

SUMMARY

The complexing polymer sodium diallyl phosphate (NaDAP) when used in conjunction with disodium ethylene diamine tetraacetate (Na₂EDTA) separates beryllium quantitatively from alkaline earths (Ca and Sr), ferric and divalent cations of the first transitional period, aluminium and lanthanides, cadmium and mercury(II), bismuth and polonium(IV). The high affinity of NaDAP for beryllium should permit its concentration by several orders of magnitude, when present as a minor or trace component in a mixture of polyvalent cations. The results are compared with those obtained using sulphonated resin.

RÉSUMÉ

L'allylphosphate de sodium polymère, en présence d'éthylènediaminetétracétate disodique, permet de séparer quantitativement le glucinium d'avec de nombreux autres cations. Les résultats sont comparés avec ceux obtenus à l'aide d'une résine sulfonée.

ZUSAMMENFASSUNG

Polymeres Diallyl-natriumphosphat, in Gegenwart des Dinatriumsalzes der Äthylendiamintetraessigsäure ermöglicht eine quantitative Abtrennung des Berylliums von zahlreichen mehrwertigen Kationen. Die Ergebnisse werden mit denjenigen, die mit Hilfe eines sulfonierten Harzes erhalten wurden, verglichen.

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SOLUBILITY PRODUCT RELATIONS IN THE RARE EARTH HYDROUS HYDROXIDES

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This paper is being presented to consider the solubility products of the rare earth hydroxides. A considerable amount of work has been directed to this topic¹. The difference between "new" and "old" precipitated hydroxides has already been well established and seems to be a kinetic phenomenon in which a more soluble material undergoes ripening through dehydration and further crystalization to become more insoluble. However, there has been some question regarding the solubility product

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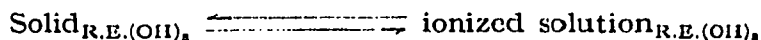
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as effected by temperature. This paper deals with this point for the freshly precipitated hydroxides. An approximation is also offered to the thermodynamic heat of solution of these precipitates.

The study was carried out by dissolving a preweighed sample of ignited oxide in a slight excess of standard perchloric acid*. This solution was then titrated with increments of standard sodium hydroxide. Readings were taken after each increment of sodium hydroxide when the pH had come to equilibrium while the temperature was held within 0.2°. This was generally accomplished in about 2 min. In this manner a curve of the type shown in Fig. 1 was obtained by recording the pH as a function of the base added. In Fig. 1, point A represents the end-point of excess perchloric acid; B, the end-point corresponding to complete precipitation of the rare earth hydroxide; and C represents the point $(B-A)/2$. For varying temperature a family of curves was obtained, as shown in Fig. 2, with $T_1 > T_2 > T_3$. By use of the pH at C, the hydroxyl concentration was obtained. By use of the fact that the concentration of rare earth in solution at point C is one-half that at A, the solubility product was obtained by substitution in:

$$L_{R.E.(OH)_3} = (R.E.) (OH)^3$$

By use of the Van 't Hoff isochore and the assumption that $L_{R.E.(OH)_3}$ represents the equilibrium between solid and solution:



the heat of the solution was calculated.

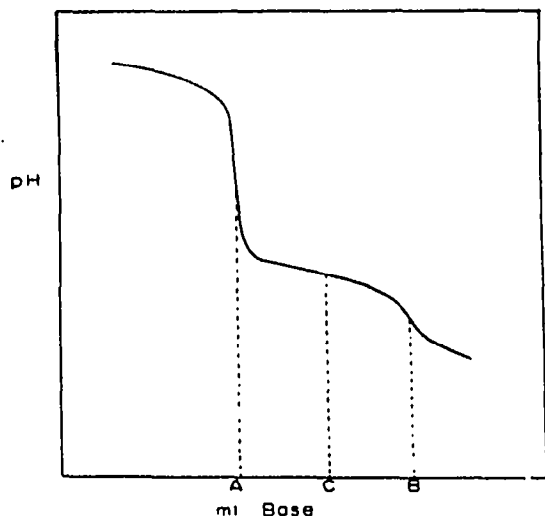


Fig. 1. Typical titration curve.

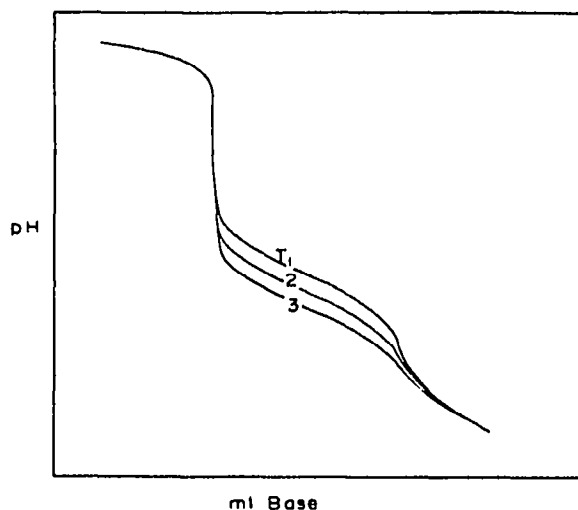


Fig. 2. Typical titration curve for variation in temperature.

* Rational atomic weights are determined by this means as:

$$\text{At. Wt. R} = \frac{\text{Wt. R}_2\text{O}_3 \times 6000}{\text{mequiv. H}^+ \text{ equal to R}_2\text{O}_3} - 48$$

The data was obtained with a Beckman model H-2 pH meter. A Cenco Universal Relay Control and mercury contact thermostat regulated the temperature in a 10-gallon water bath. By this means the pH could be obtained to within 0.02 pH units and the temperature to within 0.2°. The rare earths had the following purities (with major impurities) as indicated by the manufacturers: La 99.9% (Ce, Pr), Pr 99.9% (Ce, Nd), Nd 99.0% (Pr, Sm), Sm 99.0% (Gd, Eu), Gd 98% (Sm, Nd, Dy), Y 99.0% (Dy, Gd).

TABLE I
SOLUBILITY PRODUCT DATA OF RARE EARTH HYDROXIDES

Rare earth	T°C	Rare earth at point C	pH at point C	Solubility product
La	10	$5.48 \cdot 10^{-3}$	9.10	$14 \cdot 10^{-18}$
	20	$5.48 \cdot 10^{-3}$	8.68	$0.64 \cdot 10^{-18}$
	30	$5.48 \cdot 10^{-3}$	8.55	$0.25 \cdot 10^{-18}$
	40	$5.48 \cdot 10^{-3}$	8.10	$11 \cdot 10^{-21}$
Pr	10	$2.82 \cdot 10^{-2}$	8.23	$14 \cdot 10^{-20}$
	20	$2.82 \cdot 10^{-2}$	8.02	$3.3 \cdot 10^{-20}$
	30	$2.82 \cdot 10^{-2}$	7.77	$5.8 \cdot 10^{-21}$
	40	$2.82 \cdot 10^{-2}$	7.62	$2.4 \cdot 10^{-21}$
Nd	10	$3.72 \cdot 10^{-2}$	8.17	$12 \cdot 10^{-20}$
	20	$3.72 \cdot 10^{-2}$	7.90	$1.9 \cdot 10^{-20}$
	30	$3.72 \cdot 10^{-2}$	7.77	$7.61 \cdot 10^{-21}$
	40	$3.72 \cdot 10^{-2}$	7.65	$3.24 \cdot 10^{-21}$
Sm	10	$4.47 \cdot 10^{-2}$	7.82	$1.3 \cdot 10^{-20}$
	20	$4.47 \cdot 10^{-2}$	7.54	$2.0 \cdot 10^{-21}$
	30	$4.47 \cdot 10^{-2}$	7.32	$39 \cdot 10^{-23}$
	40	$4.47 \cdot 10^{-2}$	7.07	$7.2 \cdot 10^{-23}$
Gd	10	$1.21 \cdot 10^{-2}$	8.08	$2.3 \cdot 10^{-20}$
	20	$1.21 \cdot 10^{-2}$	7.86	$0.46 \cdot 10^{-20}$
	30	$1.21 \cdot 10^{-2}$	7.48	$35 \cdot 10^{-23}$
	40	$1.21 \cdot 10^{-2}$	7.25	$6.8 \cdot 10^{-23}$
Y	10	$3.75 \cdot 10^{-2}$	7.74	$6.2 \cdot 10^{-21}$
	20	$3.75 \cdot 10^{-2}$	7.65	$3.3 \cdot 10^{-21}$
	30	$3.75 \cdot 10^{-2}$	7.31	$32 \cdot 10^{-23}$
	40	$3.75 \cdot 10^{-2}$	7.10	$7.3 \cdot 10^{-23}$

TABLE II
RELATIVE BASICITY OF RARE EARTH HYDROXIDES

Ratio	10°C	20°C	30°C	40°C
La : Y	2270	192	770	150
Pr : Y	22.8	9.95	18.3	33.2
Nd : Y	19.7	5.57	23.8	44.3
Sm : Y	2.12	0.59	1.23	0.98
Gd : Y	3.67	1.38	1.09	0.92
Y : Y	1.00	1.00	1.00	1.00

TABLE III
HEATS OF SOLUTION OF RARE EARTH HYDROXIDES

<i>Rare earth</i>	<i>Temperature interval</i>	$\Delta H^\circ(\text{kcal})$
La	10-20	1.27
	20-30	0.42
	30-40	1.46
Pr	10-20	0.59
	20-30	0.75
	30-40	0.41
Sm	10-20	0.77
	20-30	0.72
	30-40	0.80
Gd	10-20	0.65
	20-30	1.13
	30-40	0.55
Nd	10-20	0.77
	20-30	0.44
	30-40	0.40
Y	10-20	0.25
	20-30	1.03
	30-40	0.69

Table I gives the major result of this work, giving vital data and calculated solubility product of the rare earth hydroxides. To be noted is the greater solubility for the greater atomic radii and lower temperature. It is fully recognized that these values do not represent equilibrium solubility data, but rather are to be associated only with the "new" hydroxide before it has had the opportunity to ripen. Table II shows the relative basicities as compared to yttrium hydroxide (comparison between like temperatures). This quite aptly characterizes the basicity which increases with increasing atomic radii and lower temperature. Table III shows the heat of solution for each hydroxide studied. It is estimated to be accurate to about 20%, considering temperature stability and accuracy in pH.

SUMMARY

The solubility products for some rare earth hydroxides and their temperature dependence have been shown. Greater solubility is shown for larger atomic radii and for lower temperature.

RÉSUMÉ

Les produits de solubilité de quelques hydroxydes de terres rares ont été déterminés.

ZUSAMMENFASSUNG

Es wird über die Löslichkeitsprodukte der Hydroxyde einer Anzahl seltener Erden berichtet.

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