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ABSTRACT

In aqueous chloride media above 2M acid the extraction of zirconium ions by Aliquat-336 depends solely on the total chloride ion concentration, and is independent of the hydrogen ion or lithium ion concentration.

For total chloride ion concentrations between 6M and 8M the addition of small amounts of nitrate ion greatly enhances the extraction of zirconium by Aliquat-336. This enhancement is a maximum at between 0.5 and 0.75M nitrate ion in the aqueous phase. This effect is also independent of hydrogen ion or lithium ion concentration. It is postulated that the species being extracted is $[ZrCl_5NO_3]^{2-}$.

These results are preliminary to selecting the optimum conditions for the extraction of zirconium, and also for the separation of zirconium from hafnium by a liquid anion exchange process.

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ACIDITY; AMMONIUM CHLORIDES; ANIONS; CHLORIDES; HYDROLYSIS; ION EXCHANGE; ION EXCHANGE MATERIALS; LITHIUM COMPOUNDS; METHYL RADICALS; NITRATES; OCTYL RADICALS; OPTIMIZATION; SEPARATION PROCESSES; ZIRCONIUM; ZIRCONIUM COMPLEXES

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1. INTRODUCTION

1.1 Background

The usefulness of the liquid anion exchanger Aliquat-336 (tricapryl (methyl) ammonium chloride) in the separation of zirconium from hafnium is predictable from the graphical results of Seely and Crouse (1966). The actual separation has been studied in some detail by Bonfanti et al. (1967), while the extraction of zirconium was studied, apparently independently, by Sato and Watanabe (1970). Where the latter publications overlap they agree very well so that both works carry conviction.

Bonfanti et al. claim the highest separation factors ever achieved for these metals (2.3×10^3) and hence the method must be considered potentially useful for analytical and industrial application. The chemistry governing the attainment of such high separation factors is also significant in the general comparative study of these very similar metals.

The Italian and Japanese workers demonstrate that extraction coefficients of zirconium in these systems increase markedly with increasing temperature. They both observe that zirconium extraction increases with increasing hydrochloric acid concentration. Bonfanti et al. (1967) show that zirconium extraction from solutions containing 8M total acid is depressed by the addition of all other strong acids with the exception of nitric acid below 1.0M which enhances the extraction. At higher concentrations it too is a depressant.

The graphs of Seely and Crouse (1966) and the experimental observations of Sato and Watanabe (1970) indicate that the extraction of zirconium is greatly reduced by the replacement of hydrochloric acid with lithium chloride in the aqueous phase. Their results are limited to acid concentrations of 0.1M and 0.2M. Sato and Watanabe suggest that this depression may be due to hydrolysis.

1.2 The Problem

Bonfanti et al. (1967) mention in passing that their process is somewhat limited by the production of noxious fumes. In preliminary experiments aimed at reproducing some of their results we observed considerable decomposition of solutions containing nitrate ions in a total acid concentration of above 6M. The elimination of such fuming is essential before this process can be turned to analytical or industrial use.

To reduce the problem of solution decomposition it is necessary to maintain the total acid concentration below 6M. To prevent hydrolysis of the zirconium it is necessary to maintain acid concentration of above 2M (Pakalns 1969). Our problem was to discover whether there existed, within this total acid concentration range of 2M to 6M, conditions favourable to the maximum extraction of zirconium. We agree with Sato and Watanabe (1970) that the probability of extensive hydrolysis obscures the significance of their results (and of those of Seely and Crouse 1966) on the restricted extraction of zirconium from lithium chloride solutions. We decided to re-investigate the dependence of zirconium extraction on chloride ion and nitrate ion concentrations under conditions minimizing hydrolysis and solution decomposition.

2. EXPERIMENTAL

2.1 Equipment

A Unicam S.P. 600 spectrophotometer with 1 cm cells was used for the zirconium analyses.

A Techtron Atomic Absorption Spectrophotometer was used for the lithium analyses.

2.2 Reagents

Zirconium (IV) Solutions: Zirconium oxychloride $\left([Zr_4(OH)_8(H_2O)_{16}]Cl_8 12H_2O\right)$ (0.322 g) is dissolved in 19.1 ml of 10.5 N hydrochloric acid and made up to 100 ml. This solution is 1.00 x 10^{-2}M in Zr^{4+}. In a typical dilution 5 ml of this 1.00 x 10^{-2}M solution was diluted with 190 ml 10.5M HCl. To the resulting solution was added 21 g LiCl and 6.15 g $LiNO_3.3H_2O$. The volume was then adjusted to 500 ml with distilled water to give a solution 10^{-4}M with respect to Zr^{4+} ion, 1M in LiCl, 0.1M in nitrate ion and 4M total acid concentration. The other solutions used were prepared in a similar manner.

Aliquat-336: A weighed sample of Aliquat-336 (5.13 g) was dissolved in A.R. toluene (100 ml) to give a 0.300M solution. The purity of the Aliquat-336 (General Mills) was established by analysis of its chloride content. The chloride was extracted from the toluene solution by shaking a 10 ml sample with two 10 ml portions of 2M nitric acid. The aqueous extract was neutralized with sodium carbonate and the chloride estimated by Mohr's method. For a series of concentrations of Aliquat-336 (0.1 to 0.5M) the calculated concentrations proved accurate to the third decimal place.

2.3 Procedure

Extraction: 5 ml of the aqueous phase and 5 ml of the organic phase were shaken together for 10 min in a separatory funnel. The phases were then allowed to settle and were separated. The amount of zirconium extracted into the organic phase was estimated from the zirconium content of the original solution and the residual zirconium in the equilibrated aqueous phase. Aliquat-336 tended to interfere with the direct determination of zirconium in the organic phase.

Analyses

Zirconium: Zirconium in the aqueous phase was estimated spectrophotometrically using Arsenazo III (Savvin 1959). Samples of 2 ml were used, and, if nitrate ion was present, they were first fumed down with 0.5 ml of concentrated perchloric acid.

Chloride: Chloride ion was analysed by Mohr's procedure. Chloride ion in the organic phase was first extracted (twice) into 2M nitric acid and the aqueous extract so obtained neutralised.

Acid: The acid concentration was ascertained by titration with sodium hydroxide using phenolphthalein as indicator.

Lithium: Lithium concentrations were estimated from atomic absorption measurements.

Nitrate: Nitrate ion concentration was measured using the dichromate-ferrous sulphate method.

Temperature: The temperature was the ambient temperature (20-23°C).

3. RESULTS AND DISCUSSION

3.1 Dependence of Zirconium Extraction on Total Chloride Ion Concentration

The extraction of zirconium from solutions which varied 6M to 12M in total chloride ion concentration was studied by varying the ratios of hydrochloric acid to lithium chloride in the aqueous phase. The results are collected in Table 1. Since little or no polymerization occurs for 10^{-4}M zirconium solutions at 2M acid and above (Pakalns 1969), these results represent the relationship of the extractability of monomeric zirconium and the concentration of other species in the solution. Figure 1 shows that, above 2M acid, the extraction of zirconium in this system depends solely on the chloride ion concentration. Table 1 shows that the extraction is independent of hydrogen ion or lithium ion concentration. These results are in accord with the postulate that the zirconium species being extracted is $[ZrCl_6]^{2-}$ (Sato and Watanabe 1970).

3.2 Nitrate Ion Enhancement of Zirconium Extraction from Chloride Media

The effect of nitrate ion on the extraction of zirconium described above was investigated. The aqueous medium was varied from 2M to 4M in hydrochloric acid adjusted by the addition of lithium chloride to give total chloride concentrations ranging from 3M to 10M. By the addition of lithium nitrate two series of solutions were prepared, in one of which the nitrate ion was 0.1M and in the other 0.2M.

Comparison of Figures 2a and 2b with Figure 1 shows dramatic enhancement of zirconium extraction by relatively small additions of nitrate ion. In these systems there is no discernible dependence of zirconium extraction on hydrogen ion concentration. This enhancement is due to the presence of nitrate ion rather than nitric acid.

Table 2 shows results of an extended study of this system in which the chloride concentration varied from 2M to 10M, acid concentrations from 2M to 8M and nitrate ion concentrations from 0.1M to 4.0M. From these results the percentage extraction of zirconium is plotted against total chloride ion concentration in Figure 3, and against nitrate ion concentration at various total chloride ion concentrations in Figures 4a and 4b.

Figure 3 demonstrates that nitrate ion enhancement of zirconium extraction is very concentration dependent at low nitrate ion concentrations. It is highest between 0.5M and 0.75M nitrate and diminishes slowly towards higher concentrations.

Figure 4a shows that the only range in which nitrate ion enhancement is significant is from 6M to 8M total chloride ion concentration. This range is shown in greater detail in Figure 4b.

Since nitrate ion to chloride ion concentration is about 1:10 at the optimum conditions for extraction, and since nitrate coordinates to zirconium about twice as well as does chloride (Nabivcinec 1961), it is proposed that the species being extracted from this system is $[ZrNO_3Cl_5]^{2-}$.

When the concentration of nitrate ion in the aqueous phase exceeds the Aliquat-336 concentration in the organic phase, nitrate ion will compete with the anionic zirconium species for sites on the liquid anion exchanger and so depress the extraction.

4. CONCLUSION

We conclude that the extraction of zirconium from dilute aqueous solutions by Aliquat-336 is dependent on the concentrations of chloride and nitrate ions provided that no hydrolysis occurs. The optimum conditions for extraction by 0.3M Aliquat-336 at room temperature are: chloride ion concentration 7.5 - 8.0M, acid concentration 2 - 3M and nitrate ion concentration 0.5 - 0.75M. Under these conditions there is no decomposition of the solutions.

Within these concentration ranges the extraction of hafnium is depressed practically to zero (Bonfanti et al. 1967). A parallel study of the extraction of hafnium will be the subject of a future report, and it will then be possible to establish optimum conditions for the separation of zirconium from hafnium.

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TABLE 1

VARIATION OF ZIRCONIUM EXTRACTION WITH TOTAL CHLORIDE ION CONCENTRATION

Total [Cl$^-$]	[HCl]	[LiCl]	% Extraction	Mean %
6M	2M	4M	1.7	1.7
6.5	2.0	4.5	7.5	
	6.0	0.5	5.2	6.4
7.0	2.0	5.0	17.7	
	4.0	3.0	16.1	
	6.0	1.0	4.9	12.9
7.5	6.0	1.5	43.2	43.2
8.0	2.0	6.0	18.6, 23.6	
	4.0	4.0	28.1, 23.6	
	6.0	2.0	42.5	27.3
8.25	2.0	6.25	87.0	87.0
8.5	2.0	6.5	90.0, 74.4, 85.4	
	4.0	4.5	81.7, 86.5, 87.0	
	6.0	2.5	90.2	85.0
9.0	2.0	7.0	97.3, 87.4	
	4.0	5.0	91.2, 87.8, 90.0	
	6.0	3.0	95.6	91.0
9.5	2.0	7.5	98.8, 97.1, 97.3	
	4.0	5.5	96.4, 96.7, 97.3	
	6.0	3.5	93.6	96.8
10.0	2.0	8.0	87.2, 95.3	
	4.0	6.0	93.2, 94.5, 95.3	
	6.0	4.0	95.2	93.5
10.5	4.0	6.5	99.5, 98.8	99.2
11.0	2.0	9.0	97.8, 90.2	94.0
12.0	4.0	8.0	97.8, 97.4	97.6

TABLE 2

VARIATION OF ZIRCONIUM EXTRACTION WITH NITRATE ION CONCENTRATION

[$LiNO_3$]	Total [Cl^-]	[HCl]	[LiCl]	% Extraction	Mean %
0.1M	3.0M	2.0M	1.0M	0	0
0.1	3.5	2.5	1.0	0	0
0.1	4.0	2.0	2.0	0	
		3.0	1.0	0	0
0.1	4.5	2.5	2.0	0	
		3.5	1.0	0	0
0.1	5.0	2.0	3.0	4.2	
		3.0	2.0	3.3	
		4.0	1.0	0	2.5
0.1	5.5	2.5	3.0	3.4	
		3.5	2.0	0	1.7
0.1	6.0	2.0	4.0	16.2	
		3.0	3.0	14.1	
		4.0	2.0	12.3	14.2
0.1	6.5	2.5	4.0	26.1	
		3.5	3.0	23.8	25.0
0.1	7.0	2.0	5.0	51.4	
		3.0	4.0	47.6	
		4.0	3.0	39.0	46.0
0.1	7.5	2.5	5.0	70.6	
		3.5	4.0	74.2	72.4
0.1	8.0	2.0	6.0	80.5	
		3.0	5.0	85.8	
		4.0	4.0	82.0	82.7
0.1	8.5	2.5	6.0	93.9	
		3.5	5.0	92.5	93.2
0.1	9.0	3.0	6.0	97.3	
		4.0	5.0	97.8	97.6

(continued)

Table 2 (continued)

$[LiNO_3]$	Total $[Cl^-]$	[HCl]	[LiCl]	% Extraction	Mean %
0.1M	9.5M	3.5M	6.0M	96.4	96.4
0.1	10.0	4.0	6.0	99.1	99.1
0.2M	3.0	2.0	1.0	0	0
0.2	3.5	2.5	1.0	0	0
0.2	4.0	2.0	2.0	1.9	
		3.0	1.0	0	1.0
0.2	4.5	2.5	2.0	5.1	
		3.5	1.0	2.5	3.8
0.2	5.0	2.0	3.0	10.7	
		3.0	2.0	9.4	
		4.0	1.0	5.6	8.6
0.2	5.5	2.5	3.0	28.4	
		3.5	2.0	17.1	22.8
0.2	6.0	2.0	4.0	29.3	
		3.0	3.0	43.9	
		4.0	2.0	35.1	36.1
0.2	6.5	2.5	4.0	66.0	
		3.5	3.0	59.9	63.0
0.2	7.0	2.0	5.0	74.7	
		3.0	4.0	81.2	
		4.0	3.0	69.4	75.1
0.2	7.5	2.5	5.0	89.5	
		3.5	4.0	88.9	89.2
0.2	8.0	2.0	6.0	94.1	
		3.0	5.0	91.8	
		4.0	4.0	92.2	92.7
0.2	8.5	2.5	6.0	96.8	
		3.5	5.0	94.1	95.5
0.2	9.0	3.0	6.0	96.3	
		4.0	5.0	97.6	97.0
0.2	9.5	3.5	6.0	97.0	97.0
0.2	10.0	4.0	6.0	97.9	97.9

(continued)

Table 2 (continued)

$[LiNO_3]$	Total $[Cl^-]$	[HCl]	[LiCl]	% Extraction	Mean %
0.25M	6.0M	6.0M	0M	40.2	40.2
0.25	8.0	8.0	0	93.2	93.2
0.5	6.0	4.0	2.0	62.4	
		6.0	0	43.4	52.9
0.5	7.0	4.0	3.0	88.5	88.5
0.5	8.0	8.0	0	82.6	82.6
0.75	4.0	4.0	0	2.3	2.3
0.75	6.0	6.0	0	72.1, 74.3	73.2
0.75	8.0	8.0	0	98.7, 95.5	97.1
1.0	6.0	4.0	2.0	66.6	
		6.0	0	36.3	51.5
1.0	7.0	4.0	3.0	88.0	88.0
1.0	8.0	8.0	0	87.4	87.4
1.25	2.0	2.0	0	0	0
1.25	4.0	4.0	0	4.5	4.5
1.25	6.0	6.0	0	70.5, 37.9	54.2
1.25	8.0	8.0	0	96.3, 96.2	96.3
1.50	6.0	4.0	2.0	56.3	
		6.0	0	16.4	36.4
1.50	7.0	4.0	3.0	81.2	81.2
1.50	8.0	8.0	0	92.2	92.2
1.75	2.0	2.0	0	0	0
1.75	4.0	4.0	0	5.6	5.6
1.75	6.0	6.0	0	62.9	
1.75	8.0	8.0	0	91.7, 95.3	93.5
2.0	6.0	4.0	2.6	57.5	57.5
2.0	7.0	4.0	3.0	81.4	81.4
2.0	8.0	8.0	0	56.4	56.4

(continued)

Table 2 (continued)

[$LiNO_3$]	Total [Cl^-]	[HCl]	[LiCl]	% Extraction	Mean %
2.5M	6.0M	4.0M	2.0M	54.9	54.9
2.5	7.0	4.0	3.0	72.9	72.9
2.5	8.0	8.0	0	87.1	87.1
3.0	6.0	4.0	2.0	54.2	
		6.0	0	49.7	52.0
3.0	7.0	4.0	3.0	70.9	70.9
3.5	6.0	4.0	2.0	52.9	52.9
3.5	7.0	4.0	3.0	68.5	68.5
4.0	6.0	4.0	2.0	53.1	
		6.0	0	45.3	49.2
4.0	7.0	4.0	3.0	67.6	67.6

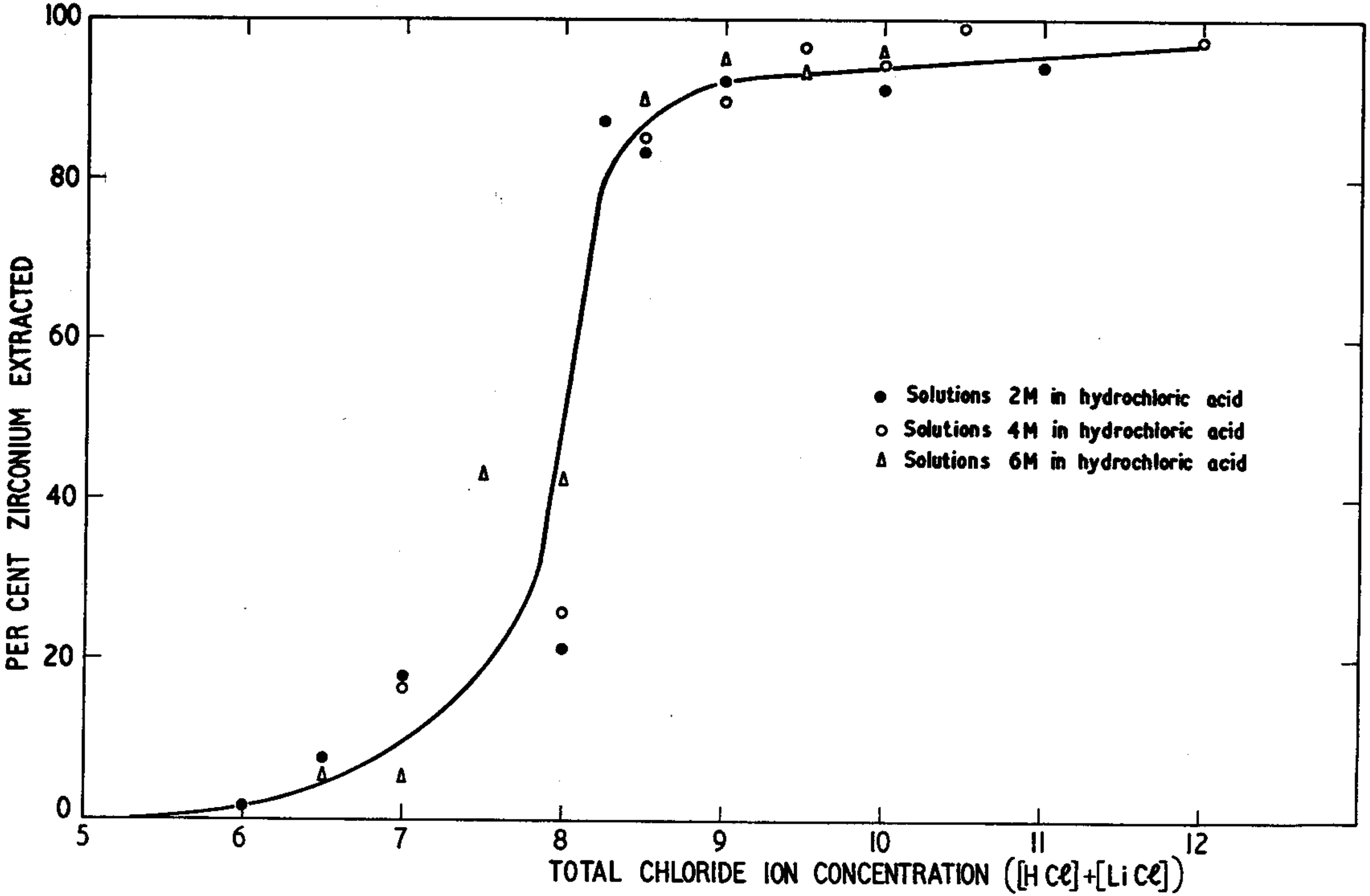

FIGURE 1. EXTRACTION OF ZIRCONIUM WITH ALIQUAT-336 AS A FUNCTION OF TOTAL CHLORIDE ION CONCENTRATION

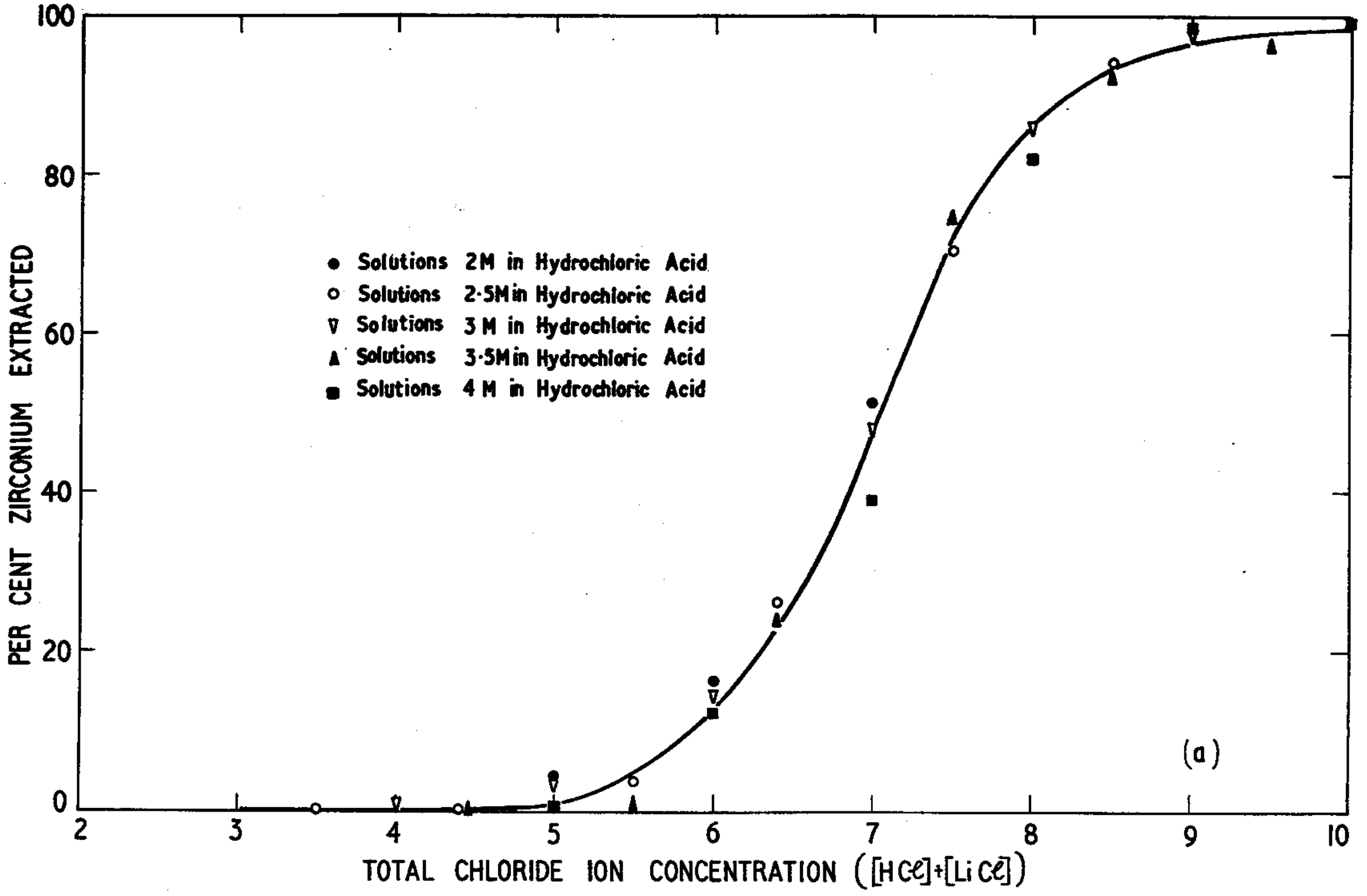

FIGURE 2A. EXTRACTION OF ZIRCONIUM WITH ALIQUAT-336 FROM 0.1M LITHIUM NITRATE SOLUTION, AS A FUNCTION OF TOTAL CHLORIDE ION CONCENTRATION

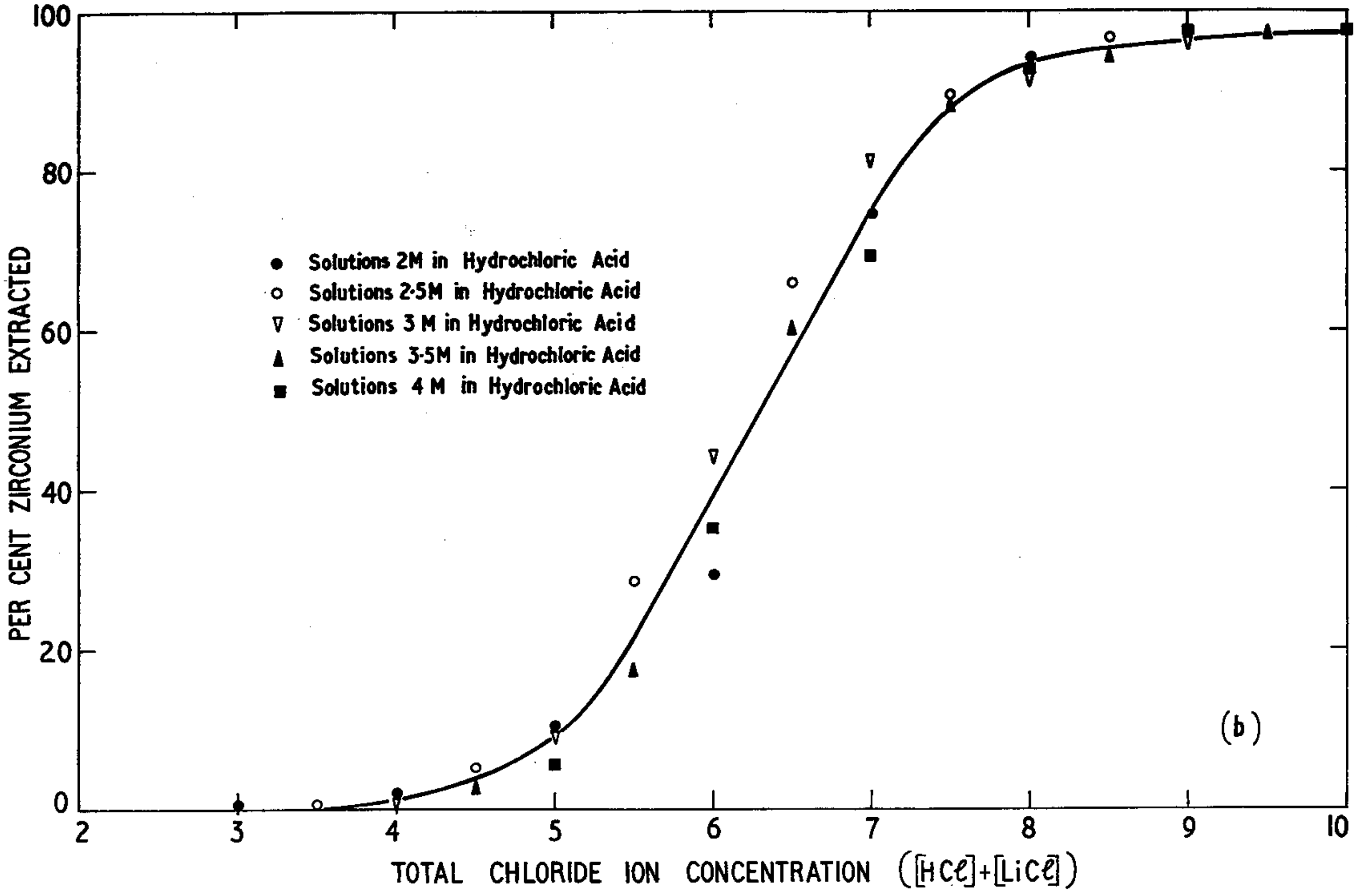

FIGURE 2B. EXTRACTION OF ZIRCONIUM WITH ALIQUAT-336 FROM 0.2M LITHIUM NITRATE SOLUTION, AS A FUNCTION OF TOTAL CHLORIDE CONCENTRATION

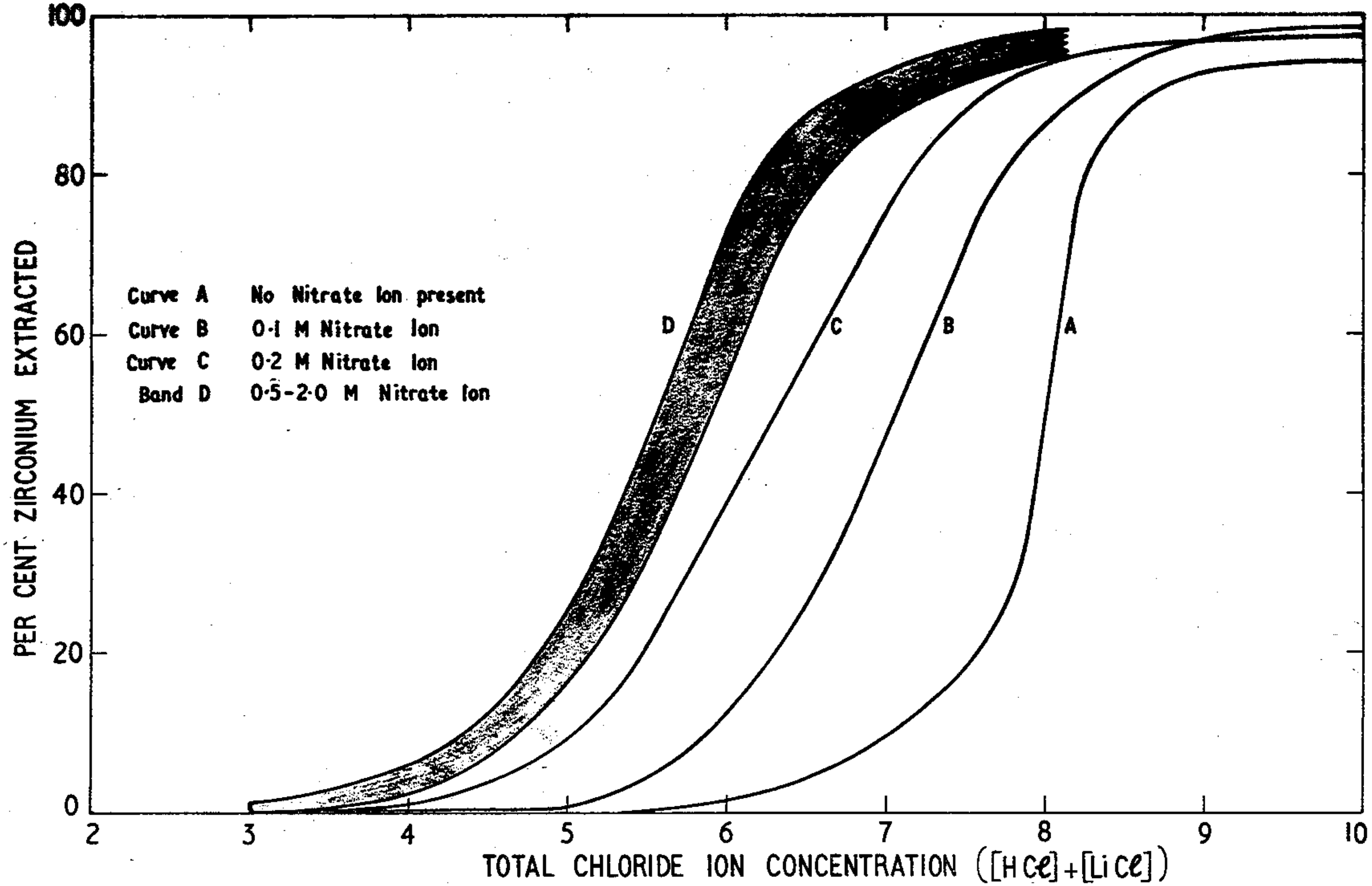

FIGURE 3. EXTRACTION OF ZIRCONIUM WITH ALIQUAT-336 FROM SOLUTIONS OF NITRATE ION AS A FUNCTION OF TOTAL CHLORIDE ION CONCENTRATION

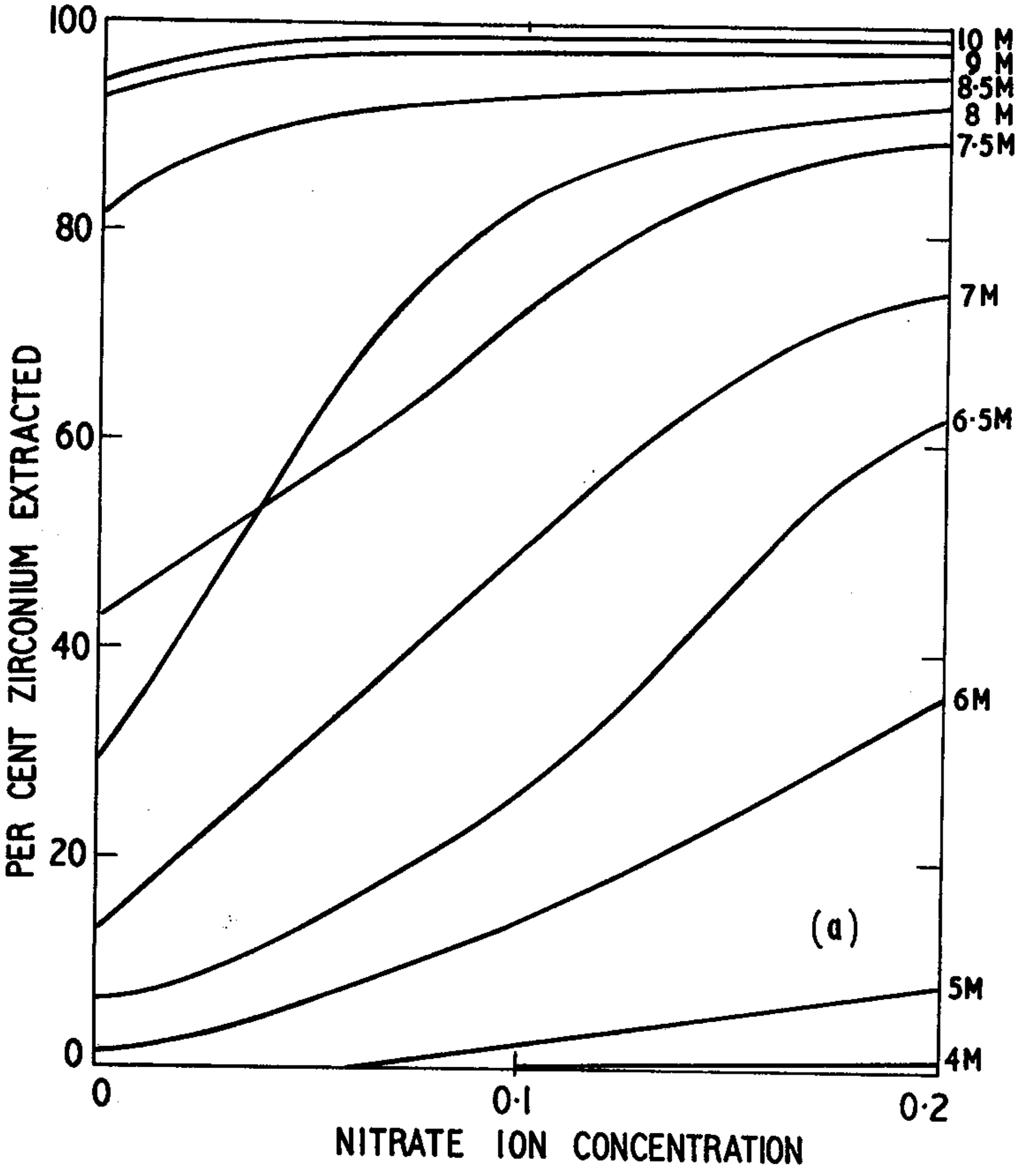

FIGURE 4A. EXTRACTION OF ZIRCONIUM WITH ALIQUAT-336 FROM SOLUTIONS OF CHLORIDE ION AS A FUNCTION OF NITRATE ION CONCENTRATION

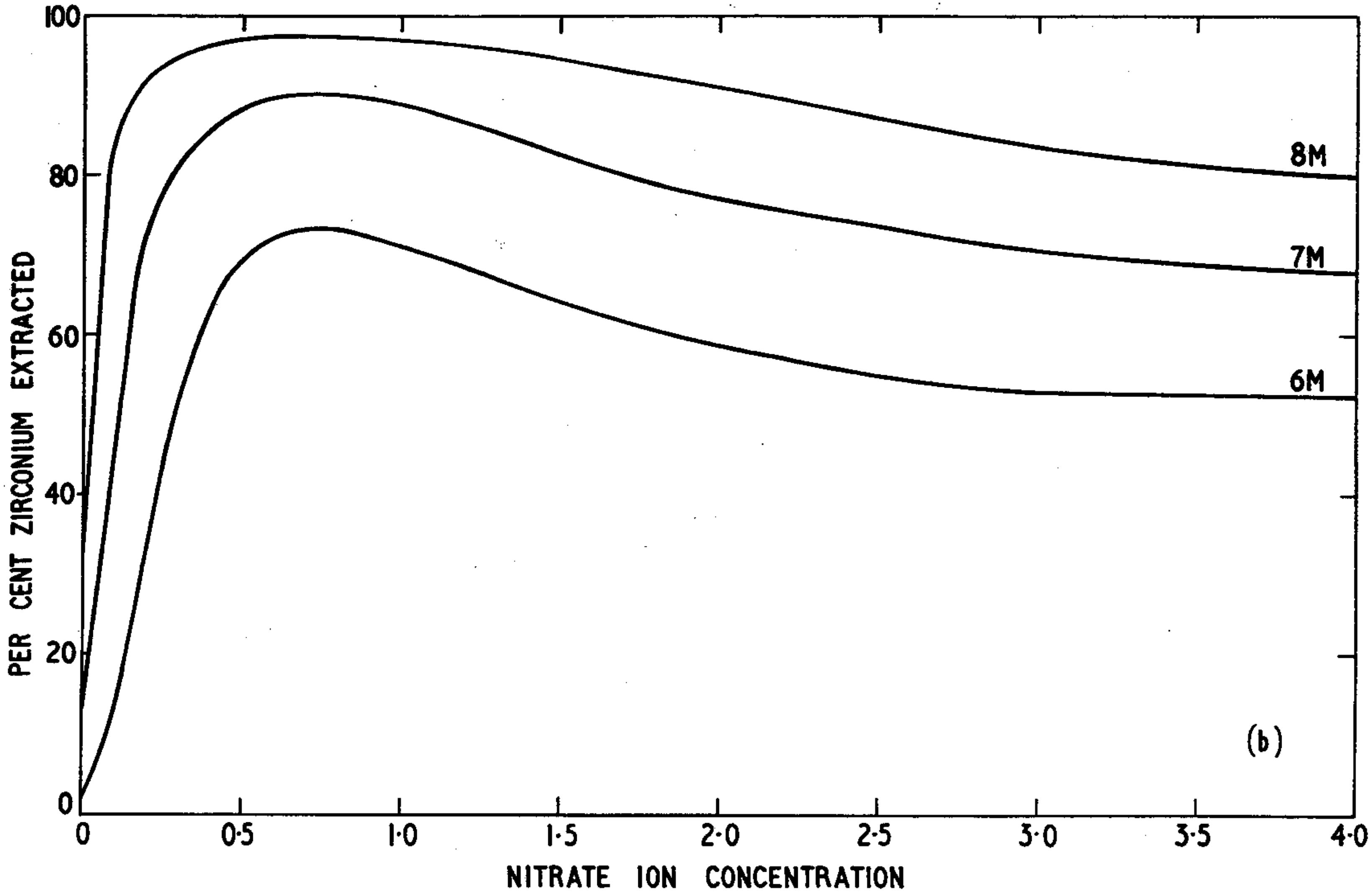

FIGURE 4B. EXTRACTION OF ZIRCONIUM WITH ALIQUAT-336 FROM SOLUTIONS 6M, 7M AND 8M IN CHLORIDE ION AS A FUNCTION OF NITRATE ION CONCENTRATION