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Recovery of Residual Lubricating Oil from Waste Clay by Flotation

A. M. A. Omar*, **R. A. El Adly**, **S. T. Keera**, and **M. S. Mohamed**

Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt

Summary. The waste clay produced from refining waste lubricating oil contains about 30% oil. Laboratory research has been carried out on the selective separation of oil by flotation using linear barium alkyl benzene sulfonates as a collector. The behaviour of this collector at the solution-air interface is studied; the critical micelle concentration (*CMC*), efficiency (Π), and effectiveness ($P_{c_{20}}$) of the collector are determined. The effects of collector concentration and addition mode are investigated. The liquid-vapour interfacial tension was controlled by methanol. The selectivity achieved by the use of methanol is explained in terms of critical surface tension of floatability and *CMC*. In addition the physico-chemical characteristics of the recovered oil at optimum conditions are determined.

Keywords. Petroleum waste clay; Pollution; Flotation.

Wiedergewinnung von Schmierölrückständen aus Abfallschlamm durch Flotation

Zusammenfassung. Der bei der Raffination von Schmierölrücksständen anfallende Abfallschlamm enthält etwa 30% Öl. Die selektive Abtrennung des Öls durch Flotation unter Verwendung von linearen Bariumalkylbenzolsulfonaten als Flotationshilfsmittel und dessen Verhalten an der Lösungs-Luft-Grenzfläche wurden im Labor untersucht, und die Parameter *CMC* (Kritische Micellenkonzentration), Π (Effizienz) und $P_{c_{20}}$ (Effektivität) wurden bestimmt. Die Einflüsse von Konzentration des Flotationshilfsmittels und der Reihenfolge der Zugabe der Reagenzien werden diskutiert. Die Grenzflächenespannung zwischen Flüssigkeit und Dampfraum wurde mit Methanol eingestellt; die dadurch erreichte Selektivität läßt sich in Abhängigkeit von kritischer Oberflächenspannung und *CMC* erklären. Zusätzlich wurden die physikochemischen Eigenschaften des unter optimalen Bedingungen wiedergewonnenen Öls bestimmt.

Introduction

Over the last years, one of the major concerns of our company has been the disposal of by-products generated during the regeneration of used lubricating oils by turning problematic by-products into saleable products. This way, the valuable resource represented by lube oil base-stocks could be conserved. Any scheme of disposal of these by-products would reduce pollution. Washing clay with solvents has been studied early [1]. The concept of critical surface tension of wetting of

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* Corresponding author

solids which has been described in the context of coal and sulfide minerals has now been extended to oil shale beneficiation [2, 3]. The adsorption of surfactants on minerals has been determined for surfactant enhanced oil recovery [4, 5]. *Somasundaran* and *Fürstenau* [6] first established that a rather characteristic adsorption isotherm shape is obtained for ionic surfactants on alumina. Adsorption isotherms for isomerically pure alkyl benzene sulfonates on alumina and kaolinite from aqueous solution have been measured [7]. Flotation techniques for the separation of bitumen from mineral tar sands as well as the technique of induced air flotation have been developed for oil separation from oil/water emulsions [8, 9]. The object of this paper is a novel approach to flotation of oil from waste clay using linear barium alkyl benzene sulfonates (Ba*LAS*) as collector.

Results and Discussion

One method of reducing interfacial tension between oil and water is the use of surfactant. Petroleum sulfonates are the most common surfactants used in oil flotation because of their ability to reduce the interfacial tension, their low cost, and their large scale availability. Sulfonation of linear alkyl benzene of an average molecular weight of 246 has been investigated by IR analysis. Strong bands appear within the 1000–1200 cm^{-1} region; symmetric and asymmetric stretching vibrations of the SO_3 groups are observed at 1050 and 1070 cm^{-1}, respectively (Fig. 1). The surface tension of Ba*LAS* has been measured at 28, 38, and 48°C for different concentrations with a Doganon Abribat tensiometer using a platinum plate (Fig. 2). The critical micelle concentration (*CMC*), the corresponding surface tension γ_{CMC}, the surface pressure at *CMC*, and the molar surfactant concentration necessary to attain 20 mNm^{-1}, ($P_{c_{20}}$) were calculated [10] (Table 1). It is obvious that *CMC* increases with increasing temperature, whereas Π_{CMC} and $P_{c_{20}}$ decrease. Fig. 3 shows that increasing collector concentration leads to increasing oil recovery at $pH = 7$; 81% of the oil could be recovered using 1.5 kg of collector (Ba*LAS*) per ton of day. On the contrary, clay recovery was much lower than that of oil and

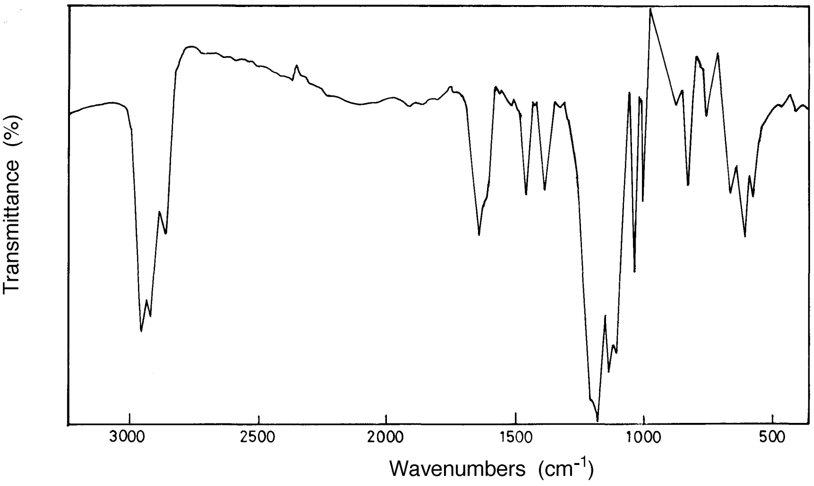

Fig. 1. Infrared spectrum of Ba*LAS*

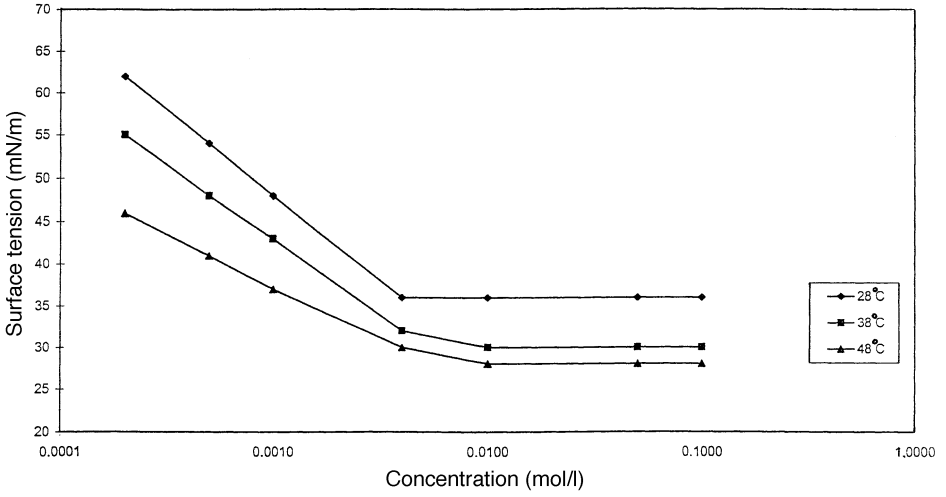

Fig. 2. Relation between the surface tension of the collector and its concentration at 28, 38, and 48°C

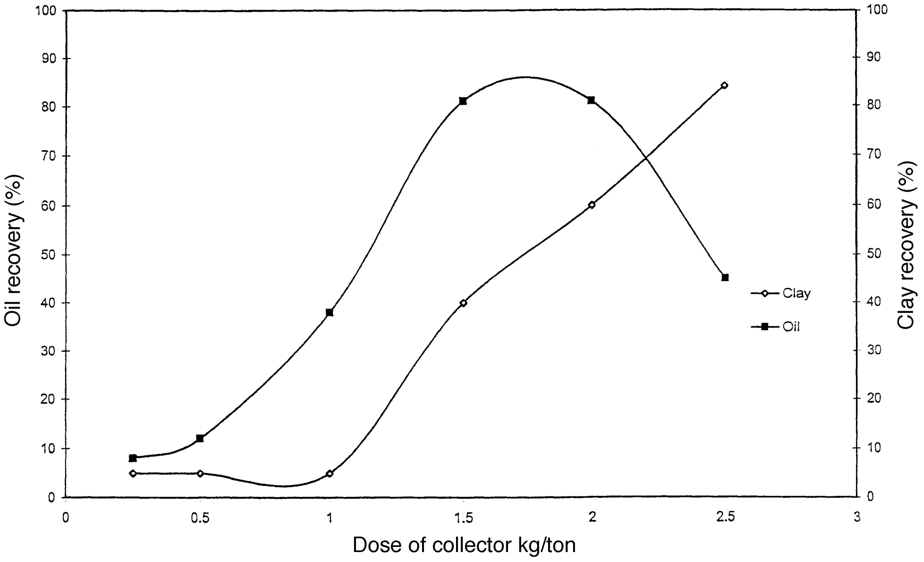

Fig. 3. Effect of Ba*LAS* on oil and clay recovery in the flotation of waste clay

reached only about 40%. Further addition of collector (above 1.5 kg/ton), resulting in increased clay recovery (60%), is accompanied by oil depression and may be attributed to the adsorption of collector at the oil taking place *via* hydrophobic bonding between the alkyl chain and the hydrophobic oil, thus extending the polar group into the aqueous solution. Increasing the collector concentration still further reverses the direction of the adsorption layer, decreases hydrophobicity and increases collector adsorption on the clay.

At optimum conditions, selectivity in flotation was evaluated in terms of separation efficiency by controlling the surface tension of the flotation medium,

Table 1. Physical properties of linear barium alkyl benzene sulfonates at various temperatures

Temperature	*CMC*	Efficiency	Effictiveness	γCMC
(°C)	(mol/l)	(Π_{CMC})	($P_{c_{20}}$)	(mN/m)
28	4×10^{-3}	36.2	2.39	36
38	6×10^{-3}	35.6	2.22	30
48	10^{-2}	30	2	28

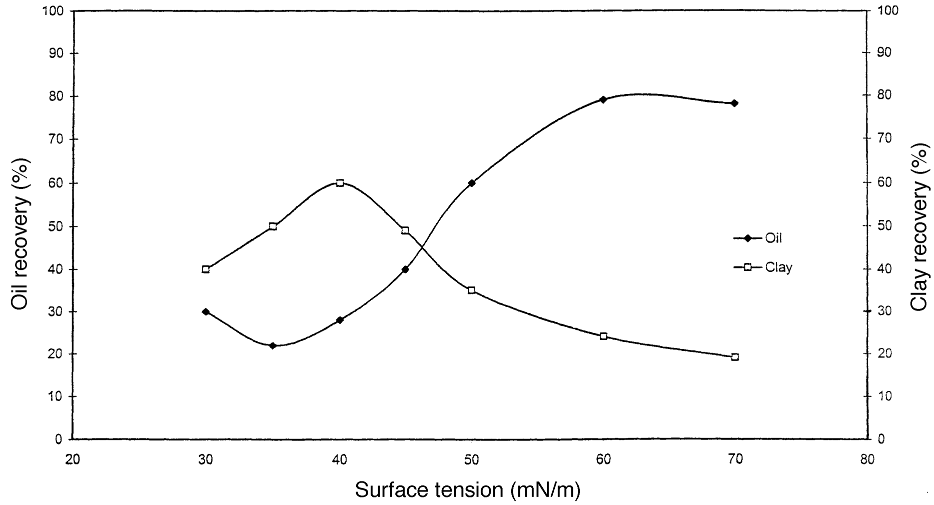

Fig. 4. Effect of surface tension on the floatability curve for waste clay

using different aqueous methanol solutions. Obviously, the surface tension of the solution corresponding to maximal clay recovery is about 40 mN/m, whereas that for best oil recovery is about 60 mN/m (Fig. 4). Therefore, the use of a reagent which controls γ_{LV} provides a means for tailoring selectivity. A similar effect has been described for oil shale [2]. The mechanism of separation may be explained in terms of the critical surface tension of floatability and the critical micelle concentration of the collector.

The mode of addition of the collector plays a certain role with respect of selectivity. The addition of the optimum dose of the collector (1.5 kg/ton) in two steps rather in one leads to an increased yield of oil (from 81% to 86%), accompanied by a relative decrease in clay recovery from 40% to 36%. (Table 2). By increasing the number of steps to three, a further improvement occurs.

The physico-chemical characteristics of the floated oil at optimum conditions are shown in Table 3 and indicate that the recovered oil is poor in quality (carbon residue 3.21% (w/w), sulfur content 1.59% (w/w). This can be explained by the fact that the waste clay includes oxygen and nitrogen containing polar organic compounds and carbonaceous residues. Therefore it is evident that the quality of the recovered oil must be improved before reuse, for example by upgrading applying hydrotreatment.

Table 2. Influence of mode of addition of the collector

Number of additions	Dose of collector (kg/ton)	Yield (%)	
		Oil	Clay
1	1.5	81	40
	0.75	75	
2			36
	0.75	11	
	0.5	70	
3	0.5	10	28
	0.5	6	

Table 3. Physico-chemical characteristics of oil recovery using flotation at optimum conditions

Specification		References
Yield (% (w/w))	86	
Density (dy^{20})	0.8904	D 1480–86
Kimematic viscosity (cSt at 40 °C)	85.7	D 445–88
Kimematic viscosity (cSt at 100 °C)	11	D 445–88
Viscosity index	112	D 2270–93
Mean molecular weight	335	D 2502–87
Carbon residue (% (w/w))	3.21	D 189–88
Ash content (% (w/w))	2.30	D 482–87
Flash point (°C)	295	D 93–85
Pour point (°C)	-13	D 97–93
Sulfur content (% (w/w))	1.59	D 1552–88
Total acid number (mg KOH/g)	0.01	D 972–92

Experimental

The linear barium alkyl benzene sulfonates (Ba*LAS*) were prepared according to a procedure described elsewhere [11]. Infrared analysis was performed using a Mattson Genesis FTIR equipment. Surface tension measurements were obtained with a Doganon Abribat tensiometer apparatus No. 03295 [12].

Waste clay was obtained from Misr Petroleum Company (Bahtim). A small quantity was subjected to treatment with light naphtha (b.p.: 85–185°C). The percentage of recovered oil represents about 30% (w/w) of the waste clay [13]. The waste clay was treated with hot water and sodium hydroxide to produce a slurry containing approximately 50% solid material. A pneumatic froth meter column [14] was used for the flotation experiments at neutral circuit. The sample was conditioned for 5 minutes; then the air flow was introduced (50 ml/min) for the duration of flotation. After the test had been completed, the recovered oil (concentrate) and the residue (tailing) were collected, and the characteristics of the recovered oil were determined according to ASTM standard methods.

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