Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Maldacker, T. A. and Rogers, L. B.(1974) 'Anion Exchange Behavior of Bromide, Chloride Nitrite, and the Lead(II)-Nitrate System at Pressures up to 3600 kg/cm^2', Separation Science and Technology, 9: 1, 27 — 33
To link to this Article: DOI: 10.1080/01496397408080041
URL: http://dx.doi.org/10.1080/01496397408080041

SEPARATION SCIENCE, 9(1), pp. 27–33, 1974

Anion Exchange Behavior of Bromide, Chloride Nitrite, and the Lead(II)-Nitrate System at Pressures up to 3600 kg/cm^2

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Abstract

The effects of high pressure (up to 3600 kg/cm^2) on the distribution coefficients of simple and complex anions have been studied on a strongly basic anion exchange resin. The retention volumes of Br^-, Cl^-, and NO_2^- were found to increase with pressure, and this was attributed primarily to an increase in the compression of the eluent, leading to greater volumetric flows at constant linear flows. The retention volume of the Pb(II) nitrate species was found to decrease significantly with pressure. This was attributed to a breakup of the anionic and neutral lead complexes to unretained cationic species and NO_3^-. The breakup occurred because of the greater ability of the more numerous dissociation products to decrease the volume of the system by electrostriction.

INTRODUCTION

The purpose of this study was to extend the technique of high-pressure liquid chromatography, at pressures up to 3600 kg/cm^2 (50,000 psi), to ion-exchange chromatography, with the idea of exploring the use of pressure as a variable for changing ion selectivities. Previous workers have used silica gel for liquid–solid adsorption (*1*), and porous glass (*2*, *3*) or Sephadex (*3*) for steric exclusion. By employing slow flow and short

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columns, most of the pressure drop occurred across a high-pressure value located between the column exit and the detector.

The weak nitrate complexes of Pb(II), which result in retention of lead on strongly basic anion exchange resins in a high nitrate background concentration (*4*), have been studied. We have also examined Br^-, Cl^-, and NO_2^- retentions on the same column using a nitrate eluent in order to examine the effects of pressure when complexation was not involved.

It is known that weak complexes dissociate under pressure, generating a greater number of charged species which take up less volume because they orient the water by electrostriction. As examples, the dissociations of $CoCl_4^{2-}$ and $CuCl_4^{2-}$ have been followed spectroscopically (*5*) as a function of pressure. Pressure dissociation of weak electrolytes has also been studied conductometrically (*6*). In the present case, pressure was expected to break up the complex into Pb^{2+} and NO_3^- species, neither of which would be retained on an anion exchange column. Thus the overall effect of pressure would be to decrease the distribution coefficient.

EXPERIMENTAL

Regents

All of the inorganic reagents were obtained from J. T. Baker Chemical Co. (Phillipsburg, New Jersey). The potassium salts were dissolved in deionized water. Chloride, bromide, and nitrite were prepared as 4-*M* solutions in water. Lead nitrate was prepared as a 1-*M* solution in water. Potassium nitrate eluent was prepared as a 2-*M* solution. The anion-exchange resin was analytical grade Dowex-1 resin in the chloride form. It was designated AG-1, with 10% cross-linking, a 230 wet mesh size, a capacity of 1.5 meq/ml, and a control number of 10701 (Bio-Rad Laboratories, Richmond, California).

Low-Pressure System

A 0.6 × 32.5 cm column was used for exploratory work. It was fabricated from borosilicate glass tubing and Teflon tube fittings (Beckman Instruments, Fullerton, California). A glass-wool plug supported the bed. Tygon tubing of 0.8 mm i.d. connected the column exit to the detector. A low-pressure peristaltic pump (Sigmamotor, Middleport, New York) delivered the eluent.

High-Pressure System

The high-pressure column, 0.6 × 30.5 cm, was made from 17–4PH stainless steel (High Pressure Equipment Corp., Erie, Pennsylvania), and 10 μ porosity frits were used at each end to support the bed. The high-pressure pump consisted of a small diameter hydraulic piston connected to an air motor-driven piston, capable of a 660-fold (hydraulic-to-air) increase in pressure (S.C. Hydraulic Engineering Corp., Los Angeles, California). A high-pressure valve was fitted to the end of the column to control the flow rate. The bulk of the pressure drop was across that valve.

Column Preparation and Use

The columns were packed by pouring an aqueous slurry of the resin, from which the fines had been removed by decantation, into a solvent-filled column. A 2-*M* KNO_3 solution was passed through the column until no silver chloride was precipitated in the eluent upon addition to a saturated solution of silver nitrate. In the case of the high-pressure column, the bed was examined visually after running several milliliters of eluent through it at 2 ml/min. Additional packing was added as needed. After that addition, the bed volume was very stable under pressure.

Sample size was 32 μl in all cases. Low-pressure syringe injections were made directly into the resin bed via a tee fitting. Injections onto the high-pressure column were made using a custom injector operated at atmospheric pressure. With the exit end of the column closed off, the pump was then turned on, the column was brought up to the desired pressure, and elution was initiated by slowly opening the exit valve to give a flow of approximately 1 ml/min. Pressure drops across the column operated in this way were approximately 50 psi. Since flow varied somewhat, volume was monitored by directing the eluent into a buret.

Other Apparatus

An R-4 differential refractometer detector was used (Waters Associates, Framingham, Massachusetts) to monitor most of the samples. For Cl^- and NO_2^-, a noisy baseline during the high-pressure runs made the use of a fraction collector necessary. The Cl^- was detected on the basis of turbidity using $AgNO_3$. The NO_2^- was monitored using a Perkin-Elmer 202 at 355 nm.

Calculations

The distribution coefficient, *D*, of the eluting ionic species was calculated using

$$D = (V_r - V_0)/V_0 \tag{1}$$

where V_r is the retention volume and V_0 the interstitial or void volume of the bed. In addition,

$$V_0 = V_t \times f \tag{2}$$

where V_t is the total bed volume and f is the fraction of the bed which is interstitial volume. The value of f varies for each ion-exchange packing, and for Dowex-1 × 10, $f = 0.396$ (*7*).

A pressure-corrected distribution coefficient is given by

$$D_p = [V_r - V_0(k + 1)]/[V_0(k_p + 1)] \tag{3}$$

where the compression, k, of water at pressure p is given by

$$k_p = -(V_w - V_p)/V_p \tag{4}$$

V_w is the volume at atmospheric pressure and V_p is the volume at the working pressure.

RESULTS

Figure 1 shows the results for high-pressure ion-exchange runs with the lead nitrate complex. There was a continuous decrease in D with pressure, apparently due to the breakup of the retained complex to $Pb(NO_3)^+$, Pb^{2+}, and NO_3^-. Presumably the larger number of charged species more strongly oriented and constricted the water.

The effects of pressure on the distribution coefficients of simple anions are also shown in Fig. 1. These results indicate a trend opposite to that of the complex. In all cases the simple ions appeared to be held up longer as the pressure increased. On a relative basis the retention volumes increased for all of these simple anions by approximately 10% on going from 350 to 3500 kg/cm^2. However, we have attributed these retention changes to compression of the liquid phase. When corrected by using compression values of water (*8*), the distribution coefficients for the simple ions showed no significant changes with pressure, as shown for Br^- by the dashed line in Fig. 1. Curves for Cl^- and NO_2^- were found to change in the same way but have been omitted from the figures for the sake of clarity. Likewise, the shape of the corrected curve for the lead complexes was not greatly changed, so it has not been shown. The corrected distribution coefficients for the lead system ranged between 2.31 and 0.79.

Actually, using the values for water produces a slight overcorrection in the resulting values for the distribution coefficients. For example, at

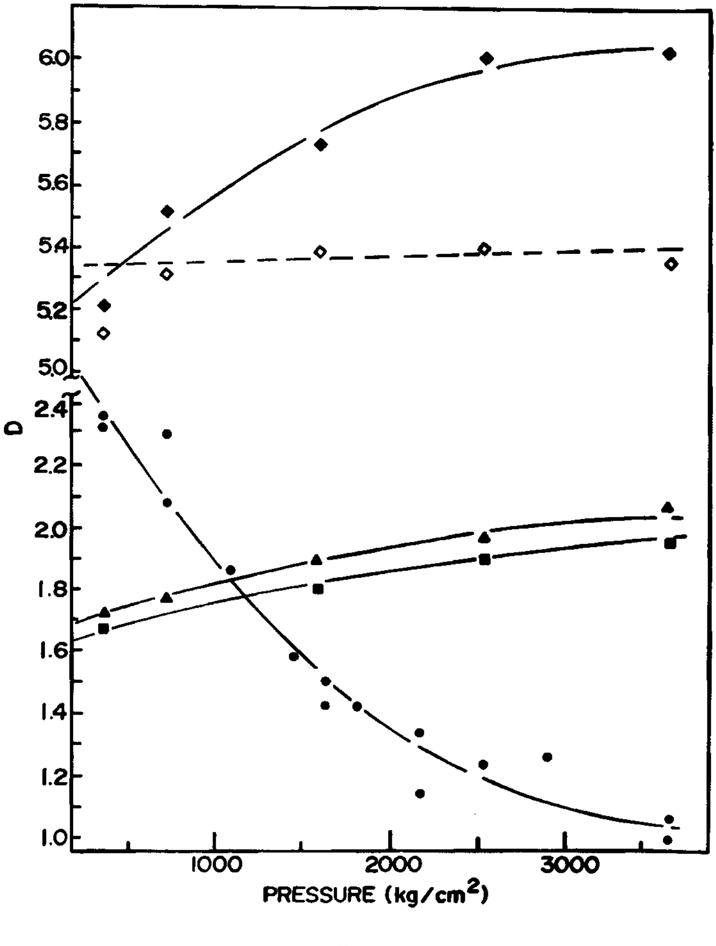

FIG. 1. Dependence of anion distribution coefficients on pressure. (■) NO_2^-, (▲) Cl^-, (◆) Br^-, (◇) Br^- corrected for compression of the eluent, and (●) $Pb(NO_3)_n^{2-n}$.

1000 kg/cm^2 a 20% by weight KNO_3 solution has a compression of 0.0328 vs 0.0393 for that of water (*9*). Therefore, using the available compression values for water alone will result in small errors. In any case, changes in *D* values for simple ions appear to be close to zero in the pressure range of our experiments.

DISCUSSION

Retention of lead nitrate species on strongly basic anion exchange resins is well documented (*4*, *10*, *11*). It is probable, however, that much of the retained species is not anionic because of the weak complexing ability of the nitrate. More than 50% of the lead ion in a 0.05-*M* Pb(II) solution has been reported to exist as neutral $Pb(NO_3)_2$ in concentrated solutions of nitrate (*12*), and the neutral species is known to adsorb on anion exchange columns (*10*, *11*).

There is disagreement in the literature concerning the relative amounts of the species, especially for the anionic complex(es). Stepwise stability constants of 1.8, 2.4, and 0.005 have been given (*12*).

In contrast, others have reported that up to 40% of the lead ion in a 0.001-*M* solution is in the form of anionic complexes in the presence of 2 *M* NO_3^- (*13*). Cumulative stability constants for $Pb(NO_3)^+$ through $Pb(NO_3)_3^-$ have been given as 3.2, 2.1, and 2.1, respectively (*14*), at 25°C using 0.001 *M* Pb(II) and up to 3 *M* NO_3^-. In any case, an increase in pressure must greatly decrease the relative amounts of the retained neutral and anionic complex species to form greater amounts of unretained species, namely $Pb(NO_3)^+$, Pb^{2+}, and NO_3^-.

The results from the lead nitrate system allow three predictions to be made. First, the present technique should be suited to increasing the resolution between two components where one is a system of weak complexes, like those of lead, and the other is a simple anion or a stronger complex having the same or larger distribution coefficient. Second, users of commercially available high-pressure chromatographs, which can operate up to 5000 to 7000 psi, may encounter band distortion in anion-exchange separations due to changes in *D* across the column. The very fine particles and narrow bore columns used in high-resolution chromatography mean that the inlet is at the state pressure while the outlet is at atmospheric pressure. Hence at 6000 psi (approximately 400 kg/cm^2) the slope of the curve for the lead nitrate suggests that there would be about a 10% increase in *D* between the inlet and the outlet of the column. Third, pressure programming of a column packed with relatively coarse particles ($>20\ \mu$) may occasionally prove to be a practical alternative to consider.

For example, one advantage of pressure programming, compared to gradient elution, is that changes throughout the column are immediate. Furthermore, the pressure can be released very quickly at the end of a run, and a second run started at once using a different pressure. In contrast, much time is usually lost when reconditioning a column with fresh solvent after a gradient-concentration run. To make pressure programming feasible while still using the currently popular, small particles for packings, larger diameter columns and smaller linear flow rates should be used in chromatographs having a valve at the column exit. In that way, one will be able to operate at or near the customary volumetric flow rates without producing pressure drops across the column which are significant compared to the operating pressures.

Acknowledgment

Supported in part by the U.S. Atomic Energy Commission under Contract AT(11–1)–1222.

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Received by editor July 2, 1973