

The Correlation between Phase Inversion Temperature in Emulsion and Cloud Point in Solution of Nonionic Emulsifier

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(Received February 5, 1964)

A model has been advanced in which it is proposed to regard the cloud point in solution of nonionic agent as akin to the phase inversion temperature in emulsion. In the latter, the mixing is macroscopic, whereas in the former the mixing is microscopic or on the bimolecular leaflet scale and the agent serves as an oil as well as an emulsifier. Phase inversion temperatures in hydrocarbon-water emulsions stabilized with polyoxyethylene alkyl phenyl ether have been determined for different hydrocarbons as a function of emulsifier concentration. It was found that the more soluble the hydrocarbon for a nonionic emulsifier, the lower is the phase inversion temperature, above which O/W type emulsions invert to W/O type. A similar rule, that the more soluble the nonionic emulsifier for a definite hydrocarbon, the lower the phase inversion temperature, also holds. The effect of polyoxyethylene chain length and hydrocarbon chain length of the emulsifier on the phase inversion temperature have been studied. It was found that the cloud points in solutions of nonionic emulsifiers saturated with various hydrocarbons and the phase inversion temperatures in emulsions were parallel, which supports the present model. The effect of temperature on the emulsion stability in connection with the phase inversion temperature is briefly discussed.

INTRODUCTION

Noionic emulsifying agents dissolve in water in a molecular dispersion up to the solubility limit, and above this concentration the excess agent separates to form a phase solution above the cloud point temperature.¹ Below the cloud point the agent forms micelles which are composed of about 100 agent molecules. Since these micelles are much smaller than the wavelength of light, the solution is transparent and the solubility increases enormously. Although the micellar solution is transparent, the formation of micelles is a phenomenon similar to a phase separation.² By analogy with the change in emulsion type at the phase inversion temperature, we may regard the change in the state of solution above and below the cloud point as follows. Above the cloud point a surfactant-rich phase containing

dissolved water separates; on this volume fraction a nonionic detergent (D) mixes with water (W). The mixing is almost on the bimolecular leaflet scale and may be regarded as the W/D type. Also, the detergent-rich phase dissolves into water as bimolecular leaflet or micelles below the cloud point. Something similar to a phase inversion on the bimolecular leaflet scale takes place in a surfactant solution near the cloud point, and the solution inverts to the D/W type. Thus, the concentrated solution readily disperses or diffuses into a dilute solution. This phenomenon may be designated as a pseudo-phase inversion.³

If we shake a 1:1 mixture of water and nonionic agent, the latter dissolves or disperses into water, and the whole system becomes an aqueous phase of the D/W type below the cloud point, whereas above the cloud point the water dissolves or disperses in the agent phase until the water phase disappears, i.e., mixes in the W/D type.

¹ R.R. Balmbra, J.S. Clunie, J.M. Corkill, and J.F. Goodman, *Trans. Faraday Soc.*, **58**, 1661 (1962).

² K. Shinoda and E. Hutchinson, *J. Phys. Chem.*, **66**, 577 (1962).

³ K. Shinoda, *Bull. Chem. Soc. Japan*, **35**, 1213 (1962).

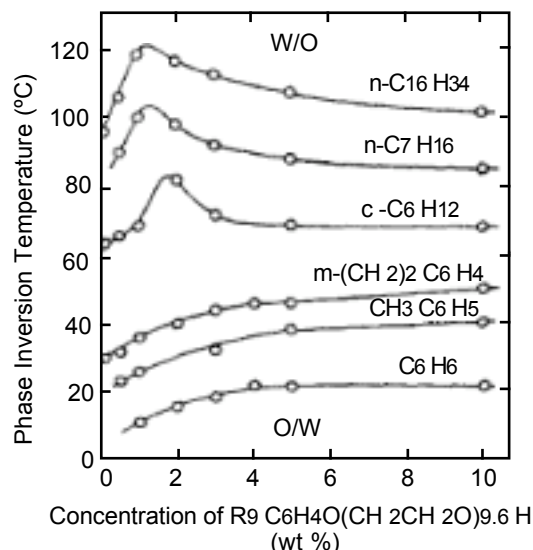


Figure 1. The effect of different hydrocarbons on the phase inversion temperature of emulsions (volume ratio = 1) vs the concentration of polyoxyethylene (9.6) nonyl phenyl ether (wt. % in water).

A similar pseudo-phase inversion may occur near the cloud point in the presence of small amounts of added hydrocarbons, because the emulsifier molecules arrange side by side and end to end regardless of whether the mixing is of the D/W or W/D type. At the same time, the cloud point may be either raised or lowered by the presence of hydrocarbons. It was then expected that near the cloud point of the solution a phase inversion would occur from the O/W to the W/O type in an emulsion stabilized with a nonionic agent when the temperature was raised. The present investigation was undertaken in order to obtain data on the phase inversion temperatures for various combinations of hydrocarbons and emulsifiers and to assure that the present model is correct. Although there are many works on emulsion type,^{4,5} the data on the effects of temperature are meager.⁶ It seemed very important to study the effect of temperature in order to eliminate confusions and get a better understanding of factors affecting the stability and type of emulsions formed. All other factors such as the phase volume ratio were held constant and only the temperature was changed to cause a phase inversion.

⁴ P. Becher, *J. Soc. Cosmetic Chemists*, **9**, 141 (1958).

⁵ J. T. Davies, *ibid.*, **12**, 193 (1961).

⁶ V.E. Wellman & H.V. Tartar, *J. Phys. Chem.*, **34**, 379 (1930).

Experimental

Materials. Polyoxyethylene nonyl phenyl ether and polyoxyethylene (9.0) dodecyl phenyl ether, were obtained from the Kao Soap Co. Samples were purified by extraction of polyethylene glycol into aqueous butanol solution.⁷ These samples showed no pattern for polyethylene glycol on paper chromatographic analysis. The average chain lengths of the ethylene oxide adducts were determined from their respective hydroxyl values. Hexadecane and heptane were the standard fuels. Liquid paraffin (Drakeol 35) and dodecene (propylene tetramer) were commercial materials. Benzene, toluene, cyclohexane, and carbon tetrachloride were extra pure grade materials. Ethyl benzene, m-xylene, and β -methyl-naphthalene were pure grade materials.

Procedure. Aqueous solutions of an emulsifier of varying concentration were placed in contact with equal volumes of hydrocarbons in test tubes end shaken vertically. Emulsion type was determined by conductivity, visual observation, dye solubility, and/or the phase dilution method. Since the emulsion was usually not stable near the phase inversion temperature visual observation was easy and reliable in most cases studied.

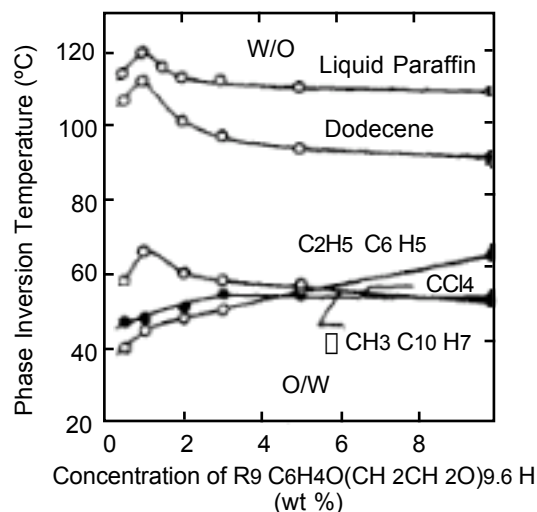


Figure 2. The effect of different hydrocarbons on the phase inversion temperature vs. the concentration of polyoxyethylene (9.6) nonyl phenyl ether.

⁷ K. Nagase & K. Sakaguchi, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **64**, 635 (1961)

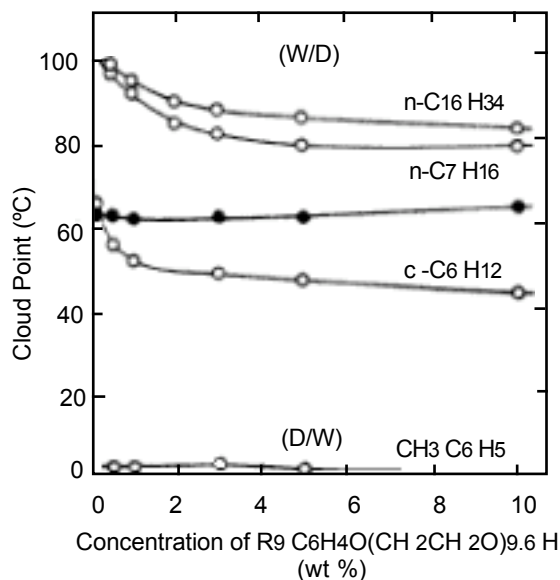


Figure 3. The cloud points of polyoxyethylene (9.6) nonyl phenyl ether solution saturated with different hydrocarbons. Filled circles express the cloud points in the absence of oil.

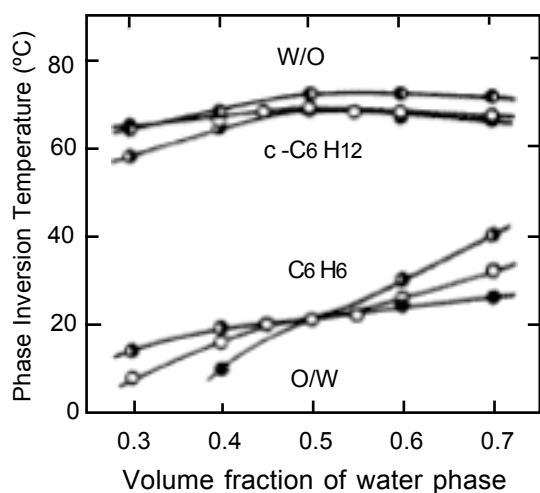


Figure 4. The effect of phase volume ratio on the phase inversion temperature for emulsions stabilized with $i\text{-R}_9\text{C}_5\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_{9.6}\text{H}$; 0, 3%; 0.4%; 0, 5%; 0, 10%.

In cases when the phase inversion temperature was higher than the boiling point of oil or water, the emulsion type was determined by visual observation only in sealed test tubes. All the phase inversion temperature values reported are averages of several values. Experimental values are reproducible within $\pm 2^\circ$. It was $1\text{-}2^\circ$ lower in the case of horizontal shaking. Unlike the usual phase inversion study, only the temperature was changed to cause a phase inversion. The cloud points of emulsifier solutions saturated with various hydrocarbons were also observed.

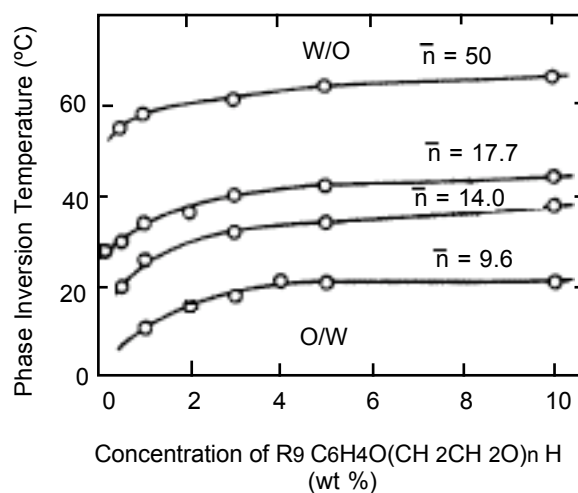


Figure 5. The effect of the hydrophilic chain length of the emulsifier on the phase inversion temperature in benzene-water emulsions (volume ratio = 1).

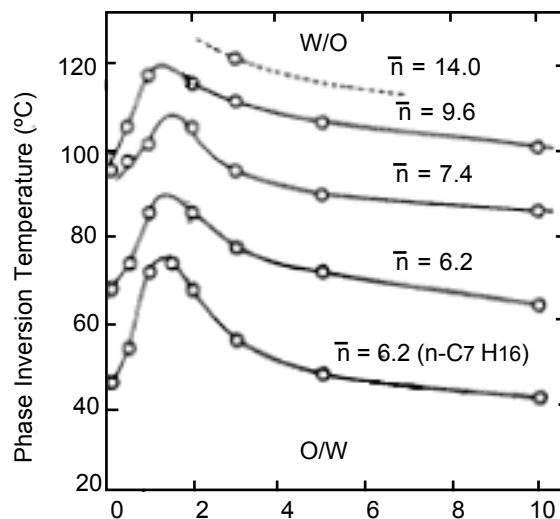


Figure 6. The effect of the hydrophilic chain length of the emulsifier on the phase inversion temperature in hexadecane-water emulsions (volume ratio = 1).

The values are not as accurate as the cloud points in the absence of hydrocarbons.

RESULTS AND DISCUSSION

The Influence of Different Hydrocarbons on the Phase Inversion Temperature. The phase inversion temperature vs. the emulsifier concentration curves were determined for different hydrocarbons and plotted in Fig. 1 and 2. The phase inversion temperature differs

widely for different hydrocarbons. Benzene gave a phase inversion temperature of about 20° which was the lowest of any of the hydrocarbons examined. Polyoxyethylene (9.6) nonyl phenyl ether dissolved well in benzene at this temperature. On the other hand, hexadecane, which was the poorest solvent for the same emulsifier, gave the highest inversion temperature, about 110°. The more soluble the hydrocarbon for a definite nonionic emulsifier, the lower was the phase inversion temperature. This rule complements Bancroft's rule at a definite temperature. The cloud point curves in aqueous solutions saturated with different hydrocarbons were determined and plotted in Fig. 3. It was found that the cloud points and the phase inversion temperatures are parallel.

As the temperature had such a remarkable effect on the emulsion type in this system, it was expected that the change in phase volume ratio would not change the phase inversion temperature very much. Actually, it did not change much for a change of volume ratio from 3/2 to 2/3 as shown in Fig. 4.

The Effect of Hydrophilic Chain Length on the Phase Inversion Temperature. It was expected that the longer the hydrophilic chain, the higher the cloud point and/or the phase inversion temperature would be. This tendency was found in benzene-water and hexadecane-water systems using various polyoxyethylene nonyl phenyl ethers. The results are plotted in Fig. 5 and 6. The larger the hydrophilic group of the nonionic emulsifier the higher was the phase inversion temperature.

The Effect of Hydrocarbon Chain Length of Emulsifier on the Phase Inversion Temperature. In order to determine the effect of the hydrocarbon chain length of the emulsifier on the phase inversion temperature, the phase inversion temperature curves were also determined for various hydrocarbons emulsified with polyoxyethylene (9.0) dodecyl phenyl ether. The results are plotted in Fig. 7.

The cloud point of 80° for polyoxyethylene (9.0) dodecyl phenyl ether saturated with hexadecane, is 7° lower than the cloud point of 87° for polyoxyethylene (9.6) nonyl phenyl ether. Thus the phase inversion temperatures are

lower by about 7-8° for respective emulsions stabilized with the former emulsifier. Although the effect of the hydrocarbon chain length of the emulsifier on the phase inversion temperature was not large, the stability of the emulsion toward coalescence was appreciably better in the case of dodecyl phenyl ether than for nonyl phenyl ether.

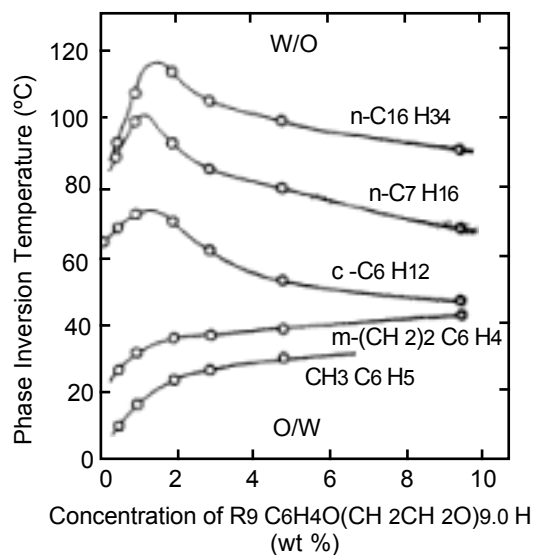


Figure 7. The effect of different hydrocarbons on the phase inversion temperature of the emulsions vs. the concentration of polyoxyethylene (9.0) dodecyl phenyl ether (wt. % in water)

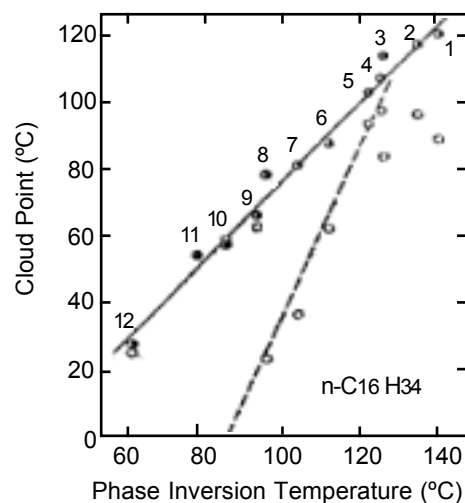


Figure 8. The correlation between the phase inversion temperatures in emulsion and the cloud points of emulsifiers in the absence of O, or saturated with hexadecane, ●; 1, Tween 40; 2, Tween 20; 3, Tween 60; 4, $R_{12}O(CH_2CH_2O)_{10}H$; 5, $i-R_9C_6H_4O(CH_2CH_2O)_{14}H$; 6, $i-R_9C_6H_4O(CH_2CH_2O)_{9,6}H$; 7, $i-R_{12}C_6H_4O(CH_2CH_2O)_{9,0}H$; 8, $i-R_9C_6H_4O(CH_2CH_2O)_{7,4}H$; 9, Pluronic L-44; 10, Pluronic L-64; 11, $i-R_9C_6H_4O(CH_2CH_2O)_{6,2}H$; 12, Pluronic L- 62.

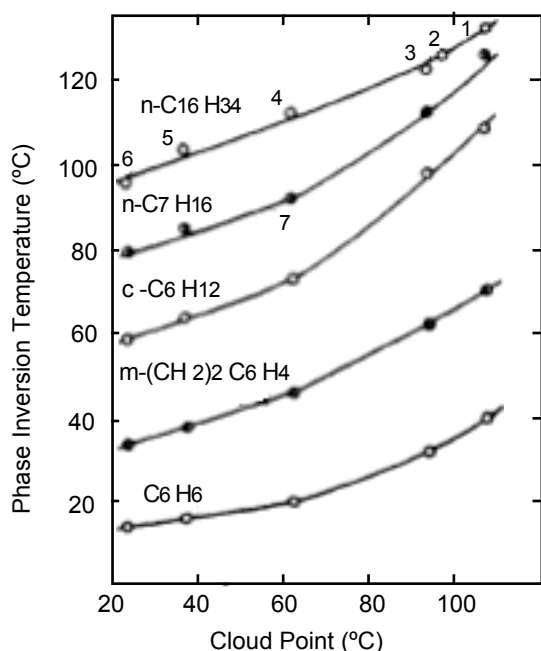


Figure 9. The correlation between the phase inversion temperatures in various hydrocarbon water emulsions (volume ratio = 1 and the cloud points of emulsifiers in the absence of hydrocarbons:

1, $i\text{-R}_{12}\text{O}(\text{CH}_2\text{CH}_2\text{O})_{10}\text{H}$; 2, $\text{R}_{12}\text{O}(\text{CH}_2\text{CH}_2\text{O})_{10}\text{H}$;
 3, $i\text{-R}_9\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_{9,6}\text{H}$; 4 $i\text{-R}_9\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_{9,5}\text{H}$;
 5, $i\text{-R}_{12}\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_{9,0}\text{H}$; 6, $i\text{-R}_9\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_{7,4}\text{H}$;
 7, $\text{C}_{18}\text{H}_{35}\text{O}(\text{CH}_2\text{CH}_2\text{O})_{10}\text{H}$.

Correlation between Phase inversion Temperature and Cloud Point. The correlation between the cloud points of aqueous solutions containing 3 wt. % of emulsifier without hexadecane and saturated with hexadecane and the phase inversion temperatures of hexadecane-water emulsions stabilized with various nonionic agents (3 wt. % for water) is shown in Fig. 8. Similar correlations were observed in solutions containing the other hydrocarbons.

It is clear from Fig. 8 that the phase inversion temperatures of emulsions and the cloud points when saturated with oil are quite parallel regardless of the type of nonionic agent.

This correlation does not hold well for cloud points in the absence of hydrocarbons as can be seen in Fig 8. As for the polyoxyethylene type of nonionic agents, the cloud points and the phase inversion temperature change monotonically as shown in Fig. 9. This correlation is very useful to estimate the phase inversion temperature from cloud points of nonionic agents in the absence of hydrocarbons.

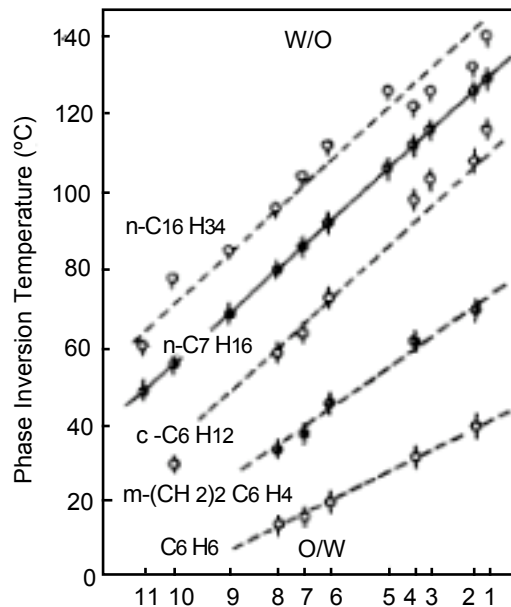


Figure 10. The correlation between the phase inversion temperatures in emulsions composed of different hydrocarbons: 1, Tween 40; 2, $i\text{-R}_9\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_{17,7}\text{H}$; 3, Tween 60; 4, $i\text{-R}_9\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_{14,0}\text{H}$; 5, $\text{R}_{12}\text{O}(\text{CH}_2\text{CH}_2\text{O})_{10}\text{H}$; 6, $i\text{-R}_9\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_{9,6}\text{H}$; 7, $i\text{-R}_{12}\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_{9,0}\text{H}$; 8, $i\text{-R}_9\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_{7,4}\text{H}$; 9, Pluronic L-64; 10, $i\text{-R}_9\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_{6,2}\text{H}$; 11, Pluronic L-62.

Correlation among Phase Inversion Temperature, Oil, Nonionic Emulsifier. The correlation between phase inversion temperatures of emulsions composed of various hydrocarbons stabilized with various nonionic agents (3 wt. % for water) is shown in Fig 10. The locations of the nonionic agents in the abscissa were determined so as to make the phase inversion temperatures in heptane-water emulsions vs. the nonionic agents fall on the straight line of slope 1. This correlation is also very useful to predict the phase inversion temperatures and/or to select the stable emulsifier in the emulsions.

Relation between the Emulsion Type and the stability. It is generally supposed that the stability toward coalescence of emulsified droplets is nearly equal for homologous hydrocarbons stabilized with the same emulsifier. On the contrary, the stability is sometimes markedly different for such homologous oils. This is clearly shown by the data on phase inversion temperature. As can be seen in Fig. 1, the emulsion in the hexadecane-water system is of the O/W type, and that of the heptane-water

system is of the W/O type at 100°. At this temperature the O/W type of emulsion of hexadecane-water is relatively stable, but that of heptane-water is unstable. At a lower temperature, for example at 80°, both systems were relatively stable, but the cyclohexane-water system was unstable. These relations on emulsion stability were qualitatively observed. The results are quite understandable with the aid of the phase inversion temperature data. The

conclusion obtained by Benerito and Singleton,⁸ "To provide emulsion stability at homogenization and sterilization temperatures the emulsifiers must be more hydrophilic than many O/W emulsifiers that are satisfactory use and must have an increased affinity for water in the temperature range of 5 to 120°," is also readily understandable from the present data.

⁸ R.R. Benerito & W.S. Singleton, *J. Am. Oil Chemists Soc.* **33**, 364 (1956)