Quantum-chemical calculation of the structure of ion exchangers in the form of multi-charged ions and predicting the sequence of their retention time in ion chromatography

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Аннотация

The structure of ion exchangers and electrostatic interaction energy of the system between counter and fixed ions were calculated using ab initio quantum-chemical method. The calculated values of electrostatic energy have been compared with the retention time of the ions in which separation of mixtures of these ions has been carried out by ion chromatography. The sequences of the retention time of ions matches with the obtained values of the electrostatic interaction energy.

Key words: Quantum chemical method, ion exchanger, multi-charged ions, Ion chromatography

Неэмпирическим методом были рассчитаны структуры ионообменников и энергии электростатического взаимодействия в них противоионов и фиксированных ионов. Проведено разделение смесей ионов методом ионной хроматографии и получено согласование последовательностей времен удерживания с величинами электростатического взаимодействия.

Ключевые слова: Квантово-химический метод, ионообменник, многозарядных ионов, ионная хроматография

Introduction

Selectivity is one of the main problems of ion-exchanger materials. Most researchers solve this problem by using equilibrium thermodynamics. To do this it needs to measure the enthalpy and the temperature dependence of heat capacity, which allows the calculation of the Gibbs energy, and then the equilibrium constant. This is a time consuming experimental work. Ab initio quantum chemical methods give principally the possibility to replace this time consuming experimental work to fast computational. The aim of this work is the quantum- chemical calculation of anion-exchangers' structure in the form of differently charged ions and to assess their selectivity.

Quantum-chemical calculations of the Columbic interaction between differently charged counter ions and fixed ions

We calculated the structure of benzyltrimethylammonium cations with hydrated forms of anions; chloride, sulfate and phosphate. For the calculation of the structure and

electrostatic interaction energy, MMMO method was applied in the sequential order in which molecular mechanics was applied to calculate the covalent bonds in the structure, and then the linear combinations of atomic orbital (LCAO MO) was used to calculate ionic and hydrogen bonds. Figure 1 shows the structure of the elementary unit of highly basic anion exchanger of a type Dowex 2, Amberlite IRA or AV-17 in the form of doubly charged sulfate ion.
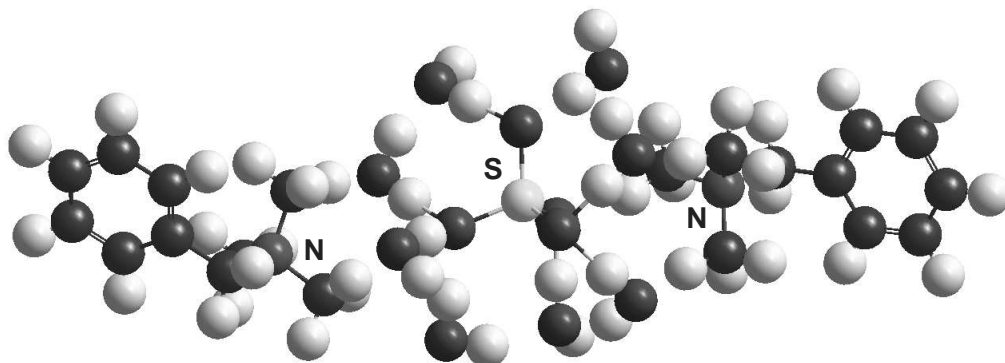

Fig. 1. the structure of the elementary unit of anion exchanger AV-17 in the form of the doubly charged sulfate ion, calculated by ab initio method

The calculated results of the optimized structure of ion exchangers allowed us to measure the effective value of the charges on the atoms, the distance between counter ions and oxygen atoms of the fixed ion (sulfo group) for cation exchanger and nitrogen atom of the ammonium ion for anion exchanger. The integral form of Coulomb's law was used to calculate the electrostatic interaction of the system as shown in equation (1).

$$E = \frac{z_+ z_- e^2}{\varepsilon r}, \tag{1}$$

where z_- - the number of charges of the anion, z_+ - number of charges of cation that calculated by quantum-chemical method, e - electron charge, r - the distance between the counter and fixed ions, ε - dielectric permittivity. Dielectric permittivity is in accordance with the theory of Debye and its modern modification [1] which is as a function of the distance between the charges and calculated by equation (2).

$$\varepsilon(r) = 78 - 77 \left(\frac{r}{2.5}\right)^2 \frac{e^{r/2.5}}{(e^{r/2.5} - 1)^2}. \tag{2}$$

The obtained results of the calculation are given in Table 1. Fig. 2 shows the structure of anion exchanger in the form of triply charged phosphate ion, which allows to calculate the effective charges and the electrostatic interaction between the counter and fixed ions by equations 1 and 2. As indicated by the results in Table 1, the electrostatic interaction energy between the fixed and counter ions of different charges naturally increases from singly to triply charged ions of chloride to phosphate.
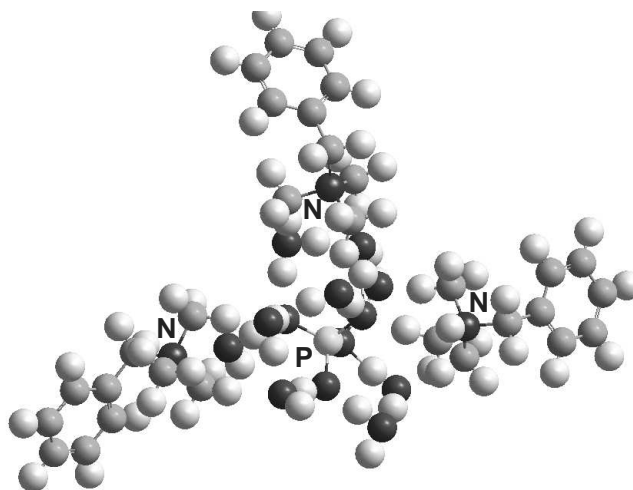
Fig.2. the structure of the elementary unit of anion exchanger AV-17 in the form of the triply charged phosphate ion calculated by ab initio method

Table1. The computational results of the electrostatic interaction of counter and fixed ions in the anion exchanger AV-17 and cation exchanger KU-2

Counter ions	$R_f - R_c$, Å	ε	Z_+	Z_-	E, kJ/mol
Cl^-	5.36	24.8	0.16	- 0.73	1.19
SO_4^{2-}	5.33	24.6	0.31	- 1.01	3.35
PO_4^{3-}	5.36	24.8	0.47	- 1.23	6.04
Na^+	5.48	25.63	0.60	- 0.38	2.25
K^+	5.22	23.79	0.73	- 0.38	3.09
Mg^{2+}	4.37	17.93	1.03	- 0.76	13.93
Ca^{2+}	3.96	15.25	1.05	-0.75	18.15
Al^{3+}	4.84	20.2	1.36	-1.10	20.80

We have also calculated the structure of sulfo-cation exchanger KU-2 in the form of ions of different charges and the results of the calculated electrostatic interaction energies for sulfo-cation exchanger are given in Table 1. The values obtained from [2] is differ from the values listed in Table 1 in that 12 water molecules were used in the calculation of the structure of the ionogenic groups not 6 water molecules for the hydration of ions. This gave us the opportunity to compare the Columbic interaction energy of cations in cation exchanger and that of anions in the anion exchanger.

As indicated in Figure 3, with increasing the number of charges of counter ions in the system, the energy of electrostatic interaction also increases. It also shows that the electrostatic interaction energy of cations in sulfo-cation exchanger is significantly higher than that of anions in anion exchanger. This is because of the smaller size of the fixed ion in sulfo-cation exchanger and the higher energy of hydration of cations as compared to the larger size of the fixed ion in the structure of benzyl-trimethyl-ammonium and smaller energy of hydration of the anions. In addition to this the sulfo-cation exchanger is more polar than benzyl-trimethyl-ammonium anion exchanger that leads to the formation of higher interaction between counter ions (cations) and fixed ion of sulfo-cation exchanger than that of counter ions (anions) and fixed ions of anion exchanger (benzyl-trimethyl-ammonium).
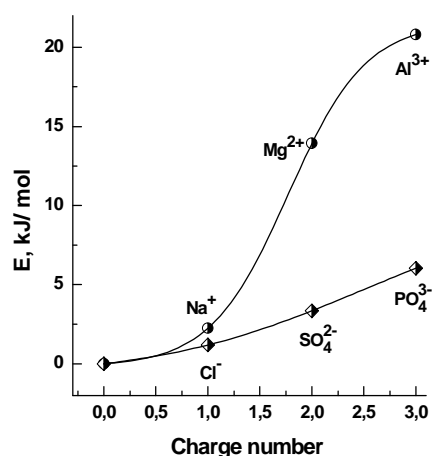
Fig. 3. Dependence of energy of electrostatic interaction on the number of charges of counter ions

Chromatographic separation of the mixtures of anions

In ion chromatography, retention is based on the attraction between solute ions and charged sites bounded to the stationary phase (ion exchange resins) frequently made by copolymerization of styrene and divinyl benzene. The benzene rings in divinyl benzene can be modified to produce either cation exchange resin (containing negatively charged groups) or anion exchange resin (containing positively charged groups) [3].

For the analysis of common cations (Na^+, Mg^{2+}, K^+, Ca^{2+}) and common anions (SO_4^{2-}, PO_4^{3-}, NO_2^-, F^-, Cl^-, Br^-); ion chromatography was carried out using a Dionex gradient HPLC system DX-600 (Dionex USA) equipped with an ED50 Electrochemical detector, Dionex LC25 chromatography oven, Electric Rheodyne injection valve, heating range of 30 to 45 °C Built-in electrochemical cell. And Autosampler (Dionex AS50) was used for sample preparation and temperature control. Isocratic separation of both cations and anions were performed on IonpacCS12A cation exchange column-Atlas suppressor, IonpacCS12A analytical column (4 x 250 mm)-046073, and IonpacAS17 anion exchange column-Atlas electrolytic suppressor, IonpacAS17 analytical column (4 x 250 mm)-055682, respectively. Dedicated IonpacCG12A guard column (4 x 50 mm)-046074 for cationic and IonpacAG17 guard column (4 x 50 mm)-055684 for anions were also used in connection with the analytical columns. Dionex GS50 Gradient pump and EG40 eluent generator containing cartridge-058900 for generating eluent to the separator system were used for the analysis of both anions and cations. The data acquisition and instrument setting were performed by PeakNet6 Software. PeakNet6 is a chromatography system for data acquisition, processing, and reporting. It provides real-time bidirectional control via DX-LAN of GS50 pumps; ED50 detector; AS50 Autosampler; and EG40 Eluent Generator.
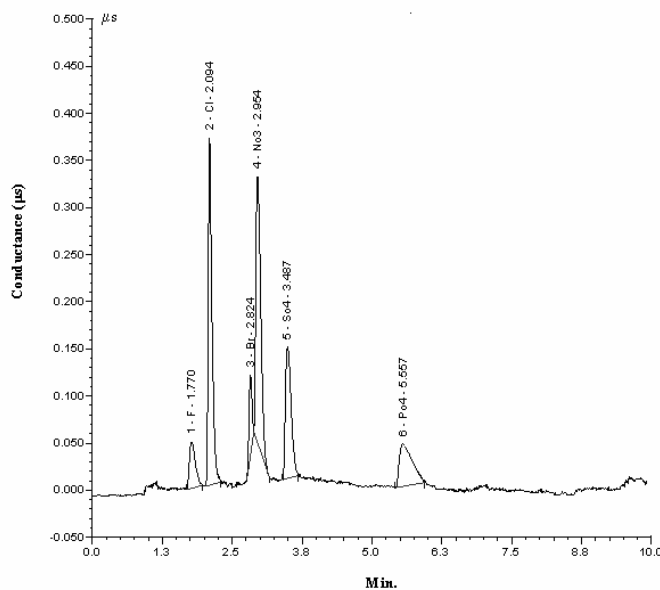
Fig.4a. Anion Chromatogram of standard solution contains
F⁻, Cl⁻, Br⁻, NO₃⁻, SO₄²⁻, PO₄³⁻ ions

The order of the retention time of anions in the chromatogram is consistent with the order of the results of electrostatic interaction energy that was obtained from the quantum chemical calculation as shown in (3).

$$Cl^- < SO_4^{2-} < PO_4^{3-}.$$ (3)

However, in the first monograph of ionic chromatography [4], the sequence of retention time of these anions differs from the calculated values (3), this is because of the used eluent was sodium bicarbonate, or whose solutions have lower pH values as compared to sodium hydroxide or potassium hydroxide. At lower pH values, phosphate exists in the form of doubly or singly charged anion [5], thus it leads to decrease its energy of electrostatic interaction with fixed ions as result lowering its retention time. The reason why lowering the eluent pH values is that to save the time of cation exchange resin of combination column that works in the form of hydrogen [4].
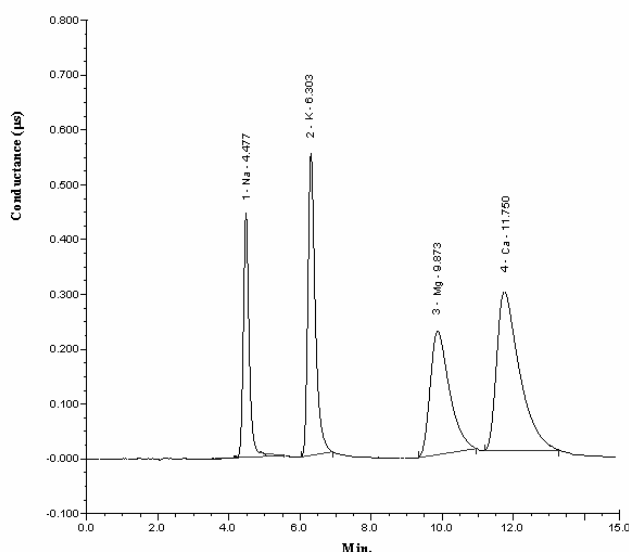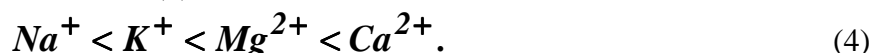

Fig. 4b. Cation Chromatogram of standard solution contains
Na⁺, K⁺, Mg²⁺, Ca²⁺ ions

The retention time of cations in the ion chromatogram shown in Fig.4b is consistent with the values of electrostatic interaction energy of the ions obtained from the quantum chemical calculation as shown in (4).

$$Na^+ < K^+ < Mg^{2+} < Ca^{2+}. \tag{4}$$

Conclusion

The structure of highly basic anion exchanger AV-17 in the form of singly charged anion chloride, doubly charged anion sulphate and triply charged phosphate, and that of strongly acidic cation exchanger KU-2 in the form of singly charged cations sodium and potassium, doubly charged cations magnesium and calcium and triply charged cation aluminum have been calculated using ab initio mothod. In calculated structures it was found that the electrostatic interaction between fixed ions and counter ions is increasing with increasing the charges of counter ions.

In the separation of the mixture of standard solutions of anions and cations on the combination column of ion chromatography it was found that the smaller the retention times of the anions and cations, the less electrostatic interaction energy of counter and fixed ions to be.

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