

# INTERACTION OF CHELATING AGENT ALUMINON AND IRON (III) IONS ON 3A ZEOLITE: A STUDY BY PHOTOMETRIC AND X-RAY DIFFRACTION METHODS

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Interaction of aluminon with 3A zeolite followed by addition of Fe(III) ions brings about changes in the composition and structure of the zeolite. Aluminon-3A zeolite behaves as the collecting agent for the precipitation of the hydroxide of Fe(III). Results of photometric and X-ray diffraction studies of the two new coloured derivatives of 3A zeolite have been reported together with their composition data.

## INTRODUCTION

Aluminon, a chelating agent, has been used in the determination of a number of elements<sup>1</sup>. A sample of synthetic zeolite 3A has been interacted with this organic reagent in aqueous medium and the solid interacted derivative used to study its behaviour with iron (III) ions. The aluminon-adsorbed and its Fe(III)-interacted derivatives were both coloured. These have been studied by X-ray diffraction and photometric methods. Some of the major constituents of two derivatives have been determined for establishing the changes occurring in the original composition of 3A zeolite. The work undertaken is aimed at verifying the mechanism of interaction between a chelating agent and a synthetic zeolite<sup>2</sup>.

## EXPERIMENTAL

An AnalaR sample of the organic reagent (ammonium salt of auro-nitrotricarboxylic acid, m.f.  $C_{22}H_{23}O_9H_3$ ) was dissolved in water and a sample of synthetic zeolite 3A in powder form (hydrated potassium aluminosilicate), supplied by Union Carbide Corporation, U.S.A., was kept in contact with this solution for a week. The filtered and dried adsorbed derivative had a dark pink colour. As soon as an aqueous ferric chloride was added to a portion of this aluminon-adsorbed 3A zeolite, coagulation of a dark brown gelatinous substance occurred. The interacted zeolite sample was repeatedly washed to free the coagulated portion from it by decantation. After filtering the final product of washing and drying a dark reddish pink zeolite derivative was obtained. Measurement of optical reflectance data of Aluminon-3A and its Fe(III)-interacted form was done on a VSU-2P type spectrophotometer between 200 nm and 840 nm. Potassium, aluminium and iron in the two samples were determined using a Varian 1475 atomic absorption spectrometer by breaking up the samples with a HF/HClO<sub>4</sub> mixture and evaporating to dryness and extracting with nitric acid. Silicon was not estimated as much of it was lost as

TABLE 1  
PHOTOMETRIC AND OTHER DATA

Sample	pH	$[H^+] \times 10^{-2}$	Absorption peaks (nm) (from UV-VIS and reflectance data)	$\lambda_{max}(nm)$
1. Aluminon-3A zeolite	—	—	240, 330, 350(sh), 540	540
2. Its solution in HCl	1.43 [1.48]	3.72 [3.24]	480, 840	480
3. Fe(III)-interacted Aluminon-3A zeolite	—	—	250, 330, 350, 380(sh), 420, 450, 540	330
4. Its solution in HCl	1.32 [1.48]	4.79 [3.24]	470, 875	470

Data for HCl in brackets, sh—shoulder

TABLE 2  
X-RAY DATA

Sample	$d(\text{\AA})$	Intensity	Sample	$d(\text{\AA})$	Intensity
Aluminon-3A zeolite	12.11	vs	Fe(III)-interacted aluminon-3A zeolite	2.61	m
	8.59	s		2.50	w
	7.08	m		2.40	w
	5.50	m		2.36	w
	5.01	w		2.17	w
	4.08	vs		2.05	w
	3.75	w		12.28	s
	3.69	vs		6.86	m
	3.40	m		3.63	s
	3.27	vs		3.31	s
	2.98	vs		3.08	m
	2.89	m		2.98	m
	2.74	m		2.73	m
2.68	w	2.53	w		

vs—very strong, s—strong, m—medium, w—weak.

the tetrafluoride. For determining aluminium acetylene/nitrous oxide flame was used while the remaining cations were determined with air/acetylene flame. X-ray diffraction studies were done on a Philips X-ray unit using copper radiation. Aluminon-3A and Fe(III)-interacted forms were not easily soluble in concentrated hydrochloric acid. The pH values of the two solutions containing  $87.4 \text{ mg ml}^{-1}$  and  $87.5 \text{ mg ml}^{-1}$  respectively and the solvent AnalaR hydrochloric acid were measured on an Elico digital pH meter with model L1 Beckman glass-calomel electrodes. A GCA/McPherson double beam spectrophotometer (Model EU/707/32) was used for photometric studies of the two solutions (Tables 1 and 2; Figs. 1 and 2).

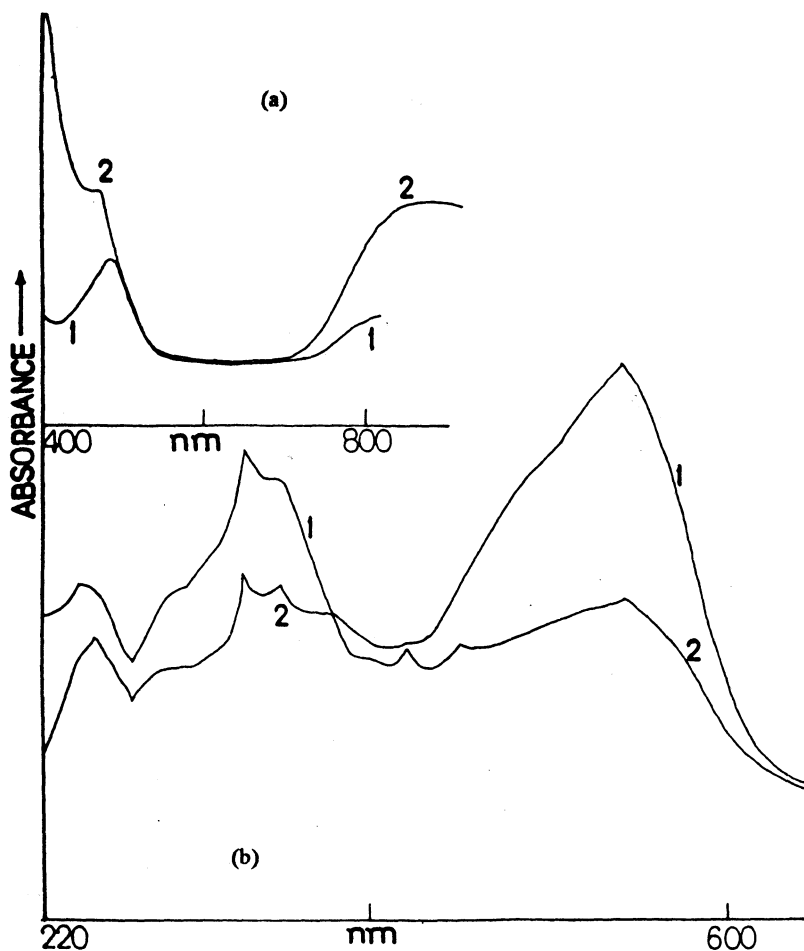


Fig. 1(a) UV-VIS spectra of the solutions in HCl for Aluminon-3A zeolite (1) and its Fe(III)-interacted derivative (2) from 400 nm onwards.  
Fig. 1(b) Reflectance data of Aluminon-3A zeolite (1) and its Fe(III)-interacted derivative between 220 nm and 800 nm.

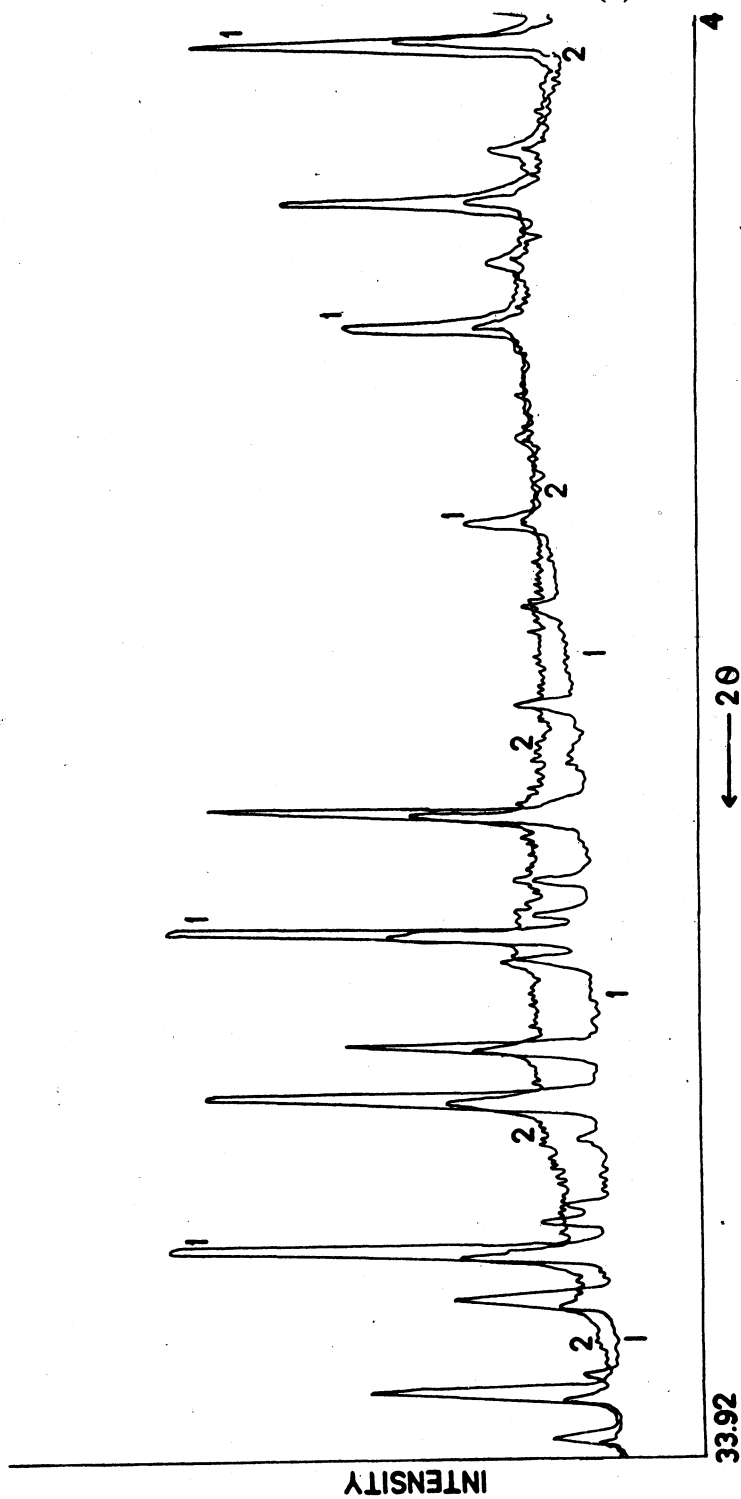


Fig. 2 X-ray diffractograms (Intensity vs  $2\theta$  plots) of Aluminon-3A zeolite (1) and its Fe(III)-interacted derivative (2) from  $4^\circ$  to  $34^\circ$ .

## RESULTS AND DISCUSSION

From the results of the present investigation it can be concluded that aluminon interaction with 3A zeolite involves cation hydrolysis with partial depletion of potassium(I) ions and adsorption of the organic reagent through O-H linkage of  $\rightarrow \text{Al}-\overset{\text{O}}{\text{---}}-\text{Si} \leftarrow$  framework structure and formation of basic sites and species like  $\text{Al}(\text{OH})_2^+$ . This is indicated by the instantaneous coagulation of iron(III) hydroxide when the adsorbed derivative is reacted with ferric chloride solution. The new adsorbed derivative, aluminon-3A, therefore, behaves like a collecting agent to induce the precipitation of ferric hydroxide as reported by earlier workers<sup>3</sup>. The analytical data for potassium(I) and aluminium(III) in Aluminon-3A zeolite show that K : Al ratio is about 3 : 4 compared to 1 : 1 in 3A. This lowering of potassium content clearly suggests partial conversion to the hydrogen form of 3A zeolite. K:Al ratio is further reduced to 1 : 3 as a result of Fe(III) interaction when K% reduces from 23.6 to 9.8. Side by side the aluminium content of Aluminon-3A derivative is also reduced by nearly 2% on addition of Fe(III) ions to it. This loss corresponds to little over one aluminium atom in the unit cell composition of original 3A zeolite (ideal composition: 20.1% K, 13.9% Al, 14.4% Si, 33.0% O and 18.6% H<sub>2</sub>O). The mechanism of interaction, therefore, is akin to the scheme suggested by Kerr<sup>4</sup>. While Aluminon adsorption results in slight dealumination of 3A zeolite, further interaction with Fe(III) ions leads to depletion in K(I) content and still more dealumination. Thus the composition of 3A zeolite undergoes changes as a result of these interactions and two new interacted derivatives are obtained. The second Fe(III)-interacted sample can be presumed to be a chelate of Fe(III) and Aluminon and dealuminated 3A zeolite containing 1.48% iron.

Fig. 1(a) shows the absorbance vs. wavelength (nm) plots of the solutions of Aluminon-3A and its Fe(III)-interacted sample in hydrochloric acid and Fig. 1(b) represents the same for the two solid derivatives. The plot marked 1 is for aluminon-3A and the one marked 2 the other sample. It can be seen that the plots differ to a considerable extent especially in the number of absorbance peaks and in  $\lambda_{\text{max}}$  values (Table 1). Similarly the X-ray characteristics of the two new 3A zeolite derivatives differ considerably from each other as well as from the reported data for 3A zeolite and its Fe(II)-exchanged form<sup>5</sup>. Aluminon-3A derivative (Fig. 2.1) has a number of well-defined high-intensity peaks comparable with the crystalline structure of the original 3A zeolite but the Fe(III)-reacted derivative has a fewer and generally low-intensity peaks in its diffractogram (Fig. 2.2). These changed characteristics relate to the diminishing crystallinity of the original zeolite as a result of the interaction and composition changes.

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