.79 \text{ \AA}$ ), penetrating between alkyl chains of TNODA, is capable to interact simultaneously with hydrogen atoms of three  $-\text{CH}_2-$  groups, nearest to the nitrogen atom, having an excessive positive charge. In the case of TMA the interaction involves the hydrogen atoms of  $\text{CH}_3$ -groups, being less efficient due to dispersion of a positive charge over a larger number of hydrogen atoms.

Fig. 5 presents the steric accessibility effect of the QAC exchange center on the value of exchange constant when sulphate is exchanged for single-charged ions.

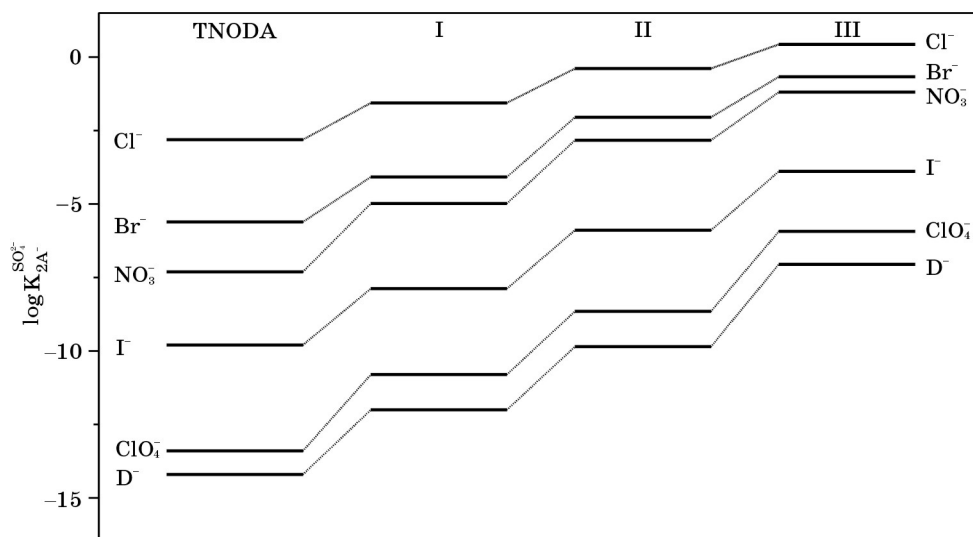


Fig. 5. The logarithms of exchange constants for the case when single-charged anions are exchanged by sulphate in a system water – toluene as a function of the exchange center steric accessibility of anion exchanger:  $[(\text{C}_{12}\text{H}_{25}\text{O})_3\text{C}_6\text{H}_2\text{CH}_2\text{N}(\text{CH}_3)_n(\text{C}_8\text{H}_{17})_{3-n}]^+\text{A}^-$ .

Roman numerals in the diagram denote the number of methyl groups in QAC

As seen, affinity of ion exchangers to the sulphate ion regularly grows with increasing of a number of methyl groups at the nitrogen atom. A maximum effect is observed for large ions, namely, perchlorate and 2,4-dinitrophenolate. In the case of chloride exchanged by sulphate the exchange constant increases by 3.2 orders of magnitude, whereas in the case of sulphate exchanged for perchlorate it increases by more than 7 orders. This derives from the fact that the ion association constants of QAC with large-size anions are less dependent on the steric accessibility of QAC exchange center. It should be noted that the observed increase in  $\log K_{2\text{ClO}_4}^{\text{SO}_4^{2-}}$  is in a good agreement with the results of calculations performed in accordance with the above assumptions. The calculations suggest that with TMA used as an ion exchanger the value of  $K_{2\text{ClO}_4}^{\text{SO}_4^{2-}}$  should have an increase by about 6 orders of magnitude.

It has been found that similar behavior is observed for other small-size double-charge anions, for example, tartrate, oxalate too, see Fig. 6.

Thus, the use of QAC with three methyl radicals results in dramatic (by  $10^3$ – $10^7$  times) growth of the exchange constants when double-charged anions are exchanged for the single-charged ones. It should be emphasized that all the foregoing is valid only for double-charged anions of small size. This follows directly from equation (11). Since the first term of the equation is a constant and the second (logarithmic term) is little dependent on  $a(\text{\AA})$ , the influence of  $a(\text{\AA})$  on the value of  $\log k_{\text{ass}}$  in media with low dielectric permeability is determined mainly by a change in the third term. Disregarding the second term changes, it is easy to show that improvement of the steric accessibility of the exchange center, leading

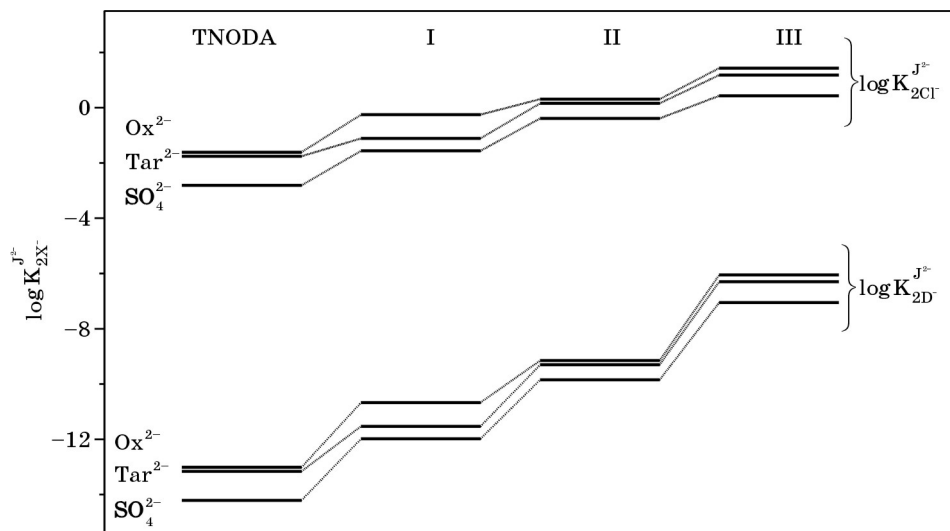


Fig. 6. The logarithms of exchange constants for the case when double-charged anions are exchanged for the single-charged ones in a system water–toluene as a function of the exchange center steric accessibility. Tar<sup>2-</sup> – tartrate, Ox<sup>2-</sup> – oxalate, D<sup>-</sup> – 2,4-dinitrophenolate. Designations for anion exchangers similar to Fig. 5

to a decrease in  $a(\text{\AA})$ , will be accompanied by an increase of  $K_{2i}^{j^2}$  so long as the following relation is fulfilled:

$$a_{Rj}(\text{\AA}) \geq \frac{3}{2} a_{Ri}(\text{\AA}), \quad (18)$$

where  $j$  is a double-charged ion,  $i$  is a single-charged ion.

Otherwise, improvement of the steric accessibility of QAC exchange center should give quite the opposite result. This is confirmed by experimental data (Fig. 7).

As seen, when the largest single-charged anions ( $\text{ClO}_4^-$ , 2,4-DNF $^-$ , Pic $^-$ ) are exchanged by a large-size double-charged ion, improvement of the steric accessibility of the ion-exchange center is accompanied by increase in the exchange constant (though not so great as in case of sulphate ion, see Fig. 5), whereas in the case of  $\text{B}_{10}\text{H}_{10}^{2-}$  exchanged for smaller single-charged ions the exchange constant passes through a maximum.

Besides, this illustrative example is also of interest since it is modeling the exchange of small-size double-charged anions for single-charged ions in the presence of neutral anion carriers used for the creation of anion-selective electrodes with nontraditional selectivity. Indeed, the picture observed when single-charged anions are exchanged by sulphate in the presence of hexyl 4-trifluoroacetyl benzoate (Fig. 8) is very similar to that observed for the exchange of  $\text{B}_{10}\text{H}_{10}^{2-}$  ion (Fig. 7).

Thus, the obtained results have demonstrated that a change in the steric accessibility of QAC exchange center may have a very strong effect on the value of the exchange constant. In the process, the charge value and sizes of exchanging anions are the key parameters.

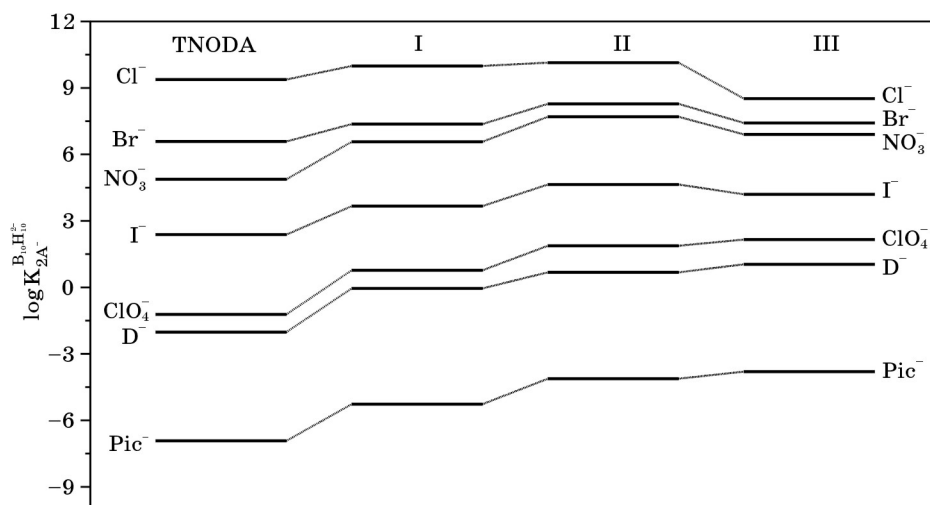


Fig. 7. The logarithms of exchange constants for the case when single-charged anions are exchanged by decaboronhydride anion in a system water – toluene as a function of the exchange center steric accessibility.

Designations for anion exchangers similar to Fig. 5

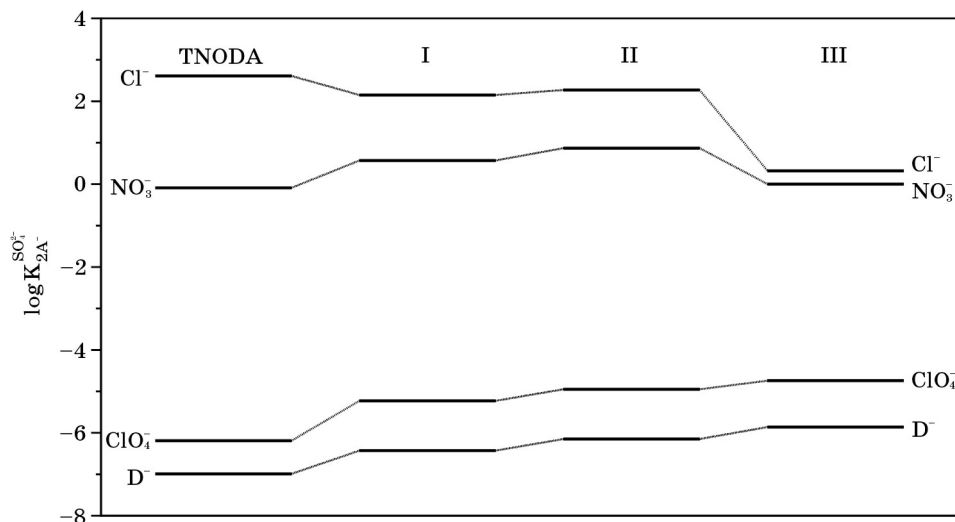


Fig. 8. The logarithms of exchange constants for the case when single-charged anions are exchanged by sulphate in a system water – toluene in the presence of hexyl 4-trifluoroacetylbenzoate ( $0.06 \text{ mol} \cdot \text{l}^{-1}$ ) as a function of the exchange center steric accessibility. Designations for anion exchangers similar to Fig. 5

## 2. ION ASSOCIATION EFFECT ON THE POTENTIOMETRIC SELECTIVITY OF QAS-BASED ANION-EXCHANGE MEMBRANES

The data presented in Fig. 9 reveal the effect of the QAC exchange center steric accessibility on the potentiometric selectivity to sulphate ion in the presence of single-charged anions. It is seen that the interfering effect of foreign anions is lowered as the steric accessibility of QAC exchange center is improved. The best selectivity to sulphate ion is observed for the membrane containing trimethyl QAS, and the worst – for the membrane containing monomethyl QAS. The membrane containing dimethyl QAS holds an intermediate position. Data for the TNODA-based membrane are lacking in the figure, because the authors have failed to obtain the sulphate function with a slope close to Nernstian one.

It is interesting that the most significant (approximately by 5 orders of magnitude) improvement of the selectivity to sulphate is achieved in the presence of large single-charged anions ( $\text{ClO}_4^-$ ,  $\text{SCN}^-$ ,  $\Gamma^-$ ), and the smallest improvement (about 1.5 orders of magnitude) is achieved in the presence of chloride. As a whole, the observed picture correlates well with the order of changes in the corresponding ion exchange constants (Fig. 5). Because of considerable differences in the solvation and dielectric properties of PVC membranes plasticized by *o*-NPOE and toluene solutions of QAS, the agreement is just qualitative.

The findings and results may be interpreted as follows. According to [50], the potentiometric selectivity coefficients determined by the separate solutions

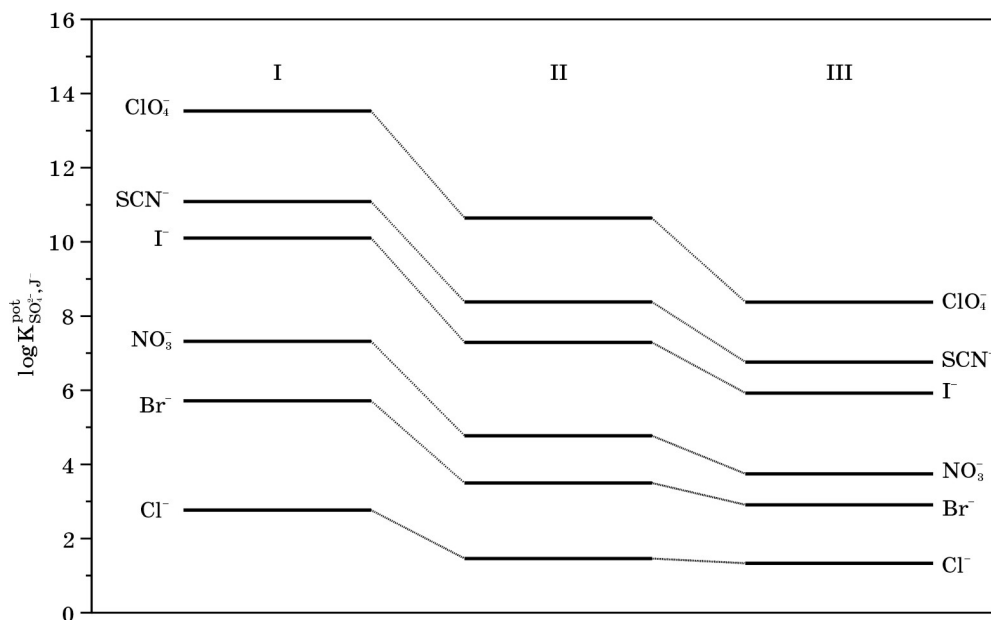


Fig. 9. The logarithms of potentiometric selectivity coefficients of QAS-based sulphate-selective electrodes as a function of the exchange center steric accessibility. Membrane composition: PVC + o-NPOE (1:2) + QAS (0,03 mol · l<sup>-1</sup>). Designations for anion exchangers similar to Fig. 5.

method for the ions differ in a charge value, are described by the following equation:

$$K_{ij}^{Pot} = \frac{\bar{C}_i}{k_i} + \frac{k_j}{\bar{C}_j} z_i/z_j, \quad (19)$$

where  $k_i$  and  $k_j$  are hypothetical individual distribution coefficients of the principal and interfering ions;  $\bar{C}_i$  and  $\bar{C}_j$  are the concentrations of «free» (forming no ion associates) ions in the membrane phase, provided all the sites in the membrane are occupied only by ions of the same type: respectively  $i$  or  $j$ . In the assumption of a perfectly associated solution, when cations and anions occurring in the membrane are predominantly in the form of ion associates and a portion of free ions is relatively small, the concentrations of free ions in the membrane may be easily obtained from analysis of the corresponding equilibria.

For single-charged (foreign) anions we have

$$\bar{C}_j = \bar{C}_R \frac{\bar{C}_R^{tot}}{(k_{ass})_{jR}}^{\frac{1}{2}}, \quad (20)$$

where  $\bar{C}_R$  is the concentration of free QAC,  $\bar{C}_R^{tot}$  is the total concentration of QAS in the membrane.

For double-charged (basic) anions we have

$$\bar{C}_i = \frac{\bar{C}_{iR}}{\bar{C}_R (k_{ass})_{iR}}, \quad (21)$$

where  $\bar{C}_i$  is the concentration of a negatively charged ion associate containing a double-charged anion  $i$  and one cation  $R$ .

In accordance with electroneutrality condition, the following equation is valid:

$$2\bar{C}_i = \bar{C}_{iR} + \bar{C}_R. \quad (22)$$

Considering that

$$(k_{ass})_{iR} \gg (k_{ass})_{iRR}, \quad (23)$$

we have

$$\bar{C}_i \ll \bar{C}_{iR} \approx \bar{C}_R, \quad (24)$$

from equations (21), (23) we obtain

$$\bar{C}_i \approx \frac{1}{(k_{ass})_{iR}}. \quad (25)$$

Then equation (19) may be written as follows:

$$K_{ij}^{Pot} = \frac{k_j^2 (k_{ass})_{jR}}{k_i (k_{ass})_{iR} \bar{C}_R^{tot}}. \quad (26)$$

Since individual distribution coefficients for ions  $i$  and  $j$  are independent of QAC nature and according to equation (11) the first association constant for a double-charged anion  $i$  with QAC has stronger dependence on the parameter  $a(\text{\AA})$  than the association constant of a single-charged anion with the same QAC, it is obvious that improved steric accessibility of the exchange center should result in reduced interference of foreign single-charged anions. Apparently, the greatest improvement of the selectivity to double-charged anions should be observed in the presence of large single-charged anions, the ion association constants of which are less dependent on the steric accessibility of QAC exchange center. A theoretical model under consideration is in a good agreement with the experimental data (Fig. 9).

It should be noted that, similar to the ion-exchange constants for ion associates formed by QAC with single-charged and double-charged anions, there is a critical relationship of the parameters  $a(\text{\AA})$  when the dependence of  $K_{ij}^{Pot}$  on the steric accessibility of QAC exchange center should be changed by just the opposite

one. It should be taken into consideration that the ion association constants involved in the expression for  $K_{ij}^{pot}$  have other relations than in the expression for an exchange constant (equations (12), (26)). Analysis of equations (11), (26) has demonstrated that in the case of membranes with rather low dielectric permeability the improvement in the steric accessibility of QAC exchange center should be accompanied by the enhanced selectivity to a double-charged anion  $i$  in the presence of a single-charged anion  $j$  until the following relation is valid:

$$a_{Ri}(\text{\AA}) \geq 2a_{Rj}(\text{\AA}), \quad (27)$$

Thus, the size restrictions in this case are less stringent than for ion exchange constants (equation (18)).

As seen in Fig. 10, the tendency for improvement of the potentiometric selectivity to sulphate anion in the presence of single-charged anions with improving steric accessibility of QAC exchange center is retained to some extent for the membranes containing a neutral anion carrier, hexyl 4-trifluoroacetylbenzoate. A considerable enhancement of the selectivity to sulphate with increasing number of methyl groups in QAC is observed in the presence of  $\text{ClO}_4^-$ ,  $\text{SCN}^-$ ,  $\text{NO}_3^-$  ions. Similar selectivity improvement has been revealed by the authors for other double-charged anions (hydrophosphate, tartrate, oxalate) as well.

It is of interest that using of the secondary amine salt  $(\text{C}_{12}\text{H}_{25}\text{O})_3\text{C}_6\text{H}_2\text{CH}_2\text{NH}(\text{CH}_3) \cdot \text{HCl}$  as anion exchanger (membrane IV) results in further significant (about an order) enhancement of the selectivity to sulphate an-

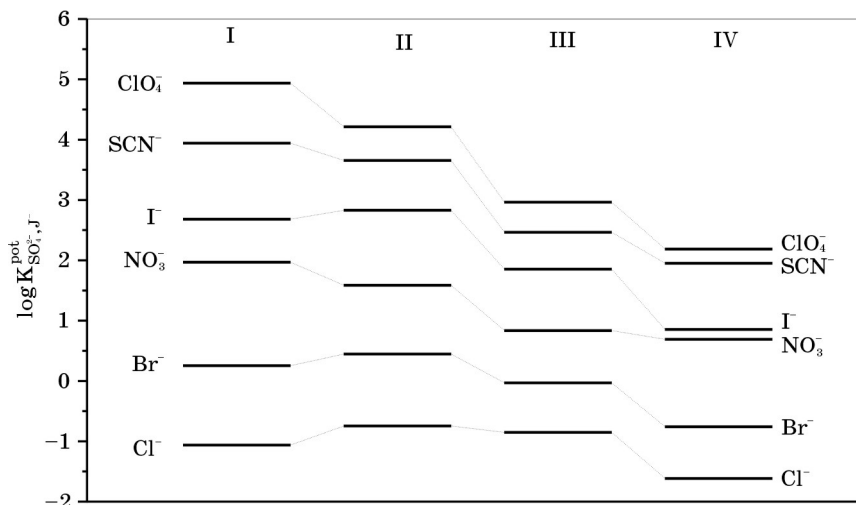
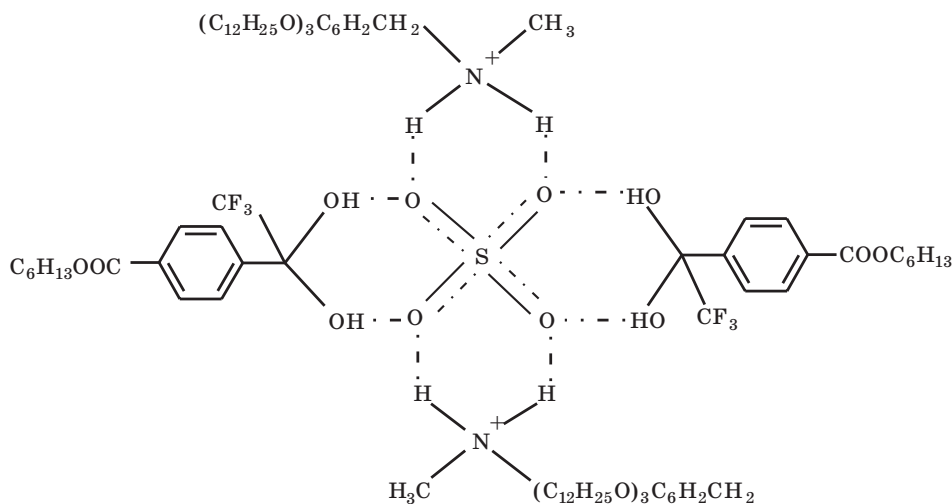


Fig. 10. The logarithms of potentiometric selectivity coefficients of neutral carrier-based sulphate-selective electrodes as a function of the nature of liquid anion exchanger. Membrane composition: PVC + 1-chloronaphthalene (1:2) + hexyl 4-trifluoroacetylbenzoate (8 % of the weight of other membrane components) + anion exchanger ( $0.03 \text{ mol} \cdot \text{l}^{-1}$ ).

Designations I, II, III in the diagram are similar to Fig. 5, and IV denotes hydrochloride of the secondary amine  $(\text{C}_{12}\text{H}_{25}\text{O})_3\text{C}_6\text{H}_2\text{CH}_2\text{NH}(\text{CH}_3) \cdot \text{HCl}$



ion in the presence of single-charged anions. It is likely that along with enhanced steric accessibility of the exchange center this is due to hydrogen bonding between hydrogen atoms of the secondary ammonium cation and sulphate ion. Specifically, the complex of the following structure may be formed:



The obtained results bear witness to the fact that the selectivity of the neutral carriers-based membranes to double-charged anions is not indifferent to the structure of liquid ion exchanger, in particular to the steric accessibility of its exchange center. This is of great importance in practice, since major progress that has been made recently in the development of anion-selective electrodes with non-traditional selectivity is due primarily to synthesis of neutral anion carriers [51–55]. A critical requirement for normal functioning of such electrodes is the presence of a liquid anion exchanger in the membrane [50]. Until the present time, the selectivity of these ISE has been attributed solely to a neutral carrier, whereas the role of a liquid ion exchanger has been reduced to the provision of anion permselectivity of the membranes and, hence, the Nernstian slope of the electrode function. Based on the results of the present study, it might be expected that proper selection of anion exchanger may be an additional means of controlling the selectivity of this type electrodes reversible to double-charged anions.

### 3. CONCLUSION

This paper is actually the first attempt at individual estimation of the contributions made by solvation and ion association effects to the exchange and potentiometric selectivity for the systems based on lipophilic QAS. The authors perceive clearly that the approaches used here are far from being perfect and necessitate further refinement. Specifically, valuable information may be acquired by a direct experimental study of the effect exerted by the steric accessibility of QAC exchange center on the ion association constants with different anions, as

well as quantum-chemical calculations of the closest approach parameters including complete structural and energy optimization for the ionic associates formed.

The most important outcome of this paper is substantiation of the effect of ion association factor on the ion exchange selectivity in QAS-based systems, the contribution of which to the ion exchange constant in solvents with low dielectric permeability may come to 10 orders and more, being comparable to the contribution of solvation interactions. A better understanding has been gained of the possibility to control the anion-exchange selectivity in such systems both by leveling and differentiation of the association constants. The revealed strong steric-accessibility effect of the exchange center of QAS (previously considered as «non-selective» anion exchangers) on the anion-exchange selectivity is of particular interest, especially when double-charged anions are exchanged for the single-charged ones producing a huge (up to  $10^7$ -fold) increase in the selectivity. This makes it possible to consider QAS with enhanced steric accessibility of the exchange center as anion exchangers selective to double-charged anions.

Among the findings of the authors, the fact that the effect of a sharp increase in the anion-exchange selectivity to double-charged anions, attained when using QAS with enhanced steric accessibility of the exchange center is of great practical significance, as this effect has been also revealed in the potentiometric selectivity of the QAS-based anion-exchange membranes and more important in the selectivity of the neutral-carriers-based membranes doped with QAS to provide the anion permselectivity.

This looks promising for a considerable improvement of ISE selectivity to  $\text{SO}_4^{2-}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{C}_2\text{O}_4^{2-}$  and some other double-charged anions, and achievement of the selectivity characteristics enabling wide use of these ISE in analytical practice.

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