INTERFACIAL INSTABILITY GENERATED BY CHEMICAL REACTION ON A BRIM MENISCUS OF WETTING

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The phenomenon of interfacial instability on a brim meniscus of wetting generated by chemosorption of carbon dioxide with water solution of a base were studied experimentally using optic interference microscope. Principal steps of evolution of instability were described and their physical explanation was given. The large-scale (i.e. at the scale of experimental cell) vortical flow observed is explained by the draining down the heavier reaction product from the brim meniscus.

INTRODUCTION

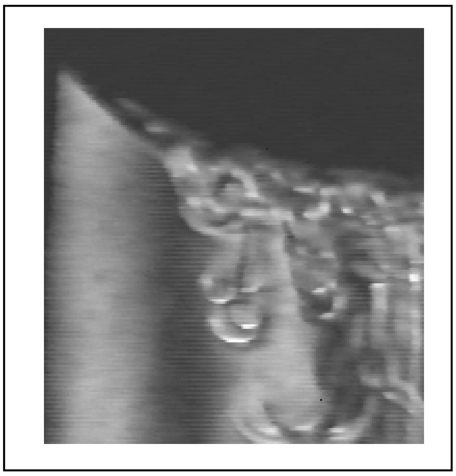
The interfacial instability generated near the gas-liquid or liquid-liquid interface results in the appearance of convective flows which increase significantly mass and heat transfer across the interface[1]. In addition, the convective flows may be considered as an example of dissipative structures in open systems. As a rule, the physical reasons for the appearance of hydrodynamic instability at the interface are local gradients of surface tension and/or the density stratification of the liquid due to gravitation. Under certain conditions, a chemical reaction between substances located in contacting phases also can give rise to such instability[2].

The conditions for the generation and evolution of interfacial instability as well as characteristics of convective flows on a flat interface have been widely studied, see, e.g.[3]. However, the conditions for the instability at a non-flat surface are considerably different, some new effects take place due to the concurrent action of gravitation and capillary forces. Because usually liquid wets solid surfaces, from the practical point of view it seems important to study the effect of interface curvature at the brim meniscus of wetting on the conditions of generation and evolution of interfacial instability caused by chemical reaction.

RESULTS AND DISCUSSION

The use of a polarizing interference microscope gives the possibility to inspect at the real time-scale the evolution of interfacial instability in a liquid on a brim meniscus of wetting near the interface CO_2 - water solution of a base, when chemosorption of the gas into the liquid occurs[4]. Our observations have shown that there are several principal steps in the evolution of such instability. At first, the instability appears only some time after the reacting phases are brought in contact. This is apparently related to the fact that chemical reaction and the accumulation of its product near the interface are limited by the diffusion of carbon dioxide into the base solution. The diffusion boundary layer is extremely thin and cannot be observed even with a high magnification. It is found that the time delay varies from 0.1 to several seconds and is defined by chemical nature of the base. For the same base it decreases with increasing base concentration in the water solution.

The appearance of instability is observed as reciprocating tangential motion of the liquid in a thin layer adjacent to the surface. The appearance of instability during this time interval may be explained by the presence of local gradients of surface tension at the interface. The appearance of low-scale motions of the liquid give rise to convective mechanism of mass transfer through the interface and a faster accumulation of the reaction product in the near-surface layer. Further, a boundary layer containing of the reaction product which is heavier than surrounding liquid develops near the interface. The layer converts with time into the system of droplets of increasing size. At a definite size, the droplets break away from the surface and begin to precipitate to the cell bottom. Due to gravitation, the heavy product seems to drain down along the meniscus as a film of increasing width. Later, this film transforms into droplet which detaches from the surface. The velocity of the droplet has both vertical and horizontal components. The precipitating droplets practically do not mix with surrounding liquid in spite that the reaction product is soluble in the liquid. It is found that the average size of droplets is defined only by the chemical nature of the base. The characteristic flow formed during the chemosorption near the brim meniscus of wetting is shown in the Figure.



The results of linear analysis of hydrodynamic stability of interface shows that critical conditions for the formation of convective flows can be reached by an increase of the width of diffusion boundary layer d. The forces leading to instability increase proportionally d (capillary forces) and to d^3 (forces of density stratification). Consequently, it is more probable that the instability at the brim meniscus of wetting arises first due to capillary mechanism. The characteristic sizes of modes which lose their stability correspond to the sizes of droplets formed near the interface.

The next, observed experimentally step of the evolution of instability is the extension of the front of precipitating heavy droplets inside the surrounding liquid. The velocity of the front extension depends on the chemical nature of the base and increases with its concentration. The front surface loses its stability at a scale of several droplets. Thus, the results of inspection of the front of precipitating droplets indicate that there exist at least two mechanisms of instability, namely, chemocapillarity and chemogravitation.

At the final step of instability evolution, due to the presence of horizontal component of the droplet velocity, two convective vortices , are formed at the scale of the whole cell. The liquid in these vortices moves from the cell walls to its centre. The velocity depends on the physico-chemical properties of the liquid and the base concentration. In a separate experiment, in the absence of brim meniscus of wetting when all the interface remain flat, no large-scale vortical flow was observed.

The work is supported by the Russian Fund of Basic Research (projects № 00-03-32055, 02-02-16294).

CONCLUSIONS

It was found experimentally that the interfacial instability during the chemosorption appears due to capillary effects and it develops only due to the accumulation of heavy reaction product near the interface according to the Rayleigh-Taylor mechanism.

The generation of a large-scale convection is caused by the brim meniscus of wetting, along which heavy reaction product drains down thus forming flows directed from the cell walls to its centre.

REFERENCES

1. Kaminsky, V.A., Vyazmin, A.V., Kulov, N.N. and Dilman, V.V., Marangoni Effect in the Presence of Bulk Turbulence, *Chem. Eng. Sci.*, Vol. 53, No. 19, pp 3347-3353, 1998.
2. Buyevich, Yu.A., Rabinovich, L.M. and Vyazmin, A.V., Chemo-Marangoni Convection. I. Linear Analysis and Criteria of Instability, *J. Coll. Int. Sci.*, Vol. 157, pp 202-210, 1993.
3. Imaishi, N. and Fujinava, K., An Optical Study of Interfacial Turbulence Accompanying Chemical Absorption, *Int. Chem. Eng.*, Vol. 290, No. 2, pp 226-232, 1980.
4. Karlov, S.P., Kazenin, D.A. and Vyazmin, A.V., The Time Evolution of Chemo-Gravitational Convection on a Brim Meniscus of Wetting, *Phys. A*, Vol. 315, No. 1-4, pp 307-313, 2002.