

par (1) et ceux fournis par théorie[3]; il fournit le nombre de transitions ainsi que leur température et leur enthalpie (Tableau 2). Il a ainsi été possible de déceler de nouvelles transitions dans les paraffines étudiées et d'estimer les températures et chaleurs de transitions.

Il est à noter que Broadhurst signale pour le nC_{36} une seconde transition, proche de la première. En tenant compte de ce fait, la variation du coefficient d'activité du nC_{36} en solution dans le Benzène, le long de la courbe d'équilibre, ne présente pas un minimum prononcé comme dans le cas du système tétracosane Benzène. Cependant les écarts entre les valeurs théoriques et les valeurs expérimentales semblent indiquer la présence d'une troisième transition que l'on peut calculer. Ces nouveaux faits expérimentaux sont en partie confirmés par les études de Mazee[8] et Templin[9] sur les paraffines solides.

CONCLUSION

Nous présentons un appareil de calorimétrie différentielle adapté à la détermination des températures de cristallisation de systèmes d'hydrocarbures. Les diagrammes de sol-

ubilité de paraffines lourdes dans les aromatiques ont été établis et leurs coefficients d'activité calculés. La comparaison faite sur la Fig. 4 avec une étude théorique des grandeurs d'excès montre que l'on doit tenir compte d'une nouvelle transition. De plus, il est possible, par une méthode numérique, d'estimer l'enthalpie de fusion et la température d'apparition de la phase solide stable dans le domaine considéré. Ces résultats sont particulièrement importants pour la détermination expérimentale des coefficients d'activité des paraffines lourdes dans des solvants polaires que ne sont pas, jusqu'à présent, calculables théoriquement.

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BIBLIOGRAPHIE

- [1] TIMMERMANS, *Physico Chemical Constants of Binary Systems*, Vol. 1. Interscience, New York 1959.
- [2] ANDREWS D. H., KOHMAN G. T. et JOHNSTON J., *J. phys. Chem.* 1925 **29** 914.
- [3] COMPANYY J. C., Thèse Université de Lyon 1972.
- [4] HILDEBRAND J. H. et WACHTER A., *J. phys. Chem.* 1949 **53** 886.
- [5] BROADHURST M. G., *J. Res. Natn. Bur. Stand.* 1962 **66A** 3 241.
- [6] ATKINSON M. L. et RICHARDSON M. J., *Trans Faraday Soc.* 1969 **5** 1749.
- [7] ATKINSON M. L., LARKIN J. A. et RICHARDSON M. J., *J. Chem. Therm.* 1969 **1** 435.
- [8] MAZEE W. H., *Rec. Trav. Chim.* 1956 **67** 197.
- [9] TEMPLIN P. R., *Ind. Engng Chem.* 1956 **48** 154.

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Surface ages in vibrating-jet experiments

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INTRODUCTION

DYNAMIC surface tensions are often measured by observing the oscillations of a jet of surfactant solution emerging from an elliptical orifice[1-3]. Because the fluid surface speed u increases gradually from zero at the orifice towards the mean jet velocity u_m , the time required for an element of surface to reach a distance z downstream is not simply z/u_m , as Defay and Hommelen[1] seem to have supposed. Hansen[4] suggested that an 'average surface age' $\bar{t} = z/u$ was a more appropriate measure of the time.

The question of appropriateness arises because one wishes to exploit the analogy between (1) the steady jet flow, in which the surface excess of surfactant is a function of position, and (2) the hydrodynamically simpler problem of adsorption on a fresh surface instantaneously created on a

liquid which thereafter is at rest, so that the surface excess is a function of time. The best measure of the time in the first case is whatever function of position corresponds to elapsed time in the second case.

It is the purpose of this note to show that Hansen's \bar{t} is approximately correct if the rate of surface aging is limited by adsorption kinetics as assumed by Tsonopoulos *et al.*[5], but that if diffusion to the surface is rate-limiting then a better measure of the time is

$$T = \frac{1}{u^2} \int_0^z u(z') dz'. \quad (1)$$

In both cases we assume that the surface tension takes much longer to reach its equilibrium value than the jet does to

reach an effectively uniform velocity profile. Unless this condition is fulfilled, any results for dynamic surface tension will be suspect: no adequate theory of waves on jets with non-uniform velocity profiles yet exists. Similar difficulties with diffusion force us to ignore deviations from axial symmetry.

ADSORPTION-LIMITED SURFACE AGING

For first-order adsorption kinetics, the boundary condition on a surface at rest is [5]

$$\frac{\partial \Gamma}{\partial t} = \ell \left(c_0 - \frac{\Gamma}{h} \right), \quad (2)$$

where ℓ is the rate constant, c_0 the subsurface concentration, Γ the surface excess and h the (constant) equilibrium value of Γ/c_0 . On a moving jet surface, Eq. (2) must be replaced, according to Levich's [6] Eqs. (73.7) and (74.1), by

$$\frac{1}{a} \frac{\partial}{\partial z} (\Gamma u a) = \ell \left(c_0 - \frac{\Gamma}{h} \right), \quad (3)$$

where a is the jet radius. In the region near the orifice where u is varying appreciably, our assumption that the surface has barely begun its approach to chemical equilibrium with the liquid implies that c_0 is close to c_∞ , the concentration far from the surface, and that $\Gamma \ll hc_0$. If so, $\Gamma = \ell c_\infty t$ to a first approximation from Eq. (2), or from Eq. (26) of [5], while $\Gamma = \ell c_\infty z/u$ from Eq. (3) if we ignore variations in a , which are usually much less important than those in u . Hence the apparent surface age is $\bar{t} = z/u$ in this case. The same result holds for any adsorption law which makes the surfactant flux into the surface a continuous function of c_0 and Γ . $R(c_0, \Gamma)$ say, because the right-hand sides of Eqs. (2) and (3) are both then approximately $R(c_\infty, 0)$.

DIFFUSION-LIMITED SURFACE AGING

For the initial stages of diffusion-limited adsorption, the relevant condition on a plane surface at rest is

$$h \frac{\partial c}{\partial t} = \frac{\partial \Gamma}{\partial t} = D \frac{\partial c}{\partial r}, \quad (4)$$

where c obeys the diffusion equation

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial r^2}, \quad (5)$$

D being the diffusivity and r the distance measured perpendicularly from the surface into the solution. At sufficiently small times, $c \ll c_\infty$ at the surface and so we have the well-known results [7] that $c = c_\infty \operatorname{erf} \left\{ \frac{1}{2} r (Dt)^{-1/2} \right\}$, and

$$\Gamma = 2c_\infty (Dt/\pi)^{1/2}, \quad (6)$$

to leading order.

Near a moving surface c will differ from c_∞ only in a thin diffusion boundary layer if u differs significantly from u_m , because the kinematic viscosity $\nu \gg D$ in all ordinary fluids likely to be used in the experiments. Because the curvature of the jet surface is negligible on the scale of the diffusion-layer thickness, the methods of Levich [6], Section 72, enable us to write the equations corresponding to (4) and (5) on

the surface and in the diffusion layer as

$$\frac{\partial}{\partial x} (\Gamma u a) = D \frac{\partial c}{\partial \psi}, \quad (7)$$

$$\frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial \psi^2}, \quad (8)$$

where x and ψ are determined by u and a as

$$x = \int_0^z a^2 u \, dz', \quad (9)$$

$$\psi = r a u. \quad (10)$$

To a sufficient approximation, ψ is the stream function of the fluid motion. With $c_\infty \gg \Gamma/h = c$ at the surface as before, $\partial c/\partial \psi = c_\infty/(\pi D x)^{1/2}$ there from Eq. (8), and so Eq. (7) gives

$$\Gamma = \frac{2c_\infty \left\{ D \int_0^z a^2 u \, dz' \right\}^{1/2}}{\pi^{1/2} a u}. \quad (11)$$

On neglecting variations of a as before, and identifying Eqs. (6) and (11), we obtain Eq. (1) for the apparent age T .

At large distances downstream where $u \rightarrow u_m$, $\bar{t} \rightarrow z/u_m$, and $\bar{t} - T$ tends to a positive constant. Consequently a diffusion-limited surfactant then behaves as if the surface were a constant amount younger than z/u_m , but an adsorption-limited surfactant reveals its true age. For a jet emerging from a capillary tube long enough for the Poiseuille parabolic velocity distribution to be developed, we find $\bar{t} - T = 0.03 a^2/\nu$ from the approximate theory of Hansen *et al.* [2], i.e. about a msec for a jet of dilute aqueous solution 0.02 mm in radius.

CONCLUSIONS

The error in Defay and Hommelen's [1] surface ages is of the right sign to reduce the discrepancy between their experimental results and the theory of Tsouopoulos *et al.* [5], but does not by itself alter the latter authors' conclusion that the experiments are inconsistent with diffusion-limited adsorption. But if the surface tension as measured after 5 msec were 2 mN m⁻¹ too high, the inconsistency would disappear. Because Defay and P  tr   [8] have shown that errors of that type and nearly that amount existed (2 mN m⁻¹ after 3 msec in a typical example), it seems that the evidence for slow adsorption from those experiments with hexanol is not conclusive. It would be preferable to use the orifice-plate technique of Caskey and Barlage [3], which minimizes velocity variations in the jet.

With decanol, which takes seconds instead of milliseconds to reach a surface equilibrium, the hydrodynamical effects are probably negligible, but evaporation can simulate slow adsorption [8]. Graves *et al.* [9], who worked with the non-volatile surfactant 'Tween 20', found the surface pressure and hence surface excess initially proportional to $t^{1/2}$, as expected for rate-limiting diffusion, rather than t as expected for rate-limiting adsorption.

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NOTATION

a jet radius
c surfactant concentration in liquid
*c*₀ value of *c* adjacent to the surface
*c*_∞ value of *c* far from the surface
D surfactant diffusivity
h equilibrium value of Γ/c_0 (assumed constant)
 ℓ adsorption rate constant
r distance from surface
t time since fluid element left orifice
 \bar{t} z/u
T apparent surface age defined by Eq. (1)

u jet surface velocity
*u*_m mean jet velocity
x streamwise variable for diffusion boundary layer, defined by Eq. (9)
z distance from orifice measured along jet surface
z' dummy variable of integration

Greek symbols

Γ surface excess of surfactant
 ν kinematic viscosity of liquid
 ψ transverse variable for diffusion boundary layer, defined by Eq. (10)

REFERENCES

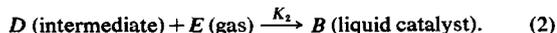
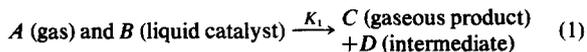
- [1] DEFAY R. and HOMMELEN J., *J. Colloid Sci.* 1958 **13** 553.
- [2] HANSEN R. S., PURCHASE M. E., WALLACE T. C. and WOODY R. W., *J. phys. Chem.* 1958 **62** 210.
- [3] CASKEY J. A. and BARLAGE, JR. W. B., *J. Colloid Interface Sci.* 1971 **35** 46.
- [4] HANSEN R. S., *J. phys. Chem.* 1964 **68** 2012.
- [5] TSONOPOULOS C., NEWMAN J. and PRAUSNITZ J. M., *Chem. Engng Sci.* 1971 **26** 817.
- [6] LEVICH V. G., *Physicochemical Hydrodynamics*. Prentice-Hall, Englewood Cliffs, N.J. 1962.
- [7] WARD A. F. H. and TORDAI L., *J. chem. Phys.* 1946 **14** 453.
- [8] DEFAY R. and PÉTRÉ G., *J. Colloid Sci.* 1962 **17** 565.
- [9] GRAVES D. J., MERRILL E. W., SMITH K. A. and GILLILAND E. R., *J. Colloid Interface Sci.* 1971 **37** 303.

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Effectiveness factors and transient behavior in gas-liquid catalyst systems

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IN A NUMBER of industrially important reactions, such as reduction, oxidation and carbonylation, reactors are employed in which two gaseous reactants are absorbed into a solution containing a dissolved involatile catalyst and react to give a product which may be a gas, or so highly volatile that the product desorbs as a gas or vapour from the catalyst solution. Some insight into the behavior of such systems and in particular the possible importance of mass transfer effects can be gained by considering the following relatively simple reaction scheme.



Here *B* and *D* are two forms of the catalyst, which in a redox process would be different valency states of a transition metal ion, or alternatively they could represent unstable complexes of the dissolved catalyst with the reactants *A* and *E*.

An interesting feature of this problem is that it may be appropriately considered in terms of the concepts and nomenclature of "gas absorption with reaction" or of effectiveness factors in porous heterogeneous catalysts, depending on the type of reactor and the magnitude of the reaction para-

meters. Rony[4] has discussed the effectiveness factor for a liquid catalyst film deposited on a porous support under steady state conditions with a first order reaction. Here we describe results for the more general catalytic reaction scheme of Eqs. (1) and (2) which provides a simple model for a number of catalytic reactions and in particular the oxidation of sulphur dioxide[2, 6] and hydrogen chloride[3] over molten salt catalysts. The calculations also give some indication of the time required to reach steady state conditions: This is negligibly short in most gas-solid catalytic reactions but might assume importance in liquid catalyst films because of the low values of diffusion coefficients in liquids.

For the above reaction scheme the relevant penetration theory equations are:

$$\frac{\partial C_A}{\partial t} = D \frac{\partial^2 C_A}{\partial y^2} - K_1 C_A C_B \quad (3)$$

$$\frac{\partial C_B}{\partial t} = D \frac{\partial^2 C_B}{\partial y^2} - K_1 C_A C_B + K_2 (C_{B0} - C_B) C_E \quad (4)$$

$$\frac{\partial C_C}{\partial t} = D \frac{\partial^2 C_C}{\partial y^2} + K_1 C_A C_B \quad (5)$$

$$\frac{\partial C_E}{\partial t} = D \frac{\partial^2 C_E}{\partial y^2} - K_2 (C_{B0} - C_B) C_E \quad (6)$$