

ELECTROKINETIC STUDIES IN THE STABILITY OF MULTIPHASE EMULSION SYSTEMS

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ABSTRACT

The stability of an emulsion may be a function of the electrical properties at the interface as the mutual repulsion of the charged particles prevent their close approach. The measurement of these electrical properties may be of importance in stability studies. The parameter of interest is often the zeta potential, which can be obtained by measuring the electrophoretic mobility of the droplets. The electrophoretic mobility changes of emulsion droplets were studied periodically by means of the Rank's Brothers Mark II particle microelectrophoretic apparatus. Over the ten-week study period the electrophoretic mobilities of the droplets did not appear to change significantly indicating lack of droplet coalescence. The zeta potential values were all above 25mV. Below this value emulsions reflect a state of instability and droplet coalescence.

The multiple emulsions can be said to be remarkably stable for the period of study.

Keywords: Electrophoretic mobilities; multiphase emulsion systems; coalescence; electro-steric stabilization; zeta potential.

INTRODUCTION

Stability of colloidal dispersion in aqueous media may be due in part to the forces of electrostatic repulsion between particles. Such repulsion is due to the presence of an electrical double layer, which arises from the electrically charged surface of the particles or droplets. The potential produced by the electrical double layer creates a repulsive effect between the droplets which therefore hinders coalescence or droplet aggregation. The significance of electrical effects in emulsion stability has long been recognised (Lewis, 1909) and Eilers and Korff (1940) found that the stability of a dispersion tends to decrease when the double layer is reduced or compressed to a point where electrostatic repulsive forces no longer hinder intimate contact of droplets.

The stability of multiphase emulsion systems may be assessed among other factors by the measurement of the electrophoretic mobility of the droplets, a parameter which is appropriate for the study of the electrophoretic behaviour as it can be measured directly (Ottowill and Halloway, 1975). The relationship between electrophoretic mobility and zeta potential is mainly theoretical (Helmholtz, 1839; Smoluchawski, 1903; Henry, 1931; Booth, 1958; Overbeek, 1950) and hence can be calculated.

The most convenient method of measuring the electrophoretic mobility is by the application of microelectrophoresis, which yields the *electrophoretic mobility*,

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which is the velocity of a particle or droplet under a potential gradient of one volt per centimetre.

EXPERIMENTAL

Materials

Cotton seed oil purchased from Real Food Ltd., New Zealand, B.P. grade light liquid paraffin oil, purchased from H.F. Stevens Ltd., Christchurch, New Zealand. Tween 20 and Tween 80 obtained from Sigma Chemical Company, St. Louis, Missouri 63178, USA. Span 80 from Koch-Light Laboratory Ltd., Colnbrook, Burks, England.

Emulsification equipment consisted of a Watson Victor Ltd. Sorvall-omni-mixer and microelectrophoresis equipment consisted of the Rank Brothers Mark II Particle Microelectrophoresis apparatus, fitted with a rectangular microelectrophoresis cell. A Fuji Optical Co. Ltd., Tokyo, Japan microscope was used for the examination of the emulsion droplets.

Methods

Multiphase emulsion (w/o/w) was prepared using cotton seed oil as the oil phase in one batch, and liquid paraffin as the oil phase in another batch. The multiphase emulsions were prepared by the two step method. Matsumoto et al., 1976 with some modification. The emulsions were coded DIT20, DIT80 to refer to multiple emulsions with oil phase being D1 that is cotton seed oil and T20 and T80 referring to the surface active agent Tween 20 and Tween 80 respectively and D for liquid paraffin.

Three multiphase emulsions water-in-oil-in-water (w/o/w) DIT20, DIT80, DT20 and DT80 were diluted 1 in 20 in 0.01 molar potassium chloride solution for the electrophoretic mobility studies. The rectangular microelectrophoresis cell was filled with one of the diluted emulsions, and the blackened platinum electrodes securely and cautiously fitted to the cell to avoid air bubbles. The temperature of the microelectrophoresis apparatus water bath was maintained at $25^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$. The transit times of ten individual droplets across a distance of $104.4\mu\text{m}$ of the eye-piece graticule were measured at both the upper and lower stationary phases and at a constant voltage. All the emulsions were similarly measured, and the measurements continued weekly for ten weeks under the same conditions as stipulated in Table 1, and the mean transit times for the droplets recorded in Table 2. From the mean transit times, the velocities (distance/time) were obtained which were used in the calculation of the electrophoretic mobilities from the expression:

$$U = V/E$$



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Where U is the electrophoretic mobility, V is the mean particle velocity, and E is the applied field strength, which can be obtained from the expression:

$$E = \frac{\text{applied voltage}}{L}$$

Where L is the effective interelectrode distance.

The resulting electrophoretic mobilities of the multiphase droplets were thus obtained in Table 3.

Table 1: Electrophoretic Mobility Measurement Conditions

Near Wall (μm)	10.778
Far Wall (μm)	10.466
Stationary Phase I (μm)	10.723
Stationary Phase II (μm)	10.531
Potential/Volts	90
Current/ μA	1.5
Conductance (K°) $\text{ohm}^{-1} \text{cm}^{-1}$	1.411×10^{-3}
Electrolyte Conc. (KCl) molar	0.01
Resistance (R) ohm	69160.427
Cross-sectional area (A) sq cm .	0.2135
Effective Interelectrode Distance (L) $\text{cm K}^{\circ}\text{A}$	20.83

Table 2: Mean Transit Times in Seconds for 40 Individual Multiphase Droplets Across 104.4 (μm)

WEEKS	0	1	2	3	4	5	6	7	8	9	10
MFLE											
IT20	10.68 ± 0.95	10.07 ± 0.62	10.82 ± 0.67	11.36 ± 0.48	10.94 ± 0.59	10.80 ± 0.35	11.16 ± 0.69	10.66 ± 0.70	10.08 ± 0.59	11.42 ± 0.76	10.73 ± 0.66
IT80	8.53 ± 0.51	9.09 ± 0.53	8.68 ± 0.94	9.92 ± 1.14	9.14 ± 0.55	10.16 ± 0.82	9.70 ± 0.71	8.54 ± 0.26	9.11 ± 0.63	9.41 ± 0.43	9.31 ± 0.48
I20	11.03 ± 0.38	11.60 ± 0.40	11.04 ± 0.69	11.70 ± 0.53	11.14 ± 0.42	11.42 ± 0.58	10.81 ± 0.68	11.09 ± 0.64	11.62 ± 0.45	10.38 ± 0.30	11.12 ± 0.22
T80	9.51 ± 0.38	9.09 ± 0.60	9.04 ± 0.51	9.88 ± 0.64	10.26 ± 1.05	9.73 ± 0.45	10.00 ± 0.48	9.53 ± 0.37	9.04 ± 0.27	8.92 ± 0.41	9.30 ± 0.40

Table 3: Electrophoretic Mobilities of Multiphase Emulsions Droplets ($\mu\text{m Sec}^{-1} \text{ Volt}^{-1} \text{cm}$)

WEEKS	0	1	2	3	4	5	6	7	8	9	10
SAMPLE											
DIT20	2.26	2.40	2.23	2.13	2.21	2.24	2.17	2.27	2.40	2.12	2.25
MEAN MOBILITY FOR PERIOD = 2.24 ± 0.088 COEFFICIENT OF VARIATION = 4.29%											
DIT80	2.83	2.66	2.79	2.44	2.64	2.38	2.49	2.83	2.65	2.57	2.60
MEAN MOBILITY FOR PERIOD = 2.63 ± 0.14 CV = 5.32%											
DT20	2.19	2.08	2.19	2.07	2.17	2.12	2.24	2.18	2.08	2.33	2.17
MEAN MOBILITY FOR PERIOD = 2.17 ± 0.070 CV = 3.23%											
DT80	2.54	2.66	2.67	2.45	2.36	2.48	2.42	2.54	2.67	2.71	2.60
MEAN MOBILITY FOR PERIOD = 2.55 ± 0.110 CV = 4.31%											

RESULTS AND DISCUSSIONS

Table 2 summarises the arithmetic means and the standard deviations of the transit times for all the batches of the multiphase emulsions studied over the ten-week period. The differences in the transit times within the batches appear small, an indication that no appreciable change in droplet size taking place over the period of study. The original interest in studying particle transit times stemmed from the fact that, droplet or particle coalescence or aggregation if occurring should affect the transit times and therefore reflect in marked variations over the period. Hence lack of droplet coalescence and rupture of the multiphase systems may be indicated. The corresponding electrophoretic mobilities for the droplets are shown in Table 3. From the electrophoretic mobilities obtained, the range of the variation the coefficient of variation obtained is 3-6%. A variation of about 6-8% is normally typical of the microscopic method (Shaw, 1969). Thus the results obtained appear typical of the microscopic method. Variation in mobility as a function of emulsion droplet radius has been reported by Mooney (1931). The trend however indicated in this study does not appear to show appreciable variation over the period and may only signify that the multiphase droplets did not show coalescence or rupture and therefore maintained their individual droplet identity and hence stable for the period.

The theoretical relationship between the zeta potential, S, and the electrophoretic mobility, U, as derived by Smoluchoski (1903) can be simplified to (Shaw, 1969).

$$S = 12.85U \text{ millivolts}$$

when the medium used is aqueous and the temperature maintained at 25°C. From the above-simplified equation, the electrophoretic mobility range for the emulsion droplets, which is 2.08 - 2.83 $\mu\text{m Sec}^{-1} \text{ volt}^{-1} \text{ cm}$. Table 3 corresponds to 26.73 - 35.37 mV zeta potential. In colloidal dispersions the zeta potential may represent the index of stability, and hence the higher the zeta potential the greater the stability of the system. The zeta potential can therefore be used as a reliable guide to the magnitude of the electric repulsive forces between particles or droplets. These multiphase emulsions did not show very high zeta potentials although the obtained zeta potentials, are all in excess of 25mV below which systems show tendencies of instability. Emulsions stabilised with non-ionic surfactants have the surfactant adsorbed onto the emulsion droplets and tend generally to reduce the zeta potential. Such surfactants tend to maintain stability more by steric forces which are dependent on the geometry and the conformation of the molecules at the particle interfaces (Florence and Attwood, 1981). The approach of particles with adsorbed hydrated macromolecules lead to steric repulsion as a result of the positive change in enthalpy, the repulsive forces however may not always be enthalpic in origin for the loss of conformational freedom also leads to a negative entropy change. Each chain loses some of its conformational freedom and its contribution to the free energy of the system increases, leading to the repulsion. This volume restriction is compounded by an "osmotic effect" which arises as the macromolecular chains on neighbouring particles crowd into each other's space and the concentration of chains in the overlap region increases. The repulsion, which arises, may therefore be due to the osmotic pressure of the solvent attempting to dilute out the concentrated region. This can only be achieved by the particles or droplets moving apart. Thus the steric repulsion is

due mainly to the volume restriction effect and the osmotic effect (Nappier, 1970; Hesselink, 1969). It is however possible to have both electrostatic and steric repulsive forces operating in a stabilised dispersion giving what is termed electro-steric stabilisation which is thought to be the case in these emulsion studies.

CONCLUSION

From the results obtained in the studies, the electrophoretic mobilities of the multiphase droplets did not appear to change significantly over the period of study. This indicates that there was no significant coalescence and thus the droplets remained stable over the period. The zeta potential was found to be within the range of 26.73 to 35.37 mV which though not too high yet nevertheless above 25mV below which dispersed phase systems show tendencies of instability.

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