

# Calculation of Spreading Pressure of Water on Cellulosic Films from Contact Angle Data

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The correlations between the surface properties of the modified cellulose papers with their toner compatibility were investigated. The surface tension components of the cellulosic films, their interfacial tension with the liquid drops and the work of adhesion components were calculated using van Oss-Good's One-Liquid contact angle approach. The electron donor (or Lewis base)  $\gamma^-$  components of the cellulosic films were found to represent the main interactions with the the electron acceptor (acidic)  $\gamma^+$  components of the contacting liquids. Allyl ketene dimer (AKD) grafting of the cellulose affected the surface properties; the higher the substitution of the hydroxyl group, the smaller the basicity of the modified cellulose and correspondingly the smaller the total surface tension. The C-AKD surfaces showed hydrophobic character in a non-polar environment. A negative value for water / unmodified cellulose acid-base interfacial tension component was found showing that the cellulose surface was adsorbing the water molecules due to hydration. The spreading film pressures of water,  $\pi_e$ , on the cellulosic films were calculated and suprisingly negative values of  $\pi_e$  were found for unmodified cellulose, cellulose acetate and C-AKD-1 films, which are impossible thermodynamically. It is probable that the hydration of the cellulosic film surface and the adsorption of water molecules resulted in the decrease of  $\gamma_{S^o}^{LW}$  values and the negative values of  $\pi_e$ .

## Introduction

In electrographic printing, the toner must spread with the use of heat and pressure to adhere to the fibers in the paper. Cellulose surfaces having lower work of adhesion requirements with the toners containing polystyrene and polyacrylate polymers were obtained by grafting the cellulose with an alkyl ketene dimer (C - AKD)<sup>1</sup>. One direction of basic research in this field is to find correlations between the surface properties of these papers and their toner compatibility<sup>2</sup>.

An appropriate experimental technique for quantifying the surface properties of the solids is the measurement of contact angles of liquids on solid surfaces. In the case of pure liquids and smooth, homogeneous, rigid and insoluble solid surfaces, the contact angle is a thermodynamic parameter which can be used to calculate the solid surface tension and solid-liquid interfacial tension by different approaches<sup>3-7</sup>. Young's equation,

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL}, \quad (1)$$

which interrelates the measurable quantities, the liquid-vapor interfacial tension  $\gamma_{LV}$  and the contact angle  $\theta$  to the non-measurable interfacial tensions  $\gamma_{SV}$  and  $\gamma_{SL}$  of the solid-vapor and solid-liquid interfaces, respectively, is the basis for all these approaches. Despite the simple form of Young's equation and the relative simplicity of the contact angle measurements, the contact angle problem is very complex and far from being completely understood<sup>8-10</sup>. Since most of the systems under investigation do not meet the ideal conditions, the contact angle hysteresis usually occurs. The hysteresis is defined as the difference between the advancing and receding (or retreating) contact angles. It is common to find hysteresis on practical surfaces in the range of  $10^\circ$  or more, and hysteresis of more than  $50^\circ$  was sometimes observed<sup>10,11</sup>. It is well established that chemical heterogeneity and surface roughness of practical solid surfaces are the main causes which lead to contact angle hysteresis<sup>8,10,12</sup>. The other hysteresis causes are the effect of the drop size, the effect of surface contamination, the effect of the molecular orientation and deformation at the solid surface and the effect of the liquid molecular transport<sup>10</sup>. In practice, many semiempirical approximations were derived to evaluate the contact angle data<sup>3-7,10,13-15</sup> and resulted in large controversy in this field<sup>10,11</sup>. These approximations depend on the data obtained by measuring the contact angle of liquids on the solid surface in air which is called the "One-Liquid Method". In all of these approximations, the spreading film pressure,  $\pi_e$ , which is the equilibrium film pressure of the adsorbed vapor of the liquid on the solid, is assumed to be zero for low-energy surfaces.

On the other hand, a new technique of measuring the contact angle of a liquid on a solid immersed in another immiscible liquid was introduced<sup>16,17</sup>. Generally, water drops in organic hydrocarbon medium or hydrocarbon drops in water medium were used in this technique, which was called as the "Two-Liquids Method"<sup>18-20</sup>. One-Liquid and Two-Liquids Methods were compared and the discrepancies were attributed to the neglect of the spreading film pressure ( $\pi_e$ ) effect<sup>17</sup>. Later, a novel analysis was developed to calculate the spreading film pressure for finite contact angles in the One-Liquid Method by the combination of both methods<sup>21</sup>. Recently, van Oss-Good's Acid-Base methodology<sup>3</sup> was applied to the Two-Liquids method in the determination of the galena surface free energy components<sup>22</sup> and van Oss-Good formalism was also used in comparison of the Two-Liquids method with the classic One-Liquid contact angle method<sup>23</sup>. A new analysis was developed to calculate  $\pi_e$  for finite contact angles in the One-Liquid Method using van Oss-Good's Acid-Base methodology by combining both methods and good agreement was obtained with the water  $\pi_e$  data on polymer surfaces obtained from independent ellipsometric measurements<sup>23</sup>.

One-Liquid as well as Two-Liquids Methods have previously been applied to determine the surface properties of cellulose films<sup>2,24,25</sup>. When the contact angle of water on the cellulosic surface immersed in several hydrocarbons was measured, the cellulosic surface is said to be "dry" and when the reversed method, whereby the contact angle of the hydrocarbons was measured on the cellulosic surface immersed in water, the cellulosic surface is said to be "fully hydrated" and different surface behavior was found in these cases<sup>2</sup>.

In the present study, the methodology to calculate  $\pi_e$  for finite contact angles in the One-Liquid Method<sup>23</sup> using van Oss-Good's Acid-Base approach<sup>3</sup> is applied to the unmodified cellulose, cellulose acetate, and various alkyl ketene dimer grafted cellulose (C-AKD) surfaces. Since Touissaint and Luner<sup>2</sup> reported precise contact angle data for the same cellulosic film samples prepared by the same procedure<sup>1</sup> with the One and the Two-Liquid Methods, these data are used in the calculations.

## Theory

### One-Liquid Method

van Oss, Good and Chaudhury<sup>3,11,26</sup> developed a more advanced approach after 1985 based on the Lifshitz theory<sup>27</sup> of the attraction between macroscopic bodies to estimate the free energy of adhesion between two condensed phases. An important result is that the contribution of dipole-dipole attraction on interfacial tension interactions,  $\gamma^p$  and the dipole-induced dipole attraction,  $\gamma^i$  were far smaller relative to the London dispersion attractions  $\gamma^d$ , than had been thought. Then they suggested that a solid surface tension consists of two terms, one is Lifshitz-van der Waals interactions,  $\gamma^{LW}$ , comprising dispersion, dipolar and induction forces and the other term is the acid-base interaction term,  $\gamma^{AB}$ , comprising all the electron donor-acceptor interactions, such as hydrogen-bonding. Then, the corresponding components of the total work of adhesion (the work required to pull the liquid away from the surface) are:

$$-W_a = \Delta G_{SL}^{TOT} = \Delta G_{SL}^{LW} + \Delta G_{SL}^{AB}. \quad (2)$$

the combining rule for the  $LW$  component in Eq.2 is its geometric-mean,

$$\Delta G_{SL}^{LW} = \sqrt{\Delta G_S^{LW} \Delta G_L^{LW}}, \quad (3)$$

which is also in concordance with Fowkes approach for London dispersion attractions<sup>4</sup>. The total interfacial tension between solid and liquid  $\gamma_{SL}^{TOT}$  is now given as

$$\gamma_{SL}^{TOT} = \gamma_{SL}^{LW} + \gamma_{SL}^{AB}, \quad (4)$$

and the total surface tension for solid,  $\gamma_{SV}^{TOT}$ , and for liquid,  $\gamma_{LV}^{TOT}$ , is accordingly given as

$$\gamma_{SV}^{TOT} = \gamma_{SV}^{LW} + \gamma_{SV}^{AB} \quad (5a)$$

$$\gamma_{LV}^{TOT} = \gamma_{LV}^{LW} + \gamma_{LV}^{AB}, \quad (5b)$$

When only  $LW$  interactions are considered, the geometric-mean combining rule is used as

$$\gamma_{SL}^{LW} = \gamma_S^{LW} + \gamma_L^{LW} - 2\sqrt{\gamma_S^{LW} \gamma_L^{LW}}, \quad (6)$$

or

$$\gamma_{SL}^{LW} \left( \sqrt{\gamma_S^{LW}} - \sqrt{\gamma_L^{LW}} \right)^2, \quad (7)$$

which is in analogy with Fowkes' approach<sup>4</sup>.

van Oss and co-workers<sup>3,11</sup> adopted Small's<sup>28</sup> combining rule for acid-base interactions which is not a geometric-mean:

$$-\Delta G_{SL}^{AB} = 2 \left( \sqrt{\gamma_S^+ \gamma_L^-} + \sqrt{\gamma_S^- \gamma_L^+} \right), \quad (8)$$

where  $\gamma_i^+$  is the Lewis acid and  $\gamma_i^-$  is the Lewis base parameter of surface tension.  $\gamma_{SL}^{AB}$  is now given as

$$\gamma_{SL}^{AB} = 2 \left( \sqrt{\gamma_S^+ \gamma_S^-} + \sqrt{\gamma_L^+ \gamma_L^-} - \sqrt{\gamma_S^+ \gamma_L^-} - \sqrt{\gamma_S^- \gamma_L^+} \right) \quad (9)$$

or

$$\gamma_{SL}^{AB} = g \left( \sqrt{\gamma_S^+} - \sqrt{\gamma_L^+} \right) \left( \sqrt{\gamma_S^-} - \sqrt{\gamma_L^-} \right). \quad (10)$$

Now, the free energy of cohesion for  $LW$  interactions in each solid and liquid phase is defined as

$$\Delta G_i^{LW} = 2\gamma_i^{LW}. \quad (11)$$

by combining Eqs.3 and 11 one obtains,

$$- \Delta G_{SL}^{LW} = 2\sqrt{\gamma_S^{LW} \gamma_L^{LW}}, \quad (12)$$

On the other hand Dupré<sup>29</sup> showed that the work of adhesion could be defined in the terms of Young's equation in 1869:

$$- \Delta G_{SL}^{TOT} = W_a = \gamma_{S^{\circ}} + \gamma_{LV} - \gamma_{SL}, \quad (13)$$

where  $\gamma_{S^{\circ}}$  is the surface tension of the solid in vacuum. Combining Young and Dupré equations yields:

$$- \Delta G_{SL}^{TOT} = (\gamma_{S^{\circ}} - \gamma_{SV}) + \gamma_{LV}(1 + \cos \theta), \quad (14)$$

where the first term is the spreading film pressure, which is the equilibrium film pressure of the adsorbed vapor of the liquid on the solid,

$$\pi_e \equiv \gamma_{S^{\circ}} - \gamma_{SV}, \quad (15)$$

and corresponds to the reduction of the surface free energy of the solid when in contact with the saturated vapor of the wetting liquid. Combining Eqs. 14 and 15 yields

$$- \Delta G_{SL}^{TOT} = \pi_e + \gamma_{LV}(1 + \cos \theta). \quad (16)$$

If  $LW$  interfacial free energy is written in conjunction with the Dupre's equation (Eq.13), one obtains

$$- \Delta G_{SL}^{LW} = \gamma_S^{LW} + \gamma_L^{LW} - \gamma_{SL}^{LW}. \quad (17)$$

It is also possible to obtain Eq.12 again by combining Eqs.6 and 17. Later by combining Eqs.2, 8 and 12 one obtains for the total interfacial free energy of adhesion as:

$$- \Delta G_{SL}^{TOT} = \left( \sqrt{\gamma_S^{LW} \gamma_L^{LW}} + \sqrt{\gamma_S^+ \gamma_L^-} + \sqrt{\gamma_S^- \gamma_L^+} \right). \quad (18)$$

By combining Eq.18 with the Young-Dupre' equation (Eq.16) for negligible spreading pressure i.e.  $\pi_e = 0$ , the general contact angle equation is obtained:

$$\gamma_L(1 + \cos \theta) = 2 \left( \sqrt{\gamma_S^{LW} \gamma_L^{LW}} + \sqrt{\gamma_S^+ \gamma_L^-} + \sqrt{\gamma_S^- \gamma_L^+} \right). \quad (19)$$

In order to find the  $AB$  interactions of cohesion in a solid or liquid phase, Eq.8 is rewritten for a single phase:

$$-\Delta G_i^{AB} = 4\sqrt{\gamma_i^+ \gamma_i^-}. \quad (20)$$

since,  $-\Delta G_i^{AB} = 2\gamma_i^{AB}$  by definition, then Eq.20 becomes,

$$\gamma_i^{AB} = 2\sqrt{\gamma_i^+ \gamma_i^-}. \quad (21)$$

If both  $\gamma_i^+$  and  $\gamma_i^-$  are present, the substance is termed “bipolar”. If one of them is not present (equals to zero), the substance is termed as “monopolar”. If both  $\gamma_i^+$  and  $\gamma_i^-$  are absent, the substance is termed “apolar”. Therefore,  $\gamma_i^{AB} = 0$  for apolar and monopolar substances and  $\gamma_i^{AB}$  is present for only bipolar substances.

The total interfacial tension is given from the sum of Eqs.7 and 10:

$$\gamma_{SL} = \left( \sqrt{\gamma_S^{LW}} - \sqrt{\gamma_L^{LW}} \right)^2 + 2 \left( \sqrt{\gamma_S^+} - \sqrt{\gamma_L^+} \right) \left( \sqrt{\gamma_S^-} - \sqrt{\gamma_L^-} \right). \quad (22)$$

The most important consequence of Eq.22 is that the contribution of acid-base interaction results in negative total interfacial tension (or free energy) in some circumstances. This occurs if  $\gamma_L^+ \gamma_S^+$  and  $\gamma_L^- \gamma_S^-$  or if  $\gamma_L^+ \gamma_S^+$  and  $\gamma_L^- \gamma_S^-$  and if  $|\gamma_{SL}^{AB}| > |\gamma_{SL}^{AB}|$ . A solid-liquid system may be stable although it has negative  $\gamma_{SL}$  <sup>11,26</sup>.

In order to use Eq.19 in determining solid surface tension components one needs a set of values of  $\gamma_L^{LW}$ ,  $\gamma_L^+$  and  $\gamma_L^-$  for reference liquids. Since,  $\gamma^{LW}$  is the entire surface tension for apolar liquids, the problem is to determine a set of  $\gamma_L^+$  and  $\gamma_L^-$  values for dipolar or monopolar liquids. Good and van Oss introduced an arbitrary relation for water. They assumed that  $\gamma_W^+ = \gamma_W^-$  for water and since  $\gamma^{AB} = 51.0$  mJ m<sup>-2</sup> is known, they calculated  $\gamma_W^+ = \gamma_W^- = 25.5$  mJ m<sup>-2</sup> from Eq.21 <sup>3,11</sup>. The values of all acid-base parameters derived therefrom are relative to those of water <sup>11,26</sup>. Good <sup>11</sup> does not exclude the presence of a possible ratio  $\alpha = \gamma_W^+ / \gamma_W^-$ ; however they suggest that they have a consistent set of liquid surface tension component data with these operational values (see Table 4). After having the reference liquid values, there are two methods to calculate the polymer surface values of  $\gamma_S^{LW}$ ,  $\gamma_S^+$  and  $\gamma_S^-$ . In the first method, three forms of Eq.19 is simultaneously solved by using the contact angle data of three different liquids with two of them being polar. In the second method,  $\gamma_S^{LW}$  can be determined first by using an apolar liquid, then two other polar liquids are used to determine  $\gamma_S^+$  and  $\gamma_S^-$ . However, sometimes negative square roots of  $\gamma_S^+$  and/or  $\gamma_S^-$  occurs which has not yet received a definitive answer <sup>10,11,26</sup>. It is recommended that if polar liquids are employed water should be used always; otherwise if only two polar liquids other than water are used (e.g.ethylene glycol and formamide) highly variable  $\gamma_S^+$  and  $\gamma_S^-$  may be obtained <sup>10,11,26</sup>.

van Oss-Good methodology was successfully applied to protein and polymer interactions with liquids, polymer solubility prediction in solvents <sup>30</sup>, critical micelle concentration estimation of surfactants, polymer phase separation and microemulsion formation <sup>11,26</sup>. This methodology was applied to liquid-liquid interactions and was found to be successful for interpreting the interactions at the liquid interfaces <sup>31-33</sup>. The change of the surface free energy properties of the copolymer films with the copolymer composition were determined by applying van Oss-Good methodology <sup>34-36</sup> and this approach was found to be more reasonable than the old semiempirical approaches <sup>10,14,15,37-39</sup>.

## Two-Liquids Method

For water-hydrocarbon systems, when a water drop in a hydrocarbon medium is used, Young's equation (Eq.1) may be written as:

$$\gamma_{WH} \cos \theta = \gamma_{SH} - \gamma_{SW}, \quad (23a)$$

where  $\theta$  is measured in the hydrocarbon phase, and when a hydrocarbon drop in water medium is used

$$\gamma_{WH} \cos \theta = \gamma_{SW} - \gamma_{SH}, \quad (23b)$$

where  $\theta$  is measured in the water phase.

According to Fowkes<sup>4</sup> and Tamai et al.<sup>16,17</sup>,  $\gamma_{SH}$  and  $\gamma_{SW}$  are given as:

$$\gamma_{SH} = \gamma_S + \gamma_H - 2\sqrt{\gamma_S^d \gamma_H^d} - I_{SH}^P \quad (24a)$$

$$\gamma_{SW} = \gamma_S + \gamma_W - 2\sqrt{\gamma_S^d \gamma_W^d} - I_{SW}^P, \quad (24b)$$

where  $I^P$  is a specific nondispersion interaction term that includes all the dipole, induced dipole and hydrogen bonding interactions. By combining Eqs.23 and 24, it leads to:

$$\gamma_W - \gamma_H + \gamma_{WH} \cos \theta = 2\sqrt{\gamma_S^d} \left( \sqrt{\gamma_W^d} - \sqrt{\gamma_H^d} \right) + I_{SW}^P - I_{SH}^P, \quad (25)$$

and  $I_{SH}^P$  may be considered equal to zero since the surface free energy of saturated hydrocarbons (n-alkanes) consists of only the London dispersion term. If the contact angles of water droplets on the solid surface are measured in several n-alkane bulk phases, the plot of  $(\gamma_W - \gamma_H + \gamma_{WH} \cos \theta)$  versus  $\left( \sqrt{\gamma_W^d} - \sqrt{\gamma_H^d} \right)$  should give a straight line with slope  $2\sqrt{\gamma_S^d}$  and intercept at the origin  $I_{SW}^P$ . ( $\gamma_H^d \equiv \gamma_H$  is accepted by definition). However, as Schultz and Nardin<sup>20</sup> pointed out this principle is based on the assumption that a droplet of water can displace the alkane layer from the solid surface at contact. They investigated the criterion for displacement that there will not remain a thin film of the hydrocarbon liquid between the solid and the water drop and concluded that the criterion corresponds to<sup>20</sup>:

$$|\gamma_{SH} - \gamma_W| < \gamma_{WH} \quad (26)$$

and

$$I_{SW}^P > 2 \left( \sqrt{\gamma_S^d} - \sqrt{\gamma_H^d} \right) \left( \sqrt{\gamma_H^d} - \sqrt{\gamma_W^d} \right). \quad (27)$$

Two-Liquids method was used to investigate the orientation of the surface molecules, that is, the variation with time of the surface energy of the grafted polymer in contact with an "orienting" polar liquid (water)<sup>40</sup>. These studies led to a new explanation of the contact angle hysteresis of wetting of polymers that is due to the polarity of materials and in particular the reorientation of polar groups at the polymer-liquid interface<sup>41</sup>.

Tamai and co-workers<sup>16,17</sup> compared the Two-Liquids method with the One-Liquid method and found that the values of  $\gamma_S^d$  from the Two-Liquids method were considerably larger than those from the One-Liquid method for PTFE, PVC and PMMA polymers. They attributed this discrepancy to the neglect of the  $\pi_e$  in

the One-Liquid method. Later both methods are combined in a single equation by using Good's interaction parameter  $\Phi$  formalism in order to calculate  $\pi_e$  values of water on the above polymers<sup>21</sup>. Recently, van Oss-Good approach was applied to the Two-Liquids method<sup>22</sup> and this formalism was adopted to calculate  $\pi_e$  for water by the combination of One and the Two-Liquids methods<sup>23</sup>. Good agreement was obtained with the water  $\pi_e$  data on these polymers obtained from the independent ellipsometric measurements<sup>21,23</sup>.

### Calculation of the Spreading Pressure:

When the interfacial free energy equation in the van Oss - Good approach (Eq.22) is applied to the Two-Liquid system of water and hydrocarbons one obtains,

$$\gamma_{SH} = \left( \sqrt{\gamma_{S^{\circ}}^{LW}} - \sqrt{\gamma_H^{LW}} \right)^2 + 2 \left( \sqrt{\gamma_{S^{\circ}}^+} - \sqrt{\gamma_H^+} \right) \left( \sqrt{\gamma_{S^{\circ}}^-} - \sqrt{\gamma_H^-} \right) - \pi_W(H) \quad (28a)$$

$$\gamma_{SW} = \left( \sqrt{\gamma_{S^{\circ}}^{LW}} - \sqrt{\gamma_W^{LW}} \right)^2 + 2 \left( \sqrt{\gamma_{S^{\circ}}^+} - \sqrt{\gamma_W^+} \right) \left( \sqrt{\gamma_{S^{\circ}}^-} - \sqrt{\gamma_W^-} \right) - \pi_H(W). \quad (28b)$$

Hydrocarbon and water are mutually soluble to some extent and it may be possible that water is adsorbed onto the solid surface from the hydrocarbon phase  $\pi_W(H)$ , or conversely, hydrocarbon is adsorbed onto the solid surface from the water phase  $\pi_H(W)$ . On the other hand, since all the used aliphatic hydrocarbons are apolar by definition,  $\gamma_H^+ = \gamma_H^- = 0$  and  $\gamma_H^{LW} = \gamma_H$ . Then Eq.28a becomes,

$$\gamma_{SH} = \left( \sqrt{\gamma_{S^{\circ}}^{LW}} - \sqrt{\gamma_H} \right)^2 + 2 \left( \sqrt{\gamma_{S^{\circ}}^+ \gamma_{S^{\circ}}^-} \right) - \pi_W(H). \quad (29)$$

Combining Eqs.23a, 28b and 29 yields,

$$\begin{aligned} \gamma_{HW} \cos \theta &= \gamma_H - \gamma_W^{LW} - 2\sqrt{\gamma_{S^{\circ}}^{LW}} \left( \sqrt{\gamma_H} - \sqrt{\gamma_W^{LW}} \right) \\ &\quad - 2 \left( \sqrt{\gamma_W^+ \gamma_W^-} - \sqrt{\gamma_{S^{\circ}}^+ \gamma_W^-} - \sqrt{\gamma_{S^{\circ}}^- \gamma_W^+} \right) - [\pi_W(H) - \pi_H(W)]. \end{aligned} \quad (30)$$

When only two hydrocarbon-water sets are considered, Eq.30 becomes,

$$\begin{aligned} \gamma_{H_1W} \cos \theta_1 - \gamma_{H_2W} \cos \theta_2 &= \gamma_{H_1} - \gamma_{H_2} - 2\sqrt{\gamma_{S^{\circ}}^{LW}} \left( \sqrt{\gamma_{H_1}} - \sqrt{\gamma_{H_2}} \right) \\ &\quad + \pi_W(H_2) - \pi_W(H_1) + \pi_{H_1}(W) - \pi_{H_2}(W). \end{aligned} \quad (31)$$

Since by definition,

$$\Delta\pi_H(W) \equiv \pi_{H_2}(W) - \pi_{H_1}(W) \quad (32a)$$

$$\Delta\pi_W(H) \equiv \pi_W(H_2) - \pi_W(H_1), \quad (32b)$$

then Eq.31 becomes

$$\begin{aligned} \gamma_{H_1W} \cos \theta_1 - \gamma_{H_2W} \cos \theta_2 &= \gamma_{H_1} - \gamma_{H_2} - 2\sqrt{\gamma_{S^{\circ}}^{LW}} \left( \sqrt{\gamma_{H_1}} - \sqrt{\gamma_{H_2}} \right) \\ &\quad + \Delta\pi_W(H) - \Delta\pi_H(W). \end{aligned} \quad (33)$$

so, even  $\pi_W(H)$  and  $\pi_H(W)$  cannot be neglected, with the difference between the  $\pi$ 's of the hydrocarbons can be considered to be negligible, that is,  $\Delta\pi_H(W) \cong 0$  and  $\Delta\pi_W(H) \cong 0$  and consequently one obtains,

$$\gamma_{H_1W} \cos \theta_1 - \gamma_{H_2W} \cos \theta_2 = \gamma_{H_1} - \gamma_{H_2} - g\sqrt{\gamma_{S^\circ}^{LW}} (\sqrt{\gamma_{H_1}} - \sqrt{\gamma_{H_2}}). \quad (34)$$

Since the left-hand side of Eq. 34 and surface tension of the hydrocarbons are all known experimentally,  $\gamma_{S^\circ}^{LW}$  can be calculated by using this equation. In the One-Liquid Method, for water drops on polymer (or solid) surfaces, Eq.19 can be rewritten as

$$\pi_W + \gamma_W(1 + \cos \theta) = 2 \left( \sqrt{\gamma_{S^\circ}^{LW} \gamma_W^{LW}} + \sqrt{\gamma_{S^\circ}^+ \gamma_W^-} + \sqrt{\gamma_{S^\circ}^- \gamma_W^+} \right). \quad (35)$$

Accordingly, when one uses a  $\gamma_{S^\circ}^{LW}$  value obtained from the Two-Liquid Method and  $\gamma_{S^\circ}^+$  and  $\gamma_{S^\circ}^-$  values obtained from the One-Liquid method or from the literature, it is possible to calculate the spreading film pressure of water  $\pi_W$  on solids by using Eq. 35.

## Experimental

All the contact angle measurement results were taken from Reference 2. The films used were unmodified cellulose, cellulose acetate, and three samples of cellulose grafted with an alkyl ketene dimer (C-AKD) 1, 2, 3 having 21.3, 28.0, 34.7 % hydroxyl groups substituted<sup>1,2</sup>. Contact angle measurements in air were made by the sessile drop method using a Ramé-Hart contact angle goniometer. 10  $\mu$ l liquid drops were placed on the surface using a micrometer syringe fitted with a stainless steel needle and only advancing contact angles were measured on both sides of the drop to assure symmetry. For each sample, contact angle measurements were made on two different films and five measurements were made on each film. Thus, a total of ten drops were used for each sample and the results averaged. For the Two-Liquids Method, the cellulosic films were placed in an environmental chamber filled with a hydrocarbon. Prior to use, doubly distilled water was shaken with the hydrocarbon phase in a separating funnel to ensure mutual saturation. The advancing contact angles were measured by placing a water drop onto the film in the hydrocarbon medium.

## Results and Discussion

The surface and interfacial tensions of the liquids used in the Two-Liquids Method are taken from Reference 40 and given in Table 1. n-Octane/water contact angle values on the cellulosic films were taken from the Fig. 2 and Table 5 of the Ref. 2. n-Hexane and cyclohexane/water contact angle values were calculated by using Table 4 of the Ref. 2. All the hydrocarbon/water contact angle values are given in Table 2. One-Liquid contact angle results were taken from the Table 3 of Ref. 2 and are reported in Table 3. The surface tension components of the liquids used in the One-Liquid Method were taken from Ref. 11 and are given in Table 4.

**Table 1.** Surface Free Energies and the Interfacial Free Energies of the Liquids<sup>†</sup> used in the Two-Liquids Method ( $\text{mJ}/\text{m}^2$ )<sup>42</sup>.

Liquid	$\gamma_{LV}$	$\gamma_{HV}$
n-Hexane	18.4	50.8
n-Octane	21.8	51.7
Cyclohexane	25.5	50.3
Water	72.8	-



**Table 2.** Water Contact Angles (in degrees) on the Cellulosic Films in the Two-Liquids Method<sup>2</sup>.

Cellulosic Film	in n-Hexane	in n-Octane	in Cyclohexane
Unmodified Cellulose	42	44	43
Cellulose Acetate	82	83	83
C - AKD - 1	74	75	75
C - AKD - 2	118	119	121
C - AKD - 3	141	141	144

**Table 3.** One-liquid Contact Angle Results (in degrees) in Air on the Cellulosic Films<sup>2</sup>.

Cellulosic Film	Water	Glycerol	Formamide	Methylene Iodide	$\alpha$ -Bromonaphthalene
Unmodified Cellulose	30	29	5	41	27
Cellulose Acetate	55	58	42	43	32
C - AKD - 1	55	36	31	32	22
C - AKD - 2	84	68	66	46	34
C - AKD - 3	110	88	81	53	43

**Table 4.** Surface Free Energy Components of the Liquids used in the One-Liquid Method (mJ/m<sup>2</sup>)<sup>11</sup>.

Liquid	$\gamma_i^{TOT}$	$\gamma_L^{LW}$	$\gamma_L^{AB}$	$\gamma_L^+$	$\gamma_L^-$
Water	72.8	21.8	51.0	25.50	25.5
Glycerol	64.0	34.0	30.0	3.92	57.4
Formamide	58.0	39.0	19.0	2.28	39.6
Methylene Iodide	50.8	50.8	0	0	0
$\alpha$ -Bromonaphthalene	44.4	43.5	$\approx 0$	0	0

The surface tension components (or surface free energy components) of the cellulosic films are calculated by using Eq.19 (by assuming  $\pi_e = 0$  in the One-Liquid Method) and are given in Table 5. As it is seen in this table, the electron acceptor (or Lewis acid)  $\gamma^+$  surface tension components of the cellulosic films are very small whereas the electron donor (or Lewis base)  $\gamma^-$  components are large and represents the main interactions with the electron acceptor (acidic)  $\gamma^+$  components of the contacting liquids. The Lifshitz-van der Waals (LW) interaction components  $\gamma^{LW}$  of the cellulosic films are very similar in magnitude except C-AKD-3 sample, which deviates 22 % from the mean value. This indicates that the modification of the cellulose does not affect LW interactions to a considerable extent (mainly London dispersion interactions) because LW forces mostly depend on the intermolecular distance between the interacting molecules. However, the modification of the cellulose very much affects the acid-base surface properties. The higher the substitution of the hydroxyl group the smaller the basicity of the modified cellulose and, correspondingly, the smaller the total surface tension of the cellulosic films.

In order to examine the single cellulosic film - contacting liquid interaction, the work of adhesion components of the films with the wetting liquids are calculated by using Eqs. 2, 8, 12 and 16 (by assuming  $\pi_e = 0$  in the One-Liquid Method) and are given in Table 6. As it is seen in the table, the ratio of the acid-base component of the work of adhesion to the total work of adhesion,  $W^{AB}/W^{TOT}$ , decreases with the decrease of the polarity and acidity (see Table 4) of the interacting liquids.  $W^{AB}/W^{TOT}$  also decreases with the increase of the hydroxyl group substitution with alkyl ketene dimers. It is interesting to note that for the highest coverage of C-AKD samples (C-AKD-3), the work of adhesion entirely consists of LW

interactions. This is probably a result of the hydrocarbon probes interacting with the alkyl chains of the AKD.

**Table 5.** Surface Free Energy Components of the Cellulosic Films obtained from the One-Liquid Method by assuming  $\pi_2 = 0$  (mJ/m<sup>2</sup>).

Cellulosic Film	$\gamma_S^{LW}$	$\gamma_S^+$	$\gamma_S^-$	$\gamma_S^{BA}$	$\gamma_S^{TOT}$
Unmodified Cellulose	39.8	2.1	38.2	17.9	57.7
Cellulose Acetate	38.4	0.3	25.8	5.4	43.8
C - AKD - 1	42.7	1.9	15.4	10.8	53.5
C - AKD - 2	37.2	0.2	3.8	1.5	38.7
C - AKD - 3	30.8	0	0	0	30.8

**Table 6.** Work of Adhesion Components of the Cellulosic Films with the Wetting Liquids in the One-Liquid Method by assuming  $\pi_e = 0$  (mJ/m<sup>2</sup>).

Cellulosic Film	Wetting Liquid	$W_{SL}^{LW}$	$W_{SL}^{AB}$	$W_{SL}^{TOT}$	$W_{SL}^{AB}/W_{SL}^{TOT}$
Unmodified Cellulose	Water	58.8	77.1	135.9	0.567
Unmodified Cellulose	Glycerol	73.6	46.4	120.0	0.387
Unmodified Cellulose	Formamide	78.9	36.9	115.8	0.319
Unmodified Cellulose	Methylene Iodide	89.1	0	89.1	0
Unmodified Cellulose	$\alpha$ -Bromonaphthalene	84.0	0	84.0	0
Cellulose Acetate	Water	57.9	56.7	114.6	0.495
Cellulose Acetate	Glycerol	69.8	28.1	97.9	0.287
Cellulose Acetate	Formamide	79.1	22.0	101.1	0.218
Cellulose Acetate	Methylene Iodide	88.0	0	88.0	0
Cellulose Acetate	$\alpha$ -Bromonaphthalene	82.0	0	82.0	0
C - AKD - 1	Water	61.1	53.5	114.6	0.467
C - AKD - 1	Glycerol	79.4	36.4	115.8	0.314
C - AKD - 1	Formamide	78.5	29.2	107.7	0.271
C - AKD - 1	Methylene Iodide	93.9	0	93.9	0
C - AKD - 1	(-Bromonaphthalene)	85.6	0	85.6	0
C - AKD - 2	Water	56.7	23.7	80.4	0.295
C - AKD - 2	Glycerol	74.4	13.6	88.0	0.155
C - AKD - 2	Formamide	70.8	10.8	81.6	0.132
C - AKD - 2	Methylene Iodide	86.1	0	86.1	0
C - AKD - 2	(-Bromonaphthalene)	81.2	0	81.2	0
C - AKD - 3	Water	47.9	0	47.9	0
C - AKD - 3	Glycerol	66.2	0	66.2	0
C - AKD - 3	Formamide	67.1	0	67.1	0
C - AKD - 3	Methylene Iodide	81.4	0	81.4	0
C - AKD - 3	$\alpha$ -Bromonaphthalene	76.9	0	76.9	0

In order to examine the single cellulosic film - contacting liquid interfacial tension, interfacial tension components of the films with the wetting liquids were calculated by using Eqs. 4, 7, 10 and 22 (by assuming  $\pi_e = 0$  in the One-Liquid Method) and are given in Table 7. In this table, the main difference is found in the

acid-base interfacial tension components,  $\gamma^{AB}$ . It is known that the decrease in the interfacial tension values indicates the high attraction between interacting molecules and it is seen in Table 7 that water / unmodified cellulose attraction was the highest whereas water / C-AKD-3 attraction was the lowest. The negative value for water / unmodified cellulose acid-base interfacial tension component indicates that the cellulose surface adsorbs water molecules (hydration). Adsorption of solvent molecules resulted in swelled polymers and if the minimum contactable surface area between two polymer molecules is known, it is possible to calculate the Flory-Huggins<sup>43</sup> polymer-solvent interaction parameter,  $\chi$ <sup>26,30</sup> from interfacial tension measurements. At present, it is conventional to apply statistical thermodynamics and dimensional change analysis to determine  $\chi$  parameter in polymer physics<sup>44</sup>, especially for polymer-solvent pairs interacting with non-polar forces, and the presence of only positive interfacial tension is assumed in this approach. However, the combination of the negative interfacial tension concept with this approach will improve our understanding on the polymer-solvent interactions, especially for specific acid-base interacting pairs<sup>45</sup>.

**Table 7.** Interfacial Tension Components of the Cellulosic Films with the Wetting Liquids in the One-Liquid Method by assuming  $\pi_e = 0$  (mJ/m<sup>2</sup>).

Cellulosic Film	Wetting Liquid	$\gamma_{SL}^{LW}$	$\gamma_{SL}^{AB}$	$\gamma_{SL}^{TOT}$
Unmodified Cellulose	Water	2.69	-8.14	-5.45
Unmodified Cellulose	Glycerol	0.23	1.48	1.71
Unmodified Cellulose	Formamide	0.004	0.014	0.018
Unmodified Cellulose	Methylene Iodide	0.67	0	0.67
Unmodified Cellulose	-Bromonaphthalene	0.08	0	0.08
Cellulose Acetate	Water	2.33	-0.29	2.04
Cellulose Acetate	Glycerol	0.13	7.24	7.37
Cellulose Acetate	Formamide	0.002	2.375	2.377
Cellulose Acetate	Methylene Iodide	0.87	0	0.87
Cellulose Acetate	$\alpha$ -Bromonaphthalene	0.16	0	0.16
C - AKD - 1	Water	3.48	8.30	11.78
C - AKD - 1	Glycerol	0.50	4.40	4.90
C - AKD - 1	Formamide	0.08	0.62	0.70
C - AKD - 1	Methylene Iodide	0.35	0	0.35
C - AKD - 1	$\alpha$ -Bromonaphthalene	0.004	0	0.004
C - AKD - 2	Water	2.05	28.86	30.91
C - AKD - 2	Glycerol	0.07	17.91	17.98
C - AKD - 2	Formamide	0.02	9.74	9.76
C - AKD - 2	Methylene Iodide	1.06	0	1.06
C - AKD - 2	$\alpha$ -Bromonaphthalene	0.25	0	0.25
C - AKD - 3	Water	0.78	51.0	51.78
C - AKD - 3	Glycerol	0.08	30.0	30.08
C - AKD - 3	Formamide	0.48	19.0	19.48
C - AKD - 3	Methylene Iodide	2.49	0	2.49
C - AKD - 3	$\alpha$ -Bromonaphthalene	1.09	0	1.09

The high increase of the total interfacial tension (or the decrease of interfacial attraction) with the increase of the hydroxyl group substitution of cellulose with alkyl ketene dimers shows that the main interfacial attraction occurs between the hydroxyl groups of the cellulose and the basic sites of the contacting

liquids and by replacing these groups with AKD molecules, this attraction vanishes. It is interesting to note that the low values of the LW interfacial tension,  $\gamma^{LW}$ , do not vary very much for all the cellulosic films showing the presence of a moderate LW attraction.

LW component of the surface tension of the cellulosic films were calculated by using Eq. 34 in the Two-Liquids Method and are given in Table 8. When the results in Tables 5 and 8 are compared a decrease of approximately 10 mJ/m<sup>2</sup> in  $\gamma_{S^{\circ}}^{LW}$  values less than  $\gamma_S^{LW}$  are seen for unmodified cellulose, cellulose acetate and C-AKD-1, whereas similar values are obtained for C-AKD-2 and C-AKD-3. Then the spreading film pressures of water,  $\pi_e$ , on the cellulosic films were calculated by using Eq.35 and  $\gamma_S^-, \gamma_S^+$  values taken from Table 5.  $\pi_e$  values are reported in Table 8. Surprisingly, negative values of  $\pi_e$  are found for unmodified cellulose, cellulose acetate and C-AKD-1 films which are impossible thermodynamically. However the values of 0.07 and 3.16 mJ/m<sup>2</sup> for C-AKD-2 and C-AKD-3, respectively, seem very reasonable. It is probable that the hydration of the film surface and the adsorption of water molecules resulted in the decrease of  $\gamma_{S^{\circ}}^{LW}$  values and the negative values of  $\pi_e$  obtained for unmodified cellulose, cellulose acetate and C-AKD-1 films. It is possible to understand what happened if the change in the contact angle with time has been followed during the above experiments. In order to follow the rapid change in the initial contact angle and the initial drop shape with time a new experimental setup has been built for such complicated situations<sup>46</sup> and two novel mathematical analyses were developed<sup>47</sup>.

**Table 8.** LW Component of the Surface Free Energy of the Cellulosic Films calculated from the Two-Liquids Method and the computed Water Spreading Pressure Values on the Cellulosic Films using Equation (mJ/m<sup>2</sup>).

Cellulosic Film	$\gamma_{S^{\circ}}^{LW}$	$\pi_e$
Unmodified Cellulose	28.03	-9.35
Cellulose Acetate	27.97	-8.33
C - AKD - 1	28.28	-11.34
C - AKD - 2	36.32	0.07
C - AKD - 3	29.89	3.16

## Conclusion

The surface tension components of the cellulosic films, their interfacial tension with the probe liquids and the work of adhesion components were calculated using van Oss-Good One-Liquid approach. The electron donor (or Lewis base)  $\gamma^-$  components were found to represent the main interactions with the electron acceptor (acidic)  $\gamma^+$  components of the contacting liquids. The modification of the cellulose very much affected the acid-base surface properties. The higher the substitution of the hydroxyl group the smaller the basicity of the modified cellulose and correspondingly the smaller the total surface tension of the cellulosic film was obtained. The C-AKD surfaces showed hydrophobic character in a non-polar environment. A negative value for water / unmodified cellulose acid-base interfacial tension component was found showing that the cellulose surface adsorbed the water molecules (hydration). The spreading film pressures of water,  $\pi_e$ , on the cellulosic films were calculated and surprisingly negative values of  $\pi_e$  were found for unmodified cellulose, cellulose acetate and C-AKD-1 films which are impossible thermodynamically. It is probable that the hydration of the film surface and the adsorption of water molecules resulted in the decrease of  $\gamma_{S^{\circ}}^{LW}$  values and the negative values of  $\pi_e$  obtained for these cellulosic surfaces.

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