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Froth-frothate Concentration Relations in Foam Fractionation

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Concentration relations between foams and their residual liquids (frothates) have been examined.

Clean air streams of 88, 91, and 96% water saturation were bubbled into aqueous solutions of isobutyl alcohol. The concentration of the alcohol in the collected and collapsed foam was plotted against its concentration in the bulk liquid.

Varying the saturation of the air stream resulted in both positive and negative enrichment of the foam with the surface-active alcohol. This suggests that where froth-frothate concentration relations are unfavorable, a change in operating conditions may advantageously affect these relations and allow the mixture to be foam separated.

Foam formation is often undesirable—for example, in stills, boilers, or fermenters. As a result, industrial study of foams has largely been directed toward (*a*) preventing their formation and (*b*) destroying them once formed. A foam, however, possesses qualities which can be usefully employed in certain instances. One of these is the fractionation of liquid mixtures.

Foaming may be used to separate the components of a homogeneous liquid mixture if one,—or more—of them is surface active. When such a liquid is formed, these components may be preferentially adsorbed in the foam layer (*froth*) and their concentration there will be greater than in either the residual liquid (*frothate*) or the original solution.

Foaming therefore offers a means of separating positively adsorbed substances from solutions the other components of which are adsorbed to a lesser degree. As such it deserves investigation for it may provide a convenient means of fractionating liquid mixtures, particularly those containing complex, heat-sensitive, and chemically unstable materials. In such cases the more conventional methods, like distillation and extraction, are frequently unsatisfactory.

A few examples of foam separation have been reported. These include the separation of ricinic acids from fatty acids (*2*), fractionation of fatty acids (*1*), and the purification of enzymes (*5*). Ore flotation (*7*), though apparently quite similar, involves a somewhat different principle in that the materials being separated are not present in a homogeneous single phase.

PRINCIPLES

Gibbs (*3*) formulated from thermodynamic considerations an adsorption equation predicting the surface excess of a solute which is in equilibrium with its bulk concentration. In modified form this relationship is

$$\Gamma = -\frac{a}{RT}\left(\frac{d\gamma}{da}\right) \tag{1}$$

where

Γ = excess solute per unit surface
a = solute activity
γ = surface tension of the solution
R = universal gas constant
T = absolute temperature

For sufficiently dilute solutions the mass concentration, x, may be substituted for activity and the equation becomes

$$\Gamma = -\frac{x}{RT}\left(\frac{d\gamma}{dx}\right) \tag{2}$$

Equation (1) says that if the solute is surface active—that is, if it lowers the surface tension of the solvent when added—it will concentrate in the surface layer. Conversely, a surface-inactive solute is negatively adsorbed (or "desorbed") and its concentration in the interior of the solution is therefore greater than at the surface. In any case, then, where the addition of solute to a solvent alters the surface tension of that solvent the surface layer of molecular depth will differ in concentration from the solution bulk.

In the work reported here, concentration relationships existing between foams and the bulk liquids from which they were formed have been measured by the rising-bubble technique. Solutions of isobutyl alcohol and water were studied and the results expressed in plots of alcohol concentration in the collected and collapsed foam (froth) vs. concentration in the residual liquid (frothate).

It is important to note that the rising-bubble method does not give equilibrium data. The values obtained are dependent upon the manner in which the bubbling apparatus is operated. Furthermore, in the case reported here the concentrations of froth and frothate were constantly changing, owing to the preferential evaporation of water by the entering air stream. Thus the data presented are for a particular arbitrary operating time (30 min.); longer or shorter periods would have given numerically different results. This point will be considered more completely in the discussion of the experimental data.

With this essential limitation of the rising-bubble technique recognized, it is still the simplest and most direct approach by far.

EXPERIMENTAL DETAILS

Filtered air was bubbled into isobutyl alcohol–water solutions in the apparatus shown in Figure 1. The resulting foam was collected, collapsed, and continuously returned to the solution to be refoamed. This method provides recirculation, making it possible to keep the bubble-retention time constant. If the foam were removed, retention time would continually decrease during the run period. *Retention time* is defined here as the total fluid volume

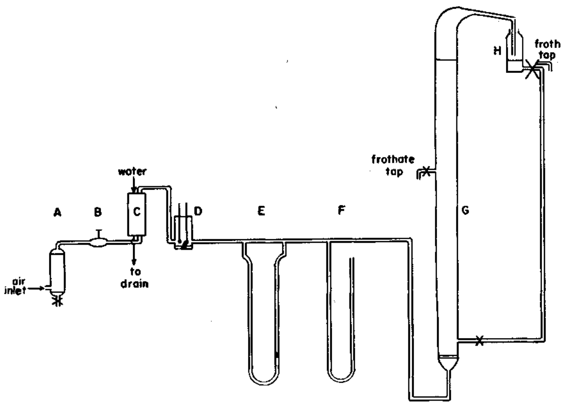

Fig. 1. Apparatus.

(liquid plus entrapped air) in the foaming chamber divided by the volumetric gas rate.

Apparatus

Dust in the air stream is removed in the filter *A*, which is packed with glass wool. A pressure regulator *B* maintains the liquid-foam interface in the column *G* at a constant height even if the pressure of the entering air stream should vary. Any degree of saturation of the inlet air stream may be obtained by varying the rate of flow of water trickling down the saturator *C* countercurrent to the rising air stream. This saturation column is a glass cylinder packed with ½-in. Raschig rings. A psychrometer *D*, with wet- and dry-bulb thermometers, permits the determination of the percentage of saturation of the air and a calibrated flow meter *E* and mercury manometer *F* indicate the rate of flow and static pressure of the air respectively.

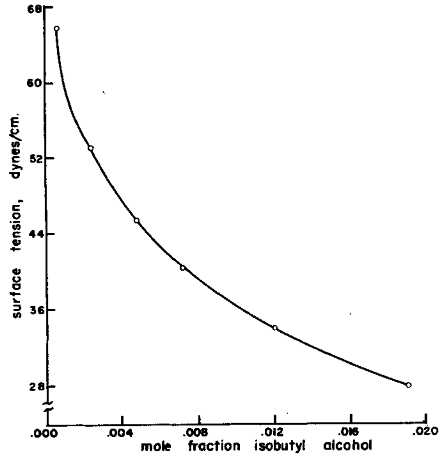

Fig. 2. Surface tension of aqueous solutions of isobutyl alcohol, 15°C.

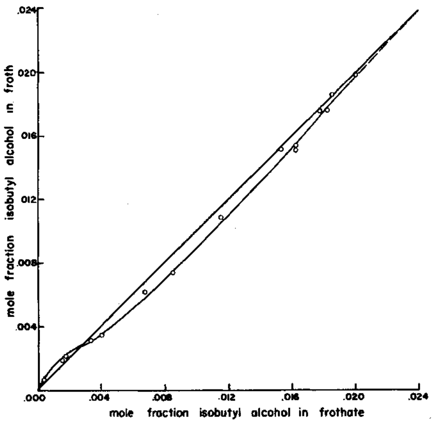

Fig. 3. Froth-frothate-concentration relations of isobutyl alcohol-water; air stream is 88% saturated at entrance.

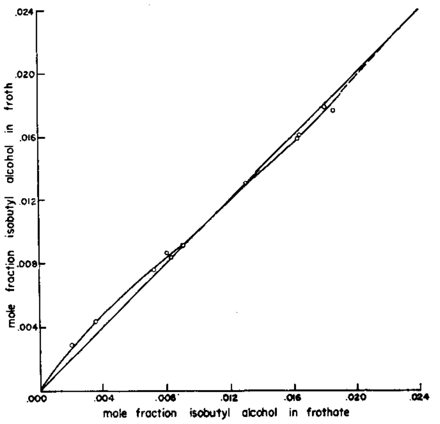

Fig. 4. Froth-frothate-concentration relations of isobutyl alcohol-water; air stream is 91% saturated at entrance.

The foaming column *G* has an inside diameter of 0.67 in. and a height of 47 in. A medium fritted-glass disk (capillary diameters: 10 to 15μ) at its base disperses the air in the solution, forming small bubbles of approximately ½-mm. diameter. An adapter leads the foam to the collecting chamber *H*, where it collapses. The resulting liquid is continuously recycled by gravity flow to the base of the column, where it is refoamed.

Procedure

Runs were made at 27°C. with solutions ranging in alcohol mole fraction from zero to concentrated solutions approaching the saturation value. The concentration curves are extrapolated to this latter value, for as the solutions approach saturation the foam persistence decreases sufficiently to prevent foam from being collected.

The air-stream velocity was kept constant during a given run to provide an average retention time of 3.6 min. for the air bubbles in the solution.

The humidity of the entering air could be varied in the saturation column *C* and measured in the psychrometer *D* before the foam column. Air streams of 88, 91, and 96% water saturation were used to note the effect of this variable. The degree of saturation of the air leaving the foam column was not measured. For the purposes of this study it was important only that it was equal to (unlikely) or greater than the entering value.

After the column was filled and the air rate adjusted, an arbitrary half-hour operating period was allowed before samples of froth and frothate (bulk liquid) were removed and analyzed for alcohol content with the Abbe refractometer.

RESULTS

Solution Surface Tensions

A surface-tension–concentration diagram for aqueous isobutanol solutions at 15°C. is shown in Figure 2. These data are taken from the literature (*4*) and show the trend even though the temperature is different from that used in the experiments reported here. Isobutyl alcohol is clearly surface active and, from the adsorption theorem [Equation (2)], adsorption should always be positive with the surface concentration exceeding that of the bulk.

Froth-frothate–concentration Relations

The froth-frothate-concentration relations actually obtained with the rising-bubble apparatus are tabulated (Table 1) and plotted in Figures 3, 4, and 5 for the different values used for air-stream saturation. They are obviously at least partially in disagreement with what one would expect from the Gibbs relationship (*1*).

The froth-frothate-concentration relations have been plotted here in the familiar y-x manner for convenience. They are not, of course, equilibrium curves, and the chosen method of plotting is not meant to imply this.

Since $d\gamma/dx$ is always negative, surface adsorption should never be zero or negative and the froth should always be richer in alcohol than the frothate. The runs reported were made randomly rather than by continuously increasing or decreasing the initial concentration. Thus the possibility that negative adsorption has been erroneously reported is discounted by the sizable negative adsorptions frequently observed and the continuous nature of the curves.

As a final check, a test of significance

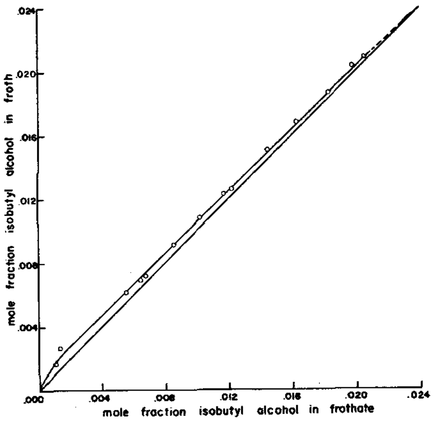

Fig. 5. Froth-frothate–concentration relations of isobutyl alcohol–water; air stream is 96% saturated at entrance.

was applied to the data of Table 1. This established the minimum difference between froth and frothate concentrations which must be equaled or exceeded before it may be said that a concentration change has actually taken place. At the 95% confidence level this difference is 0.00025 mole fraction of isobutyl alcohol. The data of Table 1 testify that significant differences in concentration between foam and residue did, in fact, occur.

Interpretation of Froth-frothate Curves

The apparent anomaly in these curves relating alcohol concentrations in froth and frothate is believed to be due to the preferential evaporation of water into the air stream during foaming. Evidently two processes were occurring during foaming. On one hand surface adsorption tended to concentrate alcohol in the foam "phase" as predicted. At the same time, however, preferential evaporation of water caused the alcohol concentration in the bulk liquid to increase. The actual froth-frothate–concentration relation observed depends on the relative rates of these two competing processes.

In dilute solutions $d\gamma/dx$, the slope of the surface tension curve (Figure 2), is large and the former effect, surface adsorption, is greater. Positive adsorption results, and froth alcohol concentrations exceed those in the frothate. As the solution concentration is increased, however, $d\gamma/dx$ decreases in absolute magnitude and adsorption falls off accordingly. At some point for each degree of air-stream saturation the two effects become equal and there is no apparent enrichment of the froth.

Support for the foregoing interpretation is afforded by the facts that the vapor pressure of water at 27°C. is twice that of alcohol and its mass transfer coefficient in air is about three times as large (*6*). A test to check this point was also made by bubbling unsaturated air through an alcohol-water solution in a bottle. After ½ hr. the alcohol concentration had increased from 0.005 to 0.00585 mole fraction.

Effect of Air-stream Saturation

If the previous interpretation is true, then the more completely saturated the air stream is with water vapor, the less will be the evaporation effect. As air-stream saturation increases, positive adsorption and alcohol enrichment of the foam should occur over a wider concentration range. This does in fact occur, as Table 1 and the curves show.

At very dilute concentrations foam enrichment results in all three degrees of saturation. As saturation increases, this enrichment is observed over a greater range of concentration before the adsorption effect is equaled by evaporation. When the air stream is least saturated (88%), zero and negative enrichment occur at a lower concentration than for higher saturations (91%). For the same reasons the degree of apparent "negative adsorption" observed at 88% saturation is greater than for 91%. When the air stream is 96% saturated (Figure 5), the adsorption effect seems to be always greater than evaporation, giving positive adsorption, or enrichment, over practically the entire concentration range.

The fact that varying saturation of the air stream permitted, in effect, both positive and negative adsorption of a surface-active agent, which should be only positively adsorbed, is extremely interesting. These results suggest that in cases where froth-frothate-concentration relations are unfavorable, alterations in operating conditions like temperature and the nature and degree of saturation of the gas with the solvent may propitiously affect these relations and permit the mixture to be separated by foaming.

Table 1.

Air-stream Moisture, % Saturation

88		91		96	
x	*y*	*x*	*y*	*x*	*y*
0.0004	0.0006	0.0021	0.00285	0.0011	0.0016
0.0016	0.00185	0.0036	0.00435	0.0014	0.0026
0.00185	0.0021	0.0073	0.0076	0.0056	0.0061
0.0034	0.0031	0.0081	0.0086	0.0065	0.00685
0.0041	0.0034	0.00835	0.00835	0.00685	0.0071
0.0088	0.0061	0.0091	0.0091	0.0086	0.0091
0.0086	0.00735	0.01305	0.01305	0.0103	0.0108
0.0116	0.0108	0.01635	0.0158	0.0118	0.0123
0.0154	0.0151	0.0165	0.01605	0.0123	0.0126
0.01635	0.0153	0.0181	0.01785	0.0145	0.01505
0.01635	0.01505	0.0186	0.0176	0.01635	0.0168
0.01785	0.0176			0.01835	0.0186
0.01835	0.0176			0.01985	0.02035
0.0186	0.0186			0.0206	0.0208
0.0201	0.01985				

x = mole fraction isobutyl alcohol in frothate.
y = mole fraction isobutyl alcohol in froth.

SUMMARY

A clean air stream of 88, 91, and 96% water saturation was bubbled into solutions of isobutyl and water. The resulting foam was collected, collapsed, and continuously returned to the solution to be refoamed. Runs were made at 27°C. for solutions ranging in concentration from 0 mole fraction alcohol to near saturation.

The concentration of the alcohol in the collected and collapsed foam was plotted against its concentration in the bulk liquid.

Varying the saturation of the air stream resulted in both positive and negative enrichment of the foam with the surface-active alcohol. This suggests that where froth-frothate–concentration relations are unfavorable, a change in operating conditions may advantageously affect these relations and allow the mixture to be foam separated.

ACKNOWLEDGMENT

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