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INFLUENCE OF TEMPERATURE AND DEGREE OF RESIN CROSSLINKING ON THE ANION EXCHANGE OF PHOSPHATE COMPLEXES OF Ga(III) AND In(III)

R. DYBCZYŃSKI, H. POLKOWSKA-MOTRENKO and R. M. SHABANA*

Department of Analytical Chemistry, Institute of Nuclear Research, ul. Dorodna 16, 03-195 Warsaw (Poland)

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SUMMARY

The effect of temperature and degree of resin crosslinking on the anion exchange of phosphate complexes of Ga(III) and In(III) on Dowex 1 has been investigated. It was found by slope analysis that gallium and indium in orthophosphoric acid solution form complexes of different charge, viz., $[\text{Ga}(\text{HPO}_4)_2]^-$ and $[\text{In}(\text{HPO}_4)_3]^{3-}$. The selectivity coefficients for the two complexes were determined from the elution curves for the temperature range 5–85° and nominal degrees of resin crosslinking of 2, 4 and 8. From the data obtained the free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) changes for the ion-exchange reactions in question were calculated. Also, the influence of temperature and degree of resin crosslinking on the plate height was evaluated and the optimal conditions for the separation of the two metals in this system were established.

INTRODUCTION

Temperature and degree of resin crosslinking are the important factors that influence the efficiency of ion-exchange separations^{1,2}. On the other hand, investigation of the thermodynamics of ion-exchange reactions sometimes permits one to achieve a deeper insight into the mechanism of these reactions³ and also to throw some light on the structure of complex ions in solution⁴.

In this paper, the effects of degree of resin crosslinking and temperature on the anion exchange of gallium and indium phosphate complexes were examined and optimal conditions for the separation of these two metals in the system Dowex 1–aqueous orthophosphoric acid were established.

EXPERIMENTAL

Resins

Dowex 1, a strongly basic ion-exchange resin with quaternary ammonium

* Guest scientist from Atomic Energy Establishment, Cairo, Egypt.

functional groups, was used. Methods of grinding and fractionating the resins and the microscopic determination of particle size have been described earlier². The resin was converted into the phosphate form by passing excess of 3 *M* orthophosphoric acid solution through the hydroxyl form of the resin and washing with deionized water. The resin was then air-dried and its water content was determined by drying it in an oven at 105° to a constant weight. The exchange capacity of the strongly basic groups (Z_s) was determined by converting a known amount of the resin in the hydroxyl form into the chloride form by using an excess of 1 *N* sodium chloride solution. After washing the bed with deionized water until chloride was no longer detected in the eluate, the chlorides were eluted from the resin with 1 *N* sodium hydroxide solution and determined titrimetrically⁵.

The total exchange capacity was determined in an analogous manner except that the resin was converted into the chloride form with 1 *N* hydrochloric acid and washed with absolute ethanol instead of water. The water content of the swollen resins was determined by a modified method of Pepper *et al.*⁶ (see ref. 7).

The bed density (d_z) (grams of dry resin in a given form per millilitre of the bed) was determined by measuring the volume of a known amount of the resin in deionized water in a graduated cylinder.

Radioactive tracers and reagents

The tracers used were ⁵⁴Mn ($t_{1/2} = 291$ days), ⁷²Ga ($t_{1/2} = 14.2$ h) and ^{114m}In ($t_{1/2} = 50$ days), where $t_{1/2}$ = half-life. ⁵⁴Mn was supplied by the Radioisotope Production and Distribution Centre (Świerk, Poland) while ⁷²Ga and ^{114m}In were prepared by neutron irradiation of the spectrally pure nitrates (Johnson Matthey, Royston, Great Britain) in the EWA nuclear reactor at Świerk. Orthophosphoric acid solutions were prepared from 85% analytical-reagent grade material (P.O.Ch., Gliwice, Poland).

Apparatus and procedures

Glass micro-columns of I.D. 0.2 cm surrounded by water-jackets were used. A constant temperature ($\pm 0.2^\circ$) was maintained by employing a Höppler ultrathermostat. A microdose pump (Unipan, Poland) was used to exert the desired pressure. The tracer solution (about 20 μ l) was applied to the top of the bed in the column and elution was carried out with 0.1–1.0 *M* orthophosphoric acid solutions. The loading did not exceed 1% of the exchange capacity of the resin. Individual fractions were collected in flat-bottomed test-tubes using a drop counter and a fraction collector (Unipan). The count rate was measured by means of a 2 \times 2-in. well-type NaI(Tl) counter. The gamma-spectrometric measurements were carried out with the aid of a Ge(Li) detector (active volume 70 cm³, resolution 3.1 keV for the 1332-keV line of ⁶⁰Co) and a Didac 4000 pulse-height analyser.

All calculations were made with the aid of a MULTI-8 (Intertechnique) minicomputer using a simple program written in Basic language.

RESULTS AND DISCUSSION

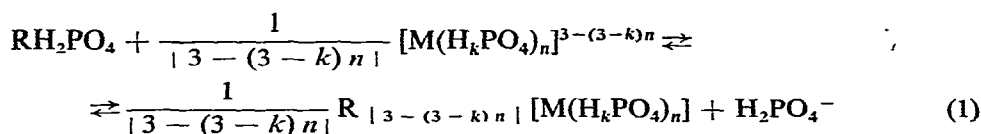
The properties of the resin used are summarized in Table I, from which it can be seen that all of the resins can be considered to be practically monofunctional. As in a previous study⁷, the degree of crosslinking of the resin could conveniently be

TABLE I
PROPERTIES OF THE RESIN USED

Resin	Exchange capacity [mequiv./g dry resin (Cl ⁻)]		Bed density [g dry resin (H ₂ PO ₄ ⁻)/ml], d _z	Maximum water content [g H ₂ O/g dry resin (Cl ⁻)]		H ₂ O in air-dried resin (%)
	Z _s	Z _c		W _{H₂O} ^o	W _{H₂O} /Z _s	
Dowex 1-X2	4.21	4.41	0.163	2.901	0.691	41.89
Dowex 1-X4	3.80	3.82	0.307	1.075	0.283	13.25
Dowex 1-X8	3.61	3.68	0.465	0.692	0.192	16.74

characterized in terms of the specific water content, W_{H_2O}/Z_s (g/mequiv.), which was a linear function of the reciprocal of the nominal divinylbenzene content.

Using the method described earlier⁸, it was found that the ion-exchange resin in 0.1–1.0 M orthophosphoric acid solution is in the [H₂PO₄⁻] form. Hence, the ion-exchange reactions in this system for anionic phosphate complexes of Ga³⁺ and In³⁺ (M³⁺) cations can be written as follows:



where R represents the resin matrix. Orthophosphoric acid is a weak tribasic acid of which the first dissociation constant ($K_1 = 7.52 \cdot 10^{-3}$) exceeds the subsequent two ($K_2 = 6.31 \cdot 10^{-8}$, $K_3 = 1.26 \cdot 10^{-12}$). Hence, in aqueous orthophosphoric acid solutions only H₂PO₄⁻ anions are present in significant amounts. The selectivity coefficient (equilibrium quotient) for reaction 1 is given by

$$K_{H_2PO_4}^{B^{p-}} = \frac{N_{RdB} \cdot m_{H_2PO_4^-}^{|\frac{1}{p}|}}{N_{RH_2PO_4} \cdot m_{B^{p-}}^{|\frac{1}{p}|}} \quad (2)$$

where B^{p-} = anionic phosphate complexes of gallium or indium, N = mole fraction of a given ion in the resin phase and m = molality in solution.

For trace amounts of the complex ions in question the following relationship exists^{1,2} between the selectivity coefficient and the weight distribution coefficient, $\lambda_{d(B^{p-})}$ (amount per gram of dry resin [H₂PO₄⁻]/amount per millilitre of the solution):

$$\lambda_{d(B^{p-})} = \frac{(K_{H_2PO_4}^{B^{p-}})^{|p|} \cdot C_r}{m_{H_2PO_4}^{|\frac{1}{p}|} \cdot d} \quad (3)$$

where C_r = concentration of the resin phase (millimoles per gram of dry resin) and d = density of the solution.

For solutions of low ionic strength and tracer loadings, $K_{\text{H}_2\text{PO}_4^-}^{\text{BP}^-}$ can be assumed to be constant (the ratio of activity coefficients in solution should not vary significantly) and, from eqn. 3, it follows that

$$\frac{d \log \lambda_{d(\text{B}^{p-})}}{d \log m_{\text{H}_2\text{PO}_4^-}} = - \left| \frac{p}{1} \right| \quad (4)$$

The values of the distribution coefficients were calculated from the elution curves by means of the equation

$$\lambda_{d(\text{B}^{p-})} = \frac{U_{\text{max}}^{(\text{BP}^-)} - (U_0 + V)}{m_j} = U_{\text{max}}^{(\text{BP}^-)} - U_{\text{max}}^{(\text{Mn}^{2+})} \quad (5)$$

where U_{max} = retention volume of the ion in question, U_0 = dead volume of the column, V = free volume of the column and m_j = weight of the dry $[\text{H}_2\text{PO}_4^-]$ form of the ion-exchange resin in the column (grams). The Mn^{2+} ion, which shows no adsorption in this system, was used for the determination of the sum $U_0 + V$.

In Fig. 1, λ_d values of Ga(III) and In(III) phosphate complexes are presented

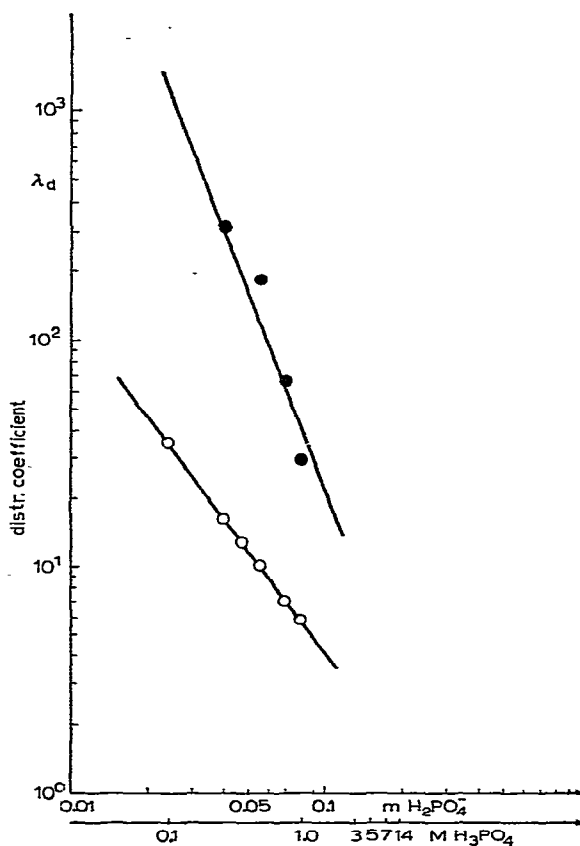
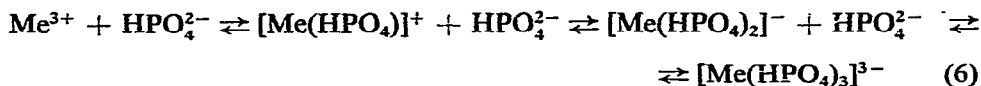


Fig. 1. Slope analysis for anionic phosphate complexes of Ga(III) and In(III). The abscissa gives the concentration of H_2PO_4^- ion (molality) and the corresponding concentration of orthophosphoric acid (molarity). \circ , Ga(III), slope = -1 ; \bullet , In(III), slope = -3 .

as a function of the molality of H_2PO_4^- ions in a log-log plot. It can be seen that straight lines with slopes of -1 and -3 for Ga(III) and In(III), respectively, were obtained, indicating that complex ions of different charge, probably $[\text{Ga}(\text{HPO}_4)_2]^-$ and $[\text{In}(\text{HPO}_4)_3]^{3-}$, respectively, exist in solution. In general, the equation of the complexing reaction for these trivalent cations could be written as



This is consistent with the suggestions of other workers⁹⁻¹¹.

As can be seen from Fig. 2, the values of $\log K$ are as a rule a non-linear function of $1/T$, indicating that the enthalpy changes are not constant throughout the temperature range investigated. By using the least-squares procedure described earlier^{4,12}, the selectivity coefficients for the ion exchange reactions

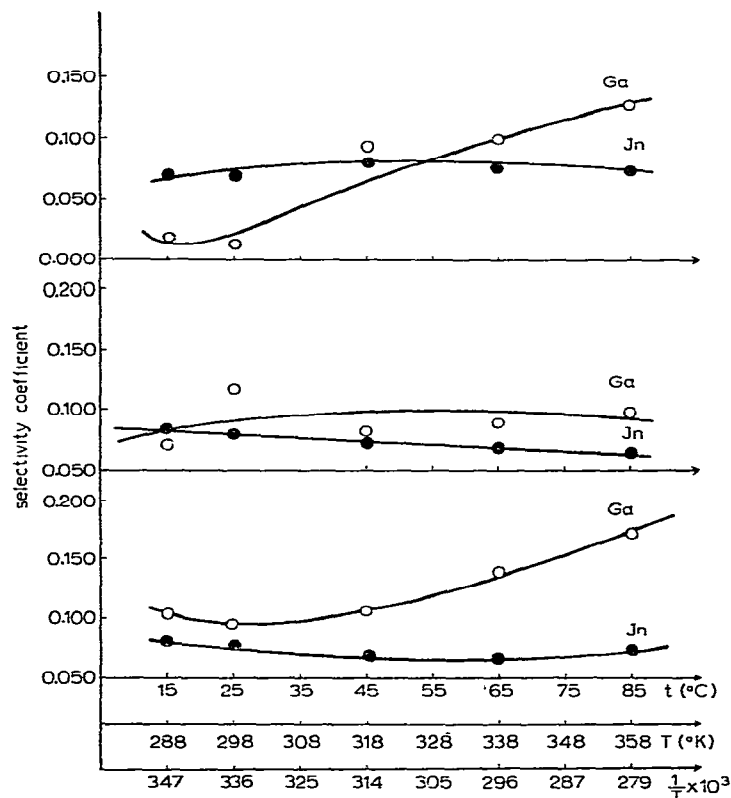
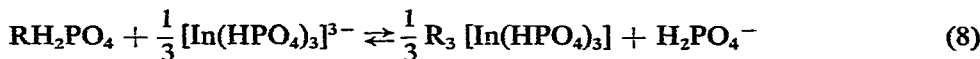


Fig. 2. Selectivity coefficients for the ion-exchange reactions 7 and 8 as a function of temperature. Points, experimental values; lines, calculated by least-squares procedure assuming $\Delta C_p^* = \text{constant}$ (i.e., $\Delta H^* = \Delta H^\circ + \Delta C_p T$). Top: Dowex 1-X8; centre, Dowex 1-X4; bottom, Dowex 1-X2.

and



were calculated for the temperature range 5–85° and are shown in Table II. From these data, the enthalpy changes:

$$\Delta H^* = -2.303 R \cdot \frac{d \log K}{d \left(\frac{1}{T} \right)} \quad (9)$$

TABLE II

SELECTIVITY COEFFICIENTS FOR ION-EXCHANGE REACTIONS 7 AND 8 AS A FUNCTION OF TEMPERATURE

Temperature (°C)	Dowex 1-X2		Dowex 1-X4		Dowex 1-X8	
	$K(\text{Ga})$	$K(\text{In})$	$K(\text{Ga})$	$K(\text{In})$	$K(\text{Ga})$	$K(\text{In})$
5	$1.072 \cdot 10^{-1}$	$8.715 \cdot 10^{-2}$	$7.801 \cdot 10^{-2}$	$8.587 \cdot 10^{-2}$	$6.263 \cdot 10^{-3}$	$6.621 \cdot 10^{-2}$
15	$1.016 \cdot 10^{-1}$	$8.134 \cdot 10^{-2}$	$8.323 \cdot 10^{-2}$	$8.362 \cdot 10^{-2}$	$1.405 \cdot 10^{-2}$	$7.182 \cdot 10^{-2}$
25	$1.004 \cdot 10^{-1}$	$7.703 \cdot 10^{-2}$	$8.745 \cdot 10^{-2}$	$8.106 \cdot 10^{-2}$	$2.677 \cdot 10^{-2}$	$7.608 \cdot 10^{-2}$
35	$1.024 \cdot 10^{-1}$	$7.388 \cdot 10^{-2}$	$9.063 \cdot 10^{-2}$	$7.827 \cdot 10^{-2}$	$4.486 \cdot 10^{-2}$	$7.895 \cdot 10^{-2}$
45	$1.088 \cdot 10^{-1}$	$7.167 \cdot 10^{-2}$	$9.282 \cdot 10^{-2}$	$7.532 \cdot 10^{-2}$	$6.677 \cdot 10^{-2}$	$8.044 \cdot 10^{-2}$
55	$1.184 \cdot 10^{-1}$	$7.028 \cdot 10^{-2}$	$9.406 \cdot 10^{-2}$	$7.228 \cdot 10^{-2}$	$8.946 \cdot 10^{-2}$	$8.066 \cdot 10^{-2}$
65	$1.321 \cdot 10^{-1}$	$6.942 \cdot 10^{-2}$	$9.443 \cdot 10^{-2}$	$6.918 \cdot 10^{-2}$	$1.092 \cdot 10^{-1}$	$7.973 \cdot 10^{-2}$
75	$1.506 \cdot 10^{-1}$	$6.917 \cdot 10^{-2}$	$9.401 \cdot 10^{-2}$	$6.609 \cdot 10^{-2}$	$1.226 \cdot 10^{-1}$	$7.781 \cdot 10^{-2}$
85	$1.739 \cdot 10^{-1}$	$6.936 \cdot 10^{-2}$	$9.290 \cdot 10^{-2}$	$6.301 \cdot 10^{-2}$	$1.278 \cdot 10^{-1}$	$7.512 \cdot 10^{-2}$

free energy changes:

$$\Delta G^* = -RT \ln K \quad (10)$$

and entropy changes:

$$\Delta S^* = \frac{\Delta H^* - \Delta G^*}{T} \quad (11)$$

were computed and are summarized in Table III. These are in fact differential values for equivalent fraction of a complex ion in the resin phase close to zero ($X_{B^m} \approx 0$).

It follows from Tables II and III that the affinities of the complex ions towards the resin are small, and usually decrease with increase in the degree of resin cross-linking. This effect probably reflects the large volumes of the ions and their strong hydration due to the presence of hydrophilic hydroxyl groups. It is interesting to note that for $[\text{Ga}(\text{HPO}_4)_2]^-$ exchange on Dowex 1-X8 at low temperatures very high ΔH^* and ΔS^* values were observed, much larger than those which usually occur in ion-exchange reactions¹. As the enthalpy changes for the two ion-exchange reactions involved are different, the separation factors ($\alpha_{\text{Ga}}^{\text{In}}$):

$$\alpha_{\text{Ga}}^{\text{In}} = \frac{\lambda_d(\text{In})}{\lambda_d(\text{Ga})} = \frac{\{K_{\text{H}_2\text{PO}_4^-}^{\text{[In(HPO}_4)_3]^{3-}}\}^3}{K_{\text{H}_2\text{PO}_4^-}^{\text{[Ga(HPO}_4)_2]^-} \cdot m_{\text{H}_2\text{PO}_4^-}^2} \quad (12)$$

TABLE III
THERMODYNAMIC FUNCTIONS ΔG^* (kcal/equiv.), ΔH^* (kcal/equiv.), AND ΔS^* (cal/equiv. °K) FOR ION-EXCHANGE REACTIONS 7 AND 8

Resin	Element	Function	Temperature (°K)									
			278	288	298	308	318	328	338	348	358	
Dowex 1-X2	Ga	ΔG^*	1.234	1.309	1.362	1.399	1.402	1.391	1.360	1.310	1.240	
		ΔH^*	-1.188	-0.535	0.119	0.773	1.427	2.081	2.735	3.388	4.042	
		ΔS^*	-8.710	-6.399	-4.168	-2.010	0.078	2.102	4.066	5.972	7.824	
	In	ΔG^*	1.349	1.437	1.519	1.595	1.666	1.732	1.792	1.848	1.899	
		ΔH^*	-1.183	-1.014	-0.845	-0.676	-0.507	-0.338	-0.170	-0.001	0.168	
		ΔS^*	-1.103	-8.507	-7.930	-7.373	-6.833	-6.310	-5.803	-5.311	-4.832	
Dowex 1-X4	Ga	ΔG^*	1.410	1.423	1.444	1.470	1.503	1.541	1.586	1.636	1.691	
		ΔH^*	1.127	0.938	0.748	0.559	0.370	0.180	-0.009	-0.198	-0.387	
		ΔS^*	-1.017	-1.686	-2.332	-2.957	-3.562	-4.148	-4.716	-5.268	-5.805	
	In	ΔG^*	1.357	1.421	1.488	1.560	1.635	1.713	1.795	1.879	1.967	
		ΔH^*	-0.369	-0.477	-0.585	-0.694	-0.802	-0.910	-0.994	-1.126	-1.234	
		ΔS^*	-6.206	-6.588	-6.957	-7.314	-7.659	-7.994	-8.319	-8.634	-8.940	
Dowex 1-X8	Ga	ΔG^*	2.804	2.445	2.145	1.901	1.711	1.574	1.488	1.452	1.464	
		ΔH^*	13.612	11.936	10.259	8.582	6.905	5.228	3.552	1.875	0.198	
		ΔS^*	38.866	32.942	27.220	21.686	16.329	11.139	6.103	1.215	-3.534	
	In	ΔG^*	1.500	1.508	1.526	1.555	1.593	1.641	1.699	1.766	1.842	
		ΔH^*	1.450	1.140	0.830	0.520	0.210	-0.100	-0.410	-0.720	-1.030	
		ΔS^*	-0.182	-1.278	-2.336	-3.359	-4.349	-5.309	-6.240	-7.143	-8.022	

also changes considerably with temperature, as shown in Table IV. The feasibility of achieving practical separations can be expressed in terms of the resolution, R_3 , which is a function of both separation factor and plate height¹³:

$$R_3 = \frac{(\alpha_{Ga}^{In} - 1) \sqrt{L}}{3 (\alpha_{Ga}^{In} + 1) \sqrt{H}} \quad (13)$$

where L is the length of the resin bed and \bar{H} is the mean plate height.

TABLE IV
SEPARATION FACTORS AS A FUNCTION OF TEMPERATURE

Temperature (°C)	α_{Ga}		
	Dowex I-X2	Dowex I-X4	Dowex I-X8
15	12.01	14.04	33.76
25	12.00	8.49	45.26
45	10.33	9.47	11.69
65	5.60	8.90	8.87
85	4.84	5.34	6.36

Some examples of elution curves illustrating the effect of temperature and degree of resin crosslinking on the separation of gallium and indium in 1 *M* orthophosphoric acid solutions are shown in Figs. 3 and 4, together with the values of α , H and R_3 .

The plate heights were calculated from the equation

$$H = \frac{L \sigma^2}{(U_{max} - U_0)^2} \quad (14)$$

where σ is the standard deviation of a chromatographic peak, and the experimental resolutions from the relationship

$$R_3 = \frac{U_{max(In)} - U_{max(Ga)}}{3 (\sigma_{In} + \sigma_{Ga})} \quad (15)$$

The dependence of α , H (normalized for the value of the weight distribution coefficient, $\lambda_d = 15$) and R_3 upon the degree of resin crosslinking is shown in Figs. 5–7, and values of the plate height and resolution at different temperatures are given in Tables V and VI.

At low temperatures, the plate height decreases with decreasing degree of resin crosslinking over the whole range of degrees of crosslinkings examined and only at higher temperatures does the minimum on the H versus W_{H_2O}/Z_s occur at $X = 4$ (*cf.*, Fig. 6). At the same time, the plate height always decreases with an increase in temperature or distribution coefficient (*cf.*, Figs. 3 and 4).

Hence, it can be concluded that the particle diffusion mechanism predominates

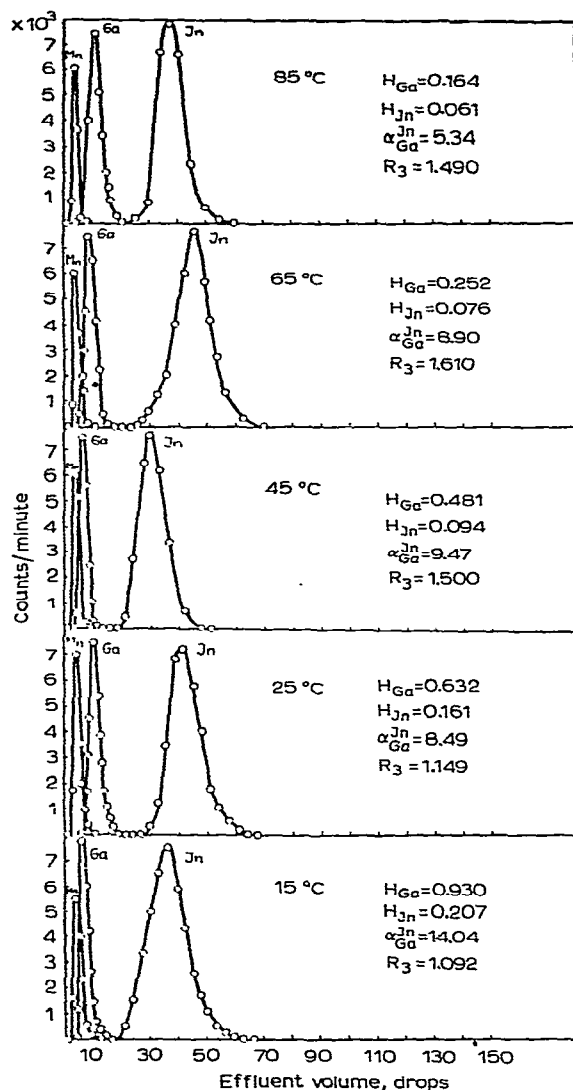


Fig. 3. Effect of temperature on elution of gallium and indium. Column: 4 cm \times 0.031 cm² Dowex 1-X4 ($H_2PO_4^-$) ($15 \mu m \leq \varnothing \leq 48 \mu m$). Eluent, 1 M H_3PO_4 ; flow-rate, 2.5 cm/min.

here and only at higher temperatures does the longitudinal diffusion in the resin phase start to contribute significantly to the total plate height. Comprehensive accounts of similar effects in other ion-exchange systems have been published elsewhere^{7,14,15}.

As the separation factor, α_{Ga}^{In} , in this system generally decreases with a decrease in the degree of crosslinking and also with increase in temperature (*cf.*, Fig. 5), the best resolution can be achieved either with Dowex 1-X4 at 65° or with Dowex 1-X2 at 45° (*cf.*, Fig. 7).

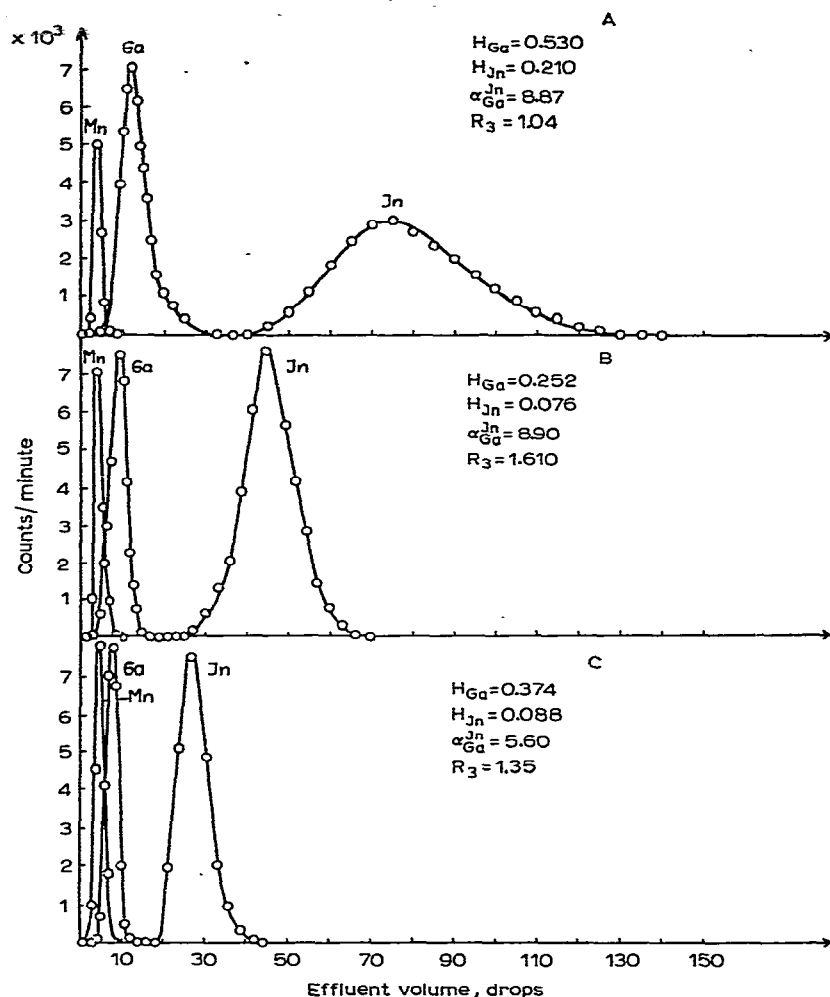


Fig. 4. Effect of degree of resin crosslinking on elution of gallium and indium. Temperature, 65°; eluent, 1 M H₃PO₄; flow-rate, 2.5 cm/min. A, Column 4 cm × 0.031 cm² Dowex 1-X8 (H₂PO₄⁻) (24 μm ≤ ∅ ≤ 42 μm); B, column 4 cm × 0.031 cm² Dowex 1-X4 (H₂PO₄⁻) (15 μm ≤ ∅ ≤ 48 μm); C, column 4 cm × 0.031 cm² Dowex 1-X2 (H₂PO₄⁻) (6 μm ≤ ∅ ≤ 38 μm).

TABLE V

PLATE HEIGHT NORMALIZED FOR A VALUE OF THE WEIGHT DISTRIBUTION COEFFICIENT $\lambda_d = 15$ (\bar{H}) AS A FUNCTION OF TEMPERATURE

Temperature (°C)	\bar{H} (cm)		
	Dowex 1-X2	Dowex 1-X4	Dowex 1-X8
15	0.590	0.710	1.723
25	0.523	0.520	1.450
45	0.305	0.330	1.412
65	0.295	0.180	0.428
85	0.235	0.100	0.220

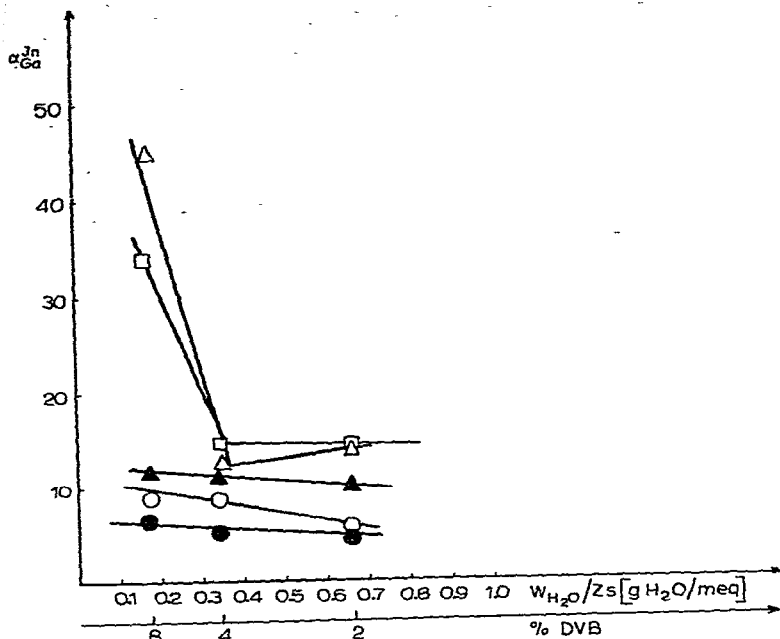


Fig. 5. Dependence of separation factor, α_{Ga}^{in} , on the specific water content of the resin for different temperatures: □, 15°; △, 25°; ▲, 45°; ○, 65°; ●, 85°.

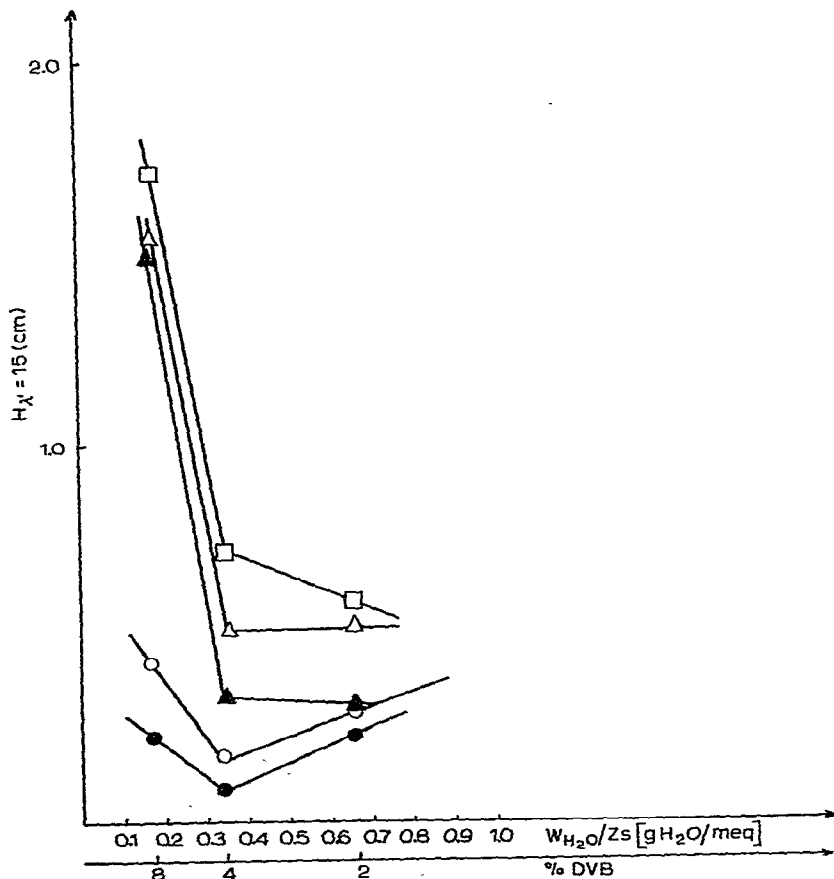


Fig. 6. Dependence of plate height normalized for a value of the weight distribution coefficient of $\lambda_d = 15$ on the specific water content of the resin for different temperatures: □, 15°; △, 25°; ▲, 45°; ○, 65°; ●, 85°.

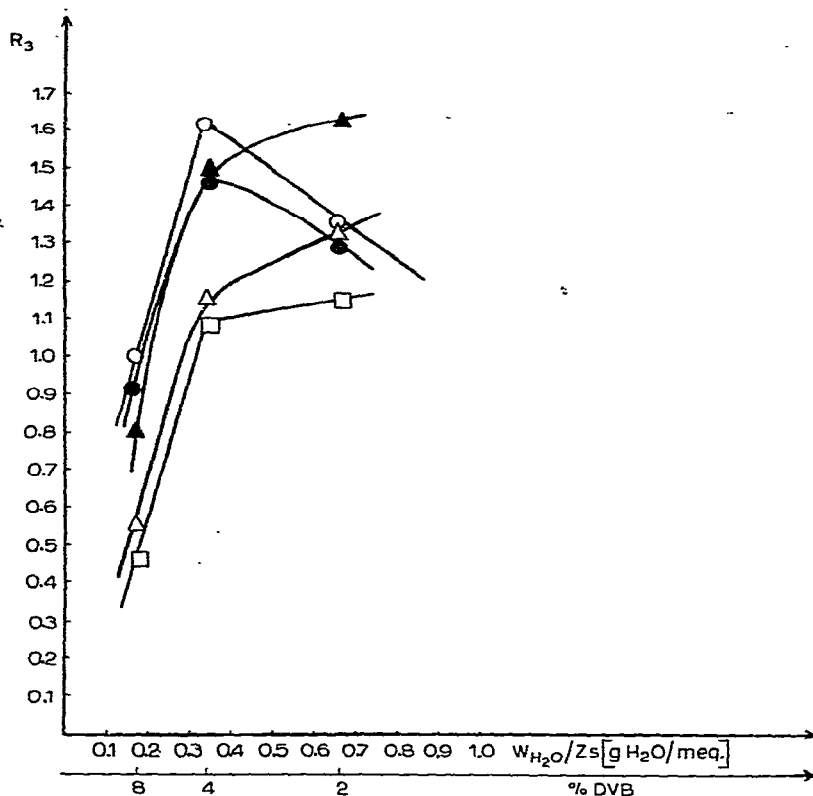


Fig. 7. Dependence of resolution, R_3 , on the specific water content of the resin for different temperatures: \square , 15°; \triangle , 25°; \blacktriangle , 45°; \circ , 65°; \bullet , 85°.

TABLE VI

RESOLUTION, R_3 , AS A FUNCTION OF TEMPERATURE

Temperature (°C)	R_3		
	Dowex I-X2	Dowex I-X4	Dowex I-X8
15	1.15	1.092	0.46
25	1.34	1.149	0.56
45	1.62	1.500	0.81
65	1.35	1.610	1.04
85	1.30	1.490	0.92

The results of this study show that for large complex ions the best separations can be obtained by using relatively lightly crosslinked resins, despite the opposite trend in separation factors. Careful choice of both degree of crosslinking and temperature can be a decisive factor in achieving good separations on small columns. Similar conclusions could also be drawn from previous studies involving rare-earth complexes with EDTA and DCTA^{7,15}.

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