

Colloid Science

The interaction of sodium caseinate with monoglyceride and diglyceride at the oil-water interface and its effect on interfacial rheological properties

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Abstract: The viscoelasticity at a corn oil-water interface of films of sodium caseinate, and of sodium caseinate plus glyceryl monostearate (GMS) and glyceryl distearate (GDS), have been examined. Caseinate films exhibited little viscoelasticity, but in the presence of GMS and GDS significant viscoelasticity developed. The magnitude of the viscoelasticity parameters was influenced by the GMS/GDS ratio employed at any caseinate concentration. Optimum values of the parameters were obtained at a 5/2 GMS/GDS ratio. This was attributed to association of caseinate with the glycerides, which had themselves entered into some form of association prior to adsorption of caseinate.

Introduction

The viscoelasticity of 60% (wt/wt) corn oil-in-water emulsions stabilised by 2.0% (wt/wt) total emulsifiers, consisting of sodium caseinate (0.5–1.5% wt/wt) and a mixture (1.5–0.5% wt/wt) of glyceryl monostearate (GMS) and glyceryl distearate (GDS) is influenced by the relative proportions of caseinate and glycerides used and also by the glyceryl monostearate/glyceryl distearate ratio when using a constant weight of caseinate [1]. Irrespective of the weights of caseinate and glycerides mixture used the highest values of the viscoelasticity parameters are obtained when using a GMS/GDS wt/wt ratio of 5/2. Under these conditions the slowest rate of drop coalescence is also exhibited.

Several workers have found a correlation between the rheological properties of films of a single emulsifier adsorbed at an extended planar oil-water interface and the stability of emulsions prepared with the same emulsifier [2–4]. Similar correlations have been observed when using mixtures of emulsifiers, e. g. blends of Spans and Tweens [5] and blends of mono- and di-glycerides [6]. With the latter systems there is a critical ratio of emulsifiers in the mixture at which the interfacial films exhibit maximum values of their viscoelasticity parameters and emulsions prepared with the emulsifiers in the same ratio exhibit optimum sta-

bility. In the fat globule membrane of milk cooperative interaction can occur between proteins and low molecular weight surfactants [7] and a similar effect has been observed with egg yolk where the complex formed between apoproteins and phospholipids is important to stability [8]. In the studies with Span-Tween mixtures it was suggested that at the critical emulsifier ratio which gave optimum values of the properties examined, association occurs between the emulsifiers, and the interfacial emulsifier film then has a liquid crystalline structure [9].

Many food emulsions contain both protein and "commercial grade" GMS. The latter emulsifier contains GMS and GDS in approximately equal proportions, so it was considered pertinent to determine whether the proteins and glycerides interact in the same way as has been observed with other emulsifier blends, how they affect the viscoelastic properties of adsorbed, mixed, interfacial films of protein and glycerides, and their effect on the stability of O/W emulsions stabilised by protein, GMS and GDS.

Experimental

Materials

Pure corn oil (density 0.917 gm cm^{-3} at 20°C) was used as the oil phase. The water used was distilled twice in an all glass apparatus

consisting of two stills in series (Autostills, England). The emulsifying agents were soluble, light white sodium caseinate (Hopkins and Williams Biochemicals, Essex, England), monoglyceride and diglyceride. The glycerides were provided by Kao-Atlas Chemicals, Tokyo, Japan, and had the following compositions —

Monglyceride; 93% (wt/wt) monoglyceride, 5% diglyceride, 1% glyceride and 1% fatty acid.

Diglyceride: 77% (wt/wt) diglyceride, 17% monoglyceride, 6% triglyceride.

The fatty acids incorporated in the glycerides were lauric, myristic, palmitic, stearic and arachidic, with the main component being stearic acid.

Viscoelastic properties of films of caseinate and glycerides at a corn oil-water interface.

The viscoelastic behaviour was studied using the biconical disc rheometer and procedure described elsewhere [4]. Sodium caseinate was dissolved in the aqueous phase and the glycerides were dissolved in the oil phase.

Using a constant low stress the creep compliance $J_s(t)$ at any time t is given by

$$J_s(t) = \frac{4\pi}{K_w} \left(\frac{1}{R_i^2} \cdot \frac{1}{R_o^2} \right)^{-1} \frac{\theta_d(t)}{\theta_s - \theta_d(t)} \quad (1)$$

where K_w is the torsion constant of the stainless steel wire from which the biconical disc of radius R_i (1.9 cm) is suspended, R_o is the radius of the glass vessel (3.4 cm) in which the oil-water interface is developed, θ_s is the rotary motion of the torsion head and $\theta_d(t)$ is the angular displacement of the biconical disc at any time t (10).

The instantaneous surface shear modulus $E_o(s)$ is given by

$$E_{o(s)} = \frac{K_w}{4\pi} \left(\frac{1}{R_i^2} \cdot \frac{1}{R_o^2} \right) \frac{\theta_s - \theta_d(t)}{\theta_d(t)} \quad (2)$$

where θ_o is the angular displacement of the biconical disc at $t = 0$.

All tests were made at $35.0^\circ \pm 0.1^\circ\text{C}$ and at pH 5.5. The following factors were examined —

1. The influence of sodium caseinate concentration (10^{-5} — $10^{-1}\%$ wt/wt) in the aqueous phase.

2. The influence of monoglyceride/diglyceride ratio (4/1, 5/2, 1/1, 1/3 and 2/9) when using $10^{-2}\%$ (wt/wt) glyceride mixture in the oil phase with $10^{-2}\%$ (wt/wt) sodium caseinate in the aqueous phase.

3. The influence of monoglyceride/diglyceride ratio (4/1, 5/2, 1/1, 1/3 and 2/9) when using $10^{-2}\%$ (wt/wt) glyceride mixture in the oil phase with $10^{-1}\%$ (wt/wt) sodium caseinate in the aqueous phase.

Table 1. Influence of sub-phase sodium caseinate concentrations (% wt/wt) on the rheological properties of sodium caseinate films at a corn oil/sodium caseinate-solution interface. Temperature 35°C , pH = 5.5

Sodium caseinate (% wt/wt)	Ageing time (h)	$E_{o(s)}$ (dyne cm^{-1})	$\eta_{N(s)}$ (s. poise)	$E_{I(s)}$ (dyne cm^{-1})	$\eta_{I(s)}$ (s. poise)	Shear stress ^{a)} (dyne cm^{-1})
10^{-1}	3	0.05	6.2	0.02	11.0	0.03
	6	0.06	7.0	0.02	12.0	0.04
	24	0.08	8.5	0.05	22.0	0.06
	45	0.08	10.0	0.07	25.0	0.08
10^{-2}	3	0.07	14.0	0.08	30.0	0.05
	6	0.07	15.0	0.08	32.0	0.06
	24	0.09	180.0	0.92	260.0	0.09
	45	0.09	200.0	0.95	570.0	0.15
10^{-3}	3	0.07	7.0	0.04	12.0	0.04
	6	0.07	7.0	0.07	14.0	0.05
	24	0.08	100.0	0.30	230.0	0.11
	45	0.08	140.0	0.60	350.0	0.13
10^{-4}	3	—	—	—	—	—
	6	0.05	5.0	0.02	10.0	0.06
	24	0.05	5.0	0.03	10.0	0.08
	45	0.06	70.0	0.07	50.0	0.12
10^{-5}	3	—	—	—	—	—
	6	0.01	4.0	0.01	6.0	0.01
	24	0.01	4.0	0.01	6.0	0.03
	45	0.02	5.5	0.02	35.0	0.09

^{a)} at 5 s

Results

No viscoelasticity was observed when mono- and di-glycerides were used independently or collectively.

Interfacial films of sodium caseinate exhibited measurable viscoelasticity only when the concentration of caseinate in the aqueous phase was very low (Table 1). The creep compliance of these films, and also of the films developed from caseinate and mixtures of mono-glyceride and diglyceride (Tables 2 and 3), could be represented by

$$J_s(t) = J_{o(s)} + J_{1(s)} [1 - \exp(-t/T_{1(s)})] + \frac{t}{\eta_{N(s)}} \quad (3)$$

where $J_s(t)$ is the surface creep compliance at any time t , $J_{o(s)}$ is the instantaneous surface elastic compliance ($= 1/E_{o(s)}$, the instantaneous surface elastic modulus), $J_{1(s)}$ represents the retarded surface elastic compliance,

$T_{1(s)}$ represents the surface retardation time and $\eta_{N(s)}$ is the surface Newtonian viscosity. Also, $J_{1(s)} = 1/E_{1(s)}$, where $E_{1(s)}$ represents the retarded surface elastic modulus, and $T_{1(s)} = J_{1(s)} \eta_{1(s)}$, with $\eta_{1(s)}$ representing the surface viscosity associated with $E_{1(s)}$.

The very low values of $E_{o(s)}$ and $E_{1(s)}$ exhibited by the sodium caseinate films increased only slightly when the films were aged for 45 hours (Table 1), but both $\eta_{1(s)}$ and $\eta_{N(s)}$ increased significantly during that time. The highest parameter values were obtained when using $10^{-2}\%$ (wt/wt) of caseinate.

All the viscoelasticity parameters were much higher, both in terms of their initial values and especially in their final values, when caseinate was used in conjunction with mixtures of monoglyceride and diglyceride (Tables 2 and 3). Now, ageing the mixed films for 45 hours produced substantial increases in all parameters with the main increase occurring within the first 24

Table 2. Influence of mono/di-glycerides ratio on the rheological properties of films adsorbed at a corn oil-glycerides $10^{-2}\%$ (wt/wt)/sodium caseinate $10^{-2}\%$ (wt/wt) solution interface. Temperature 35°C , pH = 5.5

Mono-diglycerides ratio	Ageing time (h)	$E_{o(s)}$ (dyne cm^{-1})	$\eta_{N(s)}$ (s. poise)	$E_{1(s)}$ (dyne cm^{-1})	$\eta_{1(s)}$ (s. poise)
4/1	1	0.91	5.0	0.5	10.0
	3	4.31	10.0	6.0	22.0
	6	11.29	10.0	12.0	100.0
	24	20.66	2000.0	25.0	250.0
	45	21.74	2200.0	27.0	270.0
5/2	1	1.37	7.0	0.6	30.0
	3	6.53	12.0	10.0	50.0
	6	12.73	14.0	15.0	300.0
	24	27.71	2300.0	18.0	500.0
	45	30.87	2800.0	22.0	620.0
1/1	1	0.81	6.0	0.4	20.0
	3	5.38	10.0	7.0	30.0
	6	12.21	12.0	9.0	100.0
	24	18.01	1600.0	15.0	200.0
	45	20.53	1800.0	17.0	270.0
1/3	1	0.53	5.0	0.2	10.0
	3	3.23	7.0	1.0	15.0
	6	9.31	12.0	3.0	80.0
	24	11.07	160.0	9.0	150.0
	45	12.45	220.0	11.0	180.0
2/9	1	0.37	4.0	0.2	8.0
	3	4.31	7.0	1.0	22.0
	6	8.95	15.0	2.0	110.0
	24	10.16	170.0	8.0	150.0
	45	12.25	200.0	12.0	180.0

^a) At 5 s

hours. The increase was most noticeable when using a monoglyceride/diglyceride ratio of 5/2, irrespective of whether the caseinate concentration was 10^{-2} % wt/wt or 10^{-1} % wt/wt. Caseinate concentration appeared to exert a much lower effect than the monoglyceride/diglyceride ratio. When using monoglyceride/diglycerides ratios of 1/3 and 2/9 at a constant caseinate concentration of 10^{-2} % or 10^{-1} % (wt/wt) the effects on parameter values were rather similar.

The data in Tables 2 and 3 relate to emulsions containing a constant weight (10^{-2} % wt/wt) of mixed glycerides. When a constant weight of 10^{-2} % (wt/wt) caseinate was used with a variable weight of mixed glycerides in a monoglyceride/diglyceride ratio of 5/2 the viscoelasticity parameter values were influenced by the weight of mixed glycerides. For example, Fig. 1 shows that the value of $E_{o(s)}$ increased substantially as the mixed glycerides concentration rose from 10^{-4} %

to 10^{-1} % (wt/wt), the main increase occurring between 10^{-3} % and 10^{-1} % (wt/wt). Between 10^{-1} % and 2.5×10^{-1} % (wt/wt) there was little further increase in the value of $E_{o(s)}$. $E_{o(s)}$ reflects the intact strength of the interlinked network of emulsifier molecules adsorbed at the oil-water interface and it is, therefore, the viscoelasticity parameter of greatest interest.

Discussion

Sodium caseinate diffuses to the interface mainly in the form of free casein molecules which are in equilibrium with molecules located in the casein submicelles [12]. At pH 5.5, i. e. near to its isoelectric point, the caseinate molecules are in a more compact form than at other pH values. They are adsorbed at the oil-water interface in this configuration and so should provide a higher concentration of protein molecules per unit

Table 3. Influence of mono/di-glycerides ratio on the rheological properties of films adsorbed at a corn oil-glycerides 10^{-1} % (wt/wt)/sodium caseinate 10^{-2} % (wt/wt) solution interface. Temperature 35 °C, pH 5 = 5

Mono-diglycerides ratio	Ageing time (h)	$E_{o(s)}$ (dyne cm^{-1})	$\eta_{N(s)}$ (s. poise)	$E_{I(s)}$ (dyne cm^{-1})	$\eta_{I(s)}$ (s. poise)
4/1	1	0.95	8.0	0.02	12.0
	3	4.33	15.0	10.0	22.0
	6	12.70	140.0	10.0	100.0
	24	29.75	2090.0	16.0	320.0
	45	24.78	2800.0	18.0	450.0
5/2	1	1.93	10.0	0.4	15.0
	3	7.14	16.0	8.0	20.0
	6	14.87	20.0	20.0	250.0
	24	28.37	2100.0	25.0	580.0
	45	32.43	2500.0	26.0	620.0
1/1	1	0.93	5.0	0.2	13.0
	3	5.83	7.0	3.7	18.0
	6	12.21	10.0	6.0	120.0
	24	19.01	1200.0	18.0	240.0
	45	21.32	1900.0	21.0	350.0
1/3	1	0.49	2.0	0.06	8.0
	3	3.09	3.0	1.5	14.0
	6	10.11	5.0	6.0	70.0
	24	10.12	160.0	12.0	190.0
	45	12.13	290.0	14.0	350.0
2/9	1	0.45	1.0	0.03	8.0
	3	4.78	3.0	2.0	13.0
	6	8.12	4.0	8.0	60.0
	24	12.18	120.0	10.0	190.0
	45	12.19	130.0	11.0	200.0

^a) At 5 s

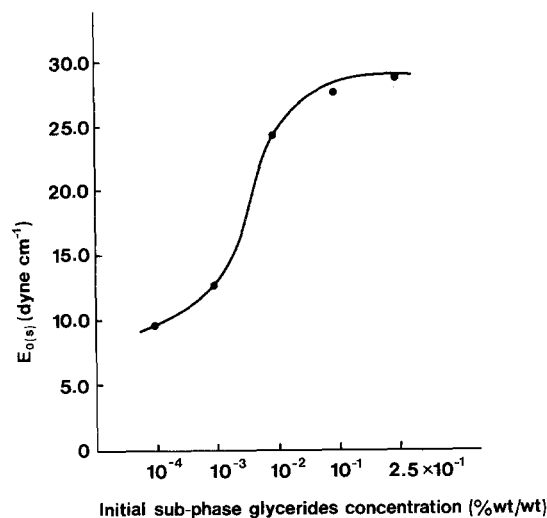


Fig. 1. Influence of 5/2 ratio of monoglyceride/diglyceride concentration on $E_{o(s)}$. Na caseinate concentration = 10^{-2} % (wt/wt). ($E_{o(s)}$ data are for interfacial films aged for 24 h)

area of interface and, consequently, a larger number of interlinkages per unit area, than at other pH values. They are adsorbed at the oil-water interface in this configuration and so should provide a higher concentration of protein molecules per unit area of interface and, consequently, a larger number of interlinkages per unit area, than at other pH values. Nevertheless, at the caseinate concentrations utilised they did not yield an interfacial film of significant viscoelasticity. The sharp increase in the values of the viscoelasticity parameters when monoglyceride/diglyceride mixtures were used in conjunction with these concentrations of sodium caseinate, suggests that there is some form of interaction between the caseinate and glycerides and that its level is influenced by the monoglyceride/diglyceride ratio. Diglyceride facilitates the interaction when it is present in not too high concentration. The 5/2 ratio of monoglyceride/diglyceride which yields the highest viscoelasticity parameters for the interfacial films is the same ratio at which emulsions prepared with the same emulsifying agents exhibit maximum viscoelasticity parameter values [1] and minimum drop coalescence rates [13]. So, this critical monoglyceride/diglyceride ratio influences several properties of O/W emulsions containing sodium caseinate.

It is interesting to note that at the 5/2 and 1/2 monoglyceride/diglyceride ratios the interfacial films exhibit a much larger increase in E_o between 6 and 24 hours

ageing than at the other ratios, with the 5/2 ratio producing the greater effect (Tables 2 and 3). Therefore, the mechanism which is responsible for increasing E_o operates over a longer time interval at the 5/2 monoglyceride/diglyceride ratio than at the other ratios.

Ageing effects in interfacial films have been reported on several occasions. For example, Izmailova [14] observed that the strength of films of α -casein, human serum albumin and egg albumin at an oil-water interface increased with time. This was attributed to slow diffusion and slow orientation of the protein molecules at the interfaces. A three-dimensional wrinkled gel-like structure developed eventually at the interface and this indicated that the adsorbed film was of considerable thickness. Similar ageing effects have been observed for interfacial films of mesquite gum [4], soy and meat proteins [15] and egg lipoproteins [16].

It has been pointed out elsewhere [1, 17] that monoglyceride and diglyceride will diffuse to, and be adsorbed at the interface before the protein, because of their substantially lower molecular weights, and enter into some form of association. Consequently, the sodium caseinate will be adsorbed against a higher surface pressure than the glycerides, and this may be one of the reasons for the effect of time on $E_{o(s)}$. The adsorbed caseinate then associates with the monoglyceride-diglyceride "complex". This may involve several mechanisms [17] including hydrogen bonding between the hydrogen atoms of the hydroxyl groups of the glycerides and the oxygen atoms of the carboxyl groups of the caseinate and non-polar dispersion forces. Presumably, the 5/2 ratio of monoglyceride/diglyceride provides adsorption of the glycerides at a level which ensures their optimum association initially and, subsequently, ensures optimum association with adsorbed caseinate molecules.

Acknowledgement

One of the authors (G. D.) gratefully acknowledges the financial assistance provided by the State Scholarships Foundation, Athens, Greece, which made this study possible.

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Received June 25, 1985;
accepted September 16, 1985

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