

**EFFECT OF FLUORIDE ADDITION ON
CONTACT ANGLE IN THE SYSTEM MICROCLINE-
DODECYLAMINE SOLUTION-NITROGEN**

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INTRODUCTION

A common procedure in the flotation separation of such silicates as the feldspars or beryl from quartz is to use a cationic collector and a pH of about 3 in the presence of fluoride. (1,2) Under such conditions the silicates float and the quartz does not. If no fluoride is present the separation cannot be made. The mechanism whereby the fluoride allows the separation to be made is not known. Indeed, the literature is not completely certain as to whether the action of the fluoride is as an activator or a depressor. (3,4) However, the recovery curves of Dean and Ambrose (5) would tend to strongly indicate an activation mechanism.

METHODS AND MATERIALS

As a preliminary part of a contemplated extensive study of the mechanism whereby fluorides act as modifiers in acid circuit with cationic collectors, contact angles were measured in the systems quartz or microcline-dodecylamine hydrochloride solution-nitrogen with and without the addition of fluorides. Quartz used was a clear, single, small crystal. Microcline used was a typical small piece of Black Hills microcline. Several surfaces of both minerals were carefully cut and polished, cleaned with hydrochloric acid and stored in distilled-deionized water. Water used in all cases was first distilled and then run through a laboratory ion exchange column. The amine used was obtained from Armour Industrial Chemical Company and was of high purity. Hydrochloric acid, hydrofluoric acid and sodium fluoride used were of reagent grade. The contact angles measurements were made in a standard captive bubble apparatus. Before each measurement mineral specimens were tested in pure water for no contact. Mineral specimens were conditioned in plastic reaction cells for 5-10 minutes before each measurement. For the contact angle measurement a bubble was brought into contact with the mineral surface and the reaction cell tapped lightly to assure an equilibrium angle. After the measurement the mineral specimen was washed in water, then hydrochloric acid, then water and then finally stored in distilled, deionized water.

RESULTS AND DISCUSSION

Figure (1) shows results obtained of contact angle versus pH at a collector concentration of 4×10^{-4} M dodecylamine hydrochloride. Fluoride was added as sodium fluoride. The quantity of sodium fluoride used was 10^{-2} N. pH was lowered in all cases by hydrochloric acid. The rise of contact angle as pH is lowered in the system microcline-dodecylamine hydrochloride-nitrogen in the presence of sodium fluoride and in none of the other systems would strongly suggest that the fluoride acts as an activator for cationic flotation of microcline. Fluorides apparently will not activate quartz.

It is of interest to note fluoride ion and hydrogen fluoride molecule concentration under the conditions of the contact angle measurements. Hydrofluoric acid has a dissociation constant of 3.53×10^{-4} and the pK value is 3.45 (6). Table I shows the relationship between fluoride ion, hydrogen fluoride and pH in solutions containing 10^{-2} N sodium fluoride. The ion actually present is probably the HF_2^- ion if HF is available (7).

TABLE I

pH	F^- or HF_2^- equiv/liter	HF equiv/liter
1	3.52×10^{-5}	9.96×10^{-3}
2	3.41×10^{-4}	9.66×10^{-3}
3	2.61×10^{-3}	7.39×10^{-3}
4	7.79×10^{-3}	2.21×10^{-3}
5	9.72×10^{-3}	2.76×10^{-4}
6	9.97×10^{-3}	2.82×10^{-5}

Thus, as pH is lowered contact angle on microcline in the presence of 4×10^{-4} M dodecylamine hydrochloride and 10^{-2} N sodium fluoride increases with increase in HF molecule concentration and pH decrease at least to a pH value of about pH 2-3.

Figure 2 shows the curve of Figure 1 for microcline with sodium fluoride addition plus several points for microcline without sodium fluoride but with pH lowered by hydrofluoric acid addition.

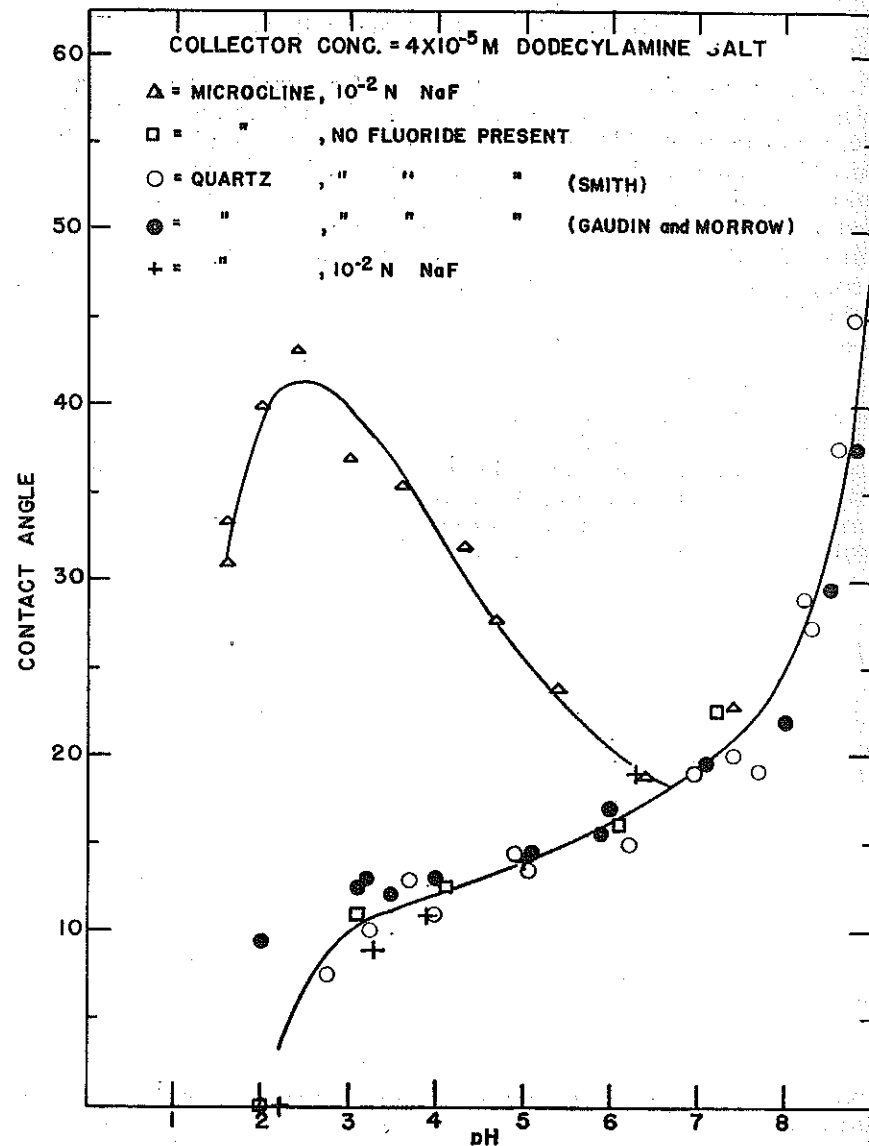


Figure 1. Contact Angle versus pH on Microcline and Quartz with and without Sodium Fluoride Addition.

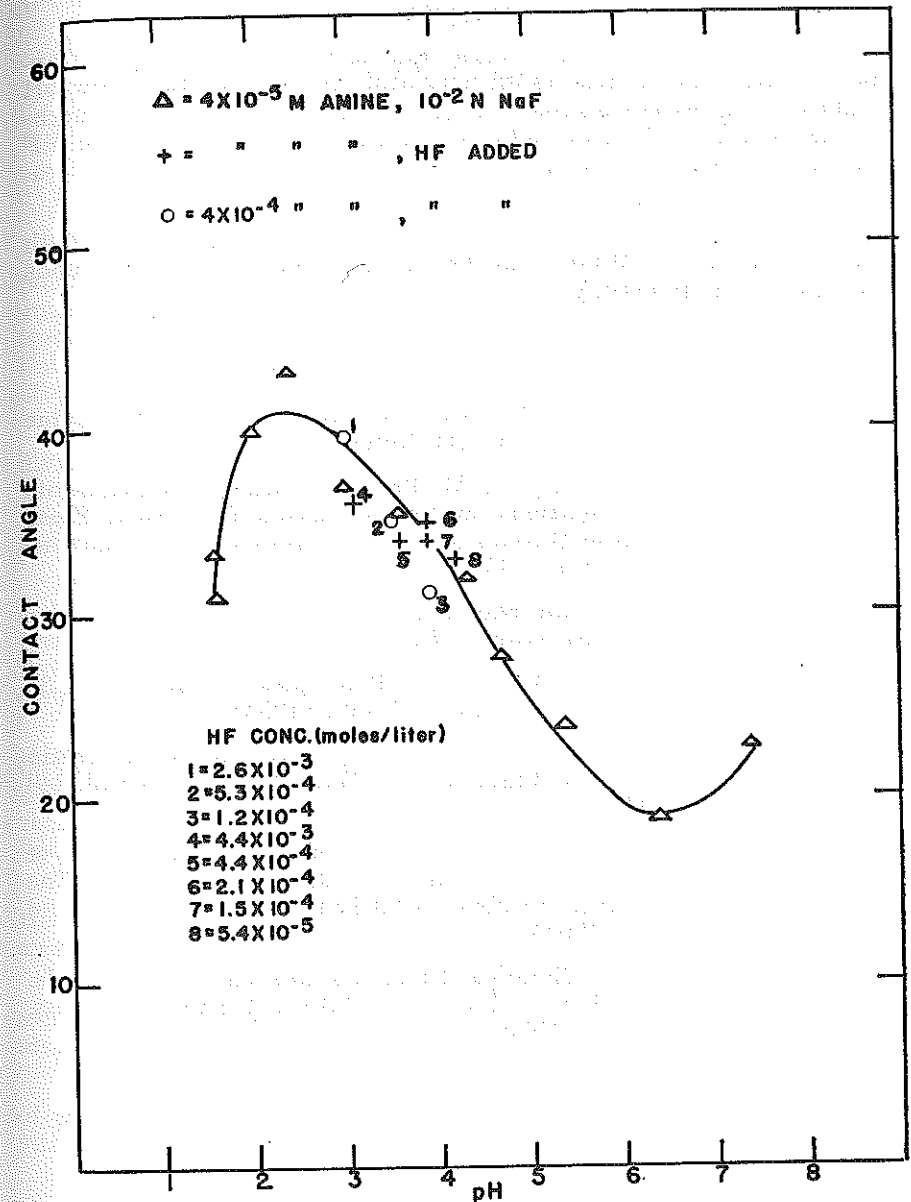


Figure 2. Contact Angle versus pH on Microcline with Fluoride Added Either as Sodium Fluoride or Hydrofluoric Acid.

SUMMARY

From the preliminary work reported on in this paper it appears that fluoride acts as an activator for microcline at low pH values using dodecylamine hydrochloride as collector. The mechanism whereby fluoride acts is unclear but apparently the HF molecule must be present in fairly large quantities for the activation to take place.

The author wishes to thank the Research Committee, South Dakota School of Mines and Technology for part of the funds necessary for this study.

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