

Influence of surfactants on contact angles of ceramic brick-aqueous solution-air and sand lime brick-aqueous solution-air

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Influence of Surfactants on Contact Angles of Ceramic Brick-Aqueous Solution-Air and Sand Lime Brick-Aqueous Solution-Air

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Surfactants influence the contact angles of ceramic brick-aqueous solution-air to a larger extent than contact angles of sand lime brick-aqueous solution-air. This applies especially to receding contact angles. Surfactants are removed from the solution by sand lime brick to a larger extent than by ceramic brick.

The increasing use of surfactants as air entrainers or superplasticizers in cementitious systems leads to the question: Do these additives influence the capillary suction exerted by bricks on the water phase in mortars? This suction is determined by the average pore size in the brick and by the contact angles at the three phase boundaries of brick-aqueous solution-air. Both factors may differ for ceramic brick versus sand lime brick.

The present investigation aims to elucidate whether surfactants influence the contact angles on those materials. Two pure compounds and two commercial substances were used as surfactants.

Experimental Procedures

Materials

A commercial brick was used, made on a clay basis by the "soft mud" process (1075°C). The fraction 36-63 μm was isolated by dry sieving. The BET nitrogen adsorption surface area (measured with an areameter*) was 0.5 m²/g. Its density, determined by a density meter† for powders, was 2720 kg/m³ (t=21°C). The main phases found by X-ray diffraction were quartz and feldspar.

A commercial sand lime brick was used. Its specifications

were: sieve fraction, 36-63 μm; surface area, 14.8 m²/g; and density (21°C), 2500 kg/m³. The main phases found by X-ray diffraction were quartz, calcium carbonate (calcite and waterite), and CSH (I).

Other materials used included: sodium dodecyl sulphate (SDS) anionic surfactant,‡ cetyl trimethylammonium bromide (CTAB) cationic surfactant,§ portland cement,|| a neutralized pine-resin-based anionic surfactant (hereafter referred to as "resin"),** a protein-based (animal keratin) nonionic surfactant (hereafter "protein"),†† calcium hydroxide, "pro analysi,"‡‡ and sand (cumulative sieve fractions: 0% > 400 μm, 53.7% > 200 μm, 89.0% > 160 μm, and 99.3% > 100 μm).§§

Method and Apparatus

Contact angles were determined by Bartell's method.¹ The velocity of flow of a liquid-gas phase boundary through a porous plug was measured at various pressure differences over the plug. Extrapolation to zero flow velocity yields the pressure ΔP₀ in this limit. ΔP₀ is related to the contact angle θ by²

$$\Delta P_0 = \frac{\gamma_{LG} \cos \theta}{M} \quad (1)$$

where *M* is the mean hydraulic pore radius in the plug in meters and γ_{LG} is the surface tension of the liquid in Newton-cubic meters.

Depending on the flow direction, the advancing or the receding contact angle is found. *M* is determined from the hydraulic permeability, *K*,³

$$K = \frac{\phi V^* \eta l}{A \Delta P} \quad (2)$$

where ϕV is the volumetric flow velocity in cubic meters per second related to a pressure difference, Δ*P*, in Newtons per square meter over the plug; η is the dynamic viscosity in Newton-seconds per square meter; *A* is the cross-sectional area of the plug in square meters; and *l* is the length of the plug in meters in the direction of flow.

K is related to the mean hydraulic radius, *M*, by

$$K = \frac{\epsilon M^2}{\kappa} \quad (3)$$

where ϵ is the volume fraction of liquid in the plug and κ is the Kozeny constant, ≈4.8 for a wide variety of porous materials.⁴

Figure 1 shows a schematic arrangement of the apparatus. The liquid flow, either with all pores filled by liquid (for determining *K*) or with a liquid-gas boundary in the plug (for determining θ), was maintained by a pump^{||} equipped with an adjustable piston stroke. The accompanying pressure was registered by a pressure transducer^{***} connected with a chart recorder.^{†††} The flow velocity was recorded with an electronic balance.^{†††}

*Of type supplied by Ströhlein & Co. GmbH, Fabrik Chemischer Apparate, Düsseldorf, West Germany.

†Model SPY-3, Quantachrome Corp., Syosset, NY.

‡Supplied by E. Merck AG, Darmstadt, West Germany.

§Supplied by Sigma Chemical Co., St. Louis, MO.

||Portland A, ENCI N.V., Maastricht, Netherlands.

**Supplied by Hercules Co., Rijswijk, Netherlands.

††Supplied by C. N. Schmidt B.V., Amsterdam, Netherlands.

‡‡Supplied by E. Merck AG, Darmstadt, West Germany.

§§Supplied by Sigrano Nederland B.V., Heerlen, Netherlands.

||Model R 409 P, Seybert & Rahier GmbH, Immenhausen, West Germany.

***Model PD 10, H. Jensen, Copenhagen, Denmark.

†††Model BD 40 X-5, Kipp & Zonen Div., Enraf-Nonius, Delft, Netherlands.

††††Model 1402 MP 7, Sartorius GmbH, Göttingen, West Germany.

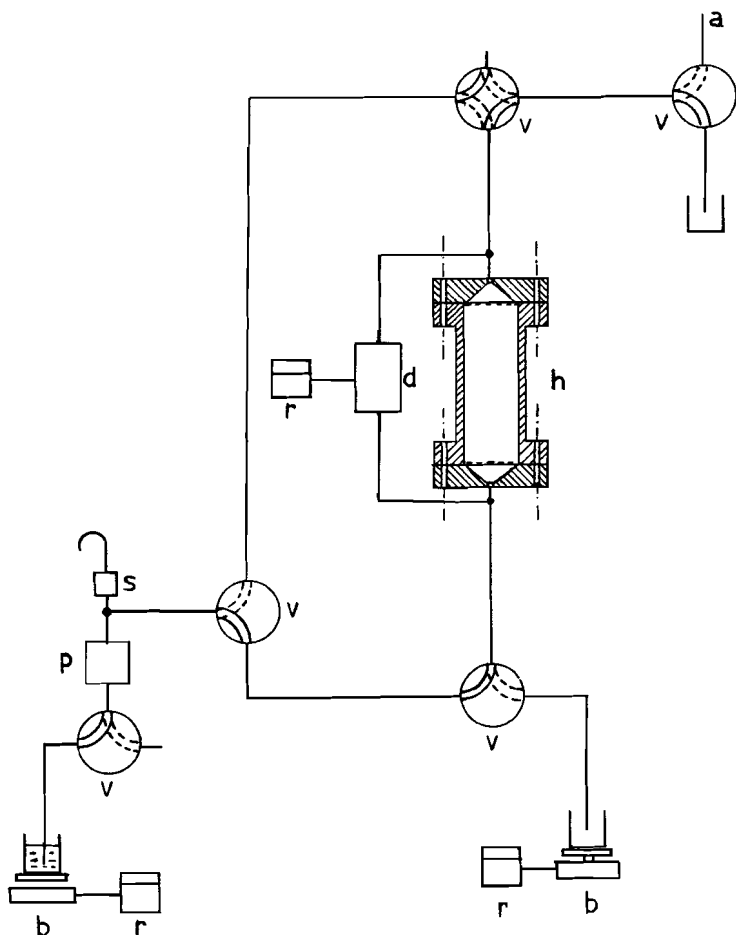


Fig. 1. Schematic of the experimental system: a, air inlet; b, electronic balance; d, differential pressure transducer; h, plug holder; p, pump; r, chart recorder; s, safety valve; v, ball valve.

The plug holder had a length of 0.10 m and an inner diameter of 0.025 m. The plug holder and all connections consisted of stainless steel; ball valves^{§§§} were used.

Procedure

The liquid used in contact angle measurements was a filtrate obtained from a suspension of ground hardened mortar in water (1:2) after standing for 1 h. The mortar was prepared from cement, sand, Ca(OH)₂, and water (or surfactant solution) in

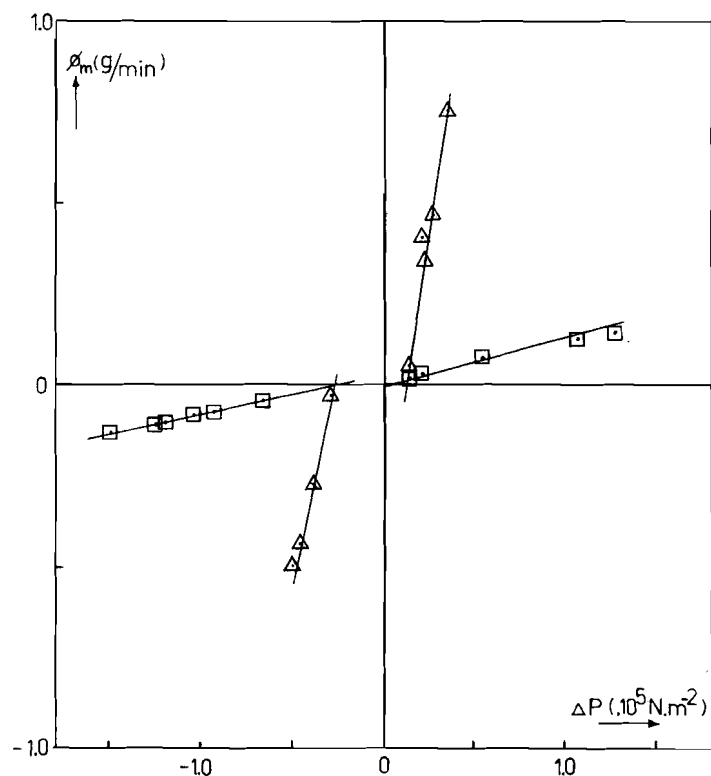


Fig. 2. Pressure difference versus flow velocity for a liquid (without surfactant)-gas interface through sand lime brick powder (□) and ceramic brick powder (△).

the ratio 1:5.25:1:2.5 and held for 14 days at room temperature before being ground. The mixing proportions were chosen to correspond with some practical formulations; aged mortars were used to avoid pronounced time effects resulting from cement hydration reactions.

The surfactant concentrations were 0.633% of the water phase for the SDS, CTAB, and resin surfactants and 2.8% for the protein surfactant. These concentrations are, at least for the commercial products, those recommended in practice.

A concentrated suspension of the powder to be investigated and this liquid was placed in the plug holder. Excess liquid was removed from the plug by suction (≈ 2 kPa at the bottom of the plug and 100 kPa at the top). The plug was then consolidated by vibration, using a 50-Hz vibrating mixer^{§§§§} with a glass needle

Table I. Results Obtained with Ceramic Brick and Sand Lime Brick

Type of surfactant	ϵ	K (m ²)	M (μ m)	γ		θ		W (mJ/m ²)
				Before plug contact (mN/m)	After plug contact (mN/m)	Advancing (°)	Receding (°)	
Ceramic Brick								
None	0.48	5.9×10^{-14}	0.72	72.9	72.9	82.6	73.9	93
SDS	0.47	7.6×10^{-14}	0.88	61	64	87.6	46.7	108
CTAB	0.48	5.2×10^{-14}	0.73	41	41	81.9	35.6	74
Protein	0.47	6.7×10^{-14}	0.83	62	66	77.7	74.0	84
Resin	0.45	9.3×10^{-14}	0.99	65	66	82.2	68.8	90
Sand Lime Brick								
None	0.49	0.26×10^{-14}	0.16	72.9	72.9	89.4	86.6	77
SDS	0.47	0.24×10^{-14}	0.16	61	69	89.9	82.2	78
CTAB	0.48	0.24×10^{-14}	0.15	41	72	89.4	89.3	73
Protein	0.47	0.24×10^{-14}	0.15	62	72	87.0	87.0	76
Resin	0.45	0.21×10^{-14}	0.14	65	72	88.5	86.1	77

^{§§§}Of type supplied by Whitey Co., Cleveland, OH.
^{§§§§}Of type supplied by Vibro-Mix AG für Chemie-Apparatebau, Zürich, Switzerland.

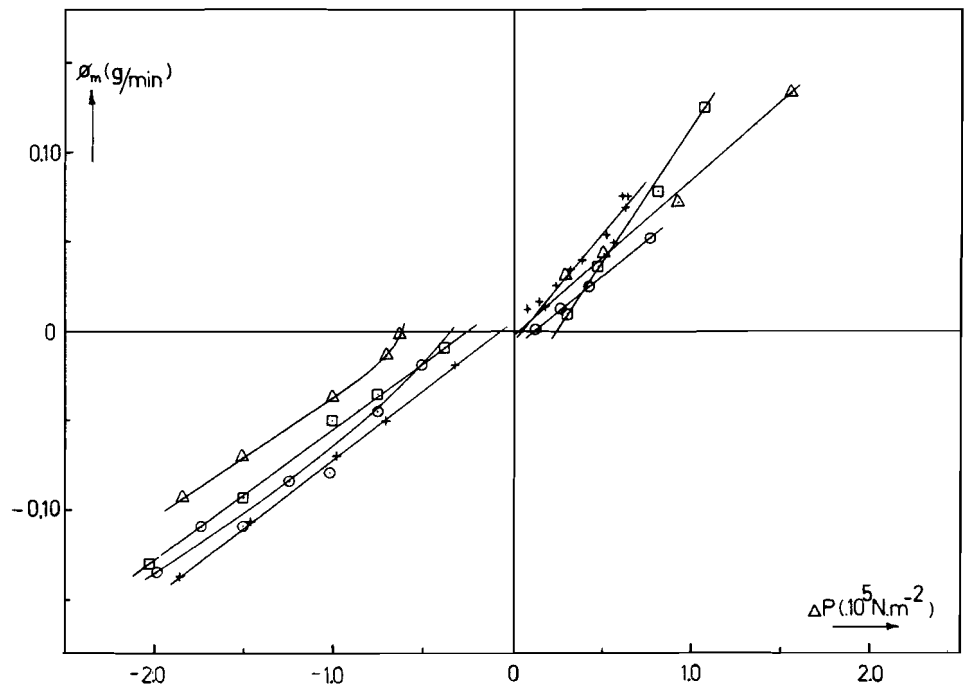


Fig. 3. ΔP versus flow velocity for the advancing and receding liquid-gas interface for sand lime brick in the presence of several surfactants: +, CTAB; O, resin; Δ , SDS; \square , protein.

(7 mm in diameter by 200 mm long).

The plug was then installed in the circuit shown in Fig. 1. The liquid obtained on filtration of the mortar was pressed into the plug, and the flow rate of this liquid was measured as a function of the pressure.

Subsequently, air was forced into the plug from the top, replacing part of the liquid in the pores. In this way, a receding liquid front was formed. Again, the flow rate was recorded at different pressures.

The liquid was then pressed from the bottom into the plug, forming an advancing liquid front. The resulting flow rate also was measured at different pressures.

The surface tensions of the liquid entering the plug and of the liquid leaving the plug were measured by the du Nouy (ring) tensiometer method.⁵ This measurement was performed in a hydrophobic vessel⁶ and in a nitrogen atmosphere to prevent formation of a precipitate. Measurements were performed at 21°C.

Results and Discussion

Figure 2 shows experiments without surfactant. Positive velocities corresponded with an advancing liquid front, whereas negative velocities corresponded with a receding front. Ceramic brick and sand lime brick differ greatly with regard to their permeability, in spite of nearly equal porosities (see Tables I and II). This difference in permeability reflects a difference in mean hydraulic radius. These differences may be surprising in view of the fact that equal sieve fractions were employed. However, it was noted by scanning electron microscopy that the sand lime brick powder was actually composed of much finer particles than those that would correspond with the sieves' mesh openings. Apparently, the sand lime brick powder forms aggregates during dry sieving which are redispersed in an aqueous medium, even in the absence of surfactants.

Figures 3 and 4 show experiments in the presence of surfactants. Values of the flow rates at different pressures were graphically extrapolated to the pressure corresponding with zero flow

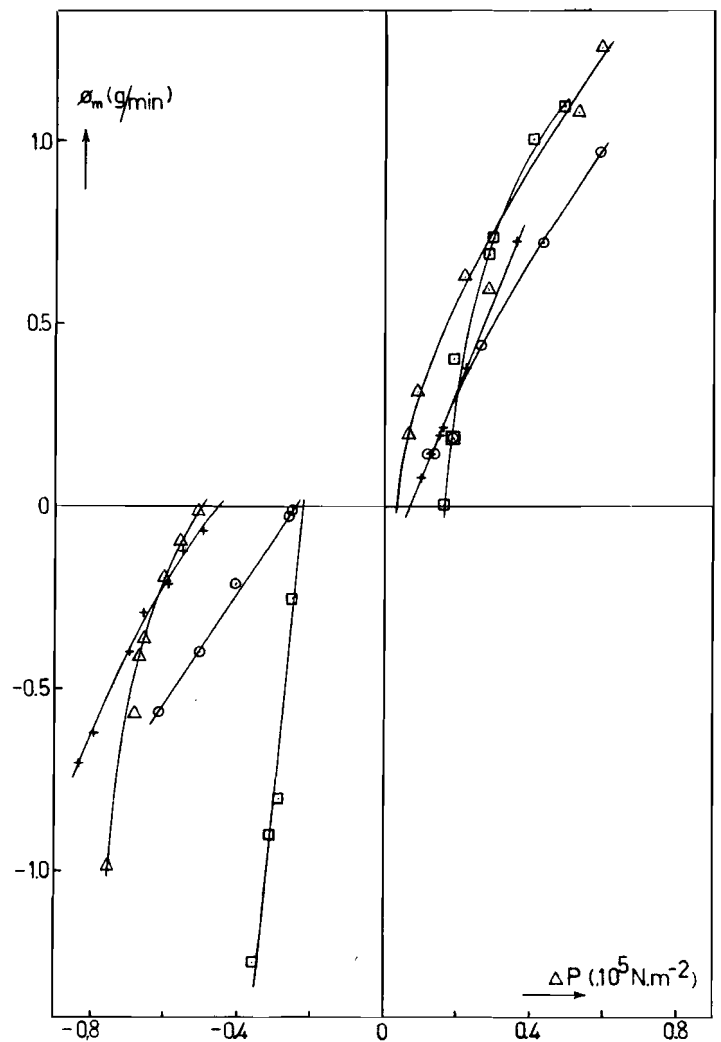


Fig. 4. ΔP versus flow velocity for the advancing and receding liquid-gas interface for ceramic brick in the presence of several reactants: +, CTAB; O, resin; Δ , SDS; \square , protein.

(ΔP_0), both for advancing and receding liquid fronts. From these ΔP_0 values and the porosities and hydraulic permeability, the contact angles were calculated using Eq. (1) through (3).

In addition, the work of adhesion was calculated by

$$W = \gamma_{LG} (1 + \cos \theta) \quad (4)$$

Here, γ_{LG} is the surface tension after contact with the plug, and θ is the receding contact angle. The work of adhesion is here the work necessary to separate a liquid from the solid, resulting in a solid surface in equilibrium with the water vapor at the temperature concerned.⁷

The following trends are noted:

- (1) With ceramic brick, the receding contact angle is significantly smaller than the advancing contact angle. This difference is apparent even in the absence of surfactants. It indicates a heterogeneous character of the surface of the ceramic brick.⁸
- (2) For ceramic brick, the presence of surfactants generally accentuates the contact-angle hysteresis, with the exception of the protein. This indicates that the other surfactants were adsorbed preferentially on part of the phases comprising the ceramic brick surface. This applies especially to CTAB.
- (3) From a comparison of γ before and after contact with the plug, it appears that CTAB is only slightly adsorbed by the brick as a whole. Thus, CTAB is strongly adsorbed on some phases in the brick but not on those forming the greater part of the surface.
- (4) The advancing contact angles are not far from 90° for ceramic brick, independent of the presence of surfactants; but, for sand lime brick the advancing contact angles are even closer to 90°.
- (5) Contact-angle hysteresis is much less pronounced for sand lime brick than for ceramic brick. This is valid both in the absence and in the presence of surfactants. It indicates that the sand lime brick surfaces are more homo-

geneous than those of ceramic brick.

- (6) Surfactants are adsorbed more strongly on sand lime brick than on ceramic brick. This is seen from a comparison of the surface tensions of the liquids before and after contact with sand lime brick.

Conclusions

During water transport through pores in ceramic brick, the surface acts as one composed of different phases. Sand lime brick surfaces behave much more homogeneously.

Surfactants are more strongly adsorbed on sand lime brick than on ceramic brick. In the absence of surfactants, the contact angle is slightly $<90^\circ$.

Acknowledgments

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