Electrostatic and van der Waals Forces in Fibrous Filters

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Organic liquids such as jet fuels which are washed with water during manufacture will often contain an emulsion of water. Similarly water effluents remain stable for long periods of time and must be removed by coalescence in a fibrous bed filter. Photomicrographic studies (Sherony, 1967) of an emulsion passing through a filter have shown that the tiny droplets of dispersed phase in the emulsion must first cling to the fibers before another droplet will coalesce on it. No coalescence of droplets has been observed apart from the fibers. Thus a study of the forces acting to attract or repel the droplet from the fiber will show whether or not the filter will be efficient. Except for the viscous forces due to the moving bulk fluid pulling on the droplet, the only other forces present are the electrostatic double layer and van der Waals forces. We shall consider both of these forces in the situation where surfactants or other adsorbed surface layers are not present in the system.

VAN DER WAALS FORCES

Sherony and Kintner (1971) have attempted to calculate the van der Waals forces for some of the filtration situations studied by Sareen et al. (1966). They used the methods of Hamaker (1937) which are applicable only when the system consists entirely of nonpolar substances. However many-body interactions between polar molecules may contribute a significant amount to the van der Waals forces as much as or even more than the two body forces. Now the theory of Lifshitz (1956) for van der Waals forces in macroscopic systems considered as continua is a very elegant theory which, through the use of measured dielectric data, allows the full calculation of these forces over a wide range of distances even for polar substances. Recently the theory has been much extended and refined, and it is now possible to apply it in a practical way to a wide class of problems. Ninham and Parsegian (1969) consider the use of readily available dielectric data to calculate the van der Waals forces, while Mitchell and Ninham (1972) have extended the theory to the case of interacting spheres. These calculations show that at short distances the force between the spheres is the same as that between two planes, except for an effective area factor readily derived by the pairwise summation methods of Hamaker (1937).

Using this theory and the appropriate dielectric data from the Handbook of Physics and Chemistry (1971), we have computed the energy of van der Waals interactions in each of the systems of fiber and emulsion studied by Sareen et al. (1966). Using the effective area factor of Mitchell and Ninham (1972) we determined the free energy of a droplet fiber system in c.g.s. units when the separation was one intermolecular distance of the field phase liquid. This gave numbers which were comparable with those of Sherony and Kitner (1971) and are given in Table 1. The symbol *A* represents an attractive force while *R* represents a repulsive force. The experimental results contain an extra symbol *Ap* which represents the observation of partial coalescence and implies a weak attractive force acting between the droplet and fiber.

ELECTROSTATIC FORCES

Although the theory of the electrostatic double layer is incomplete and full quantitative agreement with experiments is still lacking, we are able to make several qualitative deductions concerning the electrostatic forces in filters. We firstly make the conjecture that these forces dominated the van der Waals forces in the experiments of Sareen et al. (1966). We support this assumption by the following points.

1. The van der Waals forces, when calculated properly,

Table 1. The Results of Full Numerical Calculations of van der Waals Forces (Ours) Compared with Experiment (Expt.) and the Results of Sherony and Kitner (1971) (S.K.). The Numbers Are Only for Comparison and Indicate Relative Strengths of Forces

	Glass			Polyethylene			Teflon		
	Expt.	S.K.	Ours	Expt.	S.K.	Ours	Expt.	S.K.	Ours
Benzene	*A*	*A*	*A*	*R*	*A*	*A*	*Ap*	*R*	*A*
—water		−3.00	−5.44		−0.92	−4.95		0.17	−4.22
Butyl benzoate	*Ap*	—	*A*	*Ap*	—	*A*	*Ap*	—	*A*
—water			−8.24			−6.26			−5.37
Water	*A*	*R*	*R*	*Ap*	*R*	*A*	*A*	*A*	*A*
—carbon tet		1.94	0.74		0.38	−0.01		−0.42	−0.23
Chloroform	*R*	*A*	*A*	*R*	*A*	*A*	*R*	*R*	*A*
—water		−2.27	−7.54		−0.70	−5.0		0.13	−4.14
Cyclohexanol	*R*	—	*A*	*R*	—	*A*	—	—	*A*
—water			−6.11			−4.68			−4.18
Isobutanol	*R*	*R*	*A*	*R*	*R*	*A*	*R*	*A*	*A*
water		0.41	−5.07		0.13	−3.41		−0.02	−3.06
Water	*A*	*A*	*R*	*Ap*	*A*	*R*	*Ap*	*R*	*R*
—isobutanol		−0.44	0.92		−0.15	0.30		0.07	0.17
Nitrobenzene	*R*	*R*	*A*	*R*	*A*	*A*	*R*	*A*	*A*
—water		4.20	−7.10		−1.30	−5.40		−4.36	−3.92

TABLE 2. COMPARISON OF FULL EXPERIMENTAL RESULTS WITH THEORETICAL RESULTS PREDICTED BY DOUBLE LAYER THEORY. THE PREDICTION IS BASED ON THE ASSUMPTION THAT HYDROXYLIONS ARE PREFERENTIALLY ABSORBED INTO OIL

	Cotton	Dynel	Glass	Poly-ethylene	Teflon	Theory (electrostatic)
Benzene—water	*A*	*R*	*A*	*R*	*Ap*	*R*
Butyl benzoate—water	*A*	*Ap*	*Ap*	*Ap*	*Ap*	*R*
Water—carbon tetrachloride	*A*	*Ap*	*A*	*Ap*	*A*	*A*
Chloroform—water	*Ap*	*R*	*R*	*R*	*R*	*R*
Cyclohexanol—water	*R*	—	*R*	*R*	—	*R*
Isobutanol—water	*R*	*R*	*R*	*R*	*R*	*R*
Water—isobutanol	*A*	*Ap*	*A*	*Ap*	*Ap*	*A*
Water—kerosene	*A*	*Ap*	*A*	*Ap*	*A*	*A*
Nitrobenzene—water	*R*	—	*R*	*R*	*R*	*R*

did not alone agree with the experimental results.

2. The emulsion is stable because the (repulsive) electrostatic forces are dominant over the (attractive) van der Waals forces between identical droplets of the dispersed phase.

3. Heertjes and Lerk (1967) working with colloidal filtration observed that the zeta potential of the colloidal particle and the filter had to be opposite in sign before filtration would indeed occur.

4. Actual calculations based on a mathematical theory of the double layer force derived especially for the fibrous bed filter situation (Sarkies, 1972) have shown that electrostatic forces are indeed dominant at all but very small separations of droplet and fiber in the experiments of Sareen et al. (1966). This theory has so far been developed only for monovalent ions.

Until recently the main interfaces studied by colloid chemists have been the metal/water and silver iodide/water systems because of the simple mechanism by which the surface charge is produced. However, in recent times more complex systems such as the lipid/water (Parsegian and Ninham, 1971) and amphoteric oxide/water (Levine and Smith, 1971, Perram, 1972) have been considered. Here the surface charge arises from ionization of surface groups, and may be determined either from consideration of the mass-action law or from the constancy of electrochemical potential. Glass falls into this latter category, and because of its low point of zero charge (p.z.c.) of 3, will achieve a considerable negative charge in pure water. On the other hand, most plastics have no ionizable groups and being unable to acquire a charge in this way do not act as effective coalescing media.

Considerations of electrochemical potential indicate that a liquid droplet in contact with water gains a nett charge from selective adsorption of ions across the interface (Verwey and Overbeek, 1948). The process is complicated by the presence of structural effects in both phases. However, a simplified picture of the absorption process is given by the Born equation which has been applied with some success in other contexts. According to this, larger ions will be more strongly absorbed into dielectric media. Thus an organic liquid droplet in a water field phase will gain a charge with the same sign as that of the largest ion in the system. If we have water dispersed in an organic phase, the water droplets will acquire the opposite charge.

CONCLUSIONS

Thus the charge on the droplet may be changed by the addition of appropriate electrolyte whose cation and anion have different sizes (Latimer et al., 1939). When no electrolyte is present (that is, when distilled water is used), only protons and hydroxyl ions are present, and these determine the charge on the droplet. These ions are hydrated, and so very little is known about their relative sizes. The ability of, say, protons to form weak bonds with polar groups of organic molecules is a further complication. In this case the Born equation is a very rough rule of thumb at best, and we must proceed in a phenomenological fashion. Thus we cannot state conclusively that the experiments of Sareen et al. (1966) are explained in terms of the properties of the oil/water interface (because these are not known). We can say that if hydroxyl ions are preferentially absorbed into the organic phase, then these results are consistent with this hypothesis.

By supposing that an attraction *A* operates in all cases where coalescence was observed and a repulsion *R* when the emulsion remained unaffected by the filter, then the experimental results can be summarized in Table 2. We can see, apart from the first two entries, that oil droplets dispersed in water are repelled from the fibers while water droplets in oil are attracted. This is consistent with the hypothesis of preferential absorption of hydroxyl ions into the nonaqueous phase and the fiber being negatively charged. Possible mechanisms for the failure of this rule in the first two cases can be given, however. The possibility exists for hydrogen bonding of protons to the ester linkage in butyl benzoate, and hence the possibility exists that these are more strongly absorbed. The effect with benzene might find an explanation in the long range attractive force due to current-current correlations in conjugated double bond systems (Richmond, Davies, and Ninham, 1972). So far no experiments investigating the effects of electrolytes or positively charged fibers have been performed. Several predictions may be made concerning possible future experiments.

1. Addition of any electrolyte will increase the force proportionally to the concentration of electrolyte.

2. When the charges on a droplet and fiber are opposite in sign, and the dielectric constant of the droplet is greater than that of the field phase (for example, water in oil), the attractive electrostatic forces will dominate the repulsive van der Waals forces. The droplet will sit in a position of equilibrium caused by the balance of these two forces and will not necessarily wet the fiber (as observed by Sareen et al., 1966). Viscous forces from the moving bulk liquid may pull the droplet over the force barrier if the velocity is sufficiently large.

3. When the charge on a droplet and fiber are opposite in sign and the dielectric constant of the droplet is less than that of the field phase (for example, oil in water), the electrostatic forces will generally be dominated by the attractive van der Waals forces. The electrostatic forces are weakly attractive at large distances, and repulsive at

short distances. The electrolyte concentration must be carefully controlled to allow the van der Waals forces to have their full effect. Note that in this case the droplets will be able to wet the fibers.

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Convective Diffusion through Wavy Liquid Films in Horizontal Shear Flow

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The hydrodynamics of a liquid film flowing concurrently with an adjacent gas phase are complicated by the shear stress and pressure variations which result from the interactions between the gas and liquid flows. Jeffreys (1925) first analyzed the interaction between wind and waves, and renewed interest in the phenomenon was generated by Miles (1957) and Benjamin (1959). Recent measurements of the air flow characteristics over water waves made by Chang et al. (1971) emphasize the complexity of the interaction and suggest that rigorous analysis is most difficult.

The interfacial waves encountered in gas-liquid flows can significantly affect the transport of heat or mass in the two phases and across the interface, so it is desirable to develop approximate theories of the hydrodynamics to make heat and mass transfer predictions. As indicated by Frisk and Davis (1972) in their heat transfer study with horizontal air-water flow, several investigations of two-phase flow heat or mass transfer have been made—mostly experimental. Most theoretical analyses of the hydrodynamics of film flow have been for the case of zero shear stress at the wavy surface, but Leonard and Estrin (1972) applied an extended Kapitsa approach to describe the film flow for constant interfacial shear, and they applied the result to predict heat transfer through falling liquid films. By an approximate numerical solution of the thermal energy equation, they predicted significant heat transfer enhancement through the film for large amplitude waves distorted from sinusoidal shape, using the dimensionless wave velocity predicted from the Kapitsa analysis ($C = 3$).

Experimental data on waves in horizontal gas-liquid flow obtained by Narasimhan and Davis (1971, 1972) indicate that there are two important differences between falling film flows and horizontal shear flows:

1. The quasi-laminar two-dimensional waves that exist over a narrow range of gas and liquid flow rates for horizontal flow have small wave amplitudes and short wavelengths ($\lambda \approx 1$ cm).
2. The dimensionless wave speed is considerably higher for shear flows than for film flows without interfacial shear.

It is the purpose of this paper to analyze the convective diffusion in wavy film flow with interfacial shear to elucidate the effects of wave velocity and other parameters on heat or mass transport in the liquid film. The analysis of the hydrodynamics follows that by Narasimhan and Davis (1972).

HYDRODYNAMICS

Consider the fully developed wavy flow (no growth or decay of the waves) over a horizontal surface under the influence of pressure gradient ψ and with interfacial shear τ, both considered to be functions of axial distance x. Assume that the velocity profile in the wavy film has the same form as that for smooth film flow except for the fact that ψ, τ, and the film thickness a are functions of x. Then the axial velocity distribution is given by