

THE EFFECT OF HEATS OF SOLUTION ON MARANGONI CONVECTION

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Abstract—Spontaneous convective circulation arising during the unsteady state transfer of a solute across a liquid-liquid interface was investigated experimentally for the possible effects of lateral temperature variations along the interface brought about by the enthalpy change accompanying the solute transfer. The convective circulation was largely due to the Marangoni effect or surface-tension-driven flow. An additional driving force due to an unstable density was present during some runs. In addition to a study of 78 different ternary systems, detailed studies were made of two of these, both containing water and ethyl acetate as the partially miscible solvents. One system involved the transfer of acetic acid in the presence of buoyancy-driven flow; the other involved the transfer of ethyl alcohol in a buoyancy-stable system. A motion picture camera with Schlieren illumination recorded the convective patterns crossing the junction of a stationary micro-thermocouple located in the interface. Simultaneously, a fast-response, continuous measurement of the temperature at that point was recorded. Temperature perturbations as large as 0.05°C were common, and values up to 0.5°C occurred in some systems. These did not affect the interfacial tension in a significant manner. The motion picture confirmed that no consistent correspondence existed between the flow appearance and the temperature record. Thus the surface tension driving force must arise from concentration perturbations *per se* and not from the temperature perturbations which are caused by the heats of solution.

INTRODUCTION

DURING the process of heat or mass transfer in a two-phase system, certain fluid interfaces are known to exhibit an interesting convective phenomenon. The fluid in one or both of the phases shows a spontaneous motion in an often regular pattern of circulatory convection cells clustered along the interface. The circulation renders inapplicable the usual two-film model of diffusion across an interface. Instead, a higher rate of transfer results, by as much as triple the prediction based on pure diffusion.

Theoretical and experimental investigations of such spontaneous convection are widespread and date back to the late 1800's. It was not until the late 1950's [1, 2], however, that the flow was successfully shown to have two possible mechanisms, the surface tension drive and the buoyancy drive. This launched a series of analyses and experimental investigations of the surface-tension-driven convection, termed the

Marangoni effect. The most notable and universal analyses are due to Sternling and Scriven [3-5] and Smith [6], and the most interesting experimental investigation are the photographic studies of Orell and Westwater [7-9]. An excellent survey up to 1966 is given by Berg *et al.* [10], and after 1966 by Heines [11].

Analysis of the phenomenon is complicated. The cause of the spontaneous fluid circulation may be either heat or mass transfer, and the driving force may be either surface tension variations in the interface or an unstable density gradient in one or both of the bulk phases. The interaction of these possibilities and the effects of their combined presence make the applicability of certain theoretical analyses questionable in many cases.

One combination which has been investigated by several authors is that of heat and mass transfer together causing a buoyancy-driven flow process. One of the first such analyses was

by Chiang and Toor [12], who solved the problem for one spatial dimension, perpendicular to the interface. This was extended by Gardner and Hellums [13] with the inclusion of a moving interface. These were followed by linear stability analyses [14, 15] and the use of an energy theory [16]. The combination was also given experimental study, using both photography and measurement techniques [17-21].

The combined driving forces of buoyancy and surface tension gradients were analyzed by Stuart [22], Nield [23], and Krzywoblocki [24], and the relationship between the critical Rayleigh and Marangoni numbers was shown to be nearly linear in an analysis by Debler and Wolf [25]. An experimental investigation of these combined driving forces is offered by Hoard, Robertson and Acrivos [26].

The one combination which has not been investigated is that of heat and mass transfer in a surface-tension-driven convection process.

This is the area undertaken by the current investigation, whose purposes were: (1) to determine whether or not there are heat effects (as temperature perturbations) arising from the enthalpy change accompanying the transfer of a solute across a liquid-liquid interface, and (2) to determine the extent of the interaction between these spontaneous heat effects and the concentration variations in the Marangoni circulation.

APPARATUS AND PROCEDURE

The study posed a unique design problem which was twofold: (1) to put two liquid phases into contact at a zero time in such a way as to cause a minimum of agitation, and (2) to determine the lateral temperature distribution along a liquid-liquid interface without interfering with the interface shape or the spontaneous fluid motion.

The solution to both these problems lay in the structure of the diffusion test cell, pictured in

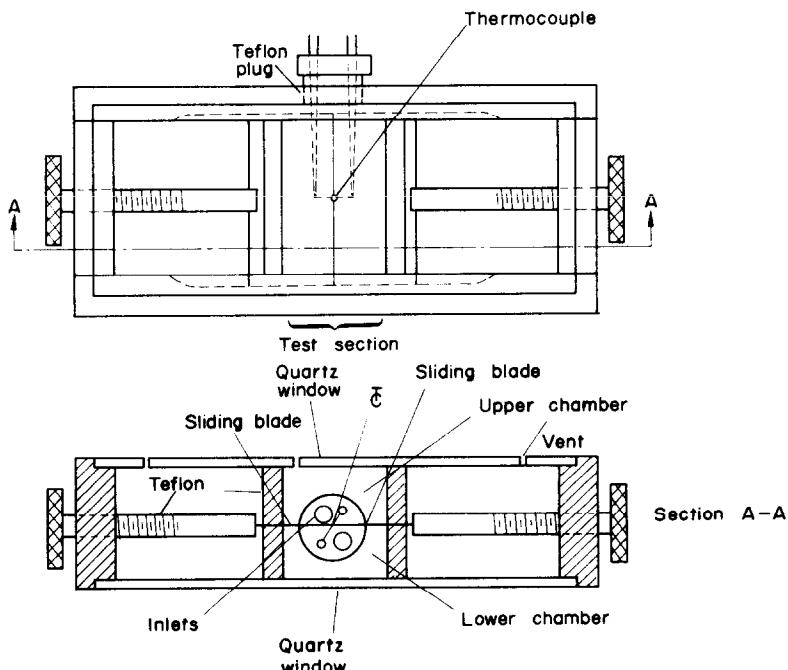


FIG. 1. Sketch of diffusion cell.

Fig. 1 The problem of putting the phases into contact was solved by dividing the diffusion cell into three sections and making use of a pair of thin metal slides. The slides when closed divided the center or test section of the cell into upper and lower chambers, each measuring 5×5 cm, 2 cm deep. This enabled one to add the solutions to the test section and keep them almost entirely sealed off from each other until the filling procedure was complete. Liquids also simultaneously filled the two end section of the cell, but mixing with the central test section was nil. The test liquids contacted only stainless steel, Teflon, glass, quartz and the chromel-alumel thermocouple.

The problem of taking a lateral temperature sweep could have been solved by use of a traversing thermocouple which moved horizontally. However, nearly all observations of interfacial convection show that the convective patterns drift horizontally. Thus it is feasible to use a stationary thermocouple and let the patterns move across it. In addition, a stationary thermocouple may cause less distortion of the fluid motion than a bulkier mobile unit.

The thermocouple was adapted from a design by Gelb, Marcus and Dropkin [27]. The wires were chromel and alumel of 1 mil (0.025 mm) diameter. Each wire extended individually through a horizontal tapered glass capillary, one in the upper phase and one in the lower. The wires extended beyond the tips of the capillaries in the center of the cell, where they were bent towards each other at right angles and met at a welded junction in the interface. The wires passed through the liquid-liquid interface at an angle of 45 degrees. Because of the wire, each slide had a notch at its contacting edge to allow an opening for the wire to pass through when the slides were closed. This opening occupied less than 0.1 per cent of the interfacial area in the test section when the slides were opened.

A reference junction was sealed in an air-filled Dewar at room temperature. Thus, only the temperature changes were detected and not the absolute temperature. All runs were carried

out at room temperature, which varied only slightly from 25°C.

The thermocouple signal was pre-amplified 50 times by a direct current amplifier and was then fed to a Sargent Model SRG potentiometric strip chart recorder. A typical setting gave a 25 cm pen deflection for a temperature jump of 1°C. The chart speed was set at 12.5 cm per min. The speed of the thermocouple response was estimated and measured [11], showing a time constant of about 0.01 s.

In order to relate the temperature variations to the concentration variations in the moving interface, the diffusion cell was built to allow a motion picture camera to record the changing Schlieren image of the liquid interface at and near the thermocouple.

The Schlieren system, pictured in Fig. 2, was built with a vertical optical path perpendicular to the liquid interface. The light source consisted of a microscope illuminator equipped with a 6 V, 108 W ribbon filament bulb and a condenser lens. Two Wollensak 75-mm, f/2.5 Fastax-Raptar lenses served as the collimating and

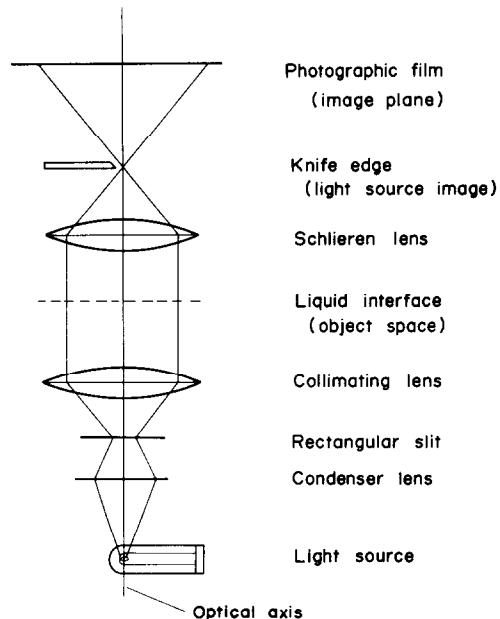


FIG. 2. Schlieren optical system.

Schlieren lenses. The test cell was located between these two lenses. The upper and lower windows of the cell were of polished quartz. Detailed descriptions of the rectangular slit and knife edge components are found in an article by Orell and Westwater [9]. The knife edge could be properly adjusted to give a sharp image of the liquid interface in intricate patterns of light and dark regions corresponding directly to the concentration variations.

A 16-mm motion picture camera was placed at the image plane. The camera lens was removed so that the image plane coincided with the film. One hundred foot rolls of film were exposed at 10-24 frames per second at a magnification of approximately $5\times$ on the Eastman Plus-X Negative film.

Solutions to be used in experimental runs were prepared by mutually saturating the solvents, then adding the solute to one of the phases. The inlet tubes pictured in the cutaway view of the cell in Fig 1. were connected to external glass funnels which could be sealed off by Teflon needle valves. The solutions were poured through these funnels to load the test cell while it was in place on the vertically mounted optical bench. After the proper amount of each phase was added, the inlet valves were closed to permit the opening and closing of the slides.

Synchronization of the motion picture and temperature records was facilitated by a remote control switch which simultaneously activated the recorder chart drive and the camera motor. When the loading of the cell was completed, the slides were opened in about 5 s and the switch was thrown. After a run of about 4 min. the switch was turned off so that the starting and stopping points on the film and the chart were well defined. This afforded an accurate synchronization.

RESULTS AND DISCUSSION

Experimental runs on 78 different ternary systems were performed in this investigation [11]. For each system, the solute was transferred across the interface first in one direction and then

in the other. The solvent pairs included: water with methyl ethyl ketone, isobutyl alcohol, ethyl acetate, toluene, and carbon tetrachloride; and ethyl acetate with ethylene glycol. The solutes used were, acetic, propionic, sulfuric, and nitric acids, ethyl, isopropyl, n-butyl, and isobutyl alcohols, acetone, methyl ethyl ketone, ethyl acetate, ammonium hydroxide, ethyl ether, and triethylamine. Starting concentrations of the solute in one phase normally were 7-10 volume per cent. Temperature vs. time records were obtained for all runs. The records for eight of these and descriptions for all are available [11].

Buoyancy instability was present in many of the diffusion processes, in addition to surface tension flow, and occasionally a chemical reaction was suspected. Many types of convection were seen, ranging from relatively large-scale motion with violent and chaotic rippling to highly ordered, intricate, slow-moving cellular patterns. Varying temperature records were also seen, but a broad view of the ternary system survey showed that the temperature fluctuations of the greatest amplitude and frequency occurred during transfer processes that involved buoyancy-unstable phases. The reasons for this are not well understood.

The solvent pair producing the most spectacular temperature records was ethyl acetate/water. The interfacial tension of 6.2 dynes/cm is the largest of all the binary solvent pairs in this investigation which show a sizeable mutual solubility, i.e. excluding carbon tetrachloride and toluene. The next highest value is around 2.5 dynes/cm (ethyl acetate/ethylene glycol). Convection during transfer across the ethyl acetate/water interface appeared solely in the form of ripples whose motion ranged from slow and lingering (ethyl alcohol diffusing downward) to swift and swirling (acetone diffusing upward). Very few temperature fluctuations were observed in buoyancy-stable diffusion processes across this interface. The large fluctuations were restricted to buoyancy-unstable flows.

The largest temperature fluctuations were observed during the transfer of acetone upward

from water to ethyl acetate, a buoyancy-unstable process. As seen in the temperature record in Fig. 3, peaks of up to 0.5°C were recorded at less than two-second intervals. Although the visual record changed chaotically during a two-second interval, the temperature fluctuations may nevertheless enhance the convection by increasing the surface tension gradients or by creating a thermal buoyancy effect.

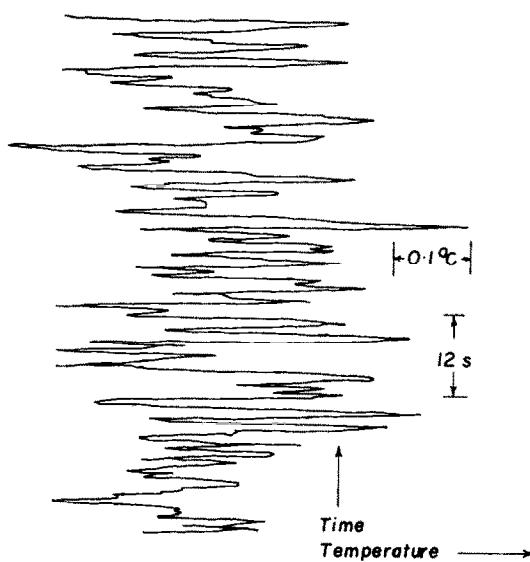


FIG. 3. System showing large temperature fluctuations at the interface. Acetone transferring upward from water to ethyl acetate; starting concentration of lower phase 10 volume per cent acetone.

One solute that showed a consistent thermal behaviour was sulfuric acid. Diffusion across the various interfaces in a buoyancy-stable direction (upward) showed no temperature fluctuations, while diffusion in the buoyancy-unstable direction (downward) showed large temperature drifts of about 0.2°C spread over several seconds. Diffusion processes with this solute were not studied in detail, since the temperature variations were clearly much slower than the moving visual patterns. Furthermore, there was a high possibility of chemical reaction.

Ethyl acetate-ethyl alcohol/water

Two diffusion processes were selected for detailed study. For these systems, the data from the temperature and motion picture records were supplemented with measurements of interfacial tension and density at various concentrations and temperatures, together with enthalpy changes and phase diagrams. The first of these two detailed studies was the downward diffusion of ethyl alcohol from ethyl acetate to water. This process was stable with respect to buoyancy forces but had a Marangoni number on the order of 10^8 , rendering it highly unstable to the Marangoni effect. Convection here, just as all other convection seen with the use of this solvent pair, took the form of ripples, whose motion was slow enough to be stopped by filming at a rate of 24 frames per s.

A typical temperature record is shown in Fig. 4, showing small temperature variations of up to 0.1°C which are broad along the time scale, spread over intervals of about 15 s. Comparison

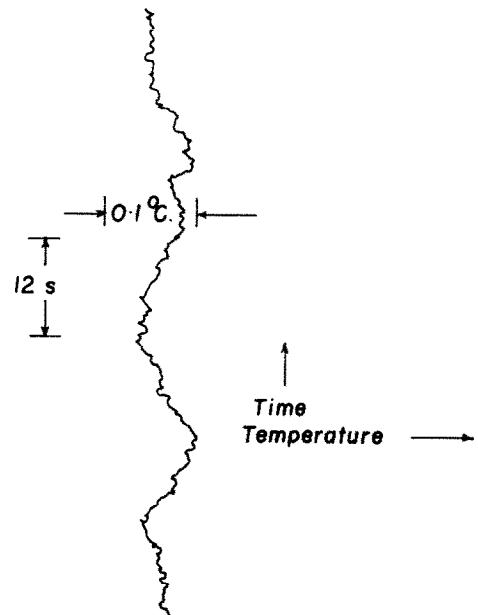


FIG. 4. System showing small temperature fluctuations at the interface. Ethyl alcohol transferring downward from ethyl acetate to water; starting concentration of upper phase 8 volume per cent ethyl alcohol.

of this with the motion picture record showed that the temperature variations were entirely out of character with the visual changes, since several ripples could be seen passing the thermocouple junction during a single second. The minute pen motions of less than 0.01°C are to be ignored. These are the level of the recorder sensitivity to electrical noise and were present even in blank runs with no solute.

The temperature fluctuations of 0.1°C were considerably smaller than the overall maximum temperature rise of 1.33°C which accompanies the complete equilibration of the system starting from an initial ethyl alcohol concentration of 8 weight per cent in the organic phase. Considering that this typical temperature fluctuation of 0.1°C is about 10 per cent of the possible maximum, a typical concentration fluctuation might be 10 per cent of its maximum, or 0.5 weight per cent.

Literature values and new measurements [11] were obtained to establish the interfacial tension and density at various concentrations and at two temperatures. From these, and assuming linearity, the typical temperature fluctuation of 0.1°C would cause an interfacial tension variation of 0.0005 dynes/cm while the "typical" concentration fluctuation would change the tension by 0.33 dynes/cm. Clearly the temperature variations for this system have little effect on the surface tension in relation to the concentration variations. The effects on density, however, are much more comparable. The greatest density variation is in the aqueous phase, where the density varies by 0.0005 g/ml over a 0.5 weight per cent range. Over a temperature range of 0.1°C , the density of ethyl acetate varies by 0.0001 g/ml while that of water varies by 0.00003 g/ml. Thus the temperature variations can counterbalance or even overbalance the stable density gradient arising from the concentration variations.

Ethyl acetate-acetic acid/water

The other diffusion process studied in detail involved combined buoyancy-driven flow and

surface-tension-driven flow. This was the diffusion of acetic acid downward from ethyl acetate to water. With the initial solute concentration of 10 weight per cent, the Rayleigh and Marangoni numbers both were on the order of 10^8 . Motion pictures showed convection largely in the form of isolated ripples, with the images ranging from sharp to indistinct. Figure 5 shows the temperature record from a typical run. The fluctuations averaged about 0.05° over two-second intervals. Here the higher frequency of the fluctuations allowed for the possibility of a correlation with the film images.

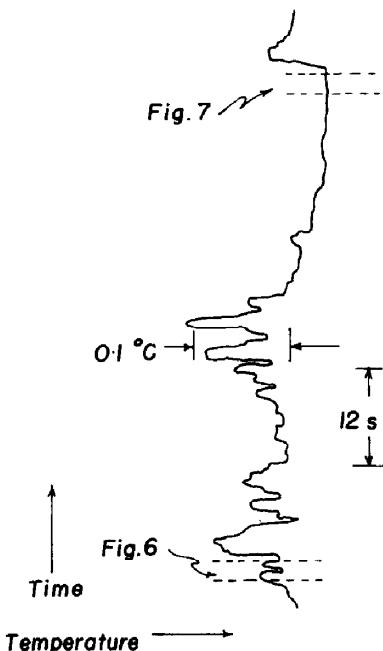


FIG. 5. Temperature record of interface as acetic acid diffuses downward from ethyl acetate to water. Starting concentration of upper phase 10 volume per cent acetic acid.

It was realized that the Schlieren motion pictures could not be used to obtain the actual concentration profile at the liquid-liquid interface, because of the interference from the integrating effects of the light beam passing through the entire liquid depth. However the picture did yield precise knowledge of where in a convection cell the thermocouple was located at any instant.

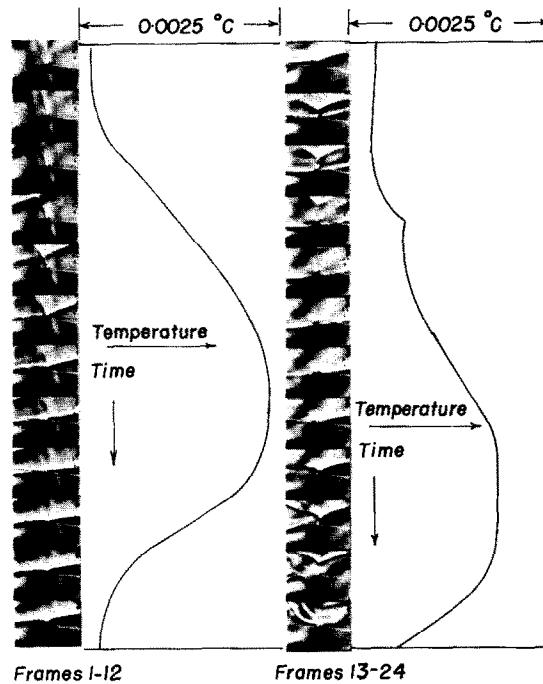


FIG. 6. Section from Fig. 5 showing temperature fluctuations; 10.5 frames per s. Each frame includes an area of 3.5×2.6 mm.

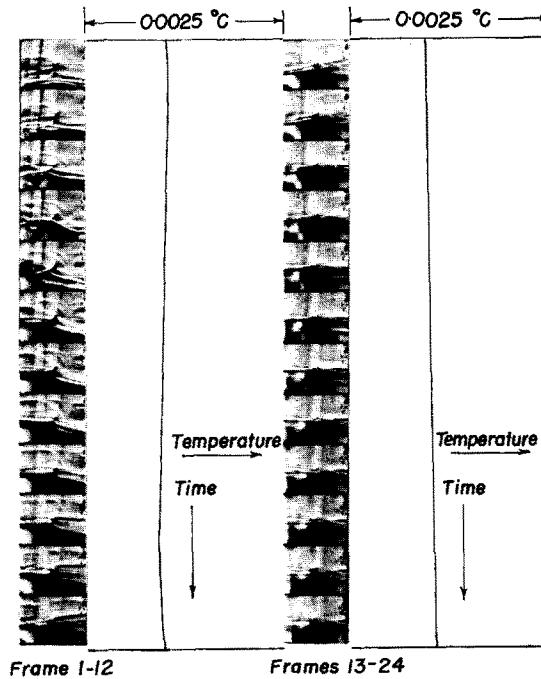


FIG. 7. Section from Fig. 5, showing no fluctuations in temperature.

Thus it was possible to answer the question as to whether the temperature at the center of a convection cell was always higher (or lower) than at the cell wall.

A correlation was indeed found in some sections of the run, where temperature peaks occurred simultaneously with the ripples crossing the thermocouple junction. An example of this is shown in Fig. 6, where an indicated section from Fig. 5 is stretched out time-wise and shown next to the corresponding movie frames. At other points, peaks appeared where no ripples passed the junction, or ripples passed the junction with no response from thermocouple. This latter is shown in Fig. 7, which is a different section taken from Fig. 5. The temperature and concentration variations probably originated in the same regions. They may have been propagated at different rates, however, because the thermal diffusivity is much greater than the molecular diffusivity.

In the first several frames of both figures, it is apparent that the meniscus formed around the wire initiates a convective ridge. Only in recent years has the importance of the effect of a meniscus on mass transfer been recognized, first by Berg and Morig [28] and most recently by Wayner and Coccio [29] and Kayser and Berg [30]. From the direction that the ridge emanates from wire, one can also determine the direction of the fluid flow at that point of origin. Thus in Fig. 6, frames 19-24 show flow toward the top of the frames.

The average temperature fluctuation in Figs. 5-7 is once again about one tenth the maximum for equilibration, which is a decrease of 0.63°C in this case. Similar to the first system, the typical interfacial tension change of 0.17 dynes/cm over a 0.5 weight per cent range is much greater than the 0.0005 dynes/cm change that is brought about by a temperature shift of 0.1°C. The density effects are 0.0015 g/ml for the concentration change and 0.0001 g/ml and 0.00003 g/ml for the temperature change in the organic and aqueous phases respectively. Density is affected almost as much by temperature

as by concentration; the interfacial tension is affected much more by concentration than by temperature.

The heat evolved or absorbed in the transfer of the solute from one solvent to another is less than 950 cal/kg of mixed liquids for each of the two cases described above. This result also encompasses the heat effects which arise from the readjustment of the mutual solvent solubilities due to the presence of the solute. We conclude from these studies and the ternary system survey that spontaneous temperature changes due to the excess enthalpy changes do not noticeably affect the surface tension drive in the Marangoni effect for systems where the enthalpy change is less than 950 cal/kg. The possibility remains, however, that the temperature variations can cause a buoyancy instability.

CONCLUSIONS

1. When spontaneous temperature fluctuations are observed in the interface in a liquid-liquid extraction process, their amplitude is approximately one tenth the temperature difference which would result from the combined enthalpy difference between the initial and equilibrated phases.
2. The frequency of the temperature fluctuations is significantly increased by the presence of an unstable density gradient.
3. In systems where the solute transfer involves an enthalpy change of less than 950 cal/kg of mixed liquids the effect of temperature fluctuations on the surface tension drive is negligible compared to the effect of the concentration fluctuations on the surface tension drive responsible for the Marangoni circulation.
4. Temperature fluctuations may affect the fluid motion because of their effect on density.

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EFFETS DES CHALEURS DE DISSOLUTION SUR LA CONVECTION DE MARANGONI

Résumé On étudie expérimentalement la circulation convective spontanée qui apparaît pendant le transfert instationnaire d'un soluté à travers un interface liquide-liquide et on recherche les effets possibles des variations latérales de température, le long de l'interface, provoquées par le changement d'enthalpie qui accompagne le transfert du soluté. La circulation convective est largement due à l'effet Marangoni sur l'écoulement piloté par la tension interfaciale. Une force supplémentaire active due à un gradient instable de masse volumique est présente dans quelques essais. Outre l'étude de 78 systèmes ternaires différents, des études détaillées sont faites pour deux d'entre eux, contenant en commun l'eau et l'acétate d'éthyle comme solvants partiellement miscibles. L'un concerne le transfert d'acide acétique en présence d'un écoulement de convection naturelle, l'autre système stable sous l'angle des forces d'Archimède est relatif au transfert d'alcool éthylique. Une caméra avec visualisation par une méthode stroboscopique enregistre les figures de convection autour d'un micro-thermocouple fixe situé à l'interface. Simultanément on enregistre la mesure instantanée et continue de la température en ce point. Des perturbations de température aussi élevées que $0,05^{\circ}\text{C}$ sont courantes et des valeurs atteignant $0,5^{\circ}\text{C}$ sont obtenues dans

quelques systèmes. Ceci n'affecte pas d'une façon sensible la tension interfaciale. Les clichés confirment qu'il n'existe pas une correspondance nette entre l'aspect de l'écoulement et l'enregistrement de la température. Ainsi la force contrôlant la tension de la surface peut provenir des perturbations de concentration et non des perturbations de température qui sont causées par les chaleurs de dissolution.

DER EINFLUSS VON LÖSUNGSWÄRMEN AUF DIE MARANGONI-KONVEKTION

Zusammenfassung—Die spontane konvektive Zirkulation, die während des instationären Übergangs eines gelösten Stoffes über die Grenzfläche zwischen zwei Flüssigkeiten einsetzt, wurde experimentell untersucht im Hinblick auf mögliche Temperaturschwankungen quer zur Grenzfläche, hervorgerufen durch Enthalpieänderungen, die mit dem Übergang des gelösten Stoffes verbunden sind. Die konvektive Zirkulation beruhte weitgehend auf dem Marangoneffekt oder auf der von der Oberflächenspannung verursachten Strömung. Eine zusätzliche treibende Kraft, die von einem instabilen Dichtegradienten herrührte, war bei einigen Versuchen vorhanden. Zusätzlich zur Untersuchung von 78 ternären Systemen wurden detaillierte Versuche ausgeführt an zwei Systemen, die Wasser und Äthylacetat als teilweise mischbare Lösungsmittel enthielten. In einem System fand der Übergang von Essigsäure unter Einfluss einer Auftriebskraft statt, im anderen der Übergang von Äthylalkohol ohne Einfluss von Auftriebskräften. Mit einer Filmkamera mit Schlierenbeleuchtung wurden die Strömungsbilder an der Lötstelle eines in der Grenzfläche fest angebrachten Mikrothermoelements aufgenommen. Gleichzeitig wurde mit einem schnellen Messgerät die Temperatur an dieser Stelle kontinuierlich aufgenommen. Temperaturschwankungen um 0.05°C waren üblich, in einigen Systemen traten Werte bis 0.5°C auf. Sie beeinflussten die Grenzflächenspannung in nicht spürbarer Weise. Der Film bestätigte, dass kein Zusammenhang bestand zwischen dem Strömungsbild und dem Temperaturverlauf. Die von der Oberflächenspannung verursachte Kraft muss also von den Konzentrationsschwankungen allein kommen und nicht von den Temperaturschwankungen, die von den Lösungswärmern herrühren.

ВЛИЯНИЕ ТЕПЛОТЫ РАСТВОРЕНИЯ НА КОНВЕКЦИЮ МАРАНГОНИ

Аннотация—Проведено экспериментальное исследование конвективной циркуляции, возникающей при нестационарном переносе растворенного вещества через границу раздела жидкость-жидкость в результате возможного бокового изменения температуры вдоль поверхности раздела, вызванного изменениями энталпии, сопровождающими перенос растворенного вещества. Конвекция, в основном, обусловлена эффектом Марангони, т.е. зависимостью поверхностного натяжения от температуры. В некоторых экспериментах имела место дополнительная движущая сила в результате неустойчивого градиента плотности. Исследовано 78 различных трехкомпонентных систем, кроме того проведено подробное исследование двух систем, содержащих воду и этилацетат в качестве частично смешивающихся растворенных веществ. В одной из этих систем происходил перенос уксусной кислоты при наличии подъемных сил; в другой исследовался перенос этилового спирта в механически равновесной системе. Конвективные потоки через спай неподвижной микротермопары, расположенной на поверхности раздела, фиксировались с помощью киносъемки с полосным освещением. Одновременно проводилось непрерывное высокоскоростное измерение температуры в этой точке. Температурные возмущения обычно достигали 0.05°C , а в некоторых системах 0.5°C . Они не оказывали существенного влияния на межфазовое натяжение. Киносъемка подтвердила отсутствие строгого соответствия между возникновением течения и изменениями температуры. Таким образом, сила поверхностного натяжения должна возникать в результате самих возмущений концентрации, а не температурных возмущений, вызванных теплотой растворения.