J. Phys. Chem. A **1998,** *102,* 697−702

Determination of C 1s Core Level Chemical Shifts in Some Langmuir−Blodgett Films Using a Modified Sanderson Formalism

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Received: April 28, 1997; In Final Form: July 9, 1997⊗

The modified Sanderson (MS) formalism for calculation of partial charge on atoms has been shown to yield extremely good correlation between the atomic partial charge in organic molecules and core level binding energies determined using X-ray photoelectron spectroscopy (XPS). The MS approach is used to determine partial charges on the carbons in Langmuir-Blodgett (LB) films of lead arachidate and chloroplatinic acid−octadecylamine complexes and from the atomic charges, expected C 1s chemical shifts. Fits to the C 1s core level spectra from the different LB films agree within experimental error with those predicted by the MS calculation. Identification of additional C 1s spectral components that arise from carbons directly coordinated to the carboxylate carbon/amine group highlights the importance of induction effects on partial atomic charges in molecules, an aspect hitherto not taken into account in XPS studies of LB films. Inclusion of the additional C 1s component in the core level fits is shown to lead to solution of a long standing problem regarding quantitative analysis based on the C 1s peak intensities. Applicability of the MS approach to such practical problems in XPS together with its simplicity and intuitiveness make this approach particularly attractive for the experimental chemist.

Introduction

It is well-known that many important properties of molecules are determined by the charges on the atoms in the molecules. The concept of effective charge on an atom is thus of considerable importance in chemistry, and many routes, both experimental[1,2] and theoretical,[3−6] have been developed for the determination of atomic charges. In the late 1960s, it was realized that core ionization energies are directly related to the charge on the atoms and thus contained information regarding the chemical properties of molecules such as acidity and basicity.[7−9] Changes in atomic charge as would occur when a particular element exists in different chemical environments lead to a shift in the core level binding energies (BEs), this being termed *chemical shifts*. This led to the rapid development and increased interest in X-ray photoemission spectroscopy (XPS) as a tool for the measurement of core level ionization energies or binding energies as they are more popularly known. Thus arose the use of the acronym ESCA, or electron spectroscopy for chemical analysis, as one major application of XPS.

The key steps in routine use of ESCA for understanding the chemical properties of molecules or in the identification of chemically shifted core level spectral components are developing a user-friendly procedure for calculation of atomic charge and establishing a correlation between the charges thus calculated and experimentally measured core level BEs. We have recently shown that there exists extremely good correlation between the C 1s BEs of a series of organic molecules (both in the solid and gas phase) and the atomic charge on carbon calculated using a modified Sanderson (MS) formalism.[10] In addition to being computationally nonintensive and intuitive, the MS formalism is known to yield better charge-BE correlation than that with charges determined using other quantum chemical techniques[10,11,12] and predicts correctly spillover and pileup effects in donor and acceptor atoms, respectively.[13]

XPS has been used extensively in the study of Langmuir−Blodgett (LB) films.[14−29] In most of the above reports, however, the information sought has been predominantly quantitative in nature. To our knowledge, there has not been a systematic attempt at understanding chemical shifts in LB films in terms of calculated atomic charges. In this paper, we present details of application of the MS protocol to C 1s core level spectra of LB films of 3 monolayers (ML) of lead arachidate (PbA) deposited on copper-coated quartz substrates[23] and octadecylamine films complexed with chloroplatinic acid (Am-HPt, 31 ML)[26] deposited on Si(111) substrates. Details regarding the film preparation and measurement conditions can be obtained from the above reports and will not be repeated here. Since the emphasis of this paper is on the application of the MS formalism for prediction of chemical shifts in the LB films mentioned above, the MS procedure is briefly outlined. It is shown that the MS formalism correctly predicts an additional C 1s spectral component arising from carbons directly coordinated to the carboxylate carbon/amine group. This highlights the importance of induction effects on atomic charges in LB films and consequently, core level chemical shifts, an aspect hitherto not taken into account in XPS studies of LB films. It is also shown that incorporation of the additional C 1s component in the core level fits leads to an accurate quantitative analysis of the LB films.

Modified Sanderson Formalism

The Sanderson method for calculation of partial charges is based on the principle of electronegativity equalization.[30] Sanderson derived an electronegativity scale based on the average electron density of atoms (this is related to the

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⊗ Abstract published in *Advance ACS Abstracts*, December 15, 1997.

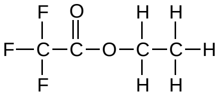
S1089-5639(97)01423-0 CCC: $15.00

TABLE 1: Sanderson Stability Ratios Used in the Atomic Charge Calculations for the Elements of This Study[a]

element	SR	ΔSR
H	3.55	3.92
C	3.79	4.05
N	4.49	4.41
O	5.21	4.75

[a] Stability ratios and normalization factors were taken from ref 30.

compactness of atoms) which he termed *stability ratios* (SR).[31,32] The atomic charge of a particular element in a molecule is then evaluated from the normalized difference in stability ratios of the molecule and element in question. It is clear that the charge determined in this way does not differentiate between an element in two different chemical environments within the same molecule nor can it differentiate between structural isomers. Without altering the basic principle of electronegativity equalization, Carver et al.[11] proposed viewing the molecule not as a collection of atoms but as a collection of groups. While the essential details are covered in ref 10a, for completeness we outline the necessary mathematical details of the modified Sanderson method through illustration with a textbook example, ethyl trifluoroacetate[33] (schematic given below).



$$F_3C-C(=O)-O-CH_2-CH_3$$

The charge on the carbon coordinated to fluorine, i.e., belonging to the CF_3 group is determined by calculating the group stability ratio involving that carbon. Mathematically, this is

$$SR_{CF_3} = (SR_C\, SR_F^{\;3}\, SR_{M'})^{1/5} \qquad (1)$$

where SR_C and SR_F are the stability ratios of carbon and fluorine, respectively, and $SR_{M'}$ is the stability ratio of the other group (rest of the molecule made up of further subgroups) attached to the carbon in question. The stability ratio of the other group $SR_{M'}$ is likewise given by:

$$SR_{M'} = \{SR_C SR_O[SR_O(SR_C SR_H^{\;2}\,(SR_C SR_H^{\;3})^{1/4})^{1/4}]^{1/2}\}^{1/3} \qquad (2)$$

The charge on the carbon in the $-CF_3$ group is then calculated as

$$\delta_C = (SR_{CF_3} - SR_C)/\Delta SR_C \qquad (3)$$

Table 1 gives the stability ratios of the different elements investigated in this study taken from ref 30. The charges for the other carbons in the molecule, i.e., $-O-C{=}O, -OCH_2$, and $-CH_3$ are determined in a similar fashion. The atomic charges on the above carbons are thus calculated using the modified Sanderson method to be 0.3131, 0.1979, 0.0159, and −0.030, respectively.

The relationship between the partial charge on carbon calculated by the MS method and C 1s BEs for organic molecules in the solid phase for which reliable values were available in the literature has been established to be linear having the form[10a]

$$\text{C 1s (BE)} = 26.0\, q_{MS} + 286.2 \qquad (4)$$

where q_{MS} is the carbon partial charge determined by the MS method. In the calculations presented below on LB films, eq 4 will be used to predict the BE positions of the C 1s spectral components.

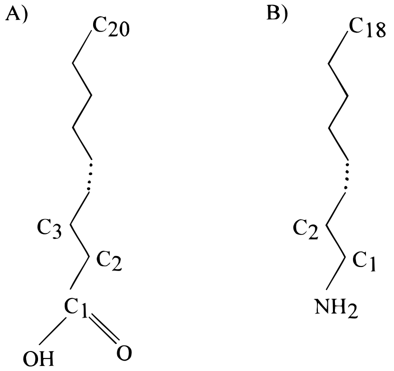


Figure 1. Schematic of arachidic acid and octadecylamine molecules with carbon numbering.

TABLE 2: Sanderson Partial Charges on Carbons in Lead Arachidate and Octadecylamine−Chloroplatinic Acid Langmuir−Blodgett Films and C 1s BEs Calculated Using Eq 4

carbon no.	Sanderson partial charge	calcd BE (eV)
	Lead Arachidate	
C_1	0.010	288.8
C_2	−0.005	286.1
C_3	−0.036	285.2
C_{20}	−0.046	285.0
	Octadecylamine−Chloroplatinic Acid	
C_1	−0.030	285.4
C_2	−0.040	285.1
C_{18}	−0.046	285.0

Results and Discussion

Figure 1a,b shows the structures of arachidic acid and octadecylamine molecules together with labeling of the carbons in the molecules. The partial charges on the carbons for the molecules shown in Figure 1 have been determined as shown in the example above (i.e., using eqs 1−3) and are given in Table 2. The carbon in the carboxylic acid group and the carbon coordinated to the amine group clearly show the largest charges due to coordination with more electronegative elements (oxygen and nitrogen, respectively, Table 1). It is seen that the “induction effect” in terms of the partial charge on carbons as one moves away from C_1 extends over a distance of only three bond lengths as observed by others.[12] Also given in Table 2 are the C 1s BEs determined from the MS partial charges using eq 4. From the table it is observed that the MS partial charge calculations predict three and two C 1s components for the arachidic acid and octadecylamine molecules, respectively, which can be identified within the resolution available in conventional laboratory-based XPS instruments. In LB films of lead arachidate, the Pb^{2+} ion coordinates to the ionized carboxylic acid group, whereas in the amine film, there is protonation of the amine group and coordination with the $(PtCl_6)^{2-}$ anion. We point out that no attempt has been made to account for the influence of the Pb^{2+} and $(PtCl_6)^{2-}$ ions on the partial charges on the C_1 atoms and consequently the other carbons through induction effects. The stability ratios of such ions are not well-studied, and there is still considerable debate over the exact nature of bond formation in such metal salts of fatty acids.[34,35] While this may lead to some discrepancy between the calculated carbon partial charges (and consequently the C 1s BE shifts) for the fatty acid/fatty amine molecules and the corresponding salts in LB film form, the *trends* arising from

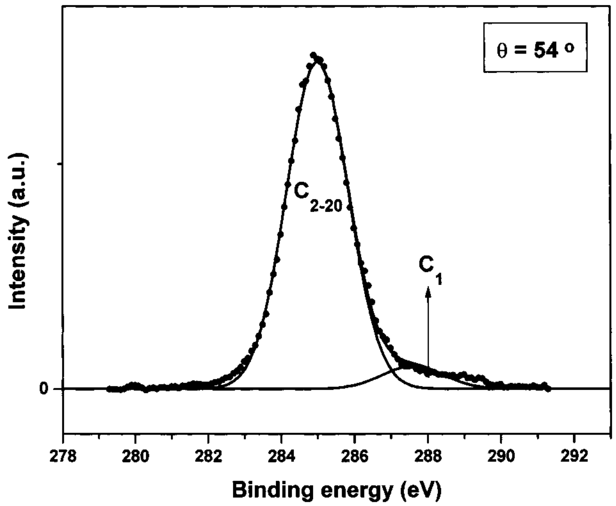


Figure 2. C 1s spectrum of a 3 ML lead arachidate film on Cu substrate at an ETOA of 54° (filled circles) together with a two-component fit (solid lines).

TABLE 3: Parameters Obtained from the Fits of the C 1s Core Level Spectra of LB Films of Lead Arachidate and Octadecylamine−Chloroplatinic Acid

carbon no.	BE (eV)	peak area	calcd area ratio	expected ratio
		Lead Arachidate (Two-Component Fit)		
C_{2-20}	285.0	3076		
C_1	287.2	214	$C_{2-20}/C_1 = 14.4$	21
		Lead Arachidate (Three-Component Fit)		
C_{3-20}	285.0 (285.0)[a]	3009 (2019)		
C_2	286.6 (286.5)	147 (50)	$C_{3-20}/C_2 = 20.5$ (40.4)	21 (37)
C_1	288.9 (288.9)	151 (50)	$C_{3-20}/C_1 = 20$ (40.4)	21 (37)
		Octadecylamine−Chloroplatinic Acid		
C_{2-18}	285.0	5214		
C_1	285.5	256	$C_{2-18}/C_1 = 20.4$	20.5

[a] The values in the parentheses refer to the fit of the C 1s spectrum measured at an ETOA of 34°.

the induction effect are expected to be reliable and may therefore be used to accurately predict the number of C 1s spectral components.

Figure 2 shows the C 1s spectrum from a 3 ML PbA film measured at an electron takeoff angle (ETOA, defined as the angle between electron emission direction and surface plane) of 54°. The spectrum shows the presence of an intense peak at ~285 eV and a smaller component at ~289 eV. The C 1s peak stripping hitherto has been performed taking into account only the two clearly visible components corresponding to the signal originating from the hydrocarbon chain and from the carboxylate group. [14,16,37] Accordingly, a nonlinear least-squares fit was performed of the C 1s spectrum shown in Figure 2 (filled circles) using two Gaussian components, and these are indicated as peaks C_{2-20} and C_1 in Figure 2 (solid lines, carbon assignment as in Figure 1a). Table 3 gives the parameters obtained from the fit. It is interesting to note that the fit yielded a high BE component at 287.2 eV and not at ~289 eV as is expected from a visual inspection of the spectrum. This indicates the presence of a component at close to 287 eV in addition to the expected carboxylate carbon at ~289 eV. Another point to be noted is that the ratios of the peak areas corresponding to the 285 eV component (hydrocarbon chain) and the 287.2 eV component (carboxylic acid carbon) is 14.4, whereas the expected ratio based on the discrete layer model[22−24] for this ETOA is ~21.[38] There is clearly an overestimation of intensity of the higher BE component relative to the 285 eV component as well as a discrepancy in the BE value when compared to the BE calculated using the MS partial charge (Table 2) and hence, the two component model is not justified in this case. However, before the high BE features at ~287 and 298 eV can be unambiguously attributed to chemical shifts arising from atomic partial charge variation, possible contributions from other physical processes need to be considered and discounted.

High BE (low kinetic energy) features can arise due to characteristic inelastic scattering losses during transport of the "no-loss" electrons within the film surface prior to emission. The "no-loss" peak would correspond to the intense component at 285 eV in the C 1s spectra of this study which arises due to emission from the alkyl chains (Figure 1a, carbons C_3-C_{20}). The features discussed above are termed "extrinsic" loss features, the energies of which can be independently determined using electron energy loss spectroscopy as has been demonstrated for cadmium arachidate films.[28] It was shown that the lowest excitation (energy loss) occurs at ~7 eV from the no-loss peak[28] which is clearly much larger than the shift of ~4 eV observed in the C 1s spectrum shown in Figure 2. This loss energy is not expected to be significantly different for PbA films. Therefore, the high BE feature at ~289 eV can be confidently attributed to atomic partial charge dependent chemical shifts as described in the MS formalism.

Figure 3a shows the same C 1s spectrum from lead arachidate (ETOA = 54°) with a fit using *three Gaussian components* as predicted by the MS charge calculation (Table 2). We mention here that *all fitting parameters were left free*. The corresponding parameters from the fit are listed in Table 3. It is observed that the carboxylate carbon BE shifts from the value of 287.2 eV obtained for the 2 component fit to 288.9 eV while the additional component has a BE of 286.6 eV. While introduction of an additional spectral component is expected to lead to reduction in the χ^2 error value and is not a justification in itself, the interesting point to note is that the BEs of the three components agree within instrumental resolution with those calculated using the MS formalism (Tables 2 and 3). The ratios of the peak areas (hydrocarbon chain, C_2; and hydrocarbon chain, C_1) are calculated from the fit to be ~20.5, which is very close to the value of 21 expected from the discrete layer model (Table 3). In going from the two-component to three-component C 1s spectrum, the standard deviation of the Gaussians decreased marginally from 0.88 to 0.85 eV.

Burns and Swalen[14] have studied the influence of the substrate on the BE of the carboxylate carbon relative to the alkyl carbon [$\Delta E_{BE} = E_{BE}$ (carboxylate carbon) − E_{BE} (alkyl carbon)] in cadmium arachidate monolayer and multilayer LB films. For Cu films as the substrate, they observed a ΔE_{BE} of 3.6 eV, whereas for the PbA LB film of this study, also on Cu substrates, a shift of 3.9 eV is obtained (Table 3). While the discrepancy is within instrumental resolution, the different counterions used in both the studies may also contribute to the discrepancy. As mentioned earlier, the exact nature of bond formation in LB films of metal salts of fatty acids is not well-understood,[34,35] and therefore, further work is required before quantification of the role of counterions on chemical shifts of carboxylate carbons can be attempted. It is interesting to note that while the ΔE_{BE} values reported for cadmium arachidate films on different substrates were obtained from a two-component fit of the C 1s spectra, Burns and Swalen have mentioned the presence of an additional component in the C 1s spectrum of cadmium arachidate at a BE of 285.5 eV.[14] Aligning the C 1s spectrum of Burns and Swalen (283.6 eV BE for the hydrocarbon chain)[14] with the value of 285 eV obtained in this study leads to a BE

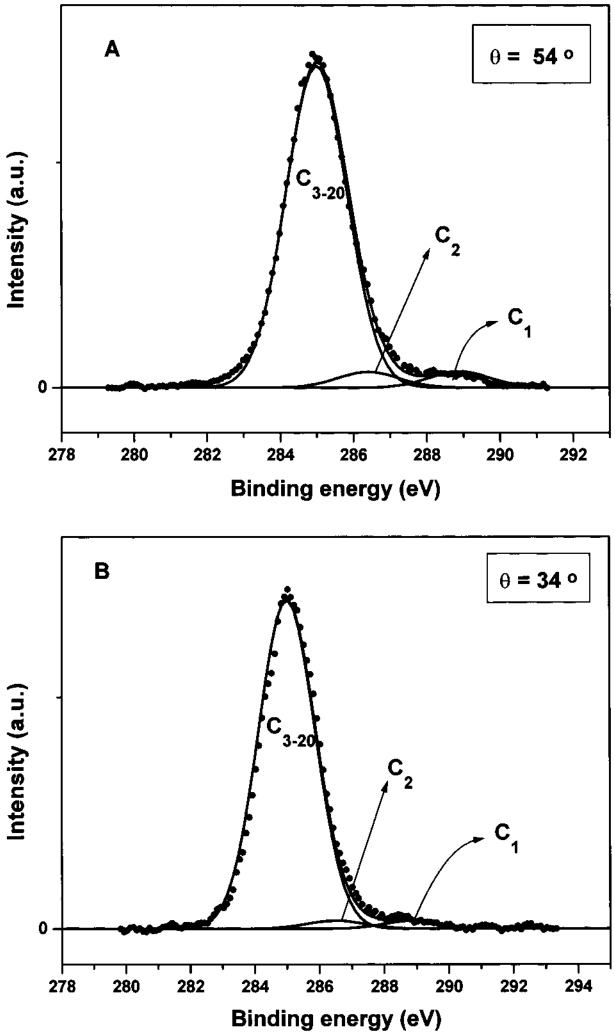


Figure 3. (A) C 1s spectrum of a 3 ML lead arachidate film on Cu substrate at an ETOA of 54° (filled circles) together with a three-component fit (solid lines). (B) C 1s spectrum of a 3 ML lead arachidate film on Cu substrate at an ETOA of 34° (filled circles) together with a three-component fit (solid lines).

of 286.9 eV for the carbon coordinated to the carboxylate carbon (C$_2$, Figure 1a) in cadmium arachidate and is in reasonable agreement with the MS predicted value of 286.1 eV (Table 2) and in excellent agreement with the value of 286.6 eV obtained from a three-component fit of PbA LB films (Figure 3a, Table 3). This lends additional support to the BE value predicted by the MS formalism for PbA films as demonstrated above. We also add here that Burns and Swalen recorded the C 1s spectra in their acid and salt LB films using monochromatized Al Kα radiation with a higher degree of spectral resolution.[14] Therefore, the three individual components are clearly seen and do not overlap significantly. Such is not the case in the spectra of this study, and therefore, identification of the true number of spectral components and their binding energies becomes more important.

We investigated the contribution of the background subtraction procedure as well as different Gaussian/Lorentzian mixing ratios for the individual spectral components used in the fits. It was observed that both linear and Shirley[39] background subtractions did not result in significantly different parameters obtained from either a two-component or three-component fit to the C 1s spectrum. Increasing the Lorentzian component in the individual spectral components resulted in an increase in the χ^2 error value for both the two- and three-component fitting procedures. Pure Gaussian spectral components gave the best fits to the C 1s core level data, and all parameters listed in Table 3 are based on such fits.

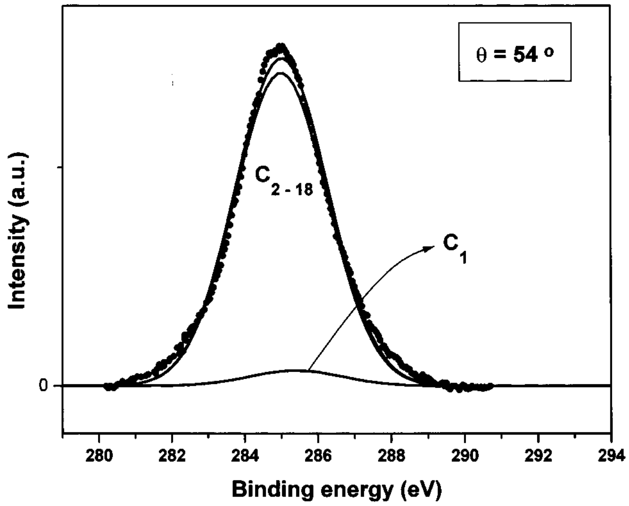


Figure 4. C 1s spectrum of a 31 ML octadecylamine−chloroplatinic acid film on Si(111) substrate at an ETOA of 54° (filled circles) together with a two-component fit (solid lines).

At low ETOA values, the discrete layer model predicts an increase in the hydrocarbon (C$_{3-20}$) to C$_1$ and C$_2$ peak area ratios.[22−24] This is due to the lamellar structure of lead arachidate films in which the hydrocarbon layer of ~27 Å thickness covers the C$_1$ and C$_2$ carbons, leading to significant attenuation of the C$_1$ and C$_2$ signals. At an ETOA of 34°, the model predicts this ratio to be ~37. Figure 3b shows the C 1s spectrum of the lead arachidate film at ETOA = 34° along with a three-component fit. As in the earlier case, all parameters were left free during the fit and are listed in Table 3. In this case as well, the BEs are close to those predicted from MS partial charge calculation (Tables 2 and 3). Another important point to note is that the peak area ratios of C$_{3-20}$:C$_1$ and C$_{3-20}$:C$_2$ calculated from the fit (40.4) are close to that expected from the model (37, Table 3). The fact that the carbon spectral component ratios agree with the expected values from a discrete layer model calculation at two vastly different electron emission angles strongly supports the MS formalism prediction of an additional “induction” effect component.

Two components are predicted in the C 1s spectra of LB films of octadecylamine−chloroplatinic acid (Table 2). Figure 4 shows the C 1s spectrum (ETOA = 54°) from the amine LB film together with a two-component fit. The parameters obtained from the fit are given in Table 3. In this case as well, the BEs of the two components from the fit agree well with those calculated using the MS formalism (Tables 2 and 3). The C$_{2-18}$:C$_1$ peak area ratio as calculated from the fit is 20.4 which is close to the value of 20.5 expected from the discrete layer model. The standard deviation of the Gaussian components was determined from the fit shown in Figure 4 to be 1.15 eV for the Am-HPt film and is considerably larger than the value of 0.85 eV determined for the PbA LB film. This broadening may be due to charging effects arising from the insulating nature of the LB films and is expected to play a role in the 31 ML Am-HPt film on Si (111) substrates whereas it is negligibly small for the 3 ML PbA film on Cu substrates. While the agreement between the BE values determined from the fit shown in Figure 4 and those predicted from the MS calculation (Table 2) is heartening, the broadening of the C 1s core level signal for the Am-HPt film mentioned above would make it difficult to assign confidence limits to the values obtained from the fits. The point

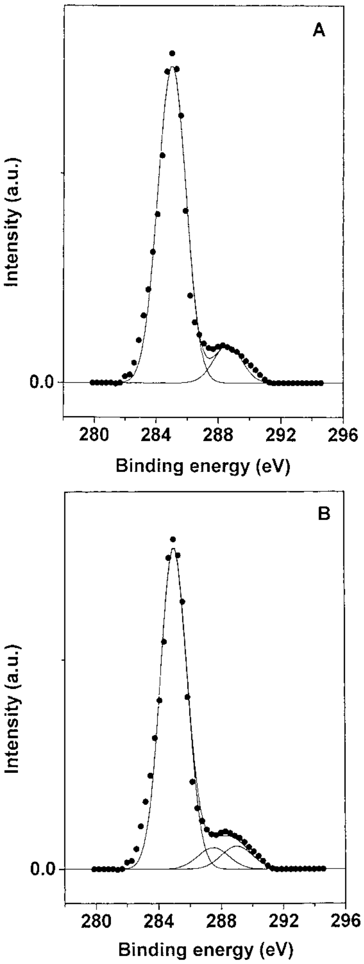


Figure 5. (A) C 1s spectrum of a 40 ML barium stearate film measured at an ETOA of 90° (filled circles) together with a two-component fit (solid lines). The C 1s spectrum has been taken from the work of Kajiyama et al. (ref 16). (B) C 1s spectrum of a 40 ML barium stearate film measured at an ETOA of 90° (filled circles) together with a three-component fit (solid lines). The C 1s spectrum has been taken from the work of Kajiyama et al. (ref 16).

we emphasize is that the induction effect would lead to a detectable component arising from the carbon coordinated to the amine group (Figure 1b).

To provide further evidence for the presence of an additional induction effect component in LB films, we have digitized and analyzed the C 1s spectra from 40 ML barium arachidate films reported by Kajiyama et al.[16] The spectrum recorded at an ETOA of 90° in particular shows the presence of a strong carboxylate carbon component due to the smaller chain length in the stearate molecules. Therefore, the confidence limits of the parameters obtained from the fits to such a spectrum will be consequently higher. We have performed a similar two- and three-component fit to the 90° ETOA C 1s data of Kajiyama et al.[16] and the results of the fits are shown in parts a and b of Figure 5, respectively. The parameters obtained from the fits are listed in Table 4. As in the case of the C 1s spectra of PbA presented earlier, a two-component fit leaves a residue at ~287 eV and therefore shows the presence of a component at close to this BE. The ratio of the alkyl carbon to carboxylate carbon intensities from the two-component fit is determined to be 8.40, which is considerably lower than the expected ratio of 18 (Table 4). A three-component fit, however, leads to intensity ratios between the alkyl carbons and the carboxylate and induction effect carbons (ca. 16 in each case) which are close to the expected value of 18. It can also be seen from a comparison of Tables 3 and 4 that the BE values of the different carbons in the barium stearate films are fairly close to those obtained for PbA films of this study and therefore close to the values predicted by the MS formalism. The above result is particularly gratifying since all fitting parameters were left free in the analysis and indicates that the MS formalism together with the MS charge−BE correlation established earlier[10a] can be seriously applied to Langmuir−Blodgett films.

TABLE 4: Parameters Obtained from the Fits of the C 1s Core Level Spectra of a 40 ML LB Film of Barium Stearate Taken from Kajiyama et al. (Ref 16)

carbon no.	BE (eV)	peak area	cald area ratio	expected ratio
		Barium Stearate (Two-Component Fit)		
C_{2-18}	285.0	1		
C_1	288.6	0.119	$C_{2-18}/C_1 = 8.40$	18
		Barium Stearate (Three-Component Fit)		
C_{3-18}	285.0	1		
C_2	287.2	0.063	$C_{3-18}/C_2 = 15.8$	18
C_1	289.1	0.064	$C_{3-18}/C_1 = 15.5$	18

From the results presented above, it is clear that the MS formalism for partial charge calculation along with the linear regression parameters of ref 10a successfully predicts C 1s core level chemical shifts in LB films of fatty acid salts and amine complexes. The MS formalism prediction of an additional “induction effect” component at ca. 286.5 and 285.5 eV for the lead arachidate and Am-HPt films leads to meaningful quantitative analysis of the films as well. Future work will be directed toward understanding and quantifying the role of the counterion on chemical shifts of carboxylate carbons in fatty acid LB films as well as application of the MS formalism to self-assembled monolayer films where interaction with the substrate is expected to play a large role in determining the chemical shifts.

Acknowledgment. The authors thank the LB and ESCA groups, NCL Pune, for assistance in film preparation and time on the XPS machine. This work was partially funded by the Indo-French Centre for Promotion of Advanced Research (IFCPAR).

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