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SELECTIVITY COEFFICIENTS OF ALIPHATIC ORGANIC ACID ANIONS ON THE METHACRYLIC MATRIX RESIN HIKS-1

In ion chromatography, a number of eluents may be applied for analysing mixtures of organic acids [1–3]. In this study we used 25 carbonate eluents [4] and analysed the mixtures of 5 homologous aliphatic organic acids $H-(CH_2)_n-COOH$, where $n=0, 1, \dots, 4$. In this report the retention times from [4] have been used to evaluate the values of the selectivity coefficient of the organic acids studied. The purpose of this study is to obtain deeper insight into the factors determining the retention of the organic anions given above.

Experimental

The retention times t_R applied in this study were obtained from [4], where all the relevant experimental details are also presented. In [4] the retention times were measured using a classical ion chromatograph equipped with a suppressor column and conductometric detector. The eluents were aqueous solutions of Na_2CO_3 and $NaHCO_3$ mixtures. In this manner a 5×5 matrix of retention times for each anion studied was constructed. In this matrix, each column corresponds to the t_R values obtained at a fixed sum $c = c_{NaHCO_3} + c_{Na_2CO_3}$ ($c=0.2, 0.4, 0.6, 0.8,$ and 1.2 mM) and each row contains the t_R values run at the fixed ratio $z = c_{NaHCO_3}/c_{Na_2CO_3}$ ($z=3.0, 1.0, 0.5, 0.33,$ and 0.0).

Table 1

Retention times (s) of the chloride ions on the ion chromatographic system applied*

$z = \frac{c_{NaHCO_3}}{c_{Na_2CO_3}}$	$c = c_{NaHCO_3} + c_{Na_2CO_3}, \text{ mM}$				
	0.2	0.4	0.6	0.8	1.2
1.0	423	298	249	222	196
0.0	322	239	200	180	170

* $t_0=50$ s (for the separator column only); $t_{0, \text{out}}=45$ s (due to moving phase outside the separator column).

In this study we measured in addition the retention times of chloride ions under the same conditions as used in [4] (see Table 1). This was done in order to associate the values of the separation coefficient for organic acid anions with the respective coefficients for the common inorganic anions published elsewhere [5].

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In order to calculate selectivity coefficient by Eq. (1), we also need the values of t_0 (void time for the separator column) and $t_{0, \text{out}}$ (time due to the eluent volume outside the separator column, see [5]). Applying the equipment and experimental conditions used in [4], we obtained $t_0 = 50$ s and $t_{0, \text{out}} = 45$ s.

Results and Discussion

The selectivity coefficient $K_{A, B}$ was calculated as in [5]:

$$K_{A, B} = \frac{\bar{c}_A \cdot c_B}{c_A \cdot \bar{c}_B} = \frac{t_{R, A} - t_0 - t_{0, \text{out}}}{t_{R, B} - t_0 - t_{0, \text{out}}}, \quad (1)$$

where \bar{c}_A and \bar{c}_B are concentrations of the ions A^{x-} B^{y-} on the resin, and c_A and c_B are concentrations of the ions A^{x-} and B^{y-} in the moving phase. It should be noted that Eq. (1) is valid only for the case where the charge numbers $x = y = 1$ [5].

Table 2

Selectivity coefficients (Eq. 1) for the anions RCOO^- of organic acids *

RCOO^-	$K_{\text{HCOO}^-, \text{RCOO}^-}^{**}$	$K_{\text{Cl}^-, \text{RCOO}^-}^{***}$
HCOO^-	—	1.46 ± 0.11
CH_3COO^-	1.109 ± 0.057	1.62 ± 0.14
$\text{C}_2\text{H}_5\text{COO}^-$	0.923 ± 0.053	1.34 ± 0.12
$\text{C}_3\text{H}_7\text{COO}^-$	0.773 ± 0.050	1.12 ± 0.11
$\text{C}_4\text{H}_9\text{COO}^-$	0.500 ± 0.048	0.73 ± 0.09

* $K_{\text{Cl}^-, \text{HCOO}^-} = 1.46$ has been calculated by Eq. (1) using the retention times from Table 1 (taking $A = \text{HCOO}^-$ and $B = \text{Cl}^-$). $K_{\text{Cl}^-, \text{RCOO}^-}$ values were obtained as $K_{\text{Cl}^-, \text{RCOO}^-} = K_{\text{HCOO}^-, \text{RCOO}^-} \cdot K_{\text{Cl}^-, \text{HCOO}^-}$;

** with root mean square errors at 24 degrees of freedom;

*** root mean square errors calculated according to [6].

Table 3

Values of the selectivity coefficient $K_{\text{HCOO}^-, \text{CH}_3\text{COO}^-}$ for different carbonate eluents

$z = \frac{c_{\text{NaHCO}_3}}{c_{\text{Na}_2\text{CO}_3}}$	$c = c_{\text{NaHCO}_3} + c_{\text{Na}_2\text{CO}_3}$, mM				
	0.2	0.4	0.6	0.8	1.2
3.00	1.077	1.087	1.128	1.150	1.091
1.00	1.231	1.086	1.052	1.049	1.098
0.50	1.095	1.075	1.071	1.152	1.127
0.33	1.148	1.069	1.147	1.106	1.132
0.0	1.037	1.286	1.113	1.067	1.061

By applying Eq. (1) to the retention times t_R published in [4], the mean $K_{A,B}$ values presented in Table 2 were obtained. The values of $K_{A,B}$ (Table 2) do not depend on the composition and concentration of the carbonate eluent used as exemplified in Table 3. The fact that HCOO^- ions were eluted between CH_3COO^- and $\text{C}_2\text{H}_5\text{COO}^-$ (see [4]) is reflected also in $K_{A,B}$ values $K_{\text{Cl}^-, \text{CH}_3\text{COO}^-} > K_{\text{Cl}^-, \text{HCOO}^-} > K_{\text{Cl}^-, \text{C}_2\text{H}_5\text{COO}^-}$.

Keeping in mind the $K_{\text{Cl}^-, \text{RCOO}^-}$ values (Table 2) one should ask why they show a tendency toward decreasing with the increasing of the length of the aliphatic group R in the organic acid anions RCOO^- . It should be noted that all the organic acids studied have the pK values in the range of 3.75–4.68, i. e. they are all practically fully ionized in the carbonate eluents applied. The application of principal component analysis (PCA) to the same sets of t_R values [4] has led to the conclusion that for all the anions considered, only one reaction mechanism is responsible for the changes in t_R . This conclusion rules out the possibility that the anions having longer aliphatic chains are retained in the separator column simply by the physical adsorption on the resin surfaces. Consequently, there should be another reason for longer retention times if the anions considered have a "fattier" character.

We are suggesting that this reason is the hydrophobic hydration of the aliphatic R-groups in RCOO^- ions [7]. The hydrophobic hydration increases with an increase in the length of the chain $\text{H}-(\text{CH}_2)_n$ ($n=1, \dots, 4$). This "structure-making" effect causes an additional stabilization for the resin-linked RCOO^- ions because the resin surface is probably itself also a "structure maker." The result of such stabilization is an increase in the concentration of resin-linked RCOO^- ions, which in turn leads to longer retention times for the RCOO^- ions with longer R-groups. The HCOO^- ions are not "structure makers" but rather "structure breakers;" therefore, they do not follow the rule described.

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**ALIFAATSETE ORGAANILISTE HAPETE SELEKTIIVSUSKOEFIITSIENT
METAKRÜÜLPOLÜMEERSE SORBENDI HIKS-1 PUHUL**

Kasutades klassikalist kahekolonnilist ionkromatograafi ja konduktomeetrilist detektorit mõõdeti metaan-, etaan-, propaan-, butaan- ja pentaanhappe anioonide retentsiooniajad elueerimisel 25 erineva koostise ($z=3,0, 1,0, 0,5, 0,33, 0$; $z=c_{\text{NaHCO}_3}/c_{\text{Na}_2\text{CO}_3}$) ja kontsentratsiooniga ($c=0,2, 0,4 \dots 1,2$ mM; $c=c_{\text{NaHCO}_3}+c_{\text{Na}_2\text{CO}_3}$) eluendi abil. Selektiivsuskoeffiitsiendi $K_{\text{Cl}^-, \text{RCOO}^-}$ arvutamiseks määrati kloriidiooni retentsiooniaeg 10 eluendiga elueerimisel ($z=2,0, 1,0$ ja $c=0,2, 0,4 \dots 1,2$ mM). Leiti, et $K_{\text{Cl}^-, \text{RCOO}^-}$ väärtus kahaneb orgaanilise happe anioonis R pikkuse suurenedes. Kätsevea piirides ei sõltu $K_{\text{HCOO}^-, \text{H}(\text{CH}_2)_n \text{COO}^-}$ väärtus eluendi koostisest ja kontsentratsioonist. Saadud tulemused ja varem tehtud peakomponentide analüüs viivad järeldusele, et hapete anioonide retentsiooni tingib nende hüdrofoobne hüdratatsioon vesilahustes.

Юло ХАЛДНА, Яан ПЕНЧУК

**КОЭФФИЦИЕНТЫ СЕЛЕКТИВНОСТИ
АНИОНОВ АЛИФАТИЧЕСКИХ ОРГАНИЧЕСКИХ КИСЛОТ
НА МЕТАКРИЛАТНОМ ИОНООБМЕННИКЕ ХИКС-1**

Измерены времена удерживания анионов метановой, этановой, пропановой, бутановой и пентановой кислот с использованием классического двухколоночного варианта ионной хроматографии с кондуктометрическим детектированием и 25 элюентов разного состава ($z = 3,0, 1,0, 0,5, 0,33, 0,0$; $z = c_{\text{NaHCO}_3}/c_{\text{Na}_2\text{CO}_3}$) и разных суммарных концентраций ($c = 0,2, 0,4, \dots, 1,2$ mM; $c = c_{\text{NaHCO}_3} + c_{\text{Na}_2\text{CO}_3}$).

Для вычисления коэффициента селективности $K_{\text{Cl}^-, \text{RCOO}^-}$ измерены времена удерживания хлорид-иона в 10 элюентах ($z = 2,0, 1,0$ и $c = 0,2, 0,4, \dots, 1,2$ mM). Установлено, что значения $K_{\text{Cl}^-, \text{RCOO}^-}$ убывают с удлинением заместителя R в анионе органической кислоты, а значения $K_{\text{HCOO}^-, \text{H}(\text{CH}_2)_n \text{COO}^-}$ не зависят в пределах ошибок эксперимента от состава и концентрации элюента. На основе сравнения полученных данных и результатов анализа того же экспериментального материала методом главных компонент можно заключить, что времена удерживания анионов органических кислот определяются в основном гидрофобной гидратацией этих анионов.

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Retention time (min)	Presented by K. Laks				
	0.0	0.2	0.4	0.8	1.2
1.001	1.001	1.001	1.001	1.001	1.001
1.127	1.127	1.127	1.127	1.127	1.127
1.211	1.211	1.211	1.211	1.211	1.211
1.311	1.311	1.311	1.311	1.311	1.311
1.401	1.401	1.401	1.401	1.401	1.401
1.501	1.501	1.501	1.501	1.501	1.501
1.601	1.601	1.601	1.601	1.601	1.601
1.701	1.701	1.701	1.701	1.701	1.701
1.801	1.801	1.801	1.801	1.801	1.801
1.901	1.901	1.901	1.901	1.901	1.901
2.001	2.001	2.001	2.001	2.001	2.001