SUPPLEMENT II:

A. On the nature of surface forces in ESP and ESP/BSA/polymer foam films

The so called "dynamic method" provides the unique possibility to measure the disjoining pressure (introduced by Deryaguin in 1936; force per unit area, acting normal to two approaching plane parallel interfaces) in non equilibrium foam films (air/liquid/air). Historically it was first applied to foam films, where just van der Waals attraction and electrostatic repulsion act as additional forces to the capillary pressure driving the foam film thinning (see Eq (1) in the main text).

All so called "colloidal forces" (relatively "long" or "short" ranged) may contribute to the disjoining pressure (as a matter of fact these different "components" of the disjoining pressure are not necessarily additive).

Israelachvili (Intermolecular and Surface Forces, Academic Press, London 1992) distinguishes
- van der Waals forces
- electrostatic forces
- solvation, structural and hydration forces (non- DLVO forces)
- steric forces (for films of polymer solutions these may be **repulsive** "steric" or "overlap" forces between polymer covered surfaces and **attractive** "intersegment", "bridging" and "depletion" forces)
- other "fluctuation" forces.

See also references in the main text and D. F. Evans and H. Wennerstrom, The Colloidal Domain where Physics, Chemistry, Biology and Technology meet, Wiley-VCH, New York, 1999 and the five ("voluminous") volumes of J.Lyklema "Fundamentals of Interface and Colloid Science" , Academic press (Vols.I-III) and Elsevier (vols. IV, V), 1999-2005.

In the context of the foam film experiments presented and discussed in the main text we consider just van der Waals attraction, steric repulsion between the two adsorption layers at the two interacting air/multicomponent solution interfaces and "depletion" osmotic attraction. Diffuse double layer electrostatic repulsion is excluded because at physiological electrolyte concentrations the Debye length is less than 1 nm.

In the complex experimental cases presented in the main text we do not have a better choice than to calculate the van der Waals attraction for a pure water film (see below).

The steric repulsion between the two adsorption layers (in a "good" solvent) manifests itself at a thickness of the order of 100 nm (see Fig 7 in the main text).

At lower thicknesses the steric repulsion is overcomed by stronger attraction. As shown in Fig 7 calculated van der Waals attraction at these thicknesses is small compared to the measured repulsive interaction. It is reasonable to attribute this stronger attraction to the "depletion" osmotic effect: when the distance between the film surfaces is small enough the solutes (particulate and polymeric) can not accomodate in the film liquid core due to their larger size; the solvent in the liquid core tends to dilute the bulk solution in the meniscus surrounding the foam film.

Unfortunately the complexity of the studied multicomponent and polydisperse suspensions does not allow us to speculate quantitatively further with the attractive "depletion" osmotic pressure (for an ideal solution its magnitude is given by the undergraduate textbook formula $\pi = cRT$).

The depletion attraction osmotic pressure represents a universal "physical" mechanism of the polymer action which does not explain the specificity of the polymer' effects registered in the current work and in previous studies (Dextrane is more effective with Curosurf, while PEG- with Survanta). The specificity is probably due to the fact that except via colloidal forces the polymers interact with ESPs via chemically specific mechanisms e.g. related with modification of surfactant dispersions microstructure (mechanism 3 discussed in the main text). As the surfactant preparations have vastly distinct compositions (Table 1), their chemical interactions with polymers are expected to strongly differ. Here we focus on the surface forces involved in ESP inhibition and recovery and the study of chemically specific interactions is outside the scope of the current work.

Table S2. 1. Consensus lipid composition (%, g/g of total lipid) and protein concentration (% phospholipid, g/g) of clinical surfactants. (Data taken from: Braun et al., Biophys. J., 2007, 93: 123–139.)

	Native Surfactant	Curosurf	Survanta
PC % (w/w)	70–85	67–74	79–87
DPPC (%PC)	36–59	50–56	45–75
LPC	0.5	<1	1
Sphingomyelin	2	8.1	4.8
Cholesterol	5	0	0
PI	4–7	3.3	0.5
PS	5		
PE	3	4.5	2.2
PG	7–10	1.2	3.2
PA			6–14
Unknown			
SP-A	4	0	0
SP-B	1	0.3	0.04–0.13
SP-C	1	0.7	0.9–1.65
SP-D	4	0	0

Abbreviations:

PC, phosphatidylcholine
DPPC, dipalmitoylphosphatidylcholine
LPC, lysophosphatidylcholine
PI, phosphatidylinositol
PS, phosphatidylserine
PE, phosphatidylethanolamine
PG, phosphatidylglycerol.

Range of reported averages are taken from the following sources: (Curosurf, Package inserts from Chiesi Farmaceutici, Parma, Italy; and Survanta, Ross Labs, Ohio).

B. Van der Waals attractive contribution to the disjoining pressure in water foam films

Despite the development in the second half of the 20th century of many more or less elaborated procedures to calculate the van der Waals disjoining pressure making use of the rigorously derived macroscopic (Lifshitz) "retarded" expression (I. E. Dzyaloshinskii, E. M. Lifshitz and L. P. Pitaevskii, Adv. Phys., 1961, 10, 165-209.) nowadays many researchers still stick to the "non-retarded" formula of Hamaker derived in 1937 (H. C. Hamaker, Physica, 1937, 4, 1058-1072.):

$$\Pi = -A/6\pi h^3 \qquad\qquad (S\ 2.1)$$

where A is the Hamaker constant. The notion of a Hamaker constant, which neglects the effect of electromagnetic retardation in the dispersion interactions and the temperature dependent "zero frequency" term, has been replaced with a Hamaker function $A(h,T)$. We shall not repeat here the lengthy expression for $A(h,T)$, which can be found in many sources (S. Nir and C. S.Vassilieff, in Thin Liquid Films, ed. I. B. Ivanov, M. Dekker, New York, 1988, pp. 207–274.; B. W. Ninham and V. A. Parsegian, Biophys. J., 1970, 10, 646-663.; V. A. Parsegian and B. W. Ninham, Biophys. J., 1970, 10, 664 – 674.).

Here we just illustrate the error introduced when using a Hamaker constant instead of a Hamaker function when calculating the van der Waals disjoining pressure in a water foam film. A further uncertainty in the theoretical prediction is introduced using different material characteristics for the dependence of complex dielectric permittivity on imaginary frequency $\varepsilon(i\xi)$.

The values of the Hamaker function for a water foam film (S. Nir and C. S.Vassilieff, in Thin Liquid Films, ed. I. B. Ivanov, M. Dekker, New York, 1988, pp. 207–274.; H. C. Hamaker, Physica, 1937, 4, 1058-1072.; C. S. Vassilieff, Annuaire Univ. Sofia Fac Chim., 1978, 71, 5-12.; D.J.Mitev, L.S.Grigorov and C.S.Vassilieff, Colloids Surf., B, 1999, 14, 149-160.), calculated from Lifshitz theory with a representation for $\varepsilon(i\xi)$, which can be considered as an upper bound with respect to uncertainty in material characteristics for water, are given in the table.

Hamaker function for a water foam film*

h, nm	0	10	20	30	40	50	60	70	80	90	100
A(h,293K) 10^{-20} J	6.44	3.75	2.49	1.90	1.56	1.34	1.18	1.07	0.98	0.91	0.86

*calculated from Lifshitz theory by numerical integration, "zero frequency" term included

It can be seen that at h=10 nm the electromagnetic retardation has lowered the value of the non-retarded Hamaker constant A(h=0) = 6.44 10^{-20} J almost twice. An exaggerated maximal possible value of the van der Waals disjoining pressure can be calculated from Eq (S 2.1) with a "non-retarded" Hamaker constant of 6.44 10^{-20} J. Israelashvili (Intermolecular and Surface Forces, Academic Press, San Diego, 1991, pp. 186-187.) recommends to use a Hamaker constant of 3.7 10^{-20} J. This value is close to the Hamaker function in Table 3 at 10 nm. The differences in the calculated values of the disjoining pressure are illustrated in Fig. S2.1.
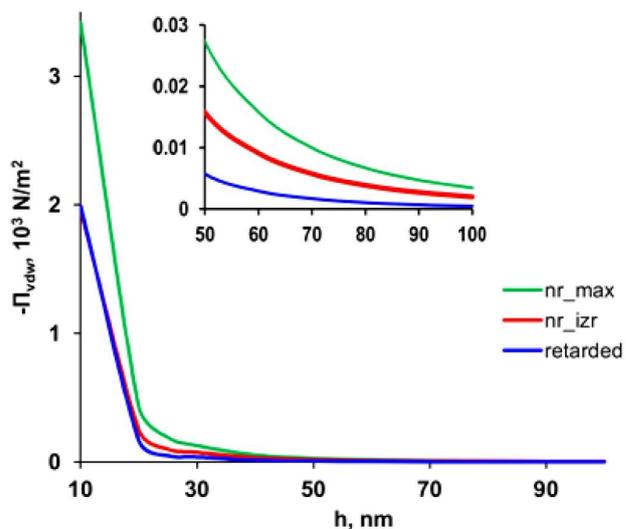
Fig. S2.1. Theoretical (red/green/blue) dependencies of Π_{vdw} on film thickness calculated with different values of the Hamaker constant or function: maximal non-retarded, non-retarded recommended by Israelaschvili and retarded. The insert shows the dependencies for the film thickness range 50-100 nm.

The stronger dependence on h^{-3} masks to a certain extent the quantitative differences between predictions for the disjoining pressure from Eq (A21) with a "non-retarded" Hamaker constant and a "retarded" Hamaker function.

These values of Π normalized by P_c are shown in Fig. 7   in the main text in order to estimate the magnitude of an additional "depletion" attraction overcoming a steric repulsion in the experimentally investigated foam films of lung surfactants.