[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY, LOS ALAMOS, NEW MEXICO

Separation of the Lanthanons at Amalgam Cathodes. IV. High Purity Ytterbium from Mixtures of Heavy Lanthanons by Aqueous Electrolysis[1]

BY E. I. ONSTOTT

RECEIVED MAY 21, 1960

Ytterbium was separated from a mixture of heavy lanthanons by electrolysis into mercury from an aqueous lithium citrate electrolyte at *p*H 6. Enrichment of the Yb_2O_3 was from 31% to >99.9% purity and the yield was quantitative. A 50-50 mixture of Yb and radioactively tagged Tm was used to study the effect of *p*H on electrolysis rates and on the purity of electrolyzed Yb. A strong *p*H dependence was found with the rate of electrolysis of Yb being 40-fold slower at *p*H 11 than at *p*H 6. The average purity of Yb electrolyzed from the 50–50 mixture of Yb–Tm was 99.98% at *p*H 6 and 99.96% at *p*H 8. A foreign impurity effect was found (believed to be platinum contamination) which affected the rate of electrolysis of Tm, and for one experiment the rate for Yb was also affected. Since the effect was different for Tm and Yb the purity of the electrolyzed Yb was variant.

The specificity of the electrochemical method for the separation of Yb from some of the lanthanons has been well known since the original work of McCoy[2] and has been further investigated,[3] but the limitations of the method still are not well known. This paper defines some of the limitations and compares the behavior of Yb with that of Eu[4,5] and Sm,[5] which also show (II) valence in aqueous solutions and are easily separated from lanthanons which show only (III) or higher valence in aqueous solutions.[6]

Experimental

Details of procedures generally used in amalgam cathode separations are described in paper III.[6]

The separability of Yb from some of the heavy lanthanons was determined with a mixture purchased from St. Eloi Corp., Newtown, Ohio. An iodate precipitation[7] was done to remove the 1% thorium impurity. Composition of the oxide mixture after the thorium removal was as follows: Ho_2O_3, 4.3%; Er_2O_3, 6.2%; Tm_2O_3, 7.3%; Yb_2O_3, 31%; Lu_2O_3, 51%. The oxide (37.16 g.) was converted to acetate and dissolved in 500 ml. of one molar trilithium citrate. The electrolysis was done in a beaker with 100 ml. of mercury in a separate polyethylene basket cathode container. The current density was 0.02 amp./cm^2. A platinum flag anode was used. Thirteen cathode fractions were taken while the electrolysis was continued for 50 hr. The mercury phase was separated with a separatory funnel, and the washings were returned to the electrolyte. Ytterbium hydroxide which precipitated underneath the mercury (due to the back reaction of Yb with the trapped solvent) was redissolved in the electrolyte by agitation prior to a subsequent fractionation. Citric acid was added to maintain the electrolyte *p*H at about 6.

The amount of Yb left in the electrolyte after 50 hr. was 0.040 g. of oxide as determined by spectrographic examination of the oxide from the amalgam of a second electrolysis. Complete removal of the Yb was confirmed by spectrographic analysis of the residual electrolyte mixed oxide, which was found to contain <0.1% Yb. Purity of the Yb from the amalgams was estimated to be < 99.9%, since no lanthanon impurities were detected (limit of detection, 0.05% each Ho, Er, Tm; 0.1% Lu).

Three experiments were done to determine the separability of Tm and Yb and to find the effect of *p*H. A 50–50 mixture of these oxides was made by combining two grams each of 99.9% pure oxide plus Tm^{170} tracer, made by irradiation of pure Tm_2O_3 in the Los Alamos Omega West reactor. The combined oxide was converted to chloride and then dissolved in 200 ml. of electrolyte containing 0.2 mole of trilithium citrate. Electrolyses were done in a 500 ml. separatory funnel with 50 ml. of mercury for the cathode and a platinum spiral wire for the anode. A c.d. of 0.02–0.025 amp./cm.^{2} was set. The cathode amalgam was removed and replaced at frequent intervals so that the Yb and the ratio Yb/Tm in the amalgams could be determined chronologically. The Tm was determined with a scintillation counter, and the Yb was determined by weighing the ignited hydroxide. A material balance on all fractions of the electrolysis done at *p*H 8 checked within 0.1%, thus showing that recovery procedures were quantitative.

One electrolysis was done at a *p*H of 6.0 ± 0.5 by adding citric acid periodically to maintain the proper *p*H. At this acidity the current density was not high enough to cause appreciable simultaneous Li electrolysis, so no Li was detected in the Yb amalgams.

A second electrolysis was continued at *p*H 8 ± 1 after the first fraction was electrolyzed with the electrolyte maintained at *p*H 9–11 by adding LiOH. Subsequently LiOH was not added, and the *p*H stabilized at about 8. The concentration of lithium in the amalgam reached saturation by the time the cathode fraction was withdrawn, and dilution with mercury was necessary for a separation of the saturated phase.

The electrolysis at *p*H 11 ± 1 was done with saturated lithium amalgam (prepared by electrolyzing lithium citrate in a separate cell) instead of starting with mercury as the cathode material. The *p*H was controlled by adding LiOH at intervals of about 30 minutes. Toward the middle of the electrolysis, a carbonate precipitate containing Yb–Tm was observed, but the total amount at the end of the electrolysis accounted for <20% of the Yb–Tm originally present. Rate data were corrected for the concentration change caused by the precipitation side reaction.

Discussion

Electrolysis Behavior of Yb.—The rate of electrolysis of Yb in the Yb–Tm mixture is first order (Fig. 1) except for the last portion of the electrolysis done at *p*H 6. The rate is slow however, compared to what would be expected for ideal behavior based on a presumption of complete concentration polarization as exhibited by Eu.[4] The slope of the straight line portion of the plot at *p*H 6 is a factor of 4 smaller than the slope drawn for the expected rate for Eu electrolysis under similar conditions. A marked *p*H dependence is demonstrated, in contrast to Eu which shows almost no *p*H dependence.[4,5] At *p*H 11 the rate is a factor of 150 slower than the expected Eu electrolysis rate.

The behavior of Yb is much more like Sm than like Eu, although Sm probably shows a greater degree of *p*H dependence.[5] Sufficient data are not now available to determine with certainty

---

(1) Work was done under the auspices of the Atomic Energy Commission. Submitted for presentation at the 138th Meeting of the American Chemical Society, September, 1960, New York.

(2) H. N. McCoy, THIS JOURNAL, **63**, 1622 (1941).

(3) H. N. McCoy and R. P. Hammond, *ibid.*, **64**, 1009 (1942); J. K. Marsh, *J. Chem. Soc.*, 398 (1943); T. Moeller and H. E. Kremers, *Ind. Eng. Chem.*, **17**, 798 (1945); D. I. Ryabchikov, Yu. S. Sklarenko and N. S. Stroganova, *Zhur. Neorg. Khim.*, **1**, 1954 (1956); *C. A.*, **51**, 5595e (1957).

(4) E. I. Onstott, THIS JOURNAL, **77**, 2129 (1955).

(5) E. I. Onstott, *ibid.*, **78**, 2070 (1956).

(6) E. I. Onstott, *ibid.*, **81**, 4451 (1959).

(7) K. Shaver, AEC Report MLM-1031, Jan. 1955, p. 8.

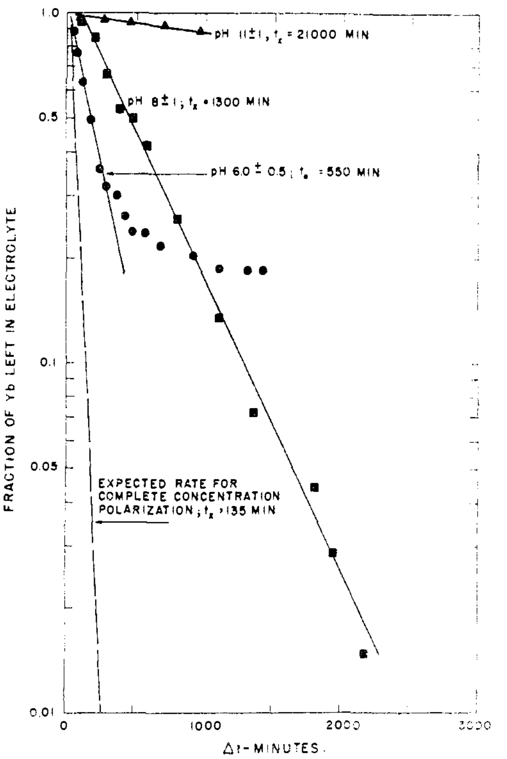

Fig. 1.—Rate of electrolysis of Yb from Yb–Tm mixtures. The straight line plot at *p*H 8 does not go through origin, since the first fraction was done at *p*H ~ 10; symbol t_x represents the time to remove 90% of the Yb.

the inherent differences. It may be presumed, however, that the electrochemical separation of Yb from Sm would be difficult by aqueous electrolysis. The separation of Eu from Yb should be easy if done at high *p*H.

In only one experiment did the electrolysis rate behavior of Yb change radically as a result of some uncontrolled change in electrolysis conditions. At *p*H 6 (Fig. 1) the rate decreased markedly after an interval of time representing about 70% removal of Yb in the electrolyte. This change in rate is so pronounced that the most likely suspect is an impurity species which increased in concentration to a point where it depolarized the cathode to such an extent that the Yb electrolysis efficiency was reduced many fold. A platinum species is the most probable impurity which would cause such a marked effect, and it could be formed rather rapidly by anodic etching in the acidic electrolyte with chloride present. Such a change in the rate of electrolysis of Yb was not noticed in the separation done at *p*H 6 with acetate as the anion. Here the removal of Yb was 99.6% complete after 50 hr.

Electrolysis Behavior of Tm.—The rate behavior of Tm can be estimated from the data in Figs. 1 and 2. There is a marked decrease in the electrolysis of Tm with time, even though the amount present in the electrolyte remains virtually constant. The decrease in rate is influenced by the electrolyte *p*H (Fig. 2), with the most rapid decrease occurring with the lowest *p*H. This behavior can most logically be attributed to a gradual buildup of an impurity which interferes with the Tm electrolysis mechanism. Most likely the impurity is a Pt species from anodic etching which steals a large portion of the hydride ion generated at the cathode and forms H_2 catalytically so that very little hydrido ligand is left for coordination with Tm. It was pointed out previously that codeposition of hydride ligand with the (III) lanthanons probably is a necessary condition for electrolysis.[6]

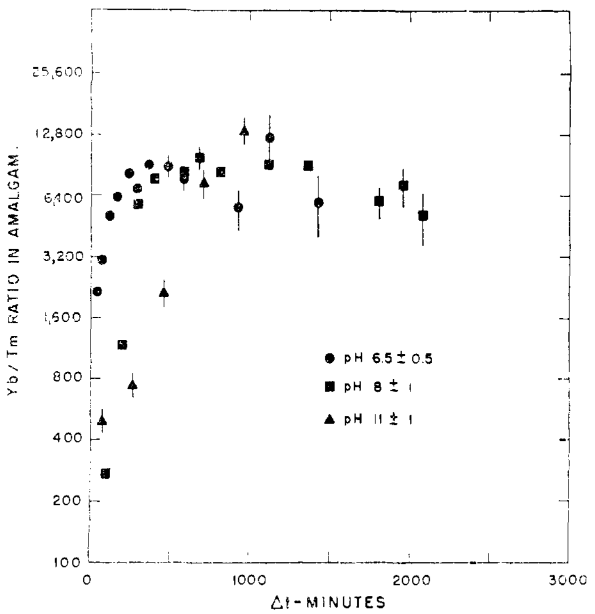

Fig. 2.—Chronological variation of purity of amalgam Yb electrolyzed from Yb–Tm mixtures.

After an interval of time the Yb/Tm ratio in the amalgam approaches a reasonably constant value even though the ratio in the electrolyte changes many fold (*i.e.*, experiment at *p*H 8). Such behavior probably has significance but cannot be interpreted with presently available data because of the probable impurity species effect.

Purity of Yb.—The Yb in the mixed lanthanon oxide was removed quantitatively and was > 99.9% pure. The average purity of amalgam Yb from the Yb–Tm mixture was 99.98% at *p*H 6 and 99.96% at *p*H 8. The purity of Yb from both of the latter electrolyses could have been improved at a sacrifice in yield by choosing middle and last fractions (Fig. 2). The yield of Yb at *p*H 6 with chloride present undoubtedly would have been improved by use of acetate instead of chloride, and the yield at *p*H 8 could have been increased to 99.9% simply by extending the electrolysis time to a total of about 3700 minutes. For a practical separation the time to remove the Yb quantitatively could be minimized by controlling the *p*H at 6. However, the same yield could be obtained at *p*H 8 without attention to *p*H control but with a sacrifice in the longer time required for completion of the electrolysis.

The chloride electrolyte should not be used with a platinum anode in acid solution if a quantitative yield of Yb is desired. Possibly a carbon anode could be substituted if the chloride anion is deemed necessary.

Acknowledgments.—The author wishes to thank O. R. Simi for the spectrographic analyses and M. M. Thorpe for the space in the Omega West Reactor.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY]

Microwave Absorption and Molecular Structure in Liquids. XXXVI. The Relaxation of the Methylene Chloride Group in Three Aromatic Molecules[1,2]

BY WILLIAM P. PURCELL,[3] KENNETH FISH AND CHARLES P. SMYTH

RECEIVED MAY 31, 1960

The dielectric constants and losses at wave lengths of 1.25, 3.22, 10, 25 and 50 cm. and 300 m. have been measured for benzyl chloride and α,α'-dichloro-*p*-xylene in benzene solution at 20, 40 and 60°, and bis-(chloromethyl)-durene has been measured in benzene solution at 20°. The data have been used to calculate the dielectric relaxation times of the molecules. The benzyl chloride absorption curve has been resolved into two peaks corresponding to over-all molecular and group relaxation. The short relaxation time for benzyl chloride is compared with the relaxation time of α,α'-dichloro-*p*-xylene, which should be associated primarily with intramolecular rotation. The durene compound has only one absorption region, that corresponding to molecular rotation. The moment measured for bis-(chloromethyl)-durene is analyzed and found to be consistent with the moments previously found for benzyl chloride and α,α'-dichloro-*p*-xylene.

Because of its possession of two rotatable polar groups, CH_2Cl, on opposite sides of a benzene ring, α,α'-dichloro-*p*-xylene offers a particularly good model for the study of intramolecular rotation by means of dielectric relaxation measurements. Measurements of dielectric loss or dielectric constant and loss have been carried out at megacycle frequencies, far below the region of maximum absorption, and the results have been discussed.[4–6] The present paper presents measurements in the kilomegacycle region on three compounds containing the CH_2Cl group with different structural factors producing very different effects of the group upon the observed relaxation times.

Experimental Methods

Apparatus.—The apparatus and the various methods of measurement have been described in previous papers.[7–9]

A Varian 4300 B apparatus equipped with a flux stabilizer was used by Mr. I. D. Kuntz to take the nuclear magnetic resonance spectrum of bis-(chloromethyl)-durene in benzene solution. The measurements were made at 25° using the side band technique.[10]

Purification of Materials.—Benzyl chloride, obtained from Eastman Kodak Co., was fractionally distilled.

α,α'-Dichloro-*p*-xylene, obtained from Eastman Kodak Co., was recrystallized twice from benzene and dried under vacuum in an Abderhalden pistol.

Bis-(chloromethyl)-durene, obtained from Shell Development Co., was recrystallized three times from benzene and dried under vacuum in an Abderhalden pistol, m.p. 197.0–198.0.

Benzene, obtained from Allied Chemical Corp., was used without further purification.

Experimental Results

The experimental results were treated in the manner previously described.[11] The slopes of the straight lines thus obtained, a', corresponding to ϵ', and a'', corresponding to ϵ'', were plotted in Cole–Cole arcs[12] in the usual fashion[11] for α,α'-dichloro-*p*-xylene and bis-(chloromethyl)-durene to obtain the critical wave lengths λ_m, the corresponding relaxation times τ, the distribution coefficients α and the arc intercepts at infinite frequency a_∞. The concentration range in mole fraction is given in parentheses for each set of solutions in Table I,

TABLE I

SLOPES FOR THE DEPENDENCE OF THE DIELECTRIC CONSTANT AND LOSS OF BENZENE SOLUTIONS UPON MOLE FRACTION OF SOLUTE

Wave length (cm.)	20°		40°		60°	
	a'	a''	a'	a''	a'	a''
Benzyl chloride (0–0.0425)						
0.435	1.25	1.30				
1.24	2.24	1.43	2.34	1.47	2.32	1.38
3.22	3.40	1.54	3.52	1.28	3.32	1.05
10	4.55	0.90	4.36	0.62	4.02	0.44
25	5.03	0.39				
300	4.98		4.58		4.10	
α,α'-Dichloro-*p*-xylene (0–0.035)						
1.24	4.50	2.31	4.75	2.03	4.90	1.67
3.22	6.17	1.52	5.90	1.11	5.51	0.84
10	6.80	0.45	6.25	0.36	5.90	.21
25	6.90	0.25	6.33	0.15	5.80	.10
300	7.05		6.45		5.79	
Bis-(chloromethyl)-durene (0–0.0057)						
1.20	0.5	0.5				
3.22	2.05	1.85				
10	3.5	2.2				
25	5.6	1.4				
50	6.5	0.8				
300	6.5					

[a] Measurements made by Mr. W. E. Vaughan.

---

[1] This research was supported by the Office of Naval Research. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

[2] This paper represents part of the work submitted by W. P. Purcell to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Allied Chemical Corporation Fellow, 1959–1960.

[4] A. Budó, *Physik. Z.*, **39**, 706 (1938).

[5] E. Fischer, *Z. Naturforsch.*, *9a*, 909 (1954).

[6] A. Aihara and M. Davies, *J. Coll. Sci.*, **11**, 671 (1956).

[7] H. L. Laquer and C. P. Smyth, THIS JOURNAL, **70**, 4097 (1948).

[8] W. M. Heston, Jr., A. D. Franklin, E. J. Hennelly and C. P. Smyth, *ibid.*, **72**, 3443 (1950).

[9] D. A. Pitt and C. P. Smyth, *J. Phys. Chem.*, **63**, 582 (1959).

[10] J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

[11] A. D. Franklin, W. M. Heston, Jr., E. J. Hennelly and C. P Smyth, THIS JOURNAL, **72**, 3447 (1950).

[12] K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).