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Gabriel Prukop[a]; L. B. Rogers[a]
[a] DEPARTMENT OF CHEMISTRY, UNIVERSITY OF GEORGIA, ATHENS, GEORGIA

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Cation Exchange at Pressures up to 400 MPa

GABRIEL PRUKOP and L. B. ROGERS

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF GEORGIA
ATHENS, GEORGIA 30602

Abstract

The effects of pressures up to 400 MPa (~60,000 psi) on the capacity factors of sodium, potassium, rubidium, lithium, and magnesium ions were studied using nitrate eluents. The capacity factors, corrected for compression, were changed by almost 25% for rubidium and potassium ions by going from atmospheric pressure to 350 MPa. The corrected capacity factor for magnesium ion changed 15%, whereas those for lithium and sodium were essentially unchanged. The effect was attributed to changes in the sizes of the hydrated cations.

INTRODUCTION

Previous work on pressurized liquid chromatography systems includes several types of separations. The adsorptions of methyl orange and ethyl orange on silica gel gave slight decreases in retention with increased pressure until about 147 MPa (22,000 psi) where sharp increases started (*1*, *2*). In another study, steric exclusion of micelles by controlled-pore glass and Sephadex gave evidence of a decrease in the stability of sodium dodecylsulfate micelles as well as an increase in the critical micelle concentration (*3*, *4*). A third study involved anion exchange of the lead(II) nitrate complex system and also simple anions. The study showed that pressure could break up anionic complexes, as indicated by a smaller retention volume, but the pressure had little effect on the simple ions (*5*).

Selectivities of cation exchange resins are related to charge densities of the hydrated ions. For alkali metal ions, a decreasing extent of exchange correlates with an increasing hydrated radius. Gregor related the order of exchange directly to the physical size of the hydrated ion due to Coulombic attraction for the hydrated ion as a single unit (*6*). For large exchange sites, Eisenman related the order of exchange to the free energy released when the ionic species were stripped of water of hydration by interaction with the exchange site (*7*). Both of these theories base the extent of exchange on the hydration of the ion. Therefore, if pressure affects the hydration of ions, it should also affect their exchange equilibria and, in turn, their retention volumes.

The effect of pressure on the hydration of a simple cation in aqueous solution is not understood. Using electrical conductivity, Horne (*8*) gave evidence that an increase in hydrostatic pressure tended to dehydrate simple ions. At a pressure of 490 MPa, even the innermost hydration sheath was destroyed due to the structure-breaking ability of pressure.

In other electrical conductivity studies up to and slightly over 490 MPa, Osugi and co-workers concluded that the hydration number increased slightly for singly-charged cations and decreased slightly for anions (*9*). However, due to an uncertainty of 0.5 in determining the hydration number, the overall conclusion was that pressure had little effect. For doubly-charged cations, hydration was constant with pressure (*10*). In contrast, based on density studies up to 98 MPa, Samoilov (*11*) concluded that the hydration of a simple cation increased with pressure. The disagreement with Horne was acknowledged. Again, the effect was attributed to a breakdown of the structure of bulk water. Another observation that reinforces that interpretation is the increased dissociation of metal complexes at higher pressures. Increased dissociation has usually been attributed to the more effective electrostriction of water by the larger number of individual ions as opposed to the complex (*12*).

In the present study the high-pressure cation exchange behaviors of lithium, potassium, rubidium, and magnesium with sodium nitrate as eluent were examined at pressures up to 343 MPa. The slight decreases in their capacity factors were attributed to the dehydration by pressure of the sodium ion in the eluent.

EXPERIMENTAL

Reagents

Laboratory distilled water was redistilled in a Corning Megapure 1-liter still (Corning Scientific Instruments, Medfield, Massachusetts). Analytical grade salts were used without further purification.

Rubidium nitrate was purchased from Fairmount Chemical Co., (Newark, New Jersey). Lithium nitrate was purchased from PCR Inc. (Gainesville, Florida). All other nitrate salts were obtained from J. T. Baker Chemical Co. (Phillipsburg, New Jersey). All mobile phases were made directly to the desired concentration, usually 1.00 *M*, and then filtered through 7 μm fritted disk filters (Nupro) prior to pumping. The 0.0100 *M* samples, made by diluting 1.00 *M* stock solutions, were filtered through 0.5 μm filters (Millipore Corp., Bedford, Massachusetts) just before injection. Blue dextran 2000 was purchased from Pharmacia Fine Chemicals (Piscataway, New Jersey).

The sulfonic acid cation-exchanger resin, AG 50WX16 (Control number 10485, BioRad Laboratories, Richmond, California) was 16% cross-linked for rigidity and low swelling. The large particle size, 37 to 74 μm (140–270 wet mesh), provided a pressure drop of less than 350 kPa (50 psi) through each column. After the fines had been removed by decantation, the resin was then allowed to swell overnight before being converted from the hydrogen form to the sodium form by passing 2 *M* sodium nitrate through a bed, held in a buret, until the pH of the eluent was constant and neutral. By converting the resin to the desired form before packing the column, acid was kept out of the high-pressure system. The potassium form of the resin was obtained by directly converting the sodium form on the column using 2 *M* potassium nitrate.

Columns were packed by adding small increments of slurry until the column was full. The high-pressure columns were consolidated by running at a flow rate of 3 to 4 ml/min and 350 MPa pressure. Additional resin was then added to fill the gap produced by compression. At the most, two compressions and additions of resin were needed. After that conditioning of the column, bed volumes were stable at different pressures under the usual flow rate of approximately 1 ml/min.

Equipment and Procedures

The low-pressure system mimicked the high-pressure column in size. It was constructed of borosilicate glass (0.6 cm × 30.5 cm) and Teflon fittings (Beckman Instruments, Fullerton, California). The bed was supported by a nylon net, and a peristaltic pump (Sigma Motor Inc., Middleport, New York) provided the flow. Injections were made during flow with an air-actuated loop injection valve (Chromatronix, Inc.).

The high pressure pumping system has been described elsewhere (*1*). The 32 μl sample volume was filled from a solenoid-controlled reservoir. The 0.0100 *M* samples were "injected" at atmospheric pressures with the exit valve closed. After the system had been brought up to pressure, the exit valve was opened, and flow adjusted to approximately 1 ml/min. Actual flow rates at high pressures varied somewhat during a run and between runs, so a drop counter (*13*) was used to trigger collection of fractions by an ISCO Model 270 fraction collector (Instrument Specialties Co., Lincoln, Nebraska).

For large retention volumes, eluent was first directed into a buret for a specified volume. Then, by means of an optical level-detector made in this laboratory, the eluent was automatically switched through the drop counter for the collection of fractions.

Most of the pressure drop occurred across the valve at the exit end of the column which was used to adjust flow rates. Pressure was monitored by a 559 MPa (80,000 psi) Bourdon gauge having a 316 SS tube (American Instrument Co., Silver Spring, Maryland) and a strain gauge pressure transducer (BLH Electronics, Waltham, Massachusetts). The power supply for the activation voltage and the amplifier circuit were built from components in our laboratory.

Metal concentrations in the eluents were analyzed using a Perkin-Elmer Model 305B flame spectrophotometer. Flame emission was usually used. Calibration curves were linear. The high background of sodium in the eluent gave higher sensitivities than reference standards in distilled water due to suppression of ionization. Therefore, references for calibration were made by diluting with the pure mobile phase.

In the case of magnesium where sodium is a spectral interferent at the main emission line, use of atomic absorption avoided the interference. A problem with the high salt background was that it required frequent cleaning of the nebulizer-burner and aspiration of distilled water at regular intervals so as to keep the system free from deposits.

All data reported in this study were taken using the stainless steel column. Because the high-pressure pump did not function well at pressures below 70 MPa, low (ambient exit) pressure data were obtained by replacing that pump with a Milton Roy peristaltic pump and completely opening the exit valve. Experiments over the entire pressure range were deliberately done in a random order so as to prevent biasing of data. For a given pressure, some replicates were run in succession while others were scattered between those at other pressures. The total number of replicates at each pressure is indicated in the diagram. One standard deviation on each side of the mean retention value is shown by a bar.

The data for a given run were obtained in volume intervals of 0.6 ml.

By curve-fitting seven points of the data, one could easily calculate the location of the peak maximum from the inflection point.

Calculations

The capacity factor, k', was calculated using the equation

$$k' = (V_r - V_i)/V_i \tag{1}$$

where V_r is the retention volume of the peak maximum. V_i is the interstitial or void volume of a column, and it was a constant for a given column.

One way of determining V_i was by multiplying the total bed volume by the fraction of bed reported to be the interstitial volume for a given resin. This fraction has been determined empirically and is relatively constant for a given resin (*14*). However, the interstitial volume plus any dead volume can be determined experimentally for an ion-exchange resin by using a molecule which is (1) uncharged, (2) totally excluded from the ion exchange bed, and (3) not adsorbed. Blue dextran 2000 was used as the unretained species. A typical value for V_i determined using 0.396 as the interstitial fraction of the AG 50X16 resin gave a value of 4.0 whereas the use of dextran gave 4.6 ml. This is good agreement considering the uncertainties in each of these approaches. All capacity factors reported for this study were based upon the value found using blue dextran. The agreement of V_i values by both methods indicated that there was little compression of the bed.

Since the retention volume was measured at atmospheric pressure, the capacity factor, k', had to be corrected for compression. The corrected capacity factor, k'_p, was calculated by using

$$k'_p = [V_a(1 - k_p) - V_i]/V_i \tag{2}$$

V_a is the volume of liquid measured at atmospheric pressure. k_p is the compression factor calculated for water from Adams data and given by (*15*)

$$k_p = V_a - V_p/V_a \tag{3a}$$

or

$$V_p = V_a(1 - k_p) \tag{3b}$$

where V_p is the compressed volume at the working pressure of the column.

The interstitial volume, V_i, needed no correction since it was measured at low pressure and was set by the physical dimensions of the column.

RESULTS AND DISCUSSION

Results are shown in Fig. 1 for samples of rubidium, potassium, magnesium, and lithium using 1.00 *M* sodium nitrate as the eluent and also for sodium ion using 1.00 *M* potassium nitrate as the eluent. The capacity factors were calculated using Eq. (1). Values for the least-squares slopes and their uncertainties are shown in Table 1 along with the values obtained when the data from Fig. 1 were corrected for compression. Only standard deviations for the uncorrected slopes are shown since the standard devia-

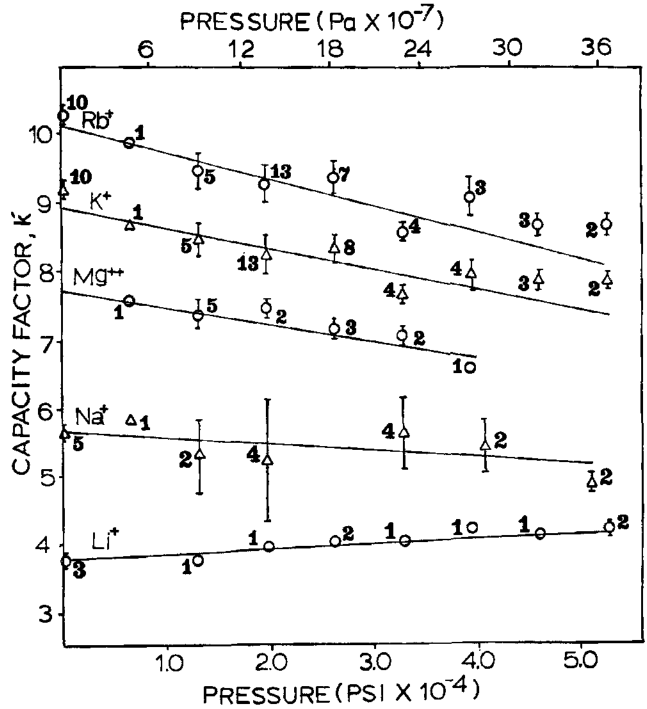

FIG. 1. Capacity factor versus pressure for simple cations using a sulfonic acid cation exchanger and 1 *M* sodium nitrate as the eluent. The exception is sodium ion where 1 *M* potassium nitrate was used as eluent. The numbers inside the figure represent replicates for each point shown.

TABLE 1

Slopes and Intercepts Before and After Correcting for Compression

Sample ion	Eluent ion[a]	Slope		Standard deviation	Intercept
		Uncorrected	Corrected		
Li^+	Na^+	1.1×10^{-5}	-2.9×10^{-8}	1.7×10^{-6}	3.8
K^+	Na^+	-2.6×10^{-5}	-4.5×10^{-5}	2.6×10^{-6}	9.0
Rb^+	Na^+	-3.1×10^{-5}	-5.2×10^{-5}	2.8×10^{-6}	10.1
Mg^{2+}	Na^+	-2.3×10^{-5}	-3.9×10^{-5}	1.2×10^{-5}	7.8
Na^+	K^+	-8.2×10^{-6}	-2.1×10^{-5}	7.6×10^{-6}	5.6

[a] 1 *M* solution of the nitrate.

tions were essentially unchanged when the data corrected for compression were fitted. The corrected capacity factors for rubidium and potassium decreased by almost 25% on going from atmospheric pressure to 350 MPa. This corresponded to a change in partial molar volume for rubidium of 1.2 ± 0.1 ml/mole. The capacity factor for magnesium decreased by about 15%, while that for lithium was essentially unchanged.

The data for sodium eluted with 1 *M* potassium did not show an increase in retention as pressure was applied. This may be due to the poor precision of the sodium data.

For sample ions that went to shorter retention with applied pressure, the size ratio of the sample ion to eluent ion must have shifted toward the larger sample ion. Either the hydrated size of the sample ion was increased or the hydrated size of the eluent ion was decreased.

An explanation of the results based on Horne's theory of dehydration would put the emphasis on the dehydration of the more highly hydrated alkali metals. The sodium ion in the eluent would become a stronger competitor as the pressure increased due to a decrease in the size of hydrated sodium ion relative to the hydrated spheres of rubidium and potassium whose hydrations apparently were not as strongly affected by pressure. The lithium results suggest that lithium and sodium ions dehydrate at approximately the same rate. Hydration of magnesium ion was relatively unaffected by these pressures due to its charge and small size (*10*). Much higher pressures would have been necessary to dehydrate the magnesium. The effects of pressure on the retentions of rubidium, potassium, and lithium ions can also be explained on the basis that the less hydrated ions became hydrated to a greater extent whereas the heavily hydrated ions lithium and sodium were essentially unaffected by pressure.

It is, however, difficult to explain the results for magnesium using the increased hydration theory since magnesium would presumably behave more like lithium and sodium than the structure breakers rubidium and potassium. In addition, Samoilov (*11*) has shown that the hydrations of sodium and potassium by pressure were parallel. The increase in concentration due to compression of the eluent might account for the slight decrease in retention for magnesium without any change in the hydration (*16*). Increasing the concentration of the eluent should have the greatest effect on magnesium (*17*) because sodium concentration is a squared term in the equilibrium expression. Although the concentration change due to compression was small, it was in the direction of shorter retention.

The behavior under pressure of simple cations on cation-exchange resins might be compared to the behavior found for simple anions on an anion-exchange resin (*3*). The retentions of bromide, chloride, and nitrite ions increased slightly with pressure. This change was greatly minimized by correcting for compression. However, compression did not totally remove the trend. Since halide ions are not strongly hydrated and References *8*, *9*, and *11* agree that halide ions are dehydrated with pressure, one cannot directly compare the behavior of halide ions and the alkali metals that are less hydrated because there is considerable H-bonding contributing to the ion–water interaction for the halide ions, approximately 50% for chloride (*11*). There is also a fundamental difference in their relations to their exchange sites. The exchange site on a cation-exchange resin is a benzene sulfonate ion, a hydrophilic species with localized charge. On the other hand, an anion-exchange site resembles a benzyltrimethylammonium ion, which is a large hydrophobic ion that probably interacts via a water structure-enforced ion-pairing force (*18*). Pressure on this system might be expected to push together an ion and its exchange site due to ease of displacing the layers of water between the ions. Thus, although pressure slightly increased retention for anions on an anion-exchange resin, it was expected to decrease retention in cation exchange.

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