Thin liquid films stabilized by polymers and polymer/surfactant mixtures

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A R T I C L E   I N F O

A B S T R A C T

The development of the topic of thin liquid films (TLF) stabilized by polymers in the last five years is outlined. Different types of TLF are considered, namely foam, emulsion (aqueous or oil) and wetting films. The reviewed results envelop a variety of polymeric surfactant and polymer(polyelectrolyte)/surfactant systems which have been probed by several methods, however mostly by the thin film pressure balance technique. The discussion addresses major factors which affect the surface forces in the TLF: type and charge of the polymer, type of the film interfaces (water/air, water/oil or water/solid), solvent conditions (salinity/polarity) and addition of a second surface active component. Linkage with studies on the corresponding single interfacial layers and macroscopic systems (foams and emulsions) is briefly discussed as well.

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1. Introduction

The state of literature results in the field of thin liquid films (TLF) was reviewed in the topical issue of Current Opinion Colloid Interface Science in 2010 [1]. In the present work we take as a baseline of our discussion the articles: of Üzüm et al. on polyelectrolyte/surfactant foam films [2]; of Mileva on the correlations between the properties of interfacial layers and TLF [3]; of Khristov and Czarnecki on emulsion films from polymeric surfactants [4]; and of Saramago on wetting films [5] as these review papers overlap to a larger or smaller extent with the present theme of TLF stabilized by polymers and polymer(polyelectrolyte)/surfactant mixtures. In addition, several other review articles [6**,7*,8*,9*,10**] published at similar time or later in different journals are considered and are highly recommended to the reader.

In this work we give an overview of results published during the last five years (some previous works are also cited as useful information) on several subtopics: Section 2 deals with aqueous foam and emulsion films stabilized by neutral polymers and includes the comparatively new subject of films from star-like polymers; Section 3 deals with foam films from mixed polymer(polyelectrolyte)/surfactant solutions; in Section 4 the relatively modern subject of water-in-crude oil emulsion films is considered; in Section 5 the development in the area of wetting films is briefly overviewed; in Section 6 some concluding remarks are given and in

addition, for the sake of curiosity, a brief retrospective overview of film stratification is presented. Section 3 envelops mostly results on foam films — this is not because of some authors' whim but just because of the fact that surprisingly the recent literature is somehow poorer of results on emulsion films in comparison to the amount of works done with foam films and moreover, to our best knowledge, works on wetting films from mixed solutions have not been published at all.

2. Aqueous foam and emulsion films stabilized by non-ionic polymeric surfactants

It is well established that electrostatic, Van der Waals and steric forces are operative in foam and emulsion films obtained from aqueous solutions of non-ionic polymeric surfactants [2,6**,11**–13]. The positive disjoining pressure (Π) which stabilizes the films is a sum of two components — electrostatic (Π_{el}) and steric (Π_{st}) as their magnitudes are controlled by both the surface charge density and the electrolyte concentration (C_{el}) [6**,11**–14], and by the intensity of the steric interaction [6**,11**,12,15,16], respectively. The action of Π_{el} in foam and O/W emulsion films stabilized by PEO–PPO–PEO polymers is suppressed at a critical electrolyte concentration ($C_{el,cr}$) and under the condition of $C_{el} > C_{el,cr}$ the thin films are stabilized by steric forces [6**,11**,12]. The critical electrolyte concentration is a characteristic parameter indicating the transition from electrostatic to steric stabilization and it has been measured also for foam and O/W emulsion films stabilized by other types of non-ionic polymeric surfactants such as hydrophobically

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Symbols

M	molecular mass
R	radius
β	asymmetry ratio in amphiphilic block polymers
h	film thickness
h_w	equivalent film thickness
h_w^{rupt}	equivalent film thickness before rupture
Π	disjoining pressure
Π_{el}	electrostatic disjoining pressure
Π_{st}	steric disjoining pressure
Π_{osc}	oscillatory disjoining pressure
$C_{Polymer}$	polymer concentration
C_S	surfactant concentration
C_{el}	electrolyte concentration
$C_{el,cr}$	critical electrolyte concentration
P_{cr}^{film}	critical pressure of film rupture
P_{cr}^{foam}	critical pressure of foam collapse

Abbreviations

TLF	thin liquid film
O/W…/O	oil-in-water … -in-oil
PEO	poly(ethylene-oxide)
PPO	poly(propylene-oxide)
HMI	hydrophobically modified inulin
EFKA	hydrophobically modified polyacrylate
DETA	diethylentriamine
TFPB	thin film pressure balance
CP-AFM	colloidal probe atomic force microscope
SFA	surface force apparatus
DBMM	drop/bubble micro-manipulator
FPD	foam pressure drop
CBF	common black film
NBF	Newton black film
CAC	critical concentration of association
CMC	critical concentration of micellization
CBC	critical bitumen (heavy oil) concentration
IEP	isoelectric point
METAC	[2-(Methacryoyloxy)ethyl]trimethylammonium chloride
$C_n(EO)_m$	n-yl m(ethylene oxide)
PVFAm	poly(vinylformamide)
PVAm	poly(vinylamine)
PNIPAM	poly(N-isopropylacrylamide)
PDADMAC	poly(diallyldimethylammonium chloride)
$C_{12}G_2$	n-Dodecyl-D-maltoside
C_8G_1	n-Octyl-D-glucoside
PAMPS	poly(2-acrylamido-2-methyl-1-propanesulfonic acid) dioctyl sulfosuccinate
AOT	Aerosol OT (Dioctyl sodium sulfosuccinate)
PSS	poly(styrene sulfonate)
SDS	sodium dodecyl sulfate
C_nTAB	n-yl trimethylammonium bromide

modified inulin (HMI) graft polymers [1,4,6**,17] and diethylentriamine (DETA) based star-like polymers [18**]. The latter can be considered as a new class of amphiphiles in respect to thin liquid films studies since such results appeared only recently in the literature.

2.1. PEO–PPO–PEO block polymers

PEO–PPO–PEO polymers are efficient stabilizers of foam and O/W emulsion films [4,6**,11**,12]. The operation of Π_{el} is suppressed at a critical electrolyte concentration ($C_{el,cr}$) as mentioned above and/or at a critical pH (denoted $pH_{cr,st}$) as the values of the latter belong to the region pH < 4 which means that the film interfaces containing adsorbed polymers molecules carry a certain negative charge, diffuse double-layer potential (φ_0) respectively, which is obliterated in acidic environments [6**,12,13]. Under solvent conditions $C_{el} \geq C_{el,cr}$ or pH ≤ $pH_{cr,st}$, the films are stabilized *brush-to-brush* steric forces and their properties, especially the film thickness, depend on the structure and molecular mass M of the respective polymers. The molecular structure is defined by the length (number of EO monomers N_{EO}) of the stabilizing PEO-chains as well as the ratio between the hydrophilic PEO (N_{EO}) and hydrophobic PPO (N_{PO}) contents. The spatial molecular state in a good solvent has been earlier described by the asymmetry ratio (β) between the radii of gyration R_{PEO} and R_{PPO}, respectively of the PEO and PPO entities in the polymer block, which is given by the relation $\beta = R_{PEO} / R_{PPO} = N_{EO}^{3/5} / N_{PO}^{1/2}$ [19]. Some of the main molecular characteristics of several polymers studied in the literature are given in Table 1. Making use of the de Gennes *brush* approach [20] one can calculate the *brush* thickness from the experimental film disjoining pressure isotherm $\Pi_{st}(h)$ and it was found that Π_{st} diminishes with decreasing the *brush* thickness [12].

The relation between the *brush* thickness and the thickness of PEO–PPO–PEO foam film was explored earlier [6**,11**,19] and recently investigated for the case of O/W emulsion films [12]. Fig. 1 shows the variation of the equivalent film thickness h_w with increasing N_{EO} per single PEO-chain for several polymers. The data for foam and emulsion films are plotted together and they obviously follow the same trend of linearly increasing h_w with increasing the PEO-chain length but the data split into two branches corresponding to lower and higher asymmetry ratios $\beta = 0.9$–1.6 and $\beta = 3.4$–3.5 respectively [19] (see Table 1 and the inset in Fig. 1). However, in all cases an increase of the film thickness by increasing the *brush* thickness is observed in every of the two branches and a quantitative interpretation is possible in the manner proposed in Ref. [19]. The reason for such differentiation by the asymmetry ratio β (valid for both foam and emulsion films) is not fully understood and the effect of this molecular parameter on the film thickness still needs further clarification.

Block polymers, as amphiphilic structures, associate in solutions at high polymer concentration as well as at a certain critical temperature (theta conditions). This gives rise to oscillatory forces (Π_{osc} component of the disjoining pressure) when such solutions got confined between surfaces as discussed by von Klitzing et al. [7*] and Langevin et al. [9*] on the basis of results obtained by TFPB, CP-AFM and SFA techniques. The interpretation suggested reveals that the reason for the high polymer concentrations required for observation of significant onset of Π_{osc} is related to the fact that these polymers are uncharged and the dominant interactions in a system consisting of closed-packed micelles are mainly controlled by steric repulsion between the PEO-chains in the corona of the polymer micelles. This is also consistent with the observed

Table 1
Pluronic polymers — values of the average molecular mass M, the average number N of EO and PO monomers and the respective asymmetry ratio β, the equivalent film thickness (h_w) of foam films (FF) [19] and emulsion films (EF) [12] at $C_{el} > C_{el,cr}$ or pH ≤ $pH_{cr,st}$ (for details look into the text).

No.	Pluronic (Synperonic)	M [kg/mol]	N_{EO} [−]	N_{PO} [−]	β [−]	h_w^{FF} [nm]	h_w^{EF} [nm]
1	L62	2.5	8.5	30	0.9	8.5	–
2	P65	3.4	18	30	1.4	–	12.5
3	P85	4.6	26.5	39	1.6	18	–
4	P104	5.9	31	54	1.5	–	13.5
5	F68	8.4	75	30	3.5	26	27
6	F88	10.8	97	39	3.5	36	–
7	F108	14.6	128	54	3.4	45	41