

CHROMSYMP. 822

## EFFECT OF HIGH PRESSURES ON ION-EXCHANGE CHROMATOGRAPHIC PROCESSES

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### SUMMARY

The changes in the interaction between an ion exchanger and solution components occurring under the effect of an external hydrostatic pressure were studied. The changes at high pressures in the ion-exchanger selectivity towards ions being sorbed in systems with weakly dissociating components are calculated by theoretically taking into account the amount and sign of the volume effects due to the partial parallel-consecutive reactions occurring in the whole system, and their contribution to the overall volume effect of the sorption process. For systems with strongly dissociating components this is done by taking into account the changes in the "swelling pressure" parameter for the ion exchangers.

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### INTRODUCTION

Ion-exchange equilibrium constants are the most important starting parameters determining the efficiency of an ion-exchange chromatographic process and they are taken into account in theoretical studies of ion-exchange chromatography. In view of the increasing tendency to use higher pressures in analytical and applied chromatographic practice, it is of interest to study the changes in ion-exchanger selectivity under extreme conditions.

The dependence of the equilibrium constant ( $K$ ) of a chemical reaction on pressure ( $p$ ) is determined by the changes in the partial molar volumes ( $\Delta V$ ) of the starting and final reaction components<sup>1</sup>:

$$\left(\frac{\partial \ln K}{\partial p}\right)_T = -\Delta V/RT \quad (1)$$

For a strongly dissociating ion exchanger, the relative solvation state of the ion being exchanged changes slightly with the transition of the ion from the ion exchanger into the solution and back and, hence,  $\Delta V$  is also small. From this Helfferich<sup>2</sup> concluded theoretically that pressure does not affect the position of the ion-exchange equilibrium. This conclusion is, however, at variance with our experimental results and those reported in the literature<sup>3-6</sup>. In fact, for systems involving weakly dissociating

ion exchangers or weak electrolyte in solution, the volume effect  $\Delta V$  will also be substantially dependent on the degree of dissociation of the weak electrolytes and the latter is strongly affected by the external pressure. This results in a decrease in the system volume as ions are formed from the molecules due to the solvation effect (electrostriction)<sup>7,8</sup>. Or strongly ionized ion exchangers, we found<sup>9</sup> that at high hydrostatic pressures there is an appreciable change in the solvent volume in the ion-exchanger grains. Consequently, a change occurs in the swelling pressure and, according to Gregor's theory<sup>10</sup>, also in selectivity. It is these pressure-induced effects which can cause the changes in the equilibrium constant under extreme conditions.

In this paper we present the results of a study of the effect of high hydrostatic pressures on two limiting systems: (1) sorption by a weakly dissociated ion exchanger of a weak electrolyte and (2) sorption by a strongly dissociated ion exchanger of a strong electrolyte. The method described for these systems can be readily extended to the description of intermediate sorption processes.

#### EXPERIMENTAL AND RESULTS

In the literature there is no experimental information on the study of the first type of heterogeneous systems at high pressures. We studied the sorption of boric acid ( $K_a = 5.8 \cdot 10^{-10}$  at  $p = 1$  bar<sup>11</sup>) by a weakly dissociated anion exchanger of the amine type (AN 22-X8) at pressures as high as 8 kbar.

The starting boric acid solutions were prepared from analytical-reagent grade boric acid and had a concentration of 0.105 *m*. The bifunctional sorbent contained weakly basic primary and secondary amino groups. It was conditioned by the usual repeated exchange cycles using 0.5 *M* hydrochloric acid and sodium hydroxide solutions and freed from low-molecular-weight impurities by extraction with ethanol. The total capacity of the swollen anion-exchanger was 3.462 mequiv./g<sup>-1</sup> (determined with an excess of 0.1 *M* hydrochloric acid) and the water content was 56% (w/w).

The procedure for studying the sorption equilibrium at 25°C and 1 bar was different from that at high pressures. In the former instance 1–3.5 g of the ion-exchange resin in the free base form were brought in contact with 15–20 g of a boric acid solution and the mixture was periodically stirred for 96 h until equilibrium was established. The amount of boric acid in the starting and equilibrium solutions was determined by titration with 0.1 *M* sodium hydroxide solution in the presence of mannitol. The amount of boric acid sorbed by the ion exchanger was calculated as the difference between its contents in the initial and equilibrium solutions.

The high-pressure studies of the sorption equilibria were carried out in the apparatus described previously<sup>12</sup>. The ion-exchange resin and the solution were placed in a cell with elastic walls which was inserted in a high-pressure cylinder. Gravitational mixing of the phases was performed by a reciprocating movement of the high-pressure cylinder.

After equilibrium had been established the pressure was rapidly raised to 12 kbar in order to "freeze" the equilibrium state. Then the pressure was released and the cell was removed from the cylinder and cut into two parts, one of which contained the frozen boric acid solution and the other a small amount of the frozen solution and grains of the ion-exchange resin. The melted ice was analysed as described above. With regard to equilibrium stabilization, this technique has considerable advantages

over the usual procedure in which the pressure is first released, then the cylinder is taken apart, the cell is removed and the solution analysed.

The apparent equilibrium constant of the sorption with boric acid for the reaction



was calculated according to

$$K = \frac{\bar{m}_{\text{RNH}_3^+\text{H}_2\text{BO}_3^-}}{\bar{m}_{\text{RNH}_2} \cdot m_{\text{H}_3\text{BO}_3}} \quad (3)$$

where  $\bar{m}_{\text{RNH}_3^+\text{H}_2\text{BO}_3^-}$  and  $\bar{m}_{\text{RNH}_2}$  are molal concentrations of ionized and non-ionized forms of the ion exchanger, respectively (the bars above the parameters denote that they refer to the ion-exchanger phase), and  $m_{\text{H}_3\text{BO}_3}$  is the molal concentration of boric acid in the equilibrium solution.

The apparent equilibrium constants calculated from the experimental data according to eqn. 3 at atmospheric and high pressures are given in Table I. The values of  $\partial \ln K / \partial p$  were obtained by graphical differentiation with respect to the  $\log K$  versus  $p$  dependence for the corresponding points, and the total volume change  $\Delta V$  was then calculated according to eqn. 1.

For the second type of system we studied the effect of pressure on the swelling

TABLE I

PARAMETERS OF BORIC ACID SORPTION BY AMINE-TYPE ANION EXCHANGER AND ELECTROSTRICTION FOR SEVERAL SUBSTANCES AT ATMOSPHERIC AND HIGH PRESSURES

System	Pressure (bar)	Equation for calculation of constant	$K$	$\partial \log K / \partial p$	$-\Delta V$ ( $\text{cm}^3 \text{mol}^{-1}$ )
AN 22-X8, boric acid sorption	1	3	$7.9 \cdot 10^{-1}$	0.21	11.8
		10	$3.2 \cdot 10^{-1}$	0.34	19.1
	3000	3	3.20	0.21	11.8
		10	3.54	0.34	19.1
	5000	3	10.03	0.14	7.9
		10	15.07	0.17	9.6
	8000	3	11.48	0.01	0.6
		10	19.68	0.02	1.1
CH <sub>3</sub> NH <sub>3</sub> OH	1	Dissociation	$4.2 \cdot 10^{-4}$	0.47*	26.4
	3000		$4.6 \cdot 10^{-3}$	0.22*	12.4*
(CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> OH	1	Dissociation	$5.9 \cdot 10^{-4}$	0.48*	27.2
	3000		$7.5 \cdot 10^{-3}$	0.28*	15.8*
H <sub>3</sub> BO <sub>3</sub>	1	Dissociation	$5.8 \cdot 10^{-10}$	0.42*	23.6
	3000		$1.3 \cdot 10^{-8}$	0.34*	19.1*
H <sub>2</sub> O	1	Dissociation,	$1.0 \cdot 10^{-14}$	0.38*	21.4*
	3000	$K_w$	$7.6 \cdot 10^{-14}$	0.23*	12.9*

\* Calculated from refs. 7, 16 and 18.

TABLE II  
 SWELLING, VOLUME AND SWELLING PRESSURE OF SULPHONATED STYRENE-DIVINYLBENZENE CATION EXCHANGERS AT ATMOSPHERIC AND HIGH PRESSURES

Cation exchanger	Counter ion	$(W_M)_H^0$	$(W_M)_M$	$(W_e)_H^0$	$(W_e)_M$	$(V_M)_H^0$	$(V_M)_M$	$(V_e)_H^0$	$(V_e)_M$	$\pi^0$ (bar)	$\pi^p$ (bar)	Degree of cross-linking (% w/w)
KU-2-X8	H <sup>+</sup>	0.96	0.97	201	203	1.59	1.60	333	335	177	179	8.11
	Li <sup>+</sup>	0.90	0.92	188	192	1.53	1.55	320	324	161	166	8.27
	Na <sup>+</sup>	0.74	0.78	155	163	1.37	1.41	287	295	120	129	8.65
	K <sup>+</sup>	0.58	0.59	121	123	1.21	1.22	253	255	77	79	8.20
	Cs <sup>+</sup>	0.63	0.65	132	137	1.26	1.28	264	269	90	96	8.53
	Ca <sup>2+</sup>	0.75	0.79	157	165	1.38	1.42	289	297	122	133	8.70
	Sr <sup>2+</sup>	0.67	0.71	140	148	1.30	1.34	271	279	99	109	8.85
	H <sup>+</sup>	2.21	2.21	476	476	2.84	2.84	612	612			(4.00)
	Li <sup>+</sup>	2.19	2.23	472	480	2.82	2.86	608	616			(4.07)
	Na <sup>+</sup>	2.02	2.11	435	454	2.65	2.74	571	590			(4.18)
Dowex 50W-X4	Mg <sup>2+</sup>	2.16	2.24	466	482	2.79	2.87	601	617			(4.15)
	Ca <sup>2+</sup>	2.04	2.15	440	464	2.67	2.78	575	599			(4.22)

properties of sulphonated polystyrene cation exchangers in their alkali and alkali-earth metal ionic forms and made an attempt to relate the values found to the change in swelling pressure in the ion-exchanger grains. Use was made of Dowex 50W-X4 and KU 2X8 ion exchangers, which were conditioned by the above procedure and converted into the ionic form with 0.5 *M* solutions of the corresponding nitrates. For use in the experiments we chose homogeneous grains of a regular spherical shape, which were additionally classified according to their specific weight. The capacity and water contents were referred to the specific (per gram of dry H<sup>+</sup> ion exchanger) or equivalent (per equivalent exchange groups) amount of the ion exchangers. The specific capacity of Dowex 50W-X4 was 4.64 mequiv. g<sup>-1</sup> and that of the KU 2-X8 was 4.78 mequiv. g<sup>-1</sup>.

The relative changes in the specific and relative volumes of the swollen ion exchangers at atmospheric and high (400 bar) hydrostatic pressures at 20–22°C were determined microscopically using a high-pressure optical cell designed by us<sup>13</sup>. In order to separate the pressure-transferring medium (condenser oil) from the material studied, the grains of the ion exchanger were placed in a leak-tight container, which was then brought into the cell. The relative changes in the grain volume were measured in the light passing through the cell and the container window using a specially developed splitting ocular and microscope. The overall magnification of the optical system was × 135 and the scale value of the splitting ocular was 0.5 μm. We measured three or four different grains (of diameter 0.5–0.7 mm) of each ionic form of the ion exchangers and the values of the relative volume changes obtained were averaged.

Table II gives the experimental values of the specific ( $V_M$ , ml g<sup>-1</sup>) and equivalent ( $V_e$ , ml equiv.<sup>-1</sup>) volumes of the ion exchangers at atmospheric (superscript zero) and high (superscript p) pressures. For the sake of correctness of the comparison, these volumes are referred to the corresponding conventional volumes of the ion exchanger in the H<sup>+</sup> form. This was done as follows. First, the water contents of each ionic form [( $W_M$ )<sup>0</sup>, g H<sub>2</sub>O per gram of dry M<sup>+</sup> ion exchanger] were determined from experiment which were then converted by the usual procedure into the specific weight [( $W_M$ )<sub>H</sub><sup>0</sup>, g H<sub>2</sub>O per gram of dry H<sup>+</sup> ion exchanger]. Then the equivalent water content was calculated using the ion-exchanger capacities. Using the value of the water content obtained, the specific volume of the ion exchanger referred to the hydrogen form was further obtained according to the equation<sup>14</sup>

$$(V_M)_H^0 = (W_M)_H^0 + 0.63 \quad (4)$$

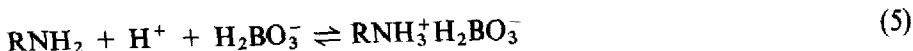
Subsequently using the capacity values, the equivalent volumes of different ionic forms of sulphonated cation exchangers were found. From the relative changes in the ion-exchanger volume at high pressures compared with atmospheric pressure, determined by means of the optical cell, it possible to calculate the corresponding values of ( $V_M$ )<sub>H</sub><sup>p</sup> and ( $V_e$ )<sub>H</sub><sup>p</sup>, using eqn. 4, also the water contents at high pressures, ( $W_M$ )<sub>H</sub><sup>p</sup> and ( $W_e$ )<sub>H</sub><sup>p</sup>. These results are also given in Table II.

## DISCUSSION

### *First type system*

The equation for calculating the apparent equilibrium constant depends on the

sorption mechanism. Thus, it is possible that, together with the mechanism of sorption of a weak acid by a polyamine (eqn. 2), boric acid sorption will proceed by the mechanism of amine interaction with a strong acid:



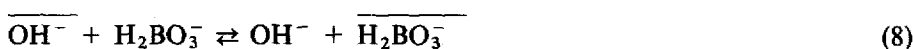
as the increase in pressure will result in an increase in boric acid dissociation:



(boric acid is assumed to be monobasic<sup>11</sup>). Then the apparent equilibrium constant for reaction 5, *i.e.*, for the acid mechanism, can also be calculated according to eqn. 3. The sorption of a weak acid from a dilute solution by a free polyamine may also proceed by the ordinary ion-exchange mechanism. Then, together with reaction 6 we must also take into account the ionization of the insoluble polybase:



the ion-exchange reaction:



and the formation of water (taking into account reactions 6 and 8):



The equation for the calculation of the apparent equilibrium constant of the ion-exchange mechanism will be

$$K = \frac{\bar{m}_{\text{RNH}_3^+} \cdot \bar{m}_{\text{H}_2\text{BO}_3^-}}{\bar{m}_{\text{RNH}_2} \cdot m_{\text{H}_3\text{BO}_3}} \quad (10)$$

Table I lists the values of  $K$  calculated according to eqn. 10 and the corresponding  $\Delta V$  values. It can be seen that the apparent equilibrium constant increases with increasing pressure and at 8 kbar it exceeds the atmospheric values by factors of 14.5 and 61.5 when calculated for the acid mechanism and the ion-exchange mechanism, respectively. However, the change in relative compressibility with pressure is not uniform (with the  $\Delta V$  values remaining negative over the whole pressure range studied). Thus, at pressures up to 3 kbar the change in the partial molar volume relative to atmospheric pressure remains constant. At higher pressures the effect of pressure on the boric acid sorption sharply decreases and is very small at 8 kbar. The values of  $\Delta V$  in Table I show the overall volume effect of the reactions, *i.e.*, they are summarized over the individual volume effects of the parallel-consecutive ionization and sorption reactions proceeding at high pressures. These volume effects may be either negative or positive. Lack of literature data on the change in  $\Delta V$  for reactions 2 and 5 does not allow us to compare directly the experimental value of the change in the total volume with the contribution to it from the individual stages of the sorption by

the acid mechanism. For the ion-exchange sorption mechanism the individual contributions can be determined as follows.

It was found<sup>15</sup> that the volume effect of reaction 6 is negative, being equal to  $23.6 \text{ cm}^3 \text{ mol}^{-1}$  at atmospheric pressure, *i.e.*, there will be a considerable decrease in the system volume with increasing pressure, which will favour reactions 5 and 8. For the ion exchangers such information is not available, but here we can make use of the known relationship that the  $pK$  values of an ion exchanger are comparable to the  $pK$  values of monomeric organic compounds having polar groups of the same chemical nature<sup>2</sup>. For example, for mono- and dimethylamine dissociation the values of  $\Delta V$  were found to be  $-26.4$  and  $-27.2 \text{ cm}^3 \text{ mol}^{-1}$ , respectively, at 1 bar pressure<sup>16</sup>. Consequently, with increasing pressure reaction 7 will be shifted forwards, which will favour the ion-exchange reaction 8.

A small increase in the degree of water dissociation due to pressure<sup>17,18</sup> is of minor importance in considering the boric acid sorption, as it is quantitatively more important to take into account the formation of water from the ions. From reaction 6 protons are liberated into the solution while the ion-exchange reaction 8 produces hydroxyl ions. The neutralization reaction 9 is accompanied by ion desolvation and, hence, the volume effect of this reaction is positive, being equal to the water ionization effect in its absolute value. Let us further assume that the ions participating in reaction 8 will only slightly change their partial molar volumes as they go from the ion-exchanger phase into the solution and *vice versa*. Such an assumption is justified by the results of a study<sup>4</sup> which showed that the values of the effective volumes of  $\text{Na}^+$  and  $\text{Cl}^-$  ions in a weakly dissociated ion-exchanger phase and in the outer solution are similar to each other. Therefore, the volume effect of reaction 8 can be neglected. The results of the above studies are summarized in the lower part of Table I for a pressure of 3 kbar, as the literature gives no dissociation data for some of the system components for higher pressures.

The expression for the overall value of  $\Delta V$  in the boric acid sorption by the ion-exchange mechanism which takes into account the partial reaction volume effects can be written as follows:

$$\Delta V = |\Delta V_{(6)}| + |\Delta V_{(7)}| + |\Delta V_{(8)}| + |\Delta V_{(9)}| \quad (11)$$

where the number of reactions is given in parentheses. Eqn. 11 makes it possible to calculate the values of  $\Delta V$  for 1 bar and 3 kbar using the data presented in Table I and to compare them with the experimental values. Thus, with the average value of the amine electrostriction of  $-26.8 \text{ cm}^3 \text{ mol}^{-1}$  and the  $\Delta V_{(8)}$  value taken to be zero, the calculated values of  $-\Delta V_{p=1 \text{ bar}}$  and  $-\Delta V_{p=3 \text{ kbar}}$  will be  $29.0$  and  $20.3 \text{ cm}^3 \text{ mol}^{-1}$ , respectively. The experimental values of these parameters are  $19.1 \text{ cm}^3 \text{ mol}^{-1}$ . For 3 kbar the difference is only  $1.2 \text{ cm}^3 \text{ mol}^{-1}$ , which appears to be a reasonable value when we consider the assumptions made. This difference is sharply increased when the values of  $\Delta V$  are compared under normal conditions. From this it can be concluded that at low pressures the sorption proceeds mainly by the acid mechanism whereas at pressures of 3 kbar and probably higher it takes the ion-exchange path.

### Second type system

From Table II, it can be seen that in all instances there is an increase in the

water contents of the ion exchangers under the effect of pressure. It appears that as the pressure is raised the dissociation of the ion pairs between the fixed ions and the counter ions in the ion-exchanger phase increases<sup>19</sup>, which, in turn, causes an increase in the number of osmotically active particles and, hence, further swelling of the ion exchanger. The considerable changes in selectivity under pressure cannot be accounted for by the electrostriction effect during the dissociation of the ion pairs, because for the 1,1-charge ions this effect is very small, being equal to approximately  $-1 \text{ cm}^3 \text{ mol}^{-1}$  (ref. 14). Within the framework of Gregor's theory, the main reason for the variation of the ion-exchange constant  $K_B^A$  under pressure is the appreciable change in the solvent content (and hence in the swelling pressure), as

$$RT \ln K_B^A = \pi (v_B - v_A) \quad (12)$$

where  $\pi$  is the swelling pressure (atm) and  $v_i$  is the partial molar volume of the  $i$ th ion.

From the values obtained of the equivalent ion-exchanger volumes in different ionic forms at atmospheric and high (400 bar) pressures, we calculated the swelling pressure in the ion-exchanger grains using the published procedure<sup>20,21</sup>. A linear correlation was found between the equivalent volumes of polystyrene  $M^+$  form ion exchangers, which were converted into the  $H^+$  form, and the swelling pressure. For an ion exchanger with a degree of cross-linking of 8% the relationship is

$$(V_e)_H = 0.807\pi + 192 \quad (13)$$

From the values of  $(V_e)_H^0$  and  $(V_e)_H$  given in Table II, we calculated according to eqn. 13 the swelling pressures for the KU 2-X8 ion exchanger at atmospheric and higher pressures, and the results are given in Table II. In several instances the swelling pressure was increased by more than 10%.

Because of the lack of such correlation dependences for ion exchangers with 4% of divinylbenzene we were not able to perform such calculations for the Dowex 50W-X4 ion exchanger. We can, however, make a comparative analysis of the changes in the matrix framework rigidity under the effect of pressure, knowing that the swelling pressure is directly proportional to the degree of cross-linking for polystyrene ion exchangers<sup>20,21</sup>. For this we can make a rough approximation that the framework rigidity is directly proportional to the water content. The conventional change in the degree of cross-linking for the Dowex 50W-X4 ion exchanger calculated in this way is given in Table II (in parentheses).

The value of the swelling pressure and the changes in the degree of cross-linking obtained in this work can form the basis for conclusions about the direction of the changes in the sorption properties of different ion pairs under the effect of pressure. For example, Horne *et al.*<sup>3</sup> found that in the  $K^+ - H^+$  system the exchange equilibrium remains unchanged for a sulphonated polystyrene cation exchanger with 8% of divinylbenzene at 400 bar. The same follows from the results in Table II, as the changes in swelling pressures for the individual components of this system are small. On the other hand, the considerable difference in the relative swelling pressure



during the sorption the ion exchanger will prefer the ion that causes least swelling.

Thus, measurements of the relative swelling of individual ionic forms of ion exchangers make it possible to predict the direction and, with a certain approximation and taking into account Gregor's eqn. 12, also the extent of the ion-exchange processes that takes place at high hydrostatic pressures. The effect of changes in the swelling pressure is also of some importance in systems with weakly dissociating ion exchangers, but its relative contribution to the final selectivity of the ion exchangers is small.

## CONCLUSION

The results of this work show that in ion-exchange chromatographic separation processes carried out at elevated pressures the shapes of the output curves may be changed relative the normal conditions. Therefore, the dependence of  $K$  on  $p$  should be taken into account and in calculations appropriate corrections should be introduced into the theoretical equations.

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