Shape, Size, Hydration and Flow Behavior of Nitrocellulose Lacquer Emulsion in Absence and Presence of Urea

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Viscometric and optical microscopic experiments, performed on nitrocellulose lacquer emulsions in the absence (Emulsion I) and presence (Emulsion II) of urea, indicate that in aqueous concentrated solutions at 30 C the emulsion droplets are spherical and non-spherical in shape, respectively. Assuming spherical shape for both emulsions, the size and volume of the aggregated particle (M_v), radius of gyration (R_g), hydrodynamic radius (R_h), diffusion coefficient (D), the correlation time for aggregate rotation (T_r), translational diffusion (T_D) and effective aggregation time (T_a) have been derived. The viscosity data for both emulsions were analyzed in terms of the Einstein, Moulik and Jones-Dole equations. Emulsion II was more hydrated than Emulsion I, although the intrinsic viscosity (η) of Emulsion II is nearly 1.5 times greater than that of Emulsion I. The Huggins and Thomas equations have been compared for both emulsions, and it has been concluded, in light of the proposed Huggins-Thomas-Mandal equation, that the Thomas constant k_1 should be 12.50 for perfect spherical shape of the particles in dilute solutions, instead of the 10.05 originally proposed by Thomas.

In recent studies we investigated (1,2) whether synthetic surfactants (syntans) form true solutions or are present as micelles in aqueous solution. By using the law of mass-action principle and phase separation concept (3), we were able to study the thermodynamics, interactions and aggregation of the systems to arrive at the effectiveness of various syntans in the presence of urea and various other environments. In light of existing controversies as to whether the shape of the nonionic Triton X-100 micelle is spherical or ellipsoid, we first determined the exact geometry of Triton X-100 micelles based on our original work (4) on micellar hydration by the conductivity method. We also have determined the geometry of nonionic Tween (Tween 20 and Tween 80) micelles (5) and the extent of hydration in mixed nonionic micelles (mixtures of different Tweens and of Tweens with Triton X-100) (8). An investigation of size and shape of anionic sodium dodecyl sulfate micelles using sophisticated quasi-elastic light-scattering spectroscopic methods has been reported recently (6). Because similar information on syntan micelles was not available, we studied the shape, size, hydration and other physicochemical properties of these large micelles (7).

In this paper, we report experiments in which shape, size, hydration, flow behavior and other physicochemical properties of aggregated nitrocellulose lacquer emulsions at high concentration in the absence and presence of urea are determined at 30 C by applying hydrodynamic and optical microscopic studies. These measurements confirm that the shape of large aggregated nitrocellulose emulsions in the absence of urea (i.e., Emulsion I) is spherical, whereas in the presence of urea (i.e., Emulsion II) it is nonspherical.

EXPERIMENTAL

Preparation of nitrocellulose (NC) lacquer emulsion. Ten g of ½ second nitrocellulose is soaked in a mixture containing 30 g of 2-ethyl hexyl acetate and 15 g of n-butyl acetate. After 24 hr, 5 g of dioctyl phthalate and 1.0 g of Noigen YX-400 are mixed and stirred well with the lacquer at a speed of 3000 rpm. This represents the nonaqueous phase. For the aqueous phase, 30 g water is mixed with 0.5 g Dodenol-OT and stirred well until a milky white emulsion is formed. Now, the

TABLE 1

Radius, Aggregated Volume, Radius of Gyration, Hydrodynamic Radius, Diffusion Coefficient and Correlation Times for Emulsion I and Emulsion II in Aqueous Solution at 30 C[a]

Radius (A^O)	$M_V \times 10^{16}$ (ml)	R_g (A^O)	$\overline{R}_H$ (A^O)	$\overline{D} \times 10^7$ ($cm^2 \cdot sec.^{-1}$)	$T_r \times 10^5$ (sec)	$T_D \times 10^5$ (sec)	$T_a \times 10^5$ (sec)
			Emulsion I				
400- 480	2.68- 4.63	309.8- 371.8	400- 480	0.693-0.578	5.13- 8.86	3.85- 6.65	2.20- 3.80
500- 600	5.23- 9.04	387.3- 464.8	500- 600	0.555-0.462	10.01- 17.30	7.51- 12.98	4.29- 7.42
800- 900	21.44- 30.52	619.7- 697.1	800- 900	0.347-0.308	41.03- 58.41	30.77- 43.81	17.58- 25.03
1500-1700	141.30-205.69	1161.9-1316.8	1500-1700	0.185-0.163	270.44-393.68	202.83-295.2	115.9 -168.72
			Emulsion II				
380- 450	2.30- 3.82	294.3- 348.6	380- 450	0.730-0.616	4.40- 7.31	3.30- 5.48	1.89- 3.13
480- 540	4.63- 6.59	371.8- 418.3	480- 540	0.578-0.514	8.86- 12.61	6.65- 9.46	3.80- 5.41

[a] The types of particles observed in the aggregates whose dimension and range are specified in Table 1, ranging from the smaller size to the bigger.

nonaqueous phase is slowly added to the aqueous phase and stirred well for 30 min. We designate the emulsion formed in this way Emulsion I. The method of preparing Emulsion II and its composition are almost identical to Emulsion I except that one g of urea is added to the aqueous phase and mixed well with the nonaqueous phase.

Reagents and solutions. Commercial nitrocellulose has grades from ¼ sec to 5000 seconds. For leather topcoats ¼, ½ and 5-6 second grades generally have been used. In the present case, ½ second grade of NC (Balmer and Lawrie Co. Ltd., Madras, India), which contains about 12% nitrogen, was used. Using the above ingredients, an NC lacquer emulsion was prepared and sprayed on leather after diluting with water in the ratio (1:0.5); the leather was dried and finally plain plated. The emulsions prepared as above in our laboratory contained Noigen YX-400 (nonylphenolethyleneoxide; HLB value: 10.0; Chika Ltd., Madras, India), Dodenol-OT (alkylsulfosuccinate base; HLB value: 16.5; HICO Products, Bombay, India), and dioctyl phthalate (BASF India Ltd.) which acts as a plasticizer. All other chemicals used were of analytical grade. In Emulsion II, the amount of urea used is calculated as ca. 0.2M; this is why 0.2M urea in water was used as a medium of reference during that experiment. Double distilled conductivity water was used throughout the experiments.

The viscosity and density of neat Emulsion I and Emulsion II at 30 C are 72.1 cps; 1.0992 g/ml and 121.1 cps; 1.0756 g/ml, respectively. The pH of the emulsions after 10-fold dilution was measured and was close to neutral, ensuring their stability. The pH values of Emulsion I and Emulsion II are 6.3 and 6.5, respectively.

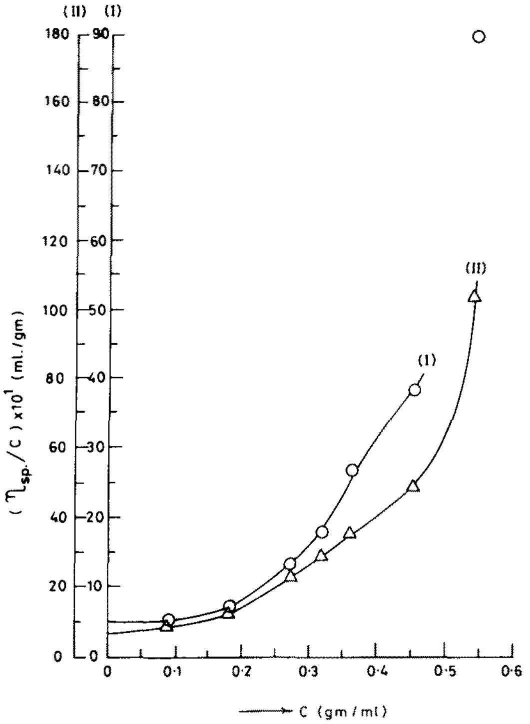

FIG. 1. Plot of η_{sp}/C vs C using Flory-Huggins equation 5 of Emulsion I (open circle) in aqueous solution and of Emulsion II (triangle) in 0.2 M urea as the medium. Temp, 30 C.

Optical microscopic study. Two to three drops of emulsions were placed on cavity slides and were covered with thin (No. 0) coverslips, taking care that no air bubbles remained under the coverslips. They were examined with an oil-immersion objective. The refractive index of the immersion oil was 1.510. Brownian motion of the aggregated particles was observed; after attaining equilibrium, measurements were taken by means of a calibrated stage micrometer scale. To minimize errors, 25 readings were taken for each type of particle. In Emulsion I four types of particles were observed and their shapes were spherical, whereas in Emulsion II two types of particles were observed and their shapes were not spherical. Assuming spherical shape in both emulsions, the average radius (R) of the particles was calculated. Regarding details of this experimental method, we refer to a recent publication (7). The measurement of R was accurate within ±5%. The volume (M_V), assuming a spherical shape of the aggregated particle, was calculated by the following equation:

$$M_V = (4/3)\pi R^3 \qquad [1]$$

For a spherical shape of the particle, the hydrodynamic radius, R_h, can be assumed to be equal to R. The radius of gyration R_g was calculated for a spherical shape by using the formula:

$$R_g = (3/5)^{1/2}R = 0.7746\ R \qquad [2]$$

The average diffusion coefficient $\overline{D}$ was calculated from R_h by using a formula analogous to the Stokes-Einstein relation for spherical particles (8):

$$\overline{D} = kT/f = kT/6\pi\eta\overline{R}_h \qquad [3]$$

where k is Boltzmann's constant, T is the absolute temperature, f is the frictional coefficient, and η is the coefficient of viscosity of the solvent. For spherical micelles or aggregated particles, $\overline{R}_h$ is the hydrated

TABLE 2

Various Physiochemical Parameters Obtained from Different Viscosity Equations for Emulsions in Aqueous Solution at 30 C

	Flory-Huggins' eqn		Thomas eqn		Einstein eqn	Moulik's eqn		Jones-Dole's eqn	
System	[η] (ml/gm)	K at dilute solution	V_h (ml/gm)	k_1^O at dilute solution	V_h (ml/gm)	M	K'	A	B (ml/gm)
Emulsion I	0.50	2.0	0.20	12.50	0.70	0.75	22.50	-2.55	6.67
Emulsion II	0.65	2.0	0.26	12.50	1.20	0	35.00	-2.95	8.40

radius of the sphere, whereas for nonspherical micelles or emulsion droplets $\bar{R}_h$ depends in a complicated way on the hydrated volume and shape of the particles through orientational averaging. $\bar{D}$ values deduced from Equation 3 will not be substantially affected by intermicellar interactions due to cancellation between thermodynamic and hydrodynamic factors under the conditions of the experiments.

Correlation time for the aggregated droplet motion of the emulsion. From the known value of radius R of the emulsion droplet, the effective correlation time (T_a) can be calculated by using the Stokes-Einstein relation (9):

$$T_r = 4\pi R^3\eta/(3kT) = M_V\eta/(kT) \qquad [4a]$$

$$T_D = R_L{}^2/(6\bar{D}) = R^2/(6kT/f)$$
$$= R^2f/(6kT) = R^2 6\pi\cdot\eta R_h/(6kT)$$

$$= \pi R^3\eta/(kT) = \frac{3}{4} M_v\eta/(kT) = \frac{3}{4} T_r \qquad [4b]$$

$$1/T_a = 1/T_r + 1/T_D \qquad [4c]$$

$$T_a = \frac{T_r T_D}{T_r + T_D}$$

If $T_D = 3/4\ T_r$, then Equation 4c can be reduced to

$$T_a = 3/7\ T_r \text{ or } T_a = 4/7\ T_D \qquad [4d]$$

Both the droplet rotation, Equation 4a, and the translational diffusion, Equation 4b, contribute to the effective correlation time (T_a) of the droplet as in Equation 4c. For the lateral diffusion process the radius has been chosen as the aggregated radius (i.e., a number of droplets held together in their movement in the continuous phase) since the rate-limiting step in this process is expected (9) to be due to diffusion of the polar head group.

Hydrodynamic studies. The viscosity of emulsions of various concentrations was measured by Ostwald viscometer with water as the solvent medium (in case of Emulsion II 0.2M urea as the solvent medium). The viscometer was calibrated with 20% sucrose solution in water, and the results are in good agreement with the literature value. The temperature of measurement was accurate within ±0.1 C. Uncertainties in temperature, density measurement and the flow detection imparted a maximum error of ±0.7% to the measured viscosity.

RESULTS AND DISCUSSION

Table 1 presents the hydrodynamic parameters calculated from the experimental data obtained as described in the Experimental Section.

The intrinsic viscosity (η) has been determined using the following equation:

$$\eta_{sp}/C = (\eta) + (\eta)^2K.C \qquad [5]$$

where $\eta_{sp} = (\eta/\eta_o - 1)$ = specific viscosity of the emulsion, and η and η_O are the viscosities of the emulsion and the solvent medium, respectively. C is the concentration of the emulsion and K is the Huggins' constant.

The plot of η_{sp}/C vs C is shown in Figure 1. The intrinsic viscosity (η) has been obtained from the intercept of the plot. The results for intrinsic viscosity are depicted in Table 2. It is difficult to get a constant value of Huggins' constant K from the slope as the slope is varying from point to point, and K is also variable with concentration. For dilute solutions of both emulsions the values of Huggins' constant K is exactly 2.0, which is consistent with the spherical shape (K = 2.0) of the particles, although the intrinsic viscosity of Emulsion II is approximately 1.5 times greater than that of Emulsion I. In concentrated emulsions, the spherical shape of particles in Emulsion I and nonspherical particles in Emulsion II also have been confirmed by microscopy as shown in Figures 2 and 3, respectively. However, if Huggins' constant K is a diagnostic criterion for the shape of particles, then it is valid for dilute emulsions only. That means the Huggins Equation 5 is applicable in dilute systems. In our case of concentrated emulsions, we have found the experimental data to agree well with the following empirical equation:

$$\eta_{sp}/C = 2.5V_h + k_1.V_h^2.C + {}^1\!/\!_c[0.00273 \exp.(16.6V_h.C)] \qquad [5a]$$

where the hydrated specific volume V_h is obtained from the intrinsic viscosity data and k_1 is the Thomas constant. The plot of Thomas constant, k_1 vs concentration of the emulsions is shown in Figure 2.

The V_h was also calculated from the following Einstein equation (10,11):

$$\eta/\eta_O = 1 + \alpha.V_h.C \qquad [6]$$

Hydrated volumes obtained by Equation 6 are always greater than those obtained by Equation 5, because the Einstein Equation 6 is valid only for dilute solutions, whereas in Equation 5a higher power concentration terms were taken into account, and eventually a decrease in the extent of hydration in concentrated solutions was witnessed.

In Emulsion I, where the particles are spherical, we can safely use $\alpha = 2.5$, but for nonspherical particles α should be greater than 2.5. The plot of η/η_O vs concentration is shown in Figure 3, and the calculated V_h values from the slopes are depicted in Table 2. We have applied the Moulik equation (12):

$$(\eta/\eta_O)^2 = M + K'.C^2 \qquad [7]$$

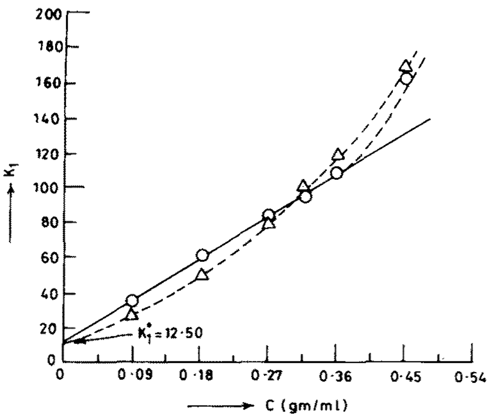

FIG. 2. Plot of k_1 vs C on Emulsion I (open circle) in aqueous solution and on Emulsion II (triangle) in 0.2 M urea as the medium. Temp, 30 C.

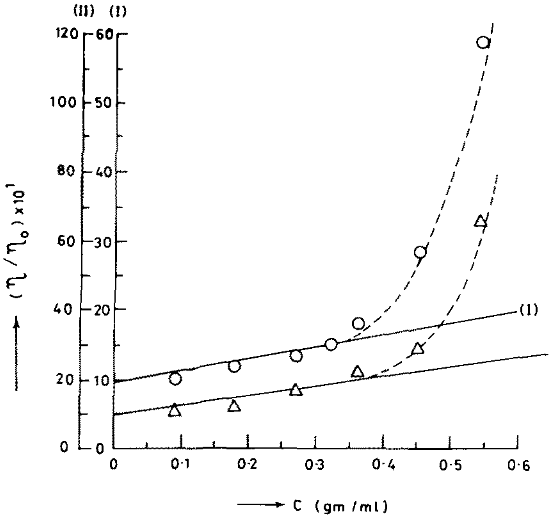

FIG. 3. Plot of η/η_0 vs C using Einstein equation 6 on Emulsion I (open circle) in aqueous solution and on Emulsion II (triangle) in 0.2 M urea as the medium. Temp, 30 C.

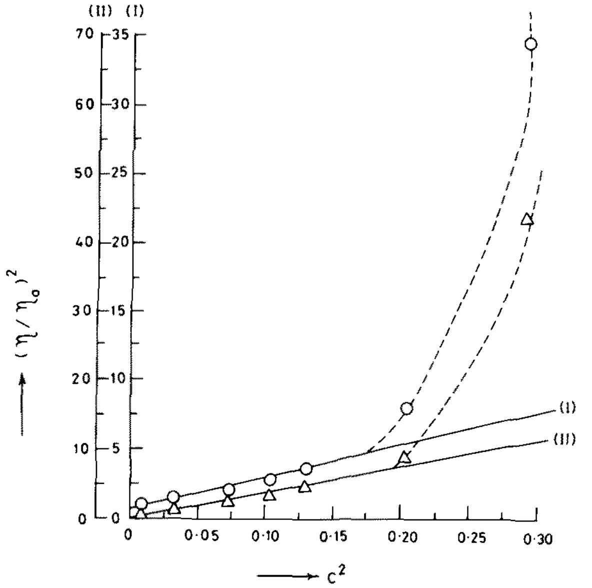

FIG. 4. Test of Moulik equation 7 on Emulsion I (open circle) in aqueous solution and on Emulsion II (triangle) in 0.2 M urea as the medium. Temp, 30 C.

The test of this equation has been shown in Figure 4, and the calculated values of the Moulik constants M and K′ are given in Table 2. The Moulik equation is usually valid for concentrated electrolyte solutions, but since our emulsions are not electrolyte solutions, Equations 6 and 7 are valid only up to a concentration of 0.35 g/ml, as shown in Figures 3 and 4 by solid lines. This corroborates our recent findings on syntans micelles (7), which also are not electrolyte solutions, but for which Equations 6 and 7 are valid up to a concentration of 0.4 g/ml. From Table 2, we find that the hydrated volume V_h (calculated from Einstein Equation 6) for Emulsion II is greater than that for Emulsion I if the particles of the emulsions are spherical. But if we assume the particles of Emulsion II not to be spherical in shape, $\alpha > 2.5$, and V_h of Emulsion II will be less than that of Emulsion I. However, we do not know the exact value of α. V_h has been calculated assuming a spherical shape. After considering the Thomas equation and Huggins' constant (Equation 9b), we have found that V_h of Emulsion I is less than that of Emulsion II. On the basis of our previous findings (4) of reduction in the extent of hydration of emulsions or micelles containing urea, we have designed our present experiment in order to get practical utility. We already have mentioned that Emulsion II contained some urea (0.2 M urea as the solvent medium). Now the question can be raised whether the increase of hydration of Emulsion II accompanies the increase of viscosity compared to Emulsion I or whether the urea involved in Emulsion II can cause the aggregated droplet structure to break. In order to address this question we turn our attention to the microscopic studies. For Emulsion II, the number of aggregated particles as well as the size is smaller than for Emulsion I. Therefore, urea contained in Emulsion II causes a progressive reduction (7,13) in $\bar{R}_h$ for the large aggregated droplet structure. The decrease in size of the aggregated droplet structure in Emulsion II is due to high solvation, and the increase in viscosity does not really contradict this view. In light of existing controversies as to whether water is trapped inside the aggregated droplet core or not, the increases in hydration and viscosity are possible only if trapped water in the aggregated core comes out, thereby reducing the compactness of the hydrophobic group and enlarging (or unfurling) the structure. The special and peculiar property of urea is thus invoked.

The viscosity data for different emulsions were analyzed in terms of the Jones-Dole equation (14):

$$(\eta/\eta_0 - 1)/\sqrt{C} = A + B\sqrt{C} \qquad [8]$$

The plots between $(\eta/\eta_0 - 1)/\sqrt{C}$ and $\sqrt{C}$ are linear and are shown in Figure 5. The intercept (A value) and the slope (B value) of the plots obtained for Emulsion I and Emulsion II are shown in Table 2. It is clear that both the negative values of A and the positive values of B are somewhat higher for Emulsion II than for Emulsion I. This supports the contention of hydration. Although our present systems are not to be treated strictly as pure electrolyte systems (systems contained anionic and nonionic surfactants with plasticizer), the Jones-Dole equation is still valid.

In terms of the concept adopted by Franks and Evans (15), the diffuse layer of the anion as well as the oxygen center of the polyoxyethylated nonionic surfactant in Emulsion II may be considered to consist of oriented water and urea molecules. The presence of urea may have caused the disruption of the so-called ordering "iceberg" structure or three-dimensional hydrogen-bonded "flickering clusters" in the solvation sphere with positive enthalpy and entropy values (1, 2). Urea is a well known structure breaker of water as well as a hydrophobic bond breaker, even in mixed systems. In our emulsions, urea acts as a structure breaker and supports our recent findings (16) where urea acts as a structure breaker even in mixed surfactant systems (anionic + cationic + nonionic). However, the B values increased in the presence of urea (Emulsion II) with decreasing size of the aggregated droplets. This is evidence for the hydration effect and may be attributed to the ability of urea to disrupt water as well as hydrophobic structures in the vicinity. In Emulsion I (control), four types of particles were observed, perhaps due to the presence of nonionic, anionic surfactants, plasticizers and their combinations, whereas in Emulsion II only two types of small particles were observed, which is due to destruction of aggregates into smaller ones by urea.

Hydrodynamic and various other physicochemical parameters are shown in Table 1. The smaller and more uniform size of the aggregated droplets of Emulsion II permits better penetration capacity into a leather matrix than does Emulsion I. Table 1 shows that the correlation times of emulsions are on the order of 10^{-5}s, and this long correlation time is due to slow motion of the large aggregates in the emulsion. This motion can consist of either the rotation of the aggregated droplet as a single entity or the translational diffusion motion of the amphiphile along the emulsion surface. Actual analysis showed that both motions take place simultaneously, are uncorrelated with each other and are approximately equally effective. Equations 4a and 4b show that both T_r and T_D are directly proportional to R^3, i.e., to the molecular volume M_V, of the aggregated droplet, and T_r is always greater than $T_D (T_r = 4/3\, T_D)$.

Since the correlation times in our emulsion systems behave qualitatively in the same way as for other micellar systems studied (9), one might expect that the overall motion of the micellar aggregation or of the emulsion droplet is also of importance in these cases. The interior of the large micellar emulsion is even more liquid, and it is then a reasonable assumption to expect the slow motion to give an important contribution to T_r and T_D (and hence to T_a) in normal hexagonal liquid crystalline phases.

Now we want to compare the following Thomas (17) equation:

$$(\eta/\eta_O - 1)/C = \eta_{sp}/C = 2.5\, V_h + k_1 \cdot V_h^2\, C \qquad [9]$$

with Equation 5, we can write:

$$[\eta] = 2.5\, V_h \qquad [9a]$$

and

$$[\eta]^2 K = V_h^2 k_1 \qquad [9b]$$

Therefore,

$$k_1 = 6.25\, K \qquad [9c]$$

Equation 9c is the relationship between Thomas' constant and Huggins' constant and can be referred to as the Huggins-Thomas-Mandal equation. The factor of 6.25 is absolutely constant for any value of k_1 or K. If Huggins' constant K for spherical particle shape is 2.0 in dilute solutions, then the value of k_1 should be 12.50, instead of 10.05 as originally proposed by Thomas (17). The value of k_1 can vary from 1 to 50 depending on the nature of the system. As shown in Figure 4, the value of k_1 in dilute solutions of both our emulsions is 12.50, which translates through Equation 9c into a K value of 2.0. This in turn shows that the emulsion particles can be considered to be spherical in their rheological behavior. This view supports our previous findings (7).

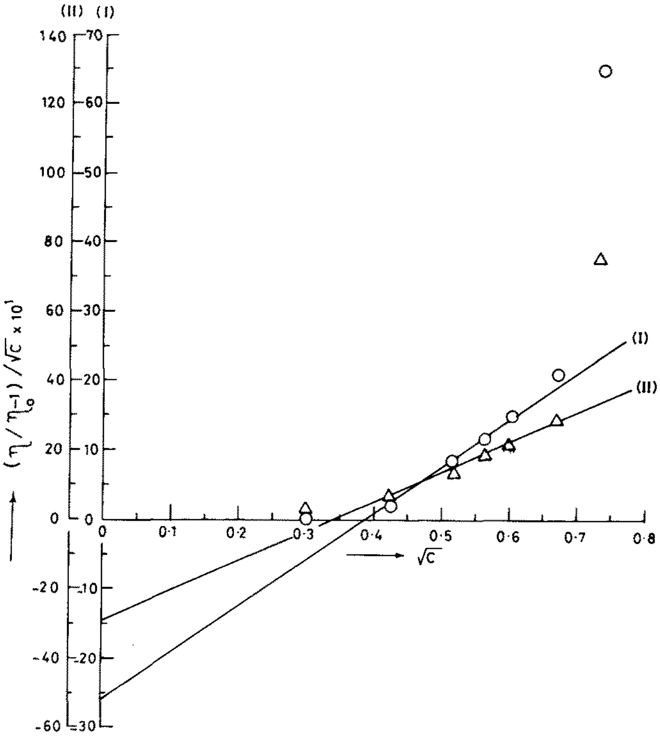

FIG. 5. Validity of Jones-Dole equation 8 on Emulsion I (open circle) in aqueous solution and on Emulsion II (triangle) in 0.2 M urea as the medium. Temp, 30 C.

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