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Solvent effects on the complexation of trivalent lanthanide cations by sugars and alditols: Chromatography–calorimetry comparison

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Abstract

A study of the solvent effects on the relative stabilities of the complexes formed between some polyols (sugars and alditols) and lanthanide cations has been performed by thin-layer ligand-exchange chromatography. The R_f values of arabinose, ribitol, ribose and glucitol in binary aqueous mixtures have been measured on TLC plates in the La^{3+} and Sm^{3+} forms. Mixtures of water with 5 to 30 wt% Me_2SO, acetonitrile, methanol, or *tert*-butanol were used as eluents. The modification of the polyols separation upon addition of the organic component has been examined. Furthermore, in order to compare the chromatographic and thermodynamic behaviours of the complexes, the stability constant for the complexation of Sm^{3+} by glucitol has been determined in the different binary mixtures using a flow microcalorimeter. © 1996 Elsevier Science Ltd.

Keywords: TLC; Microcalorimetry; Stability constants; Lanthanide cations, complexation of; Sugars; Alditols; Me_2SO, acetonitrile, methanol, *tert*-butanol, water, mixtures of

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1. Introduction

The sugar isomers that bear an axial–equatorial–axial triol on a six-membered ring or a *cis–cis* triol on a five-membered ring, and the alditols that have a *threo–threo* triol on their linear chain form weak complexes with divalent and trivalent metal cations [1]. In spite of the weakness of the interactions between the metal cations and the carbo-

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hydrates ($K < 10$), interesting selectivities are observed. It can be noticed that the univalent cations are not complexed and that the trivalent cations form stronger complexes than the divalent cations [1–4]. Furthermore, our thermodynamic characterisation of the complexation of the trivalent lanthanide cations by sugars [3] and alditols [4] in water has shown that the strength of the complex varies significantly within the lanthanide cation series and exhibits a maximum for Sm^{3+}.

The problem of the separation of mixtures of sugars prompted several researchers to compare the complexing ability of various metal cations. Twenty years ago, Goulding [5] tried to improve the chromatographic separation of mixtures of sugars and related polyhydric alcohols on columns of cation-exchange resin [6,7] by testing a wide variety of cations. Since then, many papers have been published [8–17] on the subject and columns in the calcium, barium, and lanthanum forms were recommended. More recently, a TLC study of the complexing properties of several lanthanide cations with polyols was published by Angyal and Craig [18]. Shortly after, we reported [19] a systematic study of the relative stabilities of the complexes formed between several polyols (sugars, alditols) and the whole series of trivalent lanthanide cations in water. In that work, we established a correlation between the R_f values and the stability constants previously determined by calorimetry [2–4] and compared the efficiencies of plates in the Ca^{2+}, La^{3+}, and Sm^{3+} forms.

The chromatographic separation can be improved by changing the eluent [8]. Although most of the sugars and alditols are only slightly soluble or even insoluble in pure organic solvents, mixed aqueous solvents can be conveniently used as eluents. We present here the results of our investigation of the solvent effects on the chromatographic behaviour of some polyols in binary mixtures of water with Me_2SO, acetonitrile, methanol, or *tert*-butanol, containing 5 to 30 wt% of organic component. Although it has been pointed out [20] that the solution composition of sugars may vary with the solvent, it seems reasonable to consider that the addition of up to 30% of organic component does not bring about significant changes.

The TLC study was restricted to two complexing (ribose, glucitol) and two non-complexing (arabinose, ribitol) polyols on thin layers in La^{3+} and Sm^{3+} forms. These polyols have been selected because they show typical chromatographic behaviour in water [19]. Furthermore, the thermodynamic properties of complexation of the lanthanide cations by ribose and glucitol in water are well known [3,4]. On the other hand, the interactions of the lanthanide cations with arabinose and ribitol can be used to estimate the non-specific contributions to the thermodynamic properties of complexation [3,4]. The choice of the cation La^{3+} has been motivated by the fact that cation-exchange resins in the lanthanum form have often been recommended for the separation of polyols [1,5,9,11,12,14,15]. Furthermore, we have shown [19] that thin layers in the La^{3+} and Ca^{2+} forms have similar efficiencies for the separation of sugars. Sm^{3+} has also been selected because it is the cation that binds more efficiently the sugars and the alditols in water [18,19].

It is interesting to compare the TLC results with the complexation constants determined by calorimetry. Linear correlations have been observed in water [19] between the capacity factors of ribose, xylitol or glucitol on different lanthanide cation plates ($La^{3+} \rightarrow Tb^{3+}$) and the stability constants, indicating that variations in the distribution coefficient and equilibrium constant are governed by the same factors. In order to check if the correlation observed in water still exists in organic media, we have determined calorimetrically the stability constants for the complexation of Sm^{3+} by glucitol in binary mixtures of water with 5–30 wt% Me_2SO, acetonitrile, methanol, or *tert*-butanol.

2. Results and discussion

The R_f values of arabinose, ribitol, ribose, and glucitol measured on TLC plates in the La^{3+} and Sm^{3+} forms are listed in Table 1. Addition of acetonitrile, methanol or *tert*-butanol decreases the R_f values of the complexing polyols (ribose and glucitol) on both the lanthanum and samarium plates. Me_2SO has the opposite effect on the samarium plate.

Changes in the separation of the polyols on both types of plate upon addition of 20 wt% of organic component in the eluent are shown in Fig. 1. The choice of this composition has been motivated by the fact that the R_f values in 30% *tert*-butanol are

Table 1
R_f values of polyols on TLC plates in the La^{3+} and Sm^{3+} forms

Eluent	Wt% of organic component	[R_f (La^{3+} form)]				[R_f (Sm^{3+} form)]			
		arabinose	ribitol	ribose	glucitol	arabinose	ribitol	ribose	glucitol
Water		0.81	0.80	0.56	0.51	0.82	0.69	0.33	0.28
Me_2SO–water	10	0.82	0.79	0.56	0.47	0.83	0.72	0.37	0.31
	20	0.82	0.79	0.54	0.44	0.81	0.72	0.40	0.32
	30	0.90	0.85	0.54	0.42	0.85	0.75	0.46	0.39
Acetonitrile–water	5	0.81	0.78	0.52	0.47	0.80	0.69	0.31	0.26
	10	0.82	0.77	0.52	0.39	0.82	0.68	0.23	0.22
	15	0.84	0.78	0.50	0.36	0.82	0.69	0.22	0.19
	20	0.84	0.75	0.48	0.34	0.82	0.65	0.26	0.16
	25	0.81	0.71	0.44	0.27	0.81	0.61	0.19	0.11
	30	0.80	0.70	0.38	0.14	0.79	0.57	0.15	0.07_2
Methanol–water	5	0.79	0.76	0.50	0.43	0.82	0.69	0.26	0.22
	10	0.80	0.74	0.47	0.37	0.80	0.68	0.25	0.16
	15	0.80	0.71	0.43	0.33	0.78	0.63	0.20	0.13
	20	0.78	0.67	0.39	0.26	0.74	0.58	0.16	0.12
	25	0.76	0.65	0.37	0.21	0.76	0.54	0.15	0.10
	30	0.76	0.63	0.30	0.18	0.76	0.51	0.13	0.07_5
tert-Butanol–water	5	0.82	0.74	0.53	0.41	0.82	0.69	0.31	0.22
	10	0.80	0.74	0.48	0.37	0.79	0.62	0.24	0.17
	15	0.77	0.72	0.42	0.33	0.77	0.61	0.17	0.15
	20	0.65	0.65	0.29	0.26	0.66	0.59	0.13	0.13
	25	0.68	0.62	0.24	0.21	0.70	0.51	0.13	0.09_3
	30	0.66	0.55	0.27	0.15	0.68	0.49	0.12	0.07_8

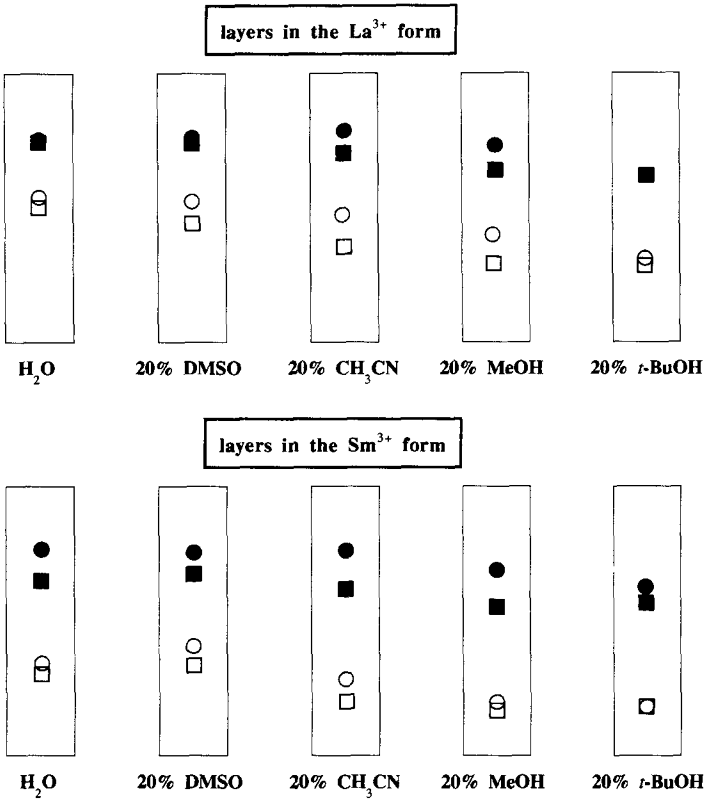

Fig. 1. Solvent effects on the separation of arabinose (●), ribitol (■), ribose (○), and glucitol (□) on TLC plates in the La^{3+} and Sm^{3+} forms upon addition of 20 wt% of Me_2SO, acetonitrile, methanol, or *tert*-butanol in the eluent.

not reliable due, as will be shown below, to an important pre-loading effect. More generally, the experimental problems encountered in highly concentrated media lead us to believe that the trends observed in mixtures containing 30 wt% of organic component are less significant than those shown in Fig. 1. As can be seen, the addition of 20 wt% of Me_2SO does not significantly modify the R_f values of the non-complexing polyols (arabinose, ribitol); however, slightly larger effects are observed with complexing ribose and glucitol, effects that are negative (R_f decreases) on the lanthanum layer and positive (R_f increases) on the samarium layer. Acetonitrile is the solvent that gives the strongest separation improvement; the Sm^{3+} plate appears to be more efficient for the separation of the non-complexing polyols whereas the La^{3+} plate is better for the separation of the complexing polyols. Addition of alcohol (methanol or *tert*-butanol) induces the largest decrease in the R_f values of the four studied polyols. However, depending on the alcohol the separation of the polyols either improves or worsens; in fact, methanol is almost as efficient as acetonitrile whereas *tert*-butanol does not separate the sugars from the alditols.

Table 2
Stability constants for the complexation of Sm^{3+} by glucitol in four mixed aqueous solvents at 25 °C [a]

Wt% of organic component	K in water +			
	Me_2SO	acetonitrile	methanol	*tert*-butanol
0	6.5	6.5	6.5	6.5
5		8.8	8.6	
10	8.9	11.8	10.2	8.1
16		14.4		
20	8.9	16.1	14.8	14.9
30	9.2			

[a] Molar scale.

The decrease in R_f values of the polyols can be explained by the importance for highly charged cations of the desolvation contribution to the thermodynamic properties of complexation. Our previous studies of the Gibbs energies, enthalpies, and entropies of association of the lanthanide cations by ribose [3] and glucitol [4] in water showed that the cation hydration shell is not noticeably modified by substitution of three OH groups of the polyol for water molecules. However, complex formation with the polyol should be strengthened if the solvent is less strongly solvating than water [8]. It is more difficult, on the other hand, to explain the changes in the separation because these second-order effects imply comparison of the polyols.

We have determined the stability constants in binary mixtures of water with 5–30 wt% Me_2SO, acetonitrile, methanol, or *tert*-butanol for the complexation of Sm^{3+} by glucitol, and these values are reported in Table 2. The K values in the mixed aqueous solvents are all larger than in pure water. Acetonitrile produces the largest increase whereas Me_2SO gives the smallest one. Thus, all of the mixtures studied here behave like less solvating media than water. Unfortunately, this behaviour cannot be easily related to quantities characterizing the solvating abilities of the organic components of the solvent mixtures (donor number, polarity index, etc.) because of selective solvation [21]. Nevertheless, what is observed here is consistent with the qualitative selectivity series given by Marcus [21] for a cation like Na^+: Me_2SO > methanol > acetonitrile.

A better way to compare the chromatographic and calorimetric results is to relate the stability constants to the distribution coefficients. To do so, one must first correct the measured R_f values for the different disturbing factors (frontal volume gradient, pre-loading effect, etc.) [22]. The true migration rates, R'_f, are simply obtained by multiplying the measured R_f values by a correction factor ξ, which is a constant in a given solvent. The correction factor can be determined by studying species that should migrate with $R_f = 1$. In the present case, the ξ value can be estimated by measuring the migration rates of the polyols on layers in the H^+ form since this cation is not complexed by the sugars or the alditols. These measurements were made with arabinose, ribitol, ribose, and glucitol in each of the binary mixtures studied here. The average of the R_f values of the four polyols was taken and reported with the standard error in Table 3. The value of ξ is equal to the reciprocal of the average R_f value.

The results show that the addition of Me_2SO does not modify the ξ value (1.16 in

Table 3
Solvent effect on the average values of R_f measured for the polyols on TLC plates in the H^+ form

Eluent	Wt% of organic component	Average R_f
Water		0.86 ± 0.01
Me_2SO–water	30	0.86 ± 0.02
Acetonitrile–water	5	0.85 ± 0.01
	10	0.85 ± 0.02
	15	0.86 ± 0.02
	20	0.83 ± 0.02
	25	0.83 ± 0.01
	30	0.81 ± 0.02
Methanol–water	5	0.86 ± 0.02
	10	0.86 ± 0.02
	15	0.82 ± 0.01
	20	0.81 ± 0.02
	25	0.80 ± 0.02
	30	0.80 ± 0.02
tert-Butanol–water	5	0.86 ± 0.02
	10	0.81 ± 0.02
	15	0.78 ± 0.01
	20	0.78 ± 0.01
	25	0.72 ± 0.02
	30	0.68 ± 0.02

pure water). Thus, the perturbing factors encountered with the Me_2SO–water mixtures seem to be the same as those experienced in pure water. The situation is different upon addition of acetonitrile, methanol or *tert*-butanol. Here the average R_f value decreases and, accordingly, ξ increases (1.23 in 30% acetonitrile, 1.25 in 30% methanol, and 1.47 in 30% *tert*-butanol). The correction factor becomes relatively important in concentrated *tert*-butanol–water mixtures, which may be due to a pre-loading effect resulting from the very slow development (7.3 h in 30% *tert*-butanol) in these highly viscous media [23]. According to Geiss [22] 'the greater the pre-loading the greater the front migration velocity and the smaller the R_f values'. The data reported in Table 3 for the *tert*-butanol–water mixtures thus seem to indicate that the pre-loading effect increases when the composition is changed from 15 to 30 wt% of *tert*-butanol. This result also implies that in such media the measurements are technically more difficult and the R_f values are less reliable.

The distribution coefficient K_d is related to the true migration rate R'_f, (i.e., ξR_f) through the following equation:

$$K_d(W_a/V_m) = \frac{1}{R'_f} - 1 = k, \qquad (1)$$

where W_a is the weight of the adsorbent in the stationary phase and V_m is the volume of

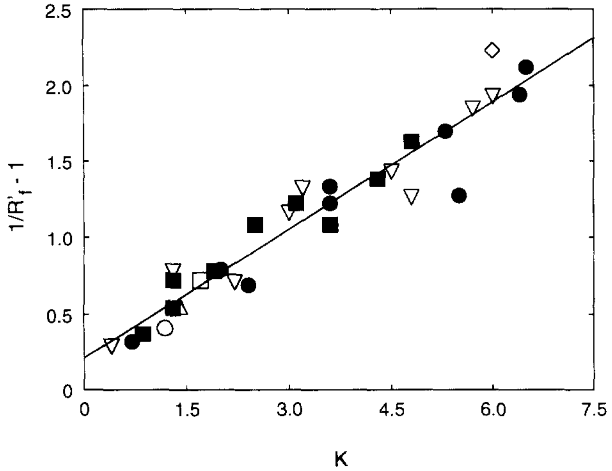

Fig. 2. Complexation of Ca^{2+} and Ln^{3+} by polyols in water: arabinitol (□), galactitol (◇), glucitol (●), mannitol (△), ribose (■), talose (○), and xylitol (▽). Correlation between the capacity factors of the polyols [19] and the stability constants [2–4,24–26] determined by calorimetry.

the mobile phase. The capacity factor k corresponds to the ratio of the weight of sorbate in the stationary phase to the weight of sorbate in the mobile phase.

We showed previously [19] that, in water, the capacity factors of ribose on several lanthanide cation layers (Ln^{3+}: $La^{3+} \rightarrow Tb^{3+}$) are linearly correlated with the complexation constants determined by calorimetry. The same thing was observed with glucitol. More interestingly, one can show that the data for different cations, sugars, and alditols in water fall on a single straight line. This is demonstrated in Fig. 2 where the capacity factors of several sugars and alditols (ribose, talose, arabinitol, galactitol, glucitol, mannitol, and xylitol) on plates in different cationic forms (Ca^{2+}, Ln^{3+}: $La^{3+} \rightarrow Tb^{3+}$) have been plotted against the complexation constants. Obviously, in water, the variations of the distribution and complexation constants are both governed by the desolvation of the cation and are independent of the polyol [19].

But does this correlation hold in other media? Data in aqueous solvent mixtures being now available, this can be easily checked. To do so, all of the experimental points for the complexation of Ln^{3+}: $La^{3+} \rightarrow Tb^{3+}$ by glucitol in water and for the complexation of Sm^{3+} by glucitol in binary mixtures of water with 5–20 wt% Me_2SO, acetonitrile, methanol, or *tert*-butanol have been plotted in Fig. 3. The latter points are more scattered than the former points because the R'_f values in the binary mixtures are, for the reasons mentioned above, less reliable than in pure water. The straight line obtained in Fig. 2 for pure water is also shown in Fig. 3 and extended to cover the whole K range. The data in aqueous solvent mixtures, without falling exactly on the correlation line obtained in water, are not very far from it. This means that, upon addition of an organic component, the solvation of the cation attached to the TLC layer and the solvation of the free cation in the homogeneous phase are modified in the same way. It must be pointed out, however, that even if a unique k–K correlation could fit the data perfectly, it would

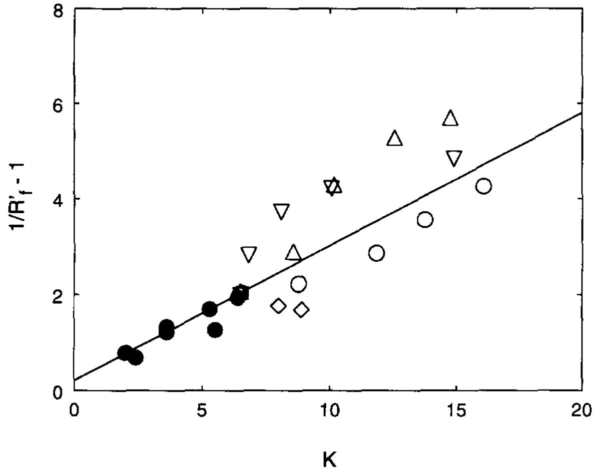

Fig. 3. Complexation of Ln^{3+} by glucitol in water (●) and complexation of Sm^{3+} by glucitol in mixed aqueous solvents: Me_2SO–water (◇), acetonitrile–water (○), methanol–water (△), and *tert*-butanol–water (▽). Correlation between the capacity factors of glucitol and the stability constants determined by calorimetry. The straight line corresponds to the straight line in pure water (Fig. 2) extended over the whole K range.

not account for the modification of the polyols separation. In fact, such a correlation can be written as $1/R'_f - 1 = sK$, where s is a constant corresponding to the slope of the correlation line. It thus implies that the modification of the separation of polyols A and B [i.e., $(R'_{fA} - R'_{fB})$] upon addition of an organic component depends on the K_A, K_B, and $(K_A - K_B)$ values in the different media. Obviously, predicting the solvent effect on the separation of the polyols is not simple.

3. Experimental

Reagents.—D-Ribose, D-arabinose, and ribitol (adonitol) were commercial products from Fluka, whereas D-glucitol (sorbitol) was obtained from Merck. Their purity was > 99%. $LaCl_3 \cdot 7H_2O$ and $SmCl_3 \cdot 6H_2O$ (99.9%) were bought from Strem. HCl was obtained from Merck (1 M Titrisol). Me_2SO (dimethyl sulphoxide) (Merck, p.a. > 99.5%, max. 0.03% H_2O), acetonitrile (methyl cyanide) (Janssen, p.a. > 99.5%), methanol (Merck, p.a. > 99.5%, max. 0.01% H_2O), and *tert*-butanol (2-methyl-2-propanol) (Labosi, p.a. > 99.5%) were used as received and mixed with triply distilled water. All solutions and binary solvents were prepared by weight.

Chromatography.—Complexing of the polyhydroxy compounds with La^{3+} and Sm^{3+} was observed by thin-layer chromatography (TLC). Resin-coated chromatosheets in the sodium form (Macherey–Nagel Polygram Ionex-25 SA Na sheets) were converted into the H^+, La^{3+}, and Sm^{3+} forms in the usual way [10,11,19,27]. First, the sheets were immersed in triply distilled water until the thin layers were completely wet. Next, the plates in the H^+ form were prepared by dipping the Ionex-25 SA Na sheets for four to five hours into 1 M HCl. For the preparation of the plates in the La^{3+} (or Sm^{3+})

form, the Ionex-25 SA Na sheets were dipped for one hour into a 0.1 M aqueous solution of $LaCl_3$ (or $SmCl_3$). Finally, the sheets were washed several times with triply distilled water and dried in air at room temperature for approximately 24 h. The sugars and alditols were spotted individually (1 μL of a 0.1 M aqueous solution) and the chromatograms were developed, without prior equilibration, in a saturated rectangular tank (N-chamber) equipped with a lid. The elution time was markedly dependent on the nature of the organic component and increased with the percentage composition of the solvent: 1.7–3 h with Me_2SO–water mixtures, 1.5–2 h with acetonitrile–water mixtures, 1.3–2.5 h with methanol–water mixtures, and 2–7.3 h with *tert*-butanol–water mixtures. For comparison, the development time in pure water was 1–1.75 h [19]. The products were detected with a saturated solution of potassium permanganate in acetone.

Microcalorimetry.—The stability constants for the complexation of Sm^{3+} by glucitol in Me_2SO–water, acetonitrile–water, methanol–water, and *tert*-butanol–water mixtures were determined by microcalorimetry. Association of glucitol with Sm^{3+} was followed by measuring the heats of mixing of a solution of $SmCl_3$ at constant concentration in a binary solvent (0.01 mol kg^{-1} before mixing) with solutions of glucitol at initial concentrations varying from 0.1 to 0.6 mol kg^{-1} in the same solvent. The heats of mixing were measured with an LKB 2277 TAM microcalorimeter [28] equipped with a flow-mix measuring cylinder as described previously [2,3]. The lanthanide and alditol solutions were injected into the mixing vessel at about the same flow rate (ca. 11 cm^3 h^{-1}). Each measurement of a heat of mixing was immediately followed by the measurements of the heats of dilution of the electrolyte solution and of the alditol solution at exactly the same flow rate. All measurements were performed at 298.15 K. Non-linear regression analysis of the data gave the stability constant and the standard enthalpy of complexation in each mixed aqueous solvent.

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