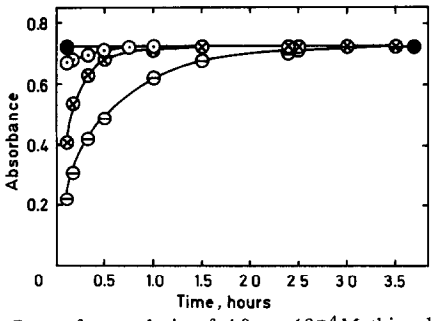

Fig. 1. Rate of cyanolysis of 4.0 × $10^{-4}M$ thiosulphate at various pH values. ●, expected value; ⊖, pH 9.1; ⊗, pH 9.3; ⊙, pH 9.5. All other conditions are as in the procedure.

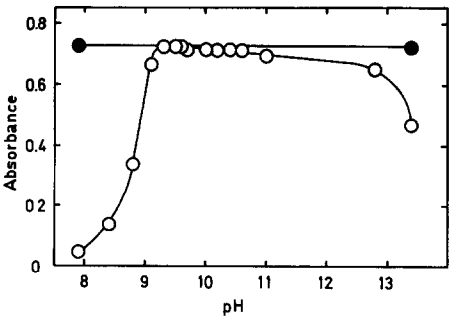

Fig. 2. Effect of pH on the cyanolysis of 4.0 × $10^{-4}M$ thiosulphate. ●, expected value; ○, experimental values. All other conditions are as in the procedure.

The effect of amount of cyanide was examined by using 3.5 ml of 0.05, 0.1, 0.5, 2, and 4*M* cyanide, the other conditions being optimal. The cyanolysis was incomplete with the 0.05–2*M* cyanide, though the calibration graphs were linear. When 4*M* cyanide was used, the calibration graph for thiosulphate coincided exactly with that for thiocyanate. It was also confirmed that the cyanolysis was quantitative with 3–4 ml of 4*M* cyanide and that excess of cyanide had no adverse effect.

A similar investigation of the amount of lanthanum(III) needed as catalyst showed that 1 ml of 0.5, 0.6, or 0.7*M* lanthanum was insufficient but 0.8–1.3 ml of 1.5*M* lanthanum gave a calibration curve in exact accord with that of thiocyanate. Excess of lanthanum has no adverse effect.

Effect of diverse ions

Aliquots (10 ml) of solution containing various amounts of diverse ions, in the presence and absence of thiosulphate, were treated exactly as in the procedure. The maximum permissible amounts of other ions in the determination of 437 μg of thiosulphate with an error of 2% are shown in Table 3. Phosphate and arsenate interfered by forming insoluble lanthanum salts. Sulphide interfered by being oxidized aerially to sulphur, which reacted with cyanide to form thiocyanate.

Precision

Eleven solutions (thiosulphate 44.9 μg/ml) were analysed and gave a relative standard deviation of 0.3%.

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Talanta, Vol 24, pp 761–762 Pergamon Press, 1977 Printed in Great Britain

USE OF THE CELLULOSE EXCHANGERS CELLEX D AND CELLEX T TO SEPARATE PLATINUM AND RHODIUM

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(*Received* 8 *March* 1977. *Revised* 19 *July* 1977. *Accepted* 23 *August* 1977)

Summary—Conditions for the separation of Pt and Rh by ion-exchange on two cellulose anion-exchangers have been established.

Our aim was to verify the feasibility of using the cellulose anion-exchangers Cellex D and Cellex T to separate platinum and rhodium. The affinity of these exchangers for chloride and other complexes of platinum metals is lower[1] than that of other anion-exchangers, and this should facilitate the separation and quantitative isolation of the components separated from the exchanger phase.

According to the literature, with the usual ion-exchangers there is difficulty in eluting the last traces of some platinum metals.[1–8] This is usually attributed to irreversible sorption. In the case of chloride complexes of Rh there is irreversible sorption on anion-exchangers, probably caused by retention of the polymerized sodium salts in small quantities.[9]

In this work the platinum and rhodium chloride complexes were separated by use of two systems: (1) exchanger with metal-ion solution in aqueous sodium (or potassium) chloride/hydrochloric acid medium at constant pH value, and (2) exchanger with metal-ion solution in hydrochloric acid medium. The effect of acetic acid on retention of chloride complexes[10] was also checked.

EXPERIMENTAL

Reagents

Exchangers. The DEAE-cellulose and TEAE-cellulose exchangers Cellex D and Cellex T (Bio-Rad Laboratories) were used.

Solutions of Pt and Rh. A 2.45 × $10^{-4}M$ solution of platinum was prepared from H_2PtCl_6 solution of known

Table 1. Distribution coefficients of Pt and Rh (15 μg ml) at various HCl concentrations

[HCl], *M*	Cellex D Pt	Cellex D Rh	Cellex T Pt	Cellex T Rh
0.01		31.6		28.9
0.1	941	15.2	926	16.1
0.3	117	8.2	94	4.4
0.5	53	6.0	58	3.3
1.0	32	4.2	28	1.7
1.5	27	1.8	23	0.5
2.0	21	1.3	20	0.3

platinum content. Solutions of other concentrations were obtained by further dilution. Rhodium solutions were prepared from a solution of known Rh content.

Distribution coefficient

The distribution coefficient is defined as:

$$K_d = \frac{\text{mmole/g of dry exchanger}}{\text{mmole/ml of solution}}.$$

The distribution coefficient was determined by the static method with 400 mg of exchanger and 40 ml of solution containing 7.7 μmole of Pt and 9.8 μmole of Rh. The distribution coefficients were determined as a function of hydrochloric acid concentration (0.01–2.0*M*) and sodium chloride concentration (0.1–0.8*M*) at constant pH. The results are given in Tables 1 and 2.

In the static-method investigations Rh and Pt were determined colorimetrically by the stannous chloride method.[11,12] In the dynamic method investigations flameless atomic-absorption spectroscopy was used (Perkin-Elmer Model 300 atomic-absorption spectrophotometer and Perkin-Elmer platinum and rhodium lamps).

Static investigations

Retention of Pt and Rh decreases with increase in hydrochloric acid concentration and the distribution coefficients are markedly higher for Pt.

The differentiation in affinity is even greater in the chloride solution at pH 2 for Cellex D, and when this exchanger is used a better separation ought to be obtained in chloride salt media than in hydrochloric acid solutions.

Interesting results were obtained for the effect of acetic acid on retention of Pt and Rh. In solutions with an initial hydrochloric acid concentration of 0.01*M* (pH 2.0) the distribution coefficient for Pt decreases on addition of acetic acid and increases with increasing acetic acid concentration but never to the same level as in its absence, whereas the coefficient for Pt is always increased, becoming larger with higher acetic acid concentration.

Table 2. Distribution coefficients of Pt (15 μg ml) and Rh (10 μg ml) on Cellex D at pH 2.1 and various NaCl concentrations

$[Cl^-]$, *M*	Pt	Rh
0.1	1620	6.7
0.3	233	2.4
0.5	120	1.9
0.8	81	1.0

Table 3. Distribution coefficients of Pt and Rh at various acetic acid concentrations

$[CH_3COOH]$, % *v/v*	Cellex D Pt (15 μg ml)	Cellex D Rh (15 μg ml)	Cellex T Pt (15 μg ml)	Cellex T Rh (15 μg ml)
40	77	124	63	120
70	185	141	210	137
90	713	302	560	286

The difference in affinity is thus decreased (Table 3). The optimum sodium chloride concentration has been determined statistically and should make it possible to separate Pt from Rh. The feasibility of separation has been checked under dynamic conditions.

Separation of Pt and Rh by column process

Pt and Rh solutions (10 ml) were introduced into an exchanger column (9.8 mm diameter) in presence of 0.1*M* sodium chloride and 0.01*M* hydrochloric acid. The bed length was 8.5 cm (1.4 g of exchanger). The flow-rate was regulated at 0.6 ml/min by means of a pump. Rh was eluted with 80 ml of 0.1*M* sodium chloride in 0.01*M* hydrochloric acid. Pt was eluted with 100 ml of 1*M* hydrochloric acid. Rh and Pt were determined both spectrophotometrically and by atomic absorption. The mean error for four determinations was 1% for 4.7 mg of Pt and 3% for 2.5 mg of Rh. Non-equivalent quantities of Pt and Rh were similarly separated, Rh being eluted with 40 ml of 0.1*M* sodium chloride in 0.01*M* hydrochloric acid and then 20 ml of 0.3*M* sodium chloride in 0.01*M* hydrochloric acid. Pt was eluted with 100 ml of 1*M* hydrochloric acid. The elution conditions were changed to give better resolution. The reduced volume of eluent used for Rh meant that a higher concentration had to be used to ensure complete elution, but that entailed a risk of loss of Pt. For this reason the volume of the more concentrated eluent had to be restricted. The mean error for three determinations was 7% for 0.3 mg of Pt and 1% for 2.5 mg of Rh, irrespective of whether 1.4 or 1.5 g of exchanger was used.

Acknowledgement—The authors wish to express their gratitude to Zygmunt Vorbrodt, M.Sc., for his help in carrying out measurements with the AAS method.

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