

Isolation and characterization of the tertiary amine Alamine 304 hydrochloride. Its application on the extraction of Co(II), Au(III) and Pt(IV)^(*)

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Abstract Amine Alamine 304 dissolved in xylene reacts with hydrochloric acid to form the amine chloride ($R_3NH^+Cl^-$) and the amine dichloride ($R_3NH_2Cl_2$). The former compound was isolated and characterised by chemical analysis, X-ray powder diffraction, infrared spectroscopy and scanning electron microscopy. Lattice parameters of the isolated amine chloride were determined and refined by least-square numerical treatment (monoclinic cell, with $a = 29.017(4) \text{ \AA}$, $b = 14.564(7) \text{ \AA}$, $c = 5.043(1) \text{ \AA}$, $\beta = 95.68(3)^\circ$ and $V = 2,120 \text{ \AA}^3$). The amine chloride is a potential anion-exchanger with metals, thus data on the liquid-liquid extraction of Co(II), Au(III) and Pt(IV) are also reported.

Keywords Solvent extraction. Alamine 304 hydrochloride. Cobalt. Gold. Platinum.

Síntesis y caracterización del cloruro de la amina terciaria Alamine 304. Su aplicación en la extracción líquido-líquido de Co(II), Au(III) y Pt(IV)

Resumen La amina Alamine 304 disuelta en xileno reacciona con el ácido clorhídrico para formar el cloruro de la amina ($R_3NH^+Cl^-$) y el dicloruro de amina ($R_3NH_2Cl_2$). El primero de estos compuestos se aisló y caracterizó mediante análisis químico, difracción de rayos X, espectroscopía de IR y microscopía electrónica de barrido. Se determinaron y refinaron los parámetros de red del cloruro de amina (monoclínico, $a = 29,017(4) \text{ \AA}$, $b = 14,564(7) \text{ \AA}$, $c = 5,043(1) \text{ \AA}$, $\beta = 95,68(3)^\circ$ and $V = 2.120 \text{ \AA}^3$). El cloruro de amina actúa como un intercambiador aniónico con ciertos metales, por lo que se incluyen datos sobre la extracción líquido-líquido de Co(II), Au(III) y Pt(IV).

Palabras clave Extracción líquido-líquido. Cloruro de Alamine 304. Cobalto. Oro. Platino.

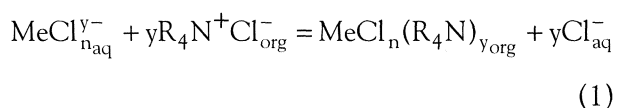
1. INTRODUCTION

Solvent extraction is an unit operation in hydrometallurgy which has been extended to the separation and/or recovery of a wide range of metals from different resources.

The extraction of metals can be explained by different mechanisms, but in the case of amines the most common reaction occurs by an anion exchange reaction^[1]. Thus two conditions are required for metal extraction:

- i) the metal forms an anionic complex in the aqueous solution,
- ii) the amine forms a salt in the organic solution,

when these two conditions are reached, the overall extraction reaction, i.e. in chloride media, is:



The formation of the amine salt can occur *in situ*, prior to metal extraction, or in a previous stage. In some cases when the concentration of the mineral acid in the aqueous solution is not enough to form the amine salt, it is desirable to form this compound previously to metal extraction and thus obtaining maximum efficiency in the metal extraction stage. Furthermore, this could be useful

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because allows optimise the concentration of the active extractant species in the organic solution and decreases the overall economic input of the process.

The extent from which reaction (1) is performed depends strongly on the concentration and type of amine used, thus, extraction is greater for tertiary>secondary>primary^[2]. In the case of tertiary amines, the corresponding chloride salts react well with a wide range of metals (e.g. precious metals), and accordingly these compounds are widely being used in metal extraction processes. Literature reports on Co(II)^[3-6], Au(III)^[7-9] and platinum group metals^[2 and 10] extractions using these reagents. A major knowledge of how these salts are formed and the proper isolation of them can help in the further understanding of the metal extraction reaction.

The present work reports investigations carried out on the formation of the hydrochloride salt of the commercially available tertiary amine Alamine 304. The reaction of HCl with the amine was deeply studied and the corresponding hydrochloride salt was isolated and described. Furthermore, some results on the application of this salt in the extraction of various metals are also presented.

2. EXPERIMENTAL METHOD

Specifications for the commercially available aliphatic tertiary amine Alamine 304 (Henkel Ireland, Ltd.), trilauryl amine, were the follows: composition C₃₆H₇₅N, molecular weight 521 and density (20 °C) 820 kg/m³. The amine content of the sample used in the present study was checked by titration with a standard HCl solution using bromothymol blue as indicator. The tertiary amine content corresponds to a 99 % according to the expected value. All other chemicals were of AR grade.

Extraction experiments were performed by the next procedure: equal volumes of organic (containing the amine chloride salt) and aqueous phases (containing each metal separately) were placed in mechanically shaken and thermostatically controlled separatory funnels.

Acidities of both aqueous and organic solutions were determined by titration with standard sodium hydroxide solutions using bromothymol blue as indicator. Metals were determined by atomic absorption spectroscopy (AAS). Fourier-transform infrared (FTIR) spectrum were recorded on CsI

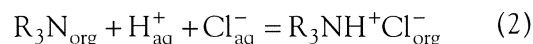
discs, using a Nicolet 550 spectrophotometer (CsI beam splitter). X-ray powder diffraction (XRD) pattern was obtained using a Siemens D-500 diffractometer with monochromatized CuK_α radiation. Pattern was recorded in the step scanning mode with a 0.025° (2θ) step and 2 sec counting time. The powder diffraction data obtained were analysed by means of the indexing program Treor 4^[11] and the calculated lattice parameters were refined by least-squares refinement.

Morphological observations were performed by scanning electron microscopy (SEM), using a Jeol 840 microscope. Conducting samples for SEM were prepared by subjecting the powder specimens to gold sputtering.

3. RESULTS AND DISCUSSION

Results on the extraction of hydrochloric acid by the amine Alamine 304 dissolved in xylene were reported in the literature^[10]. These were summarized as:

- a) the extraction of the acid may be represented by the reactions:



- b) the extraction of the acid decreases as the temperature increases ($\Delta H^\circ = -1.2$ kJ/mol) and below 17 °C a white waxy solid is formed after contacting aqueous and organic phases.
c) The extraction constant for reaction (2) tends to increase as the initial hydrochloric acid concentration increases.

As mentioned above, extractions carried out at temperatures below 17 °C led to the formation of a white waxy solid. The amine-xylene solution at these temperatures do not exhibit this behaviour, thus it may be inferred that the amine chloride precipitates under these experimental conditions. When an aliphatic diluent such as n-decane was used in HCl extraction experiments, the amine chloride precipitated even at 25 °C.

A pure trilauryl (tridodecyl) amine chloride, more properly hydrochloride, was obtained by reaction of HCl and amine-xylene solutions at 25

°C, followed by evaporation of the organic diluent and precipitation and recrystallization of the solid. The amine hydrochloride is a white solid which melts at 86-87 °C. Chemical analysis of chloride yielded 6.3 % (calculated for $R_3NH^+Cl^-$: 6.4 %).

The IR spectrum of the amine hydrochloride shows a band at $2,360\text{ cm}^{-1}$ that can be assigned to the N-H stretching vibration of the amine salt and two bands in the range $3,000\text{-}2,800\text{ cm}^{-1}$ assigned to the C-H stretching vibration (antisymmetrical and symmetrical modes) of the carbon chains. In the spectrum of the salt, the band at $1,302\text{ cm}^{-1}$ was not observed, which is attributable to the CN stretching/scissoring vibration modes in the unreacted amine. The spectrum of the organic salt also shows the presence of a broad band at $3,450\text{ cm}^{-1}$ and other band of medium intensity at $1,637\text{ cm}^{-1}$ that suggests the presence of water in the isolated compound^[12].

Morphologically, the amine salt tends to form aggregates (micelles) as may be seen in the SEM image shown in figure 1. This is a common characteristic of the long-chain aliphatic amine salts.

Crystal structure of this compound was studied by XRD. Powder diffraction data are collected in table I. The X-ray pattern was indexed in a monoclinic cell with lattice parameters: $a = 29.017(4)\text{ \AA}$, $b = 14.564(7)\text{ \AA}$, $c = 5.043(1)\text{ \AA}$, $\beta = 95.68(3)^\circ$ and $V = 2,120\text{ \AA}^3$. From the list of unambiguous peaks detected in the powder pattern the observed indexed lines were in agreement with the P2, Pm and P2/m space groups. This crystalline phase has been not reported previously in the literature, but a tetragonal phase of this amine salt was described elsewhere^[13]. It may be assumed that differences among the preparation and recrystallization processes conduce to different crystalline phases. In the same manner, it

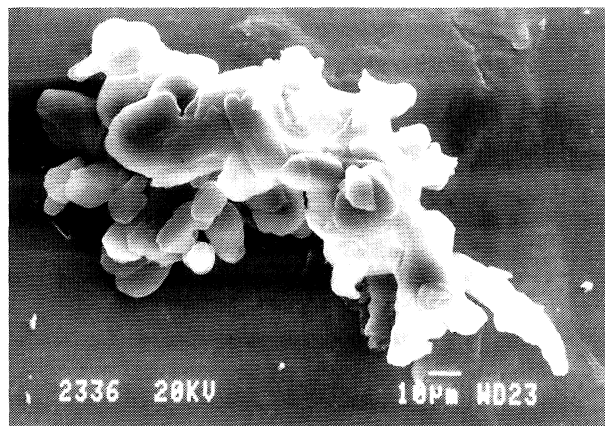


Figure 1. SEM micrograph of amine hydrochloride.

Figura 1. Micrografía de MEB del cloruro de amina.

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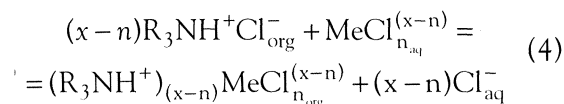
Table I. X-ray powder data for amine hydrochloride

Tabla I. Datos de difracción de rayos X correspondientes al cloruro de amina

h	k	l	$2\theta_{\text{obs}}$	$2\theta_{\text{cal}}$	I/I_0
1	0	0	3.066	3.060	»100
2	0	0	6.117	6.122	1
3	0	0	9.181	9.188	100
3	1	0	11.017	11.018	12
4	0	0	12.256	12.260	3
4	1	0	13.688	13.690	2
5	0	0	15.337	15.342	8
5	1	0	16.511	16.512	27
0	0	1	17.685	17.674	6
6	0	0	18.440	18.436	2
6	1	0	19.392	19.426	2
3	0	1	20.756	20.756	38
-2	2	1	21.892	21.884	41
7	1	0	22.403	22.400	54
-3	2	1	22.729	22.716	4
8	0	0	24.677	24.664	8
-5	2	1	25.445	25.462	4
8	2	0	27.587	27.582	4
9	1	0	28.485	28.486	6
9	2	0	30.438	30.444	2
10	0	0	30.973	30.968	2
9	3	0	33.447	33.478	3
11	0	0	34.146	34.156	2
11	1	0	34.728	34.724	1
-4	5	1	37.223	37.212	3
-3	2	2	38.218	38.214	10
-6	1	2	39.303	39.306	3
4	2	2	41.142	41.150	10
13	2	0	42.588	42.552	7
-7	3	2	44.461	44.466	8

may be assumed that the presence of water molecules might affect the interplanar distance, and accordingly the lowering of the cell symmetry may be expected. Thus, this amine salt should be more tentatively formulated as the hydrate salt $R_3NH^+Cl^- \cdot nH_2O$.

As it has been mentioned, amine salts or quaternary ammonium salts react with metal which form anionic complexes. In the case of the amine chloride salt of the amine Alamine 304, the general equilibrium explaining the metal extraction may be represented by:



x being the metal charge (2 for Co, 3 for Au and 4 for Pt), n the number of chloride ions complexed to the metal (4 for Co and Au and 6 for Pt) and aq and org represent the aqueous and organic phase, respectively.

Previous experiments showed that the amine chloride salt extracts Co(II), Au(III) and Pt(IV) at high rates, but depending upon the metal some differences can be observed, i.e. for Co(II) and Au(III) equilibria were achieved within 1 min of contact time, but in the case of Pt(IV), it was required 5 min to achieve equilibrium. This may be attributable to the platinum-chloride complex structure (octahedral), which results in minor lability to coordinate with the quaternary ammonium ion (R_3NH^+).

Several experiments were performed to study the extraction of Co(II), Au(III) and compared that of Pt(IV) at different initial metal and HCl

concentrations. Results are summarised in table II. It may be observed that the variation of the initial HCl concentration does not affect appreciably the extent of metal extraction. In all the cases the decrease of the initial metal concentration leads to an increase in the metal extraction.

To study the effect of the variation of the initial extractant concentration on the metal extraction, experiments were carried out at 20 °C. Xylene was used as diluent of the amine chloride salt. Results are shown in table III. The initial extractant concentration influences the extraction of the metal (lowering of extractant concentration results in decreasing of the extraction of the corresponding metal), however, the affinity of the amine salt to extract the metal seems to respond to the sequence Au(III) > Co(II) > Pt(IV): better metal loadings can be obtained at lower extractant concentrations.

Table II. Extraction of Co(II), Au(III) and Pt(IV) by the chloride salt of amine Alamine 304

Tabla II. Extracción de Co(II), Au(III) y Pt(IV) mediante el cloruro de amina Alamine 304

Metal	Chloride salt concentration	Metal concentration (g/L)	HCl concentration						Reference
			1M	2M	3M	4M	5M	6M	
Co	0.0785M	0.5	90.5	90.7	90.9	90.7	90.8	90.6	This work
		0.05	94.3	94.8	94.9	94.6	94.7	94.6	This work
Au	0.0031M	0.2	99.6	99.7	99.6	99.6	99.7	99.6	This work
		0.05	99.8	99.7	99.8	99.8	99.7	99.7	This work
Pt	0.157M	0.05	32.2	34.3	33.5	33.5	34.4	29.9	[10]
		0.01	89.1	90.2	90.3	90.2	90.3	89.6	[10]

All extraction values in %. Temperature 20 °C.

Table III. Influence of the amine salt concentration on metal extraction

Tabla III. Influencia de la concentración de la sal de amina en la extracción de los metales

Metal	Chloride salt concentration	Initial metal concentration (g/L)	HCl concentration						References
			1M	2M	3M	4M	5M	6M	
Co	0.039M	1	60.5	61.2	60.2	60.5	60.7	60.6	This work
	0.079M	1	85.2	85.4	85.1	85.5	85.3	85.3	This work
Au	0.03M	0.05	83.3	78.4	77.8	76.5	76.1	75.5	This work
	0.016	0.05	99.9	99.9	99.9	99.9	99.9	99.9	This work
Pt	0.079M	0.01	70.2	73.5	73.4	73.4	72.5	62.5	[10]
	0.314M	0.01	97.1	98.0	98.0	97.9	98.0	96.5	[10]

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REFERENCES

- [1] G.M. RITCEY and A.W. ASHBROOK, *Solvent Extraction, Part I*, Elsevier, Amsterdam, Holanda, 1984, pp. 371-385.
- [2] M. COX, *Principles and Practices of Solvent Extraction*, J. Rydberg, C. Musikas and G. R. Choppin (Eds.) Marcel Dekker, New York, EE.UU., 1992, pp. 397-412.
- [3] S. AMER, *Rev. Metal. Madrid*, 17 (1981) 31-49 and references therein.
- [4] M. LOGEAT, G. MANKOWSKI, J. MOLINIER and M. LENZI, *Hydrometallurgy* 9 (1982) 105-113.
- [5] T. SATO, T. SHIMOMURA, S. MURAKAMI, T. MEADA and T. NAKAMURA, *Hydrometallurgy* 12 (1984) 245-259.
- [6] F. ALGUACIL, A. HERNÁNDEZ and A. LUIS, *Proc del 7º Congreso Nacional de Ciencia y Tecnología Metalúrgicas*, Vol. I. CENIM (CSIC), 1990, pp. 299-307.
- [7] I. VILLAESCUSA, N. MIRALLES, J. de PABLO, V. SALVADÓ and A.M. SASTRE, *Solvent Extr. Ion Exch.* 11 (1993) 613-626.
- [8] I. VILLAESCUSA, V. SALVADÓ and J. de PABLO, *Hydrometallurgy*, 41 (1996) 303-311.
- [9] S. MARTINEZ, A. M. SASTRE and F. J. ALGUACIL, *Hydrometallurgy*, 52 (1999) 63-70.
- [10] F.J. ALGUACIL, A. COBO, A.G. COEDO, M.T. DORADO and A.M. SASTRE, *Hydrometallurgy* 44 (1997) 203-212 and references therein.
- [11] P.E. WERNER, L. ERIKSSON and M. WESTDAHL, *J. Appl. Cryst.*, 18 (1985) 367-372.
- [12] E. PRETSCH, T. CLERC, J. SEIBL and W. SIMON, *Tabellen zur Strukturaufklärung Organischer Verbindungen mit Spektroskopischen Methoden*, Springer, Berlin, 1976.
- [13] I. MAYER, G. MARKOVITS and A.S. KERTES, *J. Inorg. Nucl. Chem.*, 29 (1967) 1377-1378.