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Spontaneous Interfacial Cellular Convection Accompanying Mass Transfer: Ethylene Glycol-Acetic Acid-Ethyl Acetate

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Spontaneous interfacial cellular convection accompanying the extraction of acetic acid out of ethylene glycol with ethyl acetate was studied photographically with a Schlieren technique. A flat liquid-liquid interface at room temperature was photographed straight down with motion-picture and still cameras. The interface exhibited a dominant pattern of stationary and propagating polygonal cells, accompanied by stripes, cell cluster boundaries, and confined or unconfined ripples. The time-dependence of the average wave length (size) of the different patterns, their average speed of propagation, and their frequency was determined by means of an initial acetic acid concentration range of 0.1 to 10%, over a time span of 72 hr. The average wave lengths of cells, stripes, and ripples ranged from 0.02 to 0.14, 0.065 to 0.155, and from 0.03 to 0.10 cm., respectively. Cell and ripple velocities ranged from 0.27 to 1.33, and from 0.27 to 1.10 cm./min. respectively.

The relation between the observed interfacial cellular convection and the Sternling-Scriven theory of interfacial turbulence is discussed.

Mass transfer in liquid-liquid extraction, as described by the traditional two-film model, is a rather quiet and unexciting affair. Solute is visualized as transferring to and away from the interface by molecular or eddy diffusion. The interface as well as the interfacial regions of a mechanically unstirred ternary system are considered to be quiescent and motionless.

During the past decade a number of ternary systems have been discovered experimentally which challenge the universality of the two-film model. The interface in these systems is found to be disturbed during mass transfer by eruptions and spasms, while the nearby regions are agitated spontaneously. This phenomenon, known as *interfacial turbulence* (*17*), has more than an academic importance since it is invariably accompanied by mass transfer rates which may be several times higher than the theoretical ones as predicted by the two-film theory (*3, 7, 10, 18, 19, 21, 32*).

This study plans to explore the nature and form of the interfacial activity accompanying liquid-liquid extraction through a flat interface.

PREVIOUS EXPERIMENTAL OBSERVATIONS

Ward and Brooks (*38*) were the first to report the existence of spontaneous, highly localized, interfacial agitation accompanying mass transfer. Since then interfacial turbulence has been observed and studied in drops and flat interfaces both visually and photographically. Kroepelin and Neumann (*15*) photographed the flat, turbulent interface of the system ethyl acetate-acetic acid-water in profile using a Schlieren apparatus. The active interface of the system amyl alcohol-acetic acid-water was photographed by Brückner (*4*). Sherwood and Wei (*32*), while studying mass transfer with interfacial chemical reaction, noticed the occurrence of spontaneous turbulence in the phase boundary regions. Extending their observations to forty ternary and quaternary systems they found that interfacial turbulence was pronounced in the case of exothermic neutralizations. Some of Wei's experiments were repeated by Sternling and Scriven (*37*) who studied them cinematographically along with other surface-tension-driven flows.

Pendant droplets disturbed by rippling, pulsation, kicking, and eruptions were studied by Lewis and Pratt (*20*), Haydon (*11*), and Garner et al. (*8*). Haydon (*12*) investigated also the kicking of pendant drops both qualitatively and quantitatively and proposed a mechanism for it. Sigwart and Nassenstein (*33, 34*) made an extensive photographic study of eruptions in pendant droplets using a color Schlieren micro-

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scope. In particular the interfacial activity of the system carbon tetrachloride-acetic acid-water was photographed cinematographically in color (28). The Schlieren technique was employed by Kroepelin and Neumann (14) and Goltz (9) to photograph the kicking and oscillations of pendant drops. Several investigators found that rising or falling drops behave in the same manner as pendant ones (17, 32, 34).

Interfacial turbulence was observed in many ternary systems which exhibit spontaneous emulsification, spontaneous formation of emulsion in interfacial regions without the aid of external agitation (6, 13, 26, 27). Indeed interfacial turbulence has been advanced as one of the three probable mechanisms of spontaneous emulsification.

ORGANIZED INTERFACIAL ACTIVITY

All the above-mentioned experimental observations indicated that the phenomenon of interfacial turbulence, as the name implies, is a chaotic and disorganized process. Some semblance of ordered flows could however be achieved for short durations by directing a thin jet of solute toward a flat interface between two pure immiscible liquids (16, 34).

Linde (22, 23, 24) recently succeeded in producing a nonchaotic interfacial cellular convection, that lasted for 50 min., by employing highly unconventional solvents—surface active agents. Photographing the systems of 2% sodium penta decyl sulfate-isoamyl alcohol-water and 2% sodium cetyl sulfate-isoamyl alcohol-water in profile by means of a Schlieren technique, he observed the development of a single roll cell which encompassed the entire front of the test chamber. Liquid from the bulk of the two phases was conveyed to the interface along the center of the test chamber. After flowing along the interface it departed for the bulk phases running along the two opposite side walls.

The phenomenon was recorded by Linde in a motion picture (25). This film reveals that even if one disrupted the structure of an already-existing roll cell by agitating the liquid phases for a few seconds with a glass rod, the system displayed an amazing ability to re-establish the roll cell structure within minutes. Linde's observations fall in line with the theoretically based predictions of Sternling and Scriven (36) of the existence of ordered flows in the interfacial regions of an active system.

THE STERNLING-SCRIVEN THEORY

Many investigators agree that interfacial motion is triggered by local variations of interfacial tension, namely the Maragoni effect (11, 14, 16, 34). Yet until recently only the limited theory of interfacial turbulence in drops advanced by Davies and Haydon (5) was in existence. The most important theoretical contribution to the field came in 1959 from Sternling and Scriven (36) who formulated a quantitative mechanism for the onset of interfacial turbulence operating in a flat interface.

Sternling and Scriven consider interfacial turbulence to be a manifestation of hydrodynamic instability. Their theory maintains that small, ever-present fluctuations of concentration or temperature about the interface may be amplified into fully developed flows spontaneously, under favorable conditions, by the Maragoni effect. Such flows may either be highly irregular ones, corresponding to interfacial turbulence, or ordered flows that presumably may arrange themselves into a regular, cellular pattern which one may term "cellular convection." The theory deals only with the initiation of interfacial activity. However it predicts that the ultimately developed macroscopic flow patterns are dominated by the fastest growing disturbance.

Scriven and Sternling mathematically analyzed a simplified, two-dimensional model (roll cells) by means of the theory of linearized stability coupled with the traditional hydrodynamic and diffusion principles. They developed criteria for the onset of instability and determined the nature of the dominant disturbance, predicting its wave length (size), amplification factor, speed of propagation, and temporal period. Carrying out calculations for four hypothetical ternary systems on a digital computer at 0.4 sec. after the two phases are contacted they found that the computed dominant wave length ranged from 0.0014 to 0.27 cm., the amplification factor ranged from 0.32 to 250 and the speed of propagation from 0 to 0.2 cm./sec. Since the predicted magnitudes fall within the realm of experimental verification, it seemed wise to test the existence and characteristic dimensions of cellular convection under the conditions favored by the Sternling-Scriven theory.

EXPERIMENTAL PROCEDURE

A large number of ternary systems were observed for interfacial activity in a preliminary investigation. About thirty of the systems displayed either interfacial turbulence or organized interfacial activity (29). Among these the system ethylene glycol-acetic acid-ethyl acetate seemed to be a promising one for study since it developed a beautiful cellular pattern. In addition the interfacial activity was found to be rather slow and could continue for days. This particular system was therefore chosen for a thorough study.

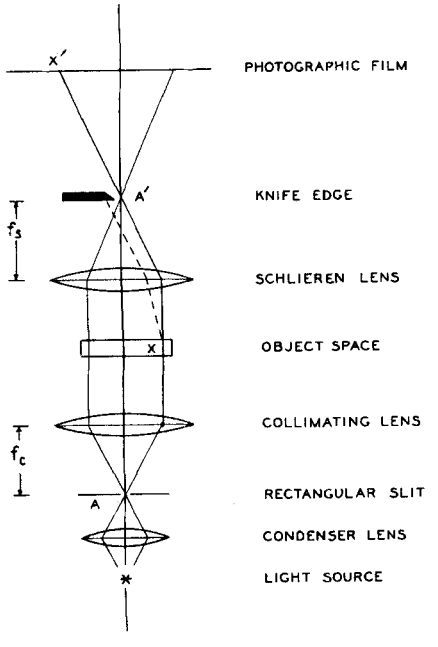


Fig. 1. Schematic side view of the Schlieren optical system. The slit A is focused at A'. The object X is focused at X'. The focal lengths of the collimating and Schlieren lenses are f_c and f_s.

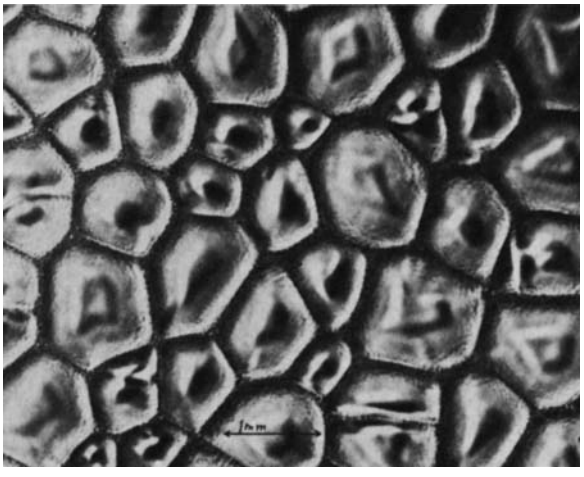


Fig. 2. Stationary cells 12 min. after formation of the interface. The lower phase contained initially 10 wt.% acetic acid in glycol. The upper phase is ethyl acetate.

Fig. 3. Propagating cells 16 hr. after formation of the interface. Lower phase initially contained 7.4% acid.

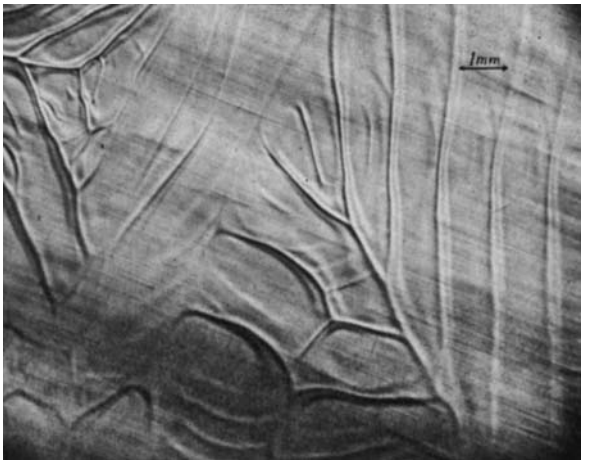


Fig. 4. Stripes at 43.5 hr. A set of five parallel stripes is located on the right side of the photo. Initial acid concentration = 7.4%.

Acetic acid, ethyl acetate, and ethylene glycol used for the preparation of the ternary system were analytical reagents, conforming to the American Chemical Society specifications. No attempt was made to purify them further.

The Schlieren technique was chosen for the photographic investigation. The apparatus consisted of a test cell, a Toepler Schlieren optical system, and photographic equipment. The test cell, originally used as a cooling cell for an arc lamp, was made of fused pyrex of good optical quality. It had internal dimensions of 32.5 × 65.5 × 85 mm. and was used with the short dimension vertical.

The conventional Toepler Schlieren arrangement was employed as shown in Figure 1. The Schlieren principles have been reviewed extensively (*31*, 35) and will not be repeated here. The Schlieren apparatus consisted of four components: light source, light source slit, optical unit, and a knife edge, all aligned and mounted on a 5½ ft. long vertical optical bench.

The light source consisted of a spherical microscope illuminator equipped with a 6 v., 108 w. ribbon filament bulb and a condenser lens. The filament size was approximately 2 × 8 mm. The light source slit was constructed of brass plates with accurately machined 45 deg. beveled edges. The gap was adjustable and was usually kept between 0.5 and 1 mm. The slit length was constant at 1 cm. The knife edge was a single-edge razor blade. It was provided with micrometer adjustments which controlled its position to within 0.001 in. The knife edge and the slit could be moved along or perpendicular to the optical axis by two traversing mechanisms.

The optical unit contained two 75 mm., f/2.5 lenses, which served as the Schlieren and the collimating lens. The Schlieren and collimating lenses were thread-mounted and were free to travel up to 1¾ in. along the optical axis of the system. Desired magnifications up to 10X were achieved by changing the distance between the test cell and the Schlieren lens. The test cell was inserted into the optical path between the Schlieren and collimating lenses and provided with means for close adjustment of its position.

Each of the components of the system was placed on a sliding block and was mounted on the rails of the optical bench. The components were rigorously aligned along a common optical axis and could be locked in position. The optical axis was vertical, and the lower end of the optical bench rested on a 1 in. thick rubber pad on the floor.

The liquid-liquid interface was photographed with a 16-mm. motion-picture camera and also with a still camera. In each case the camera, with removed lens, was placed at the top of the optical bench and aimed perpendicular to the interface. The camera was focused on the boundaries of the geometrical patterns appearing on the interface itself. The depth of focus of the optical system is estimated at ± ½mm. beyond the interface. It should be realized however that since the light rays passing through the test cell can also be deflected by refractive index gradients in the bulk of both phases, the resulting image registers any activity that may occur in the bulk liquids as well as the interfacial patterns.

The heavy phase was prepared first by making a desired solution of acetic acid in glycol which had been presaturated with ethyl acetate. This was poured into the test cell filling approximately half of its volume. A plunger, made of a cork diaphragm which fitted the cell inner walls quite snugly, was lowered until it sealed the liquid surface. The light phase, ethyl acetate, was poured next on top of the diaphragm, filling the cell to the brim. The plunger was then pulled straight up and out of the cell at an extremely slow rate to permit the formation of a calm, unperturbed interface. The completely filled cell was then sealed with a tight cover to prevent evaporation and also to prevent surface ripples which could arise from building vibrations. As soon as the cell was sealed, it was tipped from its original vertical position to a horizontal one giving an interfacial area of 65.5 by 85 mm. The instant when the interface extended and renewed itself was chosen as time zero. The interfacial activity was then photographed at various time intervals. During each run the test cell was moved horizontally, very cautiously, several times, to allow the camera to scan several regions of the interface. A run was continued until the interfacial patterns became too faint to be photographed further. For some runs this was 72 hr.

Initial solute concentration was varied between 0.1 to 10.0 wt.%. The ambient room temperature range was 21° to 26°C. The maximum deviation from the average temperature in any run however was ± 1.1°C. The acetate and glycol phases formed layers that were 15 and 17 mm. thick respectively. Duplicate runs were made at most solute concentrations. The interface was photographed with the still camera and the motion-picture camera alternately. The motion picture-framing rate was 16 frames/sec. Further details of the apparatus and procedure are available (29).

INTERFACIAL PATTERNS

Within a few seconds after the two unequilibrated liquid phases come in contact the interface starts teeming with activity as if it were a living organism. During the life time of its activity the interface exhibits a variety of geometrical patterns, the dominant one being a network of polygonal cells. In general the patterns can be grouped under three basic classes:

1. Main structure: polygonal cells, stripes.
2. Super structure: straight or closed cell-cluster boundaries.
3. Fine structure: confined or unconfined ripples.

Polygonal Cells

The cellular pattern is first to appear on the interface. The initial pattern undergoes rapid changes before being stabilized into a typical cellular pattern which may persist for many hours. This pattern usually does not encompass the whole interface, leaving some regions bare and inactive. The cells forming the network are usually irregular polygons with three to seven or more sides. With the Schlieren technique the cell boundaries are well defined. The polygonal

cells may be divided into two groups: stationary and propagating.

Stationary cells (Figure 2) are born shortly after the interface is formed. They occupy almost-fixed positions on the interface, tending to cluster in regions close to the test cell walls. The cells grow in size with time.

Propagating cells (Figure 3) resemble their living counterparts; they are born, grow, travel, multiply by splitting, and finally vanish. These cells may be born any time after the formation of the interface. They originate either by emerging from a source embedded in the cellular matrix or by splitting off from existing cells. The sources, numbering up to four or five per interface, are shaped as a line or a point. They are first visible shortly after the interface is established.

Cells emerge on both sides of a line source and travel perpendicular to it in two diametrically opposed directions. Those originating at a point source leave it traveling radially. Propagating cells tend to move along straight trajectories. Only rarely do they follow a curved path. Upon leaving the source the cells grow in size, usually retaining their original shape. Many propagating cells split, forming two new cells of either comparable or unequal size. Three-body splitting is rather rare. The newly formed cells continue to travel along straight trajectories.

Not only do new cells emerge constantly from sources and old cells grow in size, but some cells are constantly being destroyed. This occurs at sinks, straight or curved boundaries of cell clusters. The doomed cells move to the cluster boundary, shrink, and disappear. Another infrequent mode of disappearance is the merger of two cells. As the interface ages, the total number of cells decreases. Eventually they all vanish.

Stripes

The stripe pattern (Figure 4) does not appear until the interface is at least 15 hr. old. The stripes assume the form of elongated bands lying parallel to each other, side by side. As they drift slowly across the interface, their width increases with time. As time progresses, the stripes become very faint and finally disappear.

Ripples

These are shapped as an array of consecutive straight or curved fronts traveling on the interface. Ripples may appear as early as half an hour after the interface is established. They are either confined within cells or stripes or unconfined (Figure 5). Confined ripples appear first. As they emerge near a wall, they traverse their host cell (or stripe) until their front reaches an opposite wall, then they merge with the cell wall and disappear. Confined ripples always travel in the same direction as their host cell or stripe.

Unconfined ripples appear when the cellular structure or stripe structure fades out. They form around a common center, presenting an array of segmented or closed concentric rings. In time these ripples disappear too. Organized interfacial activity thus comes to a halt.

The different interfacial patterns and their behavior with time are illustrated in a motion picture which is available for loan (39).

The system ethylene glycol-acetic acid-ethyl acetate exhibits organized interfacial activity upon transfer of acetic acid from the glycol phase to the acetate phase, but solute transfer in the reversed direction results in a smooth, quiet interface. The threshold concentration of acetic acid necessary to trigger cellular activity was found to lie between 0.05 and 0.1 wt.%. Interfacial activity comes to a halt after about 72 hr. for an acetic acid initial concentration range of 2 to 10%. At acid concentrations of 0.1 and 0.5%, the activity lasts 0.5 and 3 hr. respectively. The extent to which the ternary system approaches equilibrium, defined as the ratio of the bulk solute concentration in the acetate phase to the equilibrium concentration, upon termination of interfacial activity was determined experimentally by analyzing the bulk acid content of the two phases. The extent was found to vary from 80% (for 10% acid) to 94% (for 2% acid).

PATTERN MEASUREMENTS

Polygonal Cells

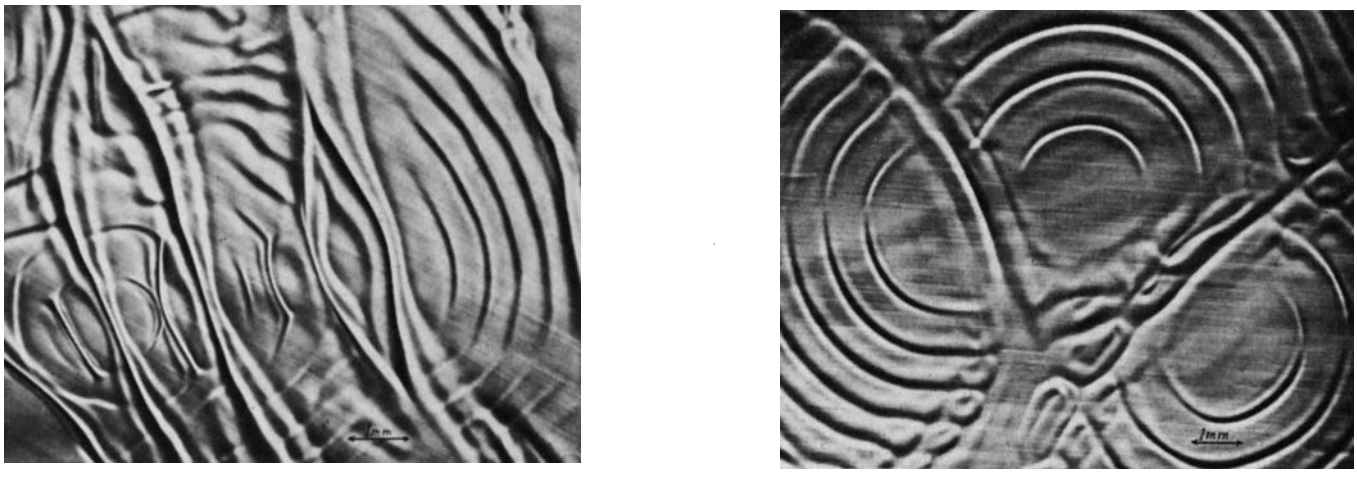
The shape and size of individual polygonal cells of a given population at any instant are not uniform. As an illustration the distribution of center-to-center distances between a cell and its surrounding neighbors is presented in Figure 6 for an elapsed time of 12 min. and at 16 hr. Normal distribution curves fit the data rather loosely. The distance range increases markedly with time.

Every polygonal cell population can be characterized by an average wave length,* which is defined here as the mean of the center-to-center distances between the cells. The time dependence of the average wave length of propagating cells over the initial acid concentration range of 0.1 to 10% is given in Figure 7. Also plotted are the average wave lengths of stationary cells at 10% acid.

The initial solute concentration dependence of the average wave length of propagating cells at 1 and 16 hr. is plotted in Figure 8. As the initial acid concentration increases, the wave lengths decrease to a minimum, near 4% acid, and then increase.

Time dependence of the average cell velocity, defined as the mean of the velocities of the centers of at least three cells along their paths, over the initial acid concentration range of 2 to 10% is given in Figure 9. Cell velocity decreases with time, and the greatest change occurs during the first 5 hr.

* This term is used by Sternling and Scriven for the size of a roll cell.



a. Ripples confined in stripes, 22 hr.

b. Unconfined ripples, 64.3 hr.

Fig. 5. Two kinds of ripples, for initial acid concentration of 10%.

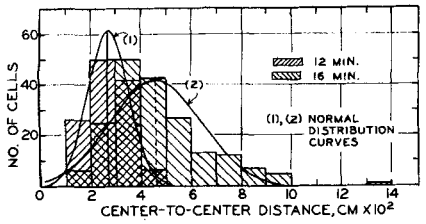


Fig. 6. Distribution of center-to-center distances for polygonal cells. Initial acid concentration = 7.4%.

When the average cell velocity is plotted vs. initial acid concentration, it is found that the velocity reaches a maximum at 7.4% and then decreases.

Propagating cells' growth curves, which relate the individual cell linear size with time after the passage of 1 hr., are presented in Figure 10. Cell linear size is defined as the square root of the cell area. Cells 1 and 2 are growing unhindered, whereas cell 3 is apparently in the process of being removed by a sink. Cell linear growth rate for 7.4% acid was found to be 0.2 cm./min. and independent of time over the time range of 1 to 30 hr. Growth rate is defined as the slope of the size vs. time graph for the linearly growing cells.

Stripes

Time dependence of the average wave length of stripes, defined as the mean width of all the individual stripes in a population, over an initial acid concentration range of 4.5 to 10%, is illustrated in Figure 11. The stripes grow with time.

Ripples

Time dependence of the average wave length of both confined and unconfined ripples, defined as the shortest distance between two consecutive fronts, is given in Figure 11. The wave length grows with time. Ripple average velocity and frequency at 10% acid were found to decrease with time and to change most during the early portion of the interface life.

DISCUSSION OF RESULTS

Effect of Time

As time progresses, at a given initial concentration the cell, stripe, and ripple average wave lengths increase. The cell and ripple velocities and the ripple frequency decrease, while the cell growth rate remains constant. As the ternary system approaches equilibrium, its chemical potential of course decreases. Consequently the energy source for interfacial activity is depleting as the solute driving force is diminishing. The concentration profile near the interface becomes less steep. Therefore cell and ripple velocities and ripple frequency of formation should decrease with time. Such trends are indeed observed experimentally.

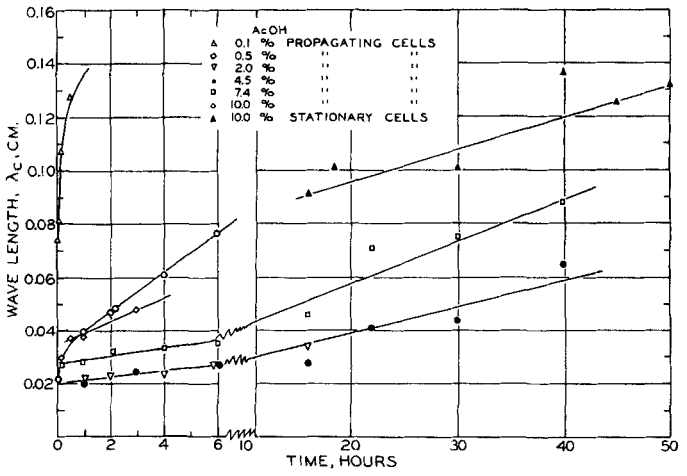


Fig. 7. Effect of time on wave length (cell size) for stationary and propagating cells.

Effect of Concentration

For a cell the average wave length and velocity at a given time depend on the initial solute concentration. The average wave lengths of stripes and ripples increase with initial concentration for a given time. Their rate of change with time however is essentially independent of concentration. As the initial concentration increases, both stripes and ripples appear earlier.

Interfacial activity is energized by the difference in chemical potential between the two phases. As this difference increases with increase of concentration difference between the two phases, it is to be expected that cell velocity will be increased by increases of initial acid concentration. The experimental data however do not follow this trend at high initial concentrations, especially at 10% acetic acid. This concentration differs from the rest of the concentrations in that it produces unusually large cells which propagate at relatively low speeds. The boundaries of the interfacial patterns at this concentration are initially delineated by numerous, tiny emulsions droplets (Figure 2) with an average diameter of roughly 0.01 mm., which disappear about 30 min. after the formation of the interface. The 10% acid composition is the only concentration at which ripples confined in cells may be observed. Possibly this abnormal behavior is to be attributed to interdiffusion of solvents. Figure 12 shows that the starting mixture of 10% acetic acid in glycol is well above the saturation curve. A second possibility for the unusual behavior may lie in some chemical reaction occurring between acetic acid and glycol.

Interfacial Motion

Local variations in interfacial tension, triggering interfacial activity, may be caused by mass or heat transfer across the interface or by any interfacial chemical reaction which releases heat. Which of these processes is operative in the ternary system under consideration?

At the start both phases were at the same temperature. A ternary system however may develop local heat effects due to heat of solution. For the present system it was possible to show that heat of solution could not be the sole cause of the observed activity. In practice heat of solution during extraction cannot be divorced from mass transfer because one causes the other. Interfacial tension could therefore be affected by both composition and temperature for any diffusion test. Consequently interfacial activity may be enhanced, reduced, or arrested, depending on the manner in which the two effects are coupled. There is little hope of separating the mass transfer effect from the heat effect unless a ternary system is used which consists of ideal solutions only. The system used is not ideal.

Heat effects accompanying the mixing of acetic acid with ethyl acetate and

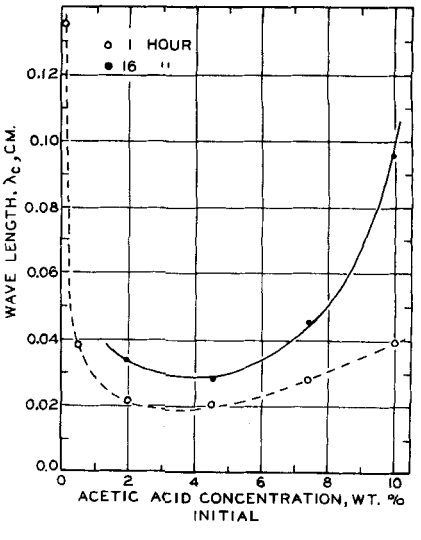


Fig. 8. Effect of initial solute concentration on average wave length for propagating cells.

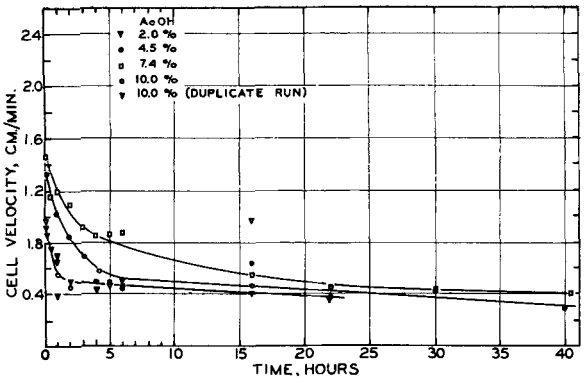


Fig. 9. Time dependence for average velocity of cells.

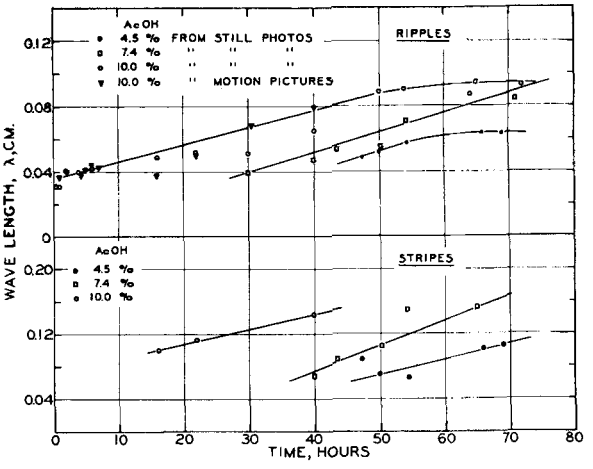


Fig. 11. Effect of time on average wave lengths for stripes and ripples.

with ethylene glycol were determined experimentally at 25°C. (29). In both cases the maximum recorded temperature rise was 0.1°C., which corresponded roughly to a heat of mixing of −3.6 cal./mole mixture. This heat is small compared with that of various other ternary systems which do not exhibit activity. Secondly, the interface of the ternary system remained quiescent upon reversing the direction of acetic acid transfer, in spite of the fact that the heat effects for transfer in both directions are of the same magnitude. Thirdly, heat effects accompanying the mixing of the two solvents were found to be twenty times larger than those for acetic acid in ethyl acetate. But upon elimination of acetic acid the system ethyl acetate-ethylene glycol failed to develop cellular activity in spite of the partial miscibility of the two components (Figure 12). All this evidence supports the conclusion that the investigated cellular activity is not caused by heat of mixing alone.

In the investigated ternary system acetic acid is dissolved in ethylene glycol and is thus available for possible chemical reactions. Is the chemical reaction fast enough at room temperature to be the sole cause of the observed activity? The extent of reactions at room temperature at the end of 72 hr. was determined experimentally (29). No reaction could be detected in the initial acid concentration range of 0.5 to 2.0%. A reaction of an extremely limited extent took place at higher concentrations. At the maximum only 4% of the initial acid reacted with the glycol in 72 hr. Very little difference in the physical appearance of the interfacial patterns between 2% and higher acid concentrations (except at 10% acid) could be detected.

Consider the reverse transfer again. If acetic acid were initially present in the ethyl acetate phase, it could react with the glycol at the interface, thus favoring interfacial activity. The interface however is found to be inactive for this reverse solute transfer. Thus chemical reaction may be ruled out as the sole activating process.

Since acetic acid is more dense than the acetate phase into which it is transferring, natural convection is prevented. Thus interfacial activity cannot be attributed to ordinary natural convection. It is concluded that the observed interfacial cellular convection is caused by mass transfer of solute across the interface and is not caused by heat of solution, heat of reaction, or conventional natural convection.

Interfacial activity should theoretically terminate when the system reaches equilibrium. The fact that the observed activity was found to subside while the system was still 9 to 20% away from equilibrium concentrations may be partly explained by a gradual buildup of unknown contaminants at the interface. However the chronological order of appearance of interfacial patterns, cells, stripes, unconfined ripples, was preserved in the initial concentration range of 2 to 10%.

Comparison with Theory

There is an inherent difficulty in trying to compare the physical appearance and the experimental characteristics of interfacial cellular convection with theoretical values. In order to obtain a mathematical model which is conducive to solution, Sternling and Scriven assumed a model which to their mind "is too simplified to be reproduced in the laboratory; therefore, direct, quantitative comparisons with experiment are impossible." In addition the Sternling-Scriven theory deals only with the initia-

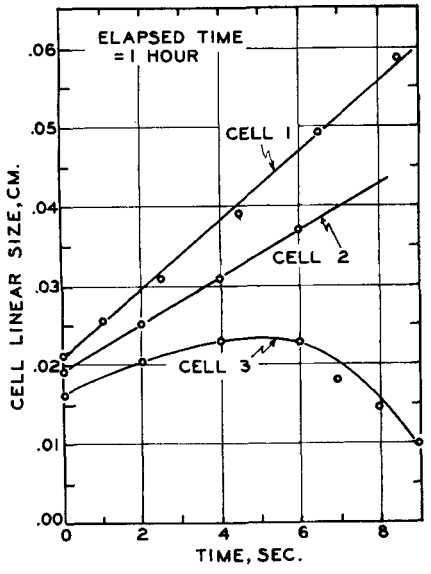


Fig. 10. Growth curves for three typical cells. The interface is 1 hr. old. 7.4% acid concentration at start.

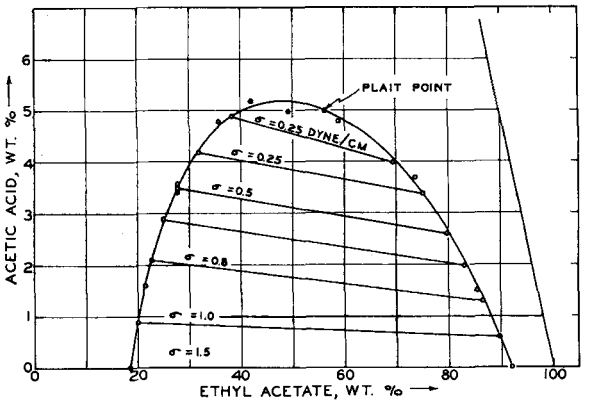


Fig. 12. Phase equilibrium for ethylene glycol-acetic acid-ethyl acetate at 25°C. Interfacial tensions are indicated on the tie lines.

tion of interfacial activity, whereas the present study considers macroscopic interfacial cellular convection.

The Sternling-Scriven model considers the active interface in profile, postulating the existence of roll cells extending on both sides of the interface. The present study discovered and investigated cellular activity occurring at the interface itself. Are the interfacial polygonal cells indicative of the existence of convection cells operating in the bulk of the liquid and are they similar to the ones observed by Linde (25)?

The answer is suggested by a comparison of interfacial cellular convection due to mass transfer with the surface tension driven thermal cellular convection observed by Bénard. The two phenomena are each triggered by an instability which is amplified by the Maragoni effect (2, 30). Bénard viewed the thermal convection cells as they appeared at the air-liquid interface, never in profile (1). Nevertheless he was able to elucidate the internal structure of the pattern and show that it consisted of circulation cells.

Bénard cells, when viewed normal to the free liquid surface, appear as a network of polygonal cells. Their boundaries are found to be raised from the mean level of the interface while their inner region is recessed. Visual observations of the active interface of the investigated ternary system at an angle show that the interface, rather than being flat and smooth, is rugged and full of indentations. Protrusions are characteristic of regions of high interfacial tension, whereas indentation denotes regions of low interfacial tension. Thus the polygonal cell boundaries may be lowered or raised depending on the particular system and the direction of solute transfer. The Schlieren technique can differentiate between protrusions and indentations, since the former act as negative lenses whereas the latter act as positive ones. An analysis of the Schlieren photographs of the investigated active interface indicates that those polygonal cells had raised boundaries.

Bénard suspended light-weight solid particles on the liquid surface and observed them collecting at the cellular boundaries. In Figure 2 of the present study tiny emulsion droplets are observed streaming towards the polygonal cell boundaries and collecting there.

The nature of the flows inside a polygonal cell can be guessed by analogy to Bénard cells. In the heavy phase of the present ternary system an acid-laden stream rises in the center of the roll cell. Reaching the interface it spreads radially over a recessed area of low interfacial tension. While flowing on the interface the stream transfers acid to the upper phase. It finally reaches the protruding cell boundaries, which are regions of high interfacial tension, to be driven down into the bulk of the phase. This interpretation of flows within a convection cell apparently will require modification before it is applied to cells or stripes which contain ripples.

Convection cells constitute only part of the story of interfacial cellular convection. The phenomenon is far more complicated than the Sternling-Scriven simple theoretical model or the Bénard-cell phenomenon. The presence of stripes, ripples, cell-cluster boundaries, and inactive interfacial areas cannot yet be explained.

Characteristic and Quantitative Features

In accordance with the stability criteria set by the Sternling-Scriven theory, the system glycol-acetic acid-ethyl acetate should be active upon transfer of acid from the glycol to the acetate phase and stable upon transfer in the reverse direction. This is indeed the case. The criteria however fail to predict the actual presence of interfacial turbulence, chaotic and unorganized activity, for the related system ethyl acetate-acetic acid-water, for solute transfer into water.

Theoretically the studied system should exhibit a diffusion-limited, stationary instability for which the roll cells grow without translation. In practice both stationary and propagating cells were observed which correspond to stationary and oscillatory instabilities.

Dominant wave lengths for theoretical roll cells in the stationary regime have been calculated (29) for initial acid concentrations of 0.5 and 10 wt.% at 1 sec. after the formation of the interface. The values are 0.01 and 0.003 cm. respectively. Although these wave lengths are characteristic of the initially growing instability, it is interesting to note that they are just one order of magnitude smaller than those of the polygonal cells in a fully developed flow.

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