ELECTRICAL CONDUCTIVITY

of

POLYAPHRONS (BILIQUID FOAMS)

by

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(ABSTRACT)

Polyaphrons (biliquid foams) are dispersions which consist of a continuous aqueous phase and a dispersed oil phase. Electrical conductivity measurements of many polyaphrons over a range of varying oil phase volume to aqueous phase volume ratio (PVR) indicate that the path of electricity through polyaphrons is independent of the nature of oil phase and aqueous phase surfactant, oil phase surfactant concentration, the nature of oil phase components, and the type of electrolyte added to aqueous phase to enhance electrical signal.

Graphs of relative electrical conductivity ratios (conductivity of polyaphron to that of aqueous phase) versus the inverse of PVR are presented. These graphs suggest characterization of polyaphrons by the identification of (1) a proportionality coefficient at high PVR, and (2) a point labelled Transition PVR associated with departure from linearity as PVR decreases. Departure from linearity occurs as geometric changes occur within polyaphron structure: spherical units called aphrons close pack until distorted polyhedral shapes result.

Graphical results of electrical conductivity measurements of polyaphrons show better agreement with Bruggeman's Equation than with Maxwell Equation or Meredith-Tobias Equation over the entire range of dispersed phase volumetric fraction.

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INTRODUCTION

Various types of gas-liquid and liquid-liquid dispersions are discussed in a large portion of the literature in surface chemistry. Publications present definitions of foams, gaseous foams, liquid foams, emulsions, gas emulsions, and microemulsions (to name a few) that are often accompanied by photographs. Fuzzy areas of identification, particularly at the limits of these general definitions, combine to leave a reader with the impression that distinct, precise definitions based on appearance and behavior are necessary.

Work by Sebba [28,29,30,31,32,33] introduces another term, polyaphrons or biliquid foams, that aids in distinguishing the behavior and appearance of liquid-liquid dispersions. A polyaphron is a three-liquid phase dispersion which contains an internal liquid phase stabilized by encapsulation in a thin aqueous soapy film. Units of internal phase so encapsulated are called aphrons.[1] The encapsulating film behaves as a phase distinct from the bulk continuous liquid phase in which the aphrons are dispersed. A concentrated dispersion of aphrons assumes a foam structure. Thus, polyaphrons are structured systems which are very stable.

A polyaphron is not an emulsion. An emulsion is a two-liquid phase dispersion containing an internal discontinuous phase, stabilized by an energy barrier composed of either a monomolecular layer of emulsifying agent or by finely divided solid particles. No stable

dispersed unit comparable to the aphron of a polyaphron is present in an emulsion. Polyaphrons exhibit a yield stress and anomalous flow properties. Their behavior is different from emulsions. In fact, polyaphrons of high ratio by volume of dispersed phase to continuous phase are similar in properties to those of a polyederschaum foam. The difference is that in a polyaphron the space inside the soap film is occupied by a non-polar liquid, not a gas.

Acceptance of the concept of polyaphrons leads to a need to characterize them. Pertinent to such a goal, this thesis investigates the relationship between the ratio by volume of dispersed phase to continuous phase and the electrical conductivity of a polyaphron.

Since the late 1800's when the work of Maxwell [23], Lorentz [21], Lorenz [22], and Rayleigh [27] was published, an extensive list of investigators have proposed equations to describe the path of electricity through dispersions of various natures. Because polyaphrons are considered liquid-liquid dispersions (the aqueous phase is the continuous phase, while the oil phase is the dispersed phase), these equations could equally apply to an investigation of electrical conductivity measurements of polyaphrons. Appropriate to this is a review of the theoretical development and experimental investigations of electrical conductivity measurements of dispersions, including foams and emulsions. Thus equations with which the results of this investigation could be compared are introduced.

Lorentz, Lorenz, and Maxwell separately derived the classical equation which now bears the name of only Maxwell. The Maxwell

Equation relates the effective conductivity (k_e) of dilute random dispersions of spherical particles of uniform diameter and conductivity (k_d) in a continuous phase of conductivity (k_c) to the volume fraction of the dispersed phase, f, as follows:

$$K_e = \frac{K_D + 2 - 2f(1-K_D)}{K_D + 2 + f(1-K_D)} \qquad (1)$$

where $K_e = \frac{k_e}{k_c}$ and $K_D = \frac{k_d}{k_c}$.

If the conductivity of the dispersed phase (k_d) equals zero, then Equation (1) simplifies to:

$$K_e = \frac{1 - f}{1 + f/2} \qquad (2)$$

The electrical conductivity of dispersions depends on the volume fraction of the dispersed phase, f. Other physical properties of dispersions, such as thermal conductivity, the dielectric constant, and magnetic permeability, exhibit identical behavior to the electrical conductivity, and thus can be included in this theory development.

To summarize assumptions of Maxwell's Equation: (1) the dispersed phase consists of spheres of a single diameter; (2) the dispersed phase is present in very low volume concentrations; (3) the average distance between the particles of the dispersed phase is large

enough so that the fields around the individual particles are undisturbed by the presence of the other particles; and (4) the conductivity of the dispersed phase (k_d) equals zero. The condition for the second assumption to be rigorously satisfied occurs only when the volume fraction of the dispersed phase (f) approaches zero. Theoretically, Equations (1) and (2) would no longer accurately represent the relation between volumetric fraction and electrical conductivity when f exceeded 0.2.

Rayleigh considered more concentrated dispersions of spheres of uniform diameter that occupy cubic lattice positions. The interactions of fields in the vicinity of neighboring, uniform-size spherical particles lead to an expression identical to Equation (2) for the case when the conductivity of the dispersed phase (k_d), equals zero, and the volume fraction of the dispersed phase (f) approaches zero.

Fricke [10] developed a more general solution. For the effective conductivity (K.) of dilute dispersions containing ellipsoidal particles:

$$K_e = \frac{1 - f(K_e - K_D)}{3(1 - f)} \sum_j \frac{1}{1 - (1 - K_D)L_i} \qquad (3)$$

for i = 1,2,3.

As with the previous equations, K_D is the relative electrical conductivity of the dispersion, and f is the volume fraction of the dispersed phase. The three values of L_i involve elliptic integrals of the second kind, and are functions of the lengths of the semiprincipal

axes (a,b,c) of the ellipsoids. Only when the particles are spheroids, that is, b is equal to c, are solutions obtained in closed form. When the particles are spheres, that is, a is equal to b is equal to c, and all three L terms equal 1/3, then Equation (3) becomes the same as Equation (1), Maxwell's Equation.

Bruggeman [3] introduced a model that represented dispersions of random particles in the concentrated range of volume fraction. This equation, using the same variables introduced above:

$$1 - f = \frac{K_e - K_D}{K_e^{1/3}(1 - K_D)} \tag{4}$$

is an expression assuming an infinite range of particle sizes within the dispersion. With K_D equal to zero, Equation (4) becomes

$$K_e = (1 - f)^{3/2} \tag{5}$$

In 1944, Miles, Shedlovsky, and Ross [26] experimentally investigated electrical conductivity as a function of the liquid in a foam. A foam made up of 0.25 percent Igepon T solution and 1 percent sodium sulfate, was measured over a narrow range of percent air in the final foam (86-95 percent). Results were presented in graphical form and no specific conclusions were drawn.

In 1946, Clark [6] conducted an experimental study to determine the expansion factor of a foam (the ratio of foam volume to volume of contained liquid) by electrical conductivity measurements. Five types of solutions were mechanically beat to produce foams which widely differed in expansion factors. Since the weight of the gaseous portion of a foam is negligible compared to the liquid portion, the expansion ratio can be equated to a density ratio--the density of the solution to the density of the foam. Clark concluded that the electrical conductivity ratio (electrical conductivity of the solution to that of the foam) was related to this density ratio by a standard curve which was independent of the nature of the foaming agent and the specific surface of the foam. Measurements were made over a wide range of expansion factors. Particularly interesting in their study was that the conductivity ratio was measured directly in the experimental system.

De La Rue and Tobias [7] suggest that theoretically a volumetric fraction of dispersed phase (f) equal to 0.25 already exhibits significant interactions of fields around spheres. Yet, many researchers have produced experimental data from moderately concentrated dispersions that satisfactorily agree with Maxwell's Equations. Fricke and Morse [12] obtained electrical conductivity data on various concentrations of cream in milk to fit Equation (2) within experimental error. De La Rue and Tobias refer to results by Eucken [9] of the systems (a) potassium chloride in water-benzene and (b) potassium iodide in water-phenol. Over the entire range of volume concentrations ($0 < f < 1$), agreement with Equation (1) was reported.

De La Rue and Tobias [7] report on studies of the electrical conductivity of electrolyte solutions in which were suspended non-conducting glass beads, sands, or polyester cylinders. High precision and reproducibility were goals of the authors to permit the evaluation of the limitations of Maxwell's Equation in the range $0 < f < 0.4$. Their results confirmed that electrical conductivity of electrolytes is lowered by the presence of randomly distributed spherical nonconductors to a larger extent than predictable from Maxwell's Equation. Bruggeman's approximation is better supported when a random dispersion of spherical non-conductors with a large size-range, such as three orders of magnitude, is used. With a narrow size range of spheres both the Maxwell and Bruggeman Equations are ineffective--yet the error with the Bruggeman Equation is less. For shapes other than spherical (especially if particles are greatly elongated or they contain cavities) neither equation holds.

Meredith and Tobias [25] initiated a study to more accurately compare results that were subject to the restrictions of Equations (1) and (4). The dependence of the electrical conductivity of water-propylene carbonate[2] emulsions (i) on volumetric fraction (f) of the dispersed phase, (ii) on the electrical conductivity of the condensed phase (k_c), and (iii) on the electrical conductivity of the disperse phase (k_d) was measured in the ranges of $0 < f < 0.5$ and $0.172 < k_d/k_c < 101$. Their objective was to identify a dispersion in which the dispersed phase not only conducted, but also conducted better than the continuous phase, that is, when k_d was much greater

than k_c. They suggest that such a dispersion was much more sensitive to changes in volumetric fractions than in the case of dispersions in which the dispersed phase did not conduct. Such a dispersion was obtainable using water and propylene carbonate. Since a wide range of ionic solutes were soluble in both phases to alter the conductivity of each phase, a desired ratio of the conductivities in both oil-in-water and water-in-oil emulsions was acquired. Results indicated that when f was greater than 0.2, neither Maxwell's Equation or Bruggeman's Equation satisfactorily represents the behavior of the data. The authors proposed a simple appproximation, based on Maxwell's Equation, that represents the electrical conductivity of emulsions in the range of conductivity they investigated with reasonable accuracy.

Their equation takes into account the interaction of fields around particles of the dispersed phase when the particle sizes are within a narrow size range--not a large number of particle size fractions as in the work of Bruggeman. In fact, their model contained particles of only two different sizes present in equal volume. If the dispersed phase consisted of spherical particles that were non-conducting, they derived this equation to describe the effective conductivity (K_e) of the dispersion:

$$K_e = \frac{8(2 - f)(1 - f)}{(4 + f)(4 - f)} \qquad (6)$$

Graphs show their equation more suitable than the Maxwell and

Bruggeman Equations for the ranges, $0 < f < 0.5$ and $0.172 < k_d/k_c < 101$. At greater f, such as the conductivity data on foam presented by Clark [6], Equation (6) shows greater deviation. The authors explain that in Clark's studies experimental conditions differ from their model: in the concentrated region of foams, very large size ranges are present, and serious deviation from spherical shape of dispersed phase particles occurs. These authors also show good correlation with a general solution to their model, assuming spheroid particles, for Stewart's electrical conductivity data [38] on dog's blood (a dispersion where the dispersed phase consists of nonconducting red blood cells which resemble oblate spheroids).

In addition, Meredith and Tobias have written a review article, "Conduction in Heterogeneous Systems", [24] that traces much of the experimental and theoretical work in this area. From the first articles by Lorentz, Lorenz, Maxwell, and Rayleigh until their own work published in 1961 [25], Meredith and Tobias discuss both the underlying assumptions and the mathematics involved with the derivations they present. Theirs is an excellent starting point for the reader interested in this area.

Figure 1 presents a summary of the Maxwell, Bruggeman, and Meredith-Tobias Equations. Maxwell's Equation assumes that the dispersion contains spherical particles of uniform diameter. The average distance between particles of the dispersed phase is large compared to the diameter of particles so that fields around particles are undisturbed by the presence of other particles. This condition is

	MAXWELL'S EQUATION	BRUGGEMAN'S EQUATION	MEREDITH-TOBIAS EQUATION
Shape of Dispersed Particle	Spherical	Spherical	Spherical
Size of Dispersed Particle	Uniform Diameter	Infinite range of diameters many small sizes, few large sizes	Narrow range of diameters two different sizes of equal volume fractions
Restrictions	1. Average distance between particles is large compared to particle diameter	1. Surroundings of large particles considered a continuum with an effective conductivity	1. Surrounding of large size fraction considered a continuum with an effective conductivity
	2. Fields around individual particles are undisturbed by other particles	2. Distribution of fields around large particles due to smaller particles is negligible	2. Distribution of fields around each fraction due to other fraction is negligible
K_D, Electrical Conductivity of Dispersed Phase	zero	zero	zero
Best Applicable Range of, f, Dispersed Phase Volumetric Fraction	Rigorously satisfied only as $f \to 0$ $0 \leq f < 0.2$	$0 \leq f < 0.2$	$0.2 < f < 0.5$
EQUATION K = Relative Conductivity f = Dispersed (oil) phase volumetric fraction	$K = \frac{1 - f}{1 + f/2}$	$K = (1 - f)^{3/2}$	$K = \frac{8(2-f)(1-f)}{(4+f)(4-f)}$

FIGURE 1. Description of the Maxwell, Bruggeman, and Meredith-Tobias Equations Which Relate a Relative Electrical Conductivity of a Dispersion to the Volumetric Fraction of the Dispersed Phase.

rigorously satisfied only as volumetric fraction of dispersed phase approaches zero. De La Rue and Tobias [7] suggest that a volumetric fraction equal to 0.25 already exhibits significant interactions of fields around spheres. The conductivity of dispersed spheres is assumed to equal zero.

Bruggeman's Equation assumes spherical particles in a broad range of sizes--particularly, few large particles compared to many small ones. Surroundings of larger particles can be considered a continuum with an effective conductivity, and distribution of fields around the large particles due to the smaller particles is negligible. Maxwell's Equation is then applied with boundary conditions that state that the effective conductivity equals the conductivity of continuous phase at f equal to zero, and equals the true conductivity of the dispersion at the upper limit of f equal to one. Electrical conductivity of dispersed phase is assumed to equal zero.

The Meredith-Tobias Equation assumes spherical dispersed particles of a narrow size range. Two different particle sizes in equal volumetric fractions are assumed. Distribution of fields around each fraction due to the other is considered negligible. Surroundings of the large size fraction can be considered a continuum with an effective conductivity. Electrical conductivity of dispersed phase is assumed to be equal to zero.

In 1959, Hanai, Koizumi, and Gotah [15] measured dielectric constants and Hanai, Koizumi, Sugano, and Gotah [16] measured electrical conductivities of oil-in-water emulsions not only over a wide

range of concentrations, but also over a wide range of measuring frequency (20 cps to 3 mc). Two different oil phases were used: either parafin oil or tetralin was weighted with carbon tetrachloride to the same density as water. The emulsifier used was an equal weight mixture of Span 20 and Tween 20. For the electrical conductivity measurements, 0.05 N potassium chloride was added to the aqueous phase. Electrical conductivity remained constant irrespective of frequency while the dielectric constant was constant only at high range of frequency and increased rapidly at lower frequency. Upon comparison of their experimental results to five theoretical equations, Bruggeman's Equation provided the best match over the entire range of concentration.

Hanai [13] subsequently presented a theoretical model of dielectric dispersion due to interfacial polarization based on Bruggeman's work. His development included equations for the limiting values of the dielectric constant and electrical conductivity at lower and higher frequencies. In 1960, he presented an experimental investigation of dielectric properties of water-in-oil emulsions [14]. In this study, the dielectric constants and electrical conductivities showed a remarkable dependence on frequency as well as shearing stress. Epstein [8]. investigated ionic and nonionic oil-in-water microemulsions and interpreted results using Hanai and Maxwell mixture theories. One conclusion was that only at lower frequencies, that is, microwave range, do dielectric properties exhibit differences.

Recently, two articles appeared in the translated Russian Journal of Colloid Chemistry. At times difficult to follow due to either a suspected translation error or inaccessibility to references cited, both studies show an active interest in the USSR with the correlation of electrical conductivity with aeration ratio of foams. In 1976, Chistyakhov and Chernin [5] started with the premise that the electrical conductivity is one of the most important characteristics of foams. They investigated eleven foam systems to evaluate an empirical coefficient (a) that relates a relative electrical conductivity ratio (K) with the degree of aeration (D) of a foam in highly aerated foams.

$$K = a\ D \tag{7}$$

They conclude by stating very narrow limits for the experimentally derived values of the coefficient (a) and state that it is independent of the concentration of the solution and the type of surfactant. They compared this experimental range for the value of the coefficient to a value of 0.33 that was theoretically derived assuming foam bubbles of highly aerated foams were shaped as uniform hexagonal prisms.

In 1980, Sharovarnikov [36] introduced the idea of an excess conductivity related to the electrical double layer of the films present in foams. He states that the presence of the electrical double layer not only increases the number of charge carriers, but also influences the effective field strength. An estimation of the contribution of surface conductance and of the possibility of polarization of the

electrical double layer is made with the use of a dimensionless relaxation criterion: no less than one fourth of the total current was estimated to be carried by ions of the electrical double layer.

The electrical conductivity of foams prepared from solutions of cationic, anionic, and nonionic surfactants were measured by Sharovarnikov with the aim of experimentally determining the influence of surface conductance on the electrical conductivity of foams with high aeration ratio. For nine systems, with film thickness constant, electrical conductivity of the foams was shown to decrease linearly with increasing aeration ratio. A relative electrical conductivity term was not used in the presentation of results. However, with foams where the film thickness was decreased as the aeration ratio increased, the electrical conductivity exhibited an increase over the linear relationship. Weakly conductive surfactants and highly dispersed foams showed the greatest increase from linearity. This deviation from linearity was attributed to surface conductance of foam films.

In 1975, Jashnani and Lemlich [19] investigated the nature and extent of coalescence in steadily ascending foams by using electrical conductivity to measure foam density. Their parameter for foam density equals the fraction of foam volume occupied by liquid. Foams were formed by bubbling prehumidified nitrogen through a Triton-X-100 (nonionic) surfactant solution containing potassium chloride. These foams continuously ascended a vertical glass column, which was equipped with electrical conductivity cells to measure foam density at various levels in the column. Two important points were made. First,

according to the authors, the presence of surface conductivity causes selective adsorption of an ionic surfactant that in turn could distort electrical conductivity results. Therefore, only foam density of foams made using nonionic surfactants were measured by electrical conductivity. Foam density of foams made using anionic and cationic surfactants were measured solely by foam collapse. Second, a slight difference was found between electrical conductivity measurements of stationary foams and of ascending foams at steady state. However, since no difference in conductivity was noted when a sudden change in foam velocity occurred, they attributed the "modest differences" largely to differences in foam morphology. As an addendum to their publication on coalescence, the relationship between foam density and the ratio of electrical conductivity of foam to that of liquid was shown graphically. The results were compared to results of earlier studies, including the work of Clark.

In 1977, Lemlich [20] introduced a model for the conductivity of a liquid foam that is composed of bubbles of any polyhedral shape at a low volumetric fraction of continuous phase (as opposed to earlier studies which discussed dispersions of spherical or ellipsoidal particles). The model specified that conduction was solely through Plateau borders of the foam. His result was the relationship:

$$\frac{k_f}{k_c} = 1/3\ D \tag{8}$$

where k_f and k_c are electrical conductivities of the bulk foam and the

continuous phase, respectively, and D is the volumetric fraction of liquid (continuous phase) in the foam. In his attempt to compare this relationship to that of four sets of published quantitative results, he stated that further experimental work was needed.

In 1979, Change and Lemlich [4] did further experiments to investigate the relationship of the electrical conductivity ratio to volumetric fraction of liquid in a foam. Foams were prepared from aqueous solutions of gelatin or Triton-X-100 surfactant to which potassium chloride was added to enhance an electrical signal. As foams slowly ascended a vertical column, samples were taken and measured. Independent of concentration of potassium chloride, choice of surfactant, and average bubble size, graphical results confirmed and extended the work of Clark [6] and confirmed Lemlich's earlier theory: that the ratio of volumetric fraction of continuous phase to relative electrical conductivity of a foam approaches a limiting value of 3.0 as the volumetric fraction approaches zero. Lemlich claims that the limiting value of this ratio equals 2.8 using experimental data of Chistyakhov and Chernin [5] and thus substantiates his theory.

In 1980, Agnihotri and Lemlich [1] proposed a model for conduction solely through lamellae of polyhedral foam bubbles. A value of 1.4 is predicted for the ratio of volumetric fraction of continuous phase to relative electrical conductivity of a foam as volumetric fraction approaches zero. In combination with the theory dealing with conduction through Plateau borders of a polyhedral foam, this result enables the relative distribution of liquid between lamellae

and Plateau borders to be determined for any experimental value of the ratio of volumetric fraction to relative electrical conductivity of a real polyhedral foam.

During 1970-1979, several Indian investigators performed physico-chemical studies on oil-in-water emulsions in which the continuous phase was water and the dispersed phase was kerosene, turpentine oil, or parafin oil [17,18,35]. During electrical conductivity measurements, no electrolyte was added to the aqueous phase; no measurements were made of the aqueous phase itself and thus, no relative conductivity term is possible; and the frequency at which electrical conductivity was measured was not noted. Tables of data led to the following conclusions: (i) high conductivity favors emulsification and increased stability of emulsions; (ii) an increase in concentration of ionic, cationic, or nonionic surfactants causes an increase in electrical conductivity; (iii) for emulsions stabilized by anionic and cationic surfactants, as oil to water ratio decreased, conductivity decreased, and for emulsions stabilized by nonionic surfactants, as oil to water ratio decreased, conductivity increased by a small amount.

In 1979, Sigrist, Dossenbach, and Ibl [37] introduced a simple conductivity method for determination of voids in a partly gas-filled electrolyte solution such as would occur in an electrolytic cell. Results were presented in graphical form; relative electrical conductivity (K/K_0, a ratio of effective electrical conductivity of the dispersion to that of the gas-free solution) as a function of void fraction (ε, ratio of

gas volume to total volume of electrolyte solution). The authors conclude that in the case of gas bubbles in an electrolye solution, Maxwell's Equation is superior to Bruggeman's and is valid up to a void fraction of 0.6 when compared to experimental results.

They propose their own equation

$$\frac{K}{K_0} = 1 - 3/2\ \varepsilon \tag{9}$$

that applies very well to experimental results up to a void fraction of 0.12. In addition, the versatility of their conductivity method was demonstrated in a study of gas voidage in a laboratory model of an electro-chemical reactor with a gas evolving electrode.

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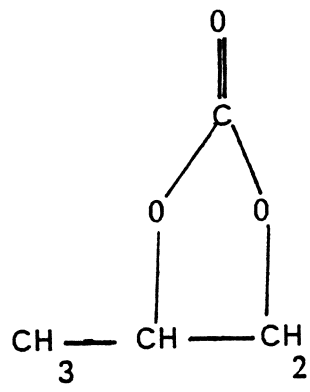
[1] Aphron is derived from the Greek word, aφρos, which means foam.

[2] Propylene carbonate is a cyclic ester of structure,



MATERIALS AND METHODS

PREPARATION OF A POLYAPHRON

During all preparations and determinations, distilled water was prepared using a metal still. The only change with the still occurred when a new steam trap was put on the condensing line. Thus, distilled water quality can be considered a constant throughout this work. Periodically the conductivity of this lab-produced distilled water was measured using a Yellow Springs Instrument Company Incorporated (YSI), Model 31 Conductivity Bridge equipped with a YSI 3400 Series conductivity cell.

A polyaphron comprises an aqueous phase and an oil phase, combined according to a certain procedure that will produce a three-phase colloidal system. The aqueous phase is an aqueous solution containing a predetermined concentration of a water soluble surfactant. If conductivity of the polyaphron were to be measured, an electrolyte, is added to the aqueous phase to enhance the electrical signal. Typically, potassium chloride is added to produce a final aqueous phase concentration equal to 0.075 molarity. The oil phase is an organic liquid to which an oil soluble surfactant is added.

Various surfactants were used in the oil and aqueous phases. The nonionic TERGITOL 15-S Series of specialty surfactants were obtained from Union Carbide. The TERGITOL 15-S Series are ethoxylates of secondary alcohols having chain lengths of eleven to

fifteen carbon atoms. The number following the TERGITOL 15-S product designation refers to average number of moles of ethylene oxide contained in the molecule. TERGITOLS 15-S-3 and 15-S-9, contain an average of three moles and nine moles of ethylene oxide per molecule, respectively.

Union Carbide provided complimentary samples of TERGITOL 15-S-3 and 15-S-9 along with specifications of samples that were sent. TERGITOL 15-S-3 is an oil soluble surfactant and has an average molecular weight of 332; a hydrophile-lipophile balance (HLB) number equal to 8.0; an iron content of two parts per million, maximum; a water content of 0.2 percent by weight, maximum; a color of 75 platinum-cobalt, maximum; and is "substantially free of suspended matter" according to specifications. TERGITOL 15-S-9 is a water soluble surfactant and has an average molecular weight of 596; an HLB number equal to 13.3; a cloud point in the range of 57.5^{0} to 62.5^{0} Celsius; a pour point of 12.8^{0} Celsius, maximum; a water content of 0.50 percent by weight, maximum; a color of 75 platinum-cobalt, maximum; and was "substantially free from dirt, lint, or other foreign material" with a permissable haze. In addition, a one percent solution of TERGITOL 15-S-9 has a pH between six to eight at 25^{0} Celsius.

Due to skin reddening and irritation, rubber gloves were used to handle TERGITOL products and solutions containing them . TERGITOL 15-S products are readily and rapidly degraded by microorganisms normally found in sewage treatment facilities. Thus, disposal of aqueous solutions containing them was no problem. Oil solutions

containing them were disposed of according to disposal procedures of the type of oil used.

All other surfactants were lab stock of the Surface Chemistry Laboratory (Room 148, Randolph Hall, Virginia Polytechnic Institute and State University, Chemical Engineering Department, Blacksburg, VA). The anionic and water soluble surfactant, sodium dodecyl benzene sulfonate (SDBS), is an orangish-tan, viscous liquid labelled Richonate, 60% by weight. Lauric Acid, an anionic and oil soluble surfactant is a solid compound labelled dodecanoic acid, $CH_3(CH_2)_{10}CO_2H$, Armour Neofat 12. The cationic and water soluble, ARQUAD, is a quaternary ammonium fatty soap. It is labelled Arquad, 15-50%, containing isopropanol, Armour Hess Chemicals, Limited. The cationic and oil soluble surfactant, ARMEEN, is a fatty amine. The crystalline powders, Armeen 12D, Lot #1911101, Armak Industries Chemical Division and Armeen SD, soyaamine, Armak Industries Chemical Division were used.

Various nonpolar compounds were used as the oil phase in the polyaphrons. The kerosene was acquired from a local service station and stored in the Surface Chemistry Laboratory in a ten gallon metal can. Since comparative determinations at varying phase volume ratios using the same ingredients was the objective of this investigation, kerosene was not distilled before use. Heavy parafin oil (Saybolt Viscosity 335/365) was laboratory grade, Fisher Scientific Company, #0-119. Cyclohexane was Mallinckrodt, lot KLRE, with density equal to 0.774 at 25° Celsius and a boiling range of 80.3° to 81.4° Celsius.

Carbon Tetrachloride was certified ACS, Fisher Scientific, lot 705243, with density equal to 1.584 at 25° Celsius and a boiling range of 76.0° to 76.5° Celsius.

Cyclohexane and carbon tetrachloride were mixed at a weight fraction equal to 0.561, cyclohexane, and 0.439, carbon tetrachloride to produce a liquid of density equal to the aqueous phase. Thus, creaming (settling due to density differences) of the polyaphron system was avoided. Due to carcinogenity of carbon tetrachloride, used samples of solutions and polyaphrons made with this oil phase mixture were pooled in a waste organic container and properly disposed.

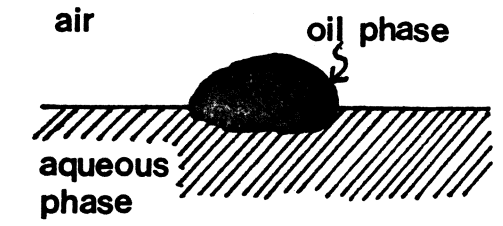
At times, one of two electrolytes was added to the aqueous phase: potassium chloride, Fisher Certified Reagent (Clark), lot 740576, and sodium chloride, U.S.P. (Mallinckrodt), lot KJJS.

There are a number of procedures that one can use to make a polyaphron. The procedure used in this work was as follows. Based on desired volume percent ratio of oil phase to aqueous phase in a polyaphron (that is, phase volume ratio, or PVR), the required total volume of aqueous phase was placed in a bottle. It is important that the bottle be one which has a tight fitting stopper to prevent loss of material during shaking. The aqueous phase was shaken in order to obtain a foam which exposed a large aqueous surface area. Then 0.5 to 1.0 milliliter of the oil phase was added to this aqueous phase. The contents of the container were shaken.

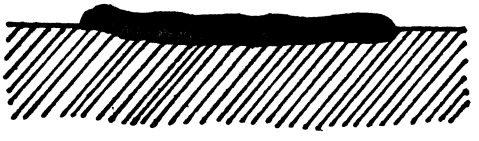
Provided spreading pressure is greater than surface pressure, the oil phase will spread on the aqueous phase. The oil film that results does not remain of uniform thickness for long. Some sections of the film thin sufficiently to allow aqueous phase to break through the thinned oil phase film. When this happens, the periphery of the isolated oil film contracts and thin strands are produced. The oil strands then break and produce globules which are encapsulated in a thin soapy film. Thus, the encapsulated oil globules are dispersed in the continuous aqueous phase. The process is summarized in Figure 2. Figure 2 also presents a sketch of the theoretical structure of a polyaphron.

Then another 1.0 mililiter of oil phase was added to the container, and the contents were shaken to reinitiate the process. Oil phase was continually added, with shaking, in 1.0 milliliter alliquots until a total of five milliliters of oil phase had been added. Volume of each alliquot was then increased to five milliliters and any remaining oil phase was added in five milliliter alliquots. At the beginning of the process, oil phase must be added in small amounts: if there is not enough surface for spreading, conditions occur which prevent the production of polyaphrons. Before long, no more foam is produced, but the aphrons that have been formed provide surfaces for similar spreading of the oil.

Most often a series of polyaphrons was prepared from the same oil and aqueous phases. Each polyaphron of the series was prepared with a different PVR. Usually each series would have fifteen polyaphrons

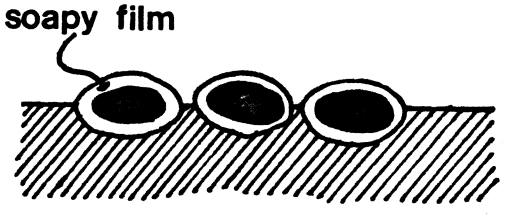


(a) Initial contact of oil phase with aqueous phase.

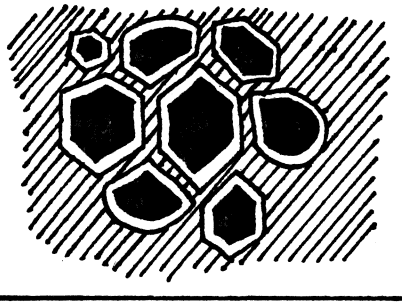


(b) If spreading coefficient exceeds surface pressure, oil phase will spread onto aqueous phase.

(c) Accidental thinning of oil phase film allows aqueous phase to break through the film. Periphery of isolated oil film contracts and thin oil strands are produced. Oil strands break and produce globules which are encapsulated in a thin soapy film.



(d) Formation of individual aphrons - encapsulated oil globules which are dispersed in the continuous aqueous phase.



(e) Schematic representation of polyaphron. As amount of oil phase increases, the number of aphrons increase. Spherical aphrons begin to close pack and assume polyhedral shapes.

FIGURE 2. Pictorial representation of the formation and structure of polyaphrons.

with PVR equal to: 9.0, 8.09, 7.33, 6.143, 5.25, 4.0, 3.0, 2.33, 2.03, 1.5, 1.0, 0.667, 0.333, 0.250, and 0.111. In other words the oil phase would equal 90%, 89%, 88%, 86%, 84%, 80%, 75%, 70%, 67%, 60%, 50%, 40%, 25%, 20%, and 10% respectively, of total volume of the polyaphron.

CONDUCTIVITY MEASUREMENTS OF A POLYAPHRON

Electrical conductance was measured by a Model 32 Yellow Springs Instrument Conductance Meter. Conductivity cell (YSI, Model 3401) with a cell constant equal to 1.0 cm^{-1} was used for all measurements. This cell constant was calibrated to $\pm$ 1 percent accuracy against a YSI standard cell. The cell is constructed of Pyrex 7740 and has dimensions: 19.05 centimeters overall length, 2.54 centimeters maximum outside diameter, and 76.2 centimeters chamber depth. Electrodes are constructed of a platinum-iridium alloy and are gold-soldered to platinum lead wires. The cell cable is 1.22 meters long and is covered with smooth rubber insulation.

The observed conductance of a solution measured with the above instrument is the value in the digital display window of the Conductivity Bridge in units of micromhos. This observed conductance value multiplied by the cell constant (cm^{-1}) becomes specific conductance or conductivity of the solution and has units of micromhos per centimeter. In equation form:

$$\text{conductivity}\left(\frac{\text{micromhos}}{\text{centimeters}}\right) = \text{conductance(micromhos)} \times \text{cell constant}_{(\text{centimeters}^{-1})}.$$

The conductivity bridge was allowed at least five minutes to warm up. To test that the bridge itself was functioning properly, one of three resistors of known value was placed directly across the terminals of the bridge. Resistors of 500, 1471, and 3000(5%) ohms were used. The registered value on the capacitance scale was recorded. It was concluded that the bridge was working properly if the capacitance values obtained were 0.338 micromhos for the 500 ohm resistor, 0.681 for the 1471, and 1.99 for the 3000(5%).

To test that the electrode/conductivity cell unit was functioning properly, a 0.075 M KC1 solution was measured at 30° Celsius. This 0.0751 KC1 was prepared periodically, but was not standardized. Thus, this check was a qualitative check. As long as the measured value of any chosen unstandardized 0.075 M KC1 solution at 30° Celsius was in the range of 9 to 11 micromhos, it was concluded that the electrode/conductivity cell unit was working correctly.

The conductivity of oil and aqueous phases that were to be used in preparing various polyaphrons within a given series was measured. Conductivites of these phases were values that later proved useful for analysis of the data. Electrical conductivities of all oil phases, as expected, were negligible. Since the aqueous phase contained 0.075M KC1 and this aqueous phase was not standardized, it was particularly important that the same aqueous phase was used to prepare all

polyaphrons in a given series. Conductivity measurements on both the aqueous phase alone and for any given polyaphron prepared from that aqueous phase were combined to calculate a relative conductivity term which is independent of KC1 molarity and characteristics of the given polyaphron. In essence, conductivity measurements were measurements of conductivity of potassium chloride solutions within the geometric framework of the polyaphron--not measurements of the polyaphron itself.

Shortly after a series of polyaphrons was prepared, aqueous and oil phases used in preparation and the polyaphrons were individually placed in a water bath at 30° Celsius and allowed to equilibrate. The water bath was an open rectangular box (30.48 centimeters wide, 60.96 centimeters long, 20.32 centimeters deep), constructed of 3.75 millimeter wide sheet aluminum and insulated by a 2.54 centimeter layer of styrofoam. A Haake Constant Temperature Circulator Model E52 controlled the water bath temperature. During the time that a polyaphron, aqueous phase, or oil phase solution was in the water bath, temperature of the solution was monitored with a Copper Constantan Precision Fine Wire Thermocouple (0.127 millimeters diameter and 0.91 meter length) produced by Omega Engineering. This thermocouple was calibrated and referenced against an ice-water mixture and boiling water. An Omega Engineering Model 199 T Copper Constantan (199-JC-A-D-DSS) Digital Meter provided Celsius temperature as measured by the thermocouple. All measurements were at 25° or 30° Celsius.

The vessel used to contain solutions being measured required the following design:

1. Sufficient space so that electrodes were submerged in solution, without entrapment of air in electrode chamber and so that conductivity cell was not touching any walls of vessel.

2. Minimum volume so that smallest volume of polyaphron could be measured--thus materials of preparation could be conserved.

3. A secure lid so that polyaphron could be shaked in between successive measurements. None of the standard laboratory vessels was appropriate. However a two ounce jar used to package Durkee Olives is of cylindrical shape with a 15 cm height, 3.1 cm inner diameter, and a volume equal to 145.0 milliliters. It fits the above design requirements and was selected as the measuring vessel.

Once the polyaphron reached desired temperature it was shaken to insure uniform distribution and poured into the measuring vessel. The vessel had previously been suspended in the water bath and thus, was at desired temperature as well.

The thermocouple and conductivity cell were then placed into the polyaphron solution. The conductivity cell was dipped into the solution several times to insure proper wetting. A soft mallet constructed of a neoprene stopper on the end of a pencil was used to lightly tap against the cell and remove any trapped air in electrode chamber. Since this mallet adequately dispelled trapped air in clear oil and aqueous solutions, it was assumed that it was also able to displace trapped air in polyaphrons. This could not be visually checked because the type of polyaphrons measured were opaque.

Conductance of the polyaphron was then read directly from the conductivity bridge and recorded. This time was designated as the starting time. Conductance was also read at 10, 20, 40, and 60 seconds from the starting time and recorded. The thermocouple and conductivity cell were then removed from the measuring vessel. The vessel was quickly closed, removed from the water bath, shaken, and returned to the water bath to be measured for the second time. This process was repeated for a third measurement. The measuring vessel was shaken before second and third measurements to compensate for possible creaming of the polyaphron and to insure a uniform distribution of polyaphron around electrode surface. Likewise, second and third measurements were taken to offset effects of possible creaming and uneven polyaphron distribution in the vicinity of electrode. The fifteen values of first, second, and third measurements were averaged for a final value which was considered the electrical conductivity of that particular polyaphron at that particular temperature.

If should be noted that these polyaprons were measured as static systems. This type of measurement is in contrast to other gas foam and emulsion conductivity measurements reported in the literature [19] where the electrical conductance was measured as the systems flowed past the surfaces of electrodes.

The conductivity cell was not cleaned as is customary with a special solution in between readings of a given series of polyaphrons. Instead, after each individual measurement, any excess polyaphron

was allowed to drain from the electrode. The electrode was then dipped two or three times in distilled water or held under a distilled water tap for one minute to rinse. The outside of the electrode was then patted dry with a Kimwipe. A Kimwipe was also used to adsorb any remaining distilled water inside electrode chamber.

However, careful cleaning was part of the procedure each time the type of solution to be measured changed. For example, a clean electrode would be used to measure an entire series of polyaphrons, differing in PVR and yet composed of the same oil and aqueous phases, without intermittant cleaning. However, when a polyaphron, composed of an oil or aqueous phase different than the phases of the series just measured was to be analyzed, the electrode would be cleaned before measuring this new polyaphron.

As recommended by the manufacturer of the cell, the cell was cleaned with the following solution: 2 parts by volume isopropyl alcohol, 2 parts ethyl ether, 1 part concentrated hydrochloric acid, and 1 part lab distilled water. The cell was dipped into this solution so that it was submerged beyond vent slots of electrode chamber. The solution was agitated for one to two minutes. Then the cell was removed from the solution and rinsed in several changes of distilled water.

Electrode surfaces were continually checked to note the appearance of the platinum black coating. When coating was uneven, cracked, or flaking off or when cleaning of electrode did not eliminate an irrational conductivity reading, the electrode was replatinized with

a YSI #3139 Platinizing Kit and YSI #3140 Platinizing Solution (3.0% platinum chloride in 0.025% lead acetate solution). The manufacturer's procedure was followed.

To summarize, the conductivity of a series of polyaphrons was measured with the following procedural steps:

(1) Preparation of the series of polyaphrons.

(2) Properly platinize electrode and clean conductivity cell.

(3) Warm up conductivity bridge.

(4) Check proper functioning of conductivity bridge with resistors.

(5) Check proper functioning of conductivity cell using reference 0.075 M KCl solution.

(6) Rinse conductivity cell. Dry well.

(7) Bring oil phase to temperature.

(8) Measure electrical conductivities of oil phase.

(9) Clean conductivity cell using cleaning solution to remove oil phase residue.

(10) Bring aqueous phase to temperature.

(11) Measure electrical conductivity of aqueous phase.

(12) Wipe excess aqueous phase from conductivity cell.

(13) With first polyaphron of series at temperature, pour into measuring vessel. Measure electrical conductivity.

(14) Close measuring vessel and shake polyaphron. Wipe excess polyaphron from conductivity cell and rinse with distilled water.

(15) Measure electrical conductivity for second time.

(16) Repeat Step 14 and measure electrical conductivity for third time.

(17) Wipe excess polyaphron from conductivity cell and rinse cell with distilled water.

(18) Repeat Steps 13 through 17 for next polyaphron of series. Continue until entire series is measured.

(19) Clean conductivity cell using cleaning solution.

ANALYSIS OF DATA

Analysis of data was as follows. As previously mentioned, observed conductance was multiplied by the cell constant to obtain conductivity. Parameters used are defined as follows:

k_{PA} = observed conductivity of polyaphron

k_C = observed conductivity of condensed phase (that is, aqueous phase)

k_D = observed conductivity of dispersed phase (that is, oil phase). For oil phases used in this investigation, k. values were so negligible that they could not be recorded with the Model 32 YSI Conductivity Bridge.

K_{PA} = relative conductivity of polyaphron

$$= \frac{\text{observed conductivity of polyaphron}}{\text{observed conductivity of continuous (aqueous) phase}}$$

$$= \frac{k_{PA}}{k_c}$$

$$PVR = \frac{\text{Volume percent of oil phase in polyaphron}}{\text{Volume percent of aqueous phase in polyaphron}}$$

All oil phase present is incorporated in the aphrons; the amount of total aqueous phase incorporated in the thin soapy film surrounding each aphron can be considered negligible compared to the remaining amount of aqueous phase because the soapy films are so thin. Thus, the PVR value can provide a concentration of aphrons per unit of continuous aqueous phase. One has a perceptive grasp of a comparison when realizing that a polyaphron of PVR equal to 9 has more than twice the concentration of aphrons dispersed in the continuous phase than does the polyaphron with PVR equal to 4. The reciprocal of PVR has been useful for graphing results: it is called Inverse PVR, or $(PVR)^{-1}$. It is, of course, the relative concentration of aqueous phase to oil phase. Figure 3 helps to explain the concept of PVR and Inverse PVR.

Thus, for each series of polyaphrons, a set of data was generated: a polyaphron of particular PVR exhibits a particular relative electrical conductivity. Values were then graphed with Inverse PVR as the independent variable.

The following experiments were performed.

(I) The effect of a change in phase volume ratio on relative electrical conductivity of a polyaphron was investigated. A series of

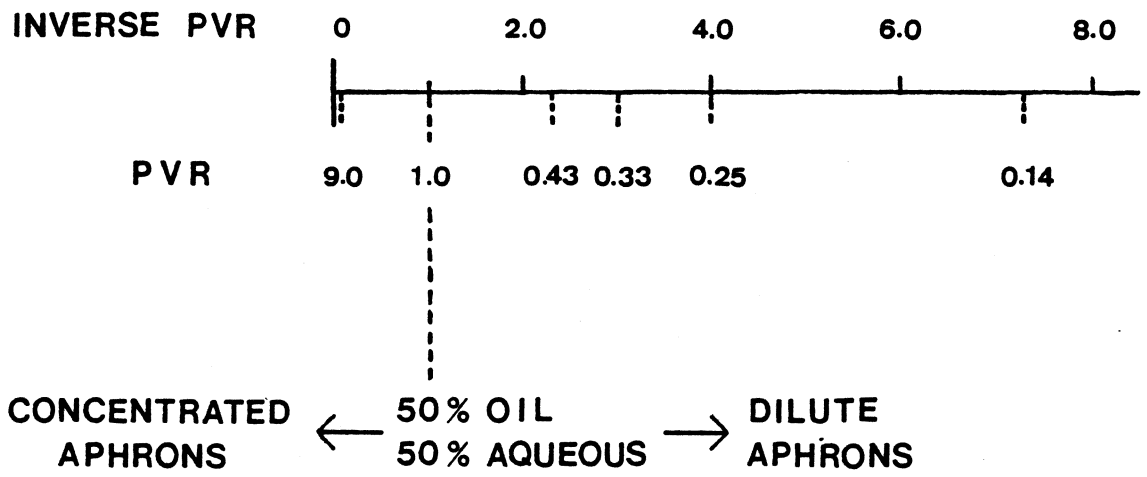


FIGURE 3. Visual representation of parameters: phase volume ratio (PVR) and reciprocal of phase volume ratio (Inverse PVR).

polyaphrons was prepared: aqueous phase was composed of 35 grams per liter TERGITOL 15-S-9 and 0.075 M potassium chloride; oil phase was a mixture of cyclohexane and carbon tetrachloride (weight fractions of 0.561 and 0.439, respectively) that contained 1.0 percent by weight of TERGITOL 15-S-3. All electrical conductivities were measured at 30° Celsius. The relationship obtained between relative electrical conductivity and inverse PVR of the polyaphrons is shown in Figure 4 located in the Result Section.

(2) The effect of oil phase surfactant concentration on relative electrical conductivity was investigated. Four series of polyaphrons were prepared. Aqueous phase in all was composed of 35 grams per liter of TERGITOL 15-S-9 and 0.075 M potassium chloride. Each series of fifteen polyaphrons contained different concentrations of TERGITOL 15-S-3 (0.2, 0.5, 1.0, and 2.0 percent by weight) in the oil phase, which was a cyclohexane/carbon tetrachloride mixture (weight fractions of 0.561 and 0.439, respectively). The above concentrations of TERGITOL 15-S-3 in the oil phase produce stable polyaphrons of aphron size which has potential industrial application. All electrical conductivities were measured at 30° Celsius. Results of this investigation are shown in Figure 5 located in the Result Section.

(3) This study was conducted to investigate the effect, if any, of varying the type of surfactant in the phases. Three series of polyaphrons were prepared. The first series contained nonionic TERGITOLS in both the aqueous and oil phases: 36 grams per liter TERGITOL 15-S-9 and 0.075 potassium chloride in the aqueous phase;

0.2 percent by weight TERGITOL 15-S-3 in the cyclohexane/carbon tetrachloride mixture (weight fractions of 0.561 and 0.439, respectively). The second series of polyaphrons used anionic surfactants, 10 grams per liter sodium dodecyl benzene sulfonate (Richonate, 60 percent by weight, as supplied) and 0.075 potassium chloride in the aqueous phase; 0.2 percent by weight lauric acid in the oil phase, which was the cyclohexane/carbon tetrachloride mixture. The third series used cationic surfactants: 2.5 grams per liter Arquad (16-50%, as supplied) and 0.075 M potassium chloride in the aqueous phase; 0.2 percent by weight Armeen SD in the oil phase, which was the cyclohexane/carbon tetrachloride mixture. Each series was measured at 30° Celsius. Results are shown in Figure 6 located in the Result Section.

(4) The effect of different oil phases on the electrical conductivity of polyaphrons was investigated. Three series of polyaphrons were prepared. The first series was one in which the oil phase was the cyclohexane/carbon tetrachloride mixture (weight fractions of 0.561 and 0.439, respectively) and contained 2.0 percent by weight TERGITOL 15-S-3. The aqueous phase contained 30 grams per liter TERGITOL 15-S-9 and 0.075 M potassium chloride. The second series comprised an oil phase made up of heavy parafin oil (Saybolt viscosity 335/365) with 1 percent by weight TERGITOL 15-S-3, and an aqueous phase containing 3 grams per liter TERGITOL 15-S-9 with 0.075 M potassium chloride. The third series of polyaphrons contained kerosene with 1.0 percent by weight TERGITOL TMN-3 as

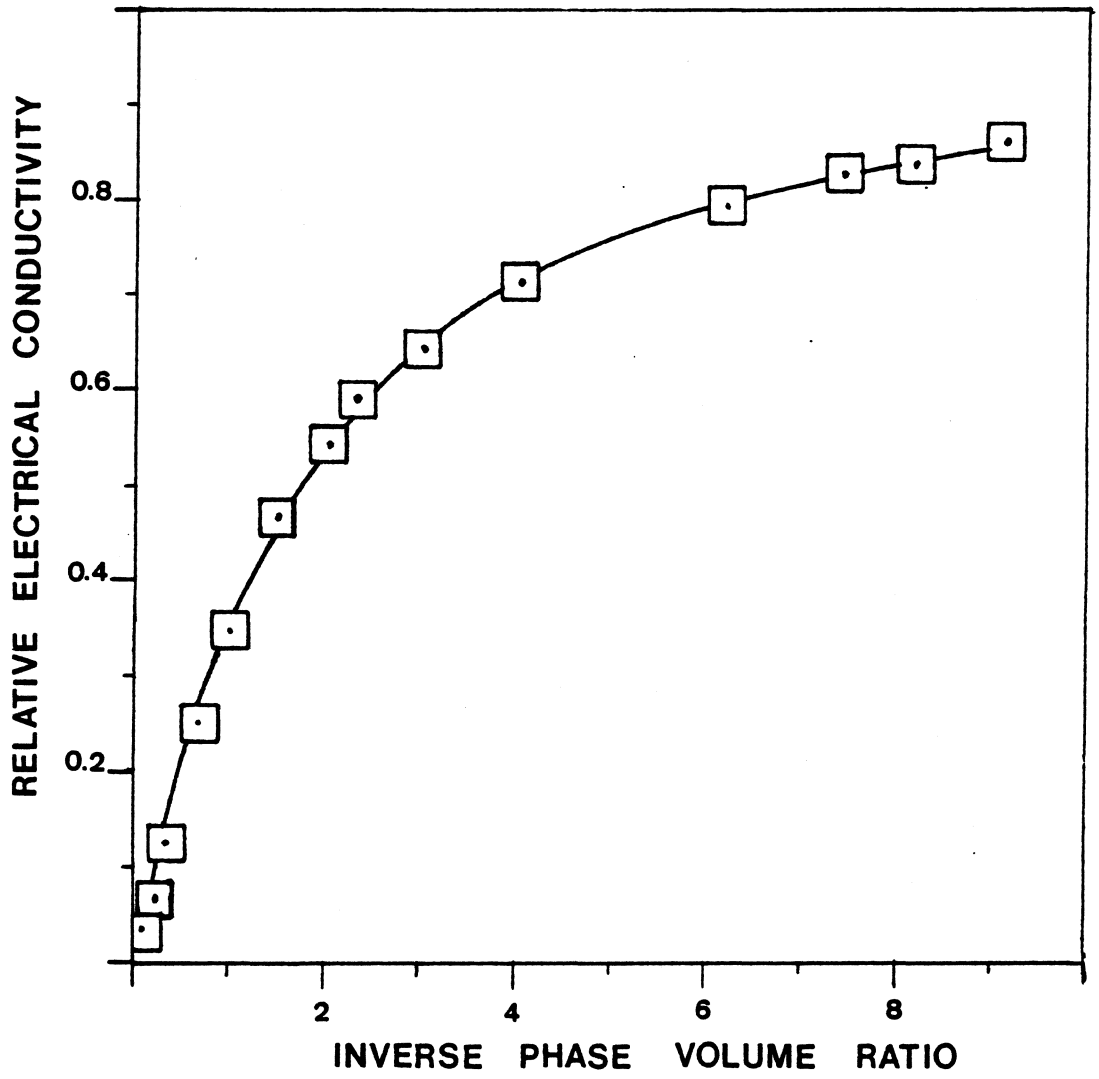
the oil phase and 3 grams per liter TERGITOL 15-S-9 with 0.075 M potassium chloride as the aqueous phase. Each series of polyaphrons was measured at 25° Celsius. Results of all three series are shown in Figure 7, located in the Result Section.

(5) The effect of using a different electrolyte in the aqueous phase was measured. Two series of polyaphrons were prepared using 1.0 percent by weight TERGITOL 15-S-3 in the oil phase consisting of the cyclohexane/carbon tetrachloride mixture (weight fractions of 0.562 and 0.439, respectively). The aqueous phase contained 35 grams per liter TERGITOL 15-S-9 and 0.075 M electrolyte. In the first series the electrolyte was potassium chloride; in the second series, the electrolyte was sodium chloride. Measurements of both series of polyaphrons were made at 30° Celsius. Figure 8, located in the Result Section, shows the outcome of this investigation.

RESULTS

Figure 4 shows the effect of a change in phase volume ratio on relative electrical conductivity of a polyaphron. The units of dispersed phase, the aphrons, cause an interruption to the electrical path between the electrodes. As the amount of oil phase increases in relationship to the aqueous (that is, as the PVR increase, or as the Inverse PVR decreases), more aphrons are present. As more aphrons are introduced, conductivity decreases. The curve shape of Figure 4 indicates a unique relationship between relative electrical conductivity and Inverse PVR. This curve has the potential to predict the PVR of a polyaphron of unknown oil phase content based on electrical conductivity measurements of the polyaphron. This idea is quite similar to the work of Miles, Shedlovsky, and Ross [26] and the work of Clark [6] that showed this pattern on gas foams. However, both investigations presented a unique relationship of relative electrical conductivity with aqueous phase volumetric fraction whereas in this investigation the inverse PVR was used.

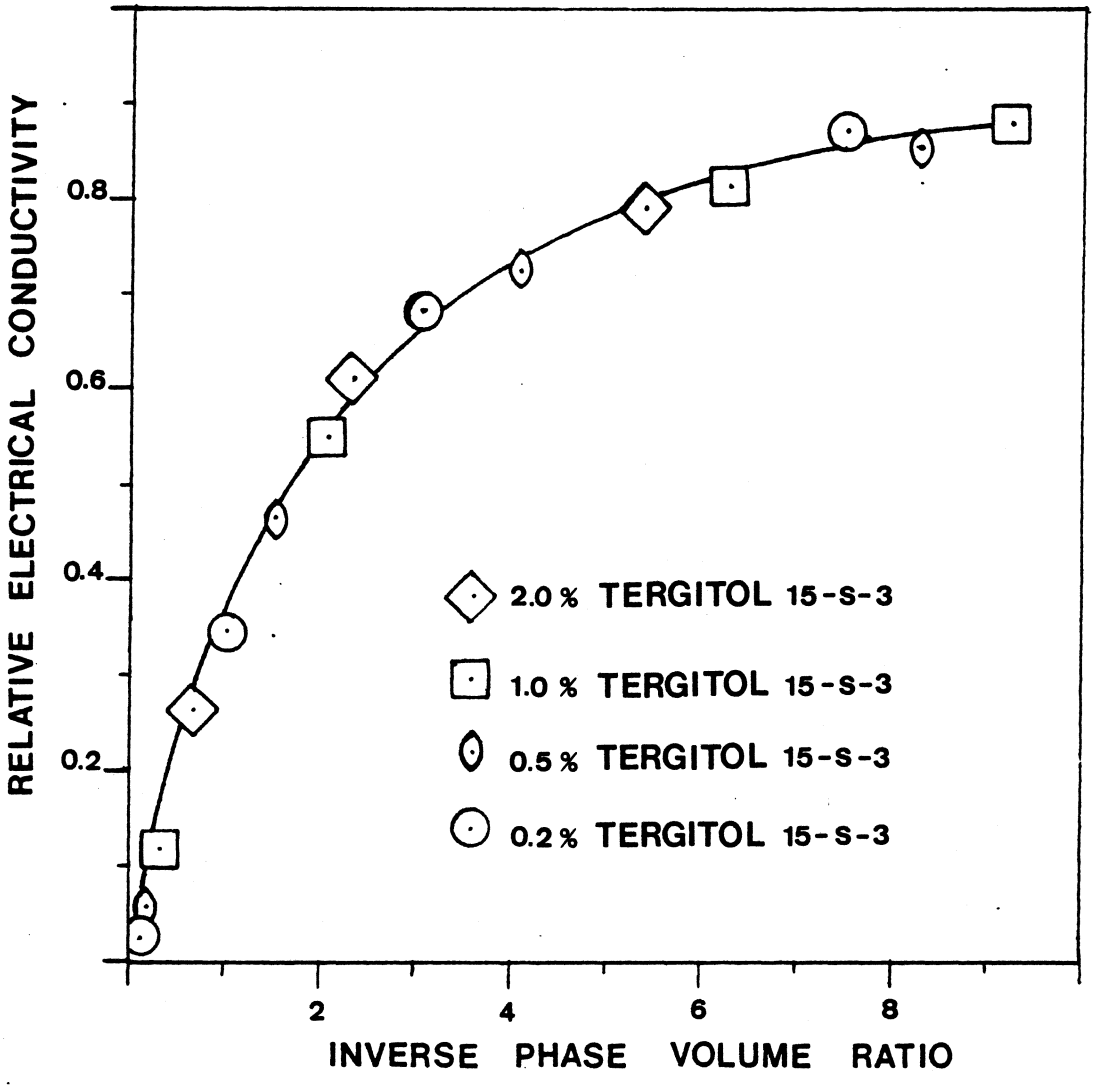
In the second investigation the surfactant in the oil phase was varied over a range of concentrations (0.2, 0.5, 1.0, and 2.0 percent by weight TERGITOL 15-S-3) as the surfactant concentration of the aqueous phase remained constant (35 grams per liter TERGITOL 15-S-9). Figure 5 summarizes the results from electrical conductivity measurements of the four polyaphron series. Each series contained at



Conditions:

Oil phase:	1.0% TERGITOL 15-S-3 in Cyclohexane/CCl_4 Mixture.
Aqueous phase:	35 grams/liter TERGITOL 15-S-9, 0.075 M KCl.
Temperature:	30° Celsius.

FIGURE 4. The relationship of inverse phase volume and relative electrical conductivity.



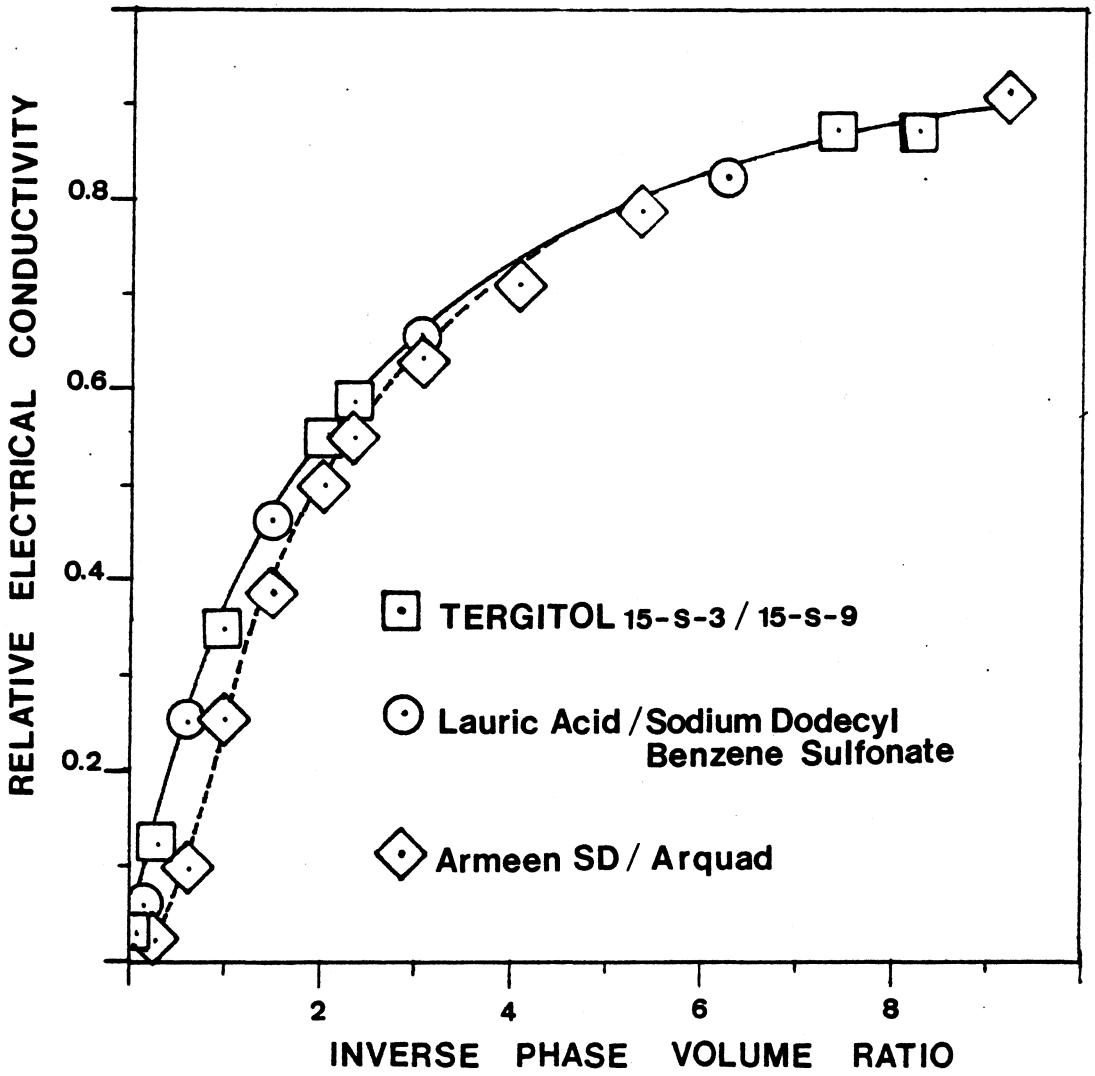
Conditions:

Oil phase:	TERGITOL 15-S-3 in Cyclohexane/CCl_4 Mixture.
Aqueous phase:	35 grams/liter TERGITOL 15-S-9, 0.075 M KCl.
Temperature:	30o Celsius.

FIGURE 5. Effect of oil phase surfactant concentration on relative electrical conductivity.

least twelve polyaphrons varying in PVR. For clarity on the figure, however, only four measurements of each level of surfactant concentration in the oil phase are included. All points shown as well as those points omitted by design, fall on the curve presented in Figure 5. Thus, Figure 5 indicates that for the conditions used, surfactant concentration in the oil phase has no effect on electrical conductivity of polyaphrons measured.

A third investigation introduced other type surfactants into the oil and aqueous phases of a polyaphron. In three series of polyaphrons, the oil phases consisted of 0.2 percent by weight oil soluble surfactant in the cyclohexane/carbon tetrachloride mixture (weight fractions of 0.561 and 0.439, respectively), and the aqueous phase consisted of the water soluble surfactant and 0.075 M potassium chloride. The first series used nonionic TERGITOLS: TERGITOL 15-S-3 in the oil phase and TERGITOL 15-S-9 (35 grams per liter) in the aqueous phase. This series is the same one reported in Figure 5. The second series incorporated anionic surfactants: lauric acid was the oil soluble surfactant and sodium dodecyl benzene sulfonate (10 grams per liter) was the water soluble surfactant. The third series of polyaphrons incorporated cationic surfactants: Armeen SD (a fatty amine) was the oil soluble surfactant, and Arquad (a quaternary ammonium fatty soap at 2.5 grams per liter) was the water soluble surfactant. The results of electrical conductivity measurements at various PVR appear in Figure 6. The nonionic series and the anionic series show the same behavior over the range of PVR investigated.



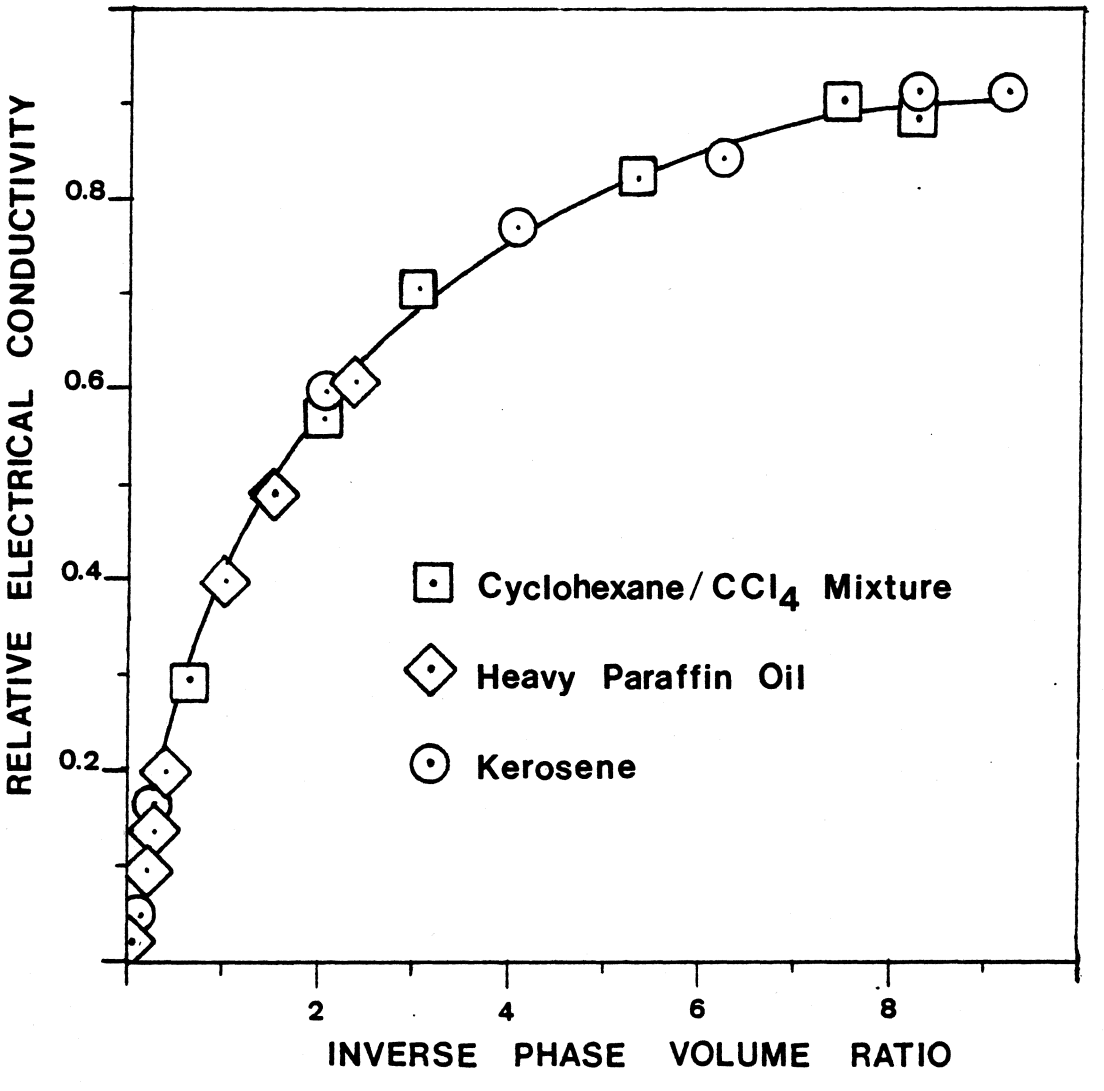
Conditions:

Oil phase:	0.2% surfactant in Cyclohexane/CCl_4 Mixture.
Aqueous phase:	surfactant 0.075 M KCl.
Temperature:	30° Celsius.

FIGURE 6. Effect of different surfactant systems on relative electrical conductivity.

However, the cationic series shows a deviation from this behavior around a PVR equal to 4, that is, 80 percent oil phase to 20 percent aqueous phase. The relative electrical conductivity decreases in comparison to the other series. Polyaphrons made with cationic surfactants did not wet glassware as did polyaphrons made with both nonionic and anionic surfactants.

Series of polyaphrons consisting of various oil phases were also investigated. The first series consisted of 2.0 percent by weight TERGITOL 15-S-3 in the cyclohexane/carbon tetrachloride mixture (weight fractions of 0.561 and 0.439, respectively) and 30 grams per liter TERGITOL 15-S-9 and 0.075 M potassium chloride in the aqueous phase. The second series contained 1 percent by weight TERGITOL 15-S-3 in heavy parafin oil of Saybolt viscosity 335/365 and 3 grams per liter TERGITOL 15-S-9 and 0.075 M potassium chloride as the aqueous phase. The third series contained 1 percent by weight TERGITOL TMN-3 in kerosene and 3 grams per liter TERGITOL 15-S-9 and 0.075 M potassium chloride as the aqueous phase. It is interesting to note that considerably less water soluble surfactant (about one tenth) was needed to produce a stable series of polyaphrons when the oil phase was changed from the cyclohexane/carbon tetrachloride mixture to either parafin oil or kerosene. Figure 7 contains the results of electrical conductivity measurements over a range of PVR for all three series of polyaphrons. Changing the nature of the oil phase did not affect curve shape for conditions investigated.

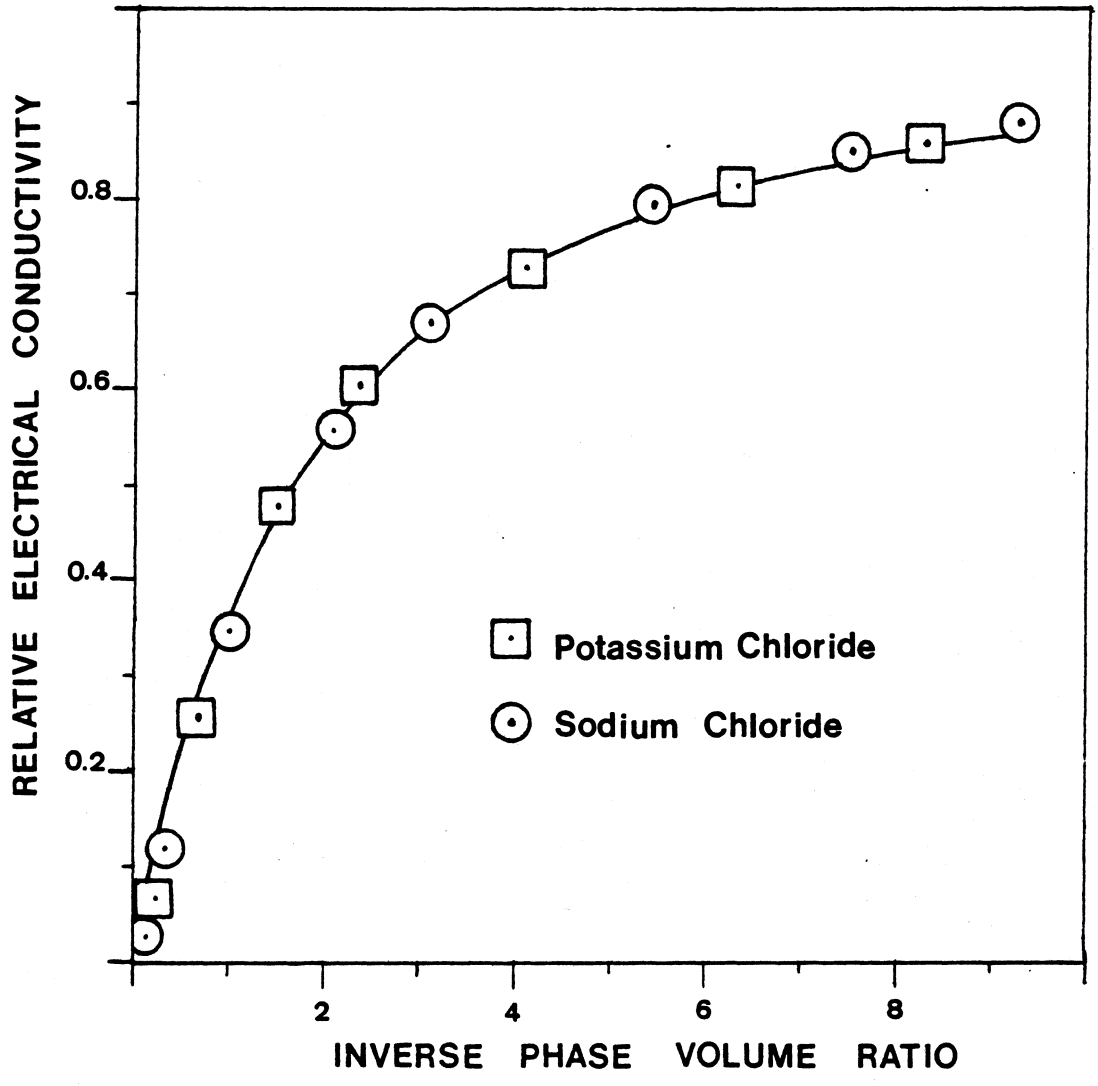


Conditions:

Oil phase:	TERGITOL surfactant
Aqueous phase:	TERGITOL surfactant, 0.075 M KCl.
Temperature:	25° Celsius.

FIGURE 7. Effect of oil phase component on relative electrical conductivity.

Figure 8 contains results of electrical conductivity measurements over a range of PVR for two series of polyaphrons. Both series were identical with an oil phase containing 1.0 percent TERGITOL 15-S-3 in a cyclohexane/carbon tetrachloride mixture (weight fractions of 0.561 and 0.439, respectively) and with an aqueous phase containing 35 grams per liter TERGITOL 15-S-9 and 0.075 M electrolyte. However, the first series contained potassium chloride as the electrolyte, and the second series contained sodium chloride. No difference in curve shape was observed.



Conditions:

Oil phase: 1% TERGITOL 15-S-3 in Cyclohexane/CCl_4 Mixture.
Aqueous phase: 35 grams/liter TERGITOL 15-S-9, 0.075 M. electrolyte.
Temperature: 30° Celsius.

FIGURE 8. Effect of aqueous phase electrolyte on relative electrical conductivity.

DISCUSSION

Results confirm a method of electrical conductivity measurements as a means to characterize a polyaphron, as many investigators have done with foams [1,4,5,6,19,26,36], emulsions [14,15,16,17,18,25], and dispersions of solids in a liquid phase [7]. Figures 4, 5, 6, 7, and 8 indicate that over a wide range of conditions, a unique relationship exists between relative electrical conductivity (a ratio of electrical conductivity of the polyaphron to that of the continuous phase of the polyaphron) and a parameter of choice to indicate amount of dispersed phase and amount of continuous phase in the polyaphron. This parameter may be a volumetric fraction of either phase, or the phase volume ratio (PVR). This unique relationship is independent of the amount of surfactant and the type of oil in the dispersed phase, or the type of electrolyte used in the continuous phase.

Whether this relationship is affected by different type surfactants is still undecided. Figure 6 shows that a polyaphron series composed of cationic surfactants in both aqueous and oil phases exhibits a deviation from the polyaphron series composed of either anionic or nonionic surfactants. At a phase volume ratio equal to 4, relative electrical conductivity of the anionic series decreases in comparison to values recorded from the other series. Jahnani and Lemlich in their article on gas foams [19], mention that selective absorption of ionic surfactants can distort electrical conductivity measurements through

the presence of surface conductivity. Sharovarnikov [36] states that an increase in electrical conductivity over values predicted by a linear relationship occurs in foams with increasing aeration and is probably due to the contribution from surface conductance of the foam films. Deviations are greater for weakly conductive foaming agents and for high volumetric fraction of dispersed phase.

Neither of these observations adequately explain the deviation found in the cationic series of polyaphrons. If this deviation were due to selective adsorption of ionic surfactants and subsequent distortion of conductivity measuremetns through the presence of surface conductivity, why does the anionic series of polyaphrons not display similar behavior? The deviation is at high volumetric fraction of dispersed phase, but it is a decrease in electrical conductivity rather than an increase as suggested by Sharovarnikov. However, it is an experimental fact that the polyaphrons prepared with cationic surfactants do not wet laboratory glass. Perhaps they do not wet the electrode surface either. This non-wetting tendency may be more significant in an explanation of the deviation in electrical conductivity behavior of cationic series of polyaphrons.

Remembering that the surface of glass is negatively charged, one might question why a cationic preparation would not wet a glass surface, that is, the conductivity cell. Based on other observations of polyaphrons, it appears that the oil soluble surfactant dominates the behavior of polyaphrons. For example, as amount of oil soluble surfactant increases, individual and average sizes of aphrons

decreases. In the case of a polyaphron in which a cationic surfactant is used in the oil phase, possibly the oil soluble cationic surfactant itself forms a stable monolayer at the surface of glass: the positively charged portion attracted to the negatively charged surface of glass, and the hydrophobic end of the molecule pointed in the direction of the contents of the glass container. In this situation, these hydrophobic ends would then repel a water continuous polyaphron. Alternatively, in the case of a polyaphron in which a cationic surfactant is used in the aqueous phase, water soluble cationic surfactant may form a stable monolayer against the surface of glass, and present a hydrophobic surface that in turn repels a water continuous polyaphron. The monolayer of cationic surfactant against the surface may also result when polyaphron breakage occurs and cationic surfactant is released into the system. Figure 9 depicts these hypotheses.

In Figure 5, surfactant in the oil phase was varied from 0.2, 0.5, 1.0, and 2.0 percent by weight. Size of an aphron is determined by concentration and nature of surfactant in the oil phase: aphrons prepared with 2.0 percent by weight TERGITOL 15-S-3 in the oil phase are considerably smaller than those prepared with 0.2 percent by weight TERGITOL 15-S-3. At the same phase volume ratio, a polyaphron that is prepared from a higher concentration of oil soluble surfactant will contain a larger amount of aqueous soap film because the film is now covering a greater number of aphrons, than in the polyaphron prepared from a lower concentration of oil soluble surfactant. Geometrically, aqueous soap films around each aphron will

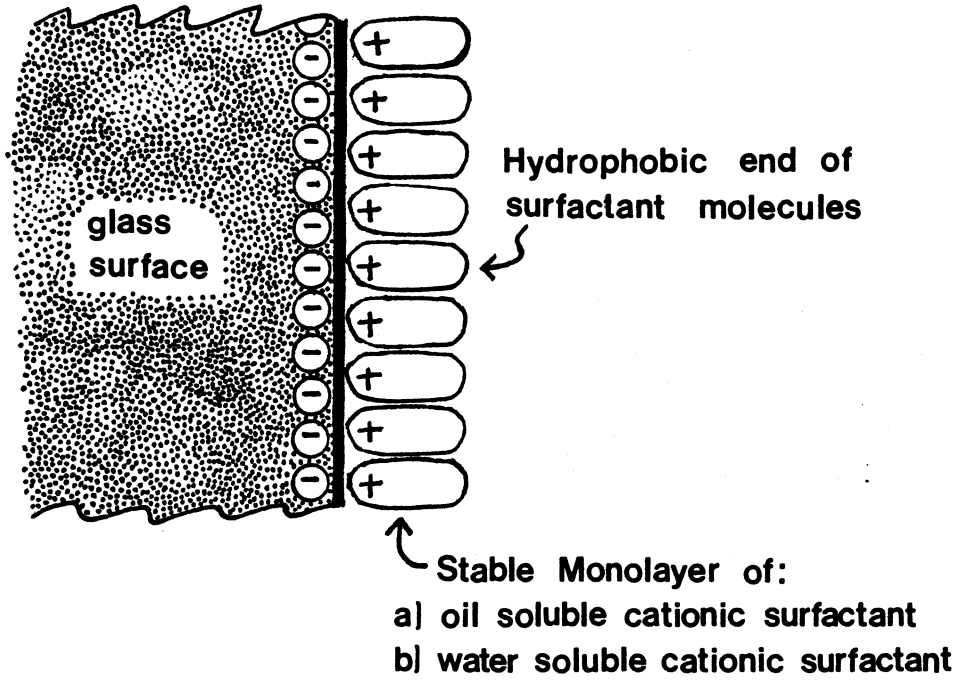


FIGURE 9. Polyaphrons prepared with cationic surfactants do not wet negatively-charged surfaces of glass. A stable monolayer, of either oil soluble surfactant or water soluble surfactant, may present a hydrophobic barrier to a water continuous polyaphron.

also be thinner. A greater amount of thinner soap film would more than likely generate a greater electrical conductivity attributable to surface conductance in the polyaphron if one were applying the hypothesis of Sharovarnikov: an experimental increase in electrical conductivity of foams from values predicted by a linear relationship was explained by the probable presence of surface conductance of foam films. A greater amount of conductance associated with surface conductance would increase the effective electrical conductivity of the polyaphron, and in turn, would increase the relative electrical conductivity of the polyaphron. Thus, an enhancement of the relative electrical conductivity for the polyaphron prepared from a higher concentration of oil soluble surfactant would be predicted for Figure 5. The enhancement is not present: no difference is noted among the four curves representing four concentrations of oil soluble surfactant. Many questions can now be voiced and direct future research. Of most importance, does surface conductance exist in a polyaphron? If it does, will it be detected in a graph of relative electrical conductivity versus Inverse phase volume ratio, or does such a graph mask the presence of certain components that contribute to the effective electrical conductivity of a polyaphron.

To testify there were any significant differences in electrical conductivity of potassium and chloride ions within the polyaphron structure, both potassium chloride and sodium chloride were used as the aqueous phase electrolyte. Figure 8 contains the results of electrical conductivity measurements on polyaphrons prepared with

sodium ions and those prepared with potassium ions. No differences were observed that would indicate a change in behavior of the two ions with the polyaphron structure.

In the literature, results of electrical conductivity measurements of dispersions from many experimental studies are compared to several historical equations and adaptions of these equations. Data obtained in this investigation have been compared to the Maxwell [23], Bruggeman [3], and Meredith-Tobias [25] Equations. The Maxwell and Bruggeman derivations are general and apply to dielectric properties of dispersions. Meredith and Tobias development was specific for electrical conductivity of emulsions. Original journal articles present in-depth developments of these equations; the introductory section of this thesis discusses the derivations briefly, and major assumptions of each theory are summarized in Figure 1.

Figure 10 presents curves of the three equations over the entire range of f and compares them to experimental data shown in Figure 5. In comparison, the Bruggeman Equation provides the best match for this polyaphron prepared with nonionic surfactants. A good agreement with Bruggeman's Equation is understandable when the assumed broad range of diameters of dispersed particles is remembered. Microscopic work shows polyaphrons to possess such a wide range of diameters of aphrons.

The data in Figure 11 was taken from an investigation where electrical conductivity measurements of emulsions were made without addition of electrolyte in the continuous phase [17]. Electrical

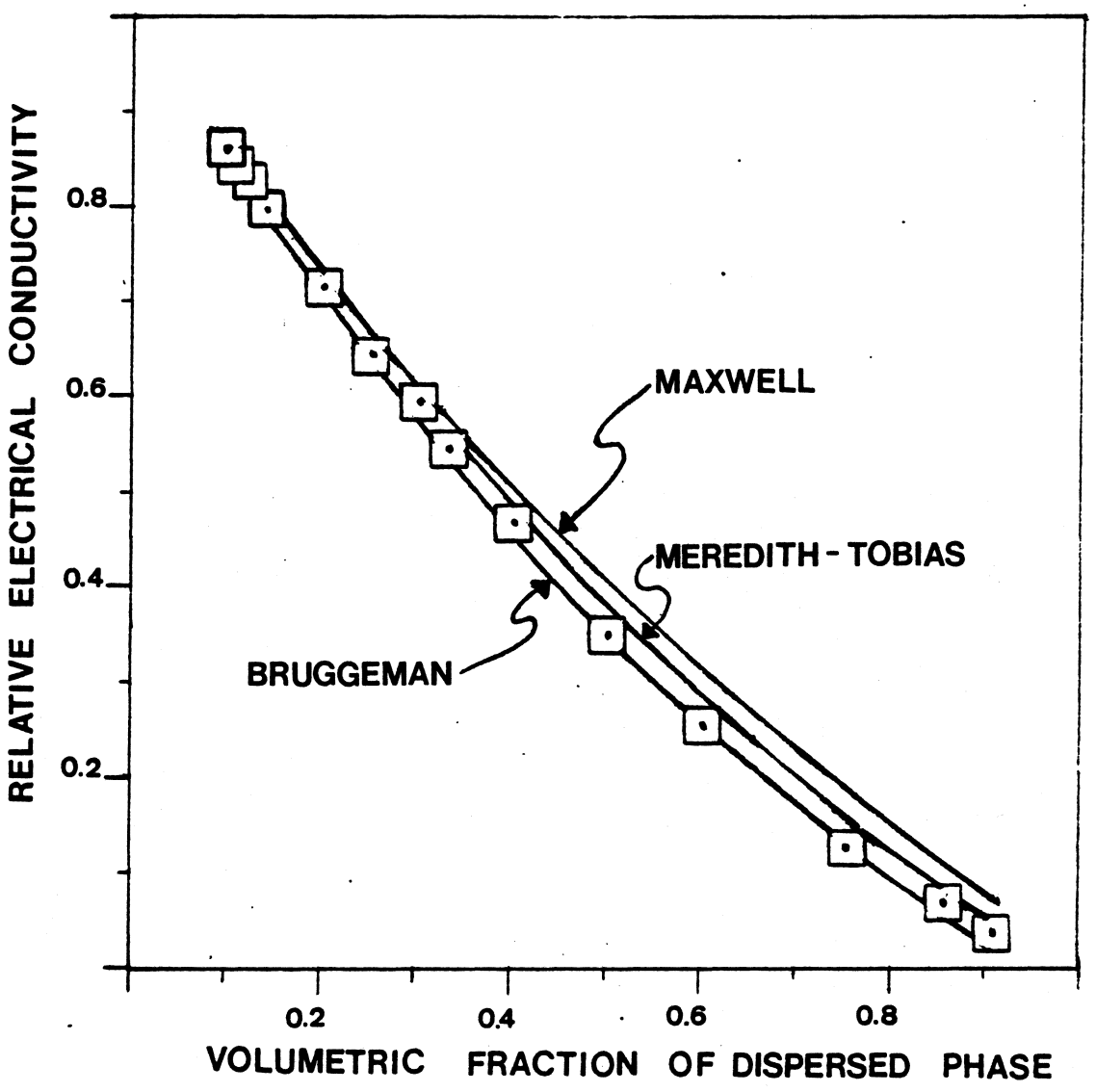


FIGURE 10. Electrical conductivity data on polyaphrons compared with Maxwell, Bruggeman, and Meredith-Tobias Equations.

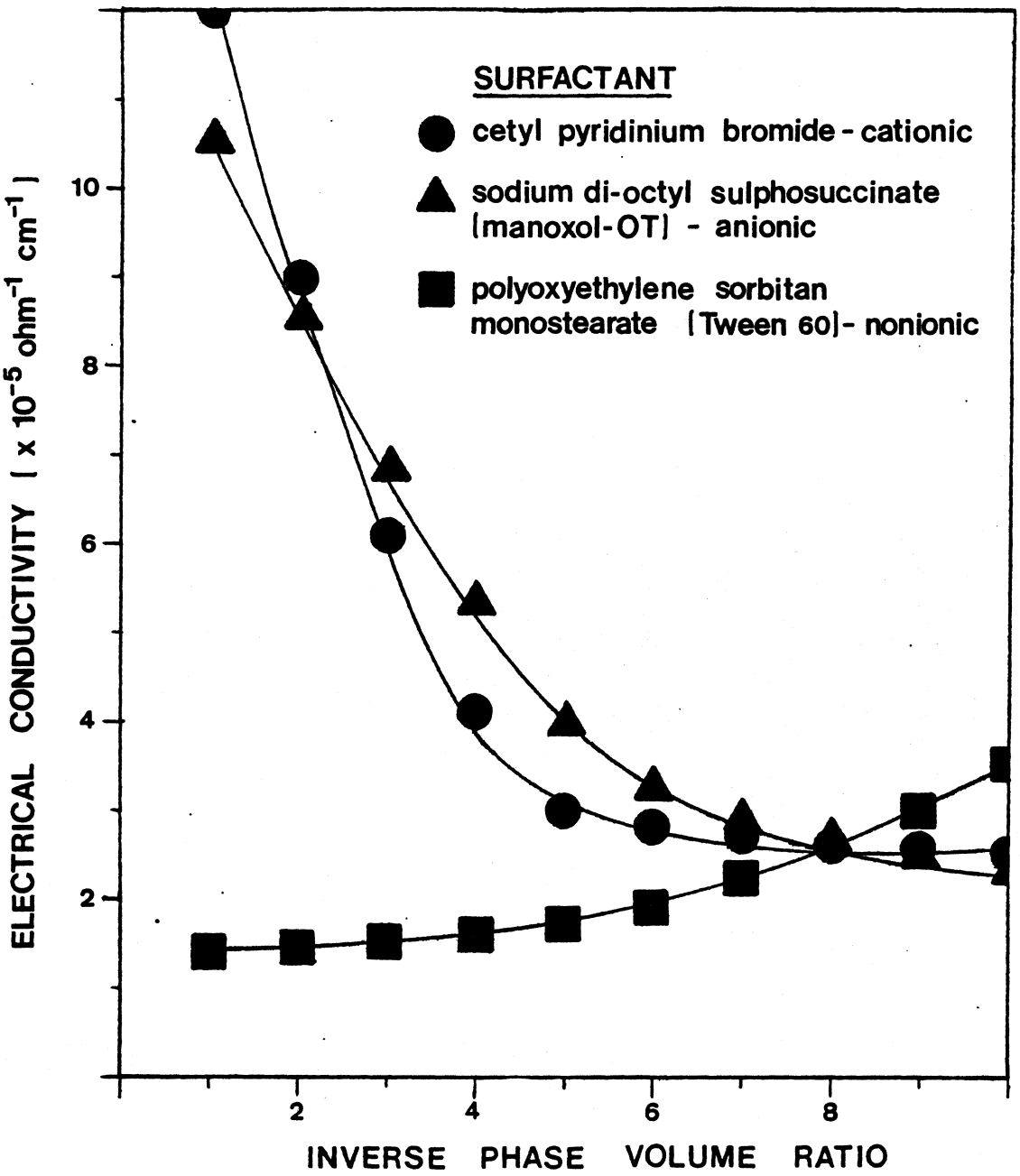


FIGURE 11. The effect of a change in inverse phase volume ratio on the electrical conductivity of kerosene oil-in-water emulsions stabilized by cationic, anionic, or nonionic surfactants at 20° Celsius [17]. No electrolyte was added to the continuous phase of the emulsions.

conductivity is graphed against inverse PVR for kerosene oil-in-water emulsions stabilized by cationic, anionic, or nonionic surfactants. Curve shape deviates markedly from results in this thesis and in much of the literature. This deviation is not so surprising when one realizes that electrical conductivity is graphed in Figure 11, not relative electrical conductivity (ratio of electrical conductivity of emulsion to that of continuous phase of emulsion).

Differences between graphs of ionic surfactant data and nonionic surfactant data indicate values of electrical conductivity presented are values which not only represent an ability of the continuous phase as a whole to conduct electricity, but also represent an ability of charges associated with surfactant molecules to conduct electricity as well. Because this enhancement of electrical conductivity is thought to be due to charges associated with the surfactant molecule, it has been labelled an electrophoretic component. Contributions to electrical conductivity due to aspects of the continuous phase have been labelled electrolytic components. An expression for the effective electrical conductivity of a polyaphron can be written as a sum of components:

$$k_{\substack{\text{effective}\\\text{conductivity}\\\text{of polyaphron}}} = k_{\substack{\text{electrophoretic}\\\text{conductivity}\\\text{of surfactant}\\\text{molecule}}} + k_{\substack{\text{electrolytic}\\\text{conductivity}\\\text{of continuous}\\\text{phase in}\\\text{bulk form}}} + k_{\substack{\text{electrolytic}\\\text{conductivity}\\\text{of continuous}\\\text{phase in}\\\text{film form}}} \qquad (10)$$

Future investigations could determine whether these components are functions of certain factors (such as geometric structure, surfactant concentration, aphron concentration); whether there are other contributing components; and whether each component enhances or detracts from electrical conductivity of polyaphrons. Equation (10) may be better expressed if, as yet, undetermined coefficients were associated with component. Sharovarnikov [36] represented electrical conductivity of foam in similar fashion. One of his components was due to surface conductance. A component due to surface conductance in polyaphrons may also be an integral term of Equation (10).

Addition of electolyte to the continuous phase is often used to enhance the electrical signal during conductivity measurements of a dispersion [4, 5, 7, 19, 25]. In studies where electrolyte is added, the electrolytic conductivity component of the continuous phase in bulk or film foam will exercise a major effect on the conductivity of polyaphrons. The electrophoretic conductivity component (in addition to other possible minor components) may be overshadowed.

Meredith and Tobias [24] not only used electrolyte in the continuous phase of emulsions to enhance electrical signal, but also used electrolytes in both phases to adjust the electrical conductivity ratio of the phases. Using this method, they were better able to investigate the effect of a change in volumetric fraction of a phase on electrical conductivity of dispersions. Identification of a polyaphron system in which the oil phase can acquire an electrical conductivity by addition of electrolyte may significantly contribute to polyaphron research.

When electrolyte is added to a phase of polyaphrons, the role of a relative electrical conductivity term becomes extremely important. Unless all polyaphrons of a series are prepared from a quantity of a phase in which amount of electrolyte has been analytically standardized, comparisons among series members based on straight electrical conductivity measurements would be invalid. Change in electrical conductivity from one polyaphron to another due to a variance in electrolyte amount can be avoided with the use of the relative term.

As Lemlich [20, 1] and Chistyakhov and Chernin [5] proposed for foams, an expression can be written for polyaphrons in the area of high phase volume ratio (PVR):

$$K = a\,\phi \qquad (11)$$

where K is relative electrical conductivity (ratio of electrical conductivity of polyaphron to that of continuous phase in polyaphron), a is an undetermined proportionality coefficient, and ϕ is the phase volume ratio. Figure 12 indicates the value of coefficient a is equal to 0.39 for the data of Figure 4. Future electrical conductivity studies on polyaphrons could evaluate this coefficient over a broader range of conditions. If a broader range of conditions were investigated, coefficient a may prove to be dependent on one or more factors. Suggested conditions include:

- additional oil phases differing in conductivity viscosity and surface tension
- additional oil soluble and aqueous soluble surfactants, as well as additional polyaphrons which are comprised of different type surfactants in the two phases (for example, nonionic surfactant in oil phase and cationic surfactant in aqueous phase)
- polyaphrons prepared with surfactants at concentrations near their critical micelle concentration
- electrical conductivity measurements over a broad range of frequency to extend the work of Hanai [13, 14, 15, 16] and Epstein [8].

Graphically a point, associated with a departure from linearity as phase volume ratio decreases, can be identified and labelled as transition PVR. Figure 12 identifies transition PVR equal to 1.5 for the data of this thesis. Transition PVR is indicative of geometric structural change in polyaphrons.

In a conductivity cell with cell constant equal to 1.0 $(\text{centimeters})^{-1}$, polarization errors are common and are detected by comparison of the ratio of sodium chloride to potassium chloride solutions at the highest resistance ratio used to the ratio found in literature. The ratio acquired from experimental values for 0.075 equivalents electrolyte per liter solution was 1.197. This compared favorably to the ratio values of 1.208 for a 0.10 equivalent electrolyte per liter solution and 1.192 for a 0.01 equivalent electrolyte per liter solution [2]. In addition, care was taken to maintain properly

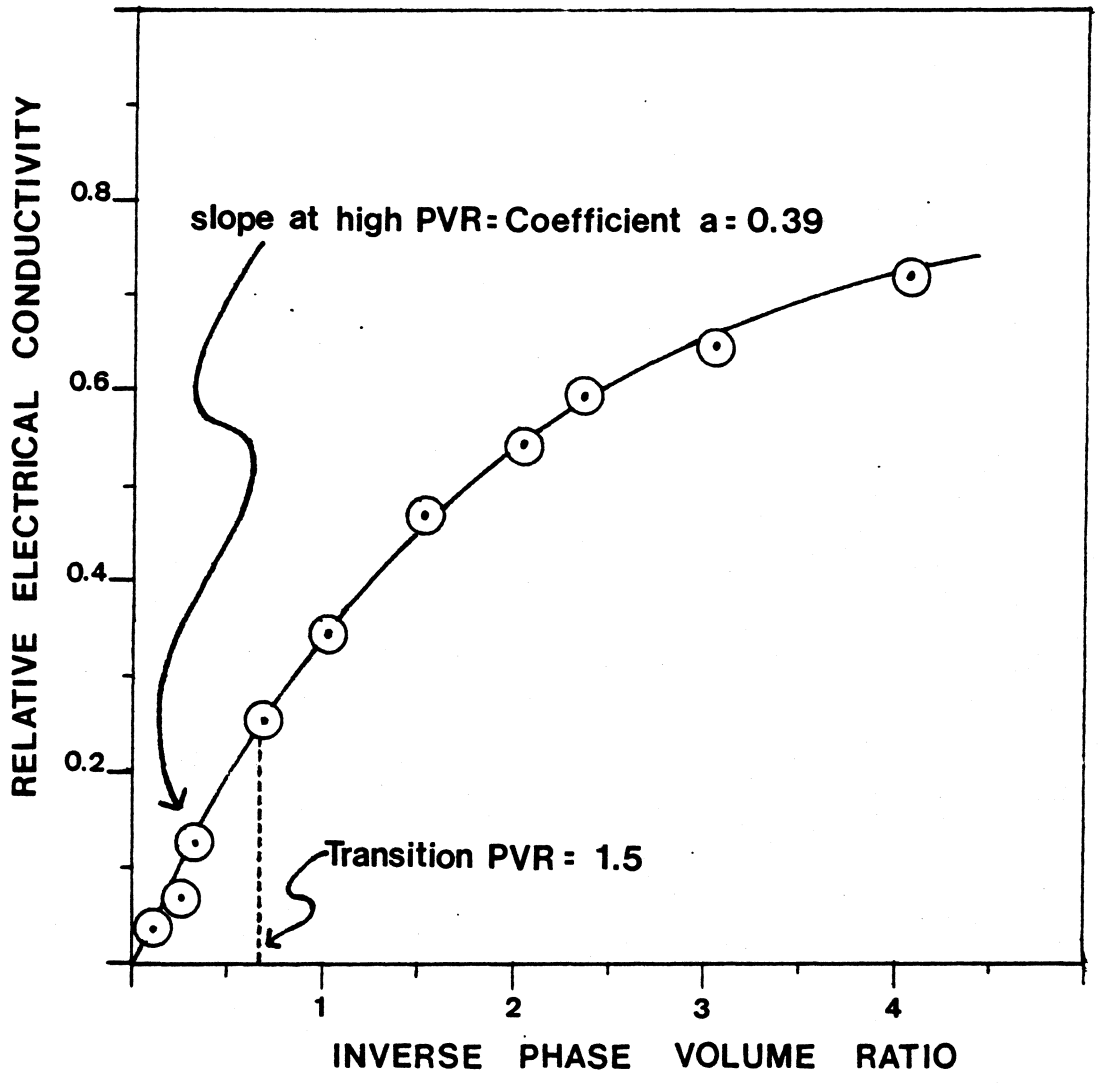


FIGURE 12. Graphical identification of coefficient a and Transition PVR from electrical conductivity data of polyaphrons.

platinized electrodes, and alternating current was used for electrical conductivity measurements--two important and well used measures to overcome electrode polarization.

Interfacial polarization is another phenomenon that may be present: Fricke and Curtis [11] write of interfacial polarization of water-dielectric interphases that is pronounced when measurement is made with direct current or with alternating current at low frequency; and Hanai [13] states that electrical conductivity shows a dielectric dispersion due to interfacial polarization only in water-in-oil type emulsions as opposed to oil-in-water type emulsions. Neither type of interfacial polarization has been considered in this investigation.

CONCLUSIONS

1. Electrical Conductivity is a measurable quantity of polyaphrons. Addition of electrolyte to the aqueous phase is useful in obtaining electrical conductivity measurements.

2. Graphs relating conductivity ratio (K) and phase volume ratio (PVR) or aqueous or oil volumetric fraction were established.

3. The existence of one standard curve to describe polyaphron phase volume ratio based on electrical conductivity measurements is a possible method to characterize polyaphrons, as many other investigators have suggested with gas foams and emulsions. Proposed characterization parameters for polyaphrons originate from a departure in linearity as PVR decreases. This departure in linearity is associated with geometric changes in polyaphron structure.

4. Bruggeman's Equation best describes the experimental curves obtained from electrical conductivity measurements of polyaphrons. This agreement between experiment and theory is probably a result of the assumption that a wide size distribution in the diameters of the dispersed particles exists.

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