Phase-Volume Relationship at the Point of Phase Inversion in Liquid Dispersions

GEORGE C. YEH, FRED H. HAYNIE, JR., and REX A. MOSES

Auburn University, Auburn, Alabama

The point of inversion of a water-in-oil type of dispersion to an oil-in-water type is investigated for several water-oil systems by studying the volume ratios of the phases in relation to their physical properties. The point of inversion for each system of an immiscible organic liquid and water and organic liquid mixture and water is obtained by varying the phase-volume ratios and determining the type of dispersion after complete mixing. The effects of temperature, interfacial tension, and density are found to have no correlation generally applicable to the systems studied. A volume-viscosity relationship is found to exist within limits. This correlation is that the phase-volume ratio at the point of inversion is equal to the square root of the ratio of the viscosities of the respective phases at the interface. The theoretical aspects of this relationship are studied along with its limitations.

The problem of making and breaking emulsions and mixing and separating dispersions has existed for many years in the chemical industry. Much research has been done regarding this problem, but in nearly every case a specific emulsion or dispersion was studied (*2*, *5*, *6*, and *14*). Only general qualitative statements have been made which apply to the problem as a whole (*6*). Phase inversion points of many emulsions have been determined, but they have been limited to the inversion of an existing dispersion to one of the opposite type (*10*, *12*, and *15*). Becher (*2*) determined the effects of various emulsifying agents on emulsion inversion. Davies (*5*) related emulsion type with coalescing rates. Schulman and Cockbain (*13*) specified that for an inversion from an oil-in-water to water-in-oil the interfacial film must possess considerable rigidity. Little if any work has been done to determine inversion points of liquids when the volumes of two separate liquid phases are first placed together and then mixed.

The phase inversion point is an important factor in the separation of two immiscible phases after an extraction or reaction because the stability of a dispersion is least at the point of phase inversion. On the other hand in the creation of emulsions the opposite effect is desired, so the point of inversion should be known in order to be avoided. Emulsions of an oil-in-water type may be more stable than those of a water-in-oil type; therefore the dispersed phase should be known. A theoretically based correlation relating inversion point with physical properties such as temperature, surface tension, density, and viscosity will greatly lessen the experimental work required to determine the phase inversion point of a particular system. The dispersed phase can also be determined without experimental analysis from such a correlation.

Since many factors including both static and dynamic properties of a system aside from phase-volume ratio may cause the phase inversion, the point of phase inversion may be defined in many different terms or ways. (For instance the intensity of agitation and the order in which the fluids are introduced into a vessel can determine the type of dispersion produced. When liquid *A* is poured into liquid *B* which is being strongly agitated, the part of liquid *A* which comes to contact with liquid *B* will be dispersed by agitation and then enveloped by liquid *B* surrounding it; thus a dispersed phase of liquid *A* is formed. Also, depending on the agitation speed, the relative importance of both viscous and inertia forces in their roles in determining the type of dispersion is different. This experimental work has been carried out with definable flow fields often laminar under noncoalescing conditions or at least under conditions in which the effect of coalescence is very small.) In this work the point of phase inversion is defined as the volume percent of the dispersed phase for a system (for example water-in-oil) in which inversion occurs (for example to oil-in-water) upon complete mixing of the system after an infinitesimal change in the phase-volume ratio has been made.

THEORETICAL CONSIDERATION

Traditionally theoretical studies on the phase-volume relationship at the point of inversion have been with regard to static forces, namely surface tension, density difference, geometry, etc. For example if other forces were not present, surface tension would cause inversion at 50% by volume. The maximum volume percent of the dispersed phase has been calculated to be 74.02%. The theory behind this value is that if the dispersed phase is made up of uniform spheres, coalescence occurs when the diameters are such that the spheres must touch. The closest packing is observed when spheres at the corners of a regular tetrahedron have diameters equal to the edges of the tetra-

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George C. Yeh is at Villanova University, Villanova, Pennsylvania.

hedron. Clayton (4) starts out with this fact, but in an effort to convert to cubic units he changes to a hexagonal close-packed system by limiting the spheres to lie in planes. These calculations resulted in the 74.02% maximum dispersed volume. In actuality higher percent volumes can be obtained because the dispersed phase is not limited to uniform spheres.

Dispersions are formed by mixing, which is a dynamic situation. Thus it would be expected that dynamic forces should play a major part in determining the type of dispersion which occurs. Bird, Stewart, and Lightfoot (3) have discussed the velocity distribution of two adjacent flows of two immiscible fluids. Their problem can be modified to apply to the point of inversion.

Two immiscible liquids α and β are flowing in a thin slit of length L and width W under the influence of a pressure gradient Δp. The liquid rates are so adjusted that the shear at the interface is zero (no tendency to mix or create a new surface, true at point of inversion). It is desired to get the volume ratio of the two liquids, in this case the ratio of the liquid thicknesses since the length and width are the same. The differential equations resulting from momentum balances in phases α and β are

$$\eta^{\alpha}\frac{d^2 u_z^{\alpha}}{dX^2} = -\frac{\Delta p}{L} \qquad (1)$$

$$\eta^{\beta}\frac{d^2 u_z^{\beta}}{dX^2} = -\frac{\Delta p}{L} \qquad (2)$$

Equations (1) and (2) integrate to give

$$u_z^{\alpha} = -\frac{\Delta p\, X^2}{2\,\eta^{\alpha} L} + C_1^{\alpha} X + C_2^{\alpha} \qquad (3)$$

$$u_z^{\beta} = -\frac{\Delta p\, X^2}{2\,\eta^{\beta} L} + C_1^{\beta} X + C_2^{\beta} \qquad (4)$$

Let X be zero at the interface and the thicknesses of phases α and β be a and b respectively. The following boundary conditions would then be true at the point of inversion:

1. Liquid α is in contact with the upper surface; hence $u_z^{\alpha} = 0$ at $X = a$.
2. Liquid β is in contact with the lower surface; hence $u_z^{\beta} = 0$ at $X = -b$.
3. Both liquids have the same velocity at the interface; hence $u_z^{\alpha} = u_z^{\beta} = u_{\max}$ at $X = 0$.
4. At the point of inversion a momentum balance exists between the two phases, and the momentum transfer at the interface is zero; hence $\eta^{\alpha}\frac{du_z^{\alpha}}{dX} = \eta^{\beta}\frac{du_z^{\beta}}{dX} = 0$ at $X = 0$.

If these boundary conditions are applied, the following relationship results:

$$C_2^{\alpha} = \frac{\Delta p\, a^2}{2\,\eta^{\alpha} L} = C^{\beta}{}_2 = \frac{\Delta p\, b^2}{2\,\eta^{\beta} L} \qquad (5)$$

$$\frac{a}{b} = \sqrt{\frac{\eta^{\alpha}}{\eta^{\beta}}} \qquad (6)$$

It must be remembered that this relationship only applies to the ratio of volumes which are flowing.

It may be assumed that the correct viscosity ratio would be that of the interfacial viscosities, which are different from bulk viscosities owing to preferential adsorption of certain components at the interface. An approximate calculation of interfacial viscosities may be made from interfacial compositions which can be determined as shown below.

In a system at equilibrium and constant pressure and temperature the Gibbs adsorption equation is given by

$$d\sigma = -\Gamma_1\, d\mu_1 - \Gamma_2\, d\mu_2 \qquad (7)$$

The Gibbs-Duhem equation for any phase is $\Sigma N_r\, d\mu_r = 0$ for r components. For a binary system

$$N_1\, d\mu_1 + N_2\, d\mu_2 = 0 \qquad (8)$$

The authors shall treat the system under investigation as did Guggenheim (6) as consisting of two bulk phases α and β and an interfacial phase γ, each of which has mass, volume, composition, and free energy. The boundaries of phase γ must be drawn so that the transition from phase α to phase β takes place entirely within phase γ; otherwise there are no restrictions in the general case on their positions. It is also assumed that both α and β phases remains sensibly constant in composition up to the boundaries. Figure 1 shows the assumed graphic representation of compositions in the three phases α, β, and γ.

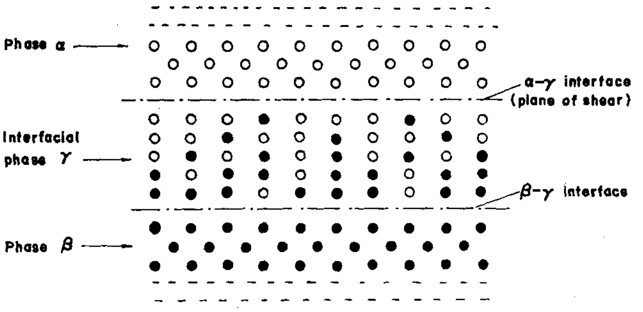

Fig. 1. Graphic representation of composition of phases α, β, and γ.

Letting component 1 be the oil and 2 the water, and phase α the bulk oil phase and phase β the bulk water phase, one has

$$d\sigma^{\alpha} = -\Gamma_1^{\alpha}\, d\mu_1 - \Gamma_2^{\alpha}\, d\mu_2 \qquad (9)$$

$$d\sigma^{\beta} = -\Gamma_1^{\beta}\, d\mu_1 - \Gamma_2^{\beta}\, d\mu_2 \qquad (10)$$

where

$\Gamma_1^{\alpha} = n_1^{\gamma} - n_1^{\alpha}$
$\Gamma_2^{\alpha} = n_2^{\gamma} - n_2^{\alpha}$
$\Gamma_1^{\beta} = n_1^{\gamma} - n_1^{\beta}$
$\Gamma_2^{\beta} = n_2^{\gamma} - n_2^{\beta}$

In a binary system in which the solubility of component 1 in phase β and of component 2 in phase α may be assumed negligible $n_2^{\alpha} = 0$ and $n_1^{\beta} = 0$, and

$\Gamma_1^{\alpha} = n_1^{\gamma} - n_1^{\alpha}$
$\Gamma_2^{\alpha} = n_2^{\gamma}$
$\Gamma_1^{\beta} = n_1^{\gamma}$
$\Gamma_2^{\beta} = n_2^{\gamma} - n_2^{\beta}$

Substituting these relations into Equation (9) and dividing by n_t^{γ}, the total number of moles in phase γ, one obtains

$$\frac{d\sigma^{\alpha}}{n_t^{\gamma}} = \left(\frac{n_1^{\alpha}}{n_t^{\gamma}} - \frac{n_1^{\gamma}}{n_t^{\gamma}}\right) d\mu_1 - \frac{n_2^{\gamma}}{n_t^{\gamma}}\, d\mu_2 \qquad (11)$$

or

$$\frac{d\sigma^{\alpha}}{n_t^{\gamma}} = \left(\frac{n_1^{\alpha}}{n_t^{\gamma}} - N_1^{\gamma}\right) d\mu_1 - N_2^{\gamma}\, d\mu_2$$

Combining Equation (8) with the above equation one gets

$$d\sigma^{\alpha} = n_1^{\alpha}\, d\mu_1 \qquad (12)$$

Similarly from Equation (10)

$$d\sigma^{\beta} = n_2^{\beta}\, d\mu_2 \qquad (13)$$

From Equation (8) for phase α, $du_2 = -\frac{N_1^{\gamma}}{N_2^{\gamma}}\, d\mu_1$.

Therefore

$$d\sigma^{\beta} = -\, n_2^{\beta} \frac{N_1^{\gamma}}{N_2^{\gamma}}\, d\mu_1 \qquad (14)$$

Since n_2^{β} and n_1^{α} occupy the same volume as phase γ, then

$$V_2 n_2^{\beta} = V_1 n_1^{\alpha} = \text{volume of phase } \gamma$$

where V is the molal volume. Rearranging this relationship one obtains

$$n_2^{\beta} = \frac{V_1}{V_2}\, n_1^{\alpha} \qquad (15)$$

Combining Equations (12), (14), and (15) one gets

$$\frac{d\sigma^{\alpha}}{d\sigma^{\beta}} = -\frac{V_2}{V_1}\frac{N_2^{\gamma}}{N_1^{\gamma}} \quad \text{or}$$

$$d\sigma^{\alpha} = -\frac{V_2}{V_1}\frac{N_2^{\gamma}}{N_1^{\gamma}}\, d\sigma^{\beta} \qquad (16)$$

To facilitate integration of Equation (16) the ratio $(N_2^{\gamma})/(N_1^{\gamma})$ is considered to be constant. This is true because phase γ is so defined that the complete transition from phase α to phase β must take place within phase γ. The surface tension limits to be used in performing the integration of Equation (16) may be established as follows. Consider phase β (that is water phase saturated with oil) to be poured into a flask containing phase α (that is oil phase saturated with water). After equilibrium between the oil and water is reached, the surface tension of phase α will have changed from σ^{α} (that is surface tension against air) to $\sigma^{\alpha\beta}$ (that is the interfacial tension of the oil against water).

Since the changes in surface tension $d\sigma$ in Equation (16) are the measures of free energy changes over unit area which result because of adsorption, the limits of integration must include only surface tension changes which are associated with adsorption. It may be assumed that none of the free energy F_s consumed in spreading the oil phase over the water was associated with adsorption. When F_s is positive, one may assume that F_s comes from the surface free energy of the β phase which has the greatest free energy. Accordingly the change in surface tensions attributed to adsorption at the surface of phase β is from $\sigma^{\beta} - F_s$ to $\sigma^{\alpha\beta}$. However the change is in the opposite direction compared with that of phase α, so the limits of integration should be reversed.

Thus integrating Equation (16) at constant temperature and pressure between the limits one gets

$$\int_{\sigma^{\alpha}}^{\sigma^{\alpha\beta}} d\sigma^{\alpha} = -\frac{V_2}{V_1}\frac{N_2^{\gamma}}{N_1^{\gamma}} \int_{\sigma^{\alpha\beta}}^{\sigma^{\beta}-F_s} d\sigma^{\beta}$$

$$\sigma^{\alpha\beta} - \sigma^{\alpha} = -\frac{V_2}{V_1}\frac{N_2^{\gamma}}{N_1^{\gamma}} (\sigma^{\beta} - \sigma^{\alpha\beta} - F_s) \qquad (17)$$

Since $F_s = \sigma^{\beta} - \sigma^{\alpha} - \sigma^{\alpha\beta}$ for the preferential adsorption of molecules at the interface, Equation (17) reduces to

$$\frac{\sigma^{\alpha\beta} - \sigma^{\alpha}}{\sigma^{\alpha}} = -\frac{V_2 N_2^{\gamma}}{V_1 N_1^{\gamma}} \quad \text{or}$$

$$\frac{\sigma^{\alpha} - \sigma^{\alpha\beta}}{\sigma^{\alpha}} = \frac{V_2 N_2^{\gamma}}{V_1 N_1^{\gamma}} \qquad (18)$$

Substituting $N_1^{\gamma} + N_2^{\gamma} = 1$ into Equation (18) one obtains

$$\frac{\sigma^{\alpha} - \sigma^{\alpha\beta}}{\sigma^{\alpha}} = \frac{V_2 N_2^{\gamma}}{V_1 (1 - N_2^{\gamma})} \qquad (19)$$

If $(\sigma^{\alpha} - \sigma^{\alpha\beta})/(\sigma^{\alpha})$ is negative, there should not be any adsorption at the interface, and both phases are pure. Experimental data show that N_2^{γ} should be considered as unity in such cases. N_1^{γ} and N_2^{γ} can be calculated from Equation (19).

There are a number of methods of estimating viscosities of liquid mixtures from the compositions and viscosities of pure components, but these methods require viscosity data for at least one composition of the mixture. Such data are not available for immiscible mixtures of oil and water, namely phase γ. Errors to be expected in predicting viscosities of chemically dissimilar liquid mixtures with Lima's equation are very great, since the method is good only for mixtures composed of chemically similar materials (*11*). An approximation of the viscosity of phase γ can be made by using the following equation:

$$\log\frac{1}{\eta_{\text{mix}}} = N_1 \log\frac{1}{\eta_1} + N_2 \log\frac{1}{\eta_2} + \ldots N_r \log\frac{1}{\eta_r} \qquad (20)$$

Since Equation (6) is based on the square root of the ratio of the viscosities at the plane of shear, the plane of shear must be found. The energy required to separate or shear two layers of liquid is equal to the work of adhesion; thus shear under flow conditions should take place at the interface which has the least work of adhesion. The work of adhesion is equal to the sum of the surface tensions of both phases less the interfacial tension. Therefore the work of adhesion should be least at the $\alpha - \gamma$ interface, since the surface tension of the α (that is oil) phase is usually much less than that of the β (that is water) phase. Thus in calculating the volume ratios of water to oil in Equation (6) η^{β} should be replaced by η^{γ}. Thus Equation (6) becomes

$$\frac{a}{b} = \sqrt{\frac{\eta^{\alpha}}{\eta^{\gamma}}} \qquad (6a)$$

However in a case where the solute is a highly surface active agent small quantities dissolved in the water phase may lower the surface tension of that phase to the point that shear will take place at the $\beta - \gamma$ interface. Multiple inversions, as experienced by Becher (*2*) while using surface active agents, may possibly be caused by a shift in the plane of shear from the $\alpha - \gamma$ interface to the $\beta - \gamma$ interface or vice versa.

Calculations of interfacial compositions for ternary systems are more complicated than for binary systems. The free energy changes of adsorption depend upon surface area changes for each component. For the binary systems the interfacial area covered by components 1 and 2 were assumed to remain constant in a unit interfacial area.

For a ternary system the change in free energy of the surface of component 1 upon adding water is given by

$$\sigma^{\alpha\beta} A_{i1} - \sigma^{\alpha} A_1 \qquad (21)$$

A portion of this free energy change is consumed in changing the area occupied by component 1 from A_1 to A_{i1}. This is equal to $(A_{i1} - A_1)\,\sigma^{\alpha\beta}$. Thus the free energy change of component 1 attributed to adsorption, that is $\Delta\sigma_1^{\alpha}$, is equal to

$$\Delta\sigma_1^{\alpha} = \sigma^{\alpha\beta} A_{i1} - \sigma^{\alpha} A_1 - (A_{i1} - A_1)\,\sigma^{\alpha\beta}$$

or

$$= A_1 (\sigma^{\alpha\beta} - \sigma^{\alpha}) \qquad (22)$$

Similarly for the solute

$$\Delta\sigma_s^{\alpha} = A_s (\sigma^{\alpha\beta} - \sigma^{\alpha}) \qquad (23)$$

Adsorption of component 1 should go from the surface of that component into phase γ, although the surface specified by A_{i1} will be included in phase γ. To simplify the calculations for the interfacial composition phase γ will be considered to consist of two portions, that is a portion under the area occupied by component 1, the composition of which depends upon the adsorption of component 1, and a second portion determined by adsorption of solute from the interfacial area occupied by the solute. The overall composition of phase γ can then be calculated from the composition of the two portions.

From the equations derived for the binary system one can calculate the composition of phase γ under the area occupied by component 1, if the area occupied against the vapor phase is known. The corresponding equation of Equation (19) becomes

$$\frac{A_1\,(\sigma^{\alpha}-\sigma^{\alpha\beta})}{\sigma^{\alpha}}=\frac{V_2\,N^{\gamma}{}_{21}}{V_1\,(1-N^{\gamma}{}_{21})} \tag{24}$$

where $N^{\gamma}{}_{21}$ is the mole fraction of water in phase γ under the area occupied by component 1. Similarly the composition of phase γ under the area covered by the solute is given by

$$\frac{A_s\,(\sigma^{\alpha}-\sigma^{\alpha\beta})}{\sigma^{\alpha}}=\frac{V_2\,N^{\gamma}{}_{2s}}{V_s\,(1-N^{\gamma}{}_{2s})} \tag{25}$$

where $N^{\gamma}{}_{2s}$ is the mole fraction of water in phase γ under the area covered by solute s.

An assumption concerning the area occupied by the solute at the vapor-phase surface was made based on the following considerations. Schulman (*13*) has indicated three types of effects of surface active molecules injected beneath a monolayer. If there is no association between polar groups of the film forming molecules, there will be no change in film characteristics. If the polar head groups associate, but there is no association between tails, then there is adsorption of surface active molecules under the film but no increase in surface pressure. It is assumed that the molecules of solute used, which were strongly adsorbed at the water interface but dissolved readily in the solvent, will have little or no association with the solvent molecules. Thus, considering that in this experiment the concentrations of solute used in the oil phases were small, one may assume that the surface areas covered by the solute molecules at the vapor-phase interface will be very small and the surface tension will evidence little or no change.

After the compositions of the two portions of phase γ have been calculated by use of Equations (24) and (25), the overall compositions of phase γ can be calculated, provided that the areas occupied by each component at the interface are known. Assuming a monolayer at the $\alpha-\beta$ interface Hutchinson (*8*) calculated the compositions from freezing point depressions of solution and surface tension changes of a number of ternary systems using the following equation:

$$\Gamma_s{}^{(1)}=\frac{N_s}{N_o}\,\frac{T_o{}^2}{LT}\,\frac{d\sigma}{d\theta} \tag{26}$$

Also the following relations were given:

$$A_{is}\,\Gamma_s{}^{(n)}+A_{io}\,\Gamma_o{}^{(n)}=1 \tag{27}$$

$$\Gamma_s{}^{(N)}=N_s\,\Gamma_s{}^{(n)}-N_s\,\Gamma_o{}^{(n)} \tag{28}$$

$$\Gamma_s{}^{(N)}=N_o\,\Gamma_s{}^{(1)} \tag{29}$$

By assuming an area per solvent molecule as given by Adam (*1*) for various organic liquids against water the interfacial area occupied by solvent can be calculated from Equation (27). When one knows the areas occupied by each component at the interface, the overall compositions of phase γ can be calculated as

$$n_1{}^{\gamma}\,V_1+n^{\gamma}{}_{21}\,V_2=A_{i1}\,x \tag{30}$$

$$n_2{}^{\gamma}\,V_2+n^{\gamma}{}_{2s}\,V_2=A_{is}\,x \tag{31}$$

where x is the thickness of interfacial phase γ. Also

$$\frac{n^{\gamma}{}_{21}}{n_1{}^{\gamma}+n^{\gamma}{}_{21}}=N^{\gamma}{}_{21} \tag{32}$$

$$n^{\gamma}{}_{21}\,(1-N^{\gamma}{}_{21})=n_1{}^{\gamma}\,N^{\gamma}{}_{21} \tag{33}$$

$$n^{\gamma}{}_{21}=n_1{}^{\gamma}\,\frac{N^{\gamma}{}_{21}}{1-N^{\gamma}{}_{21}} \tag{34}$$

$$n^{\gamma}{}_{2s}=n^{\gamma}{}_{s}\,\frac{N^{\gamma}{}_{2s}}{1-N^{\gamma}{}_{2s}} \tag{35}$$

Thus all four quantities $n_1{}^{\gamma}$, $n^{\gamma}{}_{21}$, $n_s{}^{\gamma}$ and $n^{\gamma}{}_{2s}$ can be calculated in terms of interfacial phase thickness x. The mole fractions can then be calculated from Equation (32) and corresponding equations for the other components with the interfacial phase thicknesses cancelling.

EXPERIMENTAL WORK

Accurate volume measurements were made by measuring the liquids with 50-ml. burrettes. A known quantity of both organic liquid and distilled water was added into a flask. After the system was adjusted to the right temperature, a cork stopper was placed in the mouth of the flask. The flask was then shaken vigorously by hand, and the dispersed phase was visually observed. The mode of shaking was similar to that described by Cheesman and King for O/W emulsions (*16*).

Oil dispersed in water gave globules with a shiny surface as opposed to water dispersed in oil which gave dull opaque bubbles. In most cases the dispersed phase can be determined by watching the process of coalescence. After mixing is stopped, the phases begin to separate, and the dispersion remains between the two clear layers. The phase in which the dispersed droplets break is the dispersed phase. In a few cases the dispersed phase cannot be determined by the above method because the size of the dispersed particles is so small that coalescence is very slow. In these instances a drop of the dispersion is placed in water. If the drop does not break up, the dispersed phase is water. If it does break up, the dispersed phase is oil. After the dispersion broke down, this procedure was repeated twice in order to insure that equilibrium has been established. Upon determining the dispersed phase several milliliters of that phase were added and the above procedure repeated. Gradually the volumes in the flask were brought closer to the ratio at the phase inversion point until one drop of one liquid gave a phase inversion, where one drop from the burrette used corresponds to 0.05 ml. Therefore this ratio is not the actual phase-volume ratio at the inversion point but the ratio based on the total composition of the system.

In this study surface tension and interfacial tension data for the pure components used in synthesizing various systems were taken from the International Critical Tables (*9*) and from Hutchinson's work (*8*), and viscosity and density data necessary for calculating molal volumes were found in the Handbook of Chemistry and Physics (*7*). Viscosities when not available at the desired temperature were either estimated from viscosities at other temperatures or measured with a viscometer. For all the ternary systems investigated the relative phase viscosities of organic oil mixtures were measured with a modified viscometer.

The experimental results along with the theoretically predicted values from Equations (6) and (6*a*) for the volume percent of water at the point of phase inversion are listed in Tables 1 and 2. For the ternary systems investigated two concentrations of *n*-octyl alcohol in cyclohexane vs. water system and three concentrations of the solutes in all other systems were used. For those experiments conducted in binary systems at the temperatures for which the surface tension data

Table 1. Phase Inversion Data for Various Binary Systems

Systems vs. water	T, °C.	N_2^γ	η^γ	η^α	Volume % water by Equation (6a)	Exp'l. data	Equation (6)
Nitrobenzene	25	0.697	1.107	1.81	43.8	46.3	41.1
	27			1.75		46.8	41.1
Benzene	25	1.00	0.894	0.604	54.9	55.5	55.0
	27			0.59		55.3	54.8
Cyclohexanol	16	0.838	22.902	86.1	14.0	25.0	10.2
	29			30.0		17.9	14.2
	42			18.0		18.3	15.8
Aniline	20	0.836	1.323	4.4	35.4	37.5	32.3
	26			3.65		31.1	32.9
Carbon tetrachloride	20	1.00	1.008	0.969	50.5	50.5	50.5
Chlorobenzene	20	1.00	1.008	0.799	52.9	53.2	53.0
Ethyl ether	20	0.686	0.638	0.235	62.2	66.2	67.5
Benzaldehyde	20	0.775	1.083	1.39	46.8	47.4	46.0
Anisole	20	0.616	1.117	1.32	47.9	49.5	46.5
Oleic acid	20	0.908	1.388	32.8	17.0	45.6	14.9
n-caprylic acid	23	0.850	1.219	5.45	32.1	33.0	29.3
n-octyl alcohol	25	0.855	1.210	7.21	29.0	43.7	26.5
Xylene	26			0.58		57.2	55.2

are not available in the literature no attempt was made to correlate the interfacial viscosity with the liquid volume of the systems.

DISCUSSION OF RESULTS

When the bulk-phase viscosities of liquids were used in predicting the phase inversion point by Equation (6), the agreement between theoretical and experimental values was good for many systems but rather poor for the systems such as water-cyclohexanol, water-oleic acid, water-*n*-octyl alcohol, and most of the ternary systems investigated. It is believed that a type of momentum diffusion occurs resulting in the least viscous component of the mixture concentrating at the interface, as discussed above. When one uses the interfacial viscosity rather than the bulk-phase viscosity as shown by Equation (6*a*) for the reasons described above, the agreement between theoretical and experimental values was greatly improved, though the simplified method of calculating the additive viscosity from the composition for the interfacial phase was used. If more accurate estimate of liquid mixture viscosity could be made, one would have been able to make a closer study on the applicability of Equations (6) and (6*a*).

It will be recalled that the Γ_o was calculated from experimental data found in literature from Equation (28). For ternary systems small experimental errors inherent in values for Γ_o will give large errors in the value of A_{is}, thus giving large errors in the volume percent water when viscous solutes are used. This source of errors may account

Table 2. Phase Inversion Data for Various Ternary Systems

Systems vs. water	T, °C.	N_s^α	η^γ	η^α	Vol. % water by Equation (6a)	Exp'l. data	Equation (6)
n-caprylic acid in nitrobenzene	25	0.0312	1.256	1.872	45.0	49.0	40.5
	25	0.086	1.442	1.986	45.8	50.0	39.4
	25	0.138	1.416	2.101	45.0	51.3	38.3
n-octyl alcohol in benzene	23	0.123	6.447	0.858	73.2	67.5	51.0
	23	0.0904	3.487	0.790	67.7	66.1	52.0
	23	0.0589	1.084	0.730	54.9	65.5	53.1
n-octyl alcohol in nitrobenzene	25	0.0314	1.625	1.890	48.1	50.0	43.2
	25	0.0609	1.899	1.969	49.0	49.3	39.2
	25	0.0888	2.296	2.046	51.4	49.0	38.2
n-caprylic acid in benzene	23	0.358	1.215	1.350	48.6	66.2	45.2
	23	0.228	1.334	1.018	53.2	68.5	48.8
	23	0.0584	1.487	0.703	59.2	71.0	53.4
n-decyl alcohol in benzene	23	0.102	3.215	0.826	66.3	68.8	51.5
	23	0.0491	1.770	0.712	61.2	69.1	53.3
	23	0.0238	1.304	0.663	58.3	58.2	54.2
n-lauryl alcohol in benzene	23	0.0899	2.808	0.829	64.7	66.9	51.4
	23	0.0421	1.743	0.710	61.0	63.6	53.3
	23	0.0245	1.409	0.671	59.1	64.3	54.1
n-caprylic acid in cyclohexane	25	0.0785	1.466	1.001	54.7	56.7	48.4
	25	0.0486	1.342	0.948	54.3	55.9	49.2
	25	0.0168	0.955	0.896	50.7	54.2	50.0
n-octyl alcohol in cyclohexane	25	0.0147	2.127	1.189	57.2	63.9	46.3
	25	0.0703	4.429	1.011	67.6	63.7	48.3

for the discrepancies found in the system of water-*n*-caprylic acid in benzene. The concentration of *n*-caprylic acid in benzene was considerably higher for this system than for any of the other systems investigated. The simplified assumption of a dilute solution used in calculating the interfacial composition was probably not valid for this case. For high concentrations of solute in a ternary system some other method of predicting the interfacial viscosity will be necessary.

The two binary systems water-*n*-octyl alcohol and water-oleic acid gave poor agreement between the theoretical and experimental values of phase inversion points. This probably is due to the simplified method used in predicting the viscosity of the system. It is known that where complexes are formed, or molecular association or dissociation occurs upon mixing of two or more chemically dissimilar compounds, the simplified assumption of additive viscosities from composition may not apply.

It must be remembered that Equation (6) was originally derived for two immiscible Newtonian liquids flowing under conditions in which viscous force plays a major part in determining their hydrodynamic behaviors. The equation may not be applicable if one of the following conditions prevails:

1. One or both liquids are strongly non-Newtonian.
2. The difference of liquid densities is great.
3. Inertia force rather than viscous force plays the dominant role in determining the hydrodynamic behavior of the system.

It should be noticed that Equation (6*a*) was not derived to suggest that there exists a momentum balance between α phase and γ phase which possesses negligible mass and volume in comparison to the bulk phases. It is applicable as an approximation if one may assume that the shear at the $\beta - \gamma$ interface is zero or negligible compared with that at the $\alpha - \gamma$ interface, and the velocity gradients directly opposite on either side of the plane of shear is very small or negligible in comparison with the slip velocity between the two adjacent phases at the plane when the phase inversion occurs.

CONCLUSION

It may be concluded that Equation (6) or (6*a*) may be applicable for predicting the phase-volume ratio at the point of inversion (as defined in this work) between any two liquid phases regardless of the number and concentrations of the components involved if the location of the plane of shear and also an appropriate method of predicting the viscosities of both phases at the plane of shear are known.

On the other hand one is able to predict the interfacial viscosity and in turn the interfacial composition from the experimental data of the inversion point of a system, from the above equations. This information is important in studying phenomena or processes occurring at or across the interface of two immiscible liquid phases.

NOTATION

A = surface area occupied by respective component, sq. ft.
a = thickness of α phase, ft.
b = thickness of β phase, ft.
C_1^α, C_2^α = integration constants in Equation (3)
C_1^β, C_2^β = integration constants in Equation (4)
F_s = energy of spreading = $\sigma^\beta - \sigma^\alpha - \sigma^{\alpha\beta}$, lb. force/ft.
L = length of slit in Equations (1) to (5), ft., or latent heat of fusion of solvent in Equation (26), B.t.u./lb.
N = mole fraction
n = number of moles
Δp = pressure difference, lb. force/sq. ft.
T = absolute temperature, °K.
T_o = freezing point of solvent, °K.
u = velocity, ft./sec.
V = molal volume, cu. ft.
W = width of slit, ft.
X = distance from interface, ft.
x = thickness of interfacial phase or film, ft.

Greek Letters

Γ = surface excess of component = the total number of moles of component per unit area of interface in the actual system, minus the total number of moles of the same component in purely hypothetical system, occupying the same volume in which the two phases are uniform in composition up to the interface
$\Gamma^{(1)}$ = actual number of molecules in monolayer
$\Gamma^{(u)}$ = actual number of molecules in interfacial film
$\Gamma^{(N)}$ = total number of moles of solute contained in a portion of the liquid embracing unit area of surface, minus the total number of moles of solute in an equal volume in the bulk phase containing exactly the same total number of moles of all species
η = viscosity, centipoise
θ = freezing point depression of solution, °K.
μ = chemical potential
σ = surface tension, lb. force/ft.

Superscripts

α = α phase
β = β phase
γ = interfacial phase

Subscripts

1, 2, r = components 1, 2, and r, respectively
i = interface
o = solvent
s = solute
t = total
z = z direction

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Manuscript received October 27, 1961; revision received September 6, 1963; paper accepted September 11, 1963.