

Grażyna PARA \*,  
Klaus VOLKE \*\*

## INVESTIGATION OF ADSORPTION EFFECTS ON FLOATABILITY IN SOLUTIONS OF CARBOXYLIC ACIDS AT DIFFERENT pH

Mercury floatability in aqueous solutions of carboxylic acids (n-dodecanoic, n-nonanoic, and n-octanoic) of various pH was investigated. High mercury recovery was observed for solutions containing unionized molecules. Flotation results were correlated with the adsorption of acids at the mercury/solution interface and with the mercury hydrophobization. The possibility of the formation of ionomolecular complexes in the bulk of solution and at interfaces was discussed and related to the experimental data. It was concluded that within the investigated range of acid concentrations, the formation of acid-soap associates is possible only at the mercury/solution interface.

### Introduction

Flotation is described by many mutually interrelated factors. The process is often described by using model systems. To diminish the number of factors necessary to study, we used mercury as a model of floated material [1]. Choosing mercury may seem slightly controversial because the results of studies cannot be applied directly in practice. This choice has, however, various advantages for fundamental studies. First, it allows the elimination of many factors difficult to determine and interpret, such as, for example, a "history" of samples, the heterogeneity of their size, surface, shape and chemical reactivity. Second, the wettability and physical adsorption on mercury droplets may

\* Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, 30-239 Kraków

\*\* Forschungsinstitut für Aufbereitung AdW GDR - Freiberg

be easily investigated in conditions comparable with those of model flotation. Moreover, the surface potential of droplets in solutions, after their detachment from the capillary, may be controlled by the definite composition of the bulk of flotation mixtures (using potential determining systems). This enabled us to investigate the relationship between floatability and electrocapillarity as well.

### Results and discussion

We have studied the relation between the activity of weak ionic collectors at mercury surface and their effectiveness as flotation agents in solutions of different pH values [2-5]. At extreme pHs, solutions of weak electrolytes contain either neutral molecules or ions. At pHs close to pK-value, both forms are present in solutions. At a sufficiently high concentration of an organic electrolyte the solutions may also contain complexes formed of one ion and one molecule. In the case of carboxylic acids they are called "acid-soaps".

The role in flotation of various species present in solutions of carboxylic acids of various pH has been the subject of lengthy discussion. Oxide flotation recovery attains the maximum at pH values corresponding to the region of the highest bulk concentration of ionomolecular complexes consisting of one acid molecule and one carboxylate ion or one amine molecule and one aminium ion [7-10].

The idea of the predominant role played by these complexes in the flotation process also originated from the fact that in the same pH region the surface tension of solutions attains a minimum.

Beunen, Mitchell and White [11] showed for the first time that the minimum in surface tension vs. pH relationship appeared at the solubility edge of carboxylic acids. They inferred that the most probable reason is the precipitation of the neutral acid.

Our calculations [4] as well as the above-mentioned paper [11] show that the occurrence of the minimum in surface tension curves is not necessarily connected either with a complex formation or with an increase in the mutual interaction of ions and molecules. However, this minimum always appears in the case of a limited solubility of the investigated ionic surfactant in a certain pH range.

Surface complex formation at the air-solution interface over a range of concentrations, where the formation of acid-sorp in the bulk is practically negligible, was described by Lucassen-Reynders for dodecanoic acid [12].

Our results for the chosen carboxylic acids showed that within the studied range of acid concentration, that is, from  $8 \times 10^{-4}$  M to  $10^{-3}$  M

for octanoic, from  $10^{-5}$  to  $5 \times 10^{-4}$  M for nonanoic and from  $5 \times 10^{-5}$  M to  $10^{-5}$  for dodecanoic acid concentration, there is practically no complex formation in the bulk solutions of all acids, whereas the complex may form at the air-solution interface, but only in solutions of dodecanoic acid 12.

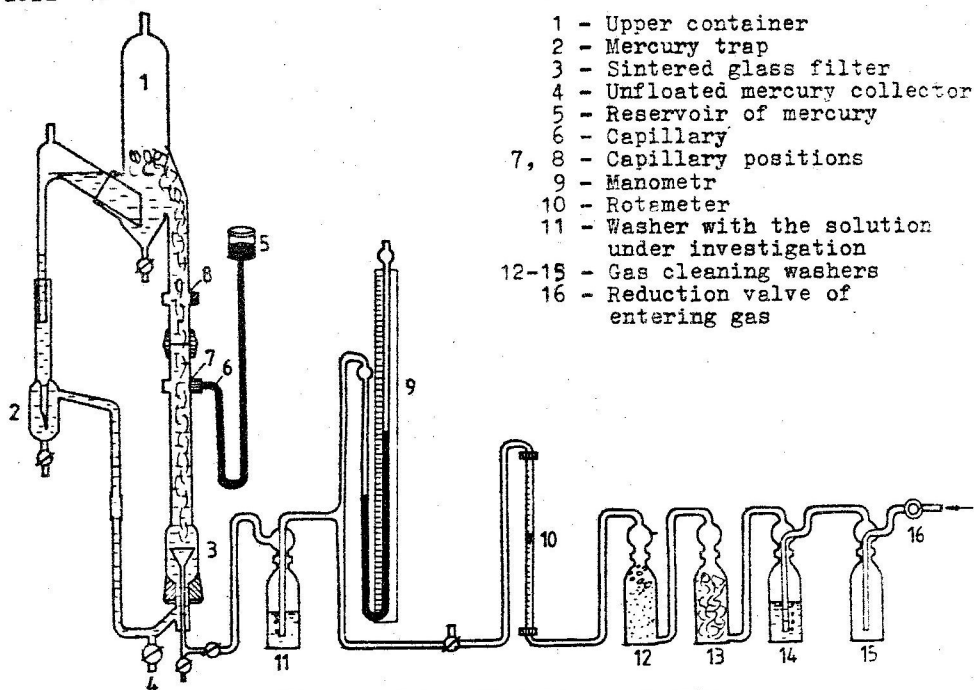


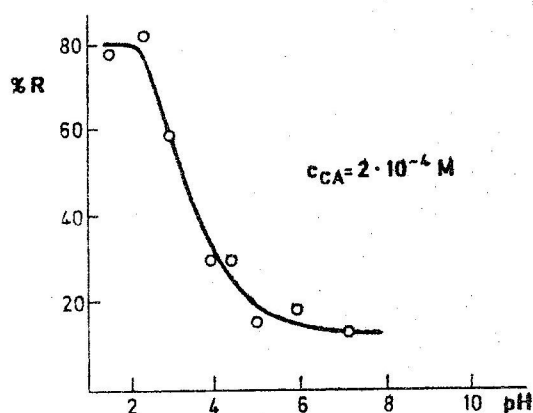
Fig. 1. Model flotation apparatus

Mercury floatability in solutions of carboxylic acids was studied in a model apparatus (shown in Fig. 1) under standard conditions: volume of solution 1300 ccm, nitrogen gas flow rate 16,6 ccm/s, capillary efficiency 3 mg Hg/s, time of flotation 6 min.

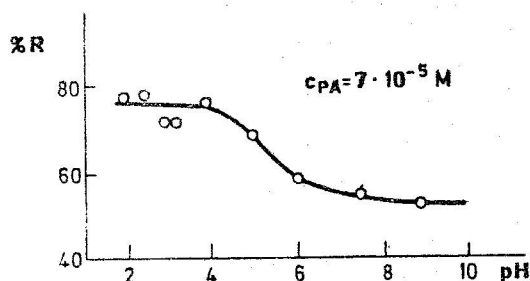
In Fig. 2, the relationship between mercury recovery and pH is shown for  $2 \times 10^{-4}$  M octanoic acid (KA),  $7 \times 10^{-5}$  M nonanoic acid (PA) and  $2.5 \times 10^{-5}$  M dodecanoic acid (LA) solutions in 0.1 M KCl. The concentrations were chosen in such a way that the surface activity of the solutions under investigation should have been comparable.

For all acids studied, the yield of mercury flotation is relatively high in acidic solutions, and decreases steadily with an increase in pH, for pH ranging from 2.5 for octanoic acid, through 4.5 for nonanoic acid, to 5 for dodecanoic acid.

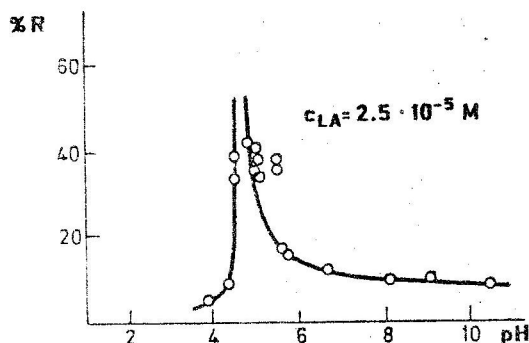
At low pH, flotation recovery in dodecanoic acid solutions decreases with the acidity of solutions. We ascribed this effect to the



foaming up of the precipitated dodecanoic acid. As the kinetics of its dissolution are relatively low, the bulk concentration of the acid decreases during the flotation process. This change in the concentration results in the formation of gas bubbles of greater size than the bubbles formed from the same gas volume in other systems. This obviously diminishes the flotation recovery.



Our hypothesis was confirmed when a small amount of propanol acting as a frother was added to the investigated dodecanoic solutions ( $2.5 \times 10^{-5}$  M) of  $\text{pH} < 5$  and the flotation recovery increased rapidly to a level comparable with the maximum of the curve.



The low flotation recoveries observed for alkaline 0.1 M KCl solutions were due to at least two factors; a low mercury hydrophobization and the formation of gas bubbles of a very small size.

Looking at Fig. 2, we may observe that the range of high floatability broadens as the chain length of carboxylic acid increases. To check the effect of mercury hydrophobization on

Fig. 2. Dependence of flotation recovery in solutions of carboxylic acids in 0.1 M KCl vs. pH

the strength of the contact between a mercury droplet and a gas bubble we have measured the contact angles on mercury.

In addition, the distance between the mercury surface and the gas bubble (attached to a teflon holder) at the moment of contact break-up caused by a slow rise of the holder was also measured.

In Fig. 3, the results of the contact angle measurements (upper curves) and the maximal distances needed to break up the drop/bubble

contact (lower curves) are shown for octanoic and nonanoic acids.

The curves describing mercury wettability in solutions of octanoic acid resemble both the curves of surface pressure vs pH and the curves showing variations of mercury floatability with pH. On the curves obtained for solutions of nonanoic acid, a maximum at pH 4.5 may be observed. This might be ascribed to the complex formation at the mercury-nonanoic acid solution interface. If it is true, a similar complex might also be formed at the mercury-dodecanoic acid solution interface.

This problem could be more precisely solved if electrochemical measure-

ments showing the equilibrium of adsorption of all components at the mercury-solution interface were performed. For short-lived drops, the kinetics of adsorption should also be simultaneously studied.

Polarographic studies of n-carboxylic acids in acidic solutions have been undertaken by many authors [13-19]. The adsorption of these acids at the mercury-solution interfaces was satisfactorily described using the Frumkin adsorption isotherm. The parameters of the adsorption of some carboxylic acids were tabularized by Jehring [16]. The adsorption of acid molecules at the Hg-solution interface is generally higher than at the free surface of aqueous solutions. In both cases, interaction parameter " $a_1$ " increases with hydrocarbon chain length. For higher homologues these values are most probably greater at the solution-mercury interface. A hysteresis of the differential capacity has been observed from nonanoic acid up to the higher members of the series. This has been ascribed to the association of the acid molecules and the film condensation on the mercury surface [14]. A dimerization

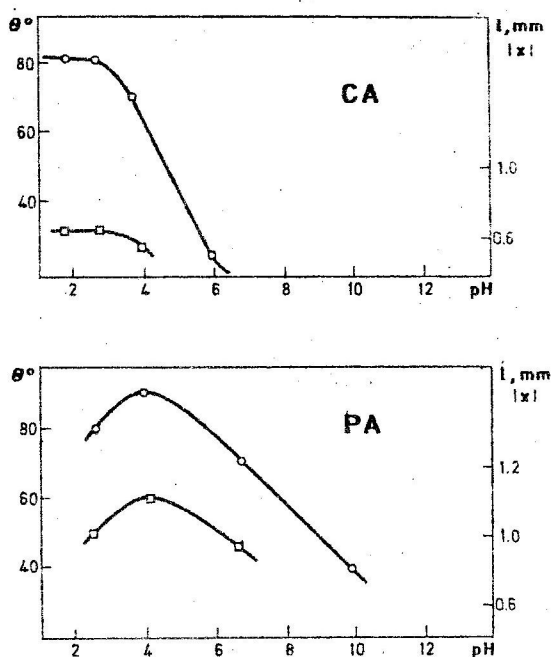


Fig. 3. The dependence of the three phase contact angle on mercury on the pH of octanoic (CA) and nonanoic (PA) acid solutions. "l"-the distance at which contact between the mercury and  $N_2$ -bubble is broken

of dodecanoic acid at Hg/solution interface was also suggested by Orzechowska and Matysik [19].

We investigated adsorption at the Hg-solution interface from mixed solutions of the undissociated acids and their ions at different pHs.

The results of the measurements of dodecanoic acid adsorption on the mercury surface were published in Coll. Polym. Sci. in 1984 [20]. An analysis of the capacity/potential and the capacity/time curves showed that the maximum of adsorption occurred at  $\text{pH} \sim 5$ . The surface coverage of mercury at that pH value exceeds the monolayer adsorption. The surface area calculated for one adsorbed molecule at pH 5 is nearly two times smaller than the area calculated at pH 10,5 (assuming the horizontal orientation of molecules). Since no reorientation of molecules was noticed on the bases of polarographic experiments, the authors suggested either the possibility of ion-molecule associates or the condensed film formation on the mercury surface (similarly to the case of nonanoic acid [14]).

For a complete comparison of the flotation and adsorption results, we performed a polarographic investigation for octanoic acid. Fig. 4 shows some selected differential capacity curves of the electrical double layer as a function of polarization potential (measured vs. SCE) for n-octanoic acid of pH = 2. The potential of maximal adsorption found on the basis of these curves equals  $-0.4$  V, and, as expected, is lower than the one in solutions of octanoate salts. Capacity curves

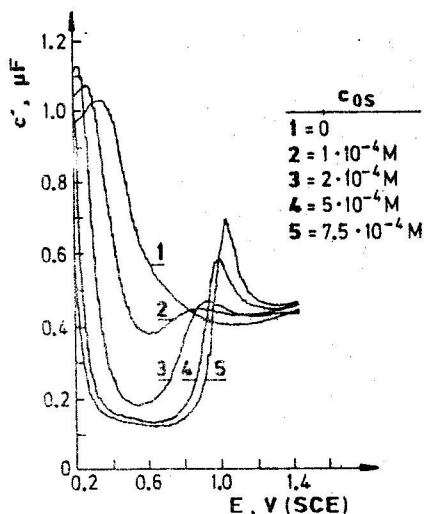


Fig. 4. Tensammetric curves in solutions of octanoic acid

for octanoic acid show only one peak of desorption, while for dodecanoic acid there are two peaks. The lack of the second peak indicates that, as opposed to dodecanoic acid, neither the condensed film nor the formation of premicellar states occurs in octanoic acid solutions.

With the decrease of the pH value, the peak occurs at a lower concentration of the acid and is more pronounced.

In the case of octanoic acid, a change in the direction of polarization did not cause hysteresis in the capacity-potential curve as it did in the case of nonanoic acid [14]. This fact also indicates that in solutions of octanoic acid only monolayer

adsorption takes place.

Fig. 5 illustrates the dependence of the maximal lowering of capacity values (normalized to the capacity in the supporting electrolyte) in octanoic acid solutions of various pH. The maximal values of the relative lowering of the capacity  $C/C_0$ , indicating strong adsorption of the components of the solution, occur in the acidic region of the pH scale. Between pH 3 and 5, the relative lowering of the capacity decreases sharply to attain a constant value of 0.3 in more alkaline solutions.

The behaviour described above corresponds closely to the changes of the undissociated octanoic acid concentration " $c_s$ " (Fig. 5).

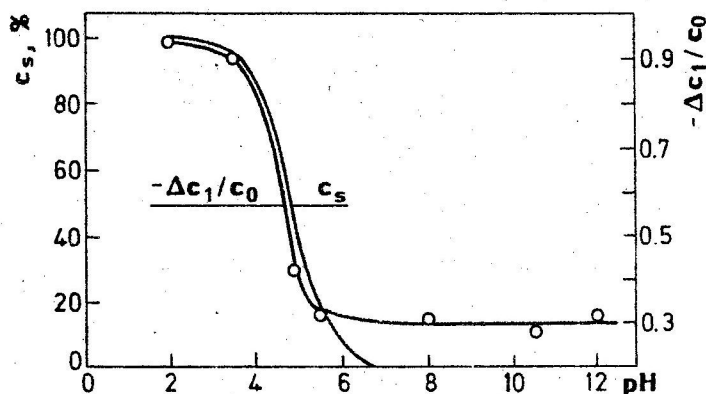


Fig. 5. Relative, maximal lowering of the specific capacity  $-\Delta C_1/C_0$  and the percentage concentration of undissociated acid molecules,  $c_s$ , vs. pH values of octanoic acid solutions.

The values of adsorption parameters: - interaction coefficient "a", equilibrium constant "B" and standard free enthalpy of adsorption " $-\Delta G$ " for acidic and alkaline solutions of octanoic acid-are collected in Table 1:

pH	a	B 1 Mol <sup>-1</sup>	$-\Delta G$ kJ Mol <sup>-1</sup>
2	1.41	2460	28.8
12	1.19	30.8	18.2

The participation of ions and undissociated molecules in the adsorption at the intermediate pH values is currently under investigation.

### Conclusions

Our analysis of flotation experiments, contact angles and polarographic measurements shows that the hydrophobization of the mercury surface is mainly caused by the adsorption of undissociated acid molecules.

The formation of acid-soap associates is possible only on the mercury/solution interface where the density of adsorbed molecules and ions is much higher. The acid-soap associates may increase mercury hydrophobization, thus increasing flotation recovery.

The formation of surface associates can also explain the maximum observed on the curve of contact angle vs pH values of nonanoic acid, as well as the broadening of the region of high mercury floatability with the increased chain length of carboxylic acids.

### References

1. Para G., Zembala M., Pomianowski A., Pol. J. Chem. 54 (1980) 77.
2. Volke K., Para G., Pawlikowska-Czubak J., Neubert H., Coll. Polym. Sci. 262 (1984) 245.
3. Para G., Pomianowski A., Volke K., Coll. Polym. Sci. 264 (1986) 260.
4. Pomianowski A., Rodkiewicz-Nowak J., Para G., Proc. 6<sup>th</sup> Int. Conf. Surf. Solution, New Delhi, 1986, in press.
5. Para G., Pomianowski A., Rodkiewicz-Nowak J., *ibid.*
6. Rosano H., Breindel K., J. Coll. Sci. 22 (1966) 58.
7. Somasundaran P., Chandar P., Chari K., Coll. Surf. 8 (1983) 121.
8. Somasundaran P., Int. J. Min. Process., 3 (1976) 35.
9. Somasundaran P., Ananthapadmanabhan K.P., Solution Chemistry of Surfactants, 1979, K.L. Mittal - ed., Plenum, N.York, vol. 2, p.777.
10. Finch J.A., Smith G., J. Coll. Interface Sci. 45 (1973) 81.
11. Beunen J.A., Mitchell D.J., White L.R., J. Chem. Soc., Faraday Trans. I 74 (1978) 2501.
12. Lucassen-Reunders E.H., J. Coll. Interface Sci. 41 (1972) 156.
13. Hansen R.S., Mitara R.E., Hickson D.A., J. Phys. Chem. 60 (1956) 1135.
14. Lorenz W., Z. Elektrochem. 62 (1958) 192.
15. Baikerikar K.G., Sathyamaryana S., J. Electroanal. Chem. 24 (1970) 33.
16. Sathyamaryana S., Baikerikar K.G., J. Electroanal. Chem. 25 (1970) 33.
17. Daniłow F.J., Panasienko S.A., Szatuchin J.G., Elektrochimija 18



(1982) 1420.

18. Jehring H., Elektrosorptionsanalyse mit Wechselstrom-polarographie, Akademie - Verlag, Berlin 1974.
19. Orzechowska M., Matysik J., J. Electroanal. Chem. 103 (1979) 251.
20. Volke K., Neubert., Z. Phys. Chem. 265 (1984) 968.

#### STRESZCZENIE

Para G., Volke K., 1987. Badania wpływu adsorpcji na flotowalność w roztworach kwasów karboksylowych różnych wartościach pH. Fizykochemiczne Problemy Mineralurgii 19; 89-97.

Badano flotowalność rtęci w roztworach kwasów karboksylowych (n-dodecylowego, n-nonylowego i n-oktylowego) o różnych wartościach pH. Stwierdzono wysokie wydajności flotacji w roztworach zawierających niezdysoცjowane cząsteczki kwasów. Wyniki flotacji skorelowano z danymi adsorpcji kwasów na powierzchni rtęci i wynikami pomiarów kątów zwilżania. Na podstawie otrzymanych rezultatów przedyskutowano możliwość powstawania jono-molekularnych asocjatów w głębi roztworu i na granicach faz. Stwierdzono, że tworzenie asocjatów jon-cząsteczka jest, w zakresie badanych stężeń kwasów karboksylowych, możliwe jedynie na powierzchni rtęci, gdzie gęstość zaadsorbowanych cząsteczek i jonów jest większa.

#### СОДЕРЖАНИЕ

Г.Пара, К.Волке, 1987. Влияние адсорбции карбоксильных кислот на флотуемость ртути в растворах с различными величинами pH. Физикохимические вопросы обогащения, 19; 89-97.

Исследована флотуемость ртути в растворах карбоксильных кислот /н-октиловой, н-нонйловой и н-додещйловой/, имеющих различные величины pH. Высокие флотационные выходы получено в растворах, содержащих недиссоциированные молекулы кислот. Результаты флотационных исследований коррелированы с адсорбцией кислот на поверхности ртути и величиной угла смачивания. На основе полученных результатов обсухлена возможность возникновения ионномолекулярных ассоциатов в объеме раствора и на границах раздела фаз /раствор-воздух и раствор-ртуть/. Обсуждено, что возникновение ионномолекулярных ассоциатов является /в пределах исследованных концентраций карбоксильных кислот /возможным лишь на поверхности ртути, где концентрация ионов и молекул выше.