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Dissolution of Aluminium and Iron Oxo Minerals in Acetylacetone. Correlation of the Digestion Rate with Mineral Density

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The series of aluminium oxo minerals such as gibbsite, boehmite, diaspore, and corundum as well as iron minerals lepidocrocite, goethite, and hematite dissolve in acetylacetone with decreasing extraction rate as the mineral density increases along each series listed above. The observed inverse dependence of the digestion rate on the mineral density for each series studied and the mechanism of digestion have been discussed.

INTRODUCTION

Solubilization of ionic compounds is still a lively issue in chemistry particularly in view of its importance in metallurgical processes, inorganic synthesis as well as in biological systems. The solubilization phenomena have been usually discussed in terms of thermodynamic functions, but the behaviour of solutes is a complicated subject and many findings remain unexplained[1–4].

The complex nature of extraction of bauxite minerals has particularly attracted a good deal of interest[5–7].

In this paper we present our results on decomposition of a series of aluminium and iron minerals in acetylacetone. Both series exhibit an inverse dependence of digestion rate on the density of minerals.

EXPERIMENTAL

Materials. — Gibbsite, γ-Al(OH)$_3$, was of purum quality, laboratory product (»Merck«). Boehmite, γ-AlOOH, was prepared from gibbsite (»Merck«) by the hydrothermal procedure of Böhm[8]. The diaspore sample was natural mixture of about 25% diaspore (α-AlOOH), pyrophyllite and a kaolinite from Nevada, USA. Corundum, α-Al$_2$O$_3$, was obtained by a published method[9]. Lepidocrocite, γ-FeOOH, was prepared by the method of Glemser[10]. The method of Fricke and Ackerman[11] was used for the preparation of goethite, α-FeOOH. Hematite, α-Fe$_2$O$_3$ was synthetized by the procedure of Richards and Baxter[12]. Acetylacetone of chromatographic »Merck« quality was distilled before use. All other chemicals were of analytical grade.

Procedure. — In some experiments 0.1500 g of sample was digested at atmospheric pressure in 3 ml acetylacetone with or without addition of 7 μl H_2SO_4 1 : 1. The course of digestion was followed gravimetrically: unextracted solid residue was filtered by using small glass filters and washed two times with 2—3 ml of hot benzene and two times with 2—3 ml of chloroform, dried at 105 °C, and weighed. The apparatus has been described in detail alsewhere[13].

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In another experiment marked in Table with the letter c, the mixture of 5 g different synthetic bauxite mineral and 1.25 g synthetic quartz was digested in 100 ml acetylacetone with or without addition of 0.2 ml H_2SO_4 1 : 1 in a thermostated glass autoclave having a volume of 250 ml. The effect of the extraction treatments on bauxite minerals was determined by comparison of peak areas of corresponding X-ray diffraction maxima in the initial sample and in the residue after digestion with those from a standard solution of this complex taking into account the ratio of this apparatus has also been reported[14]. Final products in the acetylacetone solutions were identified as tris(acetylacetonato)-aluminium(III) or tris(acetylacetonato)iron(III). For the former case the proton magnetic resonance spectra[15] were in agreement with those from a standard solution of this complex taking into account the ratio of the keto/enol peaks. After cooling of reaction mixture crystals have been separated which have been identified as tris(acetylacetonato)aluminium(III) or tris(acetylacetonato)iron(III), by X-ray diffraction.

RESULTS AND DISCUSSION

Solubilization of aluminium hydroxides and oxyhydroxides has been of great importance in the manufacture of aluminium. Limited solubility of aluminium oxo compounds in aqueous media has stimulated the use of organic solvents for the digestion of these compounds. In our case acetylacetone appears to be a moderately good solvent and under conditions used in this study, aluminium as well as iron can be brought into solution as tris(acetylacetonato)--aluminium(III) and -iron(III) complexes.

Inspection of results in the Table reveals great difference in the resistance of minerals to chemical attack by acetylacetone within either the aluminium or iron series. This resistance parallels the increase in density of minerals. Measurement of the density of bauxites as a useful adjunct to an understanding of their structure was earlier recognized[16], but to the best of our knowledge it is the first observation that the lower the density of minerals of a particular metal, the easier the digestion by an organic solvent. The recognition of this correlation may be of help in the chemistry of metal compounds including also some biochemical implications[3,4].

Some insight into the mechanism of digestion may be gained by comparison of the aluminium and iron series in the Table. In spite of the fact that minerals in both series contain anions of the same type i. e. oxides and hydroxides as well as the same lattice structure e. g. corundum and hematite, both series exhibit significant differences in the extent of dissolution. The reason for this difference in chemical behavior should be the nature of the metal ions as reflected in the strength of metal-oxygen bonds. The Al—O bond is as expected to be much stronger that the Fe—O bond since enthalpies of formation of Al_2O_3 and Fe_2O_3 are 1670 kJ/mol and 822 kJ/mol, respectively. It is obvious that if the metal-oxygen bond energy is the dominant factor responsible for the different digestion rates of the two series studied, it must also distinguish the rate of decomposition of one mineral from another within the same series. It is reasonable to assume that the higher density is a consequence of stronger metal-oxygen bond within the particular series. We suppose, therefore, that the digestion rate within the series of oxo minerals of a particular metal is inversly dependent on the metal-oxygen bond energy which is reflected in the density of minerals.

This assumption implies that the critical step in the decomposition of aluminium and iron minerals in acetylacetone is the chemical attack of acetylacetone upon aluminium or iron cations. The reactive form of acetylacetone is probably the undissociated enol form since it is reported that in aqueous solution iron(III) ions react faster with the undissociated enol form than with the keto tautomer or dissociated enol form[18]. The proposed mechanism requires the direct approach of solvent molecules to the metal ion which condition is not completely satisfied particularly in close-packed arrays of ions such as occur in the corundum or hematite structure. This suggests that steric factors should be taken into account.

In the case of steric hindrance in the vicinity of metal ions other effects leading to the weakening of the metal-oxygen bond must be considered. Such effect is illustrated in the Table where the addition of relatively small amounts of acid remarkably increase the extraction rate of each mineral studied. Acid probably weakens the metal-oxygen bond by protonating oxo anions.

TABLE

Correlation of Metal Extraction by Acetylacetone with Density of Aluminium and Iron Minerals. Extraction Data for Gibbsite, Boehmite and Diaspore are from Reference 15, and 17 (makerd with c). Extraction Data for Lepidocrocite and Hematite which are not Marked with c are from Reference 13. Other Extraction Data are from this Work.

Density Values, Calculated from X-Ray Measurements, are Taken from ASTM Hanawalt Set of Cards.

Aluminium Series

Mineral	γ-Al(OH)$_3$ Gibbsite	γ-AlO(OH) Boehmite	α-AlO(OH) Diaspore	α-Al$_2$O$_3$ Corundum	Temperature/°C
Density/(g/cm^3)	2.44	3.07	3.38	3.99	
Percent Dissolved[a]	0	0	0	0	100
	26^{b}	0^{b}	0^{b}	0^{b}	100
	0	0	0	0	120
	70^{b}	1^{b}	0^{b}	0^{b}	120
	59^{c}	5^{c}	0^{c}	0^{c}	120
	100^{bc}	92^{bc}	2^{bc}	0^{bc}	120

Iron Series

Mineral	γ-FeO(OH) Lepidocrocite	α-FeO(OH) Goethite	α-Fe$_2$O$_3$ Hematite	Temperature/°C
Density/(g/cm^3)	3.95	4.26	5.26	
Percent Dissolved[a]	100	24^{c}	0	70
	100	100^{bc}	0^{b} 0^{c} 56^{bc}	80
	100	100^{c}	0 2^{c}	100
	100	100^{bc}	0 26^{b} 77^{c} 83^{bc}	120

[a] Percent dissolved is expressed as percentage of the solid which is brought into solution over three hours of digestion at the cited temperature.

[b] Acetylacetone solution is 0.02 mol/dm^3 in H_2SO_4.

[c] Digestion is performed in autoclave over five hours under the following pressures: 1,11 atm at 70 °C, 1,16 atm at 80 °C, 1,32 atm at 100 °C, and 1,60 atm at 120 °C (1 atm = 101 325 Pa).

The extraction of other related minerals by acetylacetone is in progress, since no generalization can yet be deduced, because bauxite minerals exhibit a remarkable diversity in chemical behaviour, and artificial mineral samples, produced in the laboratory have differing solubilities compared to natural minerals from bauxite deposits.[19,20]

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SAŽETAK

Otapanje okso-minerala aluminija i željeza u acetilacetonu. Korelacija brzine otapanja i gustoće minerala

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Niz okso-minerala aluminija kao što su gibsit, bemit, dijaspor i korund kao i niz minerala željeza poput lepidokrocita, getita i hematita pokazuju obrnutu ovisnost brzine otapanja o gustoći minerala.

U radu se raspravlja o mehanizmu otapanja navedenih minerala kao i o zapaženoj inverznoj korelaciji brzine otapanja i gustoće minerala unutar studiranog niza minerala aluminija i željeza.

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