

# The Frumkin model applied to the adsorption process of benzene on a Pt electrode from sulfuric acid solutions

M.A. QUIROZ, F. CORDOVA

*Instituto de Estudios Avanzados, Universidad de las Américas-Puebla  
Apartado postal 100, Sta. Catarina Mártir, 72820 Cholula, Puebla, México*

L. SALGADO, M. VINIEGRA

*Departamento de Química. Universidad Autónoma Metropolitana-Iztapalapa  
Apartado postal 55-534, 09340 México, D.F., México*

Y. MEAS

*Centro de Investigación y Desarrollo Tecnológico en Electroquímica, S.C.  
Apartado postal 064, Pedro Escobedo 76700 Querétaro, México*

AND

G. DÍAZ

*Instituto de Física, Universidad Nacional Autónoma de México  
Apartado postal 20-364, 1000 México, D.F., México*

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**ABSTRACT.** The electroadsorption of benzene on a polycrystalline Pt electrode from 0.5 M H<sub>2</sub>SO<sub>4</sub> +  $x$  M C<sub>6</sub>H<sub>6</sub> solutions was studied as a function of the benzene concentration, time and potential of adsorption. It was observed that the maximum adsorption takes place in the double layer region, even though the adsorption process can also occur in the hydrogen region. At the potential of maximum adsorption the experimental results showed that benzene molecules are strongly adsorbed on the Pt surface, each one occupying about  $7.6 \pm 1$  accessible Pt sites and an average surface of 43 Å. The dependence of the coverage degree,  $\theta_b$ , on the adsorption time and benzene concentration was analyzed by means of the Frumkin adsorption model. However, in order to explain both the adsorption process and the value of the Frumkin interaction factor  $a$ , the quasichemical approximation developed by Guidelli for the Frumkin isotherm was used.

**RESUMEN.** En este trabajo se presenta un estudio electroquímico del proceso de adsorción de benceno sobre un electrodo de Pt policristalino, a partir de soluciones de H<sub>2</sub>SO<sub>4</sub> 0.5 M + C<sub>6</sub>H<sub>6</sub>  $x$  M, usando como variables de análisis la concentración de benceno en solución, el tiempo de contacto y el potencial de adsorción. Se observó que la adsorción ocurre en un amplio intervalo de potencial, incluida una porción de la región de hidrógeno del electrodo de Pt, con un máximo en la región de la doble capa. Los resultados experimentales mostraron que al potencial de máxima adsorción (0.39 V/erh), las moléculas de benceno son fuertemente adsorbidas (prom.  $-\Delta G_{\text{ads}}^0 = 35.4$  kJ mol<sup>-1</sup>), ocupando en promedio, cada una de ellas,  $7.6 \pm 1$  sitios accesibles de Pt y una superficie de 43 Å. La dependencia del grado de recubrimiento de la superficie de Pt por benceno  $\theta_b$ , con las variables de análisis fue tratada mediante el uso del modelo de adsorción de Frumkin. Sin embargo, tanto el proceso de adsorción como el factor de interacción calculado ( $\bar{a} = -4.3$ ) fueron explicados aplicando la aproximación cuasiquímica desarrollada por Guidelli a la isoterma de Frumkin.



## 1. INTRODUCTION

The adsorption of organic compounds over metallic electrodes, from aqueous solutions, has been a subject of special attention in electrocatalysis. This process frequently determines the activity, selectivity and reaction rate of a metal [1-7]. Owing to the solvated nature of the interfacial region, the electroadsorption can be considered as a replacement reaction of solvent molecules in the adsorbed layer by organic molecules coming from the bulk solution [8-14]. It is well known that the surface coverage degree depends on the solubility of the organic compounds, the adsorption time and, mainly, on the imposed potential at the electrode [8].

Therefore, the electroadsorption can be properly defined as the chemisorption of organic species from the aqueous solution over metallic electrodes at the potential where the process is being controlled.

It has been widely demonstrated that aromatic compounds are spontaneously and irreversibly adsorbed on Pt electrodes [15,17]. Important *ex-situ* and *in-situ* experimental evidence strongly suggests that the aromatic  $\pi$ -electrons are extensively involved in the interaction of the unsaturated molecules with the metal surface [18-21]. Moreover, the aromatic-metal interactions are unimpeded by the particular kind of chemical species of the supporting electrolyte used [22].

From the great number of aromatic compounds studied, it is important to note the scarce information reported until now about the electrosorption characteristics of benzene, even though it is the simplest aromatic compound. The adsorption of benzene labeled with C-14 was studied on platinum-plated gold electrodes in 1 N H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> by Heiland *et al.* [23]. They found, using this radiotracer method, that the benzene molecules were chemisorbed without dissociation on the surface, with the probable loss of the aromatic character. This subject was further investigated by Gileadi *et al.* [24] using electrochemical methods. The corresponding adsorption results were compared with those previously obtained by the radiotracer method, in order to establish the extent to which these methods could give consistent results. Although all potentiometric techniques agreed with the measured values of the coverage degree of benzene, it was not the case when the results obtained from these techniques were compared with those obtained through the radiotracer technique. The discrepancy was attributed by the authors to the existence on the surface of significant concentrations of intermediate radicals, formed during the oxidation of benzene at CO<sub>2</sub> at higher positive potentials. It is important to point out that, in this case, the electrochemical methods appear to offer distinct advantages over the radioactive methods. The operational methodology, essentially based on cyclic voltammetry for the study of benzene electroadsorption on platinum, has been considered in the experimental chapters of the advanced work in electrochemistry published by Gileadi *et al.* [25]. However, in this work no particular treatment was developed with respect to the partial oxidation of benzene, it was assumed that under established experimental conditions, the oxidation to CO<sub>2</sub> and water is complete. Indeed, this assumption in addition to those required to validate the use of electrochemical techniques for the measurement of electrosorption have been confirmed recently by Baltruschat *et al.* [26-28]. In this work these authors have shown that the preadsorbed benzene can be desorbed without modification in the hydrogen region if the negative potential limit is  $\geq 0.1$  V, or as hydrogenated



product (cyclohexane) if the negative potential limit is  $\leq 0.1$  V; more important yet, the desorption process can also occur by benzene oxidation yielding  $\text{CO}_2$  and water as the only detectable products. Even though in these works the adsorption process itself was scantily emphasized, the importance of the results to be based on the fact that the benzene oxidation on polycrystalline platinum electrodes in the oxygen region adsorption led to  $\text{CO}_2$  as the final product. This last conclusion provides the experimental support required to calculate the charge associated with the benzene oxidation and, hence, the surface concentration of benzene from which a detailed study of the electrosorption process can be developed.

Until recently, the values of the adsorption parameters had been interpreted on a strictly phenomenological basis, using the Frumkin adsorption model. According to this model the dependence of the coverage degree on the electrode potential is due to the change in the energy of the double-layer capacitor which results when water is replaced by organic molecules having a lower dielectric constant. Furthermore, the conditions under which the behavior of Frumkin is obtained have been examined on a non-thermodynamic basis of molecular character proposed by Guidelli [14]. This molecular model attempts to predict the behavior of the Frumkin isotherm at the greater possible range of  $\theta$ , *i.e.*, the fraction of surface covered, taking into account specifically the influence, nature of the interactions and orientation of the solvent molecules in the metal-solution interface.

Thus, it is to be expected that the molecular interpretation of the experimental data of adsorption leads to more reliable conclusions about the interactions at the monolayer when molecular models representing nearly an acceptable reality at the interface are used.

Therefore, the aim of this work has been to evaluate the experimental isotherm of the benzene adsorption on platinum in acidic media by means of a thermodynamic treatment of the results (Frumkin) which is subsequently complemented with non-thermodynamic arguments of molecular character (Guidelli) in order to interpret the corresponding adsorption parameters.

## 2. EXPERIMENTAL

All the experiments were carried out at room temperature in 0.5 M  $\text{H}_2\text{SO}_4$  solutions as supporting electrolyte, prepared from sulfuric acid (96% Suprapur Merck) and threefold distilled water (16 M $\Omega$  water system I). These solutions were deaerated by bubbling UHP nitrogen gas (99.999% Infra) before preparing the benzene (99+% Aldrich) solutions, in order to avoid the organic evaporation. The benzene concentration in solution was varied in the  $10^{-7}$ – $10^{-4}$  M range.

The working electrode was a polycrystalline Pt wire (99.999% Aldrich), 0.134 cm<sup>2</sup> geometrical area sealed at Pyrex glass, the counter electrode was a graphite rod (EG & G PARC).  $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4$  (satd.) was used as the reference electrode, in the text all the potentials are reported on the reversible hydrogen electrode (rhe) scale at room temperature.

All measurements were made by using an EG & G PARC model 273 potentiostat-galvanostat and the voltammograms recorded by means of a GRAPHTEC model WX1100 X-Y-t plotter.

## 3. RESULTS AND DISCUSSION

The adsorption and oxidation processes of benzene were carried out as a function of benzene concentration, time and potential of adsorption. A typical voltammogram is observed in Fig. 1, which is similar to those previously reported [29]. The quantity of electricity involved in these processes was measured from the corresponding potentiodynamic profiles, but some considerations about the method of calculation were taken into account in each case. The preadsorbed benzene is oxidized at potentials greater than 0.60 V but it was observed that more than one potential cycle was required for a complete oxidation, hence, the charge associated with the benzene oxidation,  $Q_b$ , was calculated from

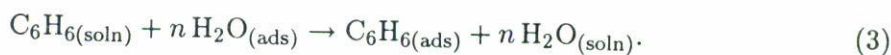
$$Q_b = \sum_i^n (Q_{\text{PtO}}^i - Q_{\text{PtO}}^0), \quad (1)$$

where  $Q_{\text{PtO}}^0$  is the charge required for the Pt oxidation in a solution free of benzene and  $Q_{\text{PtO}}^i$  the charge involved in the mutual oxidation of both, benzene and Pt during the  $i$ -th cycle. It was observed, in all of the experiments, that the total oxidation of benzene was achieved in the first five cycles, *i.e.*,  $n \leq 5$ . On the other hand, the decrease in hydrogen adsorption originated by the benzene adsorption,  $\Delta Q_H$ , was used in the traditional way [3,30–33] to measure the coverage degree of the Pt surface by benzene ( $\theta_b$ ) at a given set of experimental conditions

$$\theta_b = \frac{Q_H^0 - Q_H}{Q_H^0} = \frac{\Delta Q_H}{Q_H^0}. \quad (2)$$

In this case, the integration negative limit into the hydrogen region was restricted to 0.10V in order to avoid the reduction process of preadsorbed benzene [26].

The adsorption of benzene from an aqueous solution can be considered to take place though a replacement reaction



Mass transport from the bulk solutions to the metal surface may be expected to be the rate-controlling step if the structure of the adsorbate does not change in the adsorption process and/or its concentration in solution is very low. Therefore, the benzene coverage degree will vary with the adsorption time as [34]

$$\theta_b(t) = \left( \frac{2D^{1/2}\theta_{\text{eq}}}{\pi^{1/2}K\Gamma_m} \right) t_{\text{ads}}^{1/2}, \quad (4)$$

where  $\theta_{\text{eq}}$  and  $\theta_b(t)$  are the equilibrium and instantaneous values of fractional coverage at a given benzene concentration,  $D$  is the diffusion coefficient ( $6.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  [23]),  $K$  is the adsorption coefficient, and  $\Gamma_m$  the maximum surface coverage. Figure 2 shows this diffusional control for the mass transport of benzene to the Pt surface at short adsorption times and low concentrations.



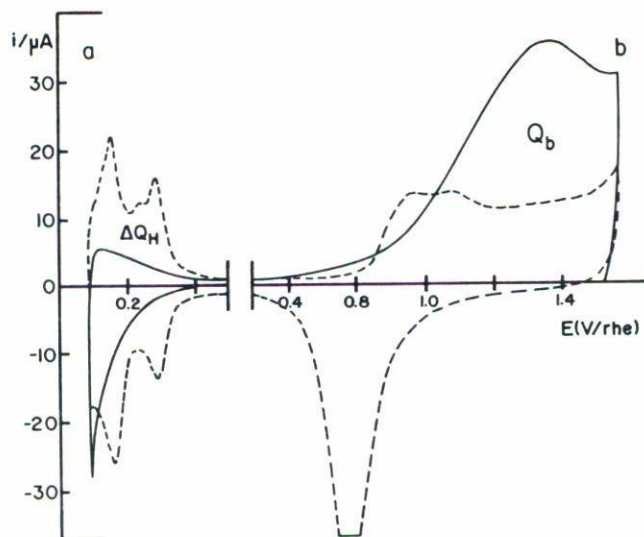


FIGURE 1. (a) Effect of the benzene adsorption on the hydrogen electroadsorption. (b) Electrooxidation process of benzene. Benzene preadsorbed at  $E_d = 0.39$  V/rhe during 600 s from a  $0.5$  M  $\text{H}_2\text{SO}_4$  +  $1.0 \times 10^{-2}$  M  $\text{C}_6\text{H}_6$  solution. Dashed curve: bare Pt electrode.

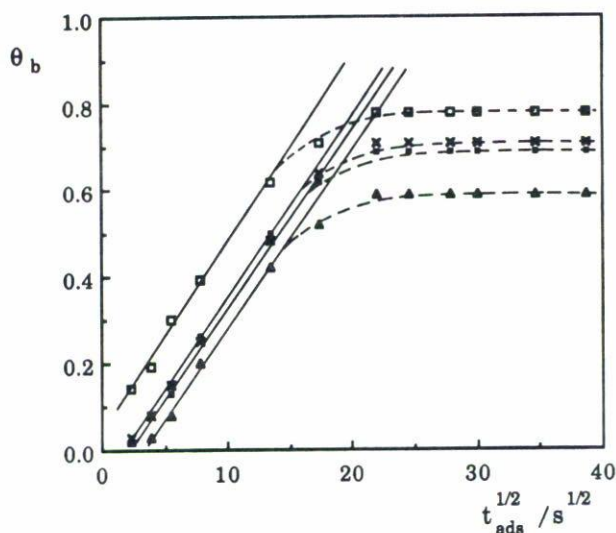


FIGURE 2. Adsorption of benzene at  $0.39$  V/rhe as a function of the adsorption time at various bulk concentrations of benzene: ( $\Delta$ )  $5 \times 10^{-7}$  M; ( $\blacksquare$ )  $1 \times 10^{-6}$  M; ( $\times$ )  $1 \times 10^{-5}$  M; ( $\square$ )  $5 \times 10^{-5}$  M.

Now, the benzene electroadsorption on Pt in  $0.5$  M  $\text{H}_2\text{SO}_4$  solution containing various amounts of benzene was analyzed as a function of the adsorption potential. For these runs the adsorption time was fixed at 600 s, it roughly correspond to the time at which the amount of adsorbed benzene remains constant in all cases. The results of these experiments are shown in Fig. 3, where the amount of adsorbed benzene  $\Gamma$ , defined as  $\Gamma = \theta_b \Gamma_m$  [14] and being  $\Gamma_m = 3.9 \times 10^{-10}$  mol  $\text{cm}^{-2}$ , is plotted against the adsorption potential. The

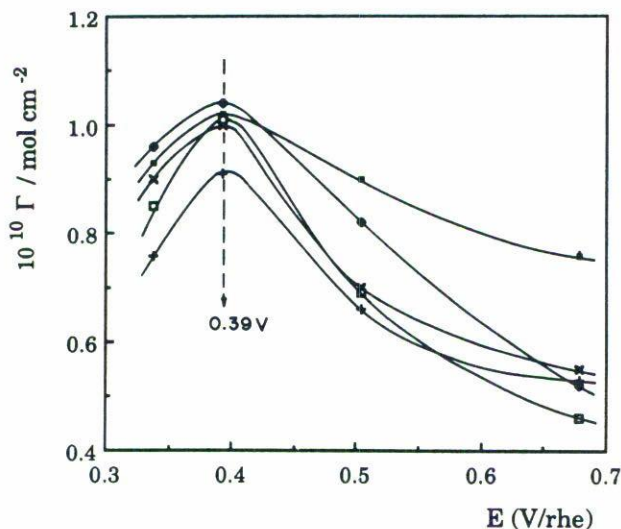


FIGURE 3. Adsorption of benzene on a Pt electrode from  $0.5 \text{ M H}_2\text{SO}_4 + x \text{ M C}_6\text{H}_6$  solutions. Bulk concentrations of benzene,  $x$ : (■)  $1 \times 10^{-6} \text{ M}$ ; (+)  $5 \times 10^{-6} \text{ M}$ ; (×)  $1 \times 10^{-5} \text{ M}$ ; (□)  $5 \times 10^{-5} \text{ M}$ ; (◇)  $1 \times 10^{-4} \text{ M}$ . Adsorption time of 600 s.

$\Gamma$ - $E$  curves have the typical dome-like shape expected for the adsorption of neutral organic compounds on Pt surfaces [12,14]. The maximum adsorption takes place in the double layer region at a potential of 0.39 V which is somewhat negative to the potential of zero charge (pzc) value of Pt (0.5–0.6 V) in acidic media [23]. Therefore, this shift of pzc should be due to the displacement of surface water by the adsorption of benzene molecules rather than to the influence of the hydrogen adsorption.

From the charge associated with the hydrogen monolayer, the initial number of surface Pt sites per sq.cm was calculated:  $n_0 = 2.5 \times 10^{15} \text{ Pt sites cm}^{-2}$ . This value allows us to estimate the number of surface Pt sites occupied by one molecule of adsorbed benzene,  $N_{\text{Pt}}$ , from the relation:  $N_{\text{Pt}} = n_0\theta/\Gamma$ . The experimental data above analyzed lead to  $N_{\text{Pt}} = 6.5\text{--}8.6$ . This result indicates that one molecule of adsorbed benzene occupies about  $7.6 \pm 1$  accessible Pt sites, which is in accordance to the data of Heilant *et al.* [23] and Stickney *et al.* [35]. In addition, the average surface occupied by one adsorbed molecule of benzene may be calculated with the aid of the following equation [15]:  $\sigma = 10^{16}/6.02 \times 10^{23} \Gamma$ , which with a  $\Gamma$  value of  $3.9 \times 10^{-10} \text{ mol cm}^{-2}$  results in a  $\sigma$  value of 43 Å in good agreement with the values reported from BET measurements [36] and theoretical methods [15]. The  $\sigma$  and  $\Gamma_m$  values support the assumption of a  $\pi$ -d-bonded benzene molecule lying flat on the Pt surface [19,20,36,37].

On the other hand, it is well known that the adsorption from solutions is a relatively complex phenomenon, which essentially depends on the nature of the interfacial region. The adsorption of organic compounds on the Pt group metal surfaces has been often viewed as a highly irreversible process, *i.e.*, with a very large  $K$  value. Thus, when the solution from which the adsorption takes place is exchanged for pure solvent, then little or no desorption occurs. Hence, it is expected that the adsorbed species are preferably desorbed through reduction and/or oxidation reactions. This is the case commonly found

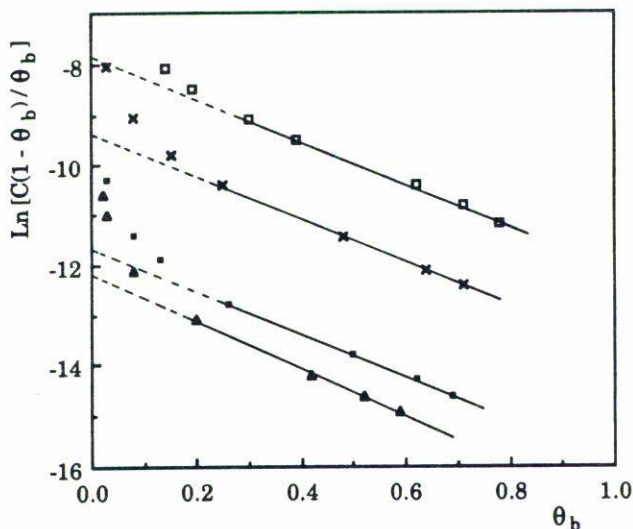


FIGURE 4. Calculated  $\ln[C(1 - \theta_b)/\theta_b]$  vs.  $\theta_b$  plot at the same potential adsorption and bulk concentrations of benzene as in Fig. 2.

in the adsorption studies of aromatic compounds from aqueous solutions, where due to the strong interaction between the surface electrode and the  $\pi$ -electrons of the aromatic ring, the adsorbed layer remains confined to a monolayer.

Owing to this fact as well as to the good concentration-coverage correlations found in many aromatic-metal systems studied [3,14,23,30,31], the adsorption data has often been fit to an equation of a particular adsorption isotherm. Even though this manner to handle the experimental data is a controversial subject yet, important experimental and theoretical evidences point out that the electroadsorption behaviour can be analyzed by means of the adsorption model of Frumkin [14]:

$$\frac{C}{55.5} \exp\left(-\frac{\Delta G_{\text{ads}}^0}{RT}\right) = \theta \exp\left(\frac{a\theta}{1-\theta}\right), \quad (5)$$

where  $(C/55.5)$  is the mol fraction of the organic compound in the bulk,  $\Delta G_{\text{ads}}^0$  the standar Gibbs energy of adsorption at zero coverage and  $a$  the Frumkin interaction factor. Rearranging Eq. (5) one has

$$\ln \frac{C(1-\theta)}{\theta} = \ln(55.5) + \frac{\Delta G_{\text{ads}}^0}{RT} + a\theta. \quad (6)$$

Substitution of the benzene adsorption data, obtained at the potential of maximum adsorption (0.39 V) as a function of the adsorption time and in the concentration range of  $5 \times 10^{-7}$ – $5 \times 10^{-5}$  M, into Eq. (6) generates the curves of Fig. 4.

By least-squares fitting of the plots in Fig. 4 to a straight line, values of  $\Delta G_{\text{ads}}^0$  and Frumkin interaction factor  $a$  are immediately obtained from the corresponding intercepts



TABLE I. Frumkin parameters obtained as a function of the bulk concentration of benzene at the potential of maximum adsorption (0.39 V).

C/mol l <sup>-1</sup>	5 × 10 <sup>-7</sup>	1 × 10 <sup>-6</sup>	1 × 10 <sup>-5</sup>	5 × 10 <sup>-5</sup>	
<i>a</i>	-4.6	-4.2	-4.3	-4.2	( $\bar{a} = -4.3$ )
-Δ <i>G</i> <sub>ads</sub> <sup>0</sup> /kJ mol <sup>-1</sup>	40.2	39.0	33.1	29.3	

and slopes. The values of *a* and Δ*G*<sub>ads</sub><sup>0</sup> for various bulk concentrations of benzene in the solution are given in Table I.

For the adsorption of aliphatic compounds on Hg, considered as a physisorption, usually the *a* parameter takes negative values in the range from -1 to -3 [12,14,38], but for the adsorption of aromatic compounds on the Pt group surfaces the information is lacking. However, from the quasichemical approximation developed by Guidelli for the Frumkin isotherm [14], an attempt to explain the average value of the *a* parameter will be made as follows. According to the Guidelli's approximation, the attractive water-water interactions, *W*<sub>WW</sub>, depends on the coverage degree of the metal surface by organic molecules, *θ*<sub>b</sub>. At low *θ*<sub>b</sub> values the water displacement should be restricted due to the predominance of the *W*<sub>WW</sub>, but at medium *θ*<sub>b</sub> values the number of interacting water-water pairs has decreased sufficiently to make the removal of water molecules from the metal surface by the adsorbing organic molecules a favourable process. This adsorption model predicts a negative slope for the ln[C(1 - *θ*)/*θ*] vs. *θ* plot with a minimum value at the potential of maximum coverage. Therefore, since this adsorption behaviour is clearly observed in the 0.2 ≤ *θ*<sub>b</sub> ≤ 0.8 range of the ln[C(1 - *θ*)/*θ*] vs. *θ* plots of Fig. 4, which were constructed from the *θ*<sub>b</sub> values calculated at the potential of maximum adsorption (0.39 V), then the average value of Frumkin interaction factor,  $\bar{a} = -4.3$  (Table I), may be considered as a satisfactory result. Furthermore, an important feature of this adsorption model is that it permits a reasonable molecular interpretation for the experimental observation that the adsorption of aromatic compounds, from an aqueous solution, takes place through a replacement reaction as showed in Eq. (3).

It is also known that reaction (3) occurs spontaneously on Pt electrodes [15], and this confirmed by the Δ*G*<sub>ads</sub><sup>0</sup> values reported in Table I. In addition, when the values of Δ*G*<sub>ads</sub><sup>0</sup> are plotted as function of ln(C/55.5) (Fig. 5), a linear relationship with a slope of 2.4 kJ mol<sup>-1</sup> is observed in the 5 × 10<sup>-7</sup>–5 × 10<sup>-5</sup> M range of benzene concentration in solution.

This result is in agreement with the Frumkin isotherm, [Eq. (5)], for which a slope of 2.5 kJ mol<sup>-1</sup> is predicted.

#### 4. CONCLUSIONS

On the basis of the results obtained we may conclude that the adsorption of benzene from sulfuric acid solutions is a spontaneous process, being its extension strongly dependent on both the time and the potential of adsorption. At the potential of maximum adsorption, 0.39 V, this process adequately satisfies the adsorption model of Frumkin.

The Frumkin isotherm is perhaps the adsorption isotherm based on molecular models



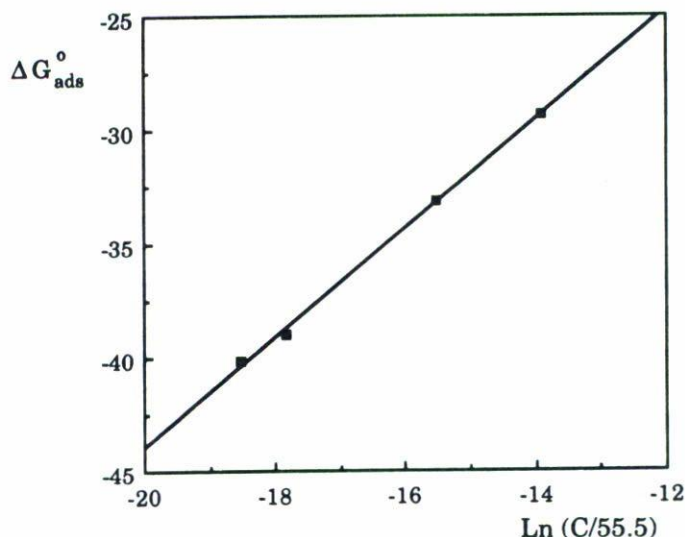


FIGURE 5. The dependence of the Gibbs energy of adsorption on the mol fraction of benzene in the bulk using the equation of the Frumkin isotherm.

more developed nowadays. Our experimental results are finely justified by the Frumkin isotherm which also provides a clear idea of the replacement process of water molecules by the adsorbing aromatic molecules. The Guidelli's theoretical treatment for the Frumkin isotherm [14] together with Hubbard's work on the adsorption of aromatic compounds [15–16], are at the present time the most important theoretical and experimental support to analyse and to interpret the adsorption data of aromatic-metal systems that present a high irreversibility degree.

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#### REFERENCES

1. H. Wroblowa and M. Green, *Electrochimica Acta* **8** (1963) 679.
2. L.L. and L. Christensen, *J. Org. Chem.* **43** (1978) 2059.
3. K. Sasaki, A. Kumai, J. Harada and S. Nakabori, *Electrochimica Acta* **28** (1983) 671.
4. T. Iwasita, W. Vielstich and E. Santos, *J. Electroanal. Chem.* **229** (1978) 367.
5. J. Zhu, Th. Hartung, D. Tegtmeier, H. Baltruschat and J. Heitbaum, *J. Electroanal. Chem.* **24** (1988) 273.
6. K. Shimazu and H. Kita, *J. Catal.* **83** (1983) 407.
7. Yu. B. Vassiliev, V.S. Bagotzky, O.A. Khazova, V.V. Cherny and A.M. Meretsky, *J. Electroanal. Chem.* **98** (1979) 253, 273.
8. E. Gileadi, *J. Electroanal. Chem.* **11** (1966) 137.

9. J.O'M. Bockris, E. Gileadi and K. Müller, *Electrochimica Acta* **12** (1967) 1301.
10. J.O'M. Bockris, M.A.V. Devanathan and K. Müller, *Proc. R. Soc. London Ser. A* **274** (1963) 55.
11. D.H. Everett, *Trans. Faraday Soc.* **60** (1964) 1803; **61** (1965) 2478.
12. B.B. Damaskin, O.A. Petrii and V.V. Batrokov, *Adsorption of Organic Compounds on Electrodes*, Plenum Press, New York (1971) p. 86.
13. S. Trasatti, *J. Electroanal. Chem.* **53** (1974) 335.
14. R. Guidelli, *Adsorption of Molecules at Metal Electrodes*, J. Lip Kowski and P.N. Ross (eds.), VCH Publishers, Inc., New York (1992) p. 1.
15. M.P. Soriaga, P.H. Wilson and A.T. Hubbard, *J. Am. Chem. Soc.* **104** (1992) 2735, 2742, 3937.
16. M.P. Soriaga, J.H. White, D. Song and A.T. Hubbard, *J. Electroanal. Chem.* **171** (1984) 359.
17. G. Horányi and E. Rizmayer, *Electrochimica Acta* **31** (1986) 401.
18. P.W. Selwood, *J. Am. Chem. Soc.* **79** (1957) 4637.
19. J.L. Gland and G.A. Somorjai, *Adv. Colloid Interface Sci.* **5** (1976) 205.
20. D.M. Haaland, *Surface Sci.* **111** (1981) 555.
21. A.W. Adamson, *Physical Chemistry of Surface*, Wiley Interscience, New York (1990) p. 421.
22. M.P. Soriaga, J.H. White, D. Song and A.T. Hubbard, *J. Phys. Chem.* **88** (1984) 2284.
23. W. Heiland, E. Gileadi and J.O'M. Bockris, *J. Phys. Chem.* **70** (1966) 1207.
24. E. Gileadi, L. Duic and J.O'M. Bockris, *Electrochimica Acta* **13** (1968) 1915.
25. E. Gileadi, E. Kirowa-Eisner and J. Penciner, *Interfacial Electrochemistry: An Experimental Approach*, Addison-Wesley Publishing Company, Inc., Advanced Book Program, Reading, Massachusetts (1975) p. 444.
26. U. Schmiemann and H. Baltruschat, *Electroanal. Chem.* (1993) (in press).
27. T. Hartung and H. Baltruschat, *Langmuir* **6** (1990) 953.
28. T. Hartung, V. Schmiemann, I. Kamphausen and H. Baltruschat, *Anal. Chem.* **63** (1991) 44.
29. M.A. Quiroz, L. Salgado, M. Viniestra, G. Díaz, Y. Meas and F. Córdova, Poster presented at the 43rd ISE Conference, Argentina (1992).
30. V.S. Bagotsky and Yu. B. Vassiliev, *Electrochimica Acta* **11** (1966) 1439.
31. P. Zelenay and J. Sobkowski, *Electrochimica Acta* **29** (1984) 1715.
32. E. Lammy-Pitara, L. Bencharif and J. Barbier, *Appl. Catal.* **18** (1985) 117.
33. B. Bittins-Cattaneo, E. Santos, W. Vielstich and V. Linke, *Electrochimica Acta* **33** (1988) 1499.
34. E. Gileadi, B.T. Rubin and J.O'M. Bockris, *J. Phys. Chem.* **10** (1965) 3335.
35. J.L. Stickney, M.P. Soriaga, A.T. Hubbard and S.A. Anderson, *J. Electroanal. Chem.* **25** (1981) 73.
36. A.L. McClellan and H.F. Harnsberger, *J. Colloid Sci.* **23** (1967) 577.
37. J.C. Bertolini and J. Massardier, *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis* Vol. 3, part B., D.A. King and D.P. Woodruff, eds. Elsevier, New York (1984) p. 107.
38. M. Carlá, G. Abisi, M.R. Moncelli and M.L. Foresti, *J. Colloid Interface Sci.* **132** (1989) 72.