

C_{AL} = concentration of A in liquid bulk
 C_B = concentration of the intermediate B
 C_B^* = concentration of B in liquid for it to be in equilibrium with the gas phase
 C_{BL} = concentration of B in liquid bulk
 D = D_B/D_A , diffusivity ratio
 D_A = diffusivity of A in liquid phase
 D_B = diffusivity of B in liquid phase
 H_B = Henry's Law constant for B
 K = k_2/k_1 , rate constant ratio
 k_1 = first-order rate constant in the first step reaction
 k_2 = first-order rate constant in the second step reaction
 k_{GB} = gas side mass transfer coefficient of B for physical absorption
 k_L = liquid side mass transfer coefficient of A for physical absorption
 L = average thickness of a liquid element or film
 M = $k_1 D_A / k_L^2$, dimensionless group
 m_1 = dimensionless group defined by Equation (8)
 m_2 = dimensionless group defined by Equation (9)
 \bar{N}_A = average chemical absorption rate of A
 \bar{N}_B = average chemical absorption rate of B
 s = surface renewal rate
 t = time
 x = distance

Y = $-\bar{N}_B/\bar{N}_A$, yield of the intermediate B in a heterogeneous system
 α = dimensionless group defined by Equation (10)
 β = dimensionless group defined by Equation (11)

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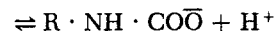
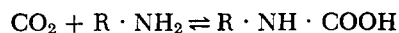
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Measurement of Interfacial Tension During the Absorption of Carbon Dioxide into Monoethanolamine-Water Mixtures Using an Oscillating Jet

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The origin of interfacial turbulence and spontaneous agitation of the interface between two unequilibrated liquids has been explained by Sterlmg and Scriven (1959) in terms of the Marangoni effect, wherein movement in an interface is caused by longitudinal variations of interfacial tension. They proposed that interfacial turbulence was a manifestation of hydrodynamic instability caused by small random fluctuations about the interface. By desorbing an inert tracer propylene simultaneously with the absorption of carbon dioxide into monoethanolamine (MEA) in a short wetted-wall column, Brian et al. (1967) showed that the physical mass transfer coefficient was increased substantially over that predicted by the Penetration theory and attributed this increase to interfacial turbulence driven by surface tension gradients. Thomas (1966) studied the absorption of carbon dioxide into aqueous MEA in a laminar jet and showed that the reaction of importance for short exposure times was that in which the carbamate is formed:



Later, with Mck. Nicholl (1969), the interfacial turbulence produced by this reaction was examined using an optical method, with a wavefront shearing interferometer, where it was shown in a stagnant pool of 2.5 M. MEA that a minimum time of 4.5 seconds elapsed before turbulence occurred. Danckwerts and Silva (1967) have investigated the surface instability produced during the absorption of carbon dioxide by MEA solutions by measuring the surface tension of the reacting amine solution using an oscillating jet. No increase in surface tension was observed, although an increase was recorded using static measurements and this increase was attributed to the ionic nature of the reaction products. Ruckenstein (1970) has qualitatively shown, using a roll-cell model, that a small-scale turbulence of small intensity due to Marangoni instability leads to a large increase in the rate of mass transfer of the same order of magnitude as that reported by Brian et al. (1967). In a subsequent

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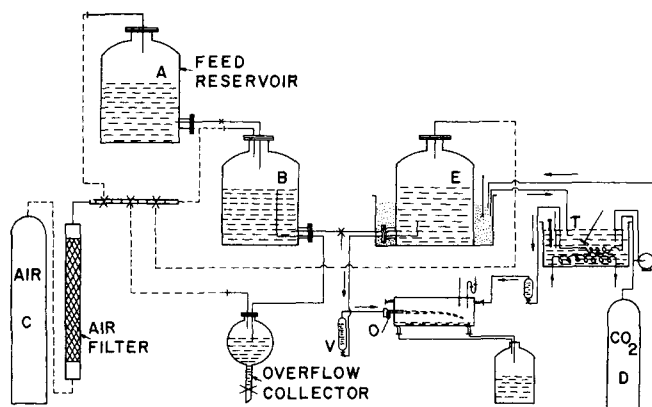


Fig. 1. Schematic diagram of apparatus.

paper Ruckenstein and Berbente (1964) have given an analytical expression for the hydrodynamic structures generated by turbulence by means of roll-cells propagating in the main direction of motion with the average velocity of the liquid. Miller and Scriven (1970) have studied the effect of electrical double layers on interfacial stability of low tension fluid interfaces and have shown that a plane interface with a diffuse layer becomes unstable to small amplitude, long wavelength disturbances when the total interfacial tension approaches zero. When the interfacial tension is zero, the interface remains stable with respect to short wavelength disturbances. Recently Mahler and Schechter (1970) have studied the stability of fluid layer subjected to nonlinear time-dependent adverse density gradients and concluded that the absolute value of surface tension is not a significant factor in determining the stability of a buoyancy-driven flow.

An analysis of these investigations shows that the increased mass transfer encountered with the MEA-CO₂ system has been attributed to interfacial turbulence, and that the conflicting absorption data presented by different workers were the result of the intensity of interfacial turbulence varying from one experimental system to another. However, the quantitative contributions that the surface tension and density gradients play to produce the turbulence is not known, and this experiment was set up primarily to investigate the changes in interfacial tension occurring during this absorption process as a first step to the solution of this problem.

EXPERIMENT

A schematic diagram of the flow system is given in Figure 1. The reservoir A containing the aqueous MEA provided a constant flow to the elliptical capillary orifice O. Vessel E damped the pressure oscillations created by the overflow in B. The flow rate from the orifice was regulated by varying the air pressure from the cylinder C or by adjusting the valve V in the line ahead of the nozzle. The constant temperature bath allowed both the liquid and the gas temperatures to be maintained at $25 \pm 0.5^\circ\text{C}$. Carbon dioxide flowed continuously from the cylinder D through the absorbing cell via the temperature bath at a velocity sufficiently low as to prevent gas drag whilst avoiding inert build-up in the cell.

The glass orifices were made by the method described by Addison (1943). The wavelength and the maximum and minimum diameters of the emerging jet were measured photographically. The method adopted to measure the wavelength was that developed by Stocker (1920). In brief, the jet was illuminated with a parallel beam of light. Each wave of the jet acts as a cylindrical lens which produces well defined line images which were recorded on a 4×5 inch photographic sheet film. The wavelengths were measured directly from the negatives with the Grant Series 400 Measuring Comparator. Similarly, the amplitudes were measured photographically.

Difficulty was experienced in obtaining good illumination of the jet, the main problem being caused by reflections from the inner surface of the walls of the jet cell, and which was partially overcome by painting the outside of the container dull black except for small windows for the passage of light. The experimental procedure has been described in greater details by Vijayan (1971).

To calibrate the apparatus, the oscillating jet was used to measure the surface tensions of the pure liquids benzene, carbon tetrachloride, methanol, iso-propanol, and water at 20°C . It was shown for a jet exposure time greater than 6 milliseconds that the results obtained were within 0.5 dynes per cm of the values measured using a Du Noüy ring tensiometer. The jet determinations were repeated with aqueous MEA solutions of concentrations ranging from 0.1 M to 2.03 M at 25°C . in both an air and a carbon dioxide environment.

The surface tensions were calculated using the simplified Bohr (1908-09) equation.

$$\frac{4(\delta + \rho)(W/\rho t) \left| 1 + \frac{37}{24} \left(\frac{b}{a} \right)^2 \right| \psi}{\left(6a\lambda^2 + 10\pi^2 a^3 + \frac{2.5\pi^4 a^5}{\lambda^2} \right)} \quad (1)$$

DISCUSSION

In Figure 2 values of interfacial tensions are presented for aqueous MEA concentrations of 0.10 M, 0.50 M, 1.02 M, and 2.03 M in a pure carbon dioxide environment for

TABLE 1.

System at 20°C .	Surface tension using ring balance, Dynes/cm.	Surface tension for large surface age using Bohr's equation
Benzene	28.9 ± 0.5	29.4
CCl ₄	26.7 ± 0.5	26.4
iso-propyl alcohol	21.7 ± 0.5	21.1
water	72.8 ± 0.5	72.3

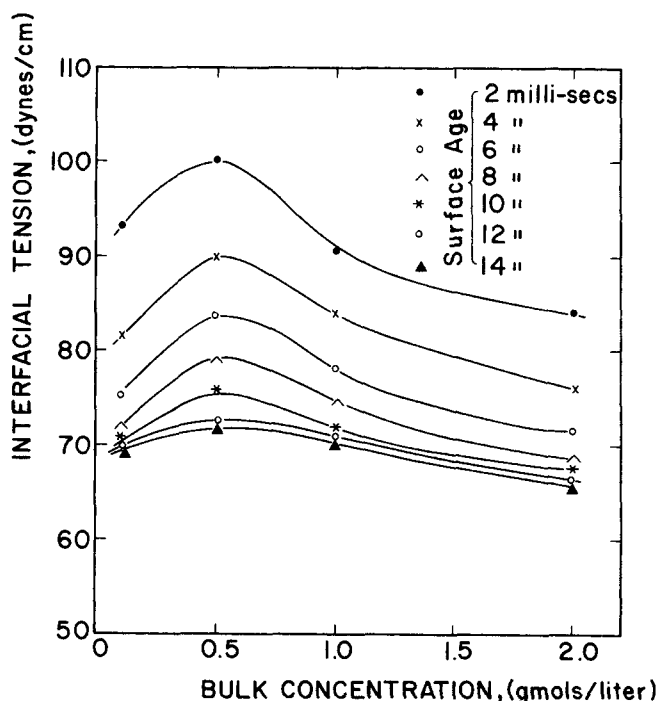


Fig. 2. Interfacial tension versus bulk concentration for MEA (aqu.)—CO₂ system at 25°C . for given surface age.

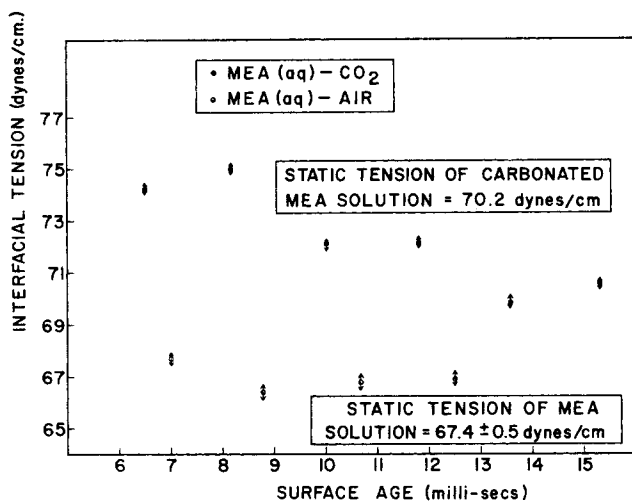


Fig. 3. Interfacial tension versus surface age for MEA (aq.)-CO₂ { system at 25°C. for bulk MEA (aq.)-air { concentration 1.02 M.

surface ages ranging from 2 to 15 milliseconds. From other experiments carried out to determine the surface tensions of the pure liquids benzene, carbon tetrachloride, methanol, iso-propanol, and water, it had been demonstrated that only for surface ages greater than 6 milliseconds did the Bohr equation accurately predict the tension. The results are given in Table 1. In the analysis of the MEA data, therefore, the low surface ages were ignored. Interfacial tensions were also measured for these concentrations in an environment of air, and static tensions were determined using a Du Noüy ring tensiometer for both the aqueous and completely carbonated MEA solutions. Illustrative data using 1.02 M MEA solution are given in Figure 3.

It is evident from Figure 2 that the interfacial tension increases with the bulk concentration up to 0.5 M approximately, for all surface ages considered. Above this concentration, the interfacial tension progressively decreases. The first effect has been attributed by Danckwerts and Silva (1967) to the presence of products of an ionic nature residing at the surface which produces an increase in surface tension. The subsequent change in behavior at higher concentrations is likely caused by the heat of reaction producing an increase in the interfacial temperature. Both Danckwerts and Kennedy (1958) and Carberry (1966) have suggested when absorbing carbon dioxide into a system exhibiting similar heats of reaction that only a surface temperature rise of approximately 1°C. may be expected. However, Chiang and Toor (1964) referred to a temperature rise of 17°C. at the gas-liquid interface when studying the absorption of ammonia into a water film, a system which exhibits similar physical properties and has a comparable heat of solution (reaction included) to that of the MEA - CO₂ system. Such a temperature increase will reduce the surface tension and at the same time produce convection currents because of density differences.

CONCLUSIONS

It has been demonstrated that interfacial tension differences exist between an aqueous MEA solution in the presence of pure carbon dioxide and air respectively. It is suggested that the interfacial behavior is influenced both by the presence of the chemical product and by the increased interfacial temperature produced by the absorption.

NOTATION

- a = average jet radius

$$= \frac{1}{2} (r_{\max} + r_{\min}) \times \left[1 - \frac{1}{6} \left(\frac{b}{a} \right)^2 \right] - \text{cm}$$

 b = wave number = $b_0 + i\epsilon$; $b = 2\pi/\lambda$ if ϵ is small
 b_0 = $2\pi/\lambda$
 b/a = amplitude of the jet, dimensionless
 $= (r_{\max} - r_{\min}) / (r_{\max} + r_{\min})$
 c = mean velocity of the fluid, cu. cm per sec.
 t = time of exposure, sec.
 t_s = surface age, millisecc.
 W = mass of liquid, g.

Greek Letters

- δ = density of carbon dioxide, gm. per cu. cm.
 ϵ = wave damping coefficient
 λ = wavelength of oscillation, cm.
 μ = absolute viscosity of liquid, poise
 ρ = density of liquid, gm. per cu. cm.
 σ = surface tension of a liquid, dynes per cm.

$$\psi = 1 + 2 \left(\frac{\mu\lambda}{\pi\rho c a^2} \right)^{3/2} + \left(\frac{\mu\lambda}{\pi\rho c a^2} \right)^2 + \dots$$

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