

A Quantitative Study of the Effect of Some Electrolytes on the Stability of the Emulsion of Xylene in Water

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A quantitative study of the stability of negatively charged dodecyl benzene sulphonate stabilized xylene-in-water emulsion in the presence of Na⁺, Ba²⁺, Pb²⁺, La³⁺ and Th⁴⁺ has been carried out by measuring electrokinetic potential microelectrophoretically. The interaction energies (as a function of interparticle distance between the two globules) have also been evaluated by summing up attractive and repulsive energies to explain the stability of the system. The flocculation of the system has been studied haemocytometrically. Combination of flocculation and electrophoretic data has been used to estimate an effective value of Hamaker constant for dodecyl benzene sulphonate coated oil globules and the value has been found to be 1.28×10^{-13} erg.

AS a part of a broad programme of studies on the effect of electrolytes on the stability of oil-in-water emulsion¹⁻³, we report here the results of our study on the effect of some electrolytes on the stability of xylene-in-water emulsion stabilized by dodecyl benzene sulphonate. An attempt has also been made to estimate an effective value of Hamaker constant.

Materials and Methods

The emulsifier, dodecyl benzene sulphonate, was a BDH reagent. All the glasswares were cleaned and steamed before use. The dispersion medium was always doubly distilled water. The flocculating electrolytes and xylene used were of BDH (AR) grade.

The xylene-in-water emulsions were prepared as reported earlier⁸ by dispersing 4% by volume of xylene in aqueous solution of 0.1% dodecyl benzene sulphonate. The final mixture also contained 0.01M KCl. The surface tension of dodecyl benzene sulphonate solution was determined at 25° by drop volume method using an 'Agla' micrometer syringe having an accuracy of ± 0.0002 ml.

The electrophoretic mobilities of the emulsion globules were measured using a Northrop-Kunitz type rectangular cell mounted on the base of a Carl-Zeiss microscope. An equi-conducting solution of potassium chloride was filled in the electrode chambers to minimize diffusion. The motion of the individual emulsion globules was timed with the help of a graticule fitted to the eyepiece of the microscope under a constant electric field.

The concentration of globules, in presence of different amounts of electrolytes, was measured with the help of an improved Neubaur model haemocytometer. The number of globules with respect to time was counted with the help of a hand tally counter (Erma, Tokyo) using the Olympus microscope. The number of monomers and dimers were also noted.

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Theoretical

The electrophoretic mobility (U) was calculated from the relation $U = V/x$, where V is the mean velocity of at least ten globules and x is the field strength. The calculations for electrokinetic potential (ζ) from mobility data were carried out using Henry's equation⁹:

$$\zeta = \frac{4\pi\eta}{\epsilon f(x_a)} \cdot U \quad \dots(1)$$

where x is the reciprocal of Debye-Hückel length in cm⁻¹, a is the radius of the emulsion particle, ϵ is the dielectric constant and η is the viscosity of the system.

The repulsive (V_R) and the attractive (V_A) energies were calculated using the Eqs. 2-4 (ref. 10).

$$V_R = \frac{\epsilon a \Psi_0^2}{2} \ln(1 + e^{-xH}) \quad \dots(2)$$

$$V_A = \frac{-Aa}{12H} \left(\frac{\lambda}{\lambda + 3.54H\pi} \right) \quad \text{(for } H < 150 \text{ A}^\circ) \quad \dots(3)$$

$$V_A = -\frac{Aa}{\pi} \left(\frac{2.45\lambda}{120H^2} - \frac{\lambda^2}{1045H^3} + \frac{\lambda^3}{5.62 \times 10^4 H^4} \right) \quad \text{(for } H > 150 \text{ A}^\circ) \quad \dots(4)$$

where the notations have their usual significance.

The total interaction energy (V) is given by Eq. 5.

$$V = V_R + V_A \quad \dots(5)$$

The degree of aggregation was calculated experimentally using Eq. 6 (ref. 10).

$$D = \frac{\text{Number of dimers}}{\text{Number of monomers} + \text{number of dimers}} \quad \dots(6)$$

The theoretical degree of aggregation (D) was determined with the help of the relation¹⁰:

$$D = 4\pi a^3 \eta_0 \int S^2 \exp(-V/kT) ds \quad \dots(7)$$

where η_0 is the initial number of particles. The integration of the equation was done graphically.

The value of Hamaker constant (A_{11}) in vacuum was determined by the relation¹¹ (Eq. 8):

$$A_{11} = 24 \pi d^2 \gamma \quad \dots(8)$$

where d is the separation of the centres of atoms in adjacent molecules, and γ is the surface tension of the material.

The value of Hamaker constant (A) in water was determined by the equation:

$$A = (A_{11}^{1/2} - A_{22}^{1/2})^2 \quad \dots(9)$$

where A_{22} is the value of Hamaker constant of water in vacuum.

Results and Discussion

Effect of electrolytes on flocculation — The initial number of globules per ml in the absence of electrolytes was found to be 4.30×10^8 . The flocculation of the system was studied by counting the change in particle concentration with ageing in the presence of various electrolytes. It is observed that the concentration of globules decreases rapidly first and becomes almost constant after a certain interval of time. The numbers of monomers and dimers were also counted for the estimation of Hamaker constant.

Effect of electrolytes on electrokinetic potential — The value of electrokinetic potential in the absence of additional electrolytes was 145.2 mV. The electrokinetic potentials in the presence of various amount of mono-, bi-, tri- and tetravalent electrolytes, viz. NaNO_3 , $\text{Ba}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, $\text{La}(\text{NO}_3)_3$ and $\text{Th}(\text{NO}_3)_4$ have been evaluated and the data are recorded in Table 1. All the electrolytes, except NaNO_3 , reversed the charge on the system. The concentrations of electrolytes at isoelectric point were $2.82 \times 10^{-3}M$, $1.68 \times 10^{-3}M$, $6.31 \times 10^{-4}M$ and $2.51 \times 10^{-4}M$ for $\text{Ba}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, $\text{La}(\text{NO}_3)_3$ and $\text{Th}(\text{NO}_3)_4$ respectively.

It is evident that the amount required for flocculation is less in the case of higher valent electrolytes. The order of their effectiveness is: $\text{NaNO}_3 < \text{Ba}(\text{NO}_3)_2 < \text{Pb}(\text{NO}_3)_2 < \text{La}(\text{NO}_3)_3 < \text{Th}(\text{NO}_3)_4$. Thus, $\text{Th}(\text{NO}_3)_4$ is most effective in bringing about charge reversal.

Hamaker constant (A) from surface tension — The value of Hamaker constant for dodecyl benzene sulphonate was estimated from its surface tension (66.50 dynes/cm). The value of A in vacuum was calculated using Eq. (8) and taking the separation (d) of the centres of atoms in adjacent molecules as 3.5 Å. Hamaker constant in vacuum for dodecyl benzene sulphonate molecule was found to be 6.14×10^{-12} erg. The value of A for water in vacuum was calculated similarly and found to be 4.50×10^{-13} erg. With the help of above values of A in vacuum, the value of A for dodecyl benzene sulphonate in water has been calculated using Eq. (9) and found to be 1.22×10^{-13} erg which is very close to the value of A for dodecyl benzene sulphonate stabilized xylene globules.

Interaction energies vis-à-vis emulsion stability — The overall interaction energies for the system in presence of different concentrations of electrolytes

TABLE 1 — VALUES OF ELECTROKINETIC POTENTIAL, DEBYE-HÜCKEL PARAMETER, HEIGHT OF MAXIMA, INTERPARTICLE DISTANCE AT WHICH ENERGY EQUALS ZERO AND DEPTH OF SECONDARY MINIMA IN PRESENCE OF DIFFERENT CONCENTRATIONS OF ELECTROLYTES

Electrolyte (M)	Debye-Hückel parameter ($\chi \times 10^{-6}$)	Electrokinetic potential (mV)	Height of maxima (kT)	Interparticle distance at $V=0$ (Å)	Depth of secondary minima (kT)
NaNO₃					
1.0×10^{-4}	3.52	115.1	3610.1	200-210	10.5
2.0×10^{-4}	3.65	110.3	3115.0	190-200	10.6
5.0×10^{-4}	3.92	97.0	2275.9	180-90	10.8
8.0×10^{-4}	4.11	87.0	1780.8	170-80	11.0
1.0×10^{-3}	4.22	84.2	1512.3	160-70	11.5
5.0×10^{-3}	5.48	64.4	1187.2	140-50	11.9
1.0×10^{-2}	6.40	54.7	897.0	110-20	12.8
Ba(NO₃)₂					
1.0×10^{-5}	3.36	114.8	3580.6	190-200	10.4
2.0×10^{-5}	3.43	107.0	3090.1	180-90	10.6
5.0×10^{-5}	3.55	94.1	2646.0	170-80	10.8
1.0×10^{-4}	3.71	85.9	2381.0	150-60	11.4
8.0×10^{-4}	4.64	46.6	1514.7	120-30	11.7
2.0×10^{-3}	5.48	14.1	241.1	70-80	13.2
5.0×10^{-3}	6.70	+27.5	362.3	90-100	12.5
8.0×10^{-3}	7.71	+54.9	903.0	110-20	12.6
Pb(NO₃)₂					
1.0×10^{-5}	3.36	110.2	3045.0	190-200	10.5
2.5×10^{-5}	3.45	98.2	2714.2	180-90	10.6
8.0×10^{-5}	3.66	82.0	2128.6	170-80	10.8
2.0×10^{-4}	3.91	63.4	1860.3	150-60	11.0
5.0×10^{-4}	4.34	48.3	1612.6	120-30	11.5
1.0×10^{-3}	4.81	30.6	394.1	80-90	13.1
2.0×10^{-3}	5.48	+27.9	374.0	80-90	12.6
5.0×10^{-3}	6.70	+42.3	811.2	110-20	12.8
La(NO₃)₃					
5.0×10^{-6}	3.36	97.2	2710.0	180-90	10.7
1.0×10^{-5}	3.43	84.3	2087.7	170-80	10.9
5.0×10^{-5}	3.71	59.0	1616.0	160-70	11.3
5.0×10^{-4}	4.81	21.8	349.8	80-90	12.6
8.0×10^{-4}	5.12	+25.0	321.6	80-90	12.8
1.0×10^{-3}	5.48	+39.6	681.0	100-110	13.1
5.0×10^{-3}	7.02	+61.4	1602.3	140-50	13.4
Th(NO₃)₄					
5.0×10^{-6}	3.41	80.0	1919.0	170-80	10.8
1.0×10^{-5}	3.50	63.7	1764.4	160-70	11.2
5.0×10^{-5}	3.86	39.1	715.2	120-30	12.3
1.0×10^{-4}	4.14	26.4	346.1	80-90	13.6
5.0×10^{-4}	5.30	+24.6	309.6	70-80	13.7
1.0×10^{-3}	6.18	+52.0	1218.5	120-30	13.8

have been evaluated by summing up attractive and repulsive energies. These values were plotted as a function of interparticle distance between the two globules. The relevant data obtained along with electrokinetic potential, Debye-Hückel parameter, interparticle distance at energy equal to zero and depth of secondary minima have been recorded in Table 1.

It is obvious that the extent of energy barriers depends upon the Debye-Hückel parameter, particle radius and electrokinetic potential which varies with the electrolyte content of the system. Thus,

the reduction in the height of maxima is more pronounced in the case of polyvalent electrolytes than monovalent electrolytes. The height of maximum is diminished continuously by the addition of electrolytes up to the stage where repulsion becomes zero, and attraction predominates indicating the flocculation of the emulsion. The maximum potential energies in presence of all the electrolytes are very high (200-3750 kT) which shows the high degree of stability of the emulsion and also obviates the occurrence of flocculation in the primary minima.

The extent of energy barriers increases after the reversal of charge of the system due to the increase in the value of electrokinetic potential. This increase in maximum energy explains the increase in emulsion stability with opposite charge on the system.

Secondary minima flocculation — The occurrence of flocculation of the system cannot be explained on the basis of high energy barriers. Therefore, to explain the flocculation of the system observed experimentally, the secondary minima flocculation curves were also drawn at larger interparticle distances. The depth of secondary minima was found to be 10-14 kT which was reasonably deep for reversible flocculation of the system.

It is observed that the depth of the secondary minima increases with electrolyte content of the system and decreases after charge reversal. The increase in the depth of secondary minima indicates an increase in the rate of flocculation of the system. Similar conclusion can also be drawn by considering the interparticle distance between the two emulsion globules at which energy is zero (H_0). The value of H_0 decreases as the concentration of electrolyte increases.

Hamaker constant — The theoretical and experimental values of degree of aggregation in presence of different amounts of electrolytes for the system have been evaluated with the help of secondary minima curves and haemocytometry respectively. The theoretical values of degree of aggregation, as a function of Hamaker constant, have been plotted in Fig. 1. The values of Hamaker constant satisfying the experimental values of degree of aggregation (D) were obtained from Fig. 1 and are given in Table 2.

The mean value of Hamaker constant (A) obtained is 1.28×10^{-13} erg which is within the same range as observed previously¹².

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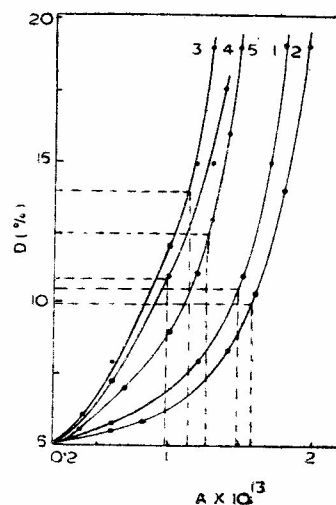


Fig. 1 — Plots of degree of aggregation (D , %) versus Hamaker constant (A) for dodecyl benzene sulphonate stabilized xylene in water emulsion in the presence of different electrolytes [Curve (1), electrolyte = $1.0 \times 10^{-4}M$ $NaNO_3$; curve (2), electrolyte = $1.0 \times 10^{-4}M$ $Ba(NO_3)_2$; curve (3), electrolyte = $2.0 \times 10^{-4}M$ $Pb(NO_3)_2$; curve (4), electrolyte = $1.0 \times 10^{-5}M$ $La(NO_3)_3$; curve (5), electrolyte = $1.0 \times 10^{-4}M$ $Th(NO_3)_4$]

TABLE 2 — THEORETICAL VALUES OF HAMAKER CONSTANT OBTAINED GRAPHICALLY BY THE OBSERVED DEGREE OF AGGREGATION

Electrolyte (conc. in moles)	$D_{obs.}$ (%)	$A^* \times 10^{13}$ (erg)
$NaNO_3$ (1.0×10^{-4})	10.5	1.48
$Ba(NO_3)_2$ (1.0×10^{-4})	10.0	1.58
$Pb(NO_3)_2$ (2.0×10^{-4})	14.0	1.14
$La(NO_3)_3$ (1.0×10^{-5})	10.9	0.98
$Th(NO_3)_4$ (1.0×10^{-4})	12.5	1.26

*Mean value of $A = 1.28 \times 10^{-13}$ erg.

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