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NOTE

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Abstract

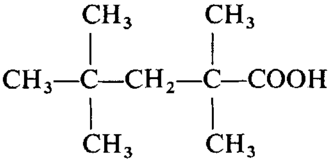
Quantitative extraction of calcium and magnesium in high molecular weight carboxylic acid, versatic-9, and amine systems is reported. Butanol was used as diluent. The study includes the extraction behavior as a function of pH by controlled addition of amines, such as monoethanol amine, diethanol amine, and triethanol amine, the effect of diluent, solvent concentration, and different high molecular carboxylic acids such as versatic-10, versatic-911, and SRS-100. A comparison with the β-diketone–buffer-extraction system and versatic-9–buffer system has also been studied. The proposed method is very simple, and quantitative extraction has been achieved.

INTRODUCTION

The application of carboxylic acids in the extraction of metals has been reported in the literature. Gindin et al., Fletcher et al., and Spitzer et al. (*1–7*) reported separations of some metals by using C_7–C_9 acids, naphthenic acids, and versatic acids, but they used the technique of gradual neutralization to avoid precipitation of metal hydroxide, i.e., the pH of the solution was gradually changed by slow addition of a neutralizing agent during the extraction period. This procedure has been much simplified in our proposed method which employs simple batch extraction at controlled pH by addition of different amines.

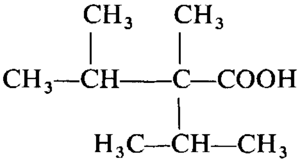
Recently Ashbrook (*14, 15*) showed the extraction of the metals cobalt and nickel from ammonium sulfate solution using versatic-911 in kerosene. Tatsuliko et al. (*16*) showed the extraction behavior of common metals using versatic-10.

Versatic-9 (Shell Chemical Co.), a branched chain aliphatic carboxylic acid having the following approximate composition, has been used as an extractant in conjunction with amines:



$CH_3-C(CH_3)_2-CH_2-C(CH_3)_2-COOH$

(56%)



$CH_3-CH(CH_3)-C(CH_3)(CH(CH_3)CH_3)-COOH$

(27%)

The organic amines can also be regarded as organic phase buffers which serve as a "sink" for hydrogen ion released from the metal–versatic acid reaction, thus pushing the latter to completion

$$M^{n+} + nRH \rightleftarrows MR_n + nH^+$$

It was found that SRS-100 is not soluble at higher pH values whereas versatic-9 and versatic-10 are soluble. Therefore, the extraction of metals with versatic acids at higher pH values is practically impossible. The use of versatic-9 for the extraction of magnesium in the presence of a buffer gave unsatisfactory results. Extraction was considerably enhanced when buffer solutions were replaced by an amine.

Perhaps the presence of an amine leads to the formation of an ion-association complex (ternary complex): metal–versatic acid–amine. The amine extraction technique is particularly important since it functions in strong acid solution and in alkaline solution. The extraction of a metal ion with a high molecular weight carboxylic acid in the presence of amines may be considered to proceed in a manner analogous to the reaction of a metal ion giving rise to an ion-association complex.

The presence of nitrogen in an ion-association complex in the organic phase has been detected by routine tests.

A comparative study of the extraction of magnesium and calcium with versatic-9 and β-diketone (TTA) (*17, 18*) has also been performed. Calcium–TTA–complex formation has already been reported (*19–23*).

EXPERIMENTAL

Apparatus

Graduated separatory funnels (250 ml) were used for extraction. All pH measurements were carried out with an Elico pH Meter Model No. LI-10.

Reagents

Versatic-9 (Shell Co., London), a high molecular weight synthetic carboxylic acid, was used as the extractant. The chemicals and solvents used were all of analytical grade unless otherwise mentioned.

A stock solution of magnesium was prepared by dissolving about 25.66 g of magnesium chloride in 500 ml of deionized water. The solution was standardized gravimetrically with 8-hydroxyquinoline.

A stock solution of calcium was prepared by dissolving about 15.5 g of calcium chloride in 1 liter of deionized water. The solution was standardized by permanganometric titration.

TTA solution (0.5 *M*) was prepared by dissolving 11.25 g TTA (Columbia Organic Chemicals, U.S.A.) in 100 ml of 150 butyl methyl ketone.

Buffer solutions of different pH values were prepared by standard procedures: pH 1.5 to 2.5, chloroacetate; pH 3.3, acetate–hydrochloric acid; pH 4 to 6 acetate–acetic acid; and pH 7.5 to 10, ammonia–ammonium chloride.

Five percent aqueous solutions of monoethanol amine, diethanolamine, and triethanol amine (Nordon, Holland) were prepared by dilution with water.

GENERAL PROCEDURE

Because of the unsatisfactory extraction hebavior of magnesium and calcium, a large number of trial runs were undertaken. A series of solvents were used: benzene, butyl alcohol, isobutyl methyl ketone, acetophenone, and amyl alcohol. The best extraction system has been found to be versatic-9–*n*-butanol–monoethanolamine.

β-Diketone (TTA) was also used for the extraction of magnesium, but the results were not satisfactory unless a salting-out agent such as lithium chloride was used.

Versatic-9–*n*-Butanol–Amine Extraction System: Magnesium and Calcium

An aliquot (2 ml) of the test solution containing 7.628 mg of magnesium/9.236 mg of calcium was mixed in a 250-ml separatory funnel with 10 ml of versatic-9–*n*-butanol (1:2). Two to 5 ml of a 5% aqueous solution of monoethanolamine, diethanolamine, or triethanolamine was added dropwise with shaking. Then the aqueous layer or the mixture was diluted to 10 ml. In each case the volume of the aqueous phase was made 10 ml and that of the organic phase 10 ml. The shaking period was varied from 2 to 15 min. The two phases were allowed to settle after equilibration. The aqueous phase was separated and the equilibrium pH was measured. To remove any traces of organic solvent entrained in the separated aqueous phase, the latter was washed with 5 ml of *n*-butyl alcohol in a separatory funnel. The resulting butyl alcohol extract was mixed with the separated organic phase. The amount of metal ion present in the aqueous phase was estimated by complexometric titration (*24*, *25*). The metal ion in the organic phase was stripped with 4 *N* nitric acid and also estimated by complexometric titration (*24*, *25*).

TTA–Isomethyl Butyl Ketone–Lithium Chloride Extraction System for Magnesium

An aliquot of 2 ml of the test solution containing 7.628 mg of magnesium was mixed in a 250-ml separatory funnel with 10 ml of buffer at the desired pH. The volume of the aqueous phase was 20 ml in each case. Lithium chloride (0.75 g) was added to it and completely dissolved. Into this mixture was added 10 ml of buffer saturated TTA-IBMK (0.5 *M*) solution. It was shaken for 10 to 15 min. The two phases were allowed to settle after equilibration. The aqueous phase was separated and the equilibrium pH was measured. However, at higher pH values the aqueous phase did not separate so easily, and so the mixture was centrifuged for 2 to 3 min. The separated aqueous phase was washed with 5 ml of IBMK to remove any traces of organic solvent. The resulting extract was mixed with the separated organic phase. The amount of the metal ion present in the aqueous phase was estimated by complexometric titration. The metal ion in the organic phase was stripped with 4 *N* nitric acid and estimated by complexometric titration (*24*, *25*).

RESULTS AND DISCUSSION

The comparative extraction behavior of magnesium and calcium with versatic-9 in three amine systems in various pH ranges is represented in

TABLE 1

Percentage Extraction of Magnesium Using Versatic-9–*n*-Butanol–Amines System[a]

No. of observations	Amine (ml)	pH			% Extraction of metal (magnesium)		
		MEA	DEA	TEA	MEA	DEA	TEA
1	0.2	6.00	5.0	5.85	17.77	12.12	11.82
2	0.5	6.1	6.05	6.00	18.74	18.33	18.17
3	0.7	6.3	6.2	6.15	23.74	21.76	21.19
4	1.00	6.6	6.4	6.35	44.62	32.91	31.77
5	1.5	6.9	6.7	6.6	74.69	55.99	52.55
6	5.0	7.6	7.5	7.2	97.23	94.36	89.13

[a] Magnesium: 7.628 mg. MEA = Monoethanolamine. DEA = Diethanolamine. TEA = Triethanolamine.

TABLE 2

Percentage Extraction of Calcium Using Versatic-9–*n*-Butanol–Amines System[a]

No. of observations	Amine (ml)	pH			% Extraction of calcium		
		MEA	DEA	TEA	MEA	DEA	TEA
1	0.2	6.1	6.0	5.9	14.78	12.48	12.20
2	0.5	6.2	6.15	6.00	28.53	25.09	19.62
3	0.7	6.3	6.25	6.15	35.85	33.25	33.90
4	1.0	6.5	6.3	6.25	54.41	42.55	40.84
5	1.2	6.6	6.5	6.4	61.28	50.44	—
6	1.5	6.9	6.8	6.75	72.24	69.92	63.95
7	5.0	7.25	7.15	7.1	97.70	95.28	94.54

[a] Calcium: 9.236 mg. MEA = Monoethanolamine. DEA = Diethanolamine. TEA = Triethanolamine.

Tables 1 and 2. These tables show that the extraction of the metals increases with increasing pH on addition of amines and becomes quantitative in the case of the monoethanolamine system. The final pH on addition of 5 ml of monoethanolamine is 7.6 in the case of magnesium and 7.25 in the case of calcium. Further addition of amine, which increases the pH above 8.5, dissolves versatic acid in the aqueous phase. No phase separation is performed. Therefore, the optimum condition for magnesium is pH 7.6 and for calcium is pH 7.25.

If buffer is added instead of amine, the extraction is unsatisfactory at pH 7.6 and 7.25. Magnesium and calcium can be extracted at higher pH in the buffer system with SRS-100, reported earlier (*8–11*). However, in the case of versatic acid, extraction is not feasible because versatic-9 is soluble at higher pH values (i.e., above 8.5).

It was found that the recommended procedure held good when the metal ion concentration was varied from 5 to 50 mg under optimum conditions. This indicates the absence of polymerization in the organic phase.

The effect of solvent concentration was studied by varying the concentration of versatic-9 from 1: 2 to 1: 9, using butanol as diluent. The results are tabulated in Table 3. It is clear from the table that dilution of versatic-9 lowers the extraction to an appreciable extent. In the case of pure solvent the tendency for emulsion formation increases. To minimize the emulsion formation tendency, most of the extractions were carried out using solvent:diluent in a 1:2 ratio, butanol being used as diluent.

Table 4 shows the effect of diluents on extraction. It follows that the diluents having high dielectric constants show favorable extraction while those with lower dielectric constant values show a tendency for

TABLE 3

Percentage Extraction of Metals as a Function of Solvent Concentration[a,b]

Versatic-9: *n*-butanol ratio	Magnesium						Calcium					
	MEA	pH	DEA	pH	TEA	pH	MEA	pH	DEA	pH	TEA	pH
1:2	97.2	7.6	94.4	7.5	89.1	7.2	97.7	7.25	95.3	7.15	94.5	7.1
1:4	80.4	7.6	77.6	7.45	72.4	7.2	90.4	7.2	86.7	7.15	80.3	7.1
1:9	69.2	7.5	68.3	7.4	63.7	7.15	79.5	7.2	74.6	7.15	71.8	7.0

[a] Magnesium: 7.628 mg; calcium: 9.239 mg. MEA = Monoethanolamine. DEA = Diethanolamine. TEA = Triethanolamine.

[b] Five milliliters of 5% aqueous amines were added in each case.

TABLE 4

Effect of Diluent on Percentage of Extraction in Different Amine Systems

Diluent	Dielectric const	Solvent: diluent ratio	Magnesium			Calcium		
			MEA	DEA	TEA	MEA	DEA	TEA
Butanol	16.1	1:2	97.2	94.4	89.1	97.7	95.3	94.5
Benzene	2.3	1:2	Emulsion	Emulsion	Emulsion	99.2	98.2	95.4
Xylene	2.4	1:2	"	"	"	98.6	97.2	94.6
Nitrobenzene	34.82	1:2	"	"	"	100.0	99.8	97.5

TABLE 5

Effect of Solvent on Percentage Extraction in Different Amine Systems[a]

	Magnesium						Calcium					
Solvent	MEA	pH	DEA	pH	TEA	pH	MEA	pH	DEA	pH	TEA	pH
Versatic-9	97.2	7.6	94.4	7.5	89.1	7.2	97.7	7.25	95.3	7.15	94.5	7.1
Versatic-911	97.2	7.7	91.3	7.7	80.2	7.4	98.2	7.5	98.3	7.4	98.2	7.3
Versatic-100	93.5	7.6	90.2	7.5	88.6	7.3	94.45	7.4	96.8	7.4	96.2	7.2
SRS-100	98.2	8.0	96.4	7.9	93.2	7.5	100.0	7.9	99.2	7.8	98.4	7.7

[a] Five milliliters of 5% aqueous amines were added.

emulsion formation. Magnesium has an emulsion formation tendency with nitrobenzene but extraction is quantitative in the case of calcium.

Different types of high molecular weight carboxylic acids—versatic-911, versatic-10, SRS-100—were used for magnesium and calcium. The results are tabulated in Table 5. Versatic-9, -911, and -10 did not make much difference in extraction, but there was noticeable increase in extraction when SRS-100 was used.

The addition of ammonium chloride or lithium chloride at various concentrations decreases the percentage of extraction.

The extraction of magnesium with TTA–benzene, TTA–chloroform, and TTA–isomethyl butyl ketone systems is unsatisfactory for there is turbidity above pH 6.9. Only 50 to 60% extraction of magnesium is possible in the TTA–acetophenone–acetylacetone system.

Nearly quantitative extraction of magnesium was possible with the TTA–IBMK–LiCl system. Extraction starts at pH 3.2, steadily increases, and becomes 98% at pH 8.00. In the pH range range 5.9 to 6.9, extraction is at least 90% complete and the pH range 7 to 8 can be used for quantitative extraction. An emulsion is formed above this pH and phase separation is not possible, even with centrifuging.

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