The Effect of Surface Phenomena on a Solvent Extraction Process

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SCOPE

Many correlations and data in the literature on the capacity of liquid-liquid extraction equipment are of doubtful general validity. Most of these were collected using saturated solvents or highly immiscible liquids with high interfacial tension. In either case the effects of interfacial phenomena are ignored or minimized, while in reality both extractor capacity and extraction rates can be markedly affected by strong surface phenomena resulting from mass transfer.

The present work resulted from an attempt to resolve seemingly inconsistent results obtained during the development of a solvent extraction desalination process using secondary and tertiary amines as solvents.

The desalination process was investigated in a bench-scale apparatus with packed and rotating disk extractors, and good but unspectacular column efficiencies were obtained. For instance, a 4-ft. section packed with ¼-in. Raschig rings gave about two and one-quarter stages. Based on these data, a 2,000-gal./day pilot plant was constructed employing mixer settlers in which 100% stage efficiencies were obtained even with the mixers turned off. Subsequent laboratory experiments in separatory funnels showed that a single rotation of the funnel followed by settling was usually sufficient to obtain equilibrium. To resolve the low rates obtained in a column with the very rapid extraction rates obtained in batch contact or in mixer settlers, it was decided to rerun the column data under conditions affording better control. Then extensive data were obtained on interfacial turbulence and drop coalescence as a function of the amine-water phase composition. It had been visually observed during many laboratory experiments that the amine-water system exhibited interfacial turbulence. Other interesting phenomena were also observed, such as a very intense dispersion resulting from minimum mixing especially with unsaturated phases. Yet when mixing ceased, very rapid coalescence occurred. It was known also from prior work that the interfacial tension was low so that the interphase phenomena might be extra sensitive to disturbances of mass transfer.

Although the coalescence studies were primarily intended to throw light on extractor performance, and did so, they represented the major contribution of this work. It has been generally reported that mass transfer out of the drop aids coalescence, but all data used for this conclusion were on systems in which the solute decreased interfacial tension. In the amine-water-salt system, salt increases interfacial tension. The results led to a detailed study of coalescence and clarification of the mechanism.

Included in this work was measurement of physical properties versus phase composition. These data are not of high absolute accuracy as no attempt at great precision was made, but their purpose is to show trends. Nearly every possible combination of phase compositions was investigated with respect to interfacial turbulence and the rate of drop coalescence. Again the techniques were crude, but the coalescence runs were repeated up to three times and were quite reproducible within the stated range of data.

SUMMARY

Extraction studies with a Scheibel column gave results similar to those previously obtained. It was impossible to realize high efficiencies with the solvent dispersed even though the dispersion was fine and the area large. Equal or better efficiency was obtained with water dispersed although the surface area of dispersed drops was much smaller. Much more power was required to disperse the water.

Studies of interfacial instability indicated that transfer of amine into unsaturated water produces eddies in the water phase while transfer of water into unsaturated amine produces no effect. The transfer of salt from the amine to water phase produced slight turbulence in the amine phase. The reverse transfer produced no effect.

Drop coalescence experiments indicated that the principal mechanism speeding or retarding coalescence during mass transfer is the effect of this transfer on film strength. It is shown that salt increases the interfacial tension of this system. The transfer of salt into the region between the drops retards coalescence while the reverse aids it. This is completely consistent with surface-tension effects, but is contrary to previous theories that stated that transfer of solute into the drop retarded coalescence. These researchers were misled in that in every case studied the solute reduced interfacial tension, while in the amine-sodium chloride-water system the reverse is true. Coalescence is also affected by the mutual solubility of the

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solvents. Increasing miscibility of solvents reduces interfacial tension and the transfer of the discontinuous phase into the region between the drops promotes coalescence.

No correlation was found between coalescence and interfacial instability. And surprisingly the tendency of the continuous phase film to dissolve in the dispersed phase was not particularly significant.

The high dispersion obtained in the column experiments with amine dispersed is confirmed by the drop experiments, corresponding to the case of salt transfer from amine drops to a continuous water phase. The poor efficiencies obtained with amine dispersed must be the result of backmixing caused by poor coalescence, as it has been demonstrated that equilibrium is rapidly approached in this system.

Satisfactory correlation of liquid-liquid extraction data is often frustrated by the sensitivity of the performance to interfacial phenomena. This can result from the effect of contaminants on the surface tension or by the formation of an additional resistance at the interface. Mass transfer itself may influence performance through interfacial turbulence or by large changes in coalescence rates. These phenomena, which are especially unpredictable, can alter the column holdup and flooding characteristics, the interfacial area, backmixing, and the mass transfer coefficient itself.

A very interesting case in point arose in the development of a solvent extraction method for desalination. In this process amines are used to extract fresh water from saline solutions. Some salt is also extracted and countercurrent extraction with extract reflux is generally required to produce a product of low salinity.

The process was investigated in a bench-scale apparatus employing packed and rotating disk extractors. The results were good, but unspectacular column efficiencies were obtained (*1*, *2*). Based on these results, a 2,000-gal./day pilot plant was constructed employing mixer settlers. It was found that 100% stage efficiency was obtained even with the mixers completely off (*3*).

Because of these results, some separatory funnel extractions were carried out in which solvent and water were mixed by slowly rotating the container an integral number of times. These data were obtained at different initial water concentrations in the solvent to see what effect the water transfer rate had on the salt transfer rate. Except for one rotation at the lowest initial water content, water saturation was closely approached; and except for one point salt saturation corresponding to the measured water content was approached.

This was surprising, for though the system exhibits interfacial instability to a marked degree at undersaturation of water, high rates at water saturation were not expected. Also, the low efficiencies obtained in the packed and rotating disk columns remained unexplained. The solvent was dispersed because this gave lower power consumption with the rotating disk column and better throughout in the packed column. In the pilot-plant mixers, the water was probably dispersed because of its lower volume, and definitely so in the settlers.

The research reported in this paper was undertaken in an attempt to answer the above questions, and to obtain more information on the process variables.

BENCH-SCALE EXTRACTION SYSTEM

The bench-scale extraction system used previously was modified. A Scheibel column was installed in the reflux section as it was suspected that backmixing was causing the low efficiencies, and it was hoped that this would be reduced by wire mesh sections between stages. Also, attention was focused on the reflux column because the solvent-to-water ratio and equilibrium salt distribution ratio are relatively constant in this section, which simplifies the calculation of the number of theoretical stages. The diisopropylamine solvent entering the reflux column had been previously saturated with water and had picked up some salt in the packed raffinate column. Product water was pumped to the top of the reflux column to extract salt from the diisopropylamine. The results of extraction in the reflux column are shown in Figure 1. Data were obtained with both phases dispersed at various revolutions per minute up to flooding. Several interesting observations were made during operation of this system: (1) The degree of dispersion, and thus the interfacial area, was very high with the solvent dispersed. (2) The dispersed solvent did not coalesce in the wire mesh sections of the Scheibel column. (3) With water dispersed, much more mixing was required to get a good dispersion; the degree of water dispersion never approached that obtainable with amine dispersed. (4) The water droplets coalesced rapidly in the wire mesh sections. (5) When the raffinate column was operated with solvent dispersed, a very fine dispersion was obtained at the bottom for about 6 in. above the fresh

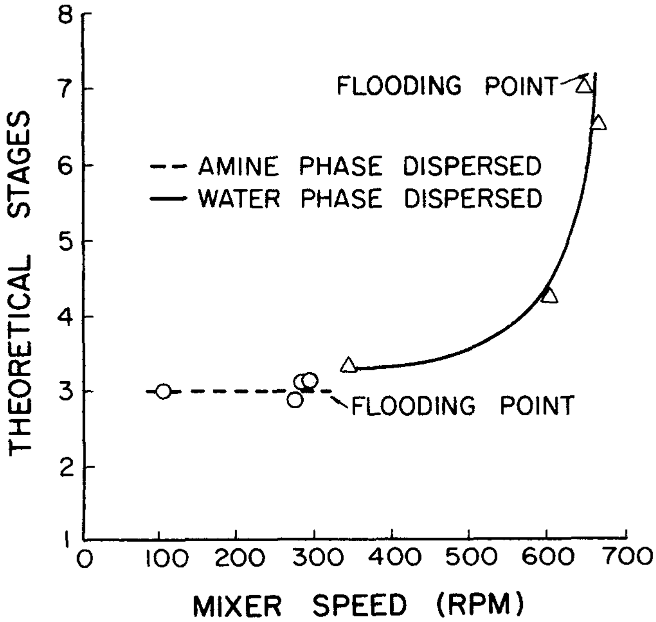

Fig. 1. Extraction efficiency in the Scheibel column at various mixer speeds.

solvent inlet. This, of course, was at a point of maximum unsaturation and mass transfer.

One further attempt was made to investigate mass transfer rates in the diisopropylamine-sodium chloride-water system. A hydrocyclone apparatus was constructed that allowed the amine-water phases to be contacted and separated in just a few seconds, but it was found that under all conditions the two phases emerged in equilibrium.

In view of the rapid mass transfer obtained in the hydrocyclone, the separatory funnel experiments, and the pilot-plant mixer sections, it is evident that the low efficiencies indicated in Figure 1 must result from backmixing. This is especially apparent with solvent dispersed, in which case the surface area is very large.

Observations indicate that this system exhibits interfacial instability, and the high dispersion at the column entrance indicates mass transfer effects on coalescence. Therefore these phenomena for this system were investigated in some detail.

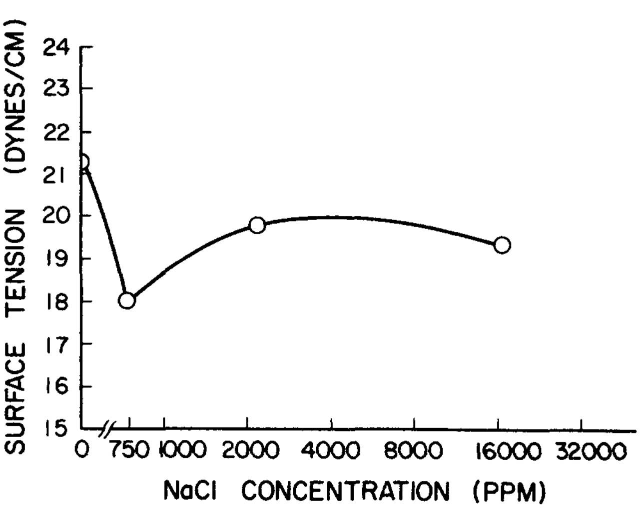

Fig. 3. Surface tension of diisopropylamine solutions (at 34°C) (amine in equilibrium with water containing the specified sodium chloride concentration).

INTERFACIAL INSTABILITY

These tests were made by placing gently a specially prepared diisopropylamine phase over a specially prepared water phase and observing what occurs at the interface. The water phase was either distilled water, distilled water saturated with amine, or 0.1, 1, or 3% sodium chloride, either with no amine or saturated with amine. The amine phase contained either 10% water or was saturated (about 30% water) and contained either no salt, 500, 1,000, or 2,000 p.p.m. The prepared phases were kept in a constant-temperature bath at about 33°C. prior to the experiments to eliminate thermal effects and to maintain saturation, which is very temperature sensitive.

One of the causes of interfacial turbulence has been demonstrated to be gradients in interfacial tension resulting from concentration gradients along the surface, the so-called Marangoni effect (*4* to *6*). The occurrence and intensity of the gradients in interfacial tension depend on the solvents and solute employed, upon solute concentrations, and upon the direction of solute transfer (*4*, *7*). Studies show that the interfacial disturbances subside in a closed system when the potential difference diminishes as thermodynamic equilibrium is approached (*7*, *8*). When interfacial turbulence is developed, the rates of convection differ in the two phases, usually [but not always (*9*)] being higher in the phase of greater kinematic viscosity (*7*). Consequently, changes in solute concentration at a point depend, in part, on the ratio of kinematic viscosities of the two phases and on the ratio of solute diffusivities of the two phases, since molecular diffusion alters the composition of each section of liquid as it is conveyed toward the interface, acting more strongly in the phase of higher diffusivity. Hence the effect of the disturbance is greater on the side of one of the phases, and the solute concentration is increased at a point in the other phase.

In the diisopropylamine-water-sodium chloride system two primary effects were consistently observed. If the water phase was initially free of amine, density eddies were visible in the water phase. If no salt was present, the amine phase showed no turbulence whether or not it was saturated with respect to water. In every case where there was salt transfer from the amine to the water phase, turbulence was present in the amine phase but unless there was a simultaneous transfer of amine into the water phase, the water phase was clear. In general transfer of salt from the water to the amine produced no effect, except in one instance at very low salt content a very slight turbulence was reported in the amine phase.

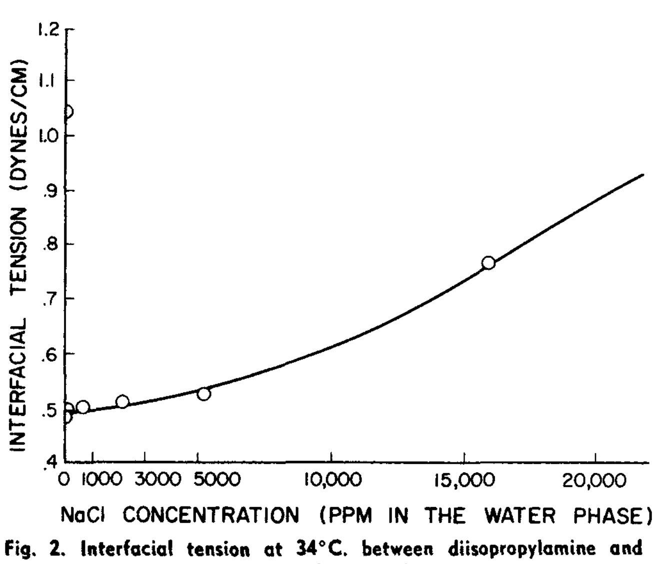

Fig. 2. Interfacial tension at 34°C. between diisopropylamine and water-sodium chloride solutions.

DROP BEHAVIOR

A number of tests were made to determine the effect of mass transfer on drop coalescence. The tests consisted of forming drops of the same solution at the end of two capillary tubes closely facing each other in a small beaker filled with the continuous phase (*11*). The rate of coalescence of the drops was observed. The results are given in Table 1. In addition, surface and interfacial tension measurements were made by the capillary rise method, and are given in Figures 2, 3, and 4. The angle of contact was not measured and a graduated scale rather than a cathetometer was used to measure the rise, so the values are probably more relative than absolute. Viscosity measurements were made of mutually saturated water and diisopropylamine phases at 32°C. The results are given in Figure 5. The measurements were made by observing the rates of flow through a capillary tube previously calibrated with water.

Much research has been done on drop behavior in re-

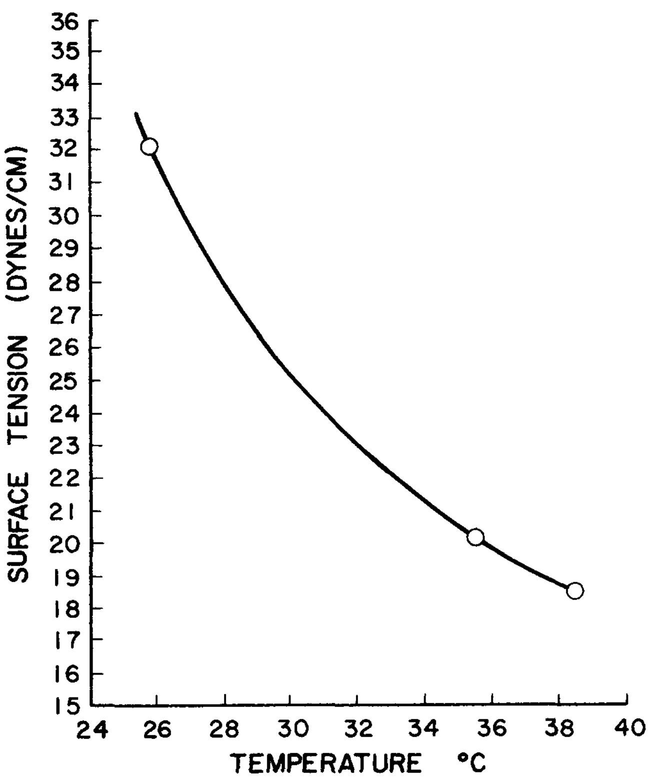

Fig. 4. Surface tension of water-saturated diisopropylamine as a function of temperature.

cent years, but little is actually known about the subject. There is very little in the way of generally accepted theory, especially with simultaneous mass transfer occurring. Each group of researchers seems to contradict other researchers. This discussion will attempt to cover most of the useful information on drop behavior in solvent extraction systems, even though all or most of what will be covered is far from accepted theory.

It has been observed (*12*) by some workers that with solute transfer from the dispersed to the continuous phase, 100 to 200% higher flooding rates are realized when compared with the reverse direction or when no solute is present. However, at least one worker has found the opposite to be true in certain cases (*13*). From these data it can easily be seen that flooding rates depend on the direction of mass transfer in some systems. Many researchers theorize that it is not the mass transfer, but the interfacial instability resulting from the mass transfer that causes the higher flooding rates to be realized.

In the Scheibel column (Figure 1), with the water phase dispersed, the flooding rate of the column is about 100% higher than when the amine phase is dispersed (the flooding rate depends on drop coalescence). It could be seen visually that the water phase had a very great tendency to coalesce and it took very high rotor speeds to keep the water phase dispersed enough to produce adequate surface area for high extraction rates.

There is some agreement that the coalescence rate is determined by interfacial tension and interfacial tension gradients (*11*), but there is disagreement on an explanation. The presence of interfacial turbulence is thought to promote drop coalescence in certain cases and to retard coalescence in others (*9*, *14* to *17*). Then, whether coalescence is promoted or retarded would apparently depend principally on the direction of mass transfer that causes interfacial turbulence (in systems that show interfacial turbulence). Workers (*11*, *15*, *17* to *19*) found that coalescence is promoted when solute transfer is out of the dispersed phase with either being dispersed.

Although the rates of coalescence shown in Table 1 varied with each case, two cases in which coalescence is strongly retarded were observed, that is, where solute is being transferred from the droplet phase. This is opposite from what would be predicted from similar tests in the literature (*11*, *15*, *17*, to *19*). Before attempting to explain these phenomena, one must consider the effect of various physical properties on the system.

A significant result of the interfacial tension measurements (Figure 2) is that interfacial tension increases with increasing salt content (except for zero salt content). This is opposite from most systems, but it is not completely unexpected since interfacial tension is usually found to increase with decreasing mutual solubility (*21*). The amine-water-salt system is a type of extraction system in which higher solute concentrations result in lower mutual solubilities. The opposite is true in most extraction systems. In the following discussion, the latter systems will be designated as type I systems and the former as type II.

The significant result of the viscosity measurements (Figure 5) is that the viscosity of the water phase increases with increasing salt concentration, while the viscosity of the amine phase decreases with increasing salt concentration.

The interfacial tests that were run show some density-type eddies in the water phase (just below the interface) when amine is being transferred to the water phase. This phenomenon could have some effect on the drainage of surface films (probably aiding drainage). Viscosity of the continuous-phase film certainly has an effect on the rate of film drainage (*22* to *24*). A low viscosity tends to aid film drainage. Temperature affects coalescence in the sense that it affects viscosity, interfacial tension, densities, probably critical thickness of the continuous film at which coalescence occurs, and probably most other variables. Density difference affects coalescence in the sense that it determines (in many cases) how hard the drops are pressed against each other, how fast drops rise or fall (which affects the thickness of surface films), and how fast the surface films drain. Salt concentration also has an effect in that it changes the physical properties of the system and may cause some film immobility.

By knowing how the physical properties vary, a coalescence theory consistent with the observed phenomena is found. Before explaining the theory, it is first necessary to understand how coalescence occurs. It is basically established that coalescence of drops occurs in five successive stages (*11*, *18*, *31*): (1) arrival of a drop at an interface; (2) mutual deformation of the drop and interface; (3) drainage of the continuous phase film which is trapped between the drop and interface; (4) rupture of the film at a certain critical thickness; and (5) deposition of the contents of the droplet into the bulk of the drop phase. The rate of drop coalescence for any particular liquid-liquid extraction system usually depends on the rate of drainage of the continuous-phase film surrounding the drops. The findings of this research suggest that the predominant factor in the drainage of continuous-phase films systems is the difference in interfacial tension produced over the surface of droplets.

By referring to Figure 6, one can see that when two interfaces approach each other (with mass transfer occurring either into or out of the droplet phase) the small volume of continuous phase between the interfaces quickly comes into equilibrium with the droplet phase. However, mass transfer continues to occur over the rest of the drops. This results in a different interfacial tension over the rest of the drops, since they now have a com-

TABLE 1. COALESCENCE RATES

Drop phase	Continuous phase	Coalescence rate	Temp., °C.	Salt concentration between drops	Effective mutual solubility between drops	Density eddies	Film tending to be dissolved
Amine	Salty water	Very rapid	32.0	Aids	Aids	No	No
Water	Salty amine	Very rapid	32.0	Aids	Aids	No	No
Pure water†	Salty amine	Very rapid	30.5	Aids	Aids	Yes	Yes
Salty amine	Pure water†	Very rapid	32.4	Retards	Aids	Yes	No
Pure water†	Salty 90% amine*	Rapid	31.0	Aids	Aids	Yes	Yes
Water	90% Amine*	Rapid	32.0	——	Aids	No	No
Pure water†	Amine	Rapid	31.0	——	?	Yes	Yes
Water	Salty 90% amine*	Rapid	31.0	Aids	Aids	No	No
Water	Amine	Rapid	31.0	——	——	No	No
Salty water	90% Amine	Fairly rapid	31.6	Retards	Aids	No	No
Pure salty water†	90% Amine*	Fairly rapid	32.7	Retards	Aids	Yes	Yes
Pure water†	90% Amine*	Fairly rapid	31.8	——	Aids	Yes	Yes
Salty water†	Amine	Fair	30.5	Retards	Retards	Yes	Yes
Amine	Salty water†	Fairly slow	33.0	Aids	Aids	Yes	No
Amine	Water	Fairly slow	33.0	——	——	No	No
Amine	Pure water†	Fairly slow	33.0	——	Aids	Yes	No
90% Amine*	Pure salty water†	Fairly slow	33.5	Aids	Retards	Yes	Yes
Pure amine†	Salty water	Fairly slow	30.8	Aids	Retards	No	Yes
90% Amine*	Salty water	Fairly slow	32.4	Aids	Retards	No	Yes
Salty 90% amine*	Water	Fairly slow	33.0	Retards	Retards	No	Yes
90% Amine*	Pure water†	Strongly retarded	33.5	——	Retards	Yes	Yes
90% Amine*	Water	Strongly retarded	33.0	——	Retards	No	Yes
Salty 90% amine*	Pure water†	Strongly retarded	33.0	Retards	Retards	Yes	Yes
Salty amine	Water	Strongly retarded	32.0	Retards	Retards	No	No
Salty amine	Amine	Strongly retarded	32.0	Retards	Retards	No	No

Approximation of coalescence rates

Very rapid	<0.1 sec.
Rapid	≈0.1 sec.
Fairly rapid	0.1 to 0.2 sec.
Fair	≈0.3 to 0.6 sec.
Fairly slow	0.3 to 0.6 sec.
Strongly retarded	1.0 to 3.0 sec.

Salt concentrations used

Parts per million weight (NaCl) on an amine-free basis
5,000 p.p.m. in the water phase
700 p.p.m. in the saturated amine phase
50 p.p.m. in the 90% amine phase

* 90% Amine contains 10% water versus approximately 30% at saturation.
† Pure means free of either water or amine.

position different from that of the part in contact with the other interface. If this difference in interfacial tension results in a smaller interfacial tension in the contact area of the two drops, the continuous-phase film between the drops will be pulled toward the back of the droplets, since the continuous-phase film is pulled toward areas of higher interfacial tension (*11*). The result is faster coalescence than would occur if mass transfer were not taking place. If the higher interfacial tension had occurred in the contact area between the drops, the continuous-phase film would have tended to be pulled into the contact area, resulting in a slower coalescence rate.

In reviewing the table of results of coalescence tests (Table 1), it is noticed that the first four columns contain experimental results, while the last four columns contain factors that might affect the rate of coalescence. One of these factors is salt concentration between drops, which can aid or retard drop coalescence. A higher salt content between drops (than over the rest of the drops) results in a higher interfacial tension in that area, which retards drop coalescence. This is due to the continuous-phase film being pulled toward areas of higher interfacial tension (between the drops). A lower salt concentration between drops results in aided coalescence. Another factor, effective mutual solubility between drops, affects coalescence in much the same way. It is found that increasing the mutual solubility of phases decreases the interfacial tension (*32*). The results are the same as when salt concentrations change the interfacial tension. As an example, consider amine-saturated water drops being coalesced in a 90% amine phase. As the water drops closely approach each other, the small amount of amine phase trapped between the drops quickly comes into equilibrium with the water drops. The amine between the drops then contains about 30 % water, while the amine surrounding the rest of

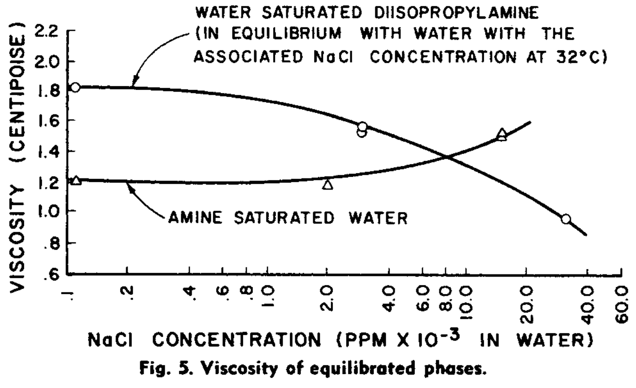

Fig. 5. Viscosity of equilibrated phases.

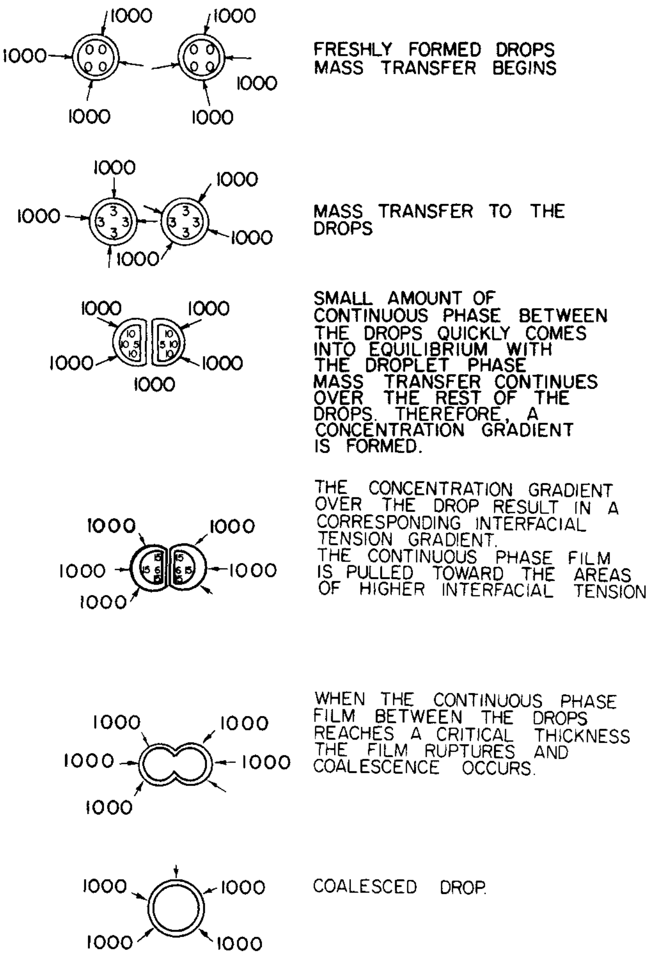

Fig. 6. Effect of interfacial tension gradients on drop coalescence.

the drops contains only 10% water. The effective mutual solubility between the drops is higher than over the rest of the drops; therefore a lower interfacial between the drops aid coalescence, since the continuous-phase films surroundings the drops are pulled toward the areas of higher interfacial tension. Density eddies are another factor that might affect coalescence by aiding in the drainage of interfacial films. In each test, it is noted if density eddies exist. The last factor listed in Table 1 is film tending to be dissolved. An example of this is when a small amount of water phase is trapped between two drops of unsaturated amine. The amine tends to quickly dissolve the small amount of water between the drops. This accelerates the thinning of the continuous-phase film, which promotes coalescence. In each test, it is noted if this effect occurs.

In evaluating the data in Table 1, it is necessary to consider all the cases where the droplet phase is water separately from the cases of amine droplets. The water phase on the average tended to coalesce more rapidly than did the amine phase, which makes it nearly impossible to compare water coalescence to amine coalescence on a case by case basis. After analyzing water and amine coalescence separately, it is then possible to compare the two on a relative basis.

Where very rapid coalescence occurs with the water drops, it is seen that both the salt concentration and the mutual solubility between drops aid coalescence (Table 1). When rapid coalescence occurs with the water drops, coalescence is either aided by one or both variables or not retarded. When only fairly rapid coalescence occurs, one case is aided by the mutual solubility effect and the other two cases are retarded by the salt concentration effect and aided by the mutual solubility effect. When only fair coalescence or strongly retarded coalescence occurs, coalescence is retarded by the salt concentration and mutual solubility effect. These cases are all in basic agreement with the theory that coalescence is dependent upon interfacial tension gradients in systems with mass transfer occurring. With the amine droplets, the results agree equally as well, except for the case of salty amine drops and pure water. Very rapid coalescence occurs in this case. Coalescence is retarded by the salt concentration effect and aided by the mutual solubility effect. The result of very rapid coalescence is unexpected. Slower coalescence than would occur with saturated amine drops and pure water (same system except for salt transfer) would be expected. No feasible explanation of this result has been found.

No significant relationship or trend between density eddies and drop coalescence can be found in the data in Table 1. The film tending to be dissolved effect is also found to have little or no effect on drop coalescence. Likewise, the absolute value of interfacial tension, which usually has a predominant effect on coalescence when no mass transfer is occurring, is found not to have a predominant effect when mass transfer is occurring.

It can be seen that mass transfer (water, amine, or salt) primarily affects coalescence in the sense that it causes differences in interfacial tension over the surfaces of drops. Of course, mass transfer can also cause interfacial turbulence in this system. It is the conclusion of these findings that interfacial instability or turbulence primarily affects coalescence in the sense that it accelerates mass transfer, which results in greater differences (than would occur without the instability) in interfacial tension over the surface of drops. Of course, interfacial instability could also affect the critical film thickness at which coalescence occurs and other properties to some extent (*6*).

In this research more than just the effect of solute transfer is evaluated. Tests were made at many conditions in an attempt also to establish the effects of amine transfer, water transfer, interfacial instability, interfacial tension, density eddies, and interfacial film dissolving. Never before have all these variables been evaluated. Only solute transfer, and sometimes interfacial tension and instability, are ever considered as being factors in drop coalescence by other works. All other variables are considered to have no effect. Workers (*11*, *14* to *18*) have suggested theories of drop coalescence, but none have proved their theories. Groothius and Zuiderweg (*11*) proposed the theory that coalescence rates are dependent upon interfacial tension gradients over drops, and ran coalescence tests that supported their theory. However, their evaluation only considered solute transfer and interfacial tension as having an effect on coalescence. It is far from a proof, since variables other than interfacial tension could also explain their observed phenomena. Neither did it disprove suggested theories by other workers. The other theories (*14* to *18*) are primarily explained with the aid of the Marangoni effect (interfacial instability or turbulence). The theories suggest that interfacial instability, which supposedly accompanies solute transfer out of drops but not into the drops, is the cause of the rapid coalescence rates observed when mass transfer is out of drops. The theories based on interfacial instability have only been suggested, rather than proved. Knowing what dramatic effects interfacial instability can have on a system, such suggested theories have appeared very feasible.

The research adds much to the proof of the theory proposed by Groothius and Zuiderweg (that coalescence, with mass transfer occurring, is primarily promoted or retarded by interfacial tension gradients over drops) and disproves other suggested theories. First, this research was done on a type II system. All other researchers have only studied type I systems. In the type II system, solute transfer into the droplet phase causes rapid coalescence. This, along with the fact that we found no correlation with interfacial instability, disproves the theories that suggest that solute transfer out of drops (being aided by interfacial instability) promotes coalescence. These theories cannot explain the rapid coalescence that occurs when solute transfer is into the droplet phase in a type II system. Second, an effort was made to determine the effect of all possible variables that might affect the rate of coalescence. This isolated the fact that coalescence is almost entirely dependent upon interfacial tension gradients in the system studied.

The results obtained from this system allow a good testing of possible coalescence theories. Perhaps one of the most fruitful results of this research is the simple fact that it brings out the role that type II systems can play in the future understanding of coalescence and liquid extraction.

From Figure 1 it can be seen that much higher stage efficiencies were obtained on the reflux column with the water phase dispersed than with the amine phase dispersed. A study of the literature (*21*) shows that low efficiencies in such columns are due to either axial mixing or limited mass transfer rates.

As concluded previously, mass transfer rates are very high and certainly not limiting if adequate mixing (interfacial area) is available. Therefore, with either the water or amine phase dispersed in the reflux column at the higher mixing rates (large interfacial area), it is concluded that near equilibrium exists in each mixing compartment.

It can be seen that only about 30% stage efficiencies were being obtained in the reflux column with the amine phase dispersed. These low efficiencies can only be accounted for by axial mixing effects.

In Table 1 it can be seen that when salt is being transferred out of amine drops, a slow rate of coalescence exists. This is the same case that we have with the amine phase dispersed in the reflux column. Due to the slow rate of coalescence, with the amine phase dispersed, the tremendous amount of interfacial area produced in the mixing compartments was also present in the wire mesh coalescing sections in the form of small uncoalesced droplets. The large interfacial area and the small droplets are very conducive to axial mixing, since the small droplets are easily affected by turbulent eddies. The large interfacial area ensures high mass transfer rates in axial direction for the axial mixing effects present. Therefore the low column efficiencies obtained in the reflux column with the amine phase dispersed are the result of the slow rate of coalescence of the amine droplets.

From Table 1 it is known that the water droplets coalesce much more rapidly than the amine droplets. Thus, one could predict that higher reflux column efficiencies would exist with the water phase dispersed. Higher efficiencies do exist. At the higher mixing rates, about 60% stage efficiencies are obtained. At the lower mixing rate the low efficiency obtained (about 30%) is due almost entirely to the lack of interfacial area produced in the mixing sections. This was visually observed. Also, it is the only logical conclusion since it has been established earlier that axial mixing increases with mixing rate.

The much smaller effect of axial mixing on the water phase, when dispersed, is entirely explained by the high coalescence rate of the water droplets. The rapid coalescence of droplets results in only a small interfacial surface area in the coalescing sections of the reflux column. The larger coalesced drops are less affected by axial mixing, and there is little interfacial area for mass transfer to occur.

These data do not completely explain the very high dispersion at the solvent inlet to the raffinate column. The results in Table 1 show only fairly slow coalescence for this case of unsaturated amine and salty water. This high dispersion might result from an extra rapid mass transfer rate caused by the low temperature of the solvent. This temperature difference could not be duplicated in the drop experiments.

ACKNOWLEDGMENT

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