

CHROM. 5349

Ion-exchange chromatography of calcium and magnesium in mixed dimethyl sulphoxide-water media

The effect of dimethyl sulphoxide (DMSO) on the anion-^{1,2} and cation-exchange³⁻⁶ behaviour of several elements has recently been investigated by several authors. JANAUER studied the ion-exchange properties of Ca^{2+} , Mg^{2+} and several other metal ions⁴. The present article describes in more detail the ion-exchange and the separation possibilities of Mg^{2+} and Ca^{2+} in this medium.

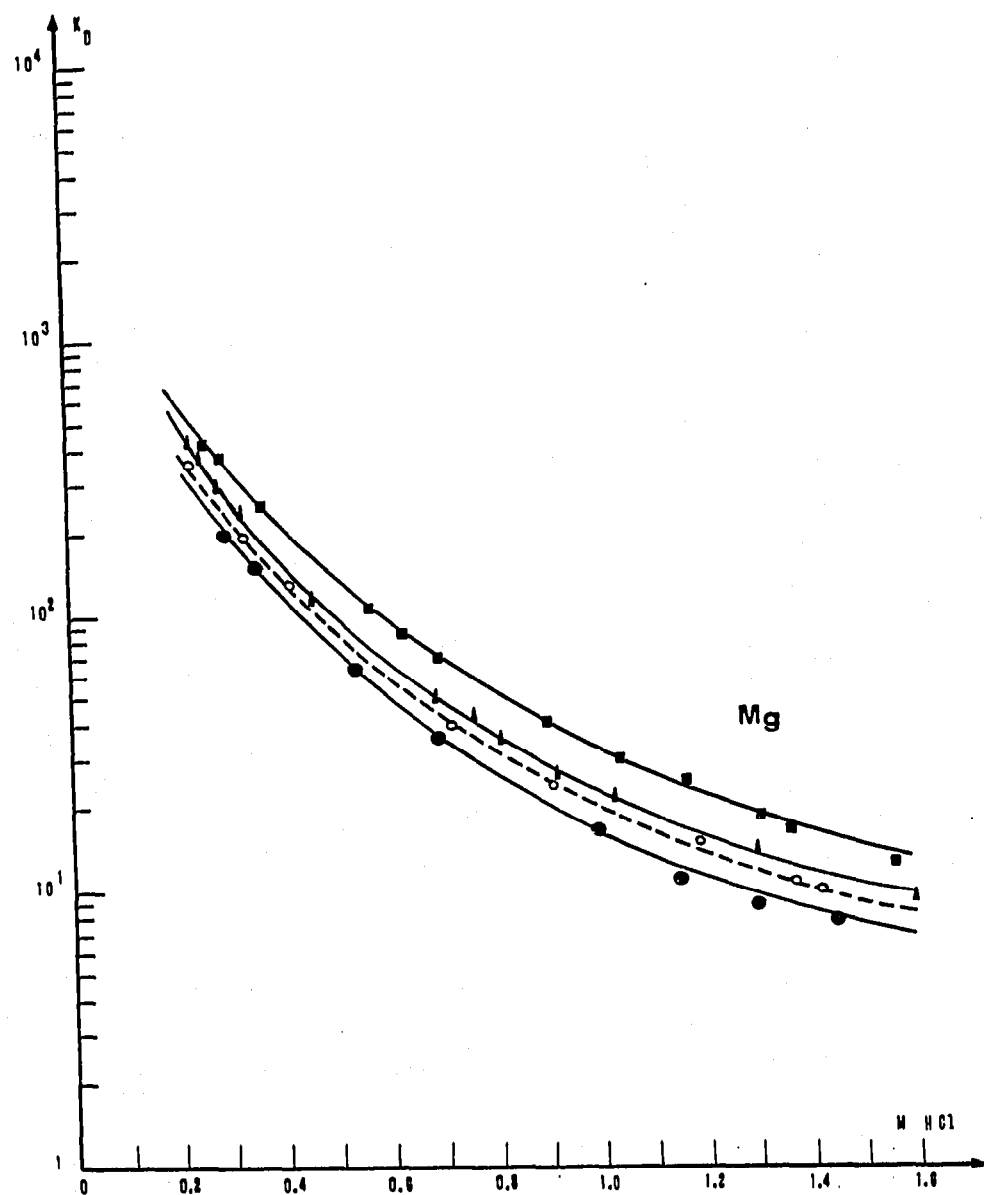


Fig. 1. Distribution coefficient of Mg^{2+} as a function of HCl concentration in mixtures of 0% (\circ — \circ), 35% (\bullet — \bullet), 50% (\blacktriangle — \blacktriangle) and 69% v/v DMSO (\blacksquare — \blacksquare).

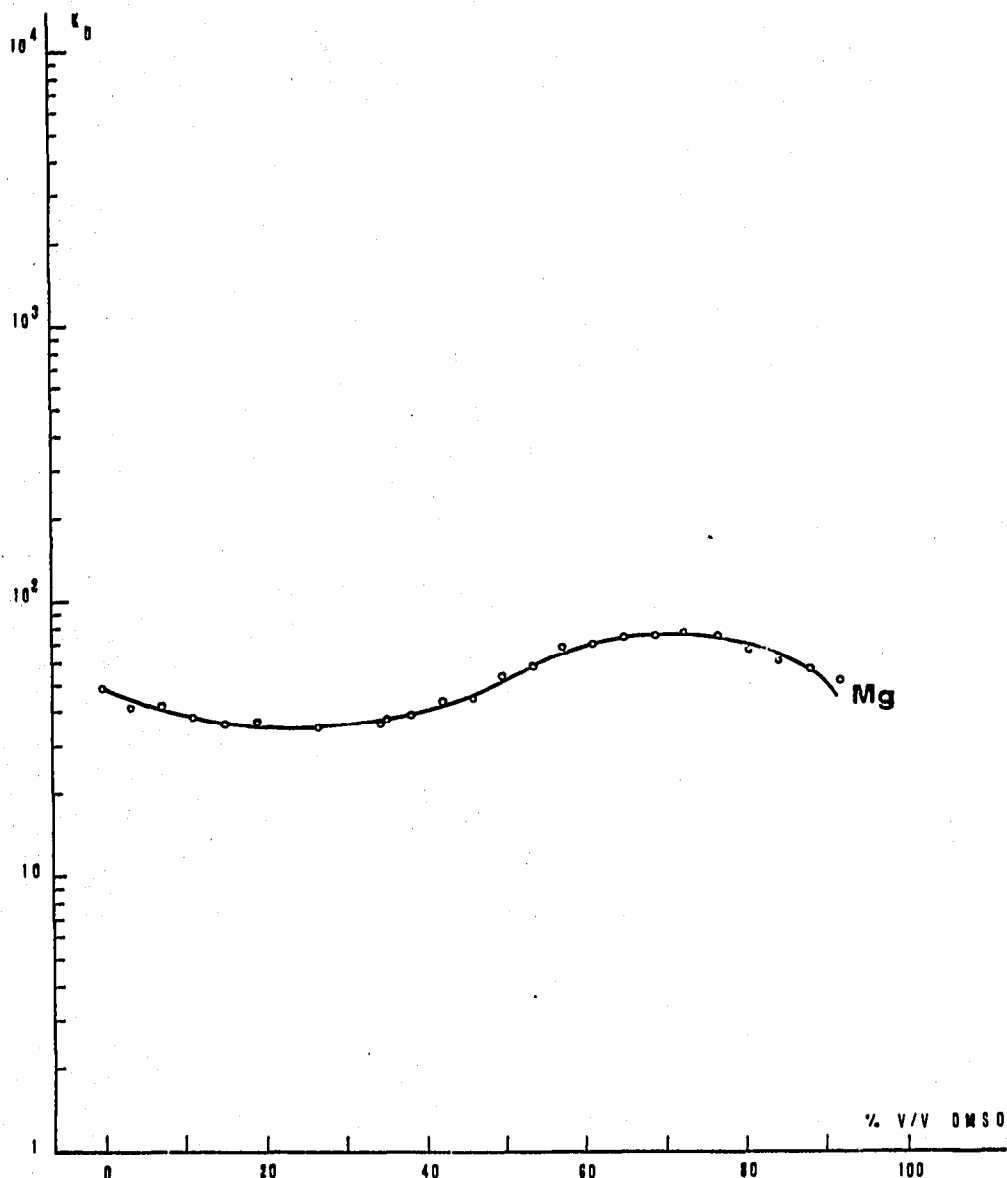


Fig. 2. Distribution coefficient of Mg^{2+} in mixtures of water -DMSO-HCl (overall concentration of HCl 0.69 *N*) as a function of the DMSO concentration.

Experimental

Apparatus. A Vitatron UC200 colorimeter microtitrator and a Radiometer automatic photometric titrator were used for the chelatometric determination of the metal ions.

Reagents. The DMSO used was spectrograde; all other reagents were reagent grade. Dowex 50W-X8 resin, 200-400 mesh, hydrogen-form, was used throughout this study. Chloride salts of Ca and Mg were used to prepare stock solutions containing 6 mg Ca/ml and 4 mg Mg/ml, respectively.

Procedure. The adsorbabilities, expressed as weight distribution coefficients, K_D , were determined by batch and column methods.

In batch experiments, exactly weighed 1.0000-g amounts of the dry, pre-

treated resin were equilibrated with 1 ml of the appropriate metal stock solution (containing 0.33 mequiv./ml of the metal ion) and 25 ml of a solvent mixture consisting of 0–100% of DMSO and 100–0% of hydrochloric acid, 1–12 *M*.

In all the column elution experiments, a column of 20 × 0.7 cm was used, packed with 1.0000 g of the dry pretreated resin. 500 μ l of a mixture containing 2 mg Mg and 4 mg Ca were pipetted on the column, which was eluted at a flow rate of 0.2–0.3 ml/min.

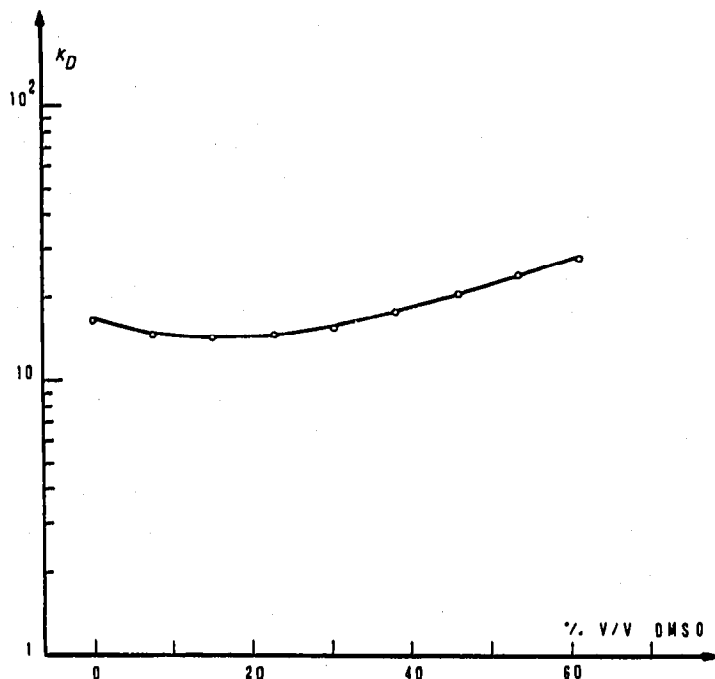


Fig. 3. Distribution coefficient of Mg^{2+} in mixtures of water–DMSO– HNO_3 (overall concentration of HNO_3 1.11 *N*) as a function of the DMSO concentration.

Results and discussion

The distribution constants decrease with increasing HCl molarities in all the DMSO– H_2O mixtures (Fig. 1). The influence of DMSO content on the distribution constants is shown in Fig. 2. A maximum is found at $\pm 70\%$ v/v DMSO. At this composition (DMSO– H_2O molar ratio 1:2) a particularly stable structure of the liquid phase exist⁷. As noted by JANAUER⁶, extreme values of viscosity, enthalpy of mixing, density, etc., occur at the same composition of the solution. According to the competitive solvation theory of ion-exchange selectivity⁸, the maximum in K_D can be interpreted as an exclusion from a highly structured external phase of the ion which is least in need of solvation.

A more unexpected result is that a minimum is also found (at $\pm 30\%$ v/v DMSO). Because it is known that anions are very reactive in DMSO media⁷, it was thought that complexation of Mg^{2+} with Cl^- could be responsible for this phenomenon. However, exactly the same behaviour was found in DMSO– H_2O – HNO_3 mixtures (Fig. 3). Since NO_3^- is a much less reactive ligand than Cl^- , this makes the complexation hypothesis improbable.

Table I gives a number of K_D values for Ca^{2+} and Mg^{2+} in different media,

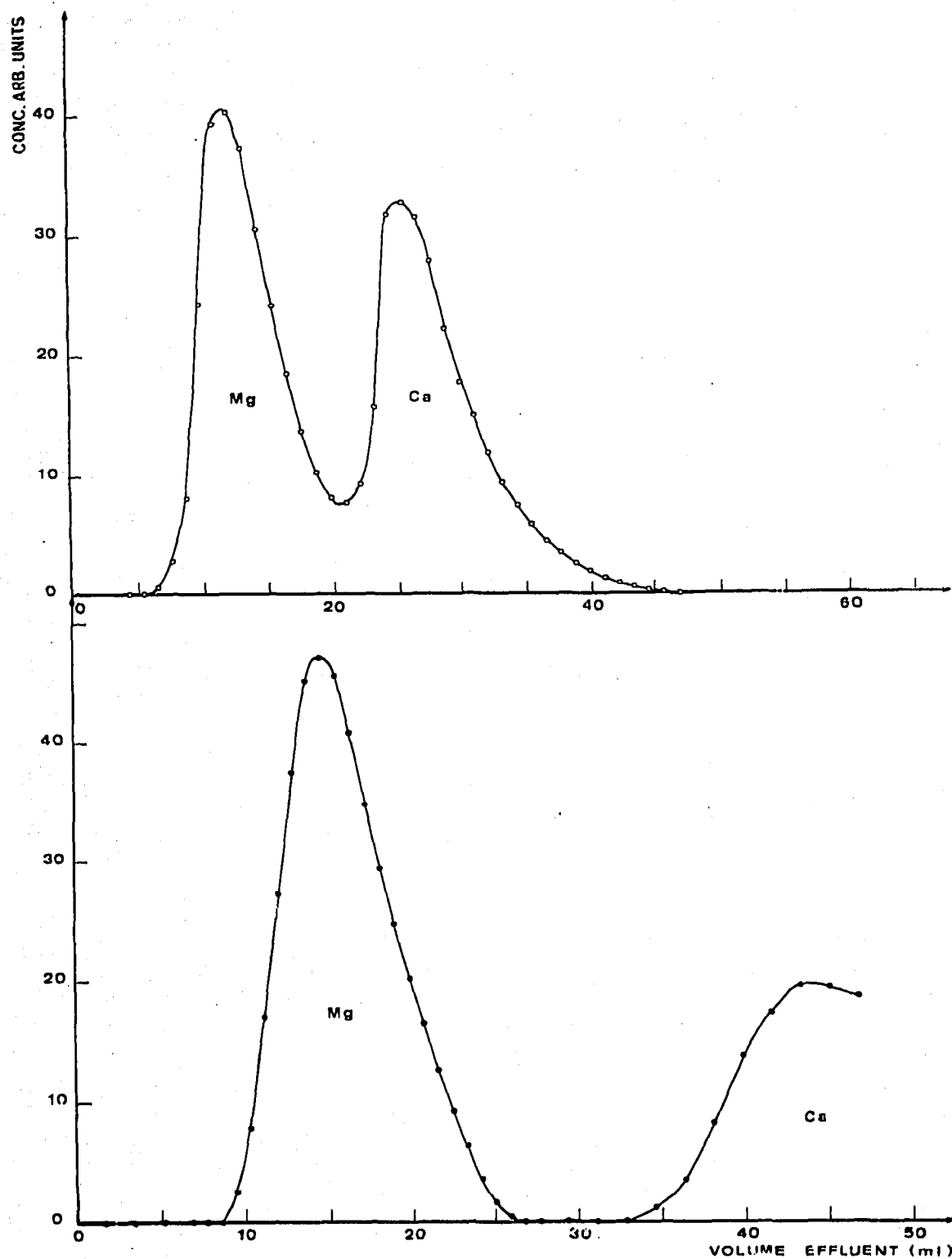


Fig. 4. Separation of Ca^{2+} and Mg^{2+} with 2.02 N HCl (○—○) and with 50% v/v DMSO/2.02 N HCl (●—●).

TABLE I

DISTRIBUTION AND SEPARATION COEFFICIENTS OF Mg^{2+} AND Ca^{2+}

DMSO (% v/v)	HCl (N)	K_D		β
		Mg^{2+}	Ca^{2+}	
0	1.01	18.8	47.4	2.5
0	2.02	5.12	11.8	2.3
35	2.61	2.41	6.90	2.9
35	3.37	1.68	5.20	3.1
35	4.67	0.61	4.04	6.6
50	1.24	13.3	43.0	3.2
50	2.02	7.27	21.4	2.9
50	2.37	3.53	15.3	4.3
50	3.08	2.36	9.76	4.1
50	4.50	2.05	7.33	3.6

and the corresponding separation factors, β . The β -value is larger in DMSO media, so that better separations should be possible. This was tested with several media of different composition. It was found that good separations can be achieved with quite small volumes of eluting agents. However, the separations are no better or only slightly better than separations in pure aqueous media (Fig. 4). This is due to the fact that the increase in β is offset by an increase of the HETP. This is not surprising since in the range considered, the viscosities increase with increasing DMSO content⁹. Therefore, the diffusion coefficient must decrease. Taking into account Glueckauf's equation for the HETP, this must lead to an increase in HETP. Because of this phenomenon, the addition of organic solvents does not always result in better resolution. In order to be able to evaluate the effect of solvent composition on HETP, a systematic investigation of HETP as a function of the composition of the mixed aqueous-organic eluting solution is now being carried out at this laboratory.

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