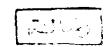
## A STUDY ON SOME FLOTATION REAGENTS FOR UPGRADING EGYPTIAN PETROLEUM COKE

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"A STUDY ON SOME FLOTATION REAGENTS FOR UPGRADING EGYPTIAN PETROLEUM COKE"

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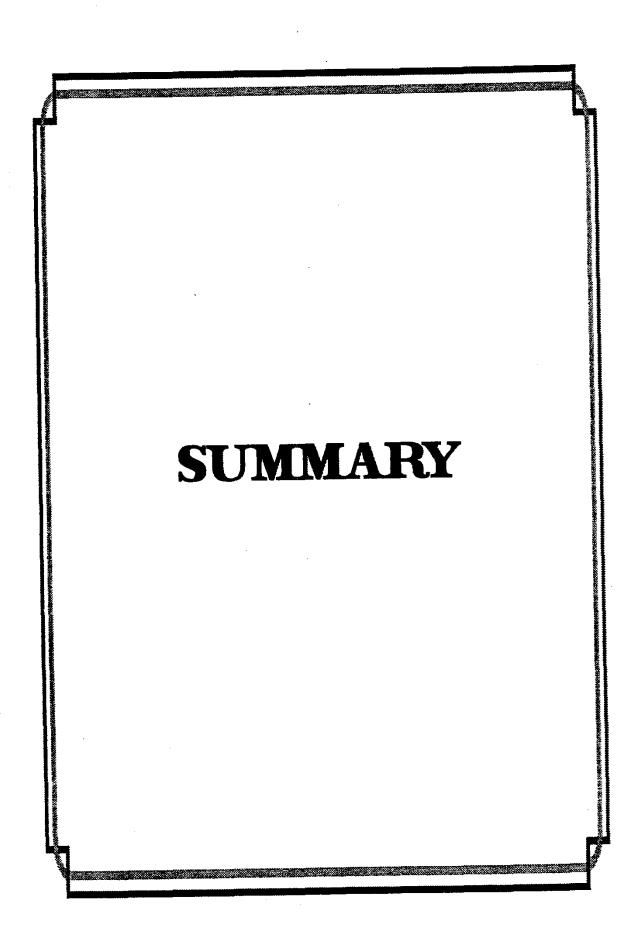
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## SUMMARY

This study is divided into two main sections. The first deals with the preparation of some anionic and cationic collectors. Some surface properties and thermodynamic parameters of these collectors are determined. The second section deals with the application of these surface-active compounds for the flotation of the Egyptian petroleum coke.

The first section: Starts with the preparation of six monoisomeric anionic collectors, namely, sodium 3-phenyl-, 4-phenyl-, 5-phenyl-, 6-phenyldodecane, 4-phenyltridecane and 4-phenyltetradecane sulphonates, then proceeds to the pereparation of other seven cationic collectors. Six of them are neutral and one is of the acidic type. The six neutral cationic collectors are: benzyltriethylammonium, benzyltriethanolammonium, dodecylbenzyltriethylammonium, dodecylbenzyltriethylammonium, dodecylbenzyltriethanolammonium chlorides. The other two are petroleum-derived quarternaryammonium chloride salts. Dodecylammonium chloride is the only acidic collector employed for the sake of comparison.

Surface properties such as critical micelle concentration. (cmc), surface tension at cmc (  $\gamma_{cmc}$ ), the effectiveness of adsorption ( $\Gamma_{max}$ ), the area occupied per molecule ( $\Lambda_{max}$ ), the effectiveness ( $\pi_{cmc}$ ) and the efficiency (pC<sub>20</sub>) of surface tension reduction are determined from the surface tension ( $\gamma$ ) - log concentration isotherms at 25,35,45 and 55 °C using the least squares regression analysis. Moreover, the thermodynamic parameters of micellization ( $\Delta G_{mic}^{\circ}$ ) and adsorption ( $\Delta G_{ad}^{\circ}$ ) are calculated. The effects of temperature, collector molecular weight and structure, on these surface and thermodynamic properties, are discussed.

Based on the analytical data obtained, the study reveals that the cmc values of the investigated anionic and cationic collectors increase with increasing temperature and decrease with increasing the length of of hydrophobic tail and/or the molecular weight. The reverse is true in case of the effectiveness of adsorption ( $\Gamma_{max}$ ). Insignificant effect of temperature variation, from 25, to 55 °C, on  $\gamma_{cmc}$  values of the investigated collectors, is observed.

At surface saturation, the area occupied by a collector molecule,  $A_{\rm max}$ , increases with increasing temperature and is inversley proportional to the effectiveness of adsorption,  $\Gamma_{\rm max}$ . Insignificant changes in  $\Gamma_{\rm max}$  or  $A_{\rm max}$  values are observed by changing the position of phenyl group along the linear alkyl chain of the investigated anionic collectors.

Data obtained reveal also that temperature variation has a minor effect on the effectiveness (  $\pi_{cmc}$ ) and the efficiency (pC<sub>20</sub>) of surface tension reduction of the employed collectors.

The standard free energy change upon micelle formation values  $\Delta G_{mic}$  of the investigated collectors become significantly more negative with increasing temperature and/or length of the collector tail. The standard free energy change upon adsorption values  $\Delta G_{ad}^{\circ}$  are all negative indicating that the adsorption of these collector molecules, at aqueous solution/solid interfaces, is spontaneous.

The second section: of this study deals with the application of the prepared compounds in the flotation of Land Belayim petroleum coke. Optimization of the

flotation process is carried out by verification of the most improtant parameters of the process, i.e. the dose of collector, the pulp density and the pH of the aqueous flotation system in presence of an ash depressant. Other parameters such as collector structure and molecular weight are also studied.

The effect of varying the dose of the anionic collectors on the yield and the quality of the flotation concentrate, is studied uisng the sodium sulphonates of  $4 \dot{\phi} C_{11}$ ,  $4 \dot{\phi} C_{12}$ ,  $4 \dot{\phi} C_{13}$ , and  $4 \dot{\phi} C_{14}$  at a dose range from 0.02 to 0.3 kg/T. The other flotation parameters are kept unchanged. The results obtained reveal that the ash percentage dropped from 1.38% by wt in the feed to 0.35, 0.40 and 0.45% by wt in the flotation concentrate obtained by using just 0.02 kg/T of  $4 \dot{\phi} C_{12}$ ,  $4 \dot{\phi} C_{13}$ , and  $4 \dot{\phi} C_{14}$  collector, respectively. The lower molecular weight  $4 \dot{\phi} C_{11}$  sulphonate collector seems uneconommic because much larger dose is required to get reasonable yield and quality of coke.

The effect of varying the dose of sodium silicate, as an ash depressant, is studied at 0.02 kg/T of sodium  $4\Phi$ ·C<sub>12</sub> sulphonate collector, pH7 and a pulp density of 10% solid. The data obtained show that at

1 kg/T of sodium silicate, a flotation yield of about 80% by wt petroleum coke assaying 0.19% by wt. ash, is obtained.

Higher yield of petroleum coke assying lower ash content is obtained by applying the multi-stage mode of addition. When the optimum dose of the  $4\Phi$   $C_{12}$  collector i.e. 0.02 kg/T, is added in two steps rather than in one step, an increase in the yield of coke concentrate from 80% to 83% by wt with a relative decrease in its ash content from 0.19% to 0.18% by wt. is obtained. By increasing the number of steps to four, further improvement occurs, the coke yield increases to 93.1% by wt assaying0.193.% by wt ash.

Under the same flotation conditions (pulp pH7 and 0.02 kg/T dose of collector) and in presence of 1 kg/T of sodium silicate depressant, the 4  $\Phi$  C<sub>14</sub> sulphonate collector gives a concentrate having an ash content of 0.18%, with a yield of 83.12% as compared with 0.19% and 80% by wt in case of 4  $\Phi$  C<sub>12</sub> collector. When different monisomeric sodium dodecylbenzene sulphonate collectors are employed, the flotation yield of the coke concentrate increases and its ash content

decreases by changing the position of the phenyl group towards the central carbon atom of the linear hydrocarbon chain.

The flotation efficiency of three pairs of neutral cationic collectors are examined at a dose rate of 0.05 kg/T, pH 7, pulp density of 10% solid and in presence of 1 kg/T sodium silicate. The study reveals that quaternized compounds containing hydroxyl group (e.g. benzyl- or alkylbenzyl- triethanol ammonium chlorides) give an appreciably reduced flotation yield with a relatively good quality of petroleum coke concentrate if compared with their corresponding benzyl- or alkylbenzyl- triethylammonium chloride collectors. The hydrophobic collector tail, of these neutral cationic collectors, seems to have insignificant influence in petroleum coke flotation.

Under the same flotation conditions and in presence or absence of silica depressant (sodium silicate), the neutral cationic petroleum-derived collector (alkylbenzyltriethanol-ammonium chloride is better than the acidic dodecylammonium chloride in respect of selectivity. Coke concentrates of higher ash content are obtained in case of this acidic collector.