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Permeability reduction of porous media on transport of emulsions through them

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Abstract

Permeability reductions, effected in a porous medium consisting of 40–60 μm glass spheres by passage of emulsions, are reported for Na oleate-stabilized emulsions at different electrolyte concentrations, and for an emulsion containing Aerosol OT (Na diocyl sulphosuccinate; AOT) at low electrolyte concentration. All emulsions show a pronounced permeability reduction, but for Na oleate-stabilized emulsions, in the absence of added electrolyte, substantial amounts of disperse phase have to be passed through in order to reduce the permeability to about 35% of its initial value. Addition of electrolyte above the critical coagulation concentration (CCC) leads to more rapid permeability reduction. AOT-stabilized emulsions, even in the absence of added electrolyte, reduce the permeability of the porous medium in a way comparable to that found for Na oleate-stabilized emulsions with [NaCl] > CCC. This is ascribed to coagulation of the AOT-containing emulsion even in the absence of added electrolyte. This coagulation is indeed observed on passing the AOT-stabilized emulsions through the porous medium. The reduced stability of the AOT-stabilized emulsion can be accounted for by the low interfacial tension in this emulsion, permitting emulsion destabilization through droplet deformation.

INTRODUCTION

Multiphase flow through porous media is of interest both because of the practical importance of systems comprising emulsions in porous media, and because of the theoretical relevance of the phenomena encountered in their study. Flow of emulsions through porous media is met, e.g. in oil recovery, in disposal of oil wastes and in paint treatment of wood. A typical phenomenon of theoretical interest encountered is the reduction of the permeability of the porous medium occurring during transport of an emulsion through it. Such a permeabil-

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ity reduction is not surprising for unstable emulsions [1] because in this case, the permeability reduction can be understood in terms of blocking of pore constrictions by large droplets formed on coalescence. Neither is the permeability reduction surprising in the cases of stable emulsions with droplet sizes exceeding the pore sizes, as reported by McAuliffe [2]. However, pronounced permeability reductions have been observed even for droplet sizes not exceeding the pore sizes while a pronounced electrostatic repulsion is expected both between the oil droplets mutually, and between the oil droplets and the walls of the porous medium [3]. In such cases blocking of the pores by individual droplets, by larger droplets formed through coalescence between primary droplets, or by attachment of the droplets to the pore walls is not expected.

From a theoretical point of view, such cases of the interaction between emulsion droplets and walls of the porous medium are interesting as an example of general colloid chemical principles on attractive, repulsive and hydrodynamical interactions between bodies immersed in a liquid. Soo and co-workers [3,4] developed a model on the basis of deep-bed filtration, in which the permeability reduction is caused by two filtration effects. The most important effect is straining: oil droplets clog in pore constrictions of sizes smaller than their own by lodging between the grains of the porous medium. This has a large effect on the permeability, since all connected pores are simultaneously blocked for emulsion flow. The second effect is the interception of oil droplets by trapping in circulation eddies or attachment to pore walls due to van der Waals forces. However, this model is not relevant as regards the compatibility of the permeability reduction with the large electrostatic repulsion expected from the zeta potentials for oil droplets and the wall material.

Devereux [5] presented a theoretical description for the flow of an emulsion through a porous medium, in which the permeability reduction is fully ascribed to the retention of oil droplets by retarding forces due to capillary effects. His model gives a good description of the experimental data, but cannot explain why the initial permeability is not recovered on subsequent passage of continuous phase free of emulsion droplets.

Neither can the irreversibility of the permeability reduction found experimentally be explained by the model presented by Alvarado and Marsden [6] which describes the flow of emulsions through porous media as the single phase flow of power-law liquids through a bundle of capillaries.

In the present investigation we report experiments on the influence of electrostatic repulsion and emulsion stability on the permeability
reduction experienced by a porous medium during flow of an emulsion through it. Two different emulsions, stabilized by Na oleate and Aerosol OT, respectively, were investigated. These emulsions happen to have very similar \( \zeta \) potential vs. [NaCl] characteristics; in addition, the bulk phases are very similar in composition. Nevertheless, they show pronounced differences in stability [7,8].

Calculations on the three types of forces experienced by an emulsion droplet approaching a pore constriction—van der Waals attraction, electrostatic repulsion, and hydrodynamic forces—will be reported separately [7,9].

**EXPERIMENTAL**

*Emulsions*

In order to prevent effects of segregation by differences in specific mass between the disperse and continuous phases, nearly density-matched emulsions were employed. These were prepared as follows [7,8]: \( n \)-decane (Janssen Chimica, 99 + %, purified on an alumina column, or Merck, zur Synthese, purified by distillation followed by purification on an alumina column) and tetrachloromethane (Merck, p.a.) were mixed to produce a composition the density of which matched the density of the aqueous phase in which the organic mixture was to be emulsified. Either Na oleate or Aerosol OT (Na dioctyl sulphosuccinate) was used as emulsifier. For the AOT-stabilized emulsions a solution of Aerosol OT (Sigma, 10% \( \text{w/v} \) solution, used as received) in water was employed with a concentration such that, after preparation of the emulsion, the desired concentration was reached. In the case of sodium oleate, the emulsifier was synthesized in situ from oleic acid and NaOH. An amount of oleic acid (Merck, reinst) was dissolved in the decane + CCl\(_4\) mixture and the resulting mixture was dispersed in a NaOH (Merck Titrisol) solution of such a concentration that, after the emulsion preparation, all the oleic acid dissolved in the oil phase was neutralized and the pH of the emulsion would be about 10.

To prepare an emulsion, 5 ml of the oil mixture was dispersed in 495 ml water phase (AOT solution or NaOH solution) using an Ystral X40 dispersing unit with a generator for media with low viscosities (diameter 20 mm). The resulting emulsions had a logarithmic normal droplet size distribution between 1 and 8 \( \mu \text{m} \). The average particle size was 2.5 \( \mu \text{m} \). The concentration of the dispersed phase was 1% (\( \text{v/v} \)) for all experiments performed. The sodium oleate concentration (calculated on the basis of the oleic acid added) was 0.5 mmol l\(^{-1}\). For the
experiments performed with the Aerosol OT-stabilized emulsions, a surfactant concentration of 1 mmol l$^{-1}$ was used.

The emulsions prepared in this way were very similar as regards the composition of the phases concerned: the oleic acid added in the case of the Na oleate-stabilized emulsion is converted into Na oleate and is assembled predominantly at the L$_1$L$_2$ phase boundary. Similarly, the $\zeta$ potentials were closely similar, increasing for Na oleate-stabilized emulsions from $-0.075$ V at [NaCl] = 0.05 $M$ to $-0.019$ V at [NaCl] = 0.5 $M$. For AOT-stabilized emulsions, these values were $-0.080$ and $-0.018$ V, respectively [7,8]. Since no polymers are present near the phase boundary, significant differences between $\zeta$ potentials and Stern potentials are not expected [10].

Droplet size distributions were determined by a Coulter Counter, model ZM, equipped with a Channelyzer 256 and a Coulter Range Expander.

**Preparation of porous cores**

To prepare a porous core, glass beads with a narrow size distribution were cleaned according to Eylander [11]. The glass was washed with a concentrated solution of NaOH in a mixture of water and ethanol (1:1 vol.:vol.), double-distilled water, hydrofluoric acid and double-distilled water. A Perspex cylinder (Fig. 1) was heated to about 80°C. A sintered glass filter was placed at the bottom of the warm cylinder. The cylinder was filled with the cleaned glass beads, closed with another sintered glass filter and slowly cooled to room temperature. The Perspex cylinder shrinks around the filter plates, so keeping them in place. After cooling, the core could be mounted in the flow apparatus.

Two types of glass beads, with size distributions shown in Fig. 2, were employed. The specific mass of the glass was 2.810 kg m$^{-3}$. A typical pore size distribution in the porous medium formed from the 40–60 $\mu$m glass bead sample, as determined by mercury porosimetry, is shown in Fig. 3. The overall porosity of the core was 0.375.

The $\zeta$ potential of the glass beads in a porous core was measured by means of the streaming potential, using Ag/AgCl electrodes for measuring the potential difference across the porous medium created by a flow. The absolute value of the $\zeta$ potential, in solutions containing both Na oleate and NaCl of total electrolyte content 0.005 $M$, increased from 101 to 110 mV with Na oleate increasing from $10^{-7}$ to $10^{-3}$ $M$.

The $\zeta$ potential of the emulsion droplets was measured by electrophoresis using a Malvern Zetasizer III.
Fig. 1. Perspex cylinder used for permeability measurements. The numbers indicate the dimensions in mm: height of the cylindrical part in the centre of the apparatus, 60.00 mm.

Fig. 2. Particle size distributions of two glass samples used for preparation of porous media.

Flow apparatus

A schematic picture of the flow apparatus is shown in Fig. 4. At the left side, two liquid containers, filled with emulsion and water respectively, are connected to the pump. The pump used was either a Verder® micro-gear pump or an ISCO model 2350 HPLC pump. The micro-gear pump had the disadvantage that the flow rate was not constant during an experiment, but decreased as the pressure increased because of the permeability reduction. The pressure difference across the core is measured using a Validyne differential pressure transducer. At the end of the apparatus the emulsion flows into a waste beaker.
RESULTS

With pure water, the flow through the cores agreed with Darcy's law, with a constant permeability.

The two types of emulsions employed containing Na oleate or AOT, respectively, in spite of being very similar as regards the composition of bulk phases (this with regard to the effective Hamaker constant) and with regard to \( \zeta \) potentials (thus with regard to electrostatic repulsion), nevertheless showed pronounced differences with regard to stability. The Na oleate-stabilized emulsion is much more stable at salt concentrations below the critical coagulation concentration than the AOT-stabilized one [7,8]. This difference has been ascribed to the low interfacial tension in the AOT-stabilized emulsion, permitting coagulation to proceed at a measurable rate even at concentrations well below the CCC, through droplet deformation.

The permeability reduction effected by a stable (Na oleate-stabilized) emulsion depends both on the droplet diameter and on the velocity with which the emulsion passes through the medium; a larger emulsion droplet size, and a lower velocity result in a more pronounced perme-
ability reduction. Figure 5 shows the influence of droplet size, at equal flow rates. Here, $K/K_0$ ($K_0$ is the initial permeability of the porous medium) is plotted vs. the number of pore volumes of disperse phase having passed through the porous medium ($\tau$ is the volume of emulsion passed through divided by the total volume of the pores and $c_i$, the volume fraction of disperse phase). It is striking that the permeability reduction is so pronounced, in view of the average size of the pores being so much in excess of the emulsion droplet diameter. Calculations on the forces experienced by a spherical emulsion droplet approaching a pore constriction [7,9] show that the forces experienced by a droplet with smaller size than the pore constriction remain finite, while especially the hydrodynamic force experienced by a droplet exceeding the pore constriction size increases very strongly as long as the emulsion droplet remains spherical. Thus, the data shown in Fig. 5 can be understood by assuming that the core investigated had a large number of pore constrictions with diameter smaller than 8.9 $\mu$m, and a much smaller number of pore constrictions smaller than 5.1 $\mu$m.

The influence of the flow rate at constant emulsion droplet size (Fig. 6) shows that a high flow rate, being accompanied by a large pressure gradient, permits some of the droplets which are blocking pore constrictions to be squeezed through them.

We investigated the droplet size distribution of an emulsion stabilized by Na oleate with a rather broad initial size distribution (Fig. 7) after having passed through the porous medium (Fig. 8). Although the droplet size distributions are rather noisy, the main effects are beyond any doubt. Initially, the larger droplets are preferentially retained, how-

![Fig. 5. Influence of average emulsion droplet size ($d_a$) on permeability $K$ of a porous medium (particles 40–60 $\mu$m). $K_0$, initial permeability; superficial velocity of liquid, 2.21 mm min$^{-1}$; $d_a = 5.1$ $\mu$m; $d_a = 8.9$ $\mu$m; $\tau$, volume of emulsion passed through/total pore volume; $c_i$, volume fraction of disperse phase.](image-url)
Fig. 6. Influence of flow rate on permeability reduction of a porous medium; $d_p = 8.0 \, \mu m$; superficial velocity, $v_s = 2.21 \, \text{mm min}^{-1}$; $v_s = 3.87 \, \text{mm min}^{-1}$. $K$, $K_0$, $\tau$, $c_i$, $d_p$ as in legend to Fig. 5.

Fig. 7. Initial droplet size distribution of bimodal Na oleate-stabilized emulsion. $K$, $K_0$, $\tau$, $c_i$, $d_p$ as in legend to Fig. 5.

ever, after some pore volumes of disperse phase have been passed through the medium, the outflowing emulsion is relatively rich in large droplets. At this stage, therefore, small droplets are retained more efficiently than larger ones. This is ascribed to the pressure gradient in the core increasing with decreasing permeability; during the initial stages of the flow, a large number of large droplets are retained in the core, but these are squeezed through the constrictions retaining them in later stages.

Figure 9 shows the influence of electrostatic repulsion. Although the experiments shown in this figure do not refer to strictly identical circumstances, the trends are clear. When the $\zeta$ potential of both
Fig. 8. Droplet size distributions of the emulsion with initial size distribution shown in Fig. 7, after passage through porous medium. η·c₁ values (volume of disperse phase passed through/total pore volume): (1) 0.004; (2) 0.01; (3) 0.02; (4) 0.90; (5) 0.00 (initial size distribution).

Fig. 9. Influence of added electrolyte and of type of emulsifier on permeability reduction by emulsions flowing through porous medium. K, K₀, τ, c₁, dₚ as in legend to Fig. 5. (a) Na oleate-containing emulsions: flow rate, 2.5 ml min⁻¹; [NaCl] = 0 M, dₚ = 6 μm; [NaCl] = 0.005 M, dₚ = 6 μm; [NaCl] = 0.1 M, dₚ = 3 μm. (b) AOT-containing emulsion: flow rate, 4 ml min⁻¹; [AOT] = 0.001 M, dₚ = 2.5 μm.

emulsion droplets and wall material is reduced by adding NaCl, the permeability reduction proceeds faster; the permeability reduction after a given number of pore volumes of disperse phase has passed through the core is about twice as large in the presence of 0.005 M NaCl as in its absence. Nevertheless, the final permeability is larger in the presence of salt than in its absence.

Figure 9 shows in addition the permeability reduction on passage of
an emulsion containing AOT as emulsifier. It is seen that the permeability reduction is comparable to that of a Na oleate-stabilized emulsion in the presence of substantial amounts of electrolyte.

DISCUSSION

Our results confirm the observations by Soo and co-workers [3,4] that both stable and unstable emulsions characterized by similar chemical composition of the disperse phase (thus similar Hamaker constants) reduce the permeability of a porous medium through which they flow, although the latter do so much more efficiently than the former. It is remarkable that the difference in permeability reduction is also found when comparing a Na oleate-stabilized emulsion at low electrolyte content with one containing AOT as emulsifier (Fig. 9), since from ζ potential values in both cases, a pronounced electrostatic repulsion is expected between emulsion droplets mutually, and emulsion droplets and wall.

In separate publications [7,8] it is shown that the difference in stability between the emulsions can be accounted for by the difference in their interfacial tensions. In the absence of added electrolyte the interfacial tension at the aqueous solution/(decane + CCl₄) interface, with molar ratio decane/CCl₄ = 0.6/0.4, in $4.3 \cdot 10^{-4}$ M AOT solution is 0.1 mN m⁻¹.

In a 0.001 M Na oleate solution, this value is 3–4 times higher. Addition of small amounts of electrolyte (up to 0.005 M) results in a very steep decrease of the interfacial tension in the case of the AOT-stabilized emulsion, whereas the interfacial tension in the Na oleate-stabilized emulsion does not change very much at such low electrolyte concentrations.

The difference in stability between the two emulsions may not come as a surprise, since the AOT concentration is less than half the CMC in pure water, which makes the interfacial film less than close-packed. However, for undeformed droplets there is a pronounced electrostatic repulsion (taking the ζ potential as an approximate value for the Stern potential), and for emulsion coalescence to occur, a coagulation step is first necessary which is expected to be prevented by electrostatic repulsion.

However, as shown in separate publications [7,8], the electrostatic repulsion between the emulsion droplets can be completely circumvented at these low interfacial tensions. Instead of a repulsion, an attraction results when two droplets approach each other, forming a flat contact area, the droplets remaining separated by the distance corresponding to the secondary minimum in the interaction energy vs.
distance graph for flat plates. This situation is the extreme end of a continuous transition starting from undeformed droplets; in reality, under kinetic conditions a "dimple" will develop as, e.g. in the experiments of the Scheludko group on horizontal films (see, e.g. Ref. [12]). The calculations show that in the flat contact area situation complete circumvention of electrostatic repulsion occurs below an interfacial tension of about 0.1 mN m\(^{-1}\), though the exact value of the interfacial tension at this transition depends somewhat on the value of the parameters introduced (e.g. the Hamaker constant and the electrical potential \(\zeta\) the beginning of the diffuse electrical double layer). The interfacial tension of the Na oleate-stabilized emulsion is not low enough to completely circumvent the electrostatic repulsion.

Recently, Aronson [13] reported that emulsions stabilized by non-ionic detergents at concentrations exceeding the CMC, may be destabilized by depletion coagulation. However, this cannot explain the low stability of the AOT-stabilized emulsion observed in the present investigation. The AOT concentration used here was lower than the CMC and, in addition, the \(\zeta\) potentials found were such that undeformed droplets should experience a pronounced electrostatic repulsion which was absent in the cases studied by Aronson. Such electrostatic repulsion should prevent the coagulation step which must precede the coalescence.

Once a flat contact area is formed between the droplets, coalescence is possible because the low interfacial tension leads to only a slight additional surface energy for the squeezing mode of interface disturbances which initiates fracture of a thin liquid film [14].

This gives us the following picture of events during pore clogging. In the case of an emulsion with AOT as emulsifier, a droplet approaching a pore constriction easily adapts its shape to that of the solid wall because only a small amount of energy is required. It may be possible that, because of the pronounced electrostatic repulsion between emulsion droplet and wall, there remains a gap between them through which some liquid may pass. This, however, leads to additional emulsion droplets being forced upon the droplet already present near the constriction concerned, and will lead to coagulation followed by coalescence, which in turn leads to a more efficient pore clogging. Thus a self-reinforcing effect occurs.

In the Na oleate-stabilized emulsion, however, in the absence of added electrolyte the interfacial tension is higher. This does not make much difference for the pore clogging by a first droplet approaching a pore constriction, since the hydrodynamic forces experienced by a spherical droplet approaching a pore constriction is found to be much more important than the electrostatic repulsion [7,9]. However in this case the
coagulation followed by coalescence between droplets near a pore constriction is of lesser importance than with the emulsion containing AOT, at least at low electrolyte content. At electrolyte concentrations above the CCC, two effects have to be taken into account. In Na oleate-stabilized emulsions the interfacial tension is not strongly changed by addition of electrolyte; however, since electrostatic repulsion at the electrolyte concentrations concerned is much reduced, coagulation will be fast and pore clogging by a sieve-like action of a pore constriction is probable. Therefore permeability reduction is rapid in this case, but not so pronounced as in the case of the emulsion containing AOT.

It should be noted that it is difficult to be sure whether in the pores the emulsions contain the same concentrations of emulsifier as they have initially, because adsorption of surfactants at the pore walls may exhaust the emulsifier, especially near the liquid front. This may cast doubt on the existence of a stability difference between the emulsions concerned during their passage through the porous medium. However, the following observations confirm the existence of a substantial difference in stability between the emulsions.

(a) The first droplets of the disperse phase appearing after having passed through the porous medium were typical emulsion droplets in the case of the Na oleate-stabilized emulsion, whereas the emulsion with AOT as emulsifier had separated into two separate liquid phases with macroscopically visible “blobs” of the non-aqueous phase.

(b) Droplet size analysis (Fig. 8) confirmed that in the Na oleate-stabilized emulsion no significant enlargement of droplets had occurred during passage through the porous medium.

The irreversibility of the permeability reduction, which was reported by Devereux [5] and Alvarado and Marsden [6] can be understood at least for coagulating emulsions, since this process will not be reversed by passage of fresh continuous phase through the porous medium.

In practical applications, low interfacial tensions should therefore be avoided when clogging of pores on passage of an emulsion through a porous medium is undesirable.

CONCLUSIONS

Stable emulsions reduce the permeability of a porous medium during passage through it, but emulsions with low interfacial tension do so much more efficiently. Electrostatic repulsion cannot prevent the effect. The very strong permeability reduction observed in the case of emulsions with very low interfacial tensions can be understood by a self-reinforcing effect of easy adjustment of a droplet to the shape of
the solid wall near a constriction, and easy coagulation followed by coalescence.

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