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Quantitative treatment of surface potentials in Langmuir films from aromatic amphiphiles

Patrycja Dynarowicz-Łątka [a,*], Ailton Cavalli [b], Demétrio A. Silva Filho [c], Piotr Milart [a], M. Cristina dos Santos [c], Osvaldo N. Oliveira [d]

[a] *Jagiellonian University, Faculty of Chemistry, Ingardena 3, 30-060 Kraków, Poland*
[b] *Universidade Estadual do Norte Fluminense, Campos dos Goytacazes, 21949 Rio de Janeiro, RJ, Brazil*
[c] *Universidade Estadual de Campinas – Instituto de Física Gleb Wataghin, Campinas, SP, Brazil*
[d] *Instituto de Física de São Carlos, Universidade de São Paulo, CP 369, CEP 13560-970, São Carlos, SP, Brazil*

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Abstract

It is shown that the surface potentials of Langmuir monolayers from aromatic compounds can be interpreted using the three-layer capacitor model of Demchak and Fort, with the same local dielectric constants employed for aliphatic compounds. Based on new data for monolayers from an acid, amine and ester compounds with an aromatic hydrophobic part, we show that the dielectric constant for the monolayer/water interface region is 6±1. Good agreement between experiment and theory was obtained by taking the dielectric constant of the monolayer/interface as 3.0±0.6, which are essentially the same as those obtained for long tail aliphatic compounds. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The surface potential technique has been used in the characterization of Langmuir monolayers for several decades, but progress in the quantitative interpretation of measured values has been rather slow. A turning point was the publication in 1974 of the Demchak and Fort (DF) three-layer capacitor model [1], in which the surface potential, ΔV, was assumed to arise from the dipole moments in distinct parts of the monolayer and with such parts possessing distinct local dielectric constants, according to Eq. (1):

$$\Delta V = (1/A\varepsilon_0)[\mu_1/\varepsilon_1 + \mu_2/\varepsilon_2 + \mu_3/\varepsilon_3], \tag{1}$$

where A is the area per molecule, ε_0 is the vacuum permittivity, μ_1 is the vertical component of the effective dipole moment due to reorientation of water dipoles caused by the introduction of film-forming molecules at the water interface, and μ_2 and μ_3 are the vertical components of group dipole moments in the hydrophilic and hydrophobic parts of the molecule, respectively. Each of such dipoles is embedded in a medium with a local dielectric permittivity, ε_i.

Using experimental data for non-ionised Langmuir monolayers of *p*-terphenyls, Demchak and Fort obtained quantitative agreement between theory and experiment by assuming that the dielectric constants were $\varepsilon_3 = 5.3$ for the air/monolayer interface, $\varepsilon_2 = 7.6$ for the monolayer/water

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[*] Corresponding author. Fax: +48-12-340515.
E-mail address: ucdynaro@cyf-kr.edu.pl (P. Dynarowicz-Łątka).

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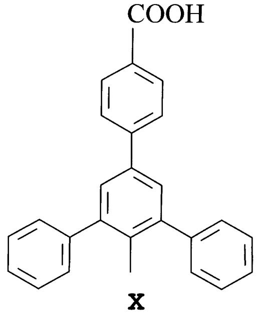
interface and that $\mu_1/\varepsilon_1 = +0.04$ D [1]. This approach was later applied to adsorbed (Gibbs) monolayers formed by small, water-soluble amphiphilic molecules [2–6] as well as for Langmuir films from insoluble amphiphiles [7,8], while a similar 2-layer model was used by Vogel and Möbius [9]. Oliveira et al. [7], in particular, demonstrated that for aliphatic compounds the value of $\varepsilon_3 = 5.3$ suggested by Demchak and Fort was far too high to explain experimental data from halogenated compounds. It was then shown [7] that for aliphatic compounds, agreement with the experiments required the following parameters: $\mu_1/\varepsilon_1 = -0.065$ D, $\varepsilon_2 = 6.4, \varepsilon_3 = 2.8$. It is worth mentioning that the latter value for ε_3 is corroborated by a theoretical treatment by Taylor and Bayes [10]. Progress has also been made in the interpretation of the double-layer contribution to the surface potential in ionized monolayers, for it has been shown [11] that at least for weakly ionized monolayers spread on aqueous subphases with monovalent ions, the simple Gouy–Chapman theory may provide good agreement with experimental results.

In summary, the monolayer surface potentials of simple aliphatic compounds could be explained quantitatively, but the question of whether different parameters should be employed for aromatic compounds remained. Testing the DF approach for the latter compounds was not possible for a number of years because surface potential data were not available for simple, purely aromatic compounds for which the contributions from the group dipole moments could be estimated. Recently, however, we have succeeded in synthesising a series of aromatic homologues of polyphenyl carboxylic acids from which stable Langmuir monolayers could be obtained [12]. Comparing the effective dipole moments of such acids differing in their hydrophobic parts, we were able to show [13] that the local dielectric constant at the monolayer/air interface, ε_3, is 3.0 ± 0.6, i.e. essentially the same as for aliphatic molecules (2.8 [7]). Important for such an achievement was the possibility of estimating the dipole moment components for relatively large molecules, which is now possible using semi-empirical quantum chemistry methods [14]. In this Letter, we present results for aromatic compounds with head groups other than the carboxylic acid, thus allowing us to also estimate the dielectric constant at the monolayer/water interface, ε_2. This is done with monolayer results from 5′-phenyl-1,1′:3′,1″-terphenyl tail attached to the amino ($-NH_2$) or methyl ester ($-COOCH_3$) head group, which were synthesised with this purpose. Both compounds are capable of stable film formation at the free water surface. The analysis of such experimental data provided a complete picture for the interpretation of surface potentials for aromatic as well as aliphatic compounds. The implications of this achievement are discussed along with the limitations in the application of the DF approach.

2. Experimental

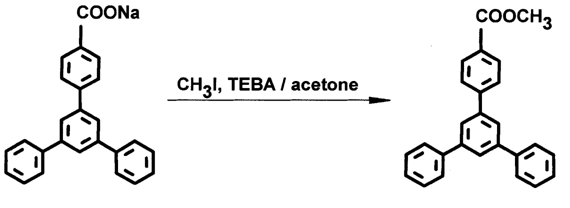
2.1. Synthesis

5′-phenyl-1,1′:3′,1″-terphenyl-4-carboxylic acid, abbreviated as PTCA (compound **1**, Scheme 1) was synthesised according to the procedure described in [15]. Methyl 5′-phenyl-1,1′:3′,1″-terphenyl-4-carboxylate **(3)** was readily obtained by alkylation of the sodium salt of the parent carboxylic acid [15] under phase transfer catalysis (Scheme 2). 5′-phenyl-1,1′:3′,1″-terphenyl-4-amine **(5)** was prepared by reduction of the appropriate nitro compound, which was synthesised applying



Compound (1) – PTCA : X = -H

Scheme 1. Chemical structure of 5′-phenyl-1,1′:3′,1″-terphenyl-4-carboxylic acid, in short PTCA (compound **1**).



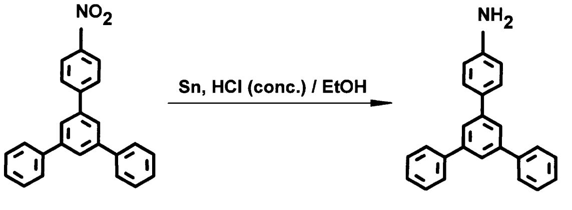
(2) (3)

Scheme 2. Synthetic path to methyl 5′-phenyl-1,1′:3′,1″-terphenyl-4-carboxylate (compound **3**).

the Zimmermann and Fischer method [16] (Scheme 3).

2.1.1. *Methyl 5′-phenyl-1,1′:3′,1″-terphenyl-4-carboxylate (3)*

A mixture of sodium 5′-phenyl-1,1′:3′,1″-terphenyl-4-carboxylate **(2)** (0.37 g, 1 mmol), methyl iodide (0.70 g, 5 mmol), TEBA (0.1 g) and dry acetone (10 ml) was stirred and refluxed for 4 h. After cooling to room temperature, a small amount of colorless material was separated by filtration and washed with acetone. The solvent was removed at reduced pressure. The crude product was treated with water, filtered off, washed with water and cold methanol (5 ml). It was purified by recrystallization from methanol and dried in air. Yield: 0.26 g (72%). M. p. 132.3°C. Anal.Calc. for $C_{26}H_{20}O_2$: %C 85.67; H 5.54. Found: %C 85.87; H 5.63. IR (KBr) í [cm^{-1}] 3061, 2998, 2954, 2841 (CH); 1718 (C=O); 1608, 1594 (aromatic rings); 1276 (C—O). ^1H NMR ($CDCl_3$) δ [ppm] 3.95 (s, 3H, OCH_3); 7.40 (t, 2H, $J_{ortho} = 7.3$ Hz, protons *para* of rings at 3′ and 5′); 7.49 (t, 4H, $J_{ortho} = 7.3$ Hz, protons *meta* of rings at 3′ and 5′); 7.69 (d, 4H, $J_{ortho} = 7.3$ Hz, protons *ortho* of rings at 3′ and 5′); 7.76 and 8.14 (2d, 4H, AA′BB′, $J_{ortho} = 8.3$ Hz, protons of the ring with $COOCH_3$ group); 7.80 (s, 2H, protons 2′ and 6′); 7.82 (s, 1H, proton 4′).



(4) (5)

Scheme 3. phenyl-1,1′:3′,1″-terphenyl-4-amine (compound **5**).

2.1.2. *5′-Phenyl-1,1′:3′,1″-terphenyl-4-amine (5)*

A vigorously stirred suspension of 4′-nitro-5′-phenyl-1,1′:3′,1″-terphenyl **(4)** (0.35 g, 1 mmol) and tin powder (0.5 g) in ethanol (10 ml) was heated to 80°C. Concentrated hydrochloric acid (5 ml) was slowly added during 2.5 h. The mixture became almost clear. Then it was cooled to room temperature and filtered. The filtrate was poured into stirred 10% sodium hydroxide solution (ca. 50 ml). The separated amine was filtered off, washed with water and a small amount of cold ethanol. For further purification, the crude product was suspended in ethanol (20 ml) and refluxed for 30 min. The colorless solid was separated and dried in vacuum at 80°C. An analytical sample was obtained by vacuum sublimation at ca. 1 mm Hg. Yield: 0.28 g (87%). M. p. 152.3°C. Anal. Calc. for $C_{24}H_{19}N$: %C 89.67; H 5.97; N 4.36. Found: %C 89.94; H 6.05; N 4.46. IR (KBr) í [cm^{-1}] 3444, 3369 (NH); 3029 (CH); 1618 (NH); 1590, 1517 (aromatic rings); 1291 (NH). ^1H NMR (DMSO-d_6) δ [ppm] 5.30 (s, 2H, NH_2); 6.69 and 7.56 (2d, 4H, AA′BB′, $J_{AB} = 8.5$ Hz, protons of the ring with —NH_2 group); 7.40 (t, 2H, $J_{ortho} = 7.3$ Hz, protons *para* of rings at 3′ and 5′); 7.50 (t, 4H, $J_{ortho} = 7.3$ Hz, protons *meta* of rings at 3′ and 5′); 7.73 (t, 1H, $J_{meta} = 1.4$ Hz, proton 4′); 7.76 (d, 2H, $J_{meta} = 1.4$ Hz, protons 2′ and 6′); 7.84 (d, 4H, $J_{ortho} = 7.3$ Hz, protons *ortho* of rings at 3′ and 5′).

2.2. *Langmuir monolayers*

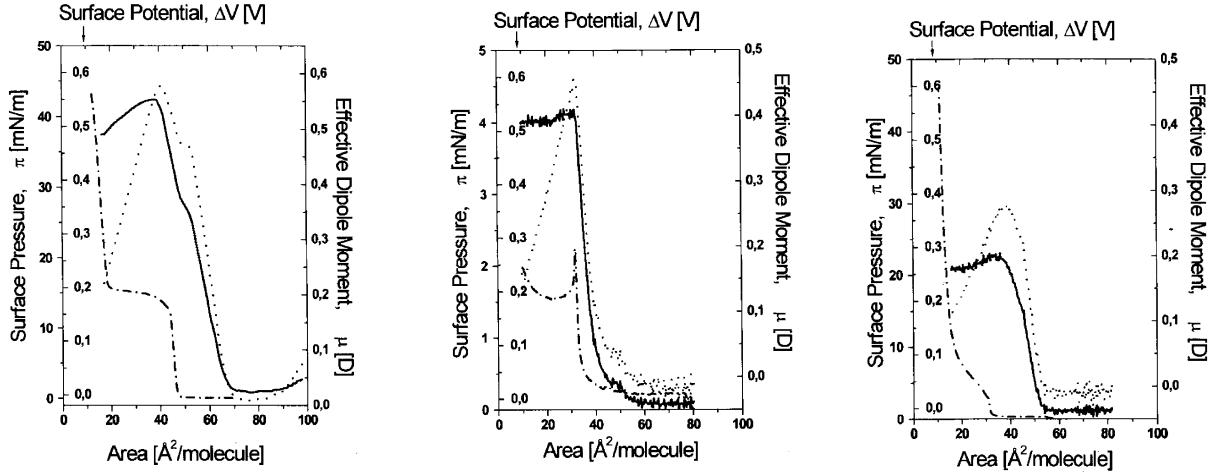
Spreading solutions were prepared by dissolving the investigated compound (~0.5 mg/ml) in freshly distilled, spectroscopic grade chloroform. Ultrapure water from a Nanopure (infinity) coupled to a Milli-Q water purification system (resistivity = 18.2 MΩ cm) was used as a subphase. To obtain non-ionised films, PTCA methyl ester was spread on pure water, while the carboxylic acid (PTCA) and amine were spread on aqueous acidic (10^{-3} M. HCl) and basic (10^{-3} M. NaOH) solutions, respectively. Monolayers were spread on a KSV-5000 LB trough (total area = 730.5 cm^2) placed on an anti-vibration table in a class 10 000 clean room. The surface pressure of the monolayer was measured to an accuracy of 0.1 m N m^{-1} with a Wilhelmy plate (made of chromatography paper, ash-less Whatman Chr 1) connected to an electrobalance. Simultaneously, the surface potential was monitored using a vibrating plate located ca. 2 mm above the water surface. The reference electrode, made from platinum foil, was placed in the water subphase. The surface potential measurements were reproducible to ±10 mV. Monolayers were usually compressed with a barrier speed of 25 mm/min (equivalent to a compression rate of 7.5×10^{17} Å^2/min) at 20°C.

2.3. Characterization methods

IR spectra were recorded on a Bruker IFS48 spectrometer as KBr pellets. ^{1}H NMR spectra were taken at 500.13 MHz with a Bruker AMX500 spectrometer using DMSO-d_6 or $CDCl_3$ as solvents and TMS as an internal standard. Elemental analyses were carried out in the Regional Laboratory of Physicochemical Analyses, Kraków, Poland. Melting points were determined with Mel-Temp II melting point apparatus in open capillaries and are uncorrected.

3. Results and discussion

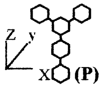
Fig. 1 presents surface pressure (π), electric surface potential (ΔV) and effective dipole moment ($\mu_\perp$)-area isotherms of the non-ionised films of PTCA **(1)**, its methyl ester **(3)** and amine **(5)**. The data for PTCA (Fig. 1a) have already been reported and are reproduced from a previous Letter [13]. The potential (solid line) and effective dipole moment (dotted line) already start to increase at ca. 60 Å^2/molecule, when the surface pressure (dashed-dotted line) is still zero. Upon further compression, the surface potential and effective dipole moment increase steeply, reach a maximum and then decrease when the surface pressure is already non-zero. For a detailed description and interpretation of the isotherms, the readers are referred to [12]. The maximum in surface potential/effective dipole moment appears at the same molecular area (36 ± 3 Å^2/molecule), regardless of the kind of hydrophilic head group of



(1) **(3)** **(5)**

Fig. 1. Surface pressure (π) (dashed-dotted), surface potential (ΔV) (solid) and effective dipole moment ($\mu_\perp^{\mathrm{exp}}$) area (A) isotherms of PTCA (compound **1**), its methyl ester (compound **3**) and amine (compound **5**) spread on 10^{-3} M HCl aq. (compound **1**), water (compound **3**) and 10^{-3} M NaOH aq. (compound **5**) at 20°C; compression speed 25 mm/min.

Table 1
Comparison of experimental and calculated dipole moments of investigated aromatic amphiphiles

Compound	Polar group (P)	Effective dipole moment, $\mu_\perp$ [D]		Dipole moments in vacuum, μ [D][a]		
		$\mu_\perp^{\text{calc}}$	$\mu_\perp^{\text{exp b}}$	μ_z [c]	μ_{x-y} [d]	μ_{total}
	—COOH	0.54	0.53	2.675	1.127	2.903
	—COOCH$_3$	0.44	0.45	2.10	1.40	2.50
	—NH$_2$	0.29	0.27	1.20	1.25	1.73

[a] Calculated with HyperChem.

[b] The values are given within an experimental error of ±0.03.

[c] Component of the dipole moment normal to the interface.

[d] Component of the dipole moment parallel to the interface.

the molecule. At this area, the molecules are assumed to take nearly vertical (to the surface) orientation as the effective (normal) dipole moment has its maximum value. Using the Demchak and Fort model and assuming that the contributions from the hydrophobic group (μ_3/ε_3) and of the oriented water dipoles (μ_1/ε_1) are independent of the head group, the difference in the total, experimentally measured dipole moment ($\mu_\perp^{\text{exp}}$) can be ascribed to differences in the contribution from the head group of the molecule (μ_2/ε_2). In order to determine ε_2, pairs of Eq. (1) have to be solved for monolayers of molecules with identical hydrophobic group and different hydrophilic heads. Assuming the same contribution from hydrated water, the resulting equation has the following form:

$$(\mu_2^{\text{a}} - \mu_2^{\text{b}})/\varepsilon_2 = \mu_\perp^{\text{exp a}} - \mu_\perp^{\text{exp b}}. \tag{2}$$

In the above formula, the superscripts a and b refer to two distinct compounds in the pair used for comparison, and $\mu_\perp^{\text{exp}}$ is the product ($\Delta VA\varepsilon_0$). The maximum values of the experimental effective dipole moments for the investigated compounds ($\mu_\perp^{\text{exp}}$) are compiled in Table 1, which also includes the calculated values, as discussed later. One also need to estimate the dipole moment from the hydrophilic groups, μ_2. Because the interactions with the neighbouring dipoles and with the medium as a whole are incorporated in the dielectric constant, μ_2 is the vertical component of the dipole moment in vacuum. These values may be obtained by subtracting the C^-H^+ dipole moment (0.4 D [17]) from the normal component of the dipole moment of the free molecule (μ_z) for benzoic acid, methyl benzoate and aniline, respectively, calculated with HyperChem [1] in the semi-empirical AM1 (Austin Model 1) parameterization [18–20]. The normal components depend on whether a *cis or trans* configuration is assumed for the carboxylic and ester head group. Table 2 contains the values of μ_2 obtained using the above-mentioned procedure.

Solving equations of type (2) for all three combinations of pairs, the mean local dielectric constant ε_2 was found to be 6.0±1.0, if the *cis* configuration is assumed for both acid and ester head groups. For *trans* conformation, a reasonable value (6.6) is obtained only when ester and acid are solved in pairs; in the other cases ε_2 is very high (14.3 and 17.7 when the acid and ester are solved in pair with the amine, respectively). It is worth pointing out that $\varepsilon_2 = 6.0 \pm 1.0$ for the aromatic compounds matches very well with the value of 6.4 found by Oliveira et al. [7] for aliphatic amphiphiles. Using the average value of $\varepsilon_3 = 3.0$, as obtained for a series of PTCA derivatives [13], and obtaining μ_3 theoretically using HyperChem, the remaining parameter, μ_1/ε_1, was found to be -0.065 ± 0.015 D for good agreement to be obtained with the experimental results. Similarly to [13], μ_3 was calculated by subtracting the normal component of the dipole moment of the respective hydrophilic group (μ_2) from the normal counterpart of the dipole moment of the free molecule of PTCA, its methyl ester and amine (μ_z). Table 1 shows the comparison with experimental data, when the three average parameters were employed, viz. $\varepsilon_2 = 6.0$, $\varepsilon_3 = 3.0$ and $\mu_1/\varepsilon_1 = 0.065$ D.

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[1] HyperChem Professional Release 5.1, A Molecular Visualization and Simulation Software Package, Hypercube, Gainesville, Florida, 1998.

Table 2
Calculated values of dipole moments of free molecules of benzoic acid, methyl benzoate and aniline

Compound		Dipole moments in vacuum, μ [D][a]		
		μ_z[b]	μ_{x-y}[c]	μ_{total}
Benzoic acid	C_6H_5—COOH	*cis* 2.13 *trans* 4.42	1.10	2.42
Methyl benzoate	C_6H_5—$COOCH_3$	*cis* 1.60 *trans* 3.89	1.30	2.11
Aniline	C_6H_5—NH_2	0.70	1.40	1.54

[a] Calculated with HyperChem.

[b] Component of the dipole moment normal to the interface.

[c] Component of the dipole moment parallel to the interface. Values presented in the table are for the *cis* configuration of the hydrophilic group.

Thus it is evident that the electrical parameters for monolayers of aliphatic and aromatic amphiphiles are practically the same. This generality may imply that any type of material can be analyzed, provided that one can estimate the group dipole moments with some degree of accuracy. In this context, the use of semi-empirical methods, as in this work, may allow extension of the analysis to larger molecules, such as the phospholipids that are widely investigated, and whose surface potential data have not been explained quantitatively in an unequivocal way. There is one important limitation, however, in the cases where the assumptions inherent in the DF approach are not valid. For instance, as emphasised in [13], when highly polar groups are incorporated into the hydrophobic part, one can no longer assume that the dielectric constant of a given medium is independent of the molecular group. Neither can one assume that a contribution from one layer does not affect the other one, which is an important tenet of the DF model. The revised Taylor and Bayes model [21] clearly shows that the value of ε_2 depends on the dipole species incorporated in the molecule. They had shown earlier [10] that the layers can be considered as non-interacting and thus treated independently (which is the basic assumption of the DF model) only for long-chain molecules where headgroup and tailgroup dipoles are more than about 10 methylene units apart. Since it is known that the hydrophobicity of a phenylene group is comparable to that of an aliphatic fragment with 4±0.5 methylene groups [22], the polyphenyl compounds investigated here, whose hydrophobic part contains four benzene rings, can be treated as analogues of alkanoic amphiphiles with 16 methylene groups. Therefore, PTCA, its methyl ester and amine are suitable materials for the DF model, which justifies the good agreement between theory and experiment reported here.

Iwamoto and co-workers [23–25] have also developed theoretical models for monolayer films, where it is found that the dielectric constant depends on the alignment and dipole density of the array of dipoles assumed to represent the monolayer [23]. They did not distinguish between the contributions from the hydrophilic and hydrophobic groups, but rather treated the molecular moments as point dipoles associated with tilted rod-like molecules arranged on a hexagonal lattice [23,24]. Considering the randomizing effect of thermal energy on molecular orientation and conformation, the relative permittivity of a simple long-chain alkanoic acid monolayer was found to be 1 in the expanded region and ca. 2 in the condensed state, which confirms earlier findings by Taylor and Bayes [10]. Moreover, they also found that for the estimation of the local dielectric constant account should be taken of the dielectric anisotropy inherent in the monolayers owing to the symmetry breaking at the air/water interface [25].

It should be stressed that the parameters obtained here to input in the DF model are only average values. It is clear that small changes in such values still lead to good agreement between theory and experiment, provided that the other parameters are also altered. Nevertheless, one may be sure that the dielectric constants are within certain ranges, which are between 5 and 8 for ε_2 and between 2 and 4 for ε_3, and these figures could be used as first input in a more refined analysis, where the assumptions of the DF models are relaxed. This can be done using models such as those of [21,23–25], by allowing the dielectric constant to vary with the molecular group, in addition to investigating the influence of a polar group in the hydrophobic tail on the dipole contributions of the other layers. From the experimental point of view, surface potential data will be required of compounds where the hydrophilic and hydrophobic parts are altered in a systematic way.

Acknowledgements

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