

Esin and Markov Effect for Adsorbed Organic Ions and Molecules

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Electrochemical adsorption of piperidine, pyridine, morpholine, dioxane, furfurylamine, tetrahydrofurfurylamine, N-methylfurfurylamine, N-methyltetrahydrofurfurylamine, *n*-propyl alcohol, allyl alcohol, and propargyl alcohol have been investigated at $25 \pm 1^\circ$ in 1 *N* aqueous potassium chloride solutions at the mercury electrode by means of an improved Lippmann electrocapillarity meter. Electrocapillary measurements were carried out for three aromatic and heterocyclic amines, which could be converted by protonation to the corresponding cations in aqueous hydrochloric acid solutions. The first objective was to verify experimentally, from a general thermodynamic standpoint suggested by Parsons, the quantitative validity of the Esin and Markov effect for specifically adsorbed *organic* cations. This effect is concerned with the linear relation of the potential of the electrocapillary maximum, measured with respect to a given reference electrode, to the logarithm of the activity of ionic additives present in the solution. A second but more important aim has been to develop a theoretical extension of Parsons' treatment to explain the possible existence of an analogous Esin and Markov effect for the specific adsorption of neutral organic molecules. Agreement and limitations in the comparison of theoretical predictions and experimental results are discussed in terms of orientation effects, electronic and molecular structure, and the dependence of the Esin and Markov coefficient on the electrode surface charge.

Introduction

The Esin and Markov effect refers to the experimental observation made by these authors¹ that the potential of zero charge (p.z.c.) on mercury varies linearly with the logarithm of activity (a_A) of surface-active anions. This subject has been examined by various workers²⁻⁵ and the thermodynamic treatment by Parsons⁶ is of special interest to the present work, since we are concerned with the correlation of the theoretical predictions of Parsons with our electrocapillary results for specifically adsorbed *organic* cations. In addition, we shall examine whether there is a comparable Esin and Markov effect for the specific adsorption of neutral organic molecules, a subject which has hitherto not been investigated. The Esin and Markov co-

efficient $\partial E / \partial \ln a_A$ is an important quantity for development of rate equations for adsorption of neutral substances at a metal-electrolyte interface⁷ where there is very little information known except for a few cases

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(2) D. C. Grahame, *Ann. Rev. Phys. Chem.*, **6**, 337 (1955).

(3) D. C. Grahame, Technical Report No. 1, Office of Naval Research, Washington, D. C., June 13, 1957.

(4) O. A. Esin and V. M. Shikov, *Russ. J. Phys. Chem.*, **17**, 236 (1943).

(5) B. V. Ershler, *ibid.*, **20**, 679 (1946).

(6) R. Parsons, *Proc. Intern. Congr. Surface Activity*, 2nd, London, 38 (1957).

(7) P. Delahay and D. M. Mohliner, *J. Am. Chem. Soc.*, **84**, 4247 (1962).

of purely diffusion-controlled processes (cf. ref. 8 and the literature cited therein).

Experimental Section

The method and experimental details for electrocapillary measurements have been described previously.⁹ More recently, improvement in instrumental design of the electrocapillarometer assembly in the form of a very sensitive pressure-regulating device led to better precision and accuracy of results,¹⁰ and the electrocapillary data used in the present paper were obtained from measurements on the modified apparatus.^{10,11} The following neutral substances were investigated in 1.0 *N* aqueous KCl solutions at 25 ± 1°: piperidine, pyridine, morpholine, dioxane, *n*-propyl alcohol, allyl alcohol, propargyl alcohol, furfurylamine, tetrahydrofurfurylamine, N-methylfurfurylamine, and N-methyltetrahydrofurfurylamine. For the adsorption of organic ions, aniline, furfurylamine, and tetrahydrofurfurylamine were examined in 1.0 *N* aqueous HCl solutions. As in previous papers, the activities of the organic compounds in neutral KCl solutions were assumed to be equal to their concentrations,^{9,10,12,13} but for the ionized aminium bases the activity coefficients were based on those for sodium toluenesulfonate.^{12,14}

The electrocapillary curves for various concentrations of the six-membered heterocyclic compounds and the aliphatic alcohols in KCl base electrolyte solutions have been reported previously,¹⁰ but the ones for the neutral five-membered heterocyclic amines and the ionized bases have not yet been published. The furfurylamines and their conjugate ions constitute a newly available class of corrosion inhibitors (Miles Chemical Co., Elkhart, Ind.), whose adsorption on mercury has been determined by electrocapillary¹¹ and capacitance methods.¹⁵ A detailed analysis of the results from the two complementary methods will be compared later in terms of their general adsorption effects and corrosion-inhibitory properties.¹⁶

The potential of zero charge for all the neutral organic molecules shifts progressively to more anodic values with increasing concentration of the additives and the greatest shifts were observed for the saturated compounds. Conversely, the smallest shift in the p.z.c. was noted for substances such as propargyl alcohol and furfurylamine. The electrocapillary curves for the organic ions were much more symmetrical than the ones for the neutral molecules. In general, the shifts in the p.z.c. and the extents of surface-tension depression were less for corresponding concentrations of the additives in HCl base electrolyte solutions.

Discussion

Theoretical Background for Specifically Adsorbed Ions. The following equation has been derived by Parsons⁶ for inorganic ion systems (the original symbols and significance are retained).

$$(\partial E_{\pm} / \partial \ln a_{\pm})_{q_M} = - (\kappa T / z_{\pm} e) (\partial q_{\mp} / \partial q_M) a_{\pm} \quad (1)$$

In applying this equation to our work where specifically adsorbed *organic* cations (derived by reaction of the base with excess HCl) are involved, we must rewrite eq. 1 in the following form

$$(\partial E_{\text{cal}} / \partial \ln a_{+})_{q_M} = - RT / F (\partial q_{\text{specific}} / \partial q_M) a_{+} \quad (2)$$

where q_{specific} now represents q_{+} , the adsorbed charge due to the cation, and a_{+} is the "activity of the cation"; a_{+} has been assumed to be equivalent to a_{\pm} , i.e., a_{\pm} for the organic salt at an ionic strength determined mainly by the excess HCl, since chloride ion activity in the base electrolyte will be almost invariant in the solutions studied. E_{-} is written as E_{cal} and refers to the electrode potential measured with respect to that of the calomel reference electrode.

The experimental electrocapillary data for anilinium, furfurylaminium, and tetrahydrofurfurylaminium ions have been used to examine the applicability of eq. 2. Values of q_{specific} , which were assumed¹⁷ to equal $F\Gamma_A$ (where F is the Faraday and Γ_A represents the surface excess of the adsorbed species,^{9,12} and under the present conditions these species are almost entirely the protonated form of the organic molecule^{12b}) were plotted against q_M , and both charge terms were computed at constant activity of the organic electrolyte for each of the above-mentioned ions. These plots are shown in Figure 1 and the slopes were then evaluated. Correspondingly, the values of E_{cal} and $RT/F \ln a_{+}$ (assuming $a_{\pm} \approx a_{+}$) at a chosen constant value of q_M (at the p.z.c.) have been plotted for the three

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(9) B. E. Conway and R. G. Barradas, *Electrochim. Acta*, **5**, 319 (1961).

(10) R. G. Barradas and P. G. Hamilton, *Can. J. Chem.*, in press.

(11) P. G. Hamilton, M.A. Thesis, University of Toronto, 1964.

(12) (a) R. G. Barradas and B. E. Conway, *Electrochim. Acta*, **5**, 349 (1961); (b) *J. Electroanal. Chem.*, **6**, 314 (1963).

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(14) R. A. Robinson, *J. Am. Chem. Soc.*, **57**, 1165 (1935).

(15) E. M. L. Valeriotte, M.A. Thesis, University of Toronto, 1964.

(16) R. G. Barradas, P. G. Hamilton, and E. M. L. Valeriotte: (a) Abstract, Corrosion Inhibitor Symposium, Electrochemical Society Meeting, Buffalo, N. Y., 1965; (b) *J. Electrochem. Soc.*, in course of preparation.

(17) This is justified since the principal nonspecifically adsorbed charge in the diffuse layer will be associated with H^{+} and Cl^{-} ions.

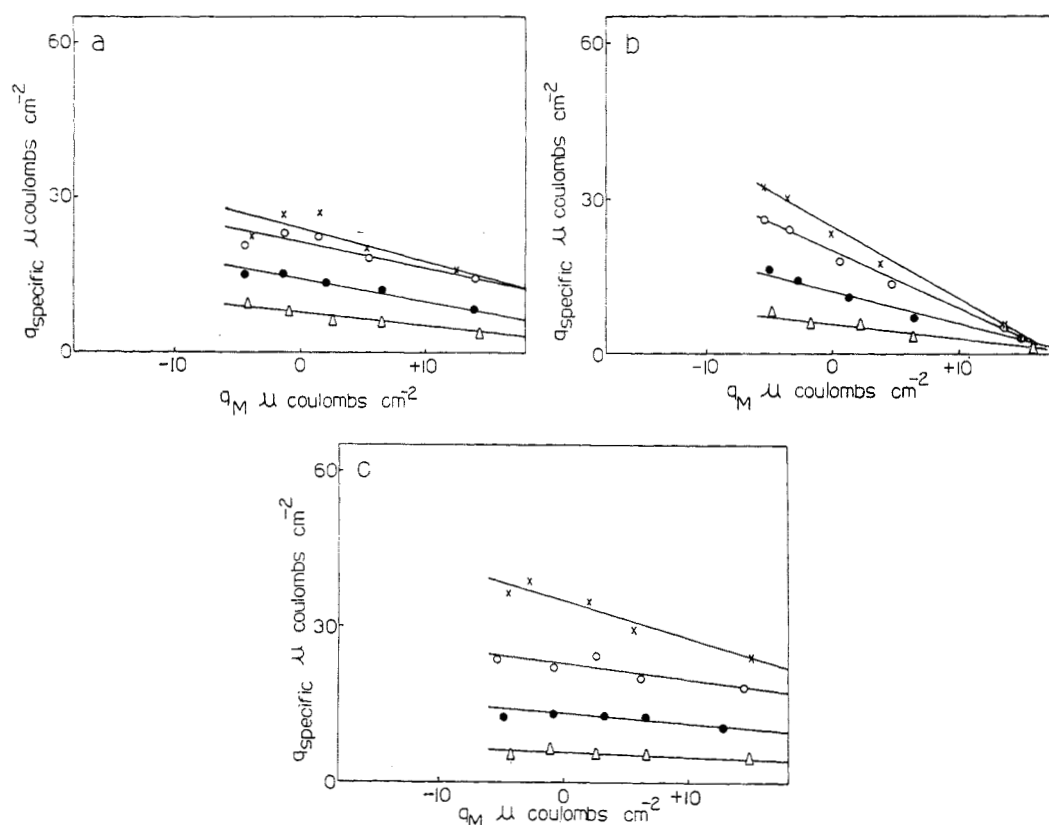


Figure 1. Plots of specific charge due to the adsorbed cations against the charge on the electrode at constant activities.

(a) Furfurylamine; activities: \times , $3.15 \times 10^{-1} M$; \circ , $2.04 \times 10^{-1} M$; \bullet , $7.60 \times 10^{-2} M$; and Δ , $2.73 \times 10^{-2} M$.
 (b) Tetrahydrofurfurylamine; activities: \times , $3.15 \times 10^{-1} M$; \circ , $2.04 \times 10^{-1} M$; \bullet , $7.60 \times 10^{-2} M$; and Δ , $2.73 \times 10^{-2} M$.
 (c) Aniline; activities: \times , $2.63 \times 10^{-1} M$; \circ , $0.75 \times 10^{-1} M$; \bullet , $2.99 \times 10^{-2} M$; and Δ , $1.07 \times 10^{-2} M$.

organic ions, and the slopes have been evaluated. For convenience, the results of these derived calculations are summarized in Table I. It is noteworthy that

within the limits of the experimental errors the average values of $(\partial q_{\text{specific}}/\partial q_M)_{a_+}$ are in reasonably satisfactory agreement with those of $[\partial E_{\text{cal}}/(RT/F \partial \ln a_+)]_{q_M}$ as required theoretically.

Thermodynamic Analysis for Neutral Molecules. A comparable new thermodynamical equation for un-ionized molecules, equivalent to that deduced by Parsons for ions, is required for describing the "Esin and Markov" behavior of neutral molecules.

$$(\partial E_{\text{cal}}/\partial \ln a_A)_{q_M} = -RT(\partial \Gamma_A/\partial q_M)_{a_A} \quad (3)$$

where a_A is the activity of the neutral molecule and will be assumed to be equal to the concentration C_A as stated previously.^{9,10,12,13} By an equivalent procedure to that described for the organic ions, we can test eq. 3 by plotting (i) E_{cal} vs. $RT \ln a_A$ at constant q_M (e.g., at the p.z.c.) and (ii) Γ_A vs. q_M at constant a_A for the neutral substances investigated. The slopes of both sets of curves have been evaluated and are compared in Tables II-IV. The comparison of the evaluated slopes shows that they are generally not in good agreement with one another, and the comparison

Table I: Test of Eq. 2 for the Esin and Markov Effect Due to Organic Cations

System	a_+, M	$(\partial q_{\text{specific}}/\partial q_M)_{a_+}$	$-(\partial E_{\text{cal}}/RT/F \partial \ln a_+)_{q_M}$
Furfurylamine in 1 N HCl	2.73×10^{-2}	-0.2	-0.4
	7.60×10^{-2}	-0.4	
	2.04×10^{-1}	-0.5	
	3.15×10^{-1}	-0.6	
	Av.	-0.4	
Tetrahydrofurfurylamine in 1 N HCl	2.73×10^{-2}	-0.3	-0.8
	7.60×10^{-2}	-0.6	
	2.04×10^{-1}	-1.1	
	3.15×10^{-1}	-1.4	
	Av.	-0.9	
Aniline in 1 N HCl	1.07×10^{-2}	-0.1	-0.2
	2.99×10^{-2}	-0.2	
	0.75×10^{-1}	-0.3	
	2.63×10^{-1}	-0.7	
	Av.	-0.3	

Table II: Test of Eq. 3 for the Esin and Markov Effect Due to Neutral Six-Membered Heterocyclic Compounds

System	a_A, M	$10^8(\partial\Gamma_A/\partial q_M)_{a_A}$	$-10^8(\partial E_{cal}/RT \partial \ln a_A)_{q_M}$
Piperidine in 1 N KCl	3.0×10^{-2}	-2.1	
	1.0×10^{-1}	-1.9	-1.5
	3.0×10^{-1}	-1.9	
	1.0	-1.8	
	Av.	-1.9	
Pyridine in 1 N KCl	3.0×10^{-2}	-1.0	
	1.0×10^{-1}	-1.9	-2.4
	3.0×10^{-1}	-1.6	
	1.0	-0.9	
	Av.	-1.4	
Dioxane in 1 N KCl	1.0×10^{-1}	-0.7	
	3.0×10^{-1}	-1.0	
	1.0	-2.0	-2.7
	2.0	-3.3	
	Av.	-1.8	
Morpholine in 1 N KCl	1.0×10^{-1}	-0.8	
	3.0×10^{-1}	-1.4	
	5.0×10^{-1}	-1.4	-1.7
	1.0	-1.4	
	Av.	-1.3	

Table III: Test of Eq. 3 for the Esin and Markov Effect Due to Neutral Aliphatic Alcohols

System	a_A, M	$10^8(\partial\Gamma_A/\partial q_M)_{a_A}$	$-10^8(\partial E_{cal}/RT \partial \ln a_A)_{q_M}$
<i>n</i> -Propyl alcohol in 1 N KCl	1.0×10^{-1}	-1.1	
	3.0×10^{-1}	-2.3	
	5.0×10^{-1}	-2.7	-3.7
	1.0	-3.5	
	Av.	-2.4	
Allyl alcohol in 1 N KCl	1.0×10^{-1}	-0.6	
	3.0×10^{-1}	-1.5	
	5.0×10^{-1}	-2.1	-2.2
	1.0	-2.8	
	Av.	-1.8	
Propargyl alcohol in 1 N KCl	1.0×10^{-1}	-0.2	
	3.0×10^{-1}	-0.6	
	5.0×10^{-1}	-1.3	-0.7
	1.0	-1.6	
	Av.	-0.9	

is less satisfactory than for the case of organic ions. From Tables III and IV it will be noted that the agreement between $(\partial\Gamma_A/\partial q_M)_{a_A}$ and $-(\partial E_{cal}/RT \partial \ln a_A)_{q_M}$ is better for the unsaturated compounds than for their corresponding saturated analogs. In general, the two derivatives are in better agreement at the higher concentrations. From the tabulated data, it is seen that $(\partial\Gamma/\partial q_M)_{a_A}$, which should be a constant

Table IV: Test of Eq. 3 for the Esin and Markov Effect Due to Neutral Five-Membered Heterocyclic Compounds

System	a_A, M	$10^8(\partial\Gamma_A/\partial q_M)_{a_A}$	$-10^8(\partial E_{cal}/RT \partial \ln a_A)_{q_M}$
Furfurylamine in 1 N KCl	1.0×10^{-2}	-0.5	
	3.0×10^{-2}	-1.1	-1.9
	1.0×10^{-1}	-1.5	
	3.0×10^{-1}	-1.6	
	Av.	-1.2	
Tetrahydrofurfurylamine in 1 N KCl	1.0×10^{-2}	-0.5	
	3.0×10^{-2}	-0.9	
	1.0×10^{-1}	-1.3	-2.1
	3.0×10^{-1}	-1.3	
	5.0×10^{-1}	-1.3	
N-Methylfurfurylamine in 1 N KCl	1.0×10^{-2}	-1.1	
	3.0×10^{-2}	-1.4	
	1.0×10^{-1}	-1.5	
	3.0×10^{-1}	-1.4	
	Av.	-1.4	-1.8
N-Methyltetrahydrofurfurylamine in 1 N KCl	1.0×10^{-2}	-1.0	
	3.0×10^{-2}	-1.3	
	1.0×10^{-1}	-1.1	-1.9
	3.0×10^{-1}	-1.3	
	Av.	-1.2	

quantity for varying concentrations of the organic additive, in fact tends to increase with increasing adsorbate concentration. It is suggested that this variation arises from orientation of the molecules of the adsorbate in the surface layer at high coverages when the additives are present at high concentrations, as we have argued from other points of view previously.^{9,12a}

Changes in the Potential of Zero Charge with $(\Gamma_A)_{pzc}$ and $\log C_A$. For the compounds listed in Tables II and III, the variation of ΔE_{pzc} with $(\Gamma_A)_{pzc}$ and with $\log C_A$ have been previously reported.¹⁰ Similar plots for the ionic species and the neutral furfurylamines are shown in Figures 2 and 3, respectively, which confirm our earlier contention^{9,10,12} that “ π -excessive” substances¹⁸ show the smallest shifts in ΔE_{pzc} while the “ π -deficient” hydrogenated derivatives show the opposite behavior. For the latter compounds, noticeable breaks are observed at certain critical $(\Gamma_A)_{pzc}$ and C_A values. We have previously attributed the sharp changes in $d\Delta E_{pzc}/d(\Gamma_A)_{pzc}$ and $d\Delta E_{pzc}/d \log C_A$ to sudden orientation effects.^{9,10,12} For the saturated six-membered heterocyclic compounds, we have demonstrated that it is not possible to discern orientation effects with increasing surface coverage or

(18) A. Albert, “Heterocyclic Chemistry,” Athlone Press, London, 1959.

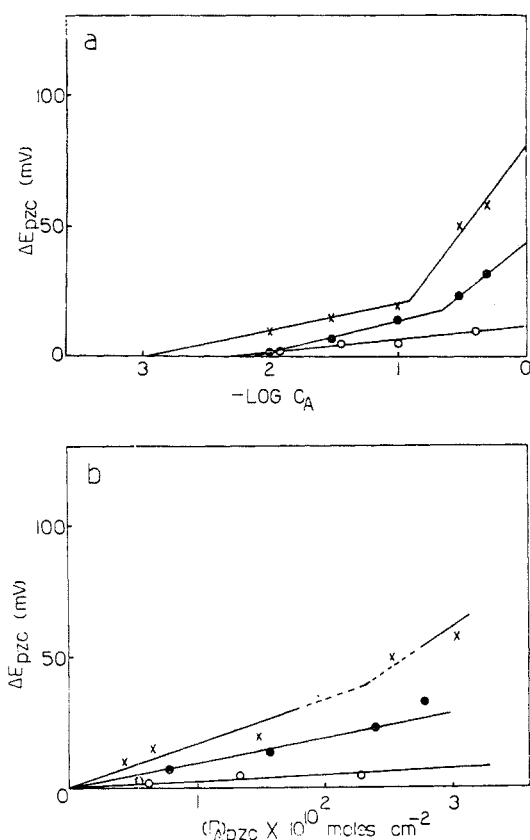


Figure 2. (a) Shifts of the potential of zero charge with additive concentrations in 1 N HCl. (b) Shifts of the potential of zero charge against surface excess at the p.z.c. in 1 N HCl. ●, furfurylamine; X, tetrahydrofurfurylamine; and O, aniline.

C_A because of the similarity of the projected molecular areas of the four possible orientational configurations (see Figure 4) involving the upright or inverted forms of either of the two conformational isomers for each of these substances¹⁰; also, the interconversion rate between the isomeric forms will generally be large unless field effects stabilize one form, *e.g.*, that with the higher dipole moment.

The change in ΔE_{pzc} with $(\Gamma_A)_{pzc}$ is a more dependable indication for discerning orientation effects than the plots of ΔE_{pzc} against $\log C_A$. It has been suggested by other workers^{19,20} that the following electrostatic formula of Helmholtz can account for the variation of ΔE_{pzc} with $(\Gamma_A)_{pzc}$.

$$\Delta E_{pzc} = 4\pi N\mu(\Gamma_A)_{pzc}/\epsilon \quad (4)$$

where μ here represents the dipole moment, ϵ the dielectric constant of the organic substance, and N is Avogadro's number. Equation 4 may be used to give indirect support for the orientation effects involved with the organic molecules investigated and also to add

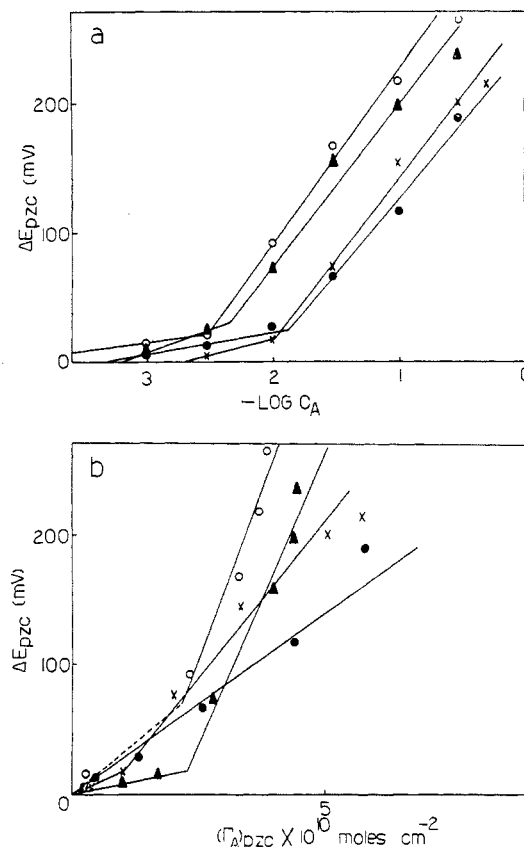


Figure 3. (a) Shifts of the potential of zero charge with additive concentrations in 1 N KCl. (b) Shifts of the potential of zero charge against surface excess at the p.z.c. in 1 N KCl. ●, furfurylamine; X, tetrahydrofurfurylamine; ▲, N-methylfurfurylamine; and O, N-methyltetrahydrofurfurylamine.

substance to our discussion of the Esin and Markov behavior. A test of eq. 4 has been made by evaluation of the slopes of ΔE_{pzc} with $(\Gamma_A)_{pzc}$ from the plots reported and are compared with $4\pi N\mu/\epsilon$ in Table V for a representative selection of compounds, the μ and ϵ values of which are available.

It has been shown that the effective μ for orientated films will be greater²¹⁻²³ than for unorientated films and this is borne out in the results of the calculations reported in Table V for pyridine, *n*-propyl alcohol, and allyl alcohol. Pyridine will tend to orient²⁴ from a planar to a perpendicular position of adsorption,

(19) F. W. Schapink, M. Ondeman, K. W. Len, and J. W. Helle, *Trans. Faraday Soc.*, **56**, 415 (1960).

(20) J. H. Schulman and E. K. Rideal, *Proc. Roy. Soc. (London)*, **A130**, 259, 270, 284 (1930); *cf.* A. N. Frumkin, *Ergeb. Exakt. Naturwiss.*, **7**, 258 (1928).

(21) J. S. Mitchell, *Trans. Faraday Soc.*, **31**, 980 (1935).

(22) M. Gerowicz, A. N. Frumkin, and D. Vargin, *J. Chem. Phys.*, **6**, 906 (1938).

(23) M. Gerowicz and A. N. Frumkin, *ibid.*, **4**, 624 (1936).

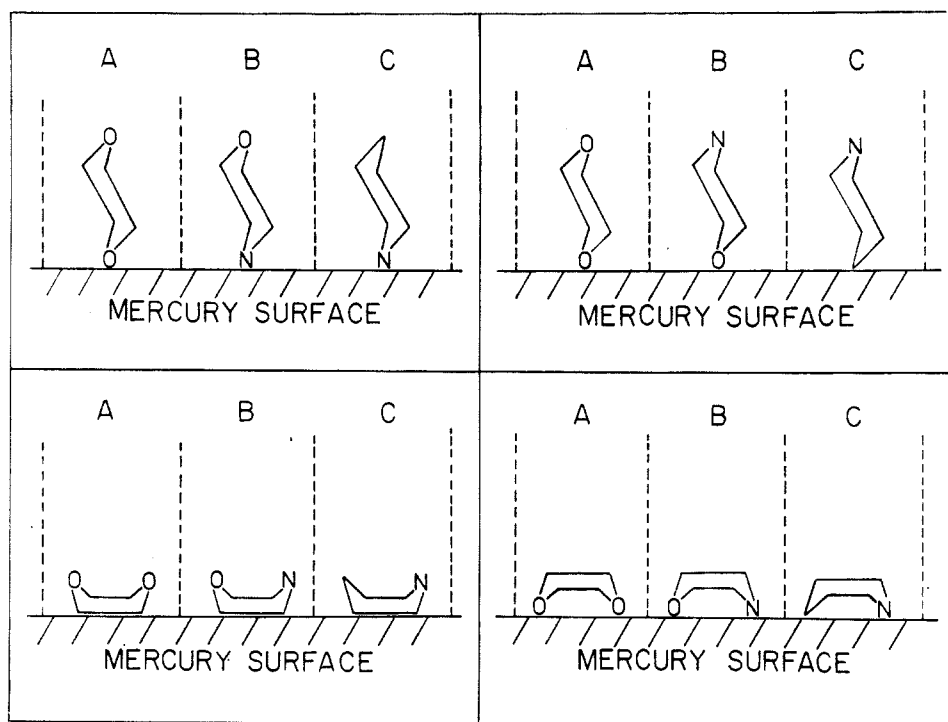


Figure 4. Schematic representation of the four possible positions involving the upright or inverted boat and chair conformations of the adsorbed molecule at the mercury-electrolyte interface: A, dioxane; B, morpholine; and C, piperidine.

Table V: Test of Eq. 4 for the Change of E_{pzc} with Respect to $(\Gamma_A)_{pzc}$

Substance	$10^{-6} d(\Delta E_{pzc}) / d(\Gamma_A)_{pzc}$	$4\pi N\mu/\epsilon \times 10^{-6}$
Dioxane	1.19	1.52
Pyridine	1.82	1.35
<i>n</i> -Propyl alcohol	3.3	0.56
Allyl alcohol	(a) 0.53	0.57
	(b) 1.10	
Propargyl alcohol	0.43	0.57

presumably with the polar group pointing towards and hydrogen bonded with the solvent as surface coverage increases,^{9,10,26} and $d(\Delta E_{pzc})/d(\Gamma_A)_{pzc}$ would be equal to $4\pi N\mu/\epsilon$ if μ increased by approximately 30% of its actual value¹⁸ of 2.2 D. (We assume that the dielectric constant of 12.3 for pyridine²⁷ remains unchanged after orientation; however, it is more probable that the ratio of μ/ϵ changes through variation in both terms.) The same change of planar to perpendicular orientation has been postulated for *n*-propyl alcohol¹⁰ and numerical agreement between the values in the second and third columns of Table V may be obtained with the fairly reasonable supposition that μ increases from 1.65²⁸ to 3.30 D. with a corresponding decrease

in ϵ from about 22²⁸ to *ca.* 7. For allyl alcohol two values of $d(\Delta E_{pzc})/d(\Gamma_A)_{pzc}$ are reported as a and b (Table V), and these slopes were evaluated over two equivalent ranges of $(\Gamma_A)_{pzc}$ since the change in slope occurs approximately at the middle region of the range of $(\Gamma_A)_{pzc}$ values plotted. We note that excellent agreement with $4\pi N\mu/\epsilon$ is obtained for slope a when $\mu = 1.63$ D.²⁹ and $\epsilon = 21.6$,³⁰ but after the onset of orientation, agreement with slope b would be obtained if μ increased from 1.63 to 3.26 D. (again we note that μ may be less than 3.26 D. after orientation, but with a corresponding decrease in ϵ). If we assume that μ and ϵ for propargyl alcohol are similar to the values

(24) As pyridine (and other neutral molecules) enter the double layer, water molecules become displaced.^{9,12} This would cause a change of surface potential even if the pyridine molecules were not oriented, since water molecules may have been oriented to an extent dependent on rational potential (*cf.* ref. 25).

(25) J. O'M. Bockris, M. A. V. Devanathan, and K. Müller, *Proc. Roy. Soc. (London)*, **A274**, 55 (1963).

(26) L. Gierst, D. Bermane, and P. Corbusier, *Ric. Sci., Suppl.*, **4**, 75 (1959).

(27) R. Parsons, "Handbook of Electrochemical Constants," Butterworth and Co. (Publishers) Ltd., London, 1959.

(28) B. E. Conway, "Electrochemical Data," Elsevier Publishing Co., London, 1952.

(29) L. G. Wesson, "Tables of Electric Dipole Moments," Massachusetts Institute of Technology, Cambridge, Mass., 1948.

(30) A. Weissberger, "Techniques of Organic Chemistry," Vol. VII, 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1955.

for allyl alcohol, then approximate agreement between the figures in the second and third columns of Table V is again observed.

The numerical values of $d(\Delta E_{pzc})/d(\Gamma_A)_{pzc}$ and $4\pi N\mu/\epsilon$ are reversed in magnitude for dioxane in comparison with the data for other molecules listed in Table V. Agreement between the two quantities can be obtained if $\epsilon = 2.2^{28}$ is increased to 2.7 or if μ ($= 0.45$ D.²⁸) is taken as 0.36 D. The latter suggestion is not unreasonable since the value of $\mu = 0.45$ D.²⁸ has been cited from a paper originating in 1923, and may possibly be in error.³¹ The calculations according to eq. 4 seem to indicate that there is no confirmation of orientation effects from the dipole moment and/or dielectric constant considerations for saturated heterocyclic compounds which exhibit conformational isomerism. The only valid conclusion that may be inferred from the applicability of the value of $\mu \approx 0.4$ D. is that it gives weight to our previous hypothesis that dioxane molecules may adsorb in the boat conformation on mercury.¹⁰ It may be noted, however, that even in the chair form the electric field, being inhomogeneous, will interact with the dioxane



molecule since one C—C end of the molecule will probably be in a higher field than the other. The field will also modify the equilibrium constant for the boat-chair equilibrium as we have implied in the earlier discussion.

Dependence of the Esin and Markov Coefficients upon Charge on the Electrode. The thermodynamic treatment for the Esin and Markov effect for inorganic ions according to Parsons⁶ is only applicable in an approximate manner for organic ions since simple inorganic ions like I^- , Cl^- , etc., do not affect the mean di-

electric constant or thickness of the inner Helmholtz layer to any great extent. Parsons has predicted that larger ions (*e.g.*, organic cations or anions) may behave like neutral molecules at the interface.³² Our experimental observations are shown in Table V and, with regard to the variation of $(\partial q_{specific}/\partial q_M)_{a+}$ with increasing activity, confirm the theoretical expectancy. For neutral molecules, the greater discrepancy between $(\partial \Gamma_A/\partial q_M)_{a_A}$ and $-(\partial E_{cal}/RT \partial \ln a_A)_{q_M}$ is probably due to the uncertainty in the dependence of the latter term on q_M .^{7,32} Γ_A is largest for neutral substances when q_M tends to a minimum, and decreases as the charge on the electrode increases anodically or cathodically with respect to the p.z.c. Furthermore, the lack of constancy in $(\partial q_{specific}/\partial q_M)_{a+}$ and $(\partial \Gamma_A/\partial q_M)_{a_A}$ for different a_+ and a_A values, respectively, may be associated with orientation effects at high surface coverages or corresponding additive concentrations. In considering the above-mentioned reasons, we conclude that the theoretical requirements of eq. 2 and 3 can provide only approximate estimates of the Esin and Markov behavior for organic species, although it is to be noted that theory and experiment agree better for organic cations and for molecules with π -orbital systems.

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(31) S. Walker in "Physical Methods in Heterocyclic Chemistry," Vol. I, A. R. Katritzky, Ed., Academic Press Inc., New York, N. Y., 1963, p. 198.

(32) R. Parsons, *Trans. Faraday Soc.*, **55**, 999 (1959).