Investigation of the depth of preferential surface ordering in liquids: A photoelectron spectroscopic investigation of liquid mixtures

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Angle resolved x-ray photoelectron spectroscopic studies of a series of liquid mixtures of a perfluoropolyether (Krytox 16350) and a polyphenylether (Santovac-5) show that the former spreads on the latter and the film thickness could even be smaller than the photoelectron mean free path. The molecular ordering in krytox remain as that of the free liquid which is manifested in the enhancement of the relative intensity of specific features in the photoelectron spectrum as the electron take-off angle is decreased. The preferential ordering is limited to the very top and an upper limit of this thickness is estimated to be about 8 Å. This observation is in accordance with molecular dynamics simulations of long chain hydrocarbon liquids. © *1997 American Institute of Physics.* [S0021-9606(97)02502-6]

I. INTRODUCTION

Molecular dynamics and related computational techniques have proved that the surface of liquids are molecularly ordered.[1–6] Simulations of long chain liquids such as decane and ecosane are available[6] which suggest that the end groups are projected outwards on the liquid surfaces. There are many studies on smaller liquids[7–9] where the interest is to study the ordering of the chemical functionality at the surface. These studies have been supported in detail by surface potential and related measurements.[10] Independent studies using second harmonic generation sum frequency spectroscopy have, also in general, supported theoretical studies.[11]

Our studies[12–14] on the surfaces of molecular liquids have shown the capabilities of photoelectron spectroscopy in understanding the finer details of molecular level ordering at the surface. Due to the short time scale of the process and the high surface sensitivity, the technique is specially well suited to study dynamic systems. In a recent investigation, we have shown that the surface chemical composition of a series of perfluoropolyethers is grossly similar, although there are differences regarding the extent of spatial order in these systems.[12] These experimental studies are in accordance with low energy ion scattering measurements,[15] in which the technique has a better surface sensitivity.

One of the fundamental issues concerning surface ordering is the depth to which the order exists. Molecular dynamics studies indicate that sharp differences in properties occur at a depth of around 5–10 Å, from the free liquid surface.[6] This difference in properties is due to variation in molecular ordering from the surface to the bulk. Although the existence of preferential surface ordering is well established, no experimental measurement so far has clearly shown the depth to which such ordering prevails. In the following, we describe an experimental approach which seems to suggest that the molecular level ordering persists only to a depth of a few angstroms from the air-liquid interface.

II. EXPERIMENT

The photoelectron spectra were measured using a VG ESCALAB MK II spectrometer with a Mg Kα radiation at a base pressure of 8×10^{-10} Torr. The liquids used for the study were perfluoropolyether, $F[CF(CF_3)CF_2O]_nCF_2CF_3$[16] ($n$, average number of repeating units, >70) and polyphenylether, $Ph-O-Ph-O-Ph-O-Ph-O-Ph$[17] with trade names krytox 16350 and santovac-5, respectively. The krytox 16350 [PFPE] liquid has a vapor pressure of $<4 \times 10^{-15}$ Torr, a density of <1.95 gm/cm^3, and a viscosity of 3500 centistokes whereas santovac-5 [PPE] has a vapor pressure of 2.6×10^{-10} Torr, density of 1.195 gm/cm^3, and a viscosity of 2400 centistokes (all at 20 °C). The krytox sample manufactured by Dupont was a gift from Professor R. G. Cooks of Purdue university. Santovac-5 is a product of Monsanto company and was obtained from Edwards Ltd. All the spectra were averages of 10 scans of 60 s duration and the x ray was maintained at a low power of 80 W to avoid any surface damage.

A series of liquid mixtures of krytox 16350 and santovac-5 were prepared and sheeted on gold coated glass substrates for x-ray photoemission spectroscopy (XPS) measurement. Above a concentration of 1:100 (by volume) between PFPE and PPE, respectively, no santovac was detected in the XPS measurements. At each composition, the surface segregation of various species was investigated by varying the electron take-off angle.

III. RESULTS AND DISCUSSION

A single molecule of krytox 16350 consists of >71 $-CF_3$ groups, >72 $-CF_2$ groups, and >69 $-CF_2$ groups. The CF_2 groups are of two kinds, two CF_2 groups at the chain ends and the remaining CF_2 groups in the repeating units. It is hard to differentiate these two kinds of $-CF_2$ groups. Moreover, it is difficult to distinguish the CF_2 and

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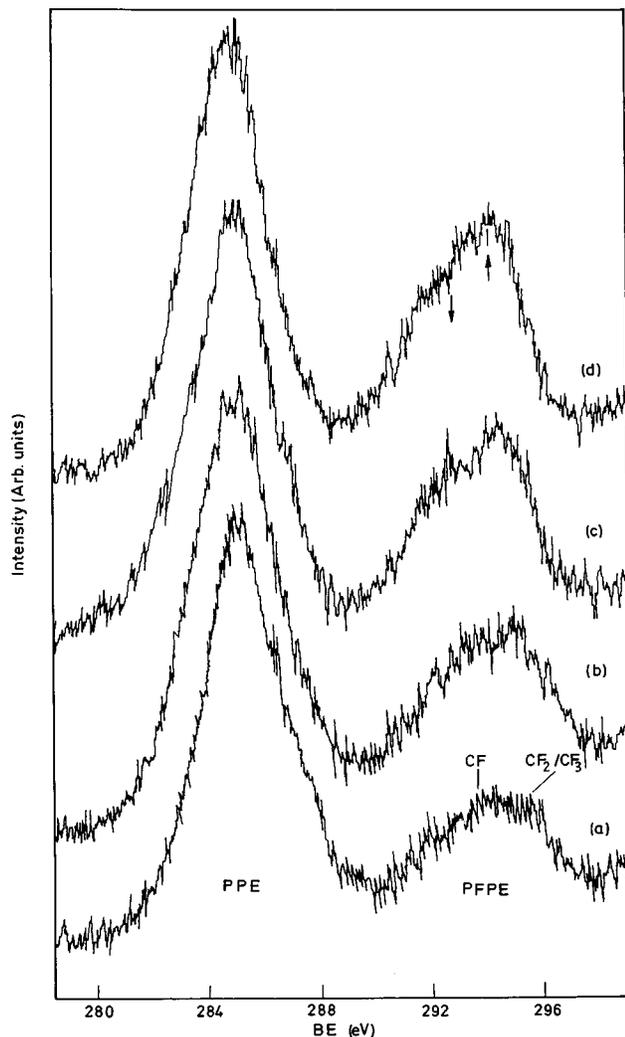
FIG. 1. X-ray photoelectron spectrum of the C 1s region of a mixture of perfluoropolyether and polyphenylether in the 1:100 volume ratio at various electron take-off angles. The various features are indicated. (a) 80, (b) 50, (c) 30, (d) 10^0. Note the increase in intensity of the CF$_2$/CF$_3$ feature as the take-off angle is decreased. Arrows show the direction of intensity variation.

FIG. 2. X-ray photoelectron spectrum of the C 1s region of a mixture of perfluoropolyether and polyphenylether in the 1:100 volume ratio at various electron take-off angles. (a) 80, (b) 50, (c) 30, (d) 10^0. Arrows indicate the direction of intensity variation.

CF$_3$ carbons with a nonmonochromatic x-ray source, since the binding energies of these two carbons will be close to each other. This is because CF$_2$ groups are attached to oxygen atoms in the repeating unit. But CF carbon will have a substantially lower binding energy. Therefore the C 1s region of PFPE is expected to show two peaks corresponding to −CF group and −CF$_2$/CF$_3$ group ionizations, with the former having a lower binding energy.

Santovac-5 is a polyphenylether with five phenyl groups connected by ether linkages at the para position with a molecular weight of 446. There are two different types of carbon atoms in the interconnecting phenyl rings in the 1:2 ratio. On the terminal phenyl rings, there are four distinctly different carbons. However, in the resolution of the present measurement, only one type of C 1s feature is observable.

In Fig. 1, we show the C 1s spectrum of a mixture of PFPE and PPE in the 1:100 volume ratio, respectively, at electron take-off angles of 80, 50, 30, and 10°. The spectra
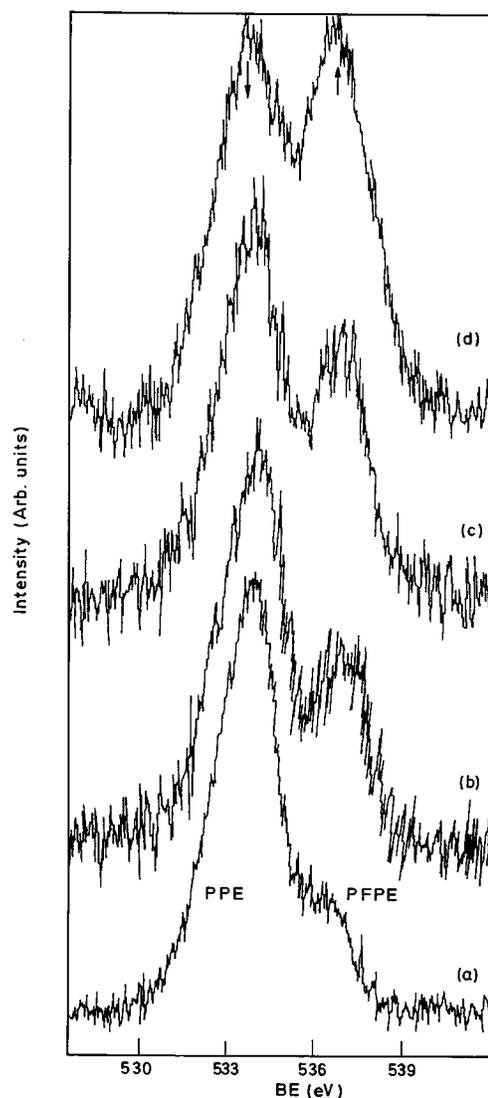
show two bands around 285.5 and 294.3 eV corresponding to santovac-5 and krytox 16350, respectively. Upon decreasing the electron take-off angle, the C 1s intensity in krytox region of the spectrum varies as in the case of pure krytox, where we see a systematic enhancement of CF$_2$/CF$_3$ intensity with decreasing take-off angle.[12–14] No variation in the C 1s spectrum of the santovac region is expected as the various C 1s species in santovac-5 exhibit similar C 1s binding energy. It is also apparent that the relative intensity of the krytox bands increase in intensity over the santovac feature and therefore it is concluded that the krytox is spread over santovac-5.

Significant differences are observed in the O 1s spectrum which is shown in Fig. 2. The spectra show two features at 533.5 and 536.6 eV, corresponding to PPE and PFPE oxygen atoms, respectively. Upon decreasing electron take-off angle, we see that the O 1s corresponding to krytox

16350 is increasing in intensity and no change in binding energy or peak width is apparent. It may be noted that the F 1s region at 688.6 eV binding energy does not show any variation with electron take-off angle just as in the case of pure krytox.[12] Increasing the krytox ratio in the sample makes the santovac features disappear completely from the C 1s and O 1s spectra.

An interpretation of experimental results requires an appreciation of the organization of the constituent liquids at the liquid-vacuum interface. Taking a photoelectron escape depth of 30 Å,[18–20] if the x-ray photoelectron spectrum has to manifest two distinct oxygens, either the liquids have to be miscible at the surface or one of the liquids form a molecular film with a thickness smaller than the escape depth. The increased intensity of C 1s and O 1s features corresponding to krytox 16350 at various electron take-off angles suggest an increased surface concentration of krytox. It has been observed that the relative intensity of the CF_2/CF_3 peak of the krytox increases with decreasing electron take-off angle. The lack of any santovac feature in krytox rich compositions indicate that the miscibility between the two liquids is extremely poor and the surface is essentially composed of either of the free liquids. Taken together, it may be concluded that the krytox forms a layer on the santovac liquid.

The foregoing suggest that the liquid surface is layered. However, there can be two possible major orientations for each of the layers. Either the constituent molecules can lie horizontally so that both the constituents are detected simultaneously with an increase in intensity of krytox as the electron take-off angle is decreased. This orientation does not support the observation of that in the liquid mixture, the C 1s intensity of krytox varies exactly like the free liquid, and is shown that krytox possesses a high degree of surface order with molecular ends protruding towards the surface.[12–14] The horizontal orientation is also not in accordance with adsorption studies of mixtures, in which we find that the surface is essentially devoid of contaminants and adsorbed species for extremely long periods of time. If the molecules of krytox were lying horizontal to the surface, it is expected that the oxygen atoms would be exposed resulting in the adsorption of contaminants. The other possible arrangement so as to account for the observed data is one in which the krytox molecules are ordered perpendicularly up to a few angstroms beneath the surface and thereafter disordered like the bulk of the liquid. Organized molecular assembly of krytox over santovac with the entire molecular chain standing up vertically although possible does not support the observation of both santovac and krytox in XPS. The suggested structure would give rise to several tens of angstroms of a krytox liquid layer followed by the santovac layer. This ordering can fully account for the observed photoelectron spectra. It may be noted that as we increase the krytox concentration, only pure krytox is detected having the same kind of surface order as in

the case of pure liquid. None of the liquid mixture compositions showed the presence of santovac alone at the surface.

There could be other possible interpretations to account for the observed C 1s and O 1s spectra. They are not in full agreement with studies of liquid mixtures of other compositions and adsorption measurements. Lack of computational studies on the molecular ordering of ultrathin liquid layers on liquid surfaces does not permit us to fully appreciate the experimental observations. It is apparent from the result that the depth to which surface order exists in liquids is substantially short. Taking a mean free path of C 1s photoelectrons to be 30 Å, an upper limit of the region of surface order could be estimated to be about 8 Å. Such assessment is in agreement with the molecular dynamics simulations of free hydrocarbon liquids.[6] It is gratifying that a simple technique such as XPS gives the most direct information as to the depth of surface order in binary liquids. It may also be noted that to the best of our knowledge no experimental evidence is available until now on this aspect.

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