Effect of temperature on retention of alkali and alkaline-earth metal ions on some aminocarboxylic acid functionalised silica based ion exchangers

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Abstract

The temperature effect on retention of alkali and alkaline-earth cations on three different carboxylic acid cation exchangers was investigated. The silica-bonded 2,6-diaminohexanoic (lysine), 2-aminoglutaric (glutamic acid) and iminodiacetic acids were used as cation exchangers and compared with bare silica. Perchloric acid was used as the eluent in all experiments. The dependence of retention ($\log k'$) from reciprocal temperature ($1/T$) is linear for all cations in the case of silica-bound lysine and glutamic acid. An abnormal parabolic dependence of $\log k'$ vs. $1/T$ was observed for iminodiacetic acid functionalized silica. The possible impact of complexation between functional groups of cation exchangers and retained cations and the effect of two carboxylic groups in a single ion-exchange site on retention are discussed. The calculated values of heats of adsorption are in the range 4–9 kJ/mol. © 1998 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

A clear trend in comprehensive ion-chromatography is the development of new generation of cation exchangers containing carboxylic acid functional groups attached to the surface of either the polymer or silica [1–3]. The main feature of these cation exchangers is a better ion-exchange selectivity for the separation of alkali and alkaline-earth metal cations and increased affinity to some transition metals due to the complexing properties of the carboxylic groups. The temperature effect is usually well expressed for systems including complexation.

On the other hand, it is known that the temperature has little influence in the case of the ''pure'' ion-exchange mechanism, e.g., for adsorption of alkali metal cations on sulphonic acid functionalised cation exchangers, and the value of sorption enthalpy does not exceed 2–3 kcal/mol (1 cal=4.184 J) [4]. So, the increase of column temperature does not change the selectivity of ion-chromatographic separation of transition metals on sulphonated polystyrene [5]. However, the change of column temperature was recently shown to be useful tool for the variation of selectivity of separation of alkaline-earth metal ions on carboxylic type cation exchanger [6].

Recently, good selectivity and ion-chromatographic performance was also demonstrated for a number

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of amino acids chemically bound to the silica surface [7–12]. Depending on the structure of amino acids attached to the silica surface the prepared ion exchangers behaved like cation, anion or zwitterion exchangers. Dicarboxylic monoamino acids (Glu-silica, Asp-silica) and monocarboxylic diamino acids (Lys-silica, Arg-silica, 2,3-diaminopropionic acid (DAP)-silica, Orn-silica) functionalized ion-exchangers demonstrated cation-exchange properties in weak acid eluents and the selectivity was similar to carboxylic cation exchangers. These were used for separation of monovalent and divalent cations with diluted perchloric or nitric acids as eluents. Usually the temperature effect is more pronounced for the complexation of metal cations so one can expect a higher temperature effect for carboxylic cation exchangers as well as a stronger influence on retention of metal cations. Moreover, the presence of amino and carboxylic functional groups together in the ion-exchange site should lead to more noticeable increase in temperature effect on retention of cations. Unfortunately, there is a lack of data on this subject in the literature except for a short study performed for iminodiacetic acid (IDA)-silica [13].

In the present work the effect of temperature on retention and selectivity of ion chromatographic separation of alkali and alkaline-earth metal ions on glutamic acid (Glu-silica), diaminohexanoic acid (Lys-silica) and iminodiacetic acid (IDA-silica) functionalised ion exchangers were examined. The adsorption enthalpies were evaluated and compared with those obtained for silica gel. The results were considered in the terms of thermodynamics and retention mechanisms.

2. Experimental

2.1. Equipment

The chromatographic system consisted of a Milton Roy A 802 high-pressure pump (USA), a Rheodyne 7125 injection valve (Cotati, CA, USA) equipped with a 20-µl loop, HPLC column oven (CBO Industrial Electronics, Vienna, Austria) with a digital thermometer, a conductivity detector LKB Conductolyzer 5300B (Bromma, Sweden) and a Spectra-Physics DP-700 integrator (USA). Stainless steel

chromatographic columns were slurry packed with silica based ion exchangers from an isopropanol–water mixture under a constant pressure of 14 MPa.

2.2. Packing materials

Amino acid stationary phases were synthesised as described [11] on the basis of Silasorb Si 600 (Lys-silica) and Silasorb Si 300 silica (Glu-silica, IDA-silica) having specific surface areas of 550 and 300 m^2/g, respectively. The particle size for all of the studied ion exchangers was either 5.0 or 7.5 µm. Both types of silica were purchased from Lachema (Brno, Czech Republic). The ion-exchange capacities of the phases were calculated from CHN elemental analysis data as follows: for the silica with attached glutamic acid – 140 µmol/g, for Lys-silica 130 µmol/g, for IDA-silica 130 µmol/g. A bare silica column was used to evaluate any other possible types of solute–surface interactions that could cause retention of cations studied.

2.3. Reagents

A 2 mM solution of perchloric acid (analytical grade, Reakhim, Russia) was used as an eluent. All the chemicals were of an analytical-reagent grade. Stock standard solutions of alkali and alkaline-earth metal cations were prepared by dissolving appropriate amounts of corresponding nitrates in deionized, distilled water. The sample concentration was 10 mM, and the sample volume 10–20 µl. This corresponds to the linear part of the adsorption isotherm. Eluent flow-rate was 1 ml/min.

3. Theory

Measurement of the capacity factor, as a function of temperature, permits the evaluation of the thermodynamic values of sorption enthalpy and entropy, which determine the sorption of solutes during chromatographic separation:

$$\ln k' = -\Delta H/RT + \Delta S/R + \ln \varphi \qquad (1)$$

where ΔH is the enthalpy change for the ion-exchange reaction, ΔS the sorption entropy and φ the

phase volume ratio, a characteristic constant for a given column. If ΔS is constant under the studied range of temperatures, a plot of ln k' vs. the reciprocal temperature should have a slope equal to $-\Delta H/R$ [14]. ΔS was accepted to be constant under the experimental conditions (a quite common assumption, although no reliable proof can be provided).

## 4. Results and discussion

4.1. Selection of stationary phases

It is a well established fact that carboxylic cation exchangers have a more optimal selectivity for the separation of alkali and alkaline-earth metal cations than sulphonic acid functionalized cation exchangers. Diaminomonocarboxylic (Lys-silica, Arg-silica, Orn-silica) and monoaminodicarboxylic (Asp-silica, Glu-silica) acid silica based substrates were found to be effective cation exchangers in ion chromatography for the simultaneous separation of alkali and alkaline-earth metal cations [8,12,15].

All the stationary phases studied here (for their preparation see Ref. [11]) were silica based with attached aminocarboxylic acids: lysine, glutamic and

iminodiacetic acid. The latter ion exchanger has a significantly higher complexing ability but can also be used for the simultaneous determination of alkali and alkaline-earth metals [16].

The structures of the ion exchangers investigated are presented below:
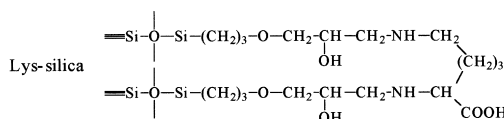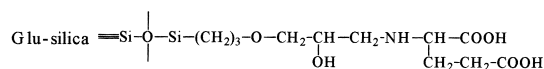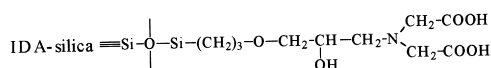
The acid–base properties of the corresponding ligands at different temperatures and related thermodynamic data are presented in Table 1.

As was found out, all the examined stationary phases combine both ion-exchange and complexing properties. The retention of cations on Lys-silica are mostly due to ion-exchange, IDA-silica showed strong complexing properties (log $\beta_1 = 1.67$–2.94 for alkaline-earth metal cations [17]), while Glu-silica is somewhere in between (log $\beta_1 = 1.33$–1.90 for those

Table 1
Values of dissociation constants and ΔH (kJ/mol), ΔS (J/mol K) for free aminocarboxylic acids [17]

Ligand/conditions	Temperature (°C)	pK_1	pK_2	pK_3
Glu/0.01 M NaClO$_4$	25[a]	2.30	4.53	9.97
	30		3.67	9.58
	40		3.55	9.45
	50		3.43	9.37
	ΔH	-3.3	-3.3	-40.5
	ΔS	7	16	11
IDA/0.1 M NaClO$_4$	25		2.70	9.73
	35		2.66	9.25
	37[b]	1.76	2.69	9.11
	45		2.44	9.07
	ΔH			-33.1
	ΔS			64.4
Lys/0.1 M NaClO$_4$	25	2.18	9.14	10.65
	37[b]	2.15	8.89	10.30
	ΔH	-2.1	-47.3	-53.6

[a] 0.1 M NaClO$_4$.
[b] 0.15 M NaClO$_4$.

cations [17]). The ratio of complexing and cation-exchange properties of attached to silica ligands was the main criterion for the selection of adsorbents for this study. In order to evaluate the influence of residual silanols on retention, bare silica was also investigated.

4.2. Selection of eluent

An aqueous solution of perchloric acid was chosen as an eluent, because of (i) the absence of complexation with metal ions and (ii) increased sensitivity of indirect conductimetric detection. The eluent concentration was equal to 2 mM (pH 2.7). That provides occurrence of a single carboxylic group dissociated in Lys-silica and Glu-silica attached amino acids. In case of IDA a partial dissociation of the second carboxylic group takes place under these experimental conditions.

So, concerning alkali metal cations one may look for only ion-exchange retention mechanism, as for alkaline-earth – complexation in the stationary phase is also possible. Moreover, the concentration of the eluent provides a reliable retention time for all cations within the investigated temperature range.

4.3. Influence of temperature

The influence of the temperature on retention of cations was investigated in the range from 23 to 67°C (Figs. 1 and 2). The experimental dependencies of log k' vs. reciprocal temperature for Lys-silica, Glu-silica and bare silica are rather linear for both alkali and alkaline-earth metal ions (Table 2). In case of Lys-silica the effect of temperature on retention was weakly expressed. As ion-exchange sites of Lys-silica contain a single carboxylic group, so one can suppose only the simple ion-exchange retention mechanism even for alkaline earth metal cations. Obviously, a low surface concentration of bonded ligand does not allow coordination of carboxylic from two adjacent attached molecules of lysine on one metal ion.

Similar dependencies were obtained for Glu-silica. The presence of two carboxylic groups in one molecule may result in complexation with divalent cations [17]. However, under the experimental conditions (pH 2.7, temperature interval from 23 to 67°C) only one carboxylic group is dissociated. It makes for retention of cations only an ion-exchange mechanism possible.

Taking into account the high stability of IDA–alkaline-earth metal complexes [17], we supposed a strong chelation of these cations with IDA groups. This should result in a noticeable difference between quantitative parameters of adsorption process and/or type of the dependencies of the log k' vs. the reciprocal temperature for cations of alkali and alkaline-earth metals. However, according to the experimental data they proved to be similar. This fact means a similar retention mechanism. Uncommonly, the dependencies of the logarithms of capacity factors on the reciprocal temperature for the retention of cations on IDA-silica are not linear, being well described by the second-order polynomial (Table 3).

The absolute values of the equation coefficients increase in the group of alkali metal cations (from Li^+ to Cs^+) and decrease in the group of alkaline-earth metal cations (from Mg^{2+} to Ba^{2+}) except those obtained for Ba^{2+} and Rb^+.

All the sorbents being investigated had a silica backbone. It is well known, that any method of surface modification does not provide a complete blocking of silanols. These residual silanols or other active hydroxyl groups from metal hydroxides due to possible presence of impurities of trivalent metals such as Al^{3+}, Fe^{3+} in the silica backbone can participate in ion-exchange [18–20] as well as carboxylic groups in attached aminocarboxylic acids. In order to evaluate their contribution to retention of cations the dependencies of the logarithms of capacity factors on the reciprocal temperature were investigated for bare silica too. They have quite a complicated character (Figs. 1 and 2), that can be connected with the presence of different types of silanol groups on the surface and change of their state and concentration with temperature.

The fully hydroxylated silica is known to contain 4.6 OH groups/nm^2 or 8–9 μmol/m^2 [21], so the maximum ion-exchange capacity would be about 2.4 mmol/g or 4.8 mmol/g for Silasorb Si 300 and Silasorb Si 600, respectively, that is one-order of magnitude higher than the surface concentration of carboxylic groups of modified silica. Of course, at least half of the original silanols cannot be blocked
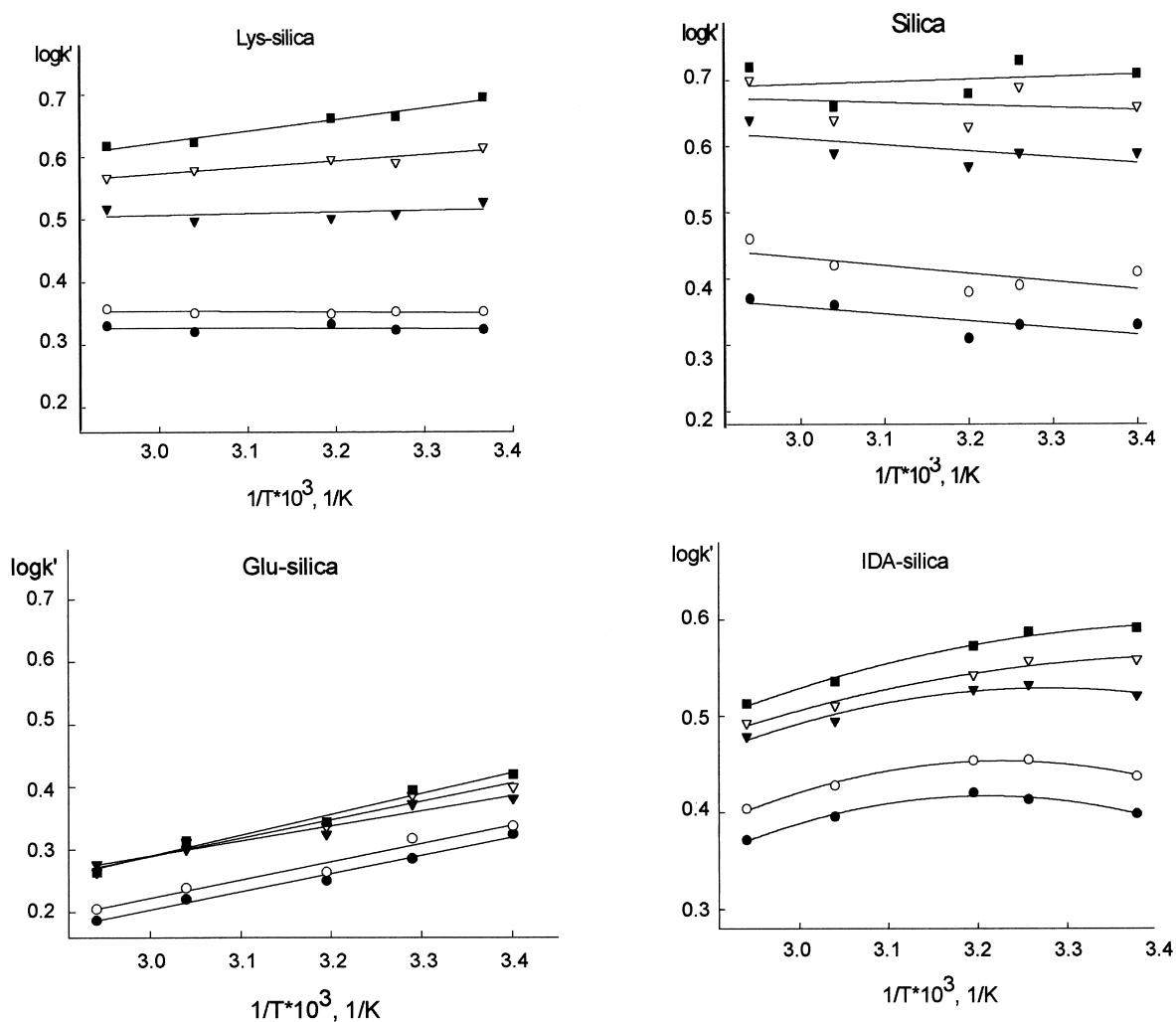
Fig. 1. Plot of log k' vs. $1/T$ for alkali metal cations: Li$^+$ (– ● –), Na$^+$ (– ○ –), K$^+$ (– ▼ –), Rb$^+$ (– ▽ –), and Cs$^+$ (– ■ –). Eluent: 2 mM perchloric acid; flow-rate: 1 ml/min.

on the reaction with silanes [21] due to the steric hindrance and nonhomogeneous distribution of silanols at the surface. Thus one can expect a possible impact of residual silanols in ion-exchange properties for amino acid bound silica having 0.13–0.14 mmol/g attached molecules. It was shown recently [20] the presence of trivalent metal ions in the silica backbone is responsible for the cation-exchange separation of alkali and alkaline-earth metals on different types of silica in 2 mM nitric acid. So, the cation-exchange properties found for

Silasorb silica can be explained by the presence of traces of trivalent metals in the silica backbone.

Also, the regularity of the retention of the cations as well as the temperature effect on their retention are different for the bare silica and for modified silica. The retention of ions decreases with the temperature growth for all studied aminocarboxylic acid stationary phases. For silica the retention of almost all cations increases with temperature rise. So, silanols or metal hydroxyls in all aminocarboxylic acid phases under investigation seem to be either
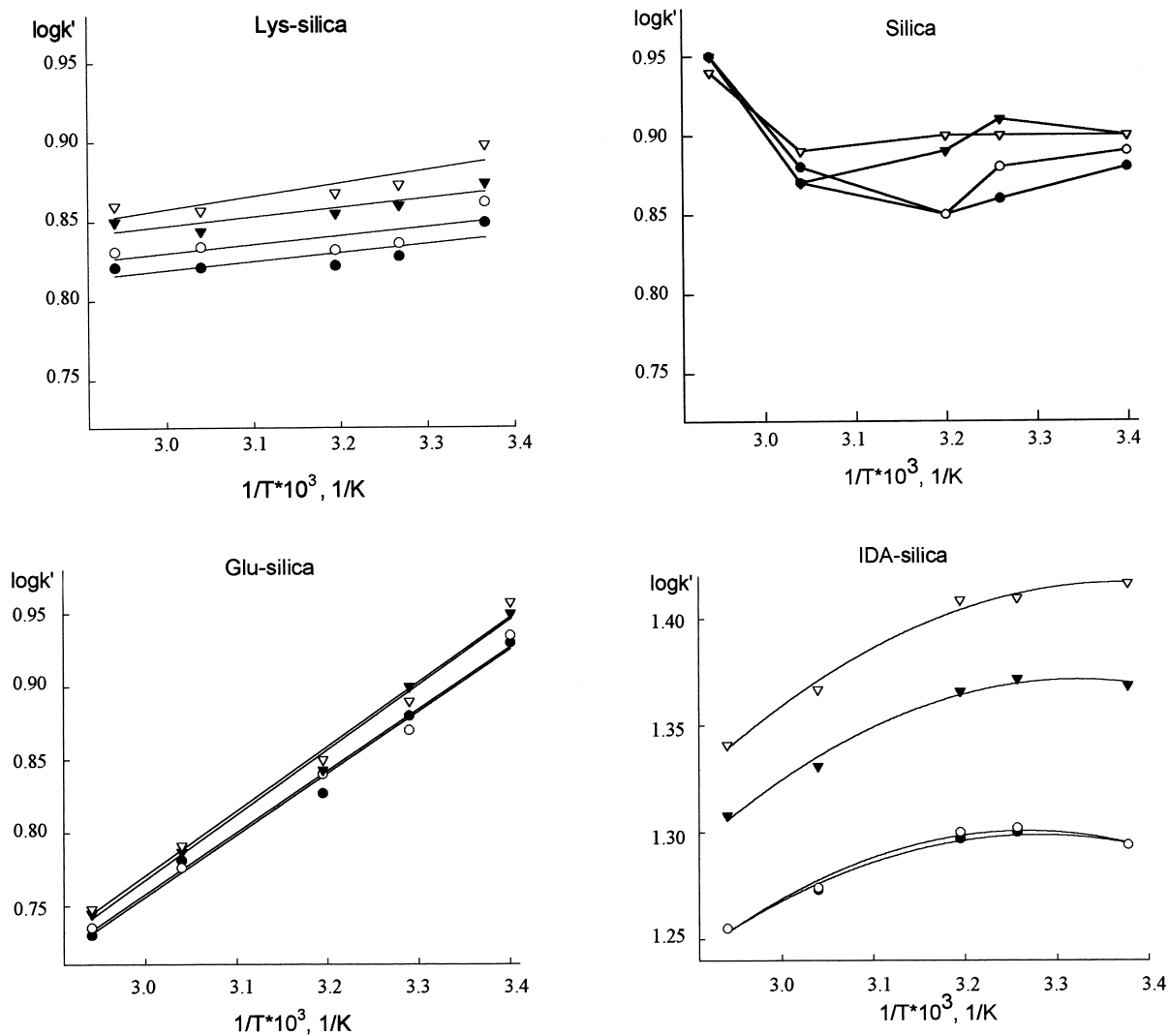
Fig. 2. Plot of log k' vs. $1/T$ for alkaline-earth metal cations: Mg^{2+} (– ● –), Ca^{2+} (– ○ –), Sr^{2+} (– ▼ –), and Ba^{2+} (– ▽ –). Eluent: 2 mM perchloric acid; flow-rate: 1 ml/min.

blocked by initial modification with silanes or by the interaction with amino groups or sterically hindered.

Anyway, the retention of alkali metal cations on all of modified silicas is weaker than that on the bare silica as it can be concluded from the dependencies log k'–$1/T$ for alkali metals (Figs. 1 and 2). Concerning alkaline earth metal ions, the affinity of the studied ion exchangers towards these cations is of one order, except a bit higher one observed for IDA-silica. Generally, the retention of cations on the bare silica was of the same strength as for modified one.

4.4. Adsorption heats

Dependencies, described earlier allow the calculation of adsorption heat ($-\Delta H$) values (Eq. (1)). As mentioned above, these data could give an opportunity for a better understanding of the retention mechanism.

Table 2
The parameters of Eq. (1) describing retention of alkali and alkaline-earth metal cations on Glu-silica, Lys-silica and bare silica as function of temperature

Metal ions	Silasorb Si 600			Lys-silica			Glu-silica		
	$\Delta S/R + \ln \varphi$	$-\Delta H/R$	r^2	$\Delta S/R + \ln \varphi$	$-\Delta H/R$	r^2	$\Delta S/R + \ln \varphi$	$-\Delta H/R$	r^2
Li^+	0.68	−0.10	0.585	0.34	$-5.77 \cdot 10^{-3}$	0.039	−0.66	0.29	0.987
Na^+	0.78	−0.12	0.469	0.38	$-8.13 \cdot 10^{-3}$	0.210	−0.66	0.29	0.987
K^+	0.89	−0.09	0.405	0.43	0.02	0.120	−0.43	0.24	0.959
Rb^+	0.78	−0.04	0.046	0.27	0.10	0.908	−0.59	0.29	0.961
Cs^+	0.78	−0.04	0.046	0.08	0.18	0.961	−0.71	0.33	0.977
Mg^{2+}	1.34	−0.14	0.437	0.65	0.06	0.624	−0.51	0.42	0.990
Ca^{2+}	1.21	−0.10	0.237	0.66	0.06	0.537	−0.51	0.42	0.993
Sr^{2+}	1.07	−0.05	0.105	0.67	0.06	0.770	−0.57	0.45	0.994
Ba^{2+}	1.09	−0.06	0.307	0.61	0.08	0.766	−0.55	0.46	0.991

Other conditions as in Figs. 1 and 2.

Table 3
The parameters describing retention of alkali and alkaline-earth metal cations on IDA-silica as function of temperature

	$\ln k' = a/T^2 + b/T + c$			
	$-a$	b	$-c$	r
Li^+	0.65	4.16	6.26	0.987
Na^+	0.64	4.10	6.16	0.994
K^+	0.48	3.15	4.63	0.977
Rb^+	0.29	1.97	2.82	0.991
Cs^+	0.32	2.22	3.24	0.994
Mg^{2+}	0.41	2.65	3.04	0.995
Ca^{2+}	0.44	2.87	3.40	0.993
Sr^{2+}	0.45	2.98	3.58	0.995
Ba^{2+}	0.43	2.88	3.43	0.995

Other conditions as in Figs. 1 and 2.

Calculated values of adsorption heat are represented in Table 4. Because the dependencies obtained for Lys-silica and Glu-silica are linear that provides the constant value of ΔH for the whole temperature range. In case of IDA-silica two values of $-\Delta H$ for each cation are presented. The reason is the parabolic dependence of log k' on $1/T$, that means $-\Delta H$ is a linear function of the reciprocal temperature. So, the highest and the lowest $-\Delta H$ values for the investigated temperature range are given in Table 4.

The values of adsorption heat increase in the groups of alkali and alkaline-earth metal cations. For the studied ion exchangers the values of $-\Delta H$ for alkali metal ions increase in the order: IDA-silica (23°C)<silica<Lys-silica<Glu-silica≈IDA-silica (67°C). For alkaline-earth metal ions this order is as follows: silica≈IDA-silica (23°C)<Lys-silica< IDA-silica (67°C)<Glu-silica.

It should be noted, that calculated adsorption heats for all ions and stationary phases under investigated conditions are in the range from −4 to −9 kJ/mol.

Table 4
Adsorption heats ($-\Delta H$, kJ/mol) of alkali and alkaline-earth metal cations on aminocarboxylic sorbents

Metal ion	IDA-silica $T = 23$°C	IDA-silica $T = 67$°C	Glu-silica	Lys-silica	Silica
Li^+	−4.43	6.43	5.5±1.1	−0.1±1.0	−1.9±3.0
Na^+	−4.29	6.41	5.6±1.8	−0.2±0.6	−2.2±4.4
K^+	−1.78	6.24	4.6±1.7	0.5±2.3	−1.8±3.9
Rb^+	0.20	5.05	5.7±2.0	1.9±1.1	−0.4±5.7
Cs^+	1.11	6.45	6.5±1.7	3.5±1.2	0.7±5.4
Mg^{2+}	−2.30	4.55	8.5±1.4	1.1±1.5	−2.6±5.6
Ca^{2+}	−1.97	5.39	8.6±1.3	1.1±1.8	−1.9±6.4
Sr^{2+}	−1.16	6.36	9.0±1.2	1.1±1.1	−1.02±5.4
Ba^{2+}	−0.49	6.70	9.1±1.4	1.6±1.6	−1.11±3.1

It is well known [4], that the change of adsorption heat values of ion-exchange processes usually does not exceed 25 kJ/mol for mono- and divalent cations. So, our supposition of a predominantly ion-exchange retention mechanism is also supported by thermodynamic data.

The column temperature was mentioned to be sometimes used as a tool for change of selectivity. In the case of these investigated substrates adsorption heat values are low and do not differ from each other noticeably. This means, that the increase of column temperature is not useful for the achievement of a better selectivity of separation. However, the improvement of kinetics of ion-exchange with increase of column temperature and, hence, the improvement of column performance should be taken into consideration. Finally, the column temperature of about 38–42°C provides an optimum quality of separation of alkali and alkaline-earth metals.

4.5. Influence of temperature on the adsorption heat values for IDA-silica

As it was stated above, adsorption heat values for IDA-silica are not constant under the experimental conditions. For alkaline-earth metal cations the adsorption heat values grow with the temperature increase in the group from Mg^{2+} to Ba^{2+} (Fig. 3). This is due to the increase of electrostatic interaction with the decrease of radii of hydrated cations. A similar elution order was obtained for the other stationary phases that is rejected in adsorption heats (Table 4).

In the case of alkali metal cations, the change of adsorption heat with the increase of temperature in the group is rather peculiar (Fig. 3). There is little correlation between the adsorption heat and the radii of hydrated ions for the whole temperature range. While the temperature is low (23–48°C), adsorption heat increase from Li^+ to Cs^+, this behaviour is similar to the group of alkaline-earth metal cations. Under higher temperatures, from 48 to 56°C, adsorption heats are close for all cations. Further increase of temperature leads to practically a mirror reflection of the adsorption heat change order, observed at 23°C (Fig. 3). It may be caused by a possibility of the coordination of sorbate with the second carboxylic group, that dissociated with the temperature increase (Table 1).

The same effect was observed by Kraus and Raridon [22] for sulphonated polystyrene–divinylbenzene copolymer cation exchanger Dowex-50. While the relative selectivity of alkali metal ions vs. H^+ is in the usual order near room temperature ($Na^+ < K^+ < Rb^+ < Cs^+$), near 150°C Rb^+ is less retained than K^+, while Cs^+ is still a bit stronger adsorbed than K^+ and Rb^+. Such reversal of order takes place for La^{3+} and Eu^{3+} also. This effect is
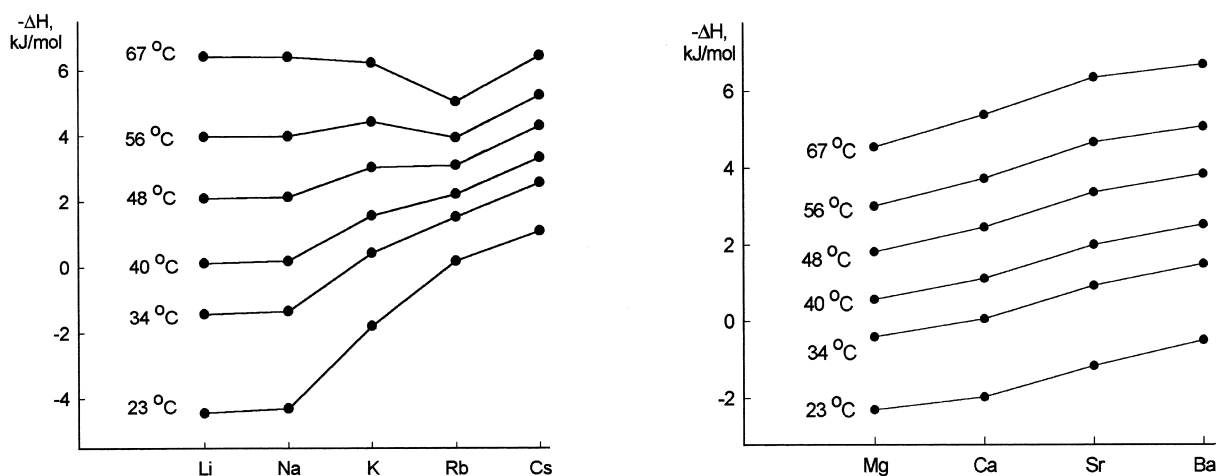

Fig. 3. Regularities of adsorption heat change of alkali and alkaline-earth metal cations on IDA-silica. Eluent: 2 m*M* perchloric acid; flow-rate: 1 ml/min.

accounted for the properties of stationary phase, but not for the change in hydrated ion radii. In particular, it can be referred to the change of solvating ability of stationary and mobile phases [23].

5. Conclusions

The study of temperature effects of some amino-carboxylic acid type silica based cation exchangers having a different complexing ability provides a number of new observations. A decrease of selectivity for all studied cation exchangers with temperature increase was observed. The dependencies of log k' on $1/T$ are linear except for IDA-silica where a parabolic type dependence was found. For latter cation-exchanger the reverse of adsorption heat increase order from $Li^+ < Na^+ < K^+ < Rb^+$ at 23°C to $Rb^+ < Na^+ < K^+ < Li^+$ at 67°C was found. The evidence of possible coordination of one alkali metal cation on two carboxylic groups in one IDA functional group was found for IDA-silica; this makes sense in our considerations of the mechanism of adsorption of alkali metals for polyfunctional ion-exchangers. At the same time the calculated values of adsorption heat are in good agreement with the domination of ion exchange in retention of alkali and alkaline-earth metals on these cation exchangers.

Acknowledgements

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