Studies on Adsorption of Organic Compounds at Mercury-Solution Interface: Individual & Simultaneous Adsorption of p-Aminobenzoic Acid & Sulphanilamide

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Adsorption of sulphanilamide and of p-aminobenzoic acid from KNO_3 solutions at mercury-solution interface has been investigated. The dipole potential has been evaluated and is found to obey the BDM theory at not too high positive charges on mercury. Surface excess values are reported over the entire range of potentials. Studies on simultaneous adsorption of the above organics have also been made from solutions containing both the entities. It is concluded that though adsorption of one takes place by displacement of the other, adsorption of both is observed over the whole range of potentials.

IN our previous paper[1], we reported our findings on the simultaneous adsorption of hydroxybenzoic acid isomers at mercury-solution interface, where it was observed that the presence of two adsorbable entities in solution reduced the extent of adsorption of either when present singly and that the fraction of surface covered by two adsorbates was not additive with respect to the individual adsorptions. A quantitative approach has been attempted for such adsorption by Tedoradze et al.[2] while Damaskin et al.[3] suggested that the argument for two position isotherm (see also Parry and Parsons[4]) be used to study adsorption of two organics at the same time. The data for such interpretation is limited in that the individual coverage in simultaneous adsorption is very seldom reported. In this paper, we report complete data regarding the individual and simultaneous adsorption of p-aminobenzoic acid (PABA) and sulphanilamide (SA) at mercury-solution interface.

The choice of these compounds was made because of the antimetabolic activity of SA which is a structural analogue to PABA, a metabolic factor in the growth of bacteria[5].

Materials and Methods

The Lipmann electrometer described elsewhere[6] was used to obtain interfacial tension at various applied potentials. The measured potentials are correct up to ± 1 mV. A saturated calomel electrode was used as reference in all the experiments and the potentials (E) reported are with respect to SCE. The base electrolyte was $0 \cdot 1M$ KNO_3, the ionic strength being maintained constant in all the experiments. Since the reference electrode was not changed, liquid junction potentials are assumed to be approximately the same in all experiments. The potentials (E) will differ from the potentials (E^-) obtained with reference to an electrode reversible to an anion in solution as required, if the general electrocapillary equation[7] is to be used. However, this difference will be a constant for all values of potentials reported involving no error in the computations from the general equation. Solutions were made in triply distilled water and deoxygenated using purified nitrogen. Triply distilled mercury was used in the electrometer. KNO_3 (BDH Analar) was purified by twice recrystallization from water and dried in a vacuum desiccator. PABA and SA (E. Merck, Analar) were purified by recrystallization from aqueous solutions. Their purity was checked by observing their melting points. The cell was thermostated at a temperature of $34° \pm 0 \cdot 2°$.

Results and Discussion

Electrocapillary curves and surface excess — The electrocapillary curves for PABA and SA for concentrations ranging from $2 \times 10^{-4}M$ to $10^{-2}M$ are shown in Figs. 1 and 2 together with the base line curve for $0 \cdot 1M$ KNO_3. The maximum concentration used in the case of SA is the saturation concentration. For these compounds, it is seen that the potential of electrocapillary maximum (e.c.m.) shifts to more negative potentials with respect to that for base solution in conformity with the observed behaviour for aromatic compounds. For equivalent concentrations, PABA is found to lower the interfacial tension to a greater extent than SA. The curves however, appear to coincide with the base curve at extreme negative and positive polarizations showing desorption of adsorbed entity at the extreme ends of the potential scale. This becomes more obvious when the surface excess which is equal to

$$-\left(\frac{\delta \Upsilon}{RT\delta \ln a}\right)_E$$

where Υ is interfacial tension and 'a' is the activity of organic (here assumed to be equal to concentration since low concentrations are employed) is calculated by differentiating the interfacial tension versus log C curves at constant potential. A graphical differentiation was carried out to obtain
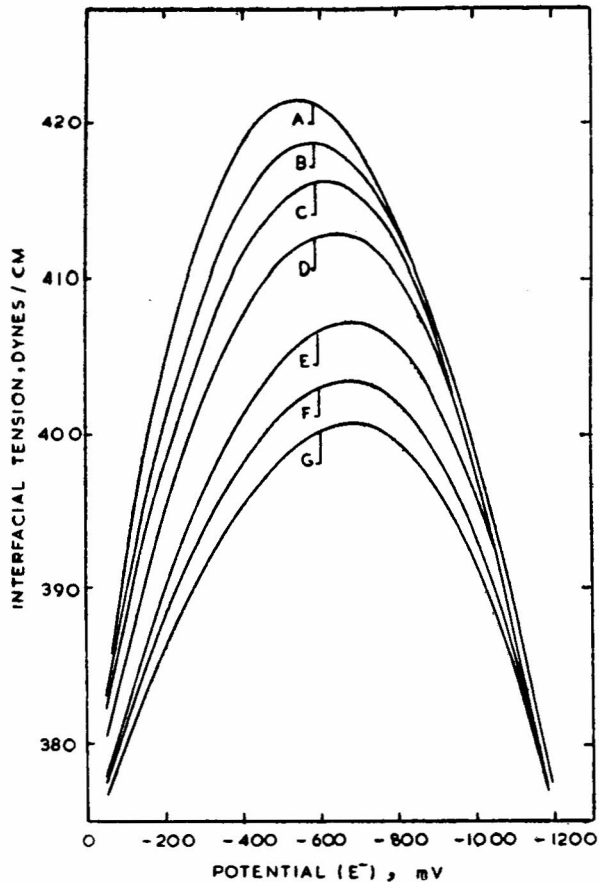
Fig. 1 — Electrocapillary curves for $0.1M$ KNO_3+(A)O; (B) 2×10^{-4}; (C) 5×10^{-4}; (D) 1×10^{-3}; (E) 3×10^{-3}; (F) 6×10^{-3}; (G) $1\times10^{-2}M$ p-aminobenzoic acid solution
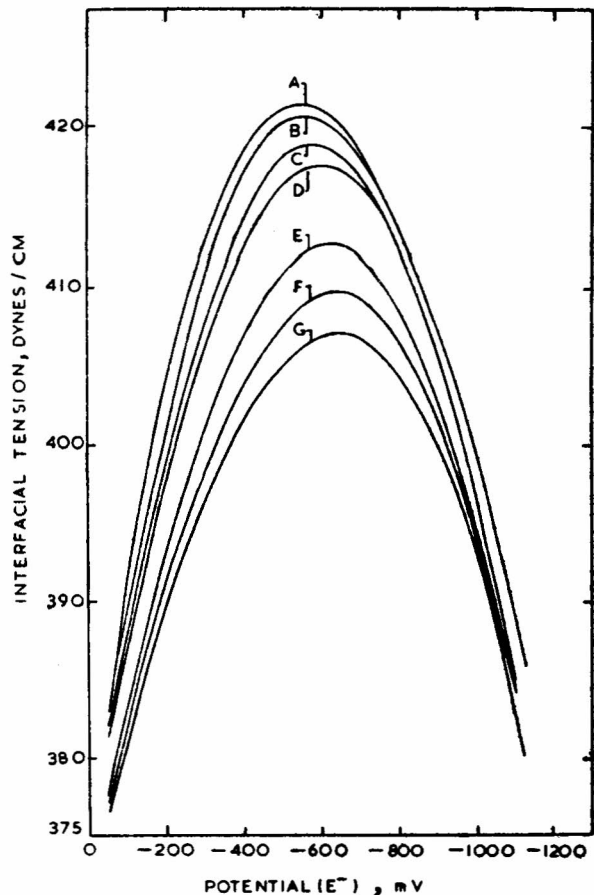
Fig. 2 — Electrocapillary curves for $0.1M$ KNO_3+(A)O; (B) 2×10^{-4}; (C) 5×10^{-4}; (D) 1×10^{-3}; (E) 3×10^{-3}; (F) 6×10^{-3} and (G) $1\times10^{-2}M$ sulphanilamide solution

the surface excess which involved a personal error of $\pm5\%$ at extreme ends of the potential scale.

The electrode charge (q) was obtained as a function of potential by differentiating the electro-capillary curves at various values of potentials. From these values, the dependence of surface excess (Γ) on charge q was plotted (Figs. 3 and 4). It is seen that the curves are symmetrical about the point of maximum adsorption which is $+3$ μ Coul. cm^{-2} for SA and 1.8 μ Coul. cm^{-2} for PABA. It is to be noted that this value is concentration dependent in the case of PABA becoming slightly negative at higher concentrations. The concentration dependence for SA is not however noticeable. Such concentration dependence of q_{max} has also been noticed previously[8]. From these curves, it is apparent that both SA and PABA adsorb in single orientation since at extreme polarization, no tendency to reorient is observed and desorption takes place. From the shift of e.c.m. with concentration to more negative potentials, it is obvious that the molecules prefer an orientation with the negative end of the dipole towards the mercury.

Shift in the potential at constant charge q due to interfacial adsorption — The observation that the potential at constant q changes with adsorption of the organic is to be correlated with the dipolar potential due to adsorption at the interface. The displacement of water molecules by the organic
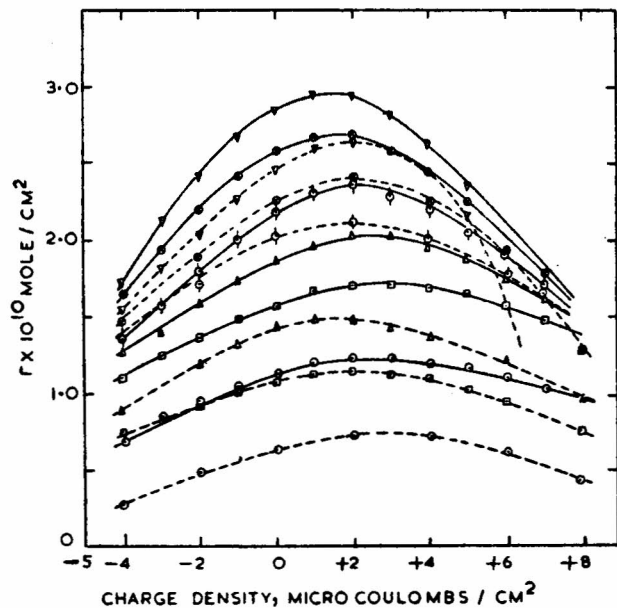

Fig. 3 — Surface excess vs charge density for PABA concentration of 2×10^{-4} (⊙); 5×10^{-4} (▣); 1×10^{-3} (△); 3×10^{-3} (⊙); 6×10^{-3} (⊗); 1×10^{-2} (▽); [Without SA (full lines) and with SA (dotted lines)]
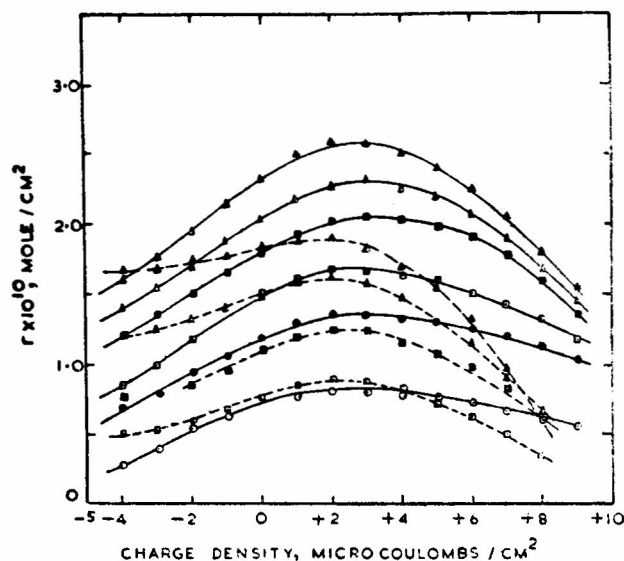
Fig. 4 — Surface excess vs charge density for SA concentration of 5×10^{-4} (●); 1×10^{-3} (□); 3×10^{-3} (■); 6×10^{-3} (△); 1×10^{-2} (▲) [Without PABA (full lines) and with PABA dotted lines]

Fig. 5 — Dependence of ΔE on Γ_{PABA} in the case of PABA at 6 (○); 4 (△); 2 (□); 0 (●); −2 (▲); −4 (⊗) q^M

contributes to the change in the χ potential which is a sum of the contribution due to water in down ($\downarrow$) and up ($\uparrow$) positions[9]. Further the organic molecules contribute their own dipolar potential proportionate to amount adsorbed. Thus, we can write

$$\Delta E = \frac{x \Gamma_{org.}}{\epsilon_s} \left[\frac{N\uparrow - N\downarrow}{N_T} \right] 4\pi \bar{\mu}_{H_2O} + \frac{4\pi \mu_{org.} \, \Gamma_{org.}}{\epsilon_s} \quad \dots (1)$$

where the factor in the bracket (called R) represents the net fractional orientation of water molecule, ϵ_s is the dielectric constant and μ's are the dipole moments, x is the size factor equal to the ratio of cross sectional areas of organic to water molecule. It has been shown that in the case of organic molecules with $\mu = 0$, the ΔE depends solely on the first term[10]. $\Delta E / \Gamma_{org.}$ plots at constant q for PABA and SA are shown in Figs. 5 and 6. Rearranging Eq. (1), we obtain

$$\Delta E = \left[x \left(\frac{N\uparrow - N\downarrow}{N_T} \right) \bar{\mu}_{H_2O} + \mu_{org.} \right] \frac{4\pi}{E} \Gamma_{org.} \quad \dots (2)$$

which shows that the shift (ΔE) is linearly dependent on $\Gamma_{org.}$ at constant q, since R is solely dependent on q as per BDM theory. From Figs. 5 and 6, it is observed that linear plots are realized only when q is less than ~4 μ Coul. cm^{-2}. The change in slope of the linear plots with charge on electrode can be attributed to change in R, i.e. net orientation of solvent molecules in the interface. At large positive q the curves deviate enormously from linearity. This is probably due to the π-electron interaction of the organic with the positively charged electrode in addition to the fact that at high positive q, specific adsorption of NO_3^- will be taking place. An implicit explanation of the nature of $\Delta E / \Gamma$ curves thus is not feasible due to complexities of the phenomenon.
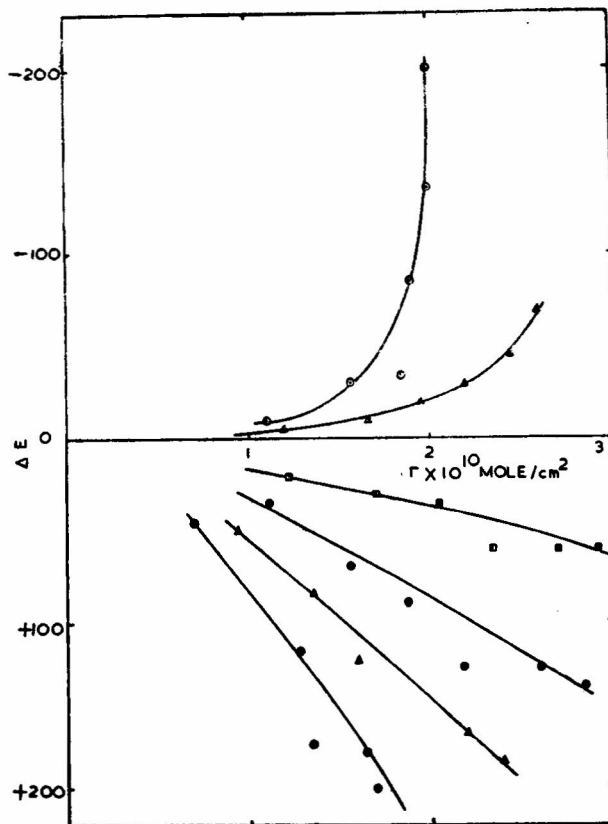

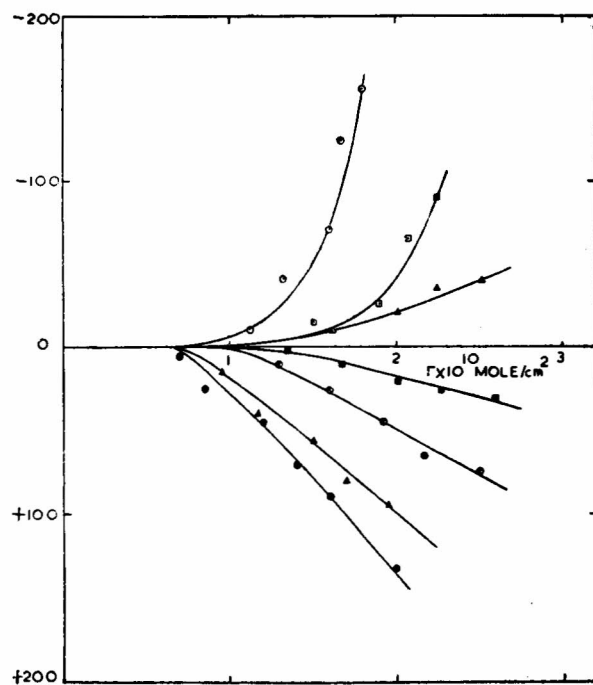Fig. 6 — Dependence of ΔE on Γ_{SA} in the case of SA at 8 (○); 6 (□); 4 (△); 2 (■); 0 (⊗); −2 (▲); −4 (●) q^M

Evaluation of surface coverage (θ) — The surface coverage (θ) is defined as Γ/Γ_{max} where Γ_{max} is the concentration in moles cm^{-2} of surface to obtain a unimolecular layer. The evaluation of Γ_{max} is usually carried out on the basis of (i) cross sectional area of the molecule which can be obtained from bond angles, covalent radii of atoms etc. and (ii) on the orientation of the adsorbed molecule. Although (i) can be evaluated satisfactorily from space filling models, the knowledge of orientation is a major indecisive factor.

For PABA, Γ_{max} calculated from bond angles and covalent radii of atoms on the basis of perpendicular and planar orientations are 7·53 and 2·4 × 10^{-10} moles cm^{-2} respectively. The maximum observed experimentally was $(3·0 \pm 0·09) \times 10^{-10}$ moles cm^{-2}. Hence, the possibility of planar orientation is ruled out for PABA unless a multilayer type of adsorption is assumed. For SA, the maximum surface excess found was $(3·0 \pm 0·09) \times 10^{-10}$ moles cm^{-2} while corresponding calculated values for planar and perpendicular orientations for maximum coverage are 2·9 and 8·3 × 10^{-10} moles cm^{-2} respectively. It is apparent that SA is also adsorbed in a perpendicular orientation. Surface coverages were calculated using the above values.

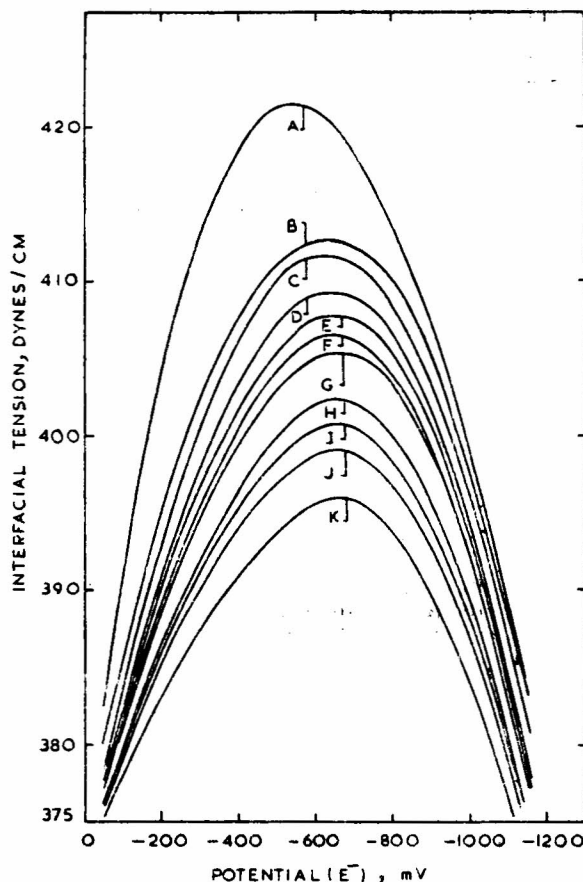*Simultaneous adsorption of PABA and SA* — For determining the dependence of adsorption of PABA

Fig. 7 — Electrocapillary curves for (A) 0·1M KNO₃;+(B) 1×10⁻⁴ SA; and+(C) 2×10⁻⁴;+(L 5×10⁻⁴;+(E) 1×10⁻³; +(F)3×10⁻³;+(G) 6×10⁻³; +(H) 8×10⁻³;+(I) 1×10⁻²;+(J) 1·5×10⁻²;+(K) 2·5×10⁻²; and +(L)4×10⁻²M PABA

Fig. 8 — Electrocapillary curves for (A) 0·1M KNO₃; +(B) 1×10⁻³ PABA; and +(C) 1×10⁻³; +(D) 3×10⁻³; + (E) 6×10⁻³; +(F) 8×10⁻³; +(G) 1×10⁻²; +(H) 1·7×10⁻²; +(I) 2·5×10⁻²; +(J) 3·5×10⁻²; and +(K) 5×10⁻²M SA

in the presence of SA on charge of the metal electrode, electrocapillary curves for the following solutions were obtained and are shown in Figs. 7 and 8.

Set-A: 0·1M KNO₃ + 1×10⁻³M SA+Y PABA where Y varies from 2×10⁻⁴M to 4×10⁻²M.
Set-B: 0·1M KNO₃ +1×10⁻³M PABA+X SA where X varies from 1×10⁻³M to 5×10⁻²M.
The electrocapillary equation for such systems at constant temperature and presure is

$$-\delta\Upsilon = q^M\delta E^- + \Gamma_{K^+}\delta\mu_{KNO_3} + \Gamma_{SA}\delta\mu_{SA} + \Gamma_{PABA}\delta\mu_{PABA}$$

...(3)

where E^- is the potential of the reference electrode reversible to NO_3^-. The reference electrode used being SCE throughout, dE^- corresponds to dE_{calc}, the small error due to change in liquid junction potentials is neglected. At constant μ_{KNO_3} and μ_{SA} (set-A).

$$\Gamma_{PABA} = -\left(\frac{\delta\Upsilon}{\delta\mu_{PABA}}\right)_{\mu_{KNO_3}, \mu_{SA}} \qquad ...(4)$$

from which surface excess due to PABA from KNO₃+SA solutions was evaluated. Similarly for Set-B,

$$\Gamma_{SA} = -\left(\frac{\delta\Upsilon}{\delta\mu_{SA}}\right)_{\mu_{KNO_3}, \mu_{PABA}} \qquad ...(5)$$

TABLE 1 — SIMULTANEOUS ADSORPTION OF PABA AND SA

q^M μ Coul./ cm^2	θ_1	θ_2	θ_3	θ_4	θ_{total} $=\theta_3+\theta_4$	θ_{total} (calc.)
6	0·211	0·175	0·146	0·060	0·206	0·324
4	0·235	0·189	0·172	0·105	0·277	0·349
2	0·247	0·195	0·184	0·111	0·295	0·363
0	0·226	0·175	0·182	0·104	0·286	0·335
−2	0·193	0·125	0·154	0·055	0·209	0·275
−4	0·154	0·098	0·122	0·042	0·164	0·225

$\theta_1=\theta$ due to PABA in $1\times10^{-3}M$ PABA$+0\cdot1M$ KNO$_3$ solution.
$\theta_2=\theta$ due to SA in $1\times10^{-3}M$ SA$+0\cdot1M$ KNO$_3$ solution.
$\theta_3=\theta$ due to PABA in $1\times10^{-3}M$ SA$+1\times10M^{-3}M$ PABA$+0\cdot1M$ KNO$_3$ solution.
$\theta_4=\theta$ due to SA in $1\times10^{-3}M$ SA$+1\times10^{-3}M$ PABA$+0\cdot1M$ KNO$_3$ solution.
$\theta_{total}=\theta$ due to PABA and SA in the mixed solution.

the adsorption due to SA was evaluated. The charge on the metal being simply $(-\delta\gamma/\delta E_{cal})\mu_{PABA}$, μ_{SA} at constant concentration of PABA and SA was evaluated for each of the above curves in sets A and B. The dependence of adsorption on charge q of SA (or PABA) from KNO$_3$ solution containing PABA (or SA) is brought out in Figs. 3 and 4. Comparing the number of moles of PABA (or SA) adsorbed to the adsorption of PABA (or SA) in the mixed solution of both, it is apparent that on the addition of SA (or PABA) to a solution containing PABA (or SA) alone, additional adsorption due to the added entity takes place to a considerable extent over the range of potentials. However, this adsorption is seen to take place by partial replacement of the already adsorbed organic species[11]. This is brought out in Table 1. It is evident that the total coverage due to both in the mixed solution is less than the sum of respective coverages in solutions of only one organic adsorbate but is nearly equal to that due to the more adsorbable entity. It has been stated by Butler et al.[12] that such a phenomenon will be obtained in the case of not very strongly adsorbed compounds. It is possible to calculate θ_3 and θ_4 (Table 1) on the basis of Langmuir-Frumkin isotherm:

$$B_{01}C_{01} = \frac{\theta_{01}}{1-\theta_{01}}.\exp[-2a_{01}\theta_{01}] \qquad ...(6)$$

where θ_{01} is the surface coverage due to the adsorbate. Hence, for a mixture of two adsorbates, the surface coverage θ_3 due to (1) in the presence of (2) can be correlated as

$$B_1C_1 = \frac{\theta_3}{1-\theta_3-\theta_4}.\exp(-2a_1\theta_3) \qquad ...(7)$$

when B is given as $(e^{-\overline{\Delta G}/RT})$ where $\overline{\Delta G}$ is the free energy of adsorption and a's are the lateral interaction coefficients. Writing similar equation for component (2) and assuming $B_1 = B_{01}$ and $a_1 = a_{01}$ for sake of simplicity, we obtain[11]

$$\theta_3 = \frac{\theta_{01}-\theta_{01}\cdot\theta_{02}}{1-\theta_{01}\cdot\theta_{02}} \text{ and } \theta_4 = \frac{\theta_{02}-\theta_{01}\cdot\theta_{02}}{1-\theta_{01}\cdot\theta_{02}} \qquad ...(8)$$

The calculated values are shown in the last column of Table 1. The calculated values are much higher than observed experimentally. This points out to the fact that simplification of the Langmuir-Frumkin equation by assuming that the free energies of adsorption are the same and that the interaction parameters are identical is not justified.

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