Submitted to Chemical Engineering Science

LBL-608
Preprint c.1

MARANGONI STABILIZATION OF DENSITY-DRIVEN CONVECTION

Ian F. Davenport and C. Judson King

January 1972

AEC Contract No. W-7405-eng-48

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA

For Reference

Not to be taken from this room

LBL-608 c.1

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

0 0 0 0 3 7 0 0 9 5 9

LBL-608

MARANGONI STABILIZATION OF DENSITY-DRIVEN CONVECTION

Ian F. Davenport and C. Judson King

Department of Chemical Engineering
Lawrence Berkeley Laboratory
University of California
Berkeley, California 97472

January 1972

MARANGONI STABILIZATION OF DENSITY-DRIVEN CONVECTION*

Surface tension data have been obtained for dilute sulfurous acid solutions. These lead to the conclusion that Marangoni (surface-tension gradient) effects, rather than the rigidity of a contaminated aqueous surface, were the cause of stabilization in a recently published report on density-driven convection.

Mahler and Schechter (7) reported conditions for the onset of convection during the absorption of sulfur dioxide into water. Absorption was initiated by suddenly increasing the partial pressure of sulfur dioxide above the water by 6 in. Hg. Once equilibrium had been obtained, the experiment was rerun by increasing the partial pressure as before. In this manner the sulfur dioxide concentration in the bulk aqueous phase at the start of absorption was increased stepwise from zero to that corresponding to equilibrium with 30 in. Hg partial pressure of sulfur dioxide in the vapor.

The convection which was observed some time later had been previously identified as density-driven by Blair and Quinn (2). Those authors had worked with a contaminated aqueous surface which acted as a rigid boundary and suppressed any Marangoni effects upon the motion. Mahler and Schechter (7) extended the work of Blair and Quinn by investigating surfaces

*Work performed under the auspices of the U. S. Atomic Energy Commission.

with and without surface active agents. They found that insoluble surfactant films acted like a rigid surface, while soluble surfactants acted like a semi-rigid surface. When the initial concentration of sulfur dioxide in the bulk liquid was greater than that corresponding to equilibrium with 6 in. Hg partial pressure of sulfur dioxide in the vapor, results in the absence of added surfactants were described by predictions for a free surface. However, when there was no sulfur dioxide initially in solution, the critical Rayleigh number (Ra_c) corresponding to the density-driven convection initiation was midway between free surface (Ra_c = 100) and rigid surface (Ra_c = 300) predictions. Analysis of these results led Mahler and Schechter to the conclusion that the "pure" water surface was contaminated and had more rigidity than the sulfurous acid surface which by comparison was not contaminated.

Marangoni effects in this system, if present, could tend to stabilize the unstable density profile and increase the observed critical Rayleigh number, as long as the liquid surface tension decreases with increasing sulfur dioxide content. This is because the convection will bring bulk liquid to the surface and increase the surface tension locally where the bulk liquid arrives. From thermodynamic considerations, systems will move or, in this case, resist motion so as to lower the total surface energy.

Submitted as a Shorter Communication to Chemical Engineering Science.

Surface tension versus composition data for sulfurous acid were measured in our laboratories using a duNouy ring tensiometer. The results are shown in Fig. 1. A special apparatus was designed to enclose the sulfur dioxide vapor so that it was in equilibrium with the aqueous phase. A close-fitting hole in the lid above the vapor permitted the tensiometer ring support to move freely, while limiting the escape of sulfur dioxide gas. The measurements were very sensitive to the cleanliness of the apparatus and solution. When the apparatus had been cleaned many times and the equilibration time was only a few minutes before the measurement, the results were higher than those with the vessel cleansed once and an equilibration time of half an hour. The surface tension measurements for the "clean" system agree well with that determined by the jet method (5). The difference in surface tension between the clean and aged surfaces can be attributed to contamination of the aqueous system which was probably brought about by self-soiling (2). The sulfur dioxide content in the aqueous solution was determined by a standard titration method (9).

Mahler and Schechter reported that the measured surface tension of sulfurous acid solution in equilibrium with 6 in. Hg partial pressure of sulfur dioxide in their experiments was 61 dyne/cm (7). This is below the value of 70.4 dyne/cm found in the present work for a clean surface, but comparable to our aged surface results. From the run descriptions given by Mahler and Schechter, their sulfurous acid surfaces appear to be aged and therefore

contaminated. Burger (4), working with the same experiment, concurs with this conclusion. However, absorption into initially pure water was probably performed with a clean system in the work of Mahler and Schechter, as indicated by the small time required for water to equilibrate and by the reported measured surface tension (71.2 dyne/cm). For this reason we assume that Marangoni stabilizing forces in the experiments of Mahler and Schechter were influential only for absorption into initially pure water. This is because the rigidity of the contaminated surface precludes the rapid renewal of the actual surface elements.

The effect of surface tension stabilization can be measured by the time-dependent Marangoni number (M). A stabilizing surface tension effect has a negative sign and a destabilizing effect has a positive sign. The Marangoni number at the onset of convection in the experiments of Mahler and Schechter for absorption into initially pure water, calculated from the "clean" curve in Fig. 1 and the critical conditions reported by Mahler and Schechter, is -1.6×10^5. Nield (8) has predicted the combined effect of surface-tension-gradient and density-gradient forces on the onset of convection for a linear composition or temperature profile in the fluid. The prediction that the normalized Rayleigh and Marangoni numbers at the critical conditions for instability are approximately additive has been partially verified by Berg and Palmer (1). A similar theory for time-dependent profiles has not yet been

published, but for the present analysis Nield's predictions may serve as a guideline.

When the Marangoni number was -1.6×10^5 for pure water in the bulk liquid, the critical Rayleigh number found by Mahler and Schechter was almost double that for the case of the sulfurous acid solutions where we presume Marangoni effects were not significant. If the critical Rayleigh number in the presence of the Marangoni stabilizing effect is double the critical Ralleigh number found in the absence of this effect, then the guideline given by Nield indicates that the stabilizing Marangoni effect is characterized by a Marangoni number equal to the negative of the critical Marangoni number (M_c) which is observed when convection results form Marangoni-driven instability alone. Since the Marangoni number for the stabilized density-driven situation is -1.6×10^5, the corresponding critical Marangoni number in the absence of a density gradient should then be $+1.6\times10^5$. This value agrees favorably with the values of the density-gradient-free critical Marangoni numbers observed by Clark and King (6), and by Brian, Vivian and Mayr (3), if the shape of the time-dependent surface concentration change is taken into account for the various studies.

Ian F. Davenport
C. Judson King

Department of Chemical Engineering,
and Lawrence Berkeley Laboratory,
University of California
Berkeley, California 97472 U.S.A.

ACKNOWLEDGEMENTS

James F. Lam assisted with the surface tension measurements.

This work was performed in the Lawrence Berkeley Laboratory under the auspices of the U.S. Atomic Energy Commission.

NOTATION

D = Liquid phase diffusivity

g = Acceleration due to gravity

M = Time-dependent Marangoni number = $(\sigma_i - \sigma_B)t^{1/2}/ D^{1/2}\mu$

R = Time-dependent Rayleigh number = $g(\rho_i - \rho_B)D^{1/2}t^{3/2}/\mu$

σ_i = Surface tension of solution at gas-liquid interface

σ_B = Surface tension of bulk solution if brought to surface

ρ_i = Liquid density at gas-liquid interface

ρ_B = Liquid density at bulk liquid composition

μ = Liquid viscosity

Subscript

c = Critical value at incipient instability

References

(1) J. C. BERG and D. E. PALMER, J. Fluid Mech. 1971 47.

(2) L. M. BLAIR and J. A. QUINN, J. Fluid Mech. 1969 36 385.

(3) P. L. BRIAN, J. E. VIVIAN and S. T. MAYR, Ind. Eng. Chem. Fund. 1971 10 75.

(4) E. D. BURGER, Ph.D. Dissertation, Univ. of Illinois, Urbana (1970).

(5) B. W. BUSSEY, Ph.D. Dissertation, Univ. of Delaware, Newark (1966).

(6) M. W. CLARK and C. J. KING, AIChE Jour. 1970 16 74.

(7) E. G. MAHLER and R. S. SCHECHTER, Chem. Eng. Sci. 1970 25 955.

(8) D. A. NIELD, J. Fluid Mech. 1964 19 341.

(9) F. P. TREADWELL and W. T. HALL, "Analytical Chemistry," John Wiley and Sons, Inc., New York (1942).

(10) R. H. PERRY et al., eds., "Chemical Engineers' Handbook," 4th ed., McGraw-Hill Book Co., Inc., New York (1963).

Fig. 1. Surface Tensions of Dilute Aqueous Sulfurous Acid Solutions.

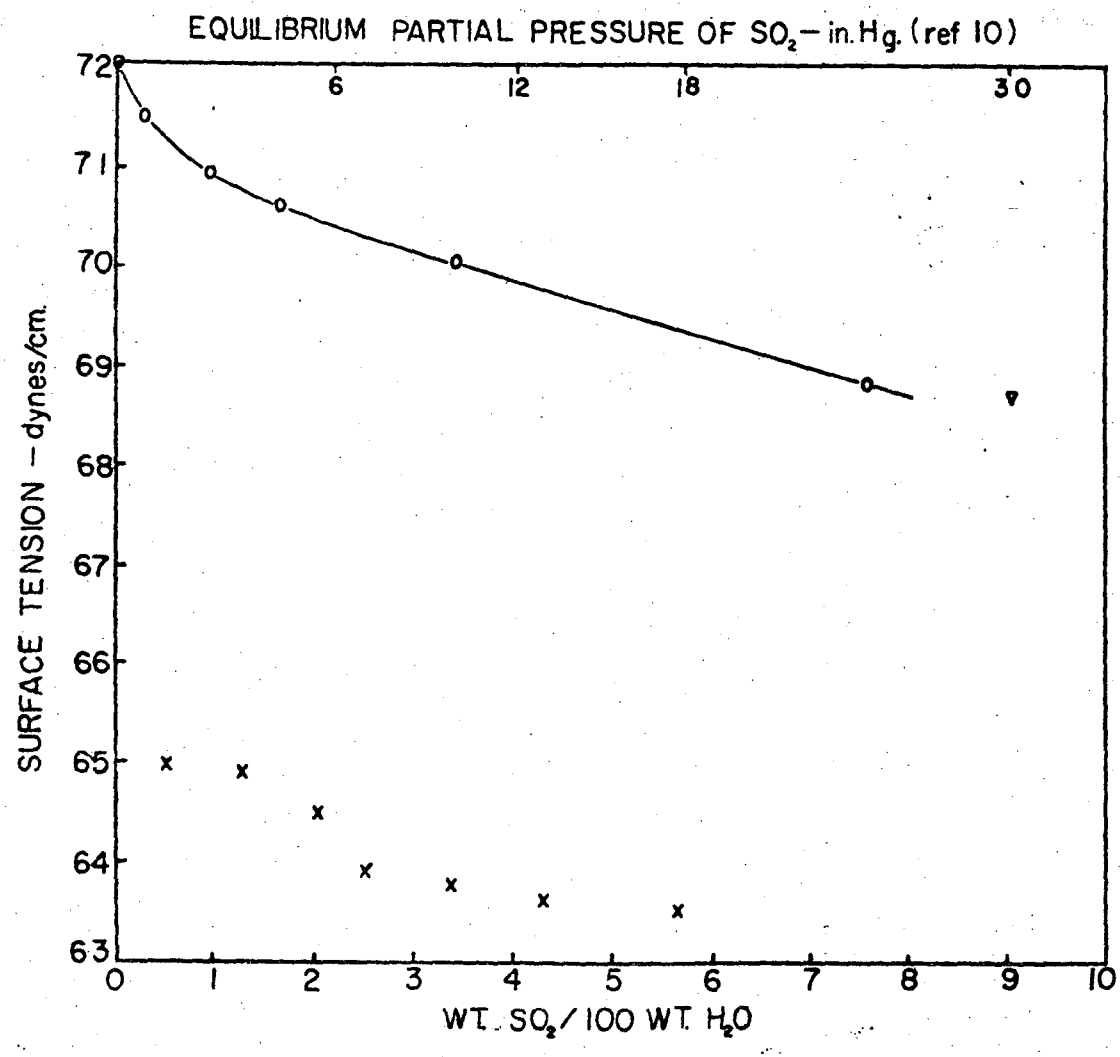
DuNouy Tensiometer (present work)

o - Clean Surface - equilibration time of approximately 5 minutes

× - Aged Surface - equilibration time of approximately 30 minutes

Laminar Jet Method

∇ - Bussey (4)


EQUILIBRIUM PARTIAL PRESSURE OF SO_2 – in. Hg. (ref 10)
6
12
18
30
72
71
70
69
68
67
66
65
64
63
SURFACE TENSION – dynes/cm.
0
1
2
3
4
5
6
7
8
9
10
WT. SO_2 / 100 WT. H_2O

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720