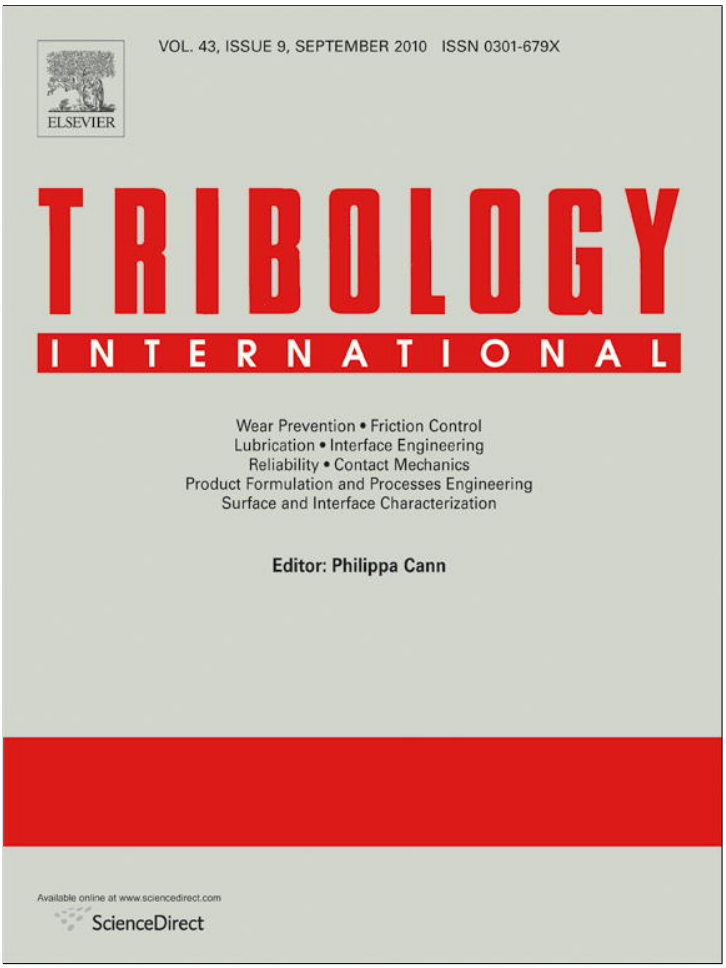

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The ultra-low friction of the articular surface is pH-dependent and is built on a hydrophobic underlay including a hypothesis on joint lubrication mechanism

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ABSTRACT

In this study, the influence of pH on interfacial energy distributed over the phospholipids-bilayer surface model and the effect of hydrophobicity on coefficient of friction (f) were investigated by using microelectrophoresis. An important clinical implication of deficiency in hydrophobicity is the loss of phospholipids that is readily observed in osteoarthritis joints. This paper establishes the influence of pH on interfacial energy upon an increase f, which might be associated with a decrease of hydrophobicity of the articular surface.

1. Introduction

1.1. Surface properties of articular cartilage

The surface properties of AC such as hydrophobicity and interfacial energy affect the adsorption and chemical affinity of biomolecules that influence the friction of this natural system [1–3]. It has been demonstrated that articular cartilage (AC) is a deformable-porous material with average Young's modulus between 12 and 50 MPa and the surface roughness varies from 1 μm for infant, 2.25 μm for adult to 5.25 μm for osteoarthritis cartilage [4].

In a recent study, the conceptualization of articular cartilage as a giant reverse micelle with a mechanism for joint biocushioning and lubrication was introduced [5]. Also, it has been hypothesized that a hydrophobic surface of AC that is covered by a highly hydrated three-dimensional network of phospholipids (PLs), namely the surface amorphous layer (SAL), on which PLs reverse micelles are created facilitates joint lubrication, while sustaining the long term efficacy of the articular surface in joint function [5–7]. Synovial fluid is non-Newtonian, in that its viscosity decreases nonlinearly with increasing shear rate. In rheumatoid arthritis, the viscosity of synovial fluid depreciates, while becoming more Newtonian in its rheological characteristics. Also, the fluid and protein content of SF is increased, while the content of HA and length decreases. The differences in the properties of synovial fluids of normal and arthritic joints are manifested in the differences in the values of their shear rate (s^{-1}) {and viscosity (Ns/m^2)}, for normal 10 {1.1}, arthritic 10 {0.3}, and rheumatologic 10 {0.03} joints [4]. The bio-surface of cartilage from a normal joint is hydrophilic (i.e. with wettability of ~40°) when undisturbed with its multi-bilayer-membrane (SAL) intact, and hydrophobic (i.e. with wettability of 105°) when washed with a detergent [3].

A hypothetical illustration of the coefficient of friction f vs. hydrophobicity of articular cartilage [PL_{AC}] was introduced recently. This "recliner seat" shaped curve is presented in Fig. 1 and it shows an inclination of ~130° [5]. It can be hypothesized that there are two regimes of synovial fluid intervention in joint lubrication. The first is the full-fluid film lubrication that corresponds to frictionless lubrication, which is characterized by complete separation of the surfaces by pressurized fluid. The second corresponds to the boundary lubrication film and is highly

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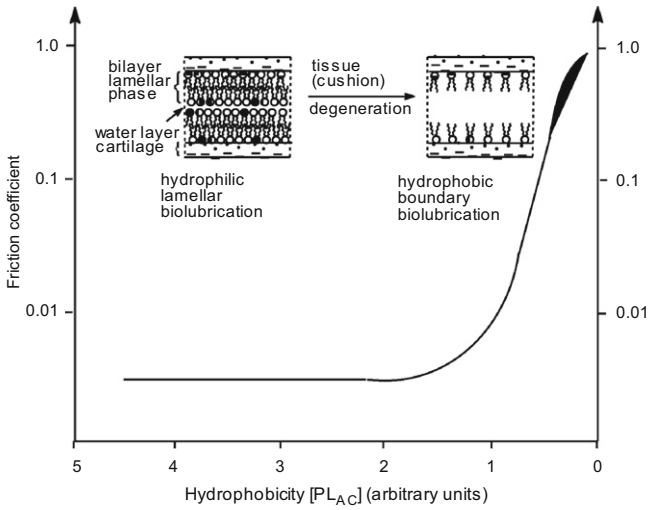

Fig. 1. A hypothetical illustration of coefficient of friction (f) vs. hydrophobicity [PLAC] of articular cartilage. Hydrophilic (HL–HL) and hydrophobic (HB–HB) tribopairs of articular cartilage at low surface velocities in synovial fluid, where HL = hydrophilic, HB = hydrophobic, [PLAC] = phospholipid concentration in articular cartilage. Lower hydrophobicity of AC $< 70^{\circ}$ is related to the decreased PLs content in cartilage. Normal articular surface wettability contact angles are about 105°.

complex, involving surface topography changes, physical and biochemical changes of the synovial fluid and articular surface/whole cartilage, and is characterized by an appreciable increase in f. This graph (cf., Fig. 1) demonstrates that the control of SAPL surface properties, e.g. surface roughness, adhesion and hydrophilicity is of importance in ensuring effective lubrication [8]. The increase in the coefficient of friction shown might be associated with decreasing hydrophobicity of the articular surface (lower amount of PL_{AC}), which may in turn result in the inability of the highly hydrated three-dimensional surface amorphous layer to resist compressive forces during joint loading [9,10].

At this juncture, it is desirable to shed more light into the phenomenon proposed in the hypothetical mechanism that is presented in Fig. 1. The fundamental premise is that a degree of surface hydrophobicity is required before the hydrophilic layer of phospholipid bilayer that is necessary for lubrication can be created. Consequently, the f of the contacting joint surfaces will increase dramatically with loss of hydrophobicity. This hypothesis or "theoretical" assertion can also be developed from an interpretation of the results by Hills and Monds [11], in which the relationship between coefficient of friction and hydrophobicity, in terms of contact angle between saline and the articular surface, was presented.

Water molecules alone, due to their inability to form a useful boundary film because of very low coefficient of viscosity and poor film-forming properties, cannot achieve the extremely low friction coefficient that is seen in natural joint systems [12–15]. We argue that in order to produce the highly efficient lubrication associated with the mammalian articular joint, a pressurized fluid film that is made of a mixture of exuded interstitial fluid (i.e. a 0.155 M aqueous electrolyte), PLs held by macromolecules of glycoprotein, lubricin and hyaluronan is required. Of relevance is that osteoarthritis has been shown to deplete the phospholipids on both the surface and within the cartilage, thereby destroying this important SAL, with significant consequences for load processing and lubrication. To date, clinicians and researchers do not fully understand the biochemical basis of cartilage lipid loss, with the consequence that there is no effective treatment for the symptom [16–18]. However, it has been demonstrated that PLs micelles can resist high shear stress/strain rates and are adsorbed in less than 50 ms, when near a surface [19], while it has also been shown that the injection of surface active phospholipids (SAPL) relieved osteoarthritic discomfort for up to 14 weeks [18]. It is possible to argue that the challenge in this context is that of how to restore the hydrophobicity of the articular cartilage surface rebuild the surface amorphous layer [20,21].

With regard to wettability (θ the contact angle), measurements of amphoteric weak polyelectrolyte bilayer with phosphate and amino functional groups in the pH range 1–10 indicate that solution pH and salt concentration change contact angle (Fig. 2) [22]. The amino-group in low solution pH is in $-NH_3^+$ form, and as the pH increases the amino groups would lose their charge resulting in increased surface wettability. In case of phosphate functional group, the contact angle decreases with increasing solution pH, screening the surface charges. Furthermore, the pH-dependent degree of dissociation of amino- and phosphate surface bilayer compounds could increase or decrease the wettability, f and swelling of weak polyelectrolyte [22].

The often prevailing opinion in the literature is that phospholipids play a role in articular joints function and that they depreciate in quality and quantity as the cartilage transforms from health to disease [23]. The degeneration is also often combined with changes in the pH of the synovial fluid with concomitant effect on the state of cartilage surface wettability (Fig. 2).

In this paper, we examine by microelectrophoresis (1) the influence of pH on the relationship between the PLs bilayer and interfacial energy, and (2) the effect of wettability/interfacial energy on the coefficient of friction of the articular surface using model phospholipid bilayer-membrane. The relationships between solution pH and wettability (θ the contact angle), interfacial energy (γ) and friction coefficient of a weak polyelectrolyte phospholipid bilayer-membrane.

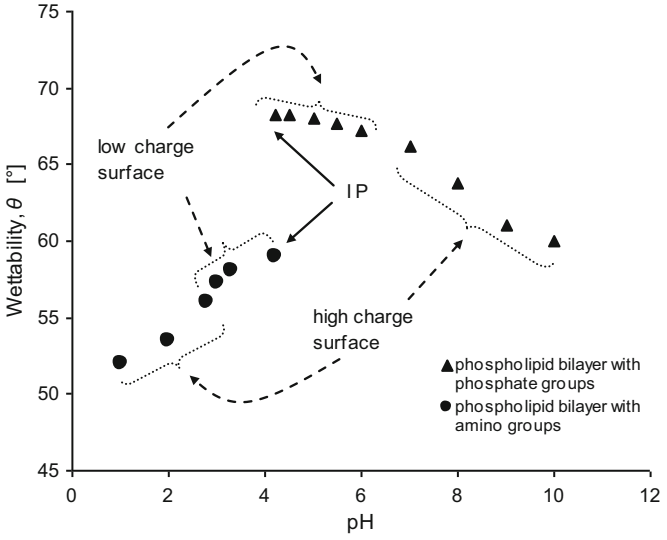

Fig. 2. Influence of solution pH on the wettability (θ) of phosphatidylcholine (PC) bilayer surface of amphotheric weak polyelectrolyte with both amino ($-NH_{3+}$/$-NH_2$) and phosphate ($-POH/-PO^-$) functional groups. Curve (–●–), the polylectrolyte (PC) with amino-group at pH 1.5 begins to poses their charge from ($-NH_{3+}$) leaving the biomembrane with a more wettable character ($-NH_2$), as the solution pH 4.2, IP (isoelectric point). Curve (–▲–) polyelectrolyte with phosphate group (–POH) at pH 4.2, IP; loosed their proton leaving the biomembrane with a less hydrophobic character ($-PO^-$) at pH 10. The PC at pH 1.5–10 showed wettability can change by charging both functional groups. Curves show that the phospholipids bilayer surface has an isoelectric point at ~pH 4.2. The wettability values of ($-NH_{3+}$/$-NH_2$) and phosphate ($-POH/-PO^-$) functional groups adapted from [28].

2. Experimental

2.1. Method, measurements and chemicals

The method used was based on Young–Laplace–Kelvin equation [1], $2\sigma = r\Delta p$, where σ designates the surface tension, r for the sphere's radius, and Δp denotes a pressure difference between inside and outside of the sphere of radius r. The factors that must be controlled in order to assure the integrity of our results were deduced from the equation (i.e. Eq. (1)), expressing the dependence of interfacial energy on the pH of an electrolyte solution [24]

$$\gamma = \gamma_{\max} + 2sRT\ln\left(\sqrt{\frac{K_a}{K_b}}+1\right) - sRT\ln\left[\left(\frac{K_a}{a_{H^+}}+1\right)\left(\frac{a_{H^+}}{K_b}+1\right)\right], \quad (1)$$

where K_a and K_b—acid and base equilibrium constant, s—surface concentration of PLs, R—gas constant, T—temperature, $\gamma_{\max}$—maximum interfacial energy of lipid membrane; a_{H^+} denotes the activity of protons. The above formula should be interpreted in a way that the interfacial energy can attain the characteristic value of $\gamma_{\max}$ at a certain acid–base equilibrium condition given by the ratio of the corresponding equilibrium constants but at some distinctive, neutral-solution that is characterised by the activity of protons which is primarily temperature dependent.

In this work, this interfacial energy (γ) for the lipid bilayer was determined from the radius of curvature r (twice the mean curvature $2/r$) of the convex surface formed when a pressure difference Δp was applied to both sides of the membrane, while all the parameters mentioned above were kept at their required levels.

The apparatus used for interfacial energy determination of lipid membranes and the approach to the measurements were described in previous papers [25,26]. The lipid membranes were formed by the Mueller–Rudin method [27]. They were formed in a Teflon diaphragm of 1.5 mm outer diameter containing an orifice along its axis. An electrolyte solution was present on both sides of the orifice. The interfacial tension was measured on freshly created membrane 10–12 times for each pH electrolyte solution. The forming solution contained 20 mg/cm^3 of lipid phosphatydylcholine in *n*-decane. Phosphatydylcholine and phosphatydylserine (PS) were dissolved in chloroform to prevent oxidisation; the solvent was evaporated in the atmosphere of argon and the residue was dissolved in *n*-decane.

Lecitin (3-sn-phosphatydylcholine, 99%) of the molecular formula $C^{40}H\ ^{80}NO\ ^{8}P\cdot H_2O$ and phosphatydylserine (99%) produced by Fluka were used in the studies. Phosphatydylcholine obtained from the egg yolk. The composition of fatty acids in the (PC) was 16:0∼33%, 18:0∼4%, 18:1∼30%, 18:2∼14%, 20:4∼4%.

Standard aqueous solutions of pH in the range of 1–12 were prepared with 0.1 M potassium chloride (KCl) and 0.2 M sodium hydroxide (NaOH) or 0.2 M hydrochloric acid (HCl) and used as the electrolyte. They were prepared by adding 0.2 M sodium hydroxide or 0.2 M hydrochloric acid to 100 cm^3 of potassium chloride.

Surface friction measurements was used AFM–LFM Nanoscope III [28], with Nanoprobes, to scan the PLL/HA multilayer film. The scan size was set at 100 nm square. The conditions used for friction scans were non-destructive to the film, and no region was scanned more than once. The coefficient of friction was calculated in accordance with the classical Coulomb–Amontons formula as the ratio of the friction force to the applied load [28].

Contact angle measurement: the contact angles of sessile droplets whose pH was in the range 2.0–11.0 at concentration 0.1 M NaCl on PLL/HA multilayer films were measured. CCD camera and goniometer (Optrel GBR Multiscope) were used to measure the contact angle of water on the surface of the film [28].

3. Results and discussion

3.1. Interfacial energy of phosphatidylcholine (PC) membrane

The dependence of interfacial energy of a lipid membrane formed from phosphatidylcholine on the pH of the electrolyte solution is presented in Fig. 3.

The maximum interfacial energy ($\gamma_{\max}$) values of the PC and PS membrane were found to be 3.53 mN/m, 2.93 mN/m at pH values of 4.2 and 3.80, respectively. The pH of the solution influences changes in electric charge of the membrane due to the variations in acid–base equilibrium of the functional groups present in the membrane. The pH-dependent degree of dissociation of the surface functional ($-NH_2$) and (–POH) groups can be used to vary and control the interfacial energy about the isoelectric point (*IP*) with a consequential change in coefficient of friction. This result strongly suggests a mechanism whereby PLs bilayer surface can have a low charge around the *IP*, and then transform into highly charged surface through a change in pH. A noteworthy aspect of the result in Fig. 3 is the closeness of the responses for the two different membranes used in this study. This is probably due to the similarity in the values of the acidity (–POH) and basicity ($-NH_2$) of their functional groups namely, (PC: $pK_a = 2.58$, $pK_b = 5.68$; PS: $pK_a = 2.42$, $pK_b = 5.98$).

Phospholipids, amphoteric molecules containing both positive and negative charges depending on the functional groups are affected by the solution's pH. At low solution pH, PLs amino-group is in protonated ($-NH_3^+$) form, and (–POH) is in molecular form; a situation that is characterized by low interfacial energy. As the pH of the solution is increased, the amino groups begin to lose partially their charge ($-NH_3^+ \rightarrow -NH_2$) and (–POH) group begin to lose partially their proton ($-POH \rightarrow -PO^-$), which causes an increase in the surface energy with the value approaching a maximum. This maximum would occur, relative to Fig. 3 at the *IP* which corresponds to the pH at which PLs or surface carriers have no net electrical charge, or where the negative and positive charges are equal [1]. As the pH of the solution is increased, the amino-group will begin to lose their charge ($-NH_3^+ \rightarrow -NH_2$) and more (–POH) groups begin to lose their proton ($-POH \rightarrow -PO^-$), living the surface charged, and leading to a decrease in the

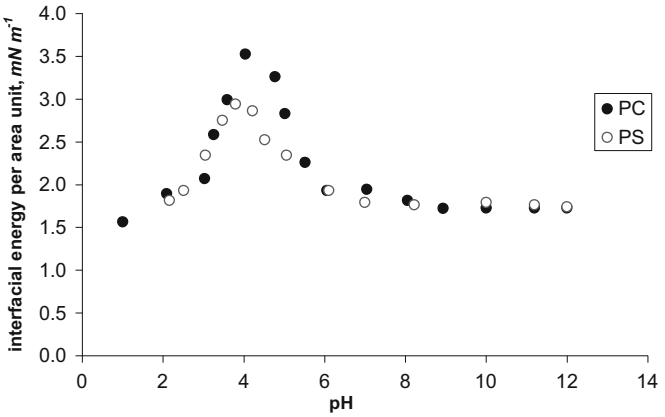

Fig. 3. The dependence of interfacial energy of phosphatidylcholine (PC) (pKa=2.58; pKb=5.68) and phosphatydylserine (PS) (pKa=2.42; pKb=5.98) membrane as the pH of the electrolyte solution with maximum surface tension value of 3.53 mN/m, 2.93 mN/m at pH equal to 4.2 and 3.80, respectively, in 0.1 M KCl aqueous solutions.

interfacial energy. In this situation, the resulting surface would become less hydrophobic with a lower f [28].

The surface energy also follows the trend described above, increasing with the charge loss in the amino-group, and decreasing for phosphate, polyelectrolyte as the solution pH is increased. A strong influence of solution pH on the wettability of phosphate group of PLs was also observed. At low solution pH, bi-layered compound with carboxylic group is in molecular form (–COOH), and the contact angle is high. As the pH of the solution is increased, the (–COOH) groups lose their proton ($-COOH \rightarrow COO^-$) leaving the surface charged with decreased wettability and a concomitant decrease in the contact angle [28,29].

The density of packed PLs molecules on a biological surface can be expressed by the wettability contact angle θ. The normal articular surface rinsed free of synovial fluid (washed with detergent) has high hydrophobicity with contact angle of between 100° and 105° [2,30]. After rigorous rinsing with lipid solvent, the wettability of the articular surface changes to a hydrophilic one with a contact angle of 37.4° [30,31] (Table 1). The presence of PLs as surfactant in synovial fluid reduces surface tension, and can transform hydrophobic surface into a hydrophilic one. This can be argued to be a micellization process in which PLs molecules arrange themselves into energetically favorable micelles and vesicles forming reservoirs for the surfactants in the lubrication process [5,32,33]. It has also been shown that the combination of a low interfacial energy and high contact angle provides effective lubrication [3].

Despite the large number of publications on the relationships between the chemical components (PLs, joint fluids) and the mechanical function of joint, there has been no research investigating the influence of pH on such relationships. The influence of interfacial energy on the wettability (contact angle, θ) for phosphatidylcholine bilayer phosphate and amino groups is shown in Fig. 4.

The characteristics of bio-surfaces namely, surface smoothness/roughness, charge density, and the hydrophobic/hydrophilic balance, play a crucial role in certain processes such as adhesion, electrostatic flow and friction [1]. The interfacial energy between solid and air (γ_S), the decrease in the interfacial energy between solid and liquid (γ_{SL}), together with the decrease of surface energy (in terms of the corresponding interfacial energy) of the lubricant containing surfactant (γ_L), lead to increase in wettability in accordance with the Young–Dupree equation [34].

$$\cos\theta = (\gamma_S - \gamma_{SL})/\gamma_L. \quad (2)$$

One of the ways in which proteins or surfactants lower their free energy is the removal of hydrophobic groups from contact with the aqueous environment. In this respect, the work of adhesion (W_{adh}) for proteins can be estimated from the equation

$$W_{adh} = \gamma_L(1+\cos\theta). \quad (3)$$

It should be noted that the value of $\cos\theta$ in Eq. (3) is estimated using an equilibrium value of the contact angle θ. The work of adhesion is an accurate reflection of the wettability of a surface, which in turn correlates to the frictional properties of such a surface [35,36]. When looking at Eq. (3), one sees that the work of adhesion can change periodically due to gradual corresponding changes in wettability characteristics, equation from normal to degenerative articular cartilage (AC), see Table 1.

The relationship between wettability (contact angle, θ) and interfacial energy (γ_L) of an aqueous solution of surfactants on e.g. PTFE (a hydrophobic solid, $\theta = 120°$) has been shown to be linear, while the same relationship for a hydrophilic glass surface with a contact angle of 37°, and some aqueous solutions of nonionic surfactants is nonlinear [29].

The wettability of soft tribopair-based lubricants is related to the characteristics of the frictional forces in the boundary area between the contacting surfaces, which decreases with decreasing contact angle [37,38]. Consequently, it can be inferred that the hydrophilization of a surface reduces the frictional forces in the associated water, a process that can be attributed to the elimination of unfavorable hydrophobic (HB) interaction. The coefficient of friction of the articular surface can be determined from the Coulomb–Amontons, Eq. (4)

$$f = F/W \quad (4)$$

where force $F = (\gamma_L)L\cos\theta$, and γ_L is the corresponding interfacial energy, which is evaluated as force per wetted perimeter L; θ is the contact angle [39]. It can be argued that relation (4) is not readily applicable in situations where the loads are applied at nanoscale level [6,15]. It therefore appears that pH dependence of the surface friction on the bilayer's phospholipid is of immense

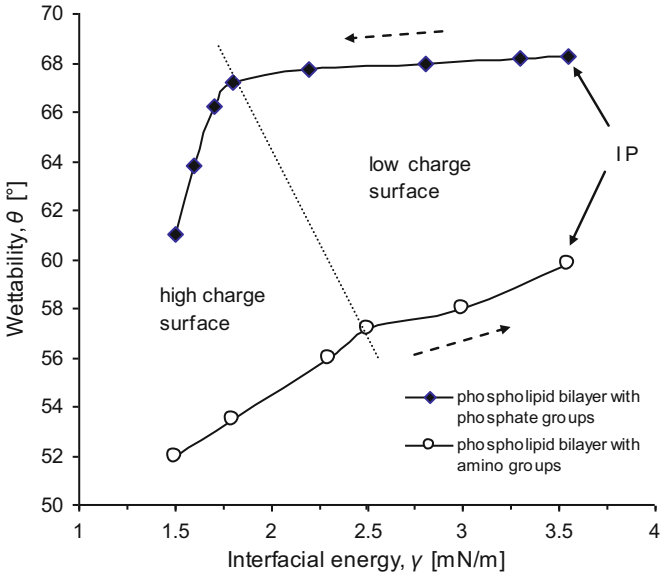

Fig. 4. Influence of interfacial energy on wettability for phosphatidylcholine bilayer surface for amino ($-NH_{3+}/-NH_2$) and phosphate ($-POH/-PO^-$) functional groups. The ($-NH_{3+}/-NH_2$) group (Curve –○–), most wettability increased for ($\gamma = 1.5$–2.5) at pH 1.0–3.0 (see Fig. 3), and for ($\gamma = 2.5$–3.5) at pH 3–4.2 (see Fig. 3), wettability changed from 52° to 59°. The phosphate group ($-POH/-PO^-$) (Curve –◆–) small change wettability for ($\gamma = 3.5$–2.0) at pH 4.2 (IP) to 6.5, most changes observed from ($\gamma = 2.0$–1.5) at pH 4.2 to 10 (see Fig. 3), wettability changed from 67° to 61°. (IP) is isoelectric point for phosphate and amino functional groups. The wettability values of ($-NH_{3+}/-NH_2$) and phosphate ($-POH/-PO^-$) functional groups were adapted from [28].

Table 1
Wettability characteristics (hydrophobicity/hydrophilicity) of biological tissue surfaces [2,11,30].

Biological tissue surface	Contact angle (θ) (°)	Wettability characteristics
Normal AC, human	103–105	h-HB_b
Normal bovine patella	100.1	h-HB
Human knee	79.7	h-HB
Hip (arthritic tissue)	56.3	h-HB
Unworn knee (worn knee)	67.8 (62.9)	h-HB
AC degenerative	70	h-HB
AC rinsed with solvent[c]	37.4	h-HL_a
AC with bilayer	<40	h-HL

[a]Highly hydrophilic, h-HL.
[b]Highly hydrophobic, h-HB.
[c] Surface extracted with $CHCl_3$/MeOH (2:1, v/v).

importance. The results in this paper demonstrate that the consideration of the charge-density effect on cartilage–cartilage surfaces and the solution pH (lubricant) condition are required if we were to properly understand how the condition of articular cartilage, dealt with as a prone-to-restructuring solid–liquid interfacial system, may influence joint lubrication. For example, at solution pH 7.4 which is above the isoelectric point (IP∼4.2), the cartilage–cartilage surfaces and lubricant are both negatively charged [32], with the charge density (repulsive interaction) of both increasing with increasing pH. This would lead to weak adhesion forces and very low coefficient of friction Fig. 5; in addition, the smallest ions in the system viz protons, being the most energetic ones, may also play, exhibit their biofriction-lowering role under a sufficient amount of permanent loading [6,32]. Moreover the amphiprotic molecules such as phospholipids (or, lubricin) can either donate or accept protons in (un)equal amounts, thereby offering an additional virtual source of these ions to facilitate, effective lubrication [32], especially when acting under the opposing electrostatic actions of oppositely charged articulating rubbing surfaces.

The biolubricant in the synovial joint contains hyaluronan (HA), proteoglycan 4 (PRG4) which is also known as lubricin, and phospholipids (PLs) (Table 2); this mixture is mostly responsible for the ultra-low friction mechanism in the joint [40]. On the other hand, the phospholipid molecules that are not involved in the development/maintenance of the surface amorphous layer (SAL) gather to form particular micellar structure (Figs. 1 and 6)

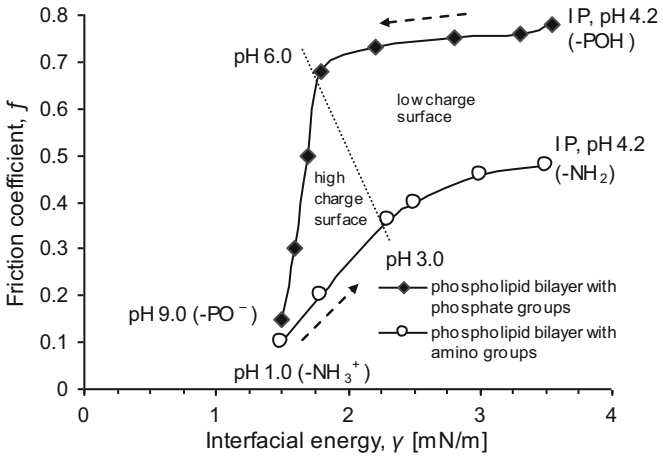

Fig. 5. Influence of interfacial energy on the coefficient of friction for phosphatydylcholine (PC) bilayer surface of amino ($-NH_{3+}/-NH_2$) and phosphate ($-POH/-PO^-$) functional groups. The amino-group (Curve –○–) most friction increase for fully charged surface by NH_{3+} group (γ=1.5–2.5) at pH 1.0–3.0 (see Fig. 3), and for (γ=2.5–3.5) at pH 3–4.2 (IP) small an increase friction for not charged surface ($-NH_2$) (see Fig. 3). The isoelectric point (IP) (γmax=3.53) of PC at solution pH value 4.2. The phosphate group ($-POH/-PO^-$) (Curve –◆–) small friction changed for not charge surface (–POH), (γ=3.5–1.9) at pH 4.2 (IP) to 6.5, most changes for charged surface ($-PO^-$), (γ=1.9–1.5) at pH 4.2–10 (see Fig. 3). (IP) is isoelectric point for phosphate and amino functional groups. The friction coefficient values for ($-NH_{3+}/-NH_2$) and phosphate ($-POH/-PO^-$) functional groups were adapted from [28].

comprising both unilamellar and bilamellar folded spheres [41]. We argue/hypothesize [5,32] that this structure acts in the manner of reverse micelles (supplied by free PLs in synovial fluid) which dissipate energy, and thus protect the cartilage from mechanical degradation. A stiff and flexible form of HA, which is known to possess unique water retention and (proper) viscoelasticity promoting properties, and hydrophobic interaction with phospholipids, is a component of this lubricant, and is believed to control the pH of synovial fluid and its protein content. As has been shown in several publications [13,42–45], we retain the notion in this work that lubricin is the carrier of PLs and the other macromolecules supporting and maintaining the structure responsible for the lubrication we have described.

Despite our present arguments, the form in which PLs exist in normal articular cartilage and SF as micelles, vesicles and lamellae, is poorly understood [50–52]. This is due to the limitation imposed on experiments; namely that while the undisturbed surface of AC *in vivo* has the ability to build lamellar bodies, surfaces *in vitro* are incapable of doing this. This is also the case with the role of water in its pressurized and unpressurized conditions. Regardless, the experimental fact that normal SF that is diluted to a third of its concentration yielded similar results in friction tests as the unmodified one [41,42,44,53–55], provides a strong indication that the synovial fluid does not play a direct role in lubrication, but instead, and in accordance with our hypothesis is a principal supplier of material for building and maintaining the near frictionless surface of articular cartilage.

The acid–base dissociation behavior of multilayer films of hyaluronic acid/poly(L-lysine), poly(acrylic acid)/poly(allylamine) or amphoteric bilayer of phospholipids is key in controlling factors such as wettability and surface friction, pH and ionic strength dependence, and some properties of film such as film swelling, wettability and surface friction. Increasing the salt concentration implies an increased screening of the surface charges, making the surface more hydrophobic in character, which causes an increase in contact angle [28]. The strong evidence between charged (NH_2^+, $-COO^-$) and uncharged ($-NH_2$, –COOH) phospholipid functional groups ($-NH_2$, –POH) of interfacial energy and hydrophobicity seen in Figs. 1 and 3 offer quantitative support for hydrophobicity, wettability and coefficient of friction.

4. Conclusions

We report and discuss here direct measurements of the local acid–base equilibria of phospholipid bilayer incorporated in liposome micelles. Microelectrophoresis has been used in this study to address the question of how surface energy and wettability of weak polyelectrolyte phospholipid bilayer surface influences the low-friction of involved biosurfaces and natural systems such as that of articular cartilage. The higher the wettability of a surface containing phospholipid bilayer, the lower the coefficient of friction. This is consistent with the results from the study on acid–base equilibrium of a weak polyelec-

Table 2
The concentration of hyaluronan (HA), proteoglycan 4 (PRG4), and PLs in synovial fluid [43,46–49].

Parameters	Healthy synovial fluid (SF)	Rheumatoid arthritis, (RA), (SF) parameter	Osteoarthritis (OA), (SF) parameter
HA (mg/ml)	1–4	0.8–1.5	0.7–1.1
PRG4 (μg/ml)	52–450	276–762	
PLs (mg/ml)	0.1–0.2	1.5–3.7	0.2–0.3
Protein (mg/ml)	15–25	36–54	29–39
AC surface θ(°)	100–105	<70	<70
pH of SF	7.30–7.43	7.4–8.1	7.4–7.6

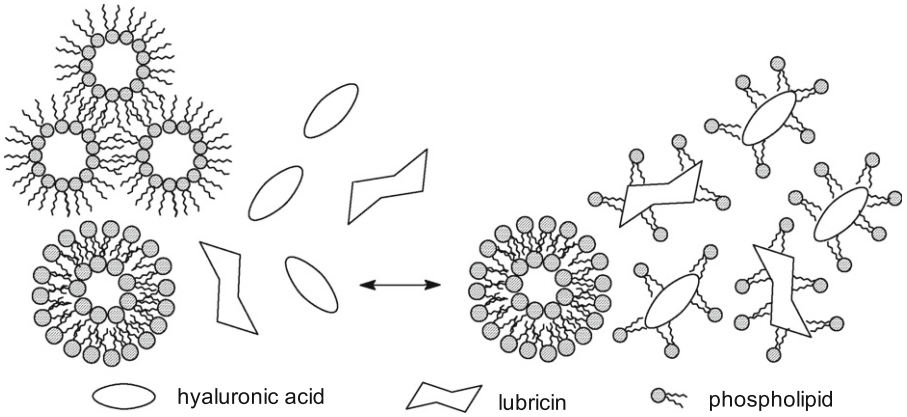

Fig. 6. Equilibrium between macromolecules of lubricin and hyaluronic acid with molecule of phospholipids in process of distribution on the surfaces in articular cartilage.

trolyte HA multilayer film/poly(L-lysine) [28]. Comparing the model of weak polyelectrolytes (non-amphoteric) adsorbed on solid surfaces [22] to our (amphoteric compound) phospholipid bilayer, we have been able to show in a semi-quantitative way the relationship between the coefficient of friction, interfacial energy and lubricant's pH on the joint lubrication mechanism.

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