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SHORT COMMUNICATION

M. Paluch

Surface mixed adsorption films of 2,4,6-trimethylphenol–2,4,6-trichlorophenol at aqueous solution/air interface

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Dr. M. Paluch (✉)
Department of Physical Chemistry
and Electrochemistry
Faculty of Chemistry
Jagiellonian University
PL-30060 Kraków
Poland

Abstract The results of experimental studies of the adsorption at the solution/air interface from an aqueous mixture: 2,4,6-trimethylphenol–2,4,6-trichlorophenol are presented. The surface properties of the above-mentioned mixture were studied by surface potential and surface tension measurements. These measurements were carried out as a function of the concentration of 2,4,6-trimethylphenol aqueous solution at a constant concentration of 2,4,6-trichlorophenol.

Using the results obtained and based on the Gibbs equation, Helmholtz formula and Motomura's method the relative surface excesses of adsorbed substances, effective dipole moments, surface molar fractions of solutes and miscibility of adsorbed films were determined.

Key words Mixed adsorption films – aqueous solution/air interface – surface potential – surface tension

Introduction

On the free surface of water exists the potential drop across the surface layer (1–4). The absolute value of this potential drop is not a measurable quantity. Introduction of surface-active compound to the surface layer causes a change in the potential drop on the surface. This change is usually called the surface potential ΔV of the solution [6–7]. The surface potential ΔV can be quantitatively interpreted by analogy with the plate condenser according to Helmholtz formula [8]

$$\Delta V = \frac{4\Pi\bar{\mu}n}{\varepsilon}\,, \tag{1}$$

where n is the number of molecules in the adsorbed film present per cm^2 of the surface, $\bar{\mu}$ is the average vertical component of the dipole moment of the molecule at the surface and ε is the relative dielectric permittivity of the adsorbed films.

Customarily, it is assumed that ε is unity, (although some authors take the value equal to 6 [9]) and that

$$\bar{\mu} = \mu \cos\theta\,, \tag{2}$$

where θ is the angle of inclination of the dipoles to the normal.

The effective dipole moment $\bar{\mu}$ can be written as a sum [7]

$$\bar{\mu} = \bar{\mu}_1 + \bar{\mu}_2 + \bar{\mu}_3 \tag{3}$$

which represents, reorientation of water molecules ($\bar{\mu}_1$) and effective dipole moments of hydrophilic ($\bar{\mu}_2$) and hydrophobic ($\bar{\mu}_3$) part of molecule.

Some authors [10–13] have completed the Eq. (3) with the local dielectric permittivities in the vicinity of the hydrophilic and hydrophobic groups of the adsorbed molecule.

In the case when there are two or more surface active compounds in a solution, mixed adsorption films are generated. The parameters which determine their surface

behaviour are different from those in the case of one-component films and depend on the kind of interaction between molecules of particular compounds in the mixed film and in the bulk of the solution, as well as between solvent and solute molecules. Mixtures of similarly structured surfactants, were aproximated well by ideal solution theory [14–16], while the mixtures of ionic–non-ionic and cationic–anionic surfactants–by regular solution theory [17, 18].

Mixed adsorption films usually have a different composition to the bulk solution from which they were generated. The composition is defined as follows:

$$X_2^s = \frac{\Gamma_2}{\Gamma_2 + \Gamma_3}\,, \tag{4}$$

$$X_3^s = \frac{\Gamma_3}{\Gamma_2 + \Gamma_3}\,, \tag{5}$$

where X_2^s, X_3^s, Γ_2 and Γ_3 represent the molar fraction and surface excess of compounds 2 and 3 at the aqueous solution/air interface, respectively. The studies of Motomura and coworkers [19–22] on mixed adsorption films clarified the relation between the composition of the adsorption film and of the bulk solution. They showed that the X_2^s value can be calculated thermodynamically from the experimental results of surface tension measured as a function of the composition and the total molarity of the surfactant mixture in aqueous solution.

$$X_2^s = X_2 - (X_3 X_2/m.)(\delta m/\delta X_2)_{p,T}\,, \tag{6}$$

where $X_2 = m_2/m.$ and $m. = m_2 + m_3$ is total molarity of bulk solution.

The plots of $m.$ vs X_2 and $m.$ vs X_2^s at constant surface tension values appear as analogues of the three-dimensional phase diagram designating the equilibrium compositions of coexisting two phases.

The above-mentioned studies share an interest in typical amphipathic solutes. However, there are many organic compounds whose molecules do not have a typical hydrophobic–hydrophilic structure, but show a tendency to accumulate at the free surface of water, forming adsorption films and altering, both the surface tension and the surface potential. In our laboratory we have studied the surface properties of such compounds [23–29]. It is especially interesting to investigate the influence of adsorbed molecules that have the same hydrophilic groups but different hydrophobic groups either of similar or different polarities on the surface potential changes. In such a situation both a decrease and an increase of surface potential may occur. This effect is relevant to the hydrophobic part of the adsorbed molecule, since the effect, from the hydrophilic group and the reorientation of water molecules would be nearly the same.

In the present paper the properties of adsorbed films prepared from 2,4,6-trimethylphenol and 2,4,6-trichlorophenol and their mixtures at the water/air interface are discussed. The molecules of these substances contain the same hydrophilic group (–OH). The difference in the polarity of the hydrophobic parts of 2,4,6-trimethylphenol and 2,4,6-trichlorophenol should give values of an opposite sign for the surface potentials of their aqueous solution. In the case of mixed films, the effects resulting from the polarity of the hydrophobic groups are additive, therefore the change in the surface potential would depend on the composition of the film and interaction between adsorbed molecules.

Experimental

2,4,6-trimethylphenol (Fluka AG, Switzerland) and 2,4,6-trichlorophenol (Aldrich-Chemie, Germany) were used as experimental materials. These substances were not purified further. Water was distilled four times.

The surface tension of the solution was measured by the drop weight method at a constant temperature (293 $\pm$ 0.1 K). The radius of the stalagmometer tip was 0.2355 cm. The accuracy of measurements was $\pm$0.1 mN/m. The time of the drop formation (30 s) was empirically established to obtain the equilibrium value of the surface tension: Harkins and Browns corrections were used in calculating the surface tension.

The surface potential measurements were based on the flowing jet method, which was described in detail by Kamieński [2]. In the case of chemical compounds of low and moderate molecular weight, this method is reliable. The measurements were performed at room temperature (ca. 293 K); measurement accuracy was $\pm$5 mV.

The investigated substances were dissolved in 0.1 M potassium chloride aqueous solution in order to reduce the streaming potential which may occur in the flowing jet method.

Results and discussion

The surface tension and surface potential were measured as a function of the concentration of 2,4,6-trimethylphenol aqueous solution at constant concentration of 2,4,6-trichlorophenol under atmospheric pressure and constant temperature. The concentrations of 2,4,6-trichlorophenol were 0, 0.00075, 0.001, 0.00125, 0.0015, 0.002 M, respectively. Figures 1 and 2 show the results obtained. As we can see from the comparison of the results in Fig. 1. the surface potential was changed by 2,4,6-trichlorophenol in an opposite way than by 2,4,6-trimethylphenol. Adsorbed

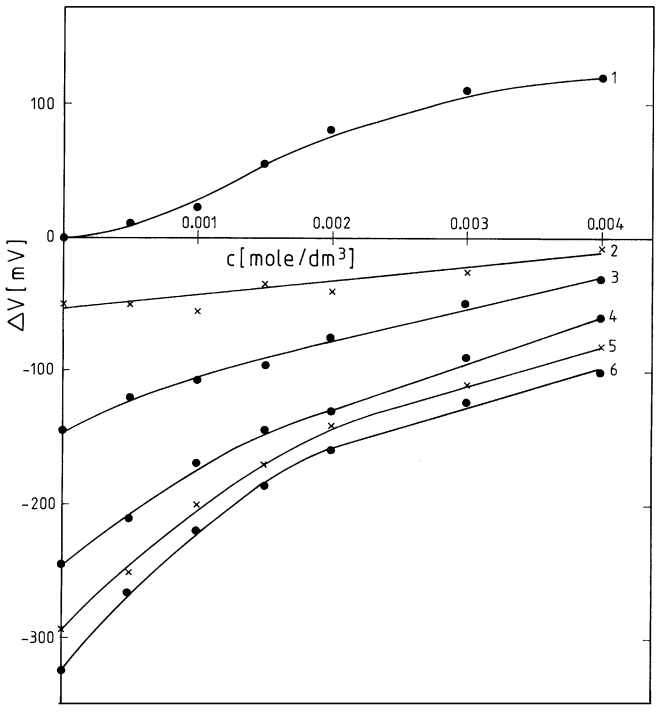

Fig. 1 Surface potential as a function of 2,4,6-trimethylphenol concentration at constant 2,4,6-trichlorophenol concentration in aqueous solution. (1) 0 M; (2) 0.00075 M; (3) 0.001 M; (4) 0.00125 M; (5) 0.0015 M; (6) 0.002 M

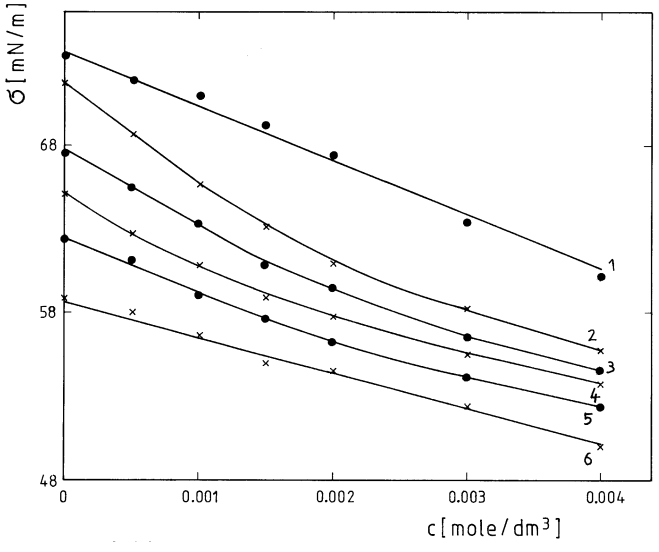

Fig. 2 Surface tension as a function of 2,4,6-trimethylphenol concentration at constant 2,4,6-trichlorophenol concentration in aqueous solution. (1) 0 M; (2) 0.00075 M; (3) 0.001 M; (4) 0.00125 M; (5) 0.0015 M; (6) 0.002 M

molecules of 2,4,6-trichlorophenol on the free surface increase the natural surface potential of water by removing a number of oriented water molecules from the water/air interface and by charging the interface with their own fields. This effect was also observed earlier [24–30]. The increase is to be expected only if we assume that the potential drop on the free surface of water has a negative sign in the direction of air and that molecules of 2,4,6-trichlorophenol orient themselves at the phase boundary with the OH group in the direction of the bulk water phase and the benzene ring with the halogenosubstituent directed towards the air.

Addition of 2,4,6-trichlorophenol to a solution of 2,4,6-trimethylphenol causes a strong change in the surface tension and the surface potential of such solutions. Using the concentration dependence of surface tension (Fig. 2) as well as the Gibbs equation in the form (assuming that surface excess for water molecules, Γ_1, equals zero):

$$\Gamma_2 = -\frac{a_2}{RT}\left(\frac{\delta\sigma}{\delta a_2}\right)_{p,T,a_3}, \tag{7}$$

$$\Gamma_3 = -\frac{a_3}{RT}\left(\frac{\delta\sigma}{\delta a_3}\right)_{p,T,a_2}, \tag{8}$$

where σ is the surface tension of the solution and Γ_2 and Γ_3 represents the surface excess and a_2, a_3 the activity of 2,4,6-trimethylphenol and 2,4,6-trichlorophenol solution, respectively. The quantities of co-adsorbed 2,4,6-trichlorophenol and 2,4,6-trimethylphenol have been determined. In the calculations of Γ_2 and Γ_3 excess activities (a) were replaced by concentration (c).

The derivatives $(\delta\sigma/\delta c)$ in these equations were estimated by fitting the surface tension results $\sigma = f(c)$ to the polynomials. The obtained polynomials were analytically differentiated to give the corresponding surface excess. The dependence of the surface excess of 2,4,6-trimethylphenol on its concentration in solution at a constant concentration of 2,4,6-trichlorophenol are presented in Fig. 3. From this figure it is evident that with low concentrations of both the compounds in the solution, the surface activity of 2,4,6-trimethylphenol is higher than in the one-component system. From the surface excess Γ, the number of molecules adsorbed on 1 cm^2 of area was obtained.

Knowing the number of adsorbed molecules at the free surface it is possible to determine the effective dipole moment, $\bar{\mu}$, of the molecule. For calculating $\bar{\mu}$ the dependence of surface potential vs number of molecules on a unit area, n, is necessary. If this dependence is linear over a wide range of n, the parameter $\bar{\mu}$ can be obtained from the slope of the straight line. The obtained dependence for 2,4,6-trimethylphenol and 2,4,6-trichlorophenol is presented in Fig. 4. From here it is evident that the orientation of molecules at the interface is constant and does not depend on the expansion of the surface phase. The values of effective dipole moments are compiled in Table 1, column II. In this Table there are also the effective dipole moments

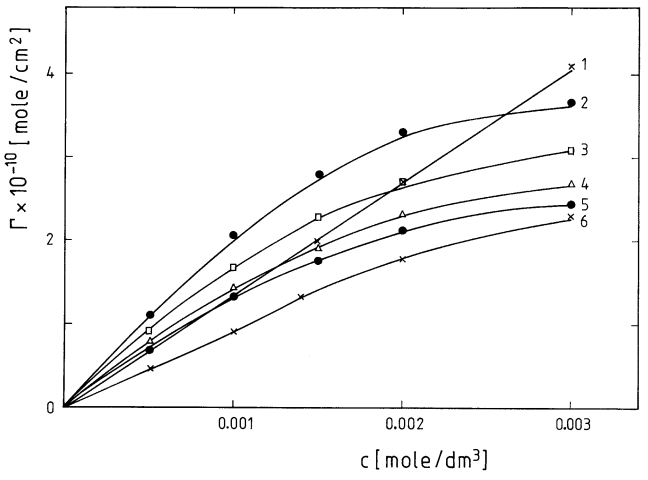

Fig. 3 Dependence of surface excess of 2,4,6-trimethylphenol on concentration at constant concentration of 2,4,6-trichlorophenol: (1) 0 M; (2) 0.00075 M; (3) 0.001 M; (4) 0.00125 M; (5) 0.0015 M; (6) 0.002 M

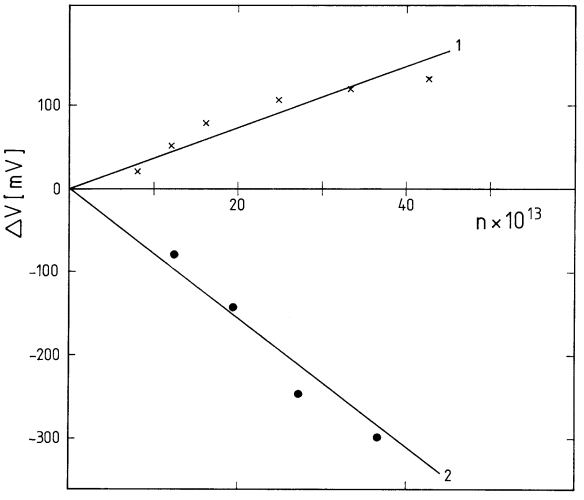

Fig. 4 Dependence of surface potential vs the number of molecules adsorbed on 1 cm^2 of surface: (1) 2,4,6-trimethylphenol, (2) 2,4,6-trichlorophenol

values for phenol, *p*-chloro and *p*-methylphenol. The dates are adopted from our earlier paper (30). The + or − sign of $\bar{\mu}$ results from the negative values of the surface potential of aqueous solutions of 2,4,6-trichlorophenol and the positive value of 2,4,6-trimethylphenol. The accuracy of the effective dipole values is ± 10 mD. When we compare the value of effective dipole moment of phenol, *p*-chlorophenol and *p*-methylphenol molecule with effective dipole moment of 2,4,6-trimethylphenol and 2,4,6-trichlorophenol we can see that they are all of the different order indicating that $\bar{\mu}$ is strongly determined by the number,

Table 1 Some data characteristic for molecules adsorbed on the air/water interface

Compound	$\bar{\mu}$ [D]	$\bar{\mu}_{\text{hydroph.}}$ [D]	μ [D]	Angle of surfacial orientation
2,4,6-Trimethylphenol	0.100	0.066	1.36	85°
2,4,6-Trichlorophenol	− 0.217	− 0.251	1.62	82°
p-Methylphenol	0.265	0.231	1.64	80°
p-Chlorophenol	− 0.590	− 0.624	2.27	75°
Phenol	0.034	—	1.45	88°

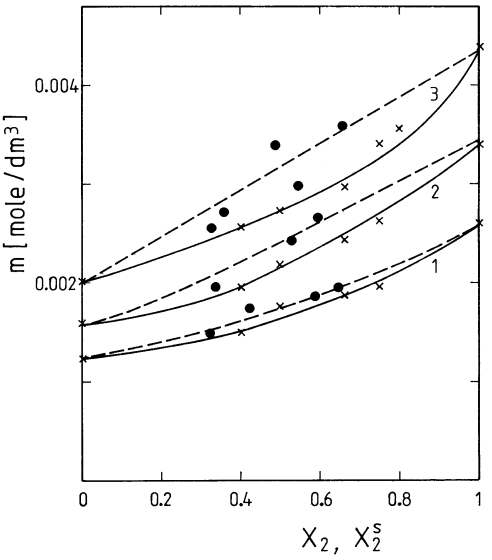

Fig. 5 Total molarity vs composition curves at fixed surface tension: (1) $\sigma = 65$ mN/m, (2) $\sigma = 62$ mN/m, (3) $\sigma = 59$ mN/m; (full line) X_2 (broken line) X_2^s, X_2 is the mole fraction of 2,4,6-trimethylphenol in the bulk solution, X_2^s is the surface mole fraction of 2,4,6-trimethylphenol

nature and position of the substituent in the hydrophobic group. Subtracting the value of the effective dipole moment of phenol from the value of the effective dipole moment of 2,4,6-trimethylphenol and 2,4,6-trichlorophenol it was possible to calculate a difference between effective dipole moments of the $-CH_3$, –Cl and –H groups.

The results are shown in Table 1, column III.

Knowing the effective dipole moments of adsorbed molecules ($\bar{\mu}$) and dipole moments of free molecules (μ) (Table 1, column IV (31)) and using Eq. (6), the surface orientation angle was determined (Table 1, column V). The larger this angle, the more horizontal the orientation of the molecule in the surface layer and smaller effect on surface potential changes.

The existence of interaction between the adsorbed molecules in the surface film was checked by using Motomuras method. To this purpose the plot of surface tension (σ) vs

total molarity (m) of solution was prepared at a constant mole fraction of 2,4,6-trimethylphenol (X_2). Using the experimental results presented in this plot and Eq. (6), the phase diagram was obtained. This phase diagram (Fig. 5) represents the total molarity vs composition in the bulk solution (X_2) and the adsorbed film (X_2^s) at constant surface tension $\sigma = 59$, 62 and 65 mN/m. It is seen from Fig. 5 that molarity vs surface mole fraction of 2,4,6-trimethylphenol curves deviate negatively from the straight line connecting the m values of pure 2,4,6-trichlorophenol and 2,4,6-trimethylphenol. This deviation is not significant. We may suggest that the mixing of 2,4,6-trichlorophenol and 2,4,6-trimethylphenol molecules in the adsorbed film is slightly non-ideal and weak attraction exists between adsorbed molecules in the surface layer.

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