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The selectivity of cellulose gels for simple salts

The separation of cations and anions in gel chromatography has been the subject of recent investigations (see, for example, the papers by EGAN[1] and UENO et al.[2] and the references contained therein. Following the synthesis of highly cross-linked cellulose gels, it was of interest to compare the selectivities of such gels for salts with those of other water-swollen gels having a comparable degree of cross-linking.

Experimental

Gel preparation. The synthesis of the cellulose gel (cellulose-20) was carried out as follows. Viscose (9.2 % cellulose, 7.5 % NaOH, 28 % CS$_2$) (1000 g) was placed in a round-bottomed flask with 3 l of ethylene dichloride, 67 g of emulsifier (Cremophor EL, BASF, Ludwigshafen) and 1 g of sodium borohydride. The contents were stirred vigorously for 2 h at room temperature to effect dispersion into microdrops. The temperature was then raised to 40° and 18.5 g of epichlorohydrin were added (20 % w/w based on cellulose). Stirring was maintained at a reduced rate for 15 h. Regeneration was accomplished by pouring the mixture into 6 l of a 50 % (v/v) mixture of ethylene dichloride and acetic acid. After 30 min with gentle stirring, the solid material was filtered off and washed well with water. The aggregated gel beads were suspended in water and dispersed with a laboratory blender. The beads were washed with acetone, then water and finally autoclaved in 3 l of 2 M sodium hydroxide solution containing 15 g of sodium borohydride at 120° for 2 h. The material was washed with acetic acid to bring the pH to 5–6. The gel beads were finally washed with hot water, then cold water and stored as a suspension in 0.02 % sodium azide solution. The beads were colourless and had a quite uniform, spherical shape with sizes in the range 20–70 μm.

Apparatus. The preparation of the columns and the instrumental set-up for gel chromatography have been described previously[3].

Results and discussion

Elution volumes and partition coefficients for some simple salts on cellulose-20 with de-ionized water as eluent are given in Table I.

Considerable differences in elution volume were observed (Fig. 1) for the chlorides of several cations. The order of elution does not bear a simple relationship to the hydrated radii of the ions. Similar results were obtained by EGAN[1] with these salts in Sephadex G-10 and polyacrylamide P-2 gels using the same eluent. Separation according to molecular size would, however, hardly be expected in this solute size range and with the gel used in this work, having a comparatively open structure, allowing fractionation of polyethylene oxides up to a molecular weight of 5000. Instead, the elution order agrees with that found for carboxylic acid cation exchangers and is exactly the reverse of that found with sulphonic acid cation exchangers[4]. The latter bind the most hydrated cations the least strongly, i.e., Li$^+$ elutes first. As found by GREGOR et al.[5], resins with carboxylic acid groups prefer the larger, more strongly hydrated and more polarisable cations. Thus association between a cation and the

TABLE I

ELUTION DATA FOR SALTS ON CELLULOSE-20 (DE-IONIZED WATER)

Blue dextran, $V_0 = 31.45$ ml; $V_T = 45.50$ ml. Column loading $= 0.3$ mg.

Salt	V_e (ml)	K_{av}[a]	Ionic radius (Å)
			Cation
LiCl	39.5₁	0.574	0.60
NaCl	39.0₅	0.541	0.95
KCl	38.2₂	0.482	1.33
MgCl₂	37.7₇	0.450	0.65
CaCl₂	37.7₄	0.447	0.99
AgNO₃	38.05	0.470	1.26
NaNO₃	37.2₈	0.415	0.95
TlNO₃	36.1₇	0.336	0.95
CsNO₃	35.7₃	0.304	1.69
			Anion
NaF	39.19	0.551	1.36
NaCl	38.40	0.541	1.81
NaBr	36.50	0.360	1.95
NaI	Adsorbed		2.20
Na₂SO₄	34.97	0.250	3.79

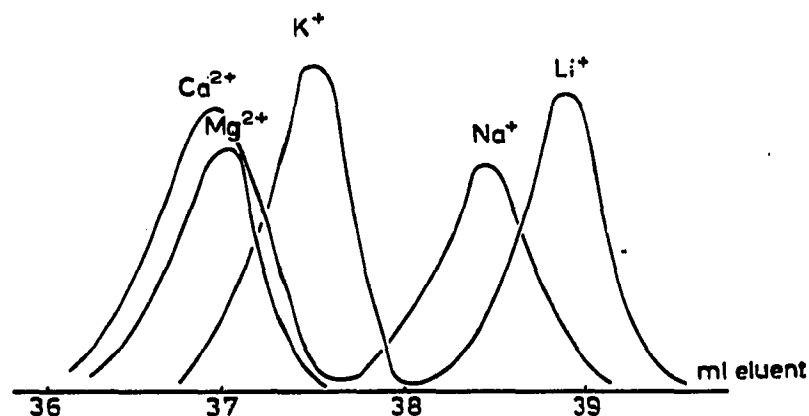[a] $K_{av} = \dfrac{V_e - V_0}{V_T - V_0}$.

Fig. 1. Cellulose gel chromatography (de-ionized water) of the chlorides of different cations. The elution sequence is the reverse of that found with sulphonic acid cation exchangers.

fixed anion appears to be the principal effect. It can be concluded that the cellulose gel behaves a typical weak-acid ion exchanger. It is surprising, however, that calcium chloride and magnesium chloride are more excluded from the gel than sodium chloride.

Cellulose gels certainly contain small quantities of carboxyl groups as the result of oxidative degradation of the polysaccharide chains. These may be non-terminal or terminal, depending on the oxidative mechanism. It has long been re-cognized that both dextran and polyacrylamide gels also possess such fixed charged groups. Their presence is observed in gel chromatography by the partial exclusion of,

TABLE II

ELUTION VOLUMES AND PARTITION COEFFICIENTS FOR SOME SIMPLE COMPOUNDS

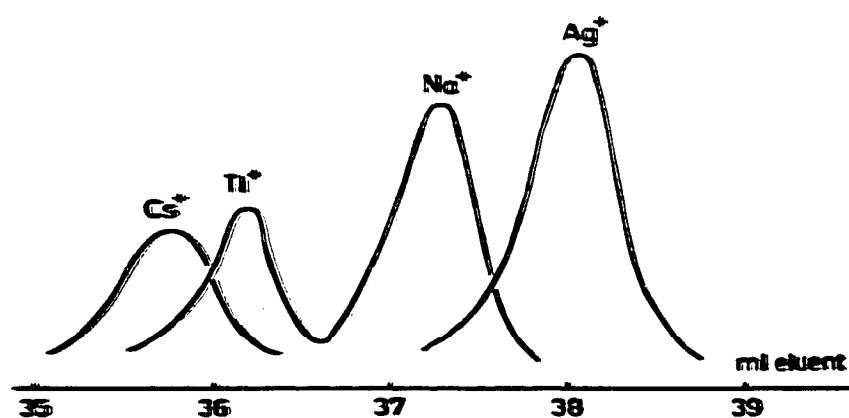| Compound	V_e (ml)	K_{av}
Glucose	43.40	0.850
Glucuronic acid	35.85	0.320
Formic acid	40.15	0.619
Formamide	44.05	0.89_n
Methanol	43.44	0.853

Fig. 2. Cellulose gel chromatography (de-ionized water) of the nitrates of different cations.

for example, acidic solutes from the gel phase; compare glucose and glucuronic acid and methanol and formic acid in Table II.

With the nitrates of Ag⁺, Na⁺, Tl⁺ and Cs⁺, the order of elution is no longer a simple reversal of that observed with sulphonic acid resins (Fig. 2). In the latter, ion binding increases in the sequence $Na^+ < Cs^+ < Ag^+ < Tl^+$. Clearly, electrostatic forces are not the only operative factors, as a heavy metal cation such as Ag^+ binds more tightly than the Na^+ cation which is smaller in size. This was anticipated, since silver nitrate has been used as a stain for cellulosic materials. Cation adsorption is thus of importance.

It is observed that sodium nitrate, for example, elutes in a smaller volume than
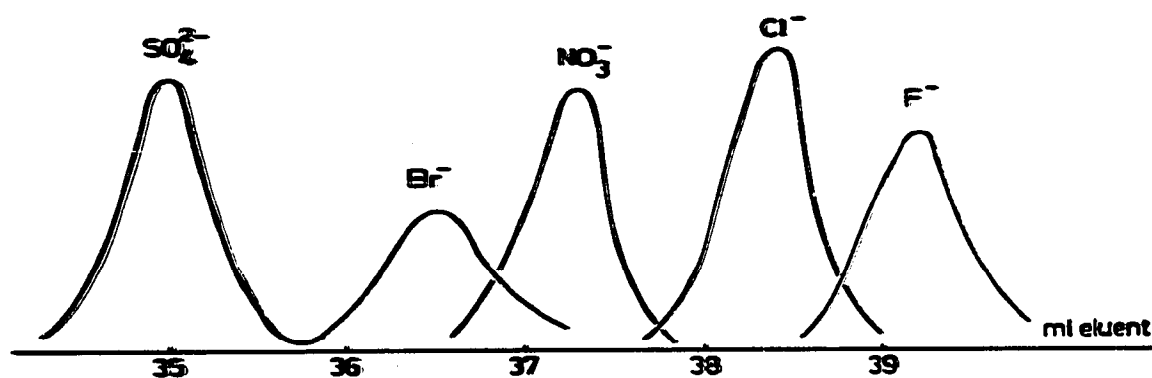

Fig. 3. Cellulose gel chromatography of the sodium salts of different anions. The elution order is the reverse of that found with sulphonic acid cation exchangers.

sodium chloride, indicating that the degree of exclusion of the co-ion from the gel matrix must be taken into consideration; cf. the elution sequence of anions in Fig. 3. This may reflect the greater tendency of sodium chloride to migrate as an ion pair owing to the higher charge: radius ratio of the chloride ion compared with that of the nitrate ion.

Data for the elution of the sodium salts of various anions are given in Table I and Fig. 3. As with the alkaline earth cations, the order is again the reverse of that for sulphonic acid cation exchangers: $F^- < Cl^- < NO_3^- < Br^-$, as would be expected for a carboxylic acid exchanger. The SO_4^{2-} ion, in accordance with the Donnan potential, is the most excluded from the gel. The I^- ion, on the other hand, is strongly adsorbed, indicating a specific interaction between the gel and this co-ion.

It is concluded that the partition coefficients of simple salts are the result of several interacting factors. These include the charge on the ion, its hydrated radius, the nature of the co-ion, the specific interaction of the counterion or co-ion with the gel matrix and fixed charges. Although an inverse relationship was noted between the elution order in the present work and that found for sulphonic acid cation exchangers, this does not appear to be generally valid for gels that have a low content of carboxyl groups. There is, unexpectedly, no obvious relationship between the present elution orders and those reported[1] for dextran and polyacrylamide gels with de-ionized water as eluent. It appears that the nature of the gel matrix, as distinct from the identity of the fixed charges, is of importance in determining elution order.

Also noteworthy are the generally low values of the partition coefficients (< 0.6), reflecting substantial exclusion of all the salts from the gel bed. These observations exemplify the unsuitability of simple salts for the determination of internal solvent volumes of gels when water is used as the eluent.

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