

Enthalpies of Solution of Lanthanum, Gadolinium and Ytterbium Trichlorides in Binary Aqueous Solvent Mixtures

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Enthalpies of solution are reported for anhydrous lanthanum trichloride in methanol, ethanol, *t*-butyl alcohol, and dimethyl sulphoxide–water mixtures, for anhydrous gadolinium trichloride in methanol–water mixtures, and for ytterbium trichloride in methanol- and dimethyl sulphoxide–water mixtures, at 298.2 K. The estimation of enthalpies of transfer of lanthanide(III) cations into these binary aqueous solvent mixtures is discussed.

Introduction

There is a considerable amount of information available on enthalpies of solution of lanthanide trichlorides in water and a few data on enthalpies of solution of these compounds in non-aqueous solvents [1, 2]. There are, however, no data on enthalpies of solution of trihalides of the lanthanides in binary aqueous solvent mixtures. In the present paper we report enthalpies of solution of anhydrous lanthanum trichloride in binary aqueous mixtures containing methanol, ethanol, *t*-butyl alcohol, or dimethyl sulphoxide, of anhydrous gadolinium trichloride in aqueous methanol, and of anhydrous ytterbium trichloride in aqueous methanol and in aqueous dimethyl sulphoxide. Enthalpy trends for these lanthanide trichlorides are compared with those for selected metal monohalides and dihalides and for iron(III) chloride. The observed variations of solution enthalpies with solvent composition for the lanthanide trichlorides are discussed in terms of the composition of the solvation shells of the constituent ions and in terms of solvent structural effects. We have also attempted to estimate enthalpies of transfer for the lanthanide cations Ln^{3+} from water into binary aqueous solvent mixtures with the aid of published enthalpies of transfer for the chloride ion.

Experimental

The lanthanide sesquioxides (Apache) were converted into the trichloride hydrates by treatment

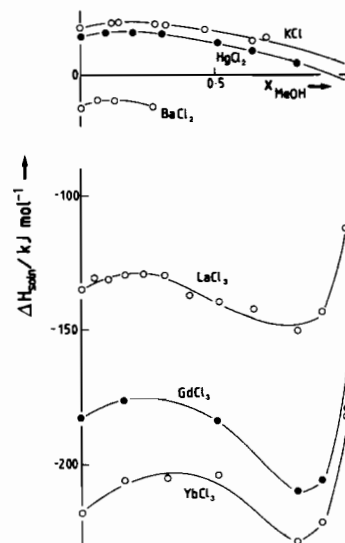


Fig. 1. Variation of enthalpies of solution of anhydrous lanthanum(III), gadolinium(III), ytterbium(III), barium(II), mercury(II), and potassium chlorides with solvent composition in aqueous methanol.

with hydrochloric acid; the anhydrous trichlorides were prepared by heating the hydrates with ammonium chloride *in vacuo* [1, 2]. Solvent mixtures were made up from distilled water and organic co-solvent suitably purified [3].

Enthalpies of solution were measured in an LKB 8700 calorimeter assembly as described earlier [4]. The performance of the calorimeter was checked periodically by measuring the enthalpy of solution of potassium chloride [5]. About 0.03 g of anhydrous trichloride and 35 cm³ of mixed solvent were used in each determination; these conditions approximate closely to infinite dilution.

Results

Our measured enthalpies of solution are reported in the Table; uncertainties in these results range

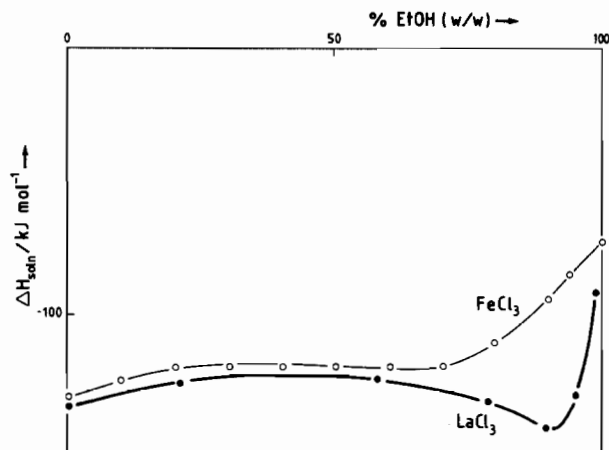


Fig. 2. Comparison of variation of enthalpies of solution of anhydrous lanthanum(III) and iron(III) chlorides with solvent composition in aqueous ethanol.

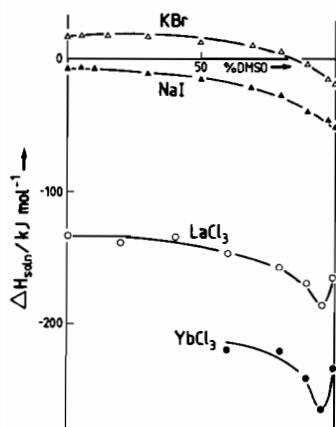


Fig. 3. Enthalpies of solution of lanthanum(III) and ytterbium(III) chlorides, and of potassium bromide and sodium iodide, in aqueous dimethyl sulphoxide (KBr and NaI data from A. S. Monaenkova, I. D. Padunova, and A. F. Vorob'ev, *Vestn. Mosk. Univ. Ser. Khim.*, 18, 667 (1977)).

between 1 and 3 kJ mol^{-1} . Enthalpies of solution in water are -137.7 , -181.6 , and -215.9 kJ mol^{-1} for anhydrous lanthanum trichloride, gadolinium trichloride, and ytterbium trichloride respectively [6].

Discussion

The trends in enthalpies of solution are shown diagrammatically in Figs. 1 to 4. Figure 1 shows the expected similarity of trends for the three lanthanide trichlorides in methanol–water mixtures. It also shows how these values and trends relate to published data on the dichlorides of mercury [7] and barium [8], and on potassium chloride [8, 9].

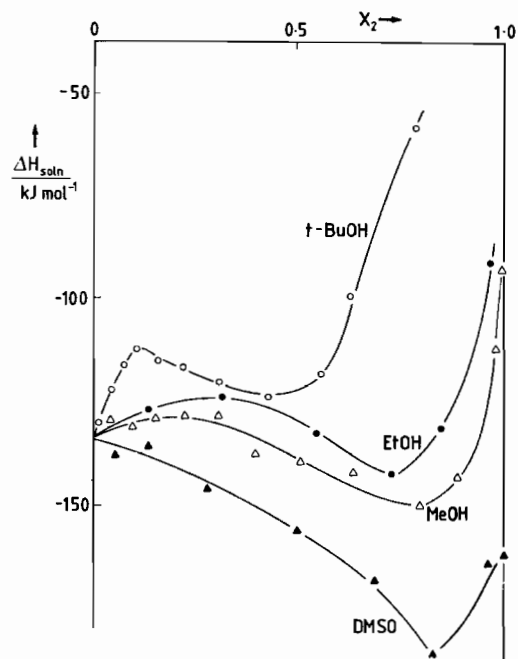


Fig. 4. Comparison of enthalpy trends for lanthanum(III) chloride in aqueous methanol, ethanol, t-butyl alcohol, and dimethyl sulphoxide.

In any given mixed solvent in this series the magnitudes of the solution enthalpies are $\text{YbCl}_3 > \text{GdCl}_3 > \text{LaCl}_3$. This is the order expected from cation radii ($\text{Yb}^{3+} = 0.998$, $\text{Gd}^{3+} = 1.08$, $\text{La}^{3+} = 1.20$ Å, for six coordination [10]) if cation solvation dominates. The extension to the dihalides and potassium chloride is consistent with this, though of course the markedly covalent nature of mercury(II) chloride (the only significantly covalent halide included in Fig. 1) affects the position of its plot greatly.

In Fig. 2 the enthalpy of solution trends for lanthanum(III) chloride and iron(III) chloride [11] in ethanol–water mixtures are depicted and compared. There is a remarkable similarity, except towards the ethanol-rich end of the plot. Figure 3 shows and compares trends in dimethyl sulphoxide–water mixtures.*

Figure 4 compares the trends in solution enthalpies for dissolution of anhydrous lanthanum trichloride in the four series of binary mixtures

*The difference in pattern between the alkali metal halides and the lanthanide(III) chlorides at high DMSO content may be assigned to the halide ions. Whereas metal ions are favourably solvated by DMSO, halide ions are not. The lanthanide(III) chlorides contain three anions per cation, the alkali metal halides only one; the unfavourable solvation of anions dominates in the former but not in the latter.

examined in this work. The existence of values for pure methanol [2] and for pure dimethyl sulphoxide [12] allows us to plot the trends for these cosolvents over the whole composition range. There is, however, no satisfactory published value for the enthalpy of solution of anhydrous lanthanum trichloride in anhydrous ethanol [1]. Low solubility and very slow dissolution have prevented us from direct measurement, but it is possible to estimate a solution enthalpy of about -60 kJ mol^{-1} for absolute ethanol from Fig. 4. The extrapolation required to make an analogous estimate for pure t-butyl alcohol is too long.

There are several factors which determine the shapes of the plots shown in Fig. 4, and it is convenient to divide the discussion of these plots into water-rich and organic-rich regions of solvent composition. The striking feature of the water-rich region of Fig. 4 is the reflection of solvent structural effects in the measured solution enthalpies. There are extrema for each of the alcohol-water mixtures, occurring at mole fractions of around 0.3 for methanol and for ethanol, and 0.1 for t-butyl alcohol. These compositions correspond with those at which extrema or points of inflection of plots of various thermodynamic and spectroscopic properties against solvent composition have been reported [13]. Moreover the sizes of the extrema, $\text{MeOH} < \text{EtOH} < \text{t-BuOH}$, parallel the relative sizes of effects reported on these other thermodynamic and spectroscopic properties. These solvent structural phenomena are generally ascribed to the effects of the alcohols on the aqueous medium structure. The addition of successive small amounts of an alcohol to water is thought to increase the structuredness up to a limit, after which further addition of alcohol results in breakdown of solvent structure. The effects of t-butyl alcohol are the greatest, and maximise at the lowest mol fraction of alcohol. It is noteworthy that there is no extremum in the water-rich region for dimethyl sulphoxide-water mixtures; addition of successive amounts of this cosolvent to water leads simply to continuous breakdown of solvent structure.

Discussion of trends in the organic-rich region is more complicated. Particularly in the alcohol-water mixtures, there is evidence that chloride enters the primary coordination shell of lanthanide cations at high mol fractions of alcohols [14-16]. Thus the plots on the right-hand sides of Figs. 1, 2 and 4 reflect enthalpy changes due to complex formation with chloride and perhaps to replacement of water by alcohol in the primary solvation sphere, as well as general solvation changes. Transfer of Ln^{3+} from water into an alcohol is enthalpically unfavourable suggesting that there will be preferential solvation by water in alcohol-water mixtures, but transfer of Ln^{3+} into dimethyl sulphoxide is

TABLE I. Enthalpies of Solution (kJ mol^{-1} ; at 298.2 K) for Lanthanide Trichlorides in Binary Aqueous Solvent Mixtures*.

Cosolvent	%	LaCl ₃	GdCl ₃	YbCl ₃
Methanol	10	-131		
	20	-129		
	30	-129	-176	-205
	40	-128		
	50	-129	-187	-206
	60	-138		
	70	-140	-184	-202
	80	-142		
	90	-151	-211	-229
	95	-143	-207	-222
Ethanol	99	-112	-179	-181
	35	-126		
	60	-124		
	80	-133		
	90	-143		
	95	-131		
	99	-91		
t-Butyl alcohol	10	-130		
	20	-122		
	30	-117		
	40	-112		
	50	-115		
	60	-117		
	70	-121		
	80	-124		
	87	-119		
	90	-99		
Dimethyl sulphoxide	95	-58		
	20	-139		
	40	-133		
	60	-147		-219
	80	-157		-220
	90	-169		-240
	95	-186		-265
	99	-163		-233

*Solvent compositions are in volume % previous to mixing.

enthalpically favourable. Hence in dimethyl sulphoxide-water mixtures there will in general be molecules of both solvents in the primary solvation shell of the Ln^{3+} cation. The plots in Fig. 3 and 4 must therefore include enthalpy changes arising from replacement of one solvent by the other in the primary solvation shell. That such plots have a minimum suggests that mixed solvates $\text{Ln}(\text{OH}_2)_n(\text{DMSO})_m^{3+}$ are enthalpically favoured over the ions Ln^{3+} aq and $\text{Ln}(\text{DMSO})_n^{3+}$. By analogy with the much-discussed carbonyl halides, unlike ligands *trans*-to each other may be favoured; possibly the total cation-solvent bond energy is minimised when the

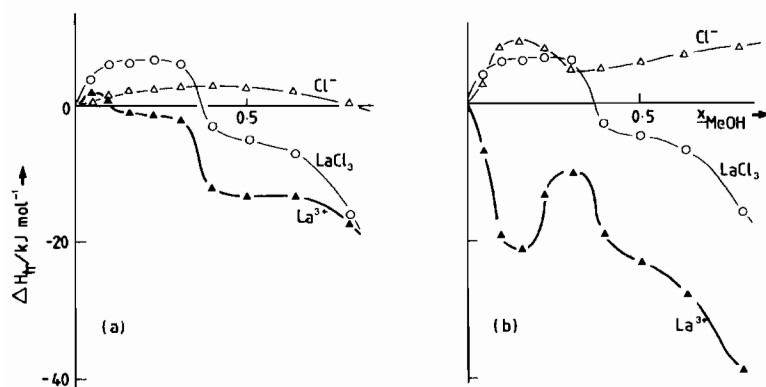


Fig. 5. Enthalpies of transfer of LaCl_3 , Cl^- , and La^{3+} from water into aqueous methanol; (a) Cl^- values from ref. [20], (b) Cl^- values from ref. [21].

numbers of water and dimethyl sulphoxide molecules in the primary solvation shell are equal. For an octahedral system, *fac*- $[\text{M}(\text{OH}_2)_3(\text{DMSO})_3]$ should be most favoured; for solvent- Ln^{3+} ions where knowledge of solvation numbers is minimal and of coordination geometries is zero [17] it is impossible to make an informed guess.

Enthalpies of transfer

It is a straightforward matter to calculate enthalpies of transfer for chlorides from water into the various binary aqueous solvent mixtures, from the results given in Table I and the sources used in constructing Figs. 1 to 4. The patterns exhibited by such enthalpies of transfer are similar to, and may be discussed in similar terms to, the solution enthalpy trends dealt with above. However it would be of considerable interest to dissect enthalpies of transfer of trichlorides LnCl_3 into contributions from lanthanide cations and chloride anions. Such transfer quantities are, of course, unlike single ion solvation enthalpies, independent of lattice enthalpies and the complications and uncertainties attendant on their calculation [18]. However in order to obtain single ion transfer functions it is impossible to avoid making an extra-thermodynamic assumption in order to split whole salt values into ionic components. This matter has been, and still is, the subject of discussion and controversy [19]. We shall relate how much progress is currently possible in determining transfer enthalpies for Ln^{3+} cations.

For transfer into aqueous methanol we have a choice of sets of values for $\Delta H_{tr}(\text{Cl}^-)$. Some years ago Krestov and Klopov derived single ion enthalpies of transfer for chloride ion from water into aqueous methanol and aqueous ethanol [20]. The basis of their single ion split is not altogether clear, but seems to involve the assumption that $\Delta H_{\text{cation}}/\Delta H_{\text{anion}}$ is a constant ratio. Recently Abraham has measured [21] sufficient enthalpies of solution of

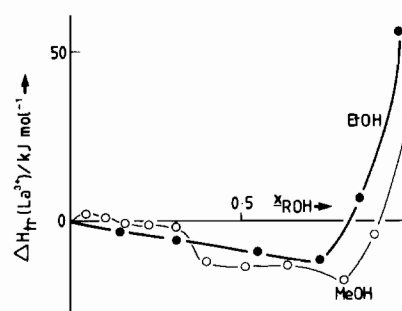


Fig. 6. Enthalpies of transfer of La^{3+} from water into aqueous methanol and into aqueous ethanol (using data for Cl^- from ref. [20]).

appropriate salts in aqueous methanol to apply the currently favoured [22] assumption of equal contributions from the large and presumably lightly solvated tetraphenylarsonium and tetraphenylborate ions, $\Delta H_{tr}(\text{Ph}_4\text{As}^+) = \Delta H_{tr}(\text{Ph}_4\text{B}^-)$. Dissections of our enthalpies of solution and transfer to give estimates for $\Delta H_{tr}(\text{La}^{3+})$ are shown in Fig. 5, for both assumptions. It will be seen that there is poor agreement. The $\Delta H_{tr}(\text{Cl}^-)$ values are themselves not in good agreement, and such disagreement is of course magnified by a factor of three in obtaining $\Delta H_{tr}(\text{La}^{3+})$.

$\Delta H_{tr}(\text{La}^{3+})$ for transfer from water into aqueous ethanol (Fig. 6) can be estimated only via Krestov and Klopov's $\Delta H_{tr}(\text{Cl}^-)$ values, as no other set is available. Trends in $\Delta H_{tr}(\text{La}^{3+})$ for aqueous methanol and aqueous ethanol, using Krestov and Klopov's $\Delta H_{tr}(\text{Cl}^-)$ values in both cases, are compared in Fig. 6. In fact the values in alcohol-rich mixtures are composite, including any incorporation of chloride into the primary coordination shell of the La^{3+} (*cf.* above).

It is possible to derive $\Delta H_{tr}(\text{La}^{3+})$ into aqueous t-butyl alcohol, in water-rich mixtures only, by using

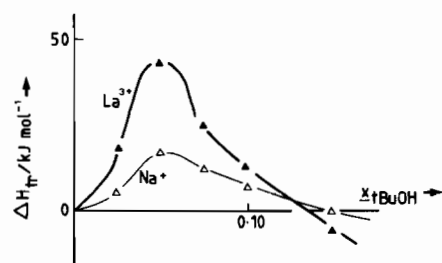


Fig. 7. Enthalpies of transfer of La^{3+} and Na^+ from water into water-rich aqueous t-butyl alcohol.

estimates for $\Delta H_{\text{tr}}(\text{Cl}^-)$ derived from published estimates of $\Delta H_{\text{tr}}(\text{Na}^+)$ [23] and enthalpies of solution of sodium chloride [24]. Our thus-derived values for $\Delta H_{\text{tr}}(\text{La}^{3+})$ and the estimates for $\Delta H_{\text{tr}}(\text{Na}^+)$ [23] are shown in Fig. 7. Solvent effects are larger for La^{3+} , as expected. The striking feature of Fig. 7, however, is the pronounced maximum at a mole fraction of t-butyl alcohol of approximately 0.05. This composition is close to that at which, on the basis of a large number of spectroscopic and thermodynamic criteria [13], the structure-making effect of the added alcohol is thought to be greatest [25].

There are several sets of enthalpies of solution of salts in dimethyl sulphoxide–water mixtures, but no single ion values have been published. Data do not exist for the estimation of these via the $\Delta H_{\text{tr}}(\text{Ph}_4\text{As}^+) = \Delta H_{\text{tr}}(\text{BPh}_4^-)$ assumption; the only solution enthalpies involving large ions of this sort refer to Bu_4NI [26]. Tantalisingly, $\Delta G_{\text{tr}}(\text{ion})$ values do exist for dimethylsulphoxide–water mixtures [27]. It would be possible for us to derive $\Delta H_{\text{tr}}(\text{Cl}^-)$, and hence $\Delta H_{\text{tr}}(\text{La}^{3+})$, by using the classical assumption that $\Delta H_{\text{tr}}(\text{K}^+) = \Delta H_{\text{tr}}(\text{Cl}^-)$, but we feel this approximation is too primitive for the results to be of value.

The estimation of $\Delta H_{\text{tr}}(\text{Ln}^{3+})$ for transfer into binary aqueous solvent mixtures thus varies from the unsatisfactory to the impossible at the moment. However as single ion splitting assumptions become more soundly based, and applied to more binary aqueous mixtures, more and better estimates for $\Delta H_{\text{tr}}(\text{Ln}^{3+})$ will be extractable from our enthalpies of solution published here.

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