

On the Complex Chemistry of the Tervalent Rare-Earth Ions

V. The Acetate and Glycolate Systems of Yttrium

ARTUR SONESSON

Department of Inorganic and Physical Chemistry, Chemical Institute, University of Lund, Lund, Sweden

The complex formation of the yttrium acetate system and the yttrium glycolate system has been studied potentiometrically. The measurements were performed at 20°C in perchlorate medium of ionic strength 2.0 M. It was found that both the systems show significant similarities with the correspondent systems in the middle of the lanthanum series.

The complexity constants of the yttrium acetate system are lower than the constants of the dysprosium system, but the ratios b_n/b_{n+1} between the consecutive stability constants coincide rather well for the two systems. The complexity constants of the yttrium glycolate system show a rather good agreement with the complexity constants of the gadolinium glycolate system. The values of the ratios b_n/b_{n+1} place the yttrium system between the samarium and the gadolinium systems.

For the trivalent yttrium ion the electron configuration of the outer shell is $4s^2 4p^6$. It is thus similar to the electron configuration of the trivalent ions of the lanthanum series — that is, $5s^2 5p^6$. Moreover the yttrium ion has about the same ionic radius (0.90 Å) as the middle rare-earth ions (Dy — 0.91 Å, Ho — 0.89 Å). Therefore the chemical similarity between yttrium and the middle rare-earths is rather great. Schwarzenbach *et al.*¹ have shown that the yttrium ions show the greatest similarity with the rare-earth ions in the middle of the lanthanum series when strong complexes are formed, *e.g.* with ethylenediamine tetra-acetate ions.

CHEMICALS USED

A stock solution of *yttrium perchlorate* was prepared by dissolving a weighed amount of yttrium oxide (99.5 % purity) in somewhat more than the calculated amount of perchloric acid. Most of the acid excess was then removed by evaporation.

The remaining excess of acid in the stock solution was determined by electrometric titration with sodium hydroxide.

The yttrium concentration of the stock solution was calculated from the weighed amount of yttrium oxide. The same value of the yttrium concentration was obtained

by means of a cation exchanger column, after having corrected for the free perchloric acid in the stock solution.

The stock solution was examined spectrographically and it was found that no foreign elements absorbing in the range 250 $m\mu$ –900 $m\mu$ were present in detectable amounts.

The other solutions used in this investigation were prepared and analyzed in the way described in the preceding parts ^{2,3,4}.

RESULTS

The investigation of the yttrium acetate and the yttrium glycolate systems was performed potentiometrically by means of quinhydrone electrodes as described in Parts I, II and III. The composition of the galvanic cells is shown in I p. 169 and III p. 999. For the notations and the functions used for the calculations of the complexity constants the reader is referred to II p. 1938.

The yttrium acetate system. It was checked that the hydrolysis of the non-complex yttrium ions did not seriously affect the complex formation. Buffer solutions having the composition 2 M HAc + 1 M NaAc and 4 M HAc + 1 M NaAc gave $\bar{n}/[A^-]$ -functions coinciding within the limits of the random errors.

As before, when the rare-earth acetate complexes were investigated, a correction has been applied for the decrease of the ionic strength caused by the complex formation. It was found that the relation between ΔE_A , the increase of E_A , and ΔI , the increase of the ionic strength I , was $\Delta E_A = -4.2 \times \Delta I$, i.e. about the same function was obtained as for the other rare-earth acetate systems (cf. I p. 171). ΔI was computed by means of approximate ligand numbers. Then, the ligand numbers \bar{n} have been computed from $E_A + \Delta E_A$.

The $\bar{n}/[A^-]$ -values at low acetate concentrations seem to increase somewhat with increasing yttrium concentrations in the same way as for the higher rare earths (cf. II). Then the system probably has a slight tendency to form polynuclear complexes. If only mono- and dinuclear complexes are assumed, the value of the complexity constant for the first dinuclear complex $\beta_1^2 = [M_2A] \cdot [M]^{-2} \cdot [A]^{-1}$ should be 20–30 M^{-2} .

The results of the measurements on the yttrium acetate system are shown in Fig. 1 and in Tables 1 and 2.

The yttrium glycolate system. The yttrium glycolate proved rather slightly soluble as was also found for the lower rare earths (cf. Jantsch and Grünkraut ⁵). However, the solution remained supersaturated for several minutes. Therefore the complex formation could be studied also at high glycolate concentrations by performing the measurements rapidly.

For the glycolate system the E_A -values measured must be increased by $\Delta E_A = -2.8 \times \Delta I$. Then the E_A -values varied with the ionic strength in about the same way as for the other rare earth glycolate systems.

No significant signs of polynuclear complexes could be detected.

The results of the measurements on the yttrium glycolate system are collected in Fig. 2 and in Tables 1 and 2.

DISCUSSION

If the complexity constants of the yttrium acetate system are compared with the corresponding constants of the rare-earth acetate systems that have

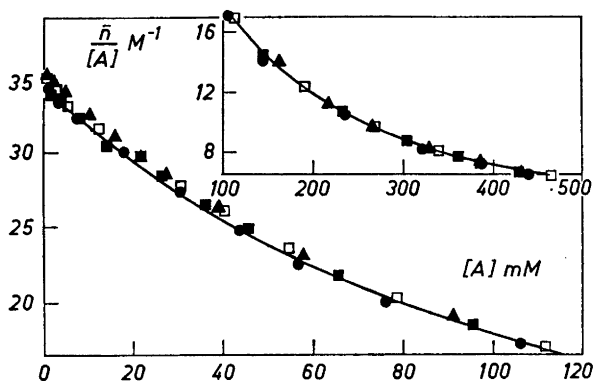


Fig. 1. $\bar{n}/[A^-]$ as a function of $[A^-]$ for the yttrium acetate system. Ionic strength 2.0 M. Open symbols: a buffer solution having the composition 2 M HAc + 1 M NaAc has been added to the yttrium perchlorate solution. Filled symbols: a buffer solution 4 M HAc + 1 M NaAc has been used. ●: C_M^0 (= the initial concentration of yttrium perchlorate) was 20 mM; ■, □: $C_M^0 = 40$ mM; ▲: $C_M^0 = 80$ mM.

been investigated before (I p. 180 and II p. 1952), it is found that the yttrium system has a considerably lower β_1 -value than the other rare-earth systems. Also the lanthanum system shows a higher value for β_1 . The increase of the complexity constants from β_1 to β_3 is, however, relatively greater for the yttrium system than for the lower rare-earth systems. Therefore the ratios b_n/b_{n+1} indicate a rather significant relationship between the acetate systems of yttrium and of the higher rare earths, especially those of dysprosium and holmium.

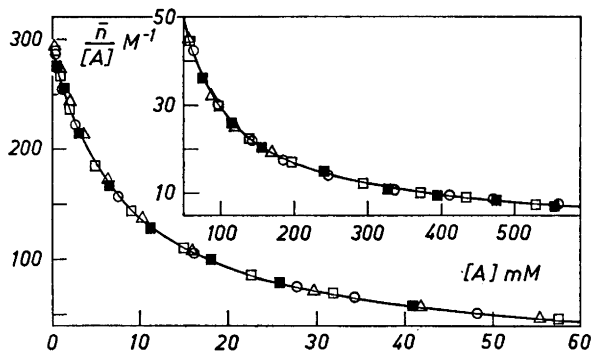


Fig. 2. $\bar{n}/[A^-]$ as a function of $[A^-]$ for the yttrium glycolate system. Ionic strength 2.0 M. Open symbols: a buffer solution 0.5 M HAcOH + 1 M NaAcOH was used. Filled symbols: a buffer solution 1 M HAcOH + 1 M NaAcOH was used. ○: C_M^0 (= the initial concentration of yttrium perchlorate) was 20 mM; ■, □: $C_M^0 = 40$ mM; △: $C_M^0 = 80$ mM.

Table 1. The complexity constants of the yttrium acetate system ($Y^{3+} - Ac^-$) and the yttrium glycolate system ($Y^{3+} - AcOH^-$) with their estimated random errors. $\beta_n = [MA_n] \cdot [M]^{-1} \cdot [A]^{-n}$ means the complexity constants of the mononuclear complexes and $\beta'_1 = [M_2A] \cdot [M]^{-2} \cdot [A]^{-1}$ the complexity constant of the first dinuclear complex. The temperature was 20°C and the ionic strength 2.0 M (perchlorate medium).

	$\beta_1 M^{-1}$	$\beta_2 M^{-2}$	$\beta_3 M^{-3}$	$\beta_4 M^{-4}$	$\beta_5 M^{-5}$	$\beta'_1 M^{-2}$
$Y^{3+} - Ac^-$	34 ± 2	460 ± 50	$2\,400 \pm 400$	$\sim 2\,000$	---	~ 20
$Y^{3+} - AcOH^-$	295 ± 15	$(25 \pm 2) \times 10^3$	$(50 \pm 7) \times 10^4$	$(18 \pm 4) \times 10^5$	$\sim 20 \times 10^6$	---

Table 2. The stability constants $b_1 = \beta_1$, $b_n = \beta_{n+1}/\beta_n$ and the ratios between the consecutive stability constants for the acetate and the glycolate systems of yttrium.

	b_1	b_2	b_3	b_4	b_1/b_2	b_2/b_3	b_3/b_4
$Y^{3+} - Ac^-$	34	13.5	5.2	0.8	2.5	2.6	6
$Y^{3+} - AcOH^-$	295	85	20	3.6	3.5	4.2	5.5

The complexity constants of the yttrium glycolate system are about the same as those of the gadolinium glycolate system (III p. 1008, 1009). Then there is also a good correspondence between the two glycolate systems concerning the stability constants as well as the ratios b_n/b_{n+1} . The values for b_n/b_{n+1} show possibly a slight tendency towards samarium.

The similarity between yttrium and the other rare earths with about the same ionic radius (especially Ho) is shown also by the ratios between the corresponding complexity constants of the glycolate and the acetate systems, *i.e.* the ratios $\beta_{n,gl}/\beta_{n,ac}$. Thus we find that the ratio $\beta_{1,gl}/\beta_{1,ac}$ is 3–5 for the lighter rare earths, 4.3 for Gd, 7.0 for Dy, 8.2 for Ho, 8.7 for Y, 10.0 for Er, and 11.8 for Yb.

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