

Influence of internal phase properties on zeta-potential and dielectric constant of o/w emulsion

DEVRAJ RAMBHAU[†], A K DORLE and B RAMI REDDY

Department of Pharmaceutical Sciences, Nagpur University Campus, Amaravati Road, Nagpur 440010, India

[†] Present address: University College of Pharmaceutical Sciences, Kakatiya University, Warangal 506009, India

Abstract. Dielectric constant (DEC) of internal phase influenced the zeta potential (ZP) of o/w emulsion prepared with or without emulgent. In both systems ZP and DEC of internal phase exhibited an approximately linear relationship. Using homologous aliphatic hydrocarbons as internal phases, emulsions were prepared with polysorbate-80. Increase in carbon chain length brought about increase in interfacial area and decrease in ZPs of emulsions. A fair inverse correlation between ZP and DEC of internal phase was revealed in this series. Increase in phase volume ratio from 0.05 to 0.3 brought about limited changes in ZPs whereas by further increasing phase volume ratio, ZP decreased steadily. Studies pertaining to the effect of phase volume ratio on DEC of o/w emulsions are in accordance with earlier observations. Increase in phase volume ratio causes a steady decrease in DEC of emulsion. Of the five equations employed, the Bruggeman equation appears to predict the observed values more accurately.

Keywords. Dielectric constant; oil-in-water emulsions; zeta potentials; emulsion stability.

1. Introduction

Most of the earlier work in the field of dielectric properties of emulsions dealt with deriving equations for predicting the DEC of emulsions (Rayleigh 1892; Weiner 1912; Bruggeman 1935; Bottcher 1952; Kubo and Nakamura 1953; Hanai 1968). These equations were based on an erroneous assumption that the dielectric constant (DEC) of an emulsion is a function of dielectric constants and concentrations of two-component phases. The presence of emulgent at globule surface constitutes a double layer and confers a certain electric charge. The influence of polarization of electrical double layer on the DEC of emulsions was extensively studied earlier in w/o emulsions under changing phase volume ratios (Fradkina 1950; Hanai 1959, 1960, 1961). However studies on o/w emulsions are scanty (Hanai 1962).

Although theoretical postulations reveal that internal phase polarity can influence DEC of emulsions, studies of varying internal phase while keeping its concentration constant, are not available. In emulsions, with a change in internal phase polarity, constitution and charge density of electrical double layer around globules are likely to be affected. It would therefore be worthwhile determining the effect of the properties of internal phase on dielectric constant and diffuse double-layer potential (ZP) in o/w emulsions. The variables pertaining to internal phase considered for this study were: polarity, carbon-chain length and concentration of internal phase.

2. Experimental

Internal phases, and their concentrations; emulsifier and its concentration; and conditions of emulsification for various studies are shown in table 1. Purity of the liquids employed as internal phases was ascertained by determining refractive index and weight per ml.

2.1 Preparation of emulsions containing polysorbate-80

In all experiments internal phase was added to the solution of polysorbate-80 and the mixture agitated for a required time continuously in a mixer at 15537 rpm. Emulsions thus formed were subjected to various measurements.

2.2 Preparation of emulsions without emulsifier

In anticipation of the delicate stability of these emulsions, they were homogenized by passing them five times through an ultrasonic homogenizer, after primary agitation.

Table 1. Materials and method of preparation of emulsions for various studies.

Study	Internal phases	Phase volume ratio	Emulgent per 100 ml of emulsion	Mixing time in minutes
I	As listed in table 3	0.33	No emulgent was used	5
II	<i>n</i> -Hexane ¹ or <i>n</i> -Hexanol ¹ or <i>n</i> -Hexane containing 1 or 10% V/V <i>n</i> -Hexanol	0.33	No emulgent was used	5
III	As listed in table 3	0.33	Polysorbate-80 1 g	3
IV	<i>n</i> -Hexane or <i>n</i> -Heptane ² or <i>n</i> -Octane or <i>n</i> -Decane ¹ or <i>n</i> , Tetradecane ³	0.10	Polysorbate-80 1 g	3
V	Liquid paraffin ⁴	0.05 0.10 0.15 0.30 0.45 0.60 0.75	Polysorbate-80 1 g	3

Study I: Effect of DEC of internal phase on ZP of o/w emulsions prepared without using any emulsifier; Study II: ZP changes in hexane-in-water emulsions (prepared without emulsifier) due to the contamination of *n*-hexanol in its internal phase; Study III: Effect of DEC of internal phase on ZP and DEC of o/w emulsions prepared using polysorbate-80; Study IV: Effect of carbon chain length of internal phase on ZP and DEC of o/w emulsions prepared using polysorbate-80; Study V: Effect of phase volume ratio on ZP and DEC of o/w emulsion prepared using polysorbate-80.

1. British Drug House, India; 2. Sisco Chemicals, India; 3. Sigma Chemical Company, St. Louis MO, USA; 4. Deepthi Pharmaceuticals, Nagpur, India.

2.3 Measurement of DEC and conductivity

Dielectric constants of the internal phases and conductivities of all the emulsions prepared with polysorbate-80 were measured on a dielectrometer (Universal dielectrometer, type 04-301, Redclikis, Hungary, which operates at a lone frequency of 3 Mc/sec).

An attempt was made to measure the DEC of emulsions without emulsifier but a majority of them started separating in the dielectrometer cell itself resulting in fluctuation in the readings. As the measurement of DEC of these emulsions was not possible, the following equations were employed to compute their theoretical values.

Rayleigh equation

$$\varepsilon = \varepsilon_m \left[1 + \frac{3\phi}{\frac{\varepsilon_p + 2\varepsilon_m}{\varepsilon_p - \varepsilon_m} - \phi - 1.65 \frac{\varepsilon_p - \varepsilon_m}{\varepsilon_p + \frac{4}{3}\varepsilon_m} \cdot \phi^{10/3}} \right] \quad (1)$$

Wiener equation

$$\frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} = \frac{\varepsilon_p - \varepsilon_m}{\varepsilon_p + 2\varepsilon_m} \cdot \phi \quad (2)$$

Bruggeman equation

$$\frac{\varepsilon - \varepsilon_p}{\varepsilon_m - \varepsilon_p} (\varepsilon_m/\varepsilon)^{1/3} = 1 - \phi \quad (3)$$

Bottcher equation

$$\frac{\varepsilon - \varepsilon_m}{3\varepsilon} = \frac{\varepsilon_p - \varepsilon_m}{\varepsilon_p + 2\varepsilon} \cdot \phi \quad (4)$$

Hanai equation

$$\frac{2\varepsilon_1 - 3\varepsilon_p}{2\varepsilon_m - 3\varepsilon_p} (1 - \phi)^{3/2} \quad (5)$$

where ε or ε_1 is the DEC of emulsion, ε_p , the DEC of internal phase, ε_m , the DEC of dispersion medium (water) and ϕ , the phase volume ratio.

3. Measurement of zeta potential (ZP)

A cylindrically bored microelectrophoresis cell equipped with platinum-iridium electrodes was used to measure the electrophoretic mobility (EM) of diluted emulsions. Emulsions were always diluted to 1 in 200, except in study V where 1 in 500 dilution was used. Dilution was usually performed with distilled water or distilled water saturated with internal phase. The latter procedure was adopted from Elworthy and Florence (1969) who suggested this method to give meaningful mobility values for emulsions containing internal phases which are partially miscible with water.

Potential drop in the cell was measured by a digital voltmeter. The current strength was kept constant during measurements. All mobility measurements were at zero electro-osmotic flow (Schott and Young 1972). By frequently changing polarity,

fifty globules were measured for their mobility. ZP was calculated from the average mobility value (Smoluchowsky 1918) using $ZP = (4\pi nu)/(\epsilon E) (9 \times 10^3)$. ZP is in mV, n is the viscosity of dispersion medium (water) in poise, u the migration velocity (cm/s), E the potential gradient voltage applied/distance between electrodes and ϵ the DEC of dispersion medium.

3.1 Globule size analysis and computation of interfacial area (IA)

Size analysis of the globules of emulsion prepared with polysorbate-80 was performed microscopically. One ml of emulsion was diluted to 25 ml with distilled water. A drop of this was mounted with a drop of glycerine water mixture (1:3) on a glass slide. Diameters of 500 globules were measured by viewing the slide under microscope equipped with a standardized eyepiece micrometer. From this data, the IA per ml of emulsion was computed. Size analysis of the emulsions without emulsifier could not be performed as a majority of them rapidly coagulated during measurements.

3.2 Assessment of stability of emulsions

Based on the shelf-life of emulsion, a scoring test was devised to make a quick appraisal of the stability where perceptible phase separation was considered as a breaking point. The test was as follows: An emulsion having a shelf-life below 15 min will be difficult to test for its ZP and other parameters of stability, it would therefore be logical to assign a score value of zero to the emulsion, breaking at or below 15 min. The highest score value of five was assigned to an emulsion, which was stable for a month or more. Using these boundary score values, a straight line was plotted between the score and shelf-life on a semi-logarithmic paper. From this line the score values for shelf-lives falling between the two boundary values were obtained (table 2).

Table 2. Assessment of emulsion stability based on score values.

Shelf-life	Score values	
	Obtained from graph	Approximated to
Emulsification not possible or breaking at or below 15 minutes	0	0
Emulsions stable for more than 15 min, but breaking within an h	0.9	1
Emulsions stable for more than one hour, but breaking within a day (24 hours)	2.85	3
Emulsions stable for more than a day but breaking within a week	4.05	4
Emulsions stable for more than a week but breaking within a month (30 days)	5.00	5

4. Results and discussion

4.1 Effect of properties of internal phase on ZP of o/w emulsion

Of the thirty seven internal phases (table 3) tried, only 25 could form emulsions without emulgents with sufficient stability (stability score 1 or more) to allow measurements.

Effect of DEC of internal phase on ZP of emulsion formed without emulsifier is illustrated in figure 1. An approximately linear relationship appears to exist between DEC of internal phase and ZP ($r = 0.7655$; $n = 23$, at $p < 0.01$). Increase in ZP with increase in DEC of internal phase may be attributed to the increasing polar nature of internal phase. With increase in polarity of internal phase, an increase in the extent of dipole-dipole interactions between globules of internal phases and dipoles from bulk medium is expected (Mackor 1951; Bockris *et al* 1963; Bijsterbosch and Lyklema 1964; Ottewill 1962), bringing about changes in χ -potentials. Mackor (1951) reported a shift in zero-point charge of an emulsion with change in χ -potential. He felt that changes in χ -potential reflect a change in the dipolar interaction at interphases.

Figure 1 shows deviations of some of the points from the regression line, *p*-cresol and methyl salicylate showing deviations to a considerable extent. For a decrease of 0.9 units of internal phase DEC (i.e. *p*-cresol DEC = 9.9 and methyl salicylate DEC = 9), an appreciable decrease in ZP from -82 mV (for *p*-cresol) to -27 mV (for methyl salicylate) is noteworthy. *p*-Cresol which belongs to phenolic group of compounds tends to dissociate in the presence of water and forms intermolecular hydrogen bonds with water molecules. These two phenomena should contribute to the high electronegative ZP observed. In methyl salicylate the lower ZP value may be attributed to its strong intramolecular hydrogen bonding and the feeble dipole interaction. The interaction of *p*-cresol and methyl salicylate with water can be confirmed from the stability behaviour of their respective emulsions. *p*-Cresol emulsion was comparatively more stable than methyl salicylate emulsion (table 3). The higher stability of *p*-cresol emulsion over methyl salicylate emulsion may be because of the combined effect of dipole accumulation and higher ZP. Increased dipole accumulation at oil-water interphase might have formed a complex condensed film of dipoles over globules, which should possibly prevent the coagulation of globules of *p*-cresol, primarily by the higher repulsive energy barriers due to higher electronegative ZP and later due to the rigidity of film of hydration in such a system.

Studies (Roberts 1936; Carruthers 1938; Growney 1941; Dickinson 1941) have earlier been carried out to evaluate the structural effect of internal phase on the EM (ZP is a direct function of EM). March (1927, 1935) believed that the stability source of an oil-hydrosol (o/w emulsion without emulsifier) is the "protective aqueous skin" around the dispersed particle. According to Mueller (1935) water molecules get attracted to the globule surface in the oil-hydrosols by electrostatic forces of double layer and hence their stabilizing influence diminishes as ZP becomes smaller. Therefore, it is generally agreed that both charge and hydration effects are important in the stability of emulsions without emulsifier against coalescence.

An approximate relationship between the DEC of internal phase and ZP indicates that not only the internal phase polarity but also the extent of dissociation of chemical groups present on globule surfaces and their specific interactions with dispersion medium are the factors governing ZP. If this mechanism is operating at interphases,

Table 3. Stability scores, average globule size and interfacial areas of o/w emulsions containing internal phases of varying polarities.

Internal phase	Internal phase DEC	Emulsions without emulsifier		Emulsions with emulsifier		Average globule size (μm)	Interfacial area (cm^2/ml)
		ZP in (mV)	Stability score	ZP in (mV)	Stability score		
<i>p</i> -cresol ⁵	9.9	-82.08	5	-44.68	1	—	—
Dichloromethane ¹	9.1	—	0	-55.8	1	—	—
Methylsalicylate ⁶	9	-28.35	4	-42.62	4	3.02	6555
Aniline ¹	6.879	—	0	-63.00	1	—	—
Methyl benzoate ¹	6.5	-41.84	4	-36.2	4	2.92	6817
Lauryl alcohol ¹	6.05	—	0	-33.0	3	2.103	9204
Chlorobenzene ⁷	5.54	-37.8	4	-36.15	4	3.02	6555
Chloroform ¹	5.2	—	0	-34.16	1	—	—
Amyl benzoate ¹	4.98	—	0	-15.4	4	3.78	5237
Amyl acetate ¹	4.834	—	0	-19.78	4	2.747	7372
Trichlorobenzene ¹	4.68	-30.06	4	-21.48	4	2.38	8320
Castor oil ⁴	4.57	-41.12	4	-25.96	5	5.93	3399
Anisole ⁸	4.4	—	0	-30.34	5	4.13	4812
Coconut oil ⁴	3.315	-20.73	4	-19.54	5	3.406	5815
Linsced oil ⁴	3.26	-51.6	4	-34.25	5	2.935	6742
Isopropylmyristate ⁹	3.219	18.29	4	-18.52	5	2.214	9028
Cotton seed oil ⁴	3.18	-27.45	4	-19.48	5	2.803	7062
Sunflower oil ⁴	3.13	-19.69	4	-19.7	5	3.43	5454
Sesame oil ⁴	3.139	-17.98	4	-23.62	4	2.815	7033
Arachis oil ⁴	3.12	-29.61	4	-23.12	5	3.595	5502
Olive oil ¹⁰	3.1	-24.43	4	-21.45	5	3.7	5351
Mustard oil ⁴	3.053	18.48	4	-20.79	4	3.516	5631
<i>m</i> -xylene ¹	2.555	—	0	-24.81	4	2.243	8822
Oleic acid ⁴	2.44	-15.63	1	-18.1	1	—	—
Xylene ¹	2.40	-14.2	1	-10.96	4	4.82	4108
Toluene ⁶	2.30	—	0	-12.6	3	2.76	7173
<i>p</i> -xylene ¹	2.23	—	0	—	—	—	—
Carbon tetra chloride ²	2.20	—	0	-17.60	1	—	—
Benzene ¹	2.20	-27.37	1	-16.04	3	3.02	6600
Lemon oil ¹¹	2.20	-13.10	1	-11.00	1	—	—
Turpentine oil ¹²	2.20	-17.81	1	-19.60	3	2.655	7449
Liquid paraffin ⁴	2.15	-25.15	4	-25.26	5	8.30	2385
Cyclohexane ⁶	2.02	-14.48	1	-12.80	3	3.12	6346
<i>n</i> -Octane ⁶	1.948	—	0	-10.78	3	3.48	5689
iso-Octane ⁶	1.94	-19.72	1	-11.64	3	2.64	7489
<i>n</i> -heptane	1.924	-18.29	1	-15.47	3	2.95	6716
<i>n</i> -hexane	1.896	-18.11	1	-18.5	3	2.99	6621

1. British Drug House, India; 2. Sisco Chemicals, India; 3. Sigma Chemical Company, St. Louis MO, USA; 4. Deepti Pharmaceuticals, Nagpur, India; 5. Pfizer, India Ltd; 6. Sarabhai M Chemicals, India; 7. Imported from USSR; 8. Bush, London, England; 9. Fluka, Switzerland; 10. Imported from Italy, supplied by Vikas Pharma, India; 11. St. Bernard, London; 12. J J Chemical, Nagpur, India.

it seems probable that ZP and stability of emulsions containing non-polar internal phase could be enhanced, provided they are contaminated with any dipole-orienting molecule. This effect has been verified experimentally in hexane-in-water emulsions, where 1 and 10% of hexanol were incorporated in *n*-hexane and emulsions were

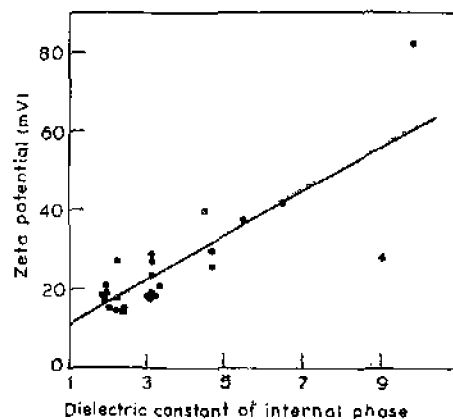


Figure 1. Effect of DEC of internal phase on ZP of o/w emulsions prepared without using any emulsifier.

Table 4. Zeta potential and stability changes due to the addition of *n*-hexanol to the internal phase of *n*-hexane-in-water emulsions prepared without using emulsifier.

Internal phase		ZP in mV	Stability score
<i>n</i> -hexanol %v/v	<i>n</i> -hexane %v/v		
0	100	-12	1
1	99	-18	4
10	90	-21	4
100	0	-26	4

formed without using any emulsifier. As expected (table 4), emulsions of *n*-hexane (hexanol)-in-water have shown an increase in their ZP and stability with increasing concentrations of hexanol.

Changes in ZPs of emulsions prepared with polysorbate-80 using internal phases of varying DEC are illustrated in figure 2. Similar to that of emulsions without emulsifier, in these systems too, there is an increase in ZP with increasing DEC of internal phase and correlation between DEC of internal phase and ZP is approximate ($r = 0.8389$; $n = 35$, $p < 0.01$). However, the presence of polysorbate-80 in these systems lowered the magnitude of ZP. Lowering the magnitude of ZP in the presence of polysorbate-80 is in accordance with earlier observations (Elworthy and Florence 1969; Riddick 1970).

Although there is considerable variation in the ZP values of all the 37 emulsions formed with various internal phases, their globule size and IA changes are limited (table 3). No relation could be traced between ZP and IA and this factor as also the existence of an approximate relationship between ZP and DEC of internal phase show, internal phase polarity as the probable factor influencing ZP.

ZP is the potential at the surface separating the immobile part of the double layer (stern layer) from the diffuse part. It is a simultaneous measure of the charge density

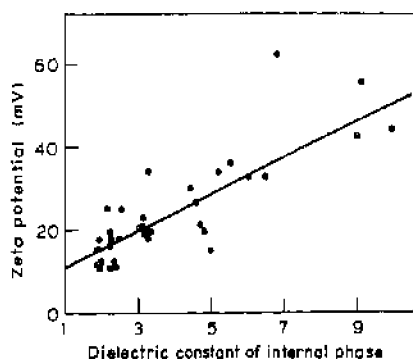


Figure 2. Effect of DEC of internal phase on ZP of o/w emulsions prepared with polysorbate 80.

of diffuse double layer (per unit surface of the globule of a particular internal phase) and also the extent to which it extends from the surface (Riddick 1968). Thus, it would depend on the mode of orientation of emulgent molecules and the number of such molecules present at the unit surface. Ottewill (1967) proposed different modes of orientation of non-ionic surfactant molecules with changing polarity of the dispersed phase in a solid/liquid dispersion. His concept as applied to present liquid/liquid dispersions (emulsions stabilized with polysorbate-80) cannot explain the increase in ZP with increase in polarity of internal phase. According to this concept, on relatively polar internal phases the orientation is through oxy-ethylene chain so that the charge conferring groups of polysorbate-80 are now engaged in the interaction with globule surface. We therefore believe that not only the internal phase DEC but surface ionogenicity, interaction of internal phase with water dipoles and mode and extent of orientation of emulgent are factors that govern the ultimate double layer structure and its charge density. As all of them contribute in a complex way to increase ZP with increasing internal phase polarity, it would be futile to explain this effect only through a single factor such as the changes of mode of orientation with a change in polarity of internal phase.

In table 3, the stability behaviour of emulsions made with or without emulsifier is recorded. In the case of emulsions without emulsifier, internal phases with lower DEC (DEC of internal phase = 1.89 to 2.55) formed emulsions which had comparatively lower stability than that of emulsions formed with internal phases having higher DEC (DEC of internal phase = 3 to 10). A similar trend was observed in emulsions made with polysorbate-80, the only exception being that they were comparatively more stable than emulsions without emulsifier.

In emulsions with or without emulsifier, the relationship between DEC of internal phase and ZP was found to be approximate. This was attributed to the wide variation in the chemical nature of internal phase. To obviate this factor and to understand clearly the influence of DEC of internal phase on ZP, internal phases belonging to the homologous series of saturated aliphatic hydrocarbons were chosen. As can be seen from figure 3, with increase in hydrocarbon chain length there is an increase in IA and decrease in ZP of emulsions. In figure 4, ZP is plotted against DEC of internal phase. They exhibit a fairly good inverse correlation between them ($r = 0.9738$; at $n = 3$; at $p < 0.01$). Thus, in homologous series ZP is an inverse function of DEC of internal phase.

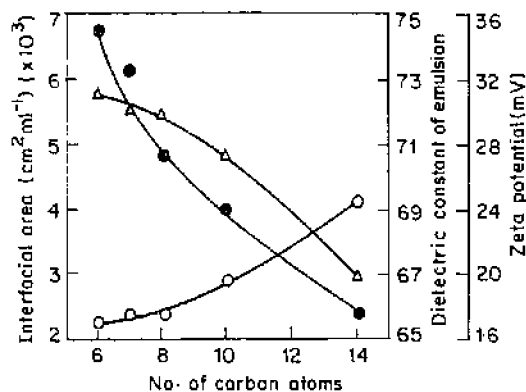


Figure 3. Changes in ZP, interfacial area and DEC of o/w emulsions prepared with polysorbate-80 due to the change in the carbon chain length of internal phase constituting these emulsions. ○—○ IA; Δ—Δ PEC; ●—● ZP.

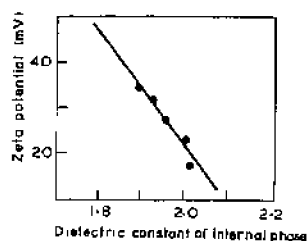


Figure 4. Relationship between DEC of internal phase and ZP of o/w emulsions prepared with polysorbate-80. Internal phases constituting these emulsions belong to the homologous series of aliphatic hydrocarbons.

Changes in IA do not decisively explain ZP changes since for a meagre change in IA in C₆ to C₈ hydrocarbon emulsions, there is a considerable drop in ZP from -35 to -27 mV (figure 3).

The increase in ZP with decrease in carbon chain length may be attributed to the increased interfacial adsorption of polysorbate-80. Consequently the stability of emulsions made with hydrocarbons of shorter chain lengths should be greater compared to the longer ones. Although we did not perform long-term stability studies of these emulsions, we presume that ZP may decisively control stability, as in these systems no parameter other than the surface coverage contributes to ZP. Davis and Smith (1972) also observed that the stability of emulsions of C₆ to C₁₆ hydrocarbons prepared with sodium dodecyl sulphate falls progressively as the alkane chain length is increased. Within the homologous series they reported an inverse correlation between DEC of internal phase and stability.

Increase in phase volume ratio from 0.05 to 0.30 brought about a meagre drop in ZP whereas a further increase in phase volume ratio brought about a considerable drop (figure 5). With increasing phase volume ratio, there is a steady increase in IA. The characteristic slow decrease in ZP up to a phase volume ratio of 0.30 and later the rapid decay can be explained by considering the emulgent concentration in relation to the total IA which is to be covered in these systems. An emulsion with a phase volume ratio of 0.75 yielded the largest IA. One gram per cent of emulgent used in

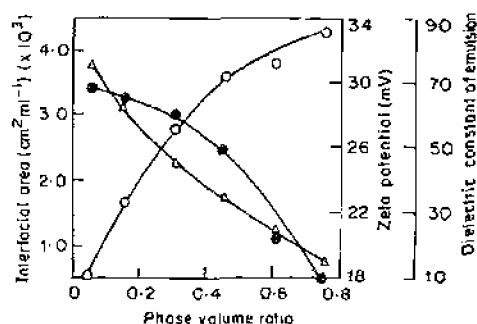


Figure 5. Effect of phase volume ratio on ZP interfacial area and DEC of o/w emulsions prepared with polysorbate-80. ○—○ IA; △—△ DEC; ●—● ZP.

the study confers a certain amount of charge to its globules, taking the ZP value to -18 mV (figure 5). As IA is decreased by decreasing the phase volume ratio, the same amount of emulgent would now cover a larger surface area per globule increasing the charge density per globule. However, once the globule surface is completely covered with a monolayer, there is hardly any more forcing of emulgent molecules to interface and thus, the ZP changes are limited. A monolayer adsorption seems to have occurred in emulsions having a phase volume ratio of 0.30. In emulsions with phase volume ratio less than 0.30 also, monolayer is formed and thus they are expected to show limited changes in ZP. Limited changes in ZP of the disperse systems after a monolayer adsorption at liquid-liquid interface or solid-liquid interface have been reported earlier (Nash and Haeger 1966; Ottewill 1967; Riddick 1968).

5. Effect of properties of internal phase on DEC of o/w emulsion

From theoretical postulations, a relationship between DEC of internal phase and DEC of emulsion is expected. However such a relationship does not appear to exist ($r = 0.2463$; $n = 35$, at $p < 0.01$) in emulsions prepared with polysorbate-80 (table 5). Further, it is obvious that the observed DEC of emulsions are higher than the values computed from any equation. Any enhancement of the observed DEC of emulsions over the theoretically computed value was attributed to either double-layer polarization or the degree of dispersion. According to Piekara (1932a, b), in emulsions stabilized by emulgents, smaller the globule size (i.e. higher the total IA per ml of emulsion), higher is the degree of dispersion and greater is its value of DEC. Since in the present systems no relationship is exhibited between DEC of emulsion and IA, it is difficult to substantiate the role played by dispersion in these systems. Thus, the enhanced values of DEC of emulsions may be due to the effect of double-layer polarization. The influence of polarization of electrical double layer on DEC of emulsions was noted by Fricke and Curtis (1937). According to them, when a dielectric dispersed in water is subjected to an electric field, a part of the current passes through the system at interfaces and the system becomes partly polarized. Dielectric properties of such systems are quite different from what would be expected from the contribution of two-component phases. As this view received much support (Piekara 1932; Fradkina 1950; Schwan 1951, 1968; Dukhin 1971) Dukhin (1971) felt that the elevated DEC

Table 5. Calculated and observed DEC of o/w emulsions prepared with polysorbate-80.

Internal phase	Internal phase DEC	DECs of emulsions					
		Calculated from equations of					Observed
		Rayleigh	Wiener	Bruggeman	Rottcher	Hanai	
<i>p</i> -Cresol	9.9	48.83	49.21	48.38	46.67	48.65	28.46
Dichloromethane	9.1	48.41	48.81	47.92	46.13	48.11	61.67
Methyl salicylate	9.0	48.35	48.75	47.86	46.65	48.04	59.71
Aniline	6.87	47.73	47.92	46.48	44.68	46.75	53.2
Methyl benzoate	6.5	46.98	47.48	46.38	44.22	46.34	53.95
Lauryl alcohol	6.05	46.73	47.23	46.11	43.87	46.04	51.94
Chlorobenzene	5.54	46.45	46.96	45.79	43.47	45.76	54.4
Chloroform	5.2	46.2	46.73	45.5	43.12	45.4	53.24
Amyl acetate	4.83	45.99	46.61	45.38	42.87	45.23	51.66
Amyl benzoate	4.98	46.04	46.65	45.45	42.98	45.31	50.38
Trichloro benzene	4.68	46.2	46.73	45.26	43.12	45.11	49.44
Castor oil	4.57	45.96	46.45	45.19	42.69	45.04	53.2
Anisole	4.4	45.81	46.36	45.02	42.56	44.93	54.1
Coconut oil	3.31	45.78	45.78	44.4	41.65	44.19	53.24
Linseed oil	3.26	45.19	45.78	44.37	41.61	44.19	55.95
Isopropyl myristate	3.2	45.1	45.73	44.34	41.58	44.12	50.65
Cottonseed oil	3.18	45.09	45.71	44.32	41.34	44.1	53.13
Sunflower oil	3.13	45.08	45.68	44.29	41.29	44.06	53.48
Sesame oil	3.13	45.08	45.69	44.29	41.3	44.07	60.00
Arachis oil	3.12	45.07	45.68	44.28	41.28	44.05	51.94
Olive oil	3.1	45.07	45.67	44.27	41.26	44.0	52.63
Mustard oil	3.05	45.06	45.64	44.24	41.22	44.01	58.7
<i>m</i> -Xylene	2.55	44.75	45.37	43.92	40.98	43.67	52.62
Oleic acid	2.44	44.71	45.31	43.85	40.88	43.59	59.33
Xylene	2.4	44.68	45.29	43.82	40.86	43.57	52.24
Toulene	2.30	44.05	45.24	43.75	40.77	43.5	51.29
<i>p</i> -Xylene	2.23	44.58	45.2	43.71	40.71	43.45	45.75
Carbon tetra chloride	2.2	44.55	45.18	43.69	40.69	43.43	53.75
Benzene	2.20	44.55	45.18	43.69	40.69	43.43	51.05
Lemon oil	2.20	44.55	45.18	43.69	40.69	43.43	49.35
Turpentine oil	2.2	44.55	45.18	43.69	40.69	43.43	53.00
Liquid paraffin	2.15	44.51	45.16	43.59	40.64	43.4	51.05
Cyclohexane	2.02	44.45	45.09	43.57	40.52	43.31	47.97
<i>n</i> -Octane	1.95	44.40	45.05	43.53	40.46	43.26	50.28
iso-Octane	1.94	44.38	45.05	43.53	40.46	43.26	48.85
<i>n</i> -Heptane	1.92	44.35	45.04	43.51	40.42	43.25	50.56
<i>n</i> -Hexane	1.89	44.32	45.02	43.49	40.41	43.22	50.48

of emulsions are due to the double-layer polarization and proposed a theory somewhat similar to that of Fricke and Curtis. According to this theory, under the influence of an external field, tangential fluxes of diffused double-layer ions arise and are redistributed along the particle surface in a dispersed system. The double layer is thus deformed and polarized, deviating from the initial spherical structure. This theory was verified with few experiments (Schwan 1951, 1968). Dukhin therefore states that the theory of diffuse double-layer polarization and its effect on DEC of dispersion

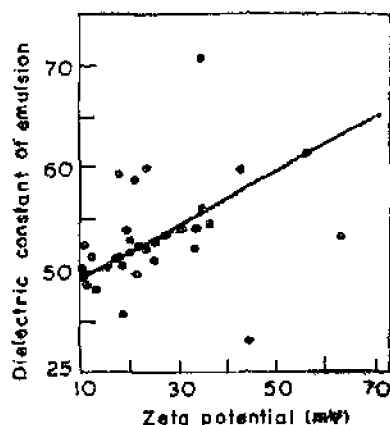


Figure 6. Plot of emulsion versus ZP for o/w emulsions, containing internal phases of varying polarity being prepared using polysorbate-80.

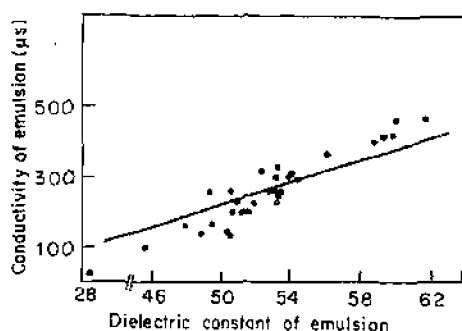


Figure 7. Plot of conductivity of emulsion versus DEC of o/w emulsion prepared with polysorbate-80.

being in good agreement with experiments, deserves further allround verification. We have therefore explored the possible relationship between DEC of emulsion and diffuse double-layer potential (ZP). Dielectric constants of emulsions (prepared with polysorbate-80) are plotted against ZP in figure 6. The correlation coefficient value ($r = 0.91$; $n = 35$, at $p < 0.01$) suggests that the relation between DEC of emulsion and ZP is approximate.

To examine the probable cause of scattering, the conductivity of emulsion was measured (figure 6). Figure 7 is a plot of conductivity versus DEC of emulsion. The relation between these two parameters is also approximate ($r = 0.854$; $n = 35$, at $p < 0.01$). It may be deduced that ZP which is a parameter whose value depends upon interfacial characters of emulsion, is not affected by the changes in conductivity which would rather depend upon the bulk properties of emulsion. Therefore, the measurement of conductivity along with DEC should always be emphasized as it could give valuable information regarding the dielectric properties of emulsions.

Because of the diversity in the chemical nature of internal phases, the relation between DEC and ZP could be approximate. A specific chemical group such as homologous series of aliphatic hydrocarbons was therefore chosen to obviate such

Table 6. Effect of carbon chain length on globule size and DEC of emulsions.

Internal phase	DEC of internal phase	Average globule size (in μm)	DECs of emulsions					
			Calculated from equations of					Observed
			Rayleigh	Wiener	Botcher	Hanai	Bruggeman	
<i>n</i> -Hexane	1.89	2.665	66.207	66.21	67.102	65.987	66.03	72.6
<i>n</i> -Heptane	1.924	2.606	66.217	66.217	67.107	65.995	66.037	72.01
<i>n</i> -Octane	1.948	2.462	66.222	66.222	67.111	66.000	66.042	72.01
<i>n</i> -Decane	2.004	2.049	66.233	66.233	67.121	66.012	66.054	70.76
<i>n</i> -Tetra decane	2.036	1.842	66.239	66.239	67.126	66.019	66.061	66.88

an effect. Figure 3 shows the dependence of parameters such as ZP, DEC and IA of emulsions on the carbon chain length of internal phase.

The DEC values of aliphatic hydrocarbons increase with increasing carbon chain length (table 6). The DEC of emulsions observed decrease with increasing DEC of internal phase. This contradicts with the theoretical postulations. The DEC values obtained experimentally are considerably higher than the values calculated from equations (1) to (5) (table 6).

Interfacial area and DEC of emulsion show excellent inverse correlation between them ($r = -0.9959$; $n = 3$, at $p, 0.01$) (figure 8A). Tetra-decane emulsion exhibits the lowest average particle size and highest IA in the series. Increasing the carbon chain length from C_6 to C_{14} causes limited change in the average particle size. The lowest DEC value (for tetradecane emulsion) being associated with an emulsion having smallest average particle size appears in contradiction to the earlier observations by Piekara (1932a, b), who found that in concentrated emulsions (emulsion containing emulgents) smaller the globule size, greater is the DEC. The relation between ZP and DEC of emulsion is difficult to linearize (figure 9A). But a linear correlation between DEC and ZP is revealed ($r = 0.9594$; $n = 3$, at $p < 0.05$) when the difference between the observed and theoretical DEC (obtained from Bruggeman equation) is plotted against ZP (figure 10).

From the above two studies it can be substantiated that the higher observed values of DEC of emulsions as compared to the theoretical one may be due to the double-layer polarization in these systems. Therefore it can be stated that adsorption of emulgent has a profound influence on the DEC of emulsion. This confirms the reports from Piekara (1932) and Fricke and Curtis (1937). Hanai *et al* (1962) stated that in o/w emulsions, the double-layer polarization is negligible and if at all envisaged can only occur, provided the internal phase has high DEC or conductivity. However the present observations indicate that the changes in bulk properties such as DEC of internal phase may not be directly responsible for double-layer polarization, but ultimately it may depend on the surface properties such as mode of emulgent orientation, extent of emulgent adsorption and its capability of interaction with bulk medium. These effects have profound influence on diffuse double-layer polarization, and hence DEC of disperse systems can be characterized by not only the bulk properties but also to a considerable extent by surface properties.

Increasing the phase volume ratio from 0.05 to 0.75 causes a steady decrease in

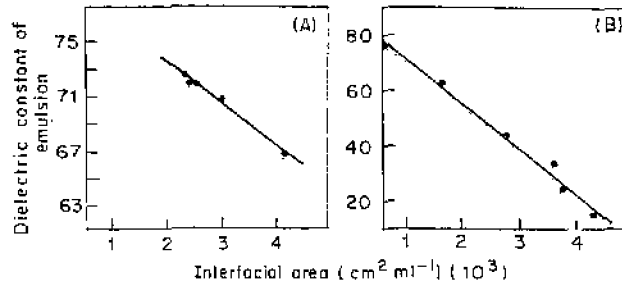


Figure 8. Relation between DEC of emulsion and interfacial area per ml of emulsion. A, study pertaining to homologous series; B, study pertaining to phase volume ratio.

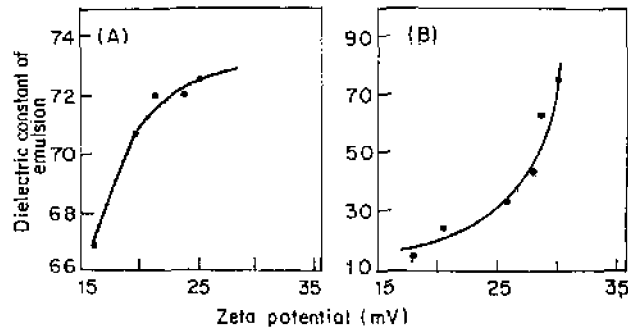


Figure 9. DEC plot of emulsion vs ZP. A, study pertaining to a homologous series; B, study pertaining to phase volume ratio.

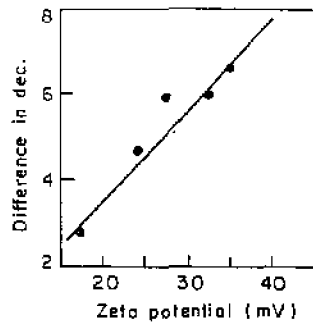


Figure 10. Relation between DEC and ZP of o/w emulsion prepared with polysorbate-80, where the difference between the observed DEC of emulsion and theoretical DEC computed by Bruggeman equation is plotted against ZP for o/w emulsion containing internal phases belonging to homologous series.

DEC of emulsion (figure 5). This agrees with earlier reports (Hanai 1959, 1961). Of all the equations, the Bruggeman equation appears to predict the observed values more accurately (table 7). Similar view was expressed by Hanai (1960).

Increase in phase volume ratio brought about a steady decrease in the DEC of emulsion and an increase in IA (figure 5). Since DEC and IA are the functions of phase volume ratio, a relation between these parameters can be expected. When DEC

Table 7. Effect of phase volume ratio on DEC of emulsions.

Phase volume ratio	DECs of emulsions					
	Observed	Bruggeman	Hanai	Bottocher	Wiener	Rayleigh
0.05	76.13	71.3783	71.29	71.28	71.30	71.39
0.15	63.38	60.9543	53.3	60.94	61.82	61.8
0.30	44.56	46.54291	35.51	45.76	48.92	48.55
0.45	33.92	33.3599	22.62	31.40	37.92	35.52
0.60	24.76	21.9329	14.07	25.98	27.26	20.72
0.75	15.11	12.4238	9.22	18.23	18.08	4.34

and IA were plotted in figure 8B an excellent inverse correlation was observed ($r = -0.9949$; $n = 4$, at $p < 0.01$). However ZP, a parameter which is a function of IA, showed an empirical relation with DEC (figure 9B). Therefore ZP changes seem to have limited importance in explaining the changes in DEC with alteration in phase volume ratio.

All the equations ((1)–(5)) employed by us to predict the DEC of emulsions under changing phase volume ratios predict the observed DEC of emulsions with some accuracy. But they fail to predict DEC values of emulsions under the changing DEC of internal phase, where phase volume ratio was kept constant. It may therefore be stated that the applicability of these equations is limited to the condition in which internal phase concentration is varied keeping DEC of internal phase constant.

References

- Bijsterbosch B H and Lyklema J 1967 *Proc. Fourth Int. Congr. Surface Activity Brussels* (London: Gordon and Breach)
- Bockris J O M, Devanathan M A V and Mutter K 1963 *Proc. R. Soc. (London)* **A274** 55
- Bottocher C J F 1952 *Theory of electric polarization* (New York: Elsevier) p 419
- Bruggeman D A 1935 *Ann. Physik.* **24** 636
- Carruthers J C 1938 *Trans. Faraday Soc.* **34** 300
- Davis S S and Smith A 1972 *J. Pharm. Pharmacol. Sci. Commun. Suppl.* **24** 155
- Dickinson W 1941 *Trans. Faraday Soc.* **37** 140
- Dukhin S S 1971 in *Surface and Colloid Sci.* (ed.) E Mategeric (New York: Wiley-Inter Science) **3** 83
- Elworthy P H and Florence A T 1969a *J. Pharm. Pharmacol.* **21** 70
- Elworthy P H and Florence A T 1969b *J. Pharm. Pharmacol.* **21** 708
- Fradkina E M 1950 *Zh. Eksp. Teor. Fiz.* **20** 1011
- Fricke H and Curtis H J 1937 *J. Phys. Chem.* **41** 729
- Growney G 1941 *Trans. Faraday Soc.* **37** 148
- Hanai T 1959 *Kolloid. Zh.* **167** 41
- Hanai T 1960 *Kolloid. Zh.* **171** 23
- Hanai T 1961 *Kolloid. Zh.* **177** 57
- Hanai T, Koizumi N and Gotoh R 1962 *Kolloid. Zh.* **184** 143
- Hanai T 1968 *Emulsion Science* (ed.) P Sherman (London: Academic Press) p 393
- Hans Mueller 1935 *Colloid Symposium Monograph* **11** 2712
- Kubo M and Nakamura S 1953 *Bull. Chem. Soc. Jpn* **26** 318
- Mackor E L 1951 *Recontrav. Chim.* **70** 663, 763
- March A 1927 *Ann. Physik.* **84** 605
- March A 1935 *Trans. Faraday Soc.* **31** 1468
- Nash R A and Haeger B E 1966 *J. Pharm. Sci.* **55** 442

- Ottewill R H 1967 *Nonionic surfactants* (ed.) M J Schick (New York: Marcel Dekker Inc.) I ed. p 636
Von Piekara A 1932a *Kolloid Zh* **58** 283
Von Piekara A 1932b *Kolloid Zh* **59** 12
Rayleigh L 1892 *Philos. Mag.* **32** 481
Riddick T M 1968a *Control of colloid stability through zeta potential* (New York: Zetameter Inc.) 1st ed. p 27
Riddick T M 1968b *Control of colloid stability through zeta potential* (New York: Zetameter Inc.) 1st ed. p 198
Riddick T M 1970 *Am. Perfum. Cosmet.* **85** 36
Roberts A L 1936 *Trans. Faraday Soc.* **32** 1705
Schott H and Young T W 1972 *J. Pharm. Sci.* **61** 183
Schwan H P 1951 *Z Nature Forsch* **66** 121
Schwan H P 1968 *New York Acad. Sci.* **148** 191
Smoluchowski M V 1918 *Z. Physik Chem.* **93** 129
Weiner O 1912 *Abh. Math. Phys. Kgl. Sach. Ges. Wissensch.* **32** 509