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ОРИГИНАЛЬНЫЕ СТАТЬИ

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Theoretical characterization of ionic liquids as stationary phases for gas chromatography

Elena A. Zaitceva[1], Alexey A. Dolgonosov[1]✉, Anatoliy M. Dolgonosov[1]
[1]Vernadsky Institute of Geochemistry and Analytical Chemistry of RAS, Moscow, Russian Federation, lex.dolgo@gmail.com✉

Abstract. The previously proposed method for the three-parameter characterization of stationary phases in gas chromatography, which proved to be accurate and informative in the description of well-studied mid-polar phases, has been adapted for ionic liquids. The three-parameter characteristic method is based on the theory of intermolecular interactions in the sorbate-sorbent system developed by the authors. It is shown that the parameters of dispersion, electrostatic and hydrogen bonds for calculating the interaction of an ionic liquid with a sorbate molecule are the sum of the corresponding characteristics of the cation and anion. Two methods of calculation are considered: according to the direct problem - the method of a priori calculation of the characteristics of an ionic liquid according to the structural formula, and according to the inverse problem - the method of characterizing stationary phases from experimental data in the form of Kovacs indices, McReynolds constants, etc. An analysis of the obtained results is carried out for mutual correspondence of the calculation results for direct and inverse problems. The possibility of classifying stationary phases based on ionic liquids according to polarity and hydrophilicity characteristics by plotting them on the chromatographic phase selectivity map is demonstrated.
Keywords: gas chromatography, intermolecular interactions, stationary phase, polarity, hydrophilicity, ionic liquids.
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Научная статья

Теоретическое описание и расчет характеристик неподвижных фаз для газовой хроматографии на основе ионных жидкостей

Елена Александровна Зайцева[1],
Алексей Анатольевич Долгоносов[1]✉, Анатолий Михайлович Долгоносов[1]
[1]Институт геохимии и аналитической химии им. В.И. Вернадского Российской академии наук (ГЕОХИ РАН), Россия, lex.dolgo@gmail.com✉

Аннотация. Предложенный ранее метод трехпараметрической характеристики неподвижных фаз в газовой хроматографии, который показал свою точность и информативность при описании хорошо изученных среднеполярных фаз, адаптирован для ионных жидкостей. Метод трехпараметрической характеристики основан на развиваемой авторами теории межмолекулярных взаимодействий в системе сорбат-сорбент. Показано, что параметры дисперсионных, электростатических и водородных связей для расчета взаимодействия ионной жидкости с молекулой сорбата являются суммой соответствующих характеристик катиона и аниона. Рассматриваются два способа расчета: по прямой задаче – способу априорного расчета характеристик ионной жидкости по структурной формуле и по обратной задаче – способу характеристики неподвижных фаз по экспериментальным данным в виде индексов Ковача, кон-

стант МакРейнольдса и т.п. Проводится анализ полученных результатов на взаимное соответствие результатов расчета по прямой и обратной задачам. Демонстрируется возможность классификации неподвижных фаз на основе ионных жидкостей по характеристикам полярности и гидрофильности путем их нанесения на карту селективности хроматографических фаз.

Ключевые слова: газовая хроматография, межмолекулярные взаимодействия, неподвижная фаза, полярность, гидрофильность, ионные жидкости.

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Introduction

Depending on the analytical task, the gas chromatography (GC) method uses capillary columns with stationary phases (SP) of low, medium, and high polarity. Ionic liquids (ILs) are promising high polarity phases. Ionic liquids are called salt melts, consisting of an organic cation paired with an organic or inorganic anion, with a melting point below 100°C. ILs became widely known in the 1980s due to their potential applications in organic synthesis, electrochemistry, and analytical chemistry for separation and extraction processes. The use of ILs as highly polar chromatographic SPs has a number of advantages over other phases, in particular, due to high polarity and thermal stability [1-6]. Despite the large number of publications on the study of ionic liquids, there is no comprehensive description of their structural properties, there is no information even on dipole moments, which greatly complicates the characterization of ILs as chromatographic phases; thus, the theoretical description of the properties of ionic liquids is extremely important.

To solve the problems of increasing the selectivity of the GC method, various methods of classifying SPs according to a number of parameters are considered. Multiparametric methods of Rohrschneider, McReynolds [7-10] and Abraham [11-12] are known for classifying phases according to Kovacs indices obtained using special chromatographic experiments. There are also a number of one-dimensional schemes for characterizing SP, which include the method of hydrophobic–hydrophilic balance [13], which determines one parameter of SP in the experimental system octanol - water. Statistical analysis of a large amount of data, carried out in [14], showed that two independent parameters are necessary and sufficient to compare the selectivity of polar phases, which indicates the redundancy of multiparameter schemes and the insufficiency of one-dimensional classification schemes. The main disadvantages of these methods are their empiricism, laboriousness, and the impossibility of predicting phase characteristics from their structural formula. These shortcomings can be avoided with the help of the theory of intermolecular interactions (IMI), in which dispersion, electrostatic and hydrogen bonds should be described.

The approach of the authors is based on the theory of generalized charges (TGC) [15], which is a quantum-statistical theory of interatomic interactions; in particular, TGC has been successfully used to calculate the adsorption of non-polar substances [16, 17]. In works [18, 19] the quantum mechanical theory of hydrogen bond (H-bond) has been developed. A new theoretical approach to the description of a general type of intermolecular interactions (IMI) was used as the basis for the method of three-parameter characteristic of SP for GC [20-26]. This method has shown its effectiveness in describing phases based on polysiloxanes and polyethylene glycol [22, 23, 25].

The purpose of this work is to describe and classify ionic liquids as SP: extension of the three-parameter characteristic method to the case of IL; obtaining characteristics of polarity and hydrophilicity of IL from experimental data; a priori calculation of IL characteristics by their structure; classification of ILs compared to traditional SPs for GC.

Theoretical part

Extension of the three-parameter characteristic method to the case of ionic liquids. The method for describing the IMI in GC is based on a general expression for the total energy of sorption of a molecule on SP, which contains three independent energy contributions [15-18]:

$$U(r) = U_{\text{np}}(Q_i, Q_{\text{sp}}, r) + U_{\text{dp}}(\mu_i^2, \mu_{\text{sp}}^2, r) + n_H E_H(r), \quad (1)$$

where U_{np} is the non-polar interaction energy is a van der Waals potential of the Lennard-Jones potential type derived using the TGC [15], U_{dp} – polar interaction energy, which is expressed as the sum of the Reinganum-Keesom orientational bond [27-28] and the Debye-Falkenhagen inductive bond; n_H is the average number of H-bonds between the adsorbate and SP, E_H is the H-bond energy (a value considered as a lower estimate); Q_i, Q_{sp} – generalized charges (CG) of the adsorbate (i) and SP (sp), respectively, μ_i, μ_{sp} are the dipole moments of the adsorbate and SP, and is the intermolecular distance.

The chromatographic and SP characteristics are related through the reduced IMI equilibrium energy u_{i}. The equation for the equilibrium distance is obtained by equating the derivative of function (1) to zero. By substituting the value of the equilibrium distance into the original expression, the equilibrium energy is obtained U_{min}. The reduced energy u_{i} is defined as the ratio U_{min} to the contribution of the non-polar interaction U_{np} to the equilibrium energy [20-23]:

$$u_i = \frac{U_{min}}{U_{\text{np}} \frac{U_{\text{dp}} E_H}{U_{\text{np}} U_{\text{np}}}^{2\,1/3}} \quad (2)$$

where the notation $A = 21.88 \cdot \frac{n_{\text{Hisp}}}{Q_i \cdot Q_{\text{sp}}}$, $B = 1 + c\left(\frac{\mu_i^2}{Q_i} + \frac{\mu_{\text{sp}}^2}{Q_{\text{sp}}} + c_T \frac{\mu_i^2}{Q_i} \frac{\mu_{\text{sp}}^2}{Q_{\text{sp}}}\right)$, $c = \frac{0.9676}{e^2 a_0^2}$, $c_T = \frac{0.1347}{a_0^3 k_B T}$, e is the elementary charge, a_0 is the Bohr radius, k_B is the Boltzmann constant, and T is the temperature.

The expressions for quantities A and B include the characteristics of the stationary phase in the form of the following relations:

polarity of the SP - the ratio of the square of the dipole moment of the SP to its GC:

$$v_{\text{sp}} = \frac{\mu_{\text{sp}}^2}{Q_{\text{sp}}}, \quad (3)$$

hydrophilicity of SP – the ratio of the average number of H-bonds that SP can form with an adsorbate to its GC:

$$w_{\text{sp}} = \frac{n_{\text{Hsp}}}{Q_{\text{sp}}}, \quad (4)$$

Polarity and hydrophilicity are responsible for different properties of the SP, expressions (3) and (4) are mathematical definitions of the desired characteristics of the SP [19]. Methods for determining the parameters of molecules (Q, μ, n_{H}) from the structural formula [22-25] are well known. It is obvious that the characteristics of polarity and hydrophilicity can also be found directly from the structure of the molecules. For brevity, the polarity and hydrophilicity characteristics are hereinafter referred to as the selectivity characteristics.

Peculiarities of describing the potential of an ionic liquid. The cationic and anionic parts of the IL are interconnected by a non-rigid ionic bond, so expression (1) is the *sum* of two parts: one for the interaction of the adsorbate with cations, the other with anions. The common terms of the summands of this expression are the adsorbate parameters. In this regard, the IL parameters are expressed through the parameters of the cationic and anionic parts as follows:

$$Q_{\text{sp}} = Q_{\text{sp+}} + Q_{\text{sp-}}, \quad (5.1)$$

$$\mu_{\text{sp}}^2 = \mu_{\text{sp+}}^2 + \mu_{\text{sp-}}^2; \quad (5.2)$$

$$n_{\text{Hsp}} = 2\left(n_{\text{Hsp+}} + n_{\text{Hsp-}}\right); \quad (5.3)$$

where the indices "+" and "–" refer to the cation and anion of the IL, respectively.

The parameter n_H in certain cases is expressed by the product [22]:

$$n_H = n_{\text{Hi}} \cdot n_{\text{Hsp}},$$

where n_{Hi} refers to the adsorbate molecule, and n_{Hsp} is the SP parameter. In the case of homogeneous phases, for example based on polyethylene glycol, the parameter n_{Hi} is 1 for hydrophilic adsorbates such as small

molecules of alcohols. The formula for calculating the parameter n_H is given in [19], it has a coefficient of $\frac{1}{2}$ due to the fact that the adsorbate molecules in the gas phase approach the SP surface on one side. In the case of IL, we have a mixture of two equal amounts of different molecules. Due to the narrow orientation of H-bonds, the adsorbate most likely interacts with either the cation or anion of the IL, so the adsorbate parameter n_{Hi} will be equal to $\frac{1}{2}$ instead of 1. From this it follows that, in order to calculate n_{Hsp} in the case of binary mixtures, to obtain a real value n_H, the total phase parameter should be doubled, as shown in formula (5.3). Due to the doubling of the phase parameter, the coefficient $\frac{1}{2}$ in formula (18) is removed (see below).

Obtaining polarity and hydrophilicity characteristics of IL from experimental data (inverse modeling method). The characteristics of polarity and hydrophilicity can be calculated from the reduced sorption energy (2), which is determined from a chromatographic experiment on the retention indices of molecules on the stationary phase under study. The reduced energy is inversely proportional to the generalized charge of the molecule and is equal to 1 for non-polar objects. The connection of GC with the Kovacs index I_n for *n*-alkane ($Q_n = (6n + 2)^{3/4} \equiv (0.06I_n + 2)^{3/4}$, where *n* is the carbon number) leads to the identity for non-polar phases: $u_i = Q_i^{-1}(0.06I_i + 2)^{3/4} \equiv 1$. As shown in [31], this dependence of the reduced energy on the Kovacs index can be approximately generalized to the case of sorption of an arbitrary molecule:

$$u_i \approx Q_i^{-1}(0.06I_i + 2)^{3/4}, \qquad (6)$$

where I_i is the Kovacs index of the adsorbate molecule on the studied SP.

The polarity and hydrophilicity characteristics of SPs are calculated from experimental data separately for polar adsorbate molecules belonging to different hydrophilicity classes. Molecules with $n_{Hi} = 0$ belong to the class M_0 and participate only in the calculation of the *SP polarity*. And hydrophilic molecules with $n_{Hi} > 0$ belong to the class M_1 and are involved in the calculation of the SP *hydrophilicity*. Our studies have shown that data for two polar molecules belonging to different hydrophilicity classes are sufficient to calculate polarity and hydrophilicity.

The stages of obtaining the polarity and hydrophilicity characteristics of ILs from experimental data are described in [32-33]. Let us consider this problem for phases based on IL.

1. Obtaining experimental data on the retention of adsorbates on the studied SP. It is convenient to use data from the literature on testing SP by traditional methods. The work uses McReynolds constants for standards from different classes given in [34].

2. Determination of polarity and hydrophilicity of test adsorbates according to their structural formula. Table 1 gives the characteristics of two standards of the McReynolds method – butanol-1 and pentanone-2 - belonging to the classes M_1 and M_0, respectively (subscripts are adopted below: "*y*" for butanol-1 and "*z*" for pentanone-2). The adsorbate parameters were obtained as follows. Generalized charges are calculated from the structure of adsorbate molecules according to the formula for an individual molecule [24-26, 33]:

$$Q = (N_\sigma + N_\pi\sqrt{2} - s)^{3/4}, \qquad (7)$$

where *N* are the numbers of σ- and π-electrons, respectively, *s* is the number of screened electrons. The experimental values of the dipole moments are given in reference books (e.g., [35]). The average number of H-bonds – in this case, the probability of the formation of one bond is calculated by the formula, derived in [19] for alcohols:

$$n_H = \sqrt{Q_d/Q_{\mathrm{mol}}}, \qquad (8)$$

where Q_d is the GC of the donor group, i.e. in this case, the hydroxyl group ($Q_d = 2.80$); Q_{mol} – GC of the butanol-1 molecule ($Q_{\mathrm{mol}} = 12.17$).

3. Calculation of the dimensionless sorption energy u_e of the standard is carried out

according to formula (6), transformed for calculation by the McReynolds constant [23, 3233]:

$$u_e \approx \left(1 + 0.06 x_e Q_e^{-4/3}\right)^{3/4} \quad (9)$$

where x_e is the McReynolds constant corresponding to the retention of the reference on the phase under study, Q_e is the reference GC.

4. Calculation of the polarity of the SP according to the formula:

$$v_{\text{sp}} = \frac{\sqrt{u_z} - 1 - c v_z}{c(1 + c_T v_z)} \quad (10)$$

5. Calculation of the hydrophilicity of SP according to the formula:

$$w_{\text{sp}} = 7.62 \times 10^{-3} \frac{u_y - [1 + c(v_y + v_{\text{sp}} + c_T v_y v_{\text{sp}})]^2}{w_y [1 + c(v_y + v_{\text{sp}} + c_T v_y v_{\text{sp}})]^{1/3}} \quad (11)$$

Table 2 presents the McReynolds constants for test analytes, 1-butanol (y) and 2-pentanone (z), and the results of inverse problem calculations for some IL-based SPs. It should be noted that the calculation of the characteristics and polarity from the McReynolds constants includes a systematic error (a decrease in the polarity value by 0.025 D^2), as evidenced by the results obtained in [22-23, 25].

Figure 1 shows the structural formulas of the ILs considered in the work (the phase numbering corresponds to Table 2).

A priori calculation of IL characteristics from their structure (method of direct modeling problem). The characteristics of polarity and hydrophilicity are determined by formulas (3) and (4) from the structural formulas of molecules by calculating the GC, dipole moments, and the average number of H-bonds between the SP and the adsorbate (conditional probabilities of participation in the formation of the H-bond). Such a priori calculation solves the direct problem of modeling.

The solution of the direct problem for IL is considered below. According to expression (5) in paragraph 1 of the GC, the dipole moments and the parameter n_{H} of the cation and anion are calculated separately as characteristics of rigid fragments, and then summed for the entire IL [24].

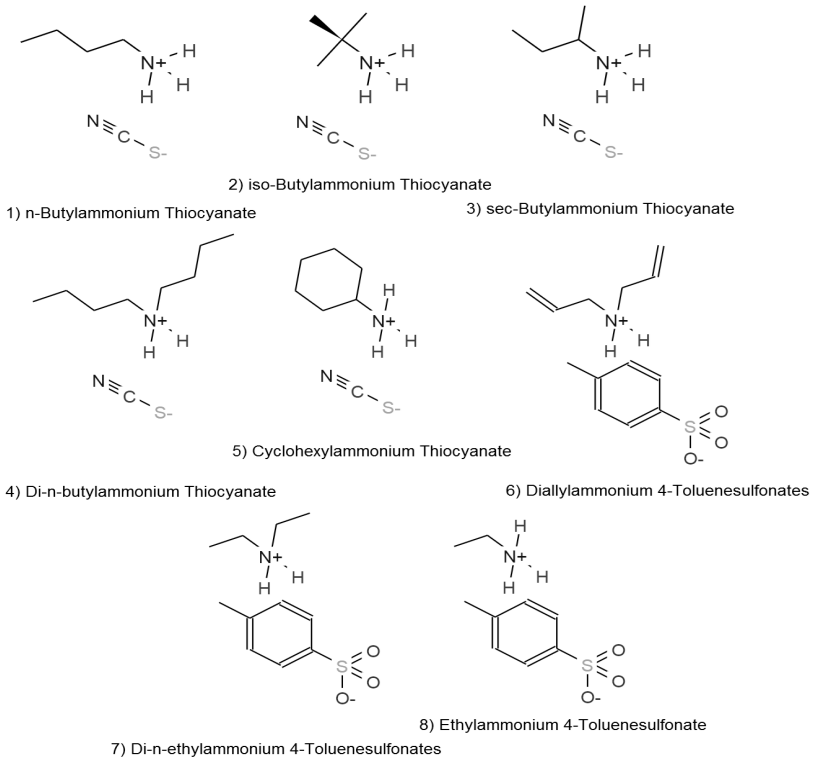

Fig. 1. Structural formulas of the ionic liquids studied in the work

Table 1. Characteristics of reference adsorbates (standards of the McReynolds method)

Reference adsorbate	Q	μ^2, D ^{2}	n_H	v , D ^{2}	w
butanol-1	12.17	2.32	0.43	0.1 9	0.036
pentanone-2	13.08	7.73	0	0.59	0

Table 2. Results of calculation of polarity and hydrophilicity for IL

No	Ionic liquid	McReynolds constants		u_y	u_z	v_{sp}, D^2	w_{sp}
		y	z				
1	n-Butylammonium Thiocyanate	1070	805	2.445	2.028	0.205	0.226
2	Iso-Butylammonium Thiocyanate	1086	830	2.464	2.057	0.211	0.227
3	Sec-Butylammonium Thiocyanate	1106	870	2.488	2.103	0.221	0.229
4	Di-n-butylammonium Thiocyanate	711	485	2.002	1.647	0.119	0.163
5	Cyclohexylammonium Thiocyanate	694	491	1.981	1.654	0.121	0.158
6	Diallylammonium 4-Toluenesulfonates	902	574	2.241	1.755	0.145	0.204
7	Di-n-ethylammonium 4-Toluenesulfonates	1077	691	2.453	1.895	0.176	0.237
8	Ethylammonium 4-Toluenesulfonate	1259	797	2.667	2.019	0.203	0.272

1. GC calculation.

The generalized charge of an IL is determined by its structural formula according to the following expression [36]:

$$Q_{sp} = \frac{\alpha}{3} \cdot \left(\frac{e^2}{2a_0 E_1}\right)^{3/2}, \qquad (12)$$

where the coefficient $\alpha = \frac{(Q^{4/3}+s)^{3/4}}{Q} \approx 1$, E_1 – the average energy of the electron.

The expression for the average energy of a valence electron follows from the condition for the average density of electrons that create GC [19]:

$$\overline{n} \propto N r_s^{-3} \propto N E_1^{3/2} = \sum_{i=1}^{N_b} z_i (E_{bi}/z_i)^{3/2},$$

from where

$$E_1^{3/2} = N^{-1} \sum_{i=1}^{N_b} z_i (E_{bi}/z_i)^{3/2} \qquad (13)$$

where $N_b = N_\sigma/2$ is the number of covalent bonds in the molecule falling within the shielding sphere; $E_{bi}$and z_i – energy and doubled multiplicity of the *i*-th covalent bond; $N = N_\sigma + N_\pi = \sum_{i=1}^{N_b} z_i$.

In a particular case, for the boundary of the electron cloud of organic molecules, we find from (13) that the average electron energy is E_1 calculated from the structural formula of SP molecules according to the formula for alkanes taken from [36] and adapted for nitrogen-containing compounds:

$$E_1(n, m_3, m_4, s) = a\left[\frac{6m_3+12m_4+14-s+2^{-3/2}(6n-12m_3-18m_4-12)}{6n+2}\right]^{2/3} \qquad (14)$$

where n is the number of carbon (C) and nitrogen (N) atoms, m_3 is the number of three-substituted C atoms, m_4 is the number of four-substituted C atoms, $a = E_{1,C-}/2$ =228.1 kJ/mol. To calculate the number of screened electrons s in the case of small molecules, you can use a simple counting rule: 1) if there are no three- and four-substituted carbon atoms in the molecule, the number of screened electrons s is equal to 0; 2) in the presence of three- and / or four-substituted C atoms, s is equal to 1 and 3, respectively, for each three- and four-substituted C atom. For nitrogen-containing compounds, the value of s increases by the number of N atoms.

Table 3. Reference data on bond energies [37-40]

Bond	Energy E, kJ/mol
C-N	873.0
S-C	550.0
C-C	456.2
C ⋮C (benzene)	490.0
S=O	400.4

Table 4. Generalized charges of IL according to formula (12) (IL numbering corresponds to Table 2)

No	Q_{sp+}	Q_{sp-}	Q_{sp}
1	7.70	8.52	16.22
2	6.78	8.52	15.30
3	7.41	8.52	15.93
4	8.81	8.52	17.33
5	15.36	8.52	23.88
6	8.08	9.69	17.77
7	7.06	9.69	16.75
8	5.52	9.69	15.21

If there is a cycle compound in the structure (IL No. 5), expression (14) takes the following form:

$$E_1(n, m_3, m_4, s) = a\left[\frac{2\sqrt{2}(6m_3+12m_4-s)+(6(n-1)-12m_3-18m_4)}{6n-1}\right]^{2/3} \quad (15)$$

For the case of a thiocyanate anion in IL, we write the expression (13) in the following form:

$$E_1 = \left(\frac{1}{2}\cdot\frac{6E_{C\equiv N}^{3/2}+7E_{SC}^{3/2}}{13}\right)^{2/3} \quad (16)$$

where $E_{C\equiv N}$ is the binding energy of C≡N divided by 3 E_{CS} is the binding energy of S-C.

For the toluenesulfonate anion, expression (13) is derived in the following form:

$$E_1 = \left(\frac{1}{2}\cdot\frac{7E_{C-}^{3/2}+20E_{C|}^{3/2}+12E_{S=O}^{3/2}}{47}\right)^{2/3} \quad (17)$$

where E_{C-} is the C-C methyl bond energy, $E_{C|}$ is the C⋮C bond energy in the benzene ring divided by 1.5, $E_{S=O}$ is the S=O bond energy. In the numerator of expression (16) there are no energies of 8 electrons of two tree-substituted C atoms, because they do not affect the formation of the boundaries of the electron cloud. The coefficients $\frac{1}{2}$ in expressions (16) and (17) are introduced to take into account the electron energy (2 electrons for each bond).

Table 3 shows the bond energies used in the calculation of the average electron energy E_1. Table 4 shows the GC for a number of ILs.

1. Determination of the dipole moment μ_{sp}. There are no reliable data on the dipole moments of ILs in the literature, and mathematical modeling programs determine the dipole moment of these rather complex molecules with a large error. The values of the squared dipole moments for ILs can be calculated from the experimental data on the McReynolds constants. To do this, the values of the GC from Table 4 and the polarity of the IL obtained from the experimental data (see Table 2) are substituted into formula (3) and the square of the dipole moment of the IL is determined, which, in accordance with formula (5.2), is equal to the sum of the squares of the dipole moment of the cation and anion. If one of the terms is known, the other can be found. In this way, it is possible to obtain experimental information about the dipole moment in the case when there are no reference data, and the quantum mechanical calculation of the structure is difficult. Table 5 presents the results of calculating the dipole moments for some ILs.

Table 5 shows how to restore the dipole moment of the second fragment if the dipole

Table 5. Squared dipole moments for ILs expressed as the sum of squared dipole moments of the cation and anion

No	Ionic liquid	v_{sp}, D^2	μ^2_{sp}, D^2	μ^2_{sp+}, D^2 [37-38]	μ^2_{sp-}, D^2
1	n-Butylammonium Thiocyanate	0.205	3.324	1.000	2.324
2	Iso-Butylammonium Thiocyanate	0.211	3.227	1.664	1.563
3	Sec-Butylammonium Thiocyanate	0.221	3.521	-	-
4	Di-n-butylammonium Thiocyanate	0.119	2.062	0.960	1.102
5	Cyclohexylammonium Thiocyanate	0.121	2.889	1.588	1.302
6	Diallylammonium 4-Toluenesulfonates	0.144	2.558	0.846	1.712
7	Di-n-ethylammonium 4-Toluenesulfonates	0.176	2.947	0.846	2.101
8	Ethylammonium 4-Toluenesulfonate	0.203	3.087	1.488	1.598

moment of one of the IL fragments is known. For example, by taking the known values of the squared dipole moments of substances similar in structure to cations [37, 38, 40], one can calculate the squared dipole moments for thiocyanate and toluenesulfonate anions. Further, by averaging the values for cations with the same functional groups, new values of the squared dipole moments for anions are calculated by subtraction from the total dipole moment, and then these values were averaged for ILs Nos. 1-5 and 6-8, respectively. In particular, we averaged the squared dipole moments for IL cations Nos. 1-3, 5, and 8 with functional groups $-\mathrm{NH}_3^+$, and the squares of dipole moments for cations Nos. 4, 6, and 7 with functional groups $-\mathrm{NH}_2^+-$. For IL cations, dipole moments (squared) were taken from reference books [37–38] for the corresponding amines: n-butylamine for IL 1 cation, tert-butylamine for IL 2, di-n-butylamine for IL 4, and etc. (see tables 5 and 6); the squared dipole moments for the anions were calculated from the difference. Table 6 gives the squares of the IL dipole moments obtained as the sum of the parameters of anions and cations, taking into account such averaging.

2. SP polarity calculation for v_{sp} is given in formula (3). For the calculation, the data of tables 4 and 6 are used, the results of the calculation are given in table 8;

3. Parameter calculation for n_H is given in formula (18) (see [19] and commentary on (5.3)):

$$n_H = \frac{a\sqrt{Q_{(d)\mathrm{sp}}}+b\sqrt{Q_{(a)\mathrm{sp}}}}{\sqrt{Q_{(\mathrm{mol})\mathrm{sp}}}}, \qquad (18)$$

where $Q_{(d)\mathrm{sp}}$ is the GC of the donor group, $Q_{(a)\mathrm{sp}}$ is the GC of the acceptor group, $Q_{(\mathrm{mol})\mathrm{sp}}$ is the GC of the entire cation or anion (see Table 4), *a* and *b* are the numbers of donor and acceptor groups, respectively. Groups for ILs Nos. 1-3, 5 and 8 $-\mathrm{NH}_2^+-$were considered as donor groups, $-\mathrm{NH}_3^+$for ILs Nos. 4 and 6-7, as acceptor groups $N \equiv C - S^-$for ILs Nos. 1-5 and $-\mathrm{SO}_3^+$for ILs Nos. 5-8 (see Figure 1). The calculation of $Q_{(d)\mathrm{sp}}$, $Q_{(a)\mathrm{sp}}$ and $Q_{(\mathrm{mol})\mathrm{sp}}$ is made according to the formula (7). The calculation results are shown in Table 7.

Table 6. Corrected squared dipole moments for IL, expressed as the sum of squared dipole moments of the cation and anion

No	Ionic liquid	μ^2_{sp+}, D^2	μ^2_{sp-}, D^2	μ^2_{sp}, D^2
1	n-Butylammonium Thiocyanate	1.44	1.64	3.08
2	Iso-Butylammonium Thiocyanate	1.44	1.64	3.08
3	Sec-Butylammonium Thiocyanate	1.44	1.64	3.08
4	Di-n-butylammonium Thiocyanate	1.08	1.64	2.72
5	Cyclohexylammonium Thiocyanate	1.44	1.64	3.08
6	Diallylammonium 4-Toluenesulfonates	1.08	1.67	2.75
7	Di-n-ethylammonium 4-Toluenesulfonates	1.08	1.67	2.75
8	Ethylammonium 4-Toluenesulfonate	1.44	1.67	3.11

Table 7. Calculated values of the H-bond index n_H for some ILs (IL numbering corresponds to Table 2)

No of ILs	$n_{H\,sp+}$	$n_{H\,sp-}$	$n_{Hsp} = 2(n_{Hsp+} + n_{Hsp-})$
1	0.81	1.00	3.62
2	0.84	1.00	3.69
3	0.82	1.00	3.64
4	0.41	1.00	2.81
5	0.74	1.00	3.47
6	0.45	1.50	3.90
7	0.51	1.50	4.10
8	0.98	1.50	4.95

When calculating the parameter n_H for cation isomers, it is important to take into account their dependence on the number *a*, the number of donor groups. So, for example, for cations Nos. 1-3, 5 and 8, in which the functional group is terminal, *a* in expression (18) is 3 - the functional group has 3 donor hydrogen atoms; for cations Nos. 4, 6-7, in which the functional group is in the middle of the carbon chain, *a*=2 - the functional group, respectively, has 2 donor hydrogen atoms. This explains the differences in the values $n_H$for the isomers. For anions, the number *b* is 2 and 3: for the thiocyanate anion, *b*=2, because it has two electronegative atoms - nitrogen and sulfur, and the toluenesulfonate anion has *b*=3, because the SO_3^- group has three acceptor oxygen atoms.

5. Calculation of the hydrophilicity of SP w_{sp}according to the formula (4). The calculation uses the data of tables 4 and 7.

Thus, we obtain theoretical selectivity characteristics for some ILs.

Results and discussion

Correspondence of a priori calculations with experimental data. Table 8 presents the results of the calculation of the selectivity characteristics for IL according to the direct and inverse problems – calculation by the structural formula of IL and calculation from experimental data on chromatographic retention in the form of McReynolds constants, respectively.

Selectivity Map: Classification of ILs vs. Conventional SPs for GC. The results of the calculation of the characteristics of polarity and hydrophilicity are presented in the form of a diagram – a selectivity map. Such a graphical way of presenting data makes it easy to classify SP [33]. Figure 2 shows the

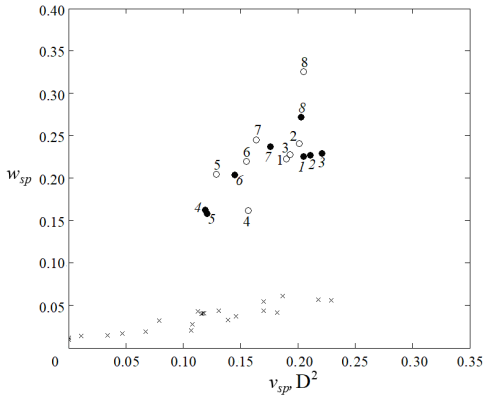

Fig. 2. SP selectivity map based on IL, phase numbering corresponds to Table 2. Designations: black circles – calculation data for the inverse problem from McReynolds constants, empty circles – calculation data for the direct problem from the IL structural formula, crosses – calculation data for the inverse problem for SP based on polyethylene glycol and polysiloxane [33].

Table 8. Characteristics of IL selectivity (IL numbering corresponds to Table 2)

No. of ILs	Direct problem		Inverse problem	
	v_{sp}, D^2	w_{sp}	v_{sp}, D^2	w_{sp}
1	0.190	0.2 2 3	0.205	0.226
2	0.201	0.241	0.211	0.227
3	0.193	0.228	0.221	0.229
4	0.157	0.162	0.119	0.163
5	0.129	0.205	0.121	0.158
6	0.155	0.220	0.144	0.204
7	0.164	0.239	0.176	0.237
8	0.205	0.326	0.203	0.272

SP selectivity map based on the ILs presented in Table 8; for comparison, experimental calculation data (●) and a priori calculation data (○) are given; crosses on the map indicate phases based on polysiloxanes and polyethylene glycol of various molecular weights.

The map shows a good agreement between the results of theoretical calculation and calculation from experimental data on retention in the form of McReynolds constants. The greatest difference in the results of the two calculation methods is observed for phases Nos. 4, 5, and 8, which can be explained by a possible inaccuracy in determining the GC and a rough estimate of the dipole moment for cyclic molecules: in the case of phase No. 8 toluenesulfonate anion. Also, the error in determining the parameters of the SP may lie in the experimental determination of the McReynolds constants, this is obvious in the case of phases Nos. 4 and 5 – ILs have large differences in the structures of cations, which do not allow them to have the same properties. This is the subject of further study. From Figure 2 and Table 8, it can be seen that during the theoretical calculation, the sequence of SP Nos. 1-3 changes - initially, when calculating from the McReynolds constants, the phases go in the order 1-2-3, however, we see that the theoretical calculation gives the sequence 1-3-2 , which is associated with differences in the isomer GCs – IL No. 2 has more shielded electrons *s* due to the presence of a four-substituted C atom, than in IL No. 3, which has only three-substituted C (see Figure 1), respectively, the GC is less (see Table 5). However, these differences can be neglected, they do not fundamentally contradict the experimental calculation from the

McReynolds constants, and it can be concluded that the three-parameter characteristic method is applicable for calculating IL.

Comparing the characteristics of ILs in Fig. 2 with the characteristics of SPs based on polyethylene glycol and polysiloxane with various substituents [33] (they are indicated by crosses on the selectivity map), it can be seen that the phases based on ILs have medium and high polarity and high hydrophilicity – the hydrophilicity values of the considered ILs are more than 2 times higher than common polysiloxane and polyethylene glycol SP. ILs are considered to be phases with high "polarity", however, we see that the main contribution to "polarity" is made by hydrophilicity, in other words, the ability of ILs to form an H-bond with analytes. However, due to the vagueness of the generally accepted definition of "polarity" for chromatographic phases, we can say that the results obtained are consistent with the results of experimental studies of the properties of ionic liquids.

Conclusion

The three-parameter characteristic method has shown its effectiveness in describing the properties of stationary phases based on ionic liquids. Methods for calculating the polarity and hydrophilicity parameters of the three-parameter characteristic method from the structural formula of ionic liquids and from chromatographic retention data in the form of McReynolds constants, adapted for ionic liquids, are presented. For the first time, ionic liquids are theoretically described by their structural formula as stationary phases for gas-liquid chromatography. The obtained results of calculating the selectivity characteristics of ionic liquids in two ways do not contradict each other, which makes it possible to classify stationary phases based on ionic liquids in the same way as phases based on polysiloxane and polyethylene glycol – according to the structural formula.

Конфликт интересов

Авторы заявляют, что у них нет известных финансовых конфликтов интересов или личных отношений, которые могли бы повлиять на работу, представленную в этой статье.

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Информация об авторах / Information about the authors

Е.А. Зайцева – к.х.н., научный сотрудник лаборатории сорбционных методов, Институт геохимии и аналитической химии им. В.И. Вернадского Российской академии наук (ГЕОХИ РАН), Москва, Россия

А.А. Долгоносов – младший научный сотрудник лаборатории геохимии углерода, Институт геохимии и аналитической химии им. В.И. Вернадского Российской академии наук (ГЕОХИ РАН), Москва, Россия

E.A. Zaitceva – Ph.D., Scientific fellow, Laboratory of Sorption Methods, Vernadsky Institute of Geochemistry and Analytical Chemistry of Russian Academy of Sciences (GEOKHI RAS), Moscow, Russian Federation, e-mail: lil-dante@mail.ru

A.A. Dolgonosov – Junior scientific fellow, Laboratory of Carbon Geochemistry, Vernadsky Institute of Geochemistry and Analytical Chemistry of Russian Academy of Sciences (GEOKHI RAS), Moscow, Russian Federation, e-mail: lex.dolgo@gmail.com

А.М. Долгоносов – д.х.н., ведущий научный сотрудник лаборатории сорбционных методов, Институт геохимии и аналитической химии им. В.И. Вернадского Российской академии наук (ГЕОХИ РАН), Москва, Россия

A.M. Dolgonosov – Dr. sci. (chem), Leading scientific fellow, Laboratory of Sorption Methods, Vernadsky Institute of Geochemistry and Analytical Chemistry of Russian Academy of Sciences (GEOKHI RAS), Moscow, Russian Federation, e-mail: amdolgo@mail.ru

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