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Solvent Structure and Molecular Orientation in the Double-Layer at the Mercury—Water Interface*

B. E. Conway and H. P. Dhar

Chemistry Department, University of Ottawa, Ottawa, Canada

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Solvent structure and molecular orientation in the Hg-water interphase is an important and previously little investigated aspect of the electrical double-layer at charged metal interfaces. By using pyrazine and pyridine in critical comparative experiments on *a)* changes of surface dipole potential difference (Esin and Markov effects), *b)* surface pressure changes and *c)* charge dependence of free energy of adsorption, it is shown how the surface dipole contribution from oriented solvent molecules may be evaluated together with the charge-dependent distribution function for water orientation. In the case of pyridine, orientation of the adsorbate molecule itself occurs in a manner dependent on surface charge on the metal and interaction with oriented and bulk solvent molecules.

INTRODUCTION

The role of solvent structure and orientation of solvent molecules at charged interfaces has, until recent years[1–3], been a relatively neglected subject in discussions of the double-layer[4]. It has obvious importance in relation to any real representation of the interphase between an electrode surface and the solution. The role of local solvent structure changes and molecular orientation has, however, played an important part in the development of the theories of solvation of spherical and linear charged particles (polyelectrolytes)[5]. Following the model by Watts-Tobin and Mott[1,2] and the application of their model to the treatment of field-dependent, substitutional adsorption at electrode-solution interfaces by Bockris, Devanathan and Müller[6], a more realistic representation of the real structure of the double-layer, particularly in the water solvent, has resulted[6].

In terms of the theory of polar dielectrics near orientation saturation, the first treatment of the condition of polarized solvent molecules at an electrode interface was that given by Conway, Bockris and Ammar[7] (*cf.* Conway[8]) followed after sometime by the related treatment by Grahame.

The problem of pollution of water by surfactants, and the resultant foaming, has provided an added impetus to the study of adsorption of organic substances at liquid interfaces. As in the case of bulk solutions of organic substances in the water solvent, rather specific solute-solvent and solute-solute interaction and structure effects may be anticipated in interphases, dependent upon the orientation of either or both species in the surface. Orientation effects

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associated with adsorption of organic substances in relation to the intrinsic orientation of solvent molecules must hence be understood; especially at electrodes, where such effects will be charge-, or potential-dependent, knowledge of solvent orientation is an essential requirement for quantitative treatments of the double-layer (*cf.*[2,6]). When the surfactant is ionic, other and longer range interaction effects arise[13] and at appreciable coverages ($\Theta > 0.2$) solvation co-sphere interaction effects[9,10] become of major importance.

In the present paper, we present some new experimental observations on the orientation of pyridine and pyrazine molecules at the mercury electrode which provide relatively direct and quantitative information on the field-dependent orientation of solvent water dipoles. Elsewhere[10], we have compared the adsorption behavior of these molecules at the air-water and mercury-water interfaces.

General Basis of the Methods of Approach Used

The orientation of solute and solvent molecules at an electrode interface can be evaluated *(a)* in terms of the shift of potential at which a given charge q_m arises, including $q_m = 0$, the e. c. m. condition; *(b)* the dependence of surface pressure due to an adsorbed solute molecule at a given coverage on surface charge or metal-solution p. d., and hence on orientation of the molecule, and *(c)* the dependence of free energy of adsorption evaluated at a given coverage Θ[9,13,14], on the electrode surface charge.

Important solvent-structure factors in the adsorption can also be deduced from the coverage and charge dependence of the isosteric[9,10] entropy and heat[11] of adsorption of the solute. This aspect of the problem has, however, been dealt with in recent previous papers from this[9,10] and other[12] laboratories.

EXPERIMENTAL

(i) Choice of Compounds Studied

Much of the work on adsorption of organic molecules at electrode interfaces has been concerned with adsorbates of such relatively complex structure and poly-functionality that quantitative interpretation of the electrochemical adsorption behavior is rendered very difficult, bearing in mind the already highly specific solvation effects that are indicated[15,16] in the aqueous medium through such properties as partial molal volume[15], compressibility[16,17], specific heat behavior, *etc.* Also the question of relative molecular size of solute and solvent molecules is an important factor to which little attention has been given[18] in studies of adsorption of organic molecules (but *cf.*[9,10,19,20] where the size factor was treated in terms of Flory-Huggins type isotherms[21]). In the present work *(a)* pyridine and *(b)* pyrazine were chosen as the adsorbates because *(a)* exhibits interesting orientation effects[22] and carries a net electric dipole while *(b)* is almost exactly the same size and has similar conjugated structure but has *no* overall dipole moment (it has, however, two local $\begin{matrix}C\\C\end{matrix}\!\!>\!\!\!\!>N$: dipole components that promote hydrophilicity) and *(c)* both molecules are rigid and hence cannot change their conformation in a field in the way that such previously studied molecules as dioxane[23] or butene- or butyne-1,4-diols[18] can, *e. g.* with respect to the direction of the OH groups.

(ii) Electrocapillary Measurements

In general, the technique employed was similar to that described in refs. 9 and 10. Surface tension measurements on an Hg electrode were made by means of a Lippmann capillary electrometer employing the special techniques[9] developed previously in this laboratory. The improved accuracy of measurements of surface tension using this apparatus, over that with conventional technique, has been discussed previously[9].

The whole electrocapillary cell, including the Hg column and reservoir, was thermostatted to ± 0.1 °C and experiments could be conducted from 5 to 75 °C. Supporting electrolyte solutions were made up from 0.03 M $NaClO_4$ in most experiments. The solutions contained 0.01 M NaOH to ensure that the bases pyridine and pyrazine remained virtually completely un-ionized.

Measurements were made at the following temperatures and some or all of the following molal concentrations of the adsorbates, pyrazine, pyridine and amyl alcohol: 281, 293, 308, 323 and 338 °K; 0.003, 0.006. 0.008, 0.012, 0.020, 0.035, 0.055, 0.090, 0.130, 0.180, 0.250, 0.350, 0.50 M

0.03 M KCl calomel or 0.01 M NaOH/HgO reference electrodes were used. Their potentials were constant to 0.2 mV during runs. The junction between the electrolyte in the cell and in the reference electrode electrolyte was made in a wetted ground glass joint covering the bottom of the reference electrodes. Liquid junction potentials were constant to better the 0.5 mV during runs and their absolute values were < 5 mV. The l. j. p. does not enter into the experimental results which were expressed in terms of surface charge.

In experiments where runs were made at various temperatures, both the reference and the capillary electrodes were maintained at the same temperature thus eliminating thermal junction potentials in the electrolyte. The advantage[9] of expressing derived results for conditions of constant q_M rather than constant E again arises here with respect to measurements over a range of temperatures where a change of reference electrode potential must occur.

(iii) Evaluation of Surface Excess Γ, Surface Pressure Φ, Coverage Θ and Surface Charge q

As in previous work[9,10,13], surface excess quantities and q were evaluated from the Gibbs-Lippmann equation for given values of q[24], the electrode surface charge. The surface pressure Φ was obtained for various coverages and q values by similar calculations[24]. Θ values were obtained from the derived Γ values taking Γ_{max} for saturation adsorption as 4.5×10^{-10} mole cm^{-1} for pyrazine. In the case of pyridine, where two orientations of the molecule can arise, Γ_{max} was taken as 4.5×10^{-10} or 8.3×10^{-10} mole cm^{-2}, based on Courtauld space-filling models.

(iv) Evaluation of Esin and Markov Effects

Esin and Markov plots were made by calculating from the experimental surface tension-potential plots, the potentials at which various surface charges arose as surface excess Γ changed with increasing adsorbate concentration. At fixed surface charges, the corresponding potentials were calculated from a computer programme as described previously[9,25].

RESULTS AND DISCUSSION

Solvent and Adsorbate Orientation

Information on orientation of adsorbate dipoles has previously been considered[23] in terms of the Esin and Markov (EM) effects (shift of potential of zero charge) related to the dipole p. d. χ_d established according to the Helmholtz relation

$$\chi_d = 4\pi \bar{N}\mu/\varepsilon_s \tag{1}$$

for N dipoles of moment μ normal to the surface in an interphase of dielectric constant ε_s [note that ε_s is itself expected limitingly to be a f (χ_d) and μ can be a f (N)].

The previous treatments of effects due to χ_d have not taken into account solvent orientation. That this is a significant, if not major, factor is indicated from Fig. 1 which shows a substantial EM effect for adsorption of the *non*-polar molecule naphthalene[25] from a methanolic 1 N H_2SO_4 solution at $q = 0$. The EM effect can also be evaluated for q values other than zero and hence provides a

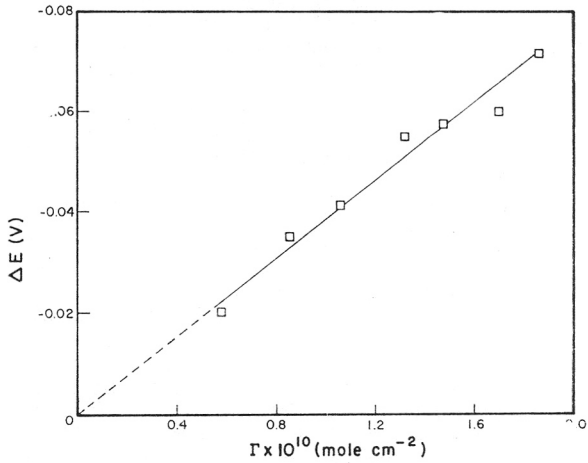

Fig. 1. Esin and Markov effect for adsorption of naphthalene at Hg from methanolic Na_2SO_4 solution at 25 °C at the potential of zero charge[25].

means of evaluating not only the qualitative role of solvent orientation, but quantitatively the solvent dipole orientation contribution in $\Delta\chi$ which determines the experimental change of potential ΔE for a given q value as the extent of solute adsorption increases.

Results for ΔE_q ($= E_{q,\text{ base solution}} - E_{q,\text{ adsorbate}}$) for a given electrode surface charge are shown in Fig. 2 for pyrazine adsorption at several temperatures from solutions in 0.3 M aq. $NaClO_4$. ΔE_q shows a linear change with Γ with a slope depending on q. At $q = 0$, there is an appreciable dependence of ΔE on Γ as in the case of naphthalene. Pyrazine is a flat molecule (like naphthalene) with zero (net) dipole moment and will not itself tend to be oriented in the double-layer field. Hence the substantial effects in Fig. 2 must be attributed to charge dependent, water dipole orientation.

Such effects will arise because adsorption of pyrazine must occur by *replacement*[6] of solvent molecules already adsorbed and oriented in the interphase, to an extent determined by q or the corresponding outer field. It is of interest that zero ΔE as f (Γ) arises not at $q = 0$ but at $-2\,\mu$ C cm^{-2} which indicates intrinsic orientation of water at the p. z. c. From the sign of ΔE, the orientation must be with the O atom *towards* the Hg surface, a direction consistent with greater image energy[6]. This is also consistent with the increasingly *negative* ΔE for more positive q where relatively greater extents of H_2O dipole orientation will arise, also with the negative ends of the dipoles disposed towards the positive Hg surface. Fig. 2 shows that the EM effect is symmetrical about $q = -2\,\mu$ c cm^{-2} for various other q values.

The standard free energy of adsorption, evaluated elsewhere[10], is also a symmetrical function of q about $q = -2\,\mu$ C cm^{-2} (Fig. 3), so that pyrazine forms an ideal molecule for examining the solvent replacement theory of electrochemical adsorption[6] and thus for providing direct information on the extent of solvent dipole orientation as a f (q) experimentally. This can be done as follows.

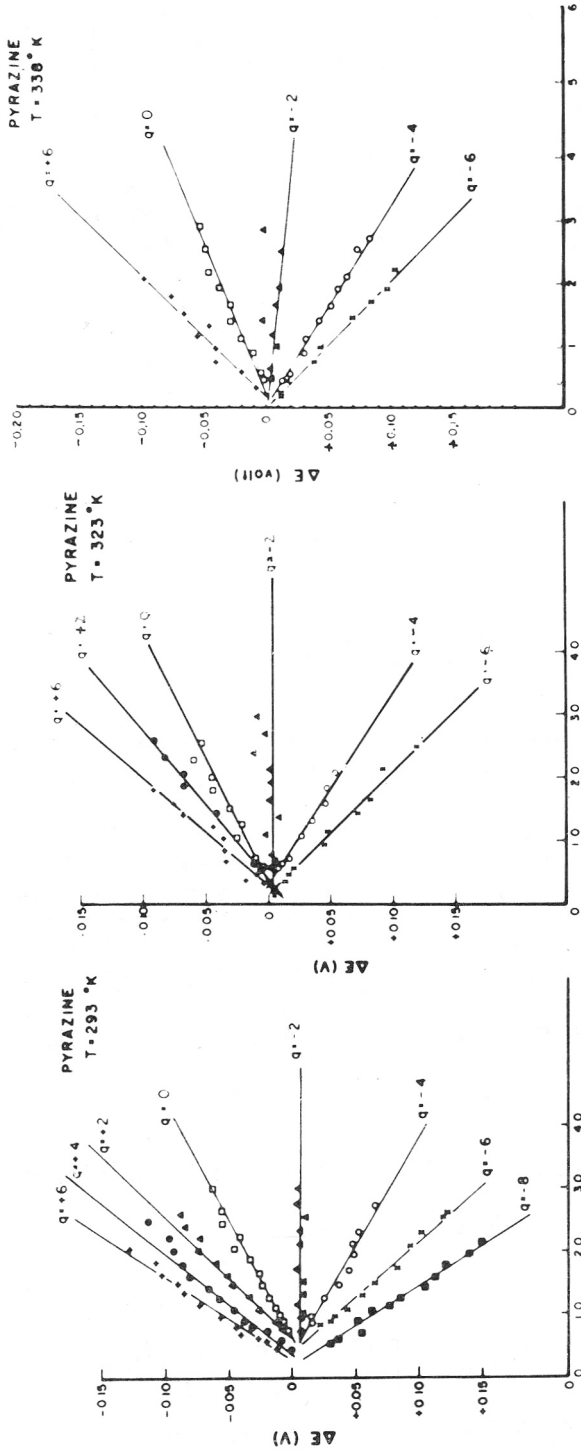

Fig. 2. Esin and Markov plots for pyrazine adsorption at Hg as a function of Γ at various q values in 0.03 M aq. $NaClO_4$. *a)* 293 °K; *b)* 323 °K; *c)* 338 °K.

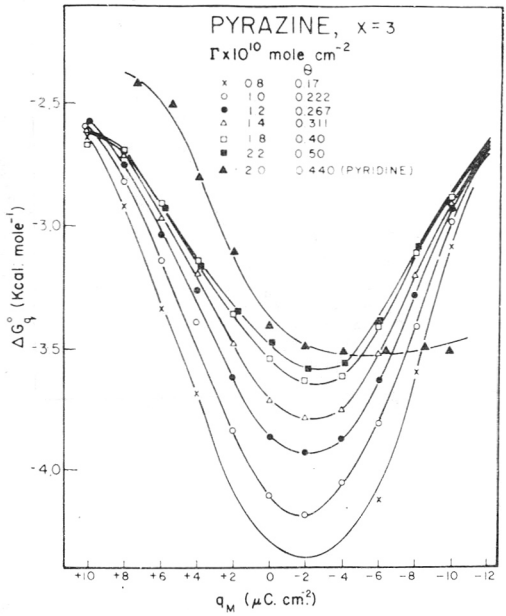

Fig. 3. Variation of »apparent standard free energy of adsorption«[13,14,25] of pyrazine at 25 °C as a function of charge q at various surface coverages (data for one coverage by pyridine is included for comparison).

Changes of χ Potential due to Replacement of Oriented Solvent Dipoles

(a) Pyrazine. — Let the experimental slope of an EM effect relation be $m = \mathrm{d}(\Delta E)/\mathrm{d}\Gamma = \delta(\Delta E)/\delta\Gamma$ where δ represents a finite change of ΔE or Γ with increasing coverage by the adsorbate, itself remaining unoriented. The number of oriented solvent dipoles can be represented[6] as $(N\uparrow - N\downarrow)_q$ cm^{-2} at a given q and will be $\mathrm{f}(q)$. At a given q, each pyrazine molecule replaces x adsorbed water molecules ($x \doteqdot 3$[10]). Hence for Γ mole cm^{-2} of adsorbed pyrazine, $x\Gamma$ mole cm^{-2} water oriented in the ratio $N\uparrow/N_\mathrm{T}$ and $N\downarrow/N_\mathrm{T}$ are replaced. Hence a degree of net solvent orientation in the double-layer has been eliminated by displacement equivalent to $x\Gamma(N\uparrow - N\downarrow)/N_\mathrm{T}$ where $N_\mathrm{T} = N\uparrow + N\downarrow$. This change of extent of solvent dipole orientation per cm^{-2} gives rise to

$$\Delta E_q = \frac{x\Gamma(N\uparrow - N\downarrow)}{N_\mathrm{T}}\, 4\pi\mu/\varepsilon_\mathrm{s} \tag{2}$$

The experimental slope m of the integral $\Delta E - \Gamma$ relation is hence

$$m = \mathrm{d}\Delta E_q/\mathrm{d}\Gamma \doteqdot \delta\Delta E_q/\delta\Gamma = \frac{x(N\uparrow - N\downarrow)}{N_\mathrm{T}}\, 4\pi\mu/\varepsilon_\mathrm{s} \tag{3}$$

Now[1,2,6]

$$\frac{N\uparrow - N\downarrow}{N_\mathrm{T}} = \tanh\left[\frac{\mu F}{kT} - \frac{Uc}{kT}\,\frac{(N\uparrow - N\downarrow)}{N_\mathrm{T}}\right] \tag{4}$$

which enables $(N\uparrow - N\downarrow)/N_\mathrm{T}$ to be estimated for various values of Uc/kT where

U is the solvent dipole-dipole interaction energy in a lattice of coordination number c (= 6) and F is the outer field given by $-4\pi q/\varepsilon_s$.

Fig. 4 shows how $(N\uparrow - N\downarrow)/N_T$ evaluated from the experimental results of Fig. 2 compares with that calculated from equation (4) taking $U c/k T = 2$, 3, 3.5 or 4, μ for water 1.87 D and $\varepsilon_s = 6$[6,7]. The experimental relation for pyrazine is consistent with the heavy curve for $U c/k T = 3.5$. (It is displaced from this line along the »X«-axis by $2\,\mu$ C cm^{-2} since the maximum adsorption of pyrazine and many other compounds usually occurs at $q = -2\,\mu$ C cm^{-2} rather than zero). The good fit for $U c/k T = 3.5$ is reasonably consistent with the value, 3.0, of this term required to fit the variation of free-energy of adsorption of pyrazine (Fig. 3) with q, discussed in ref. 10.

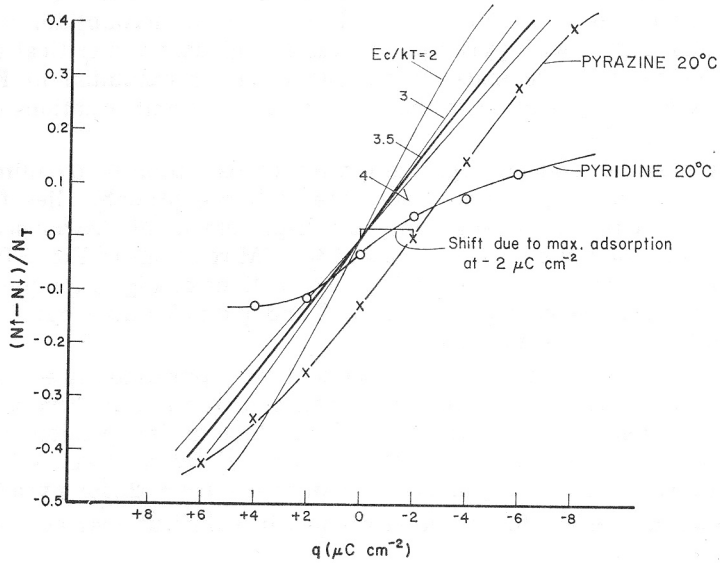

Fig. 4. Evaluation of the solvent orientation distribution function $(N\uparrow - N\downarrow)/N_T$ from data of Fig. 2 in relation to values calculated from eqn. (4) with various Uc/kT values.

Elsewhere, the behavior of the symmetrical saturated bicyclic N-molecule, 1,4-diazabicyclo(2,2,2)octane, will be described separately owing to its complex adsorption characteristics and their relation to two-stage ionization of the molecule.

Damaskin *et al.*[32], have remarked that EM effects as large as 0.5 V cannot be explained in terms of solvent orientation since the maximum χ_d given by the theory of Bockris, Devanathan and Müller is 0.1 V. This conclusion is, however, incorrect since the correct maximum value of χ_d is, in fact, *ca.* 1.2 V and its *actual* value, *e. g.* at $q = \pm 15\,\mu$ C cm^{-2}, depends on the value of $U c/k T$ and the value of N_T for the water layer, as shown by Conway, MacKinnon and Tilak[31]. It is seen from ref.[31] that a change of χ_d of the magnitude demonstrated in the present work can easily arise from displacement of oriented solvent dipoles if $U c/k T = 3$ to 6 and if $x = 3$ to 4, values which are also consistent with the dependence of standard free energy of adsorption on q (Fig. 3 and ref.[10]).

(b) Pyridine. — The results for ΔE as $f(\Gamma)$ for various q in the case of pyridine (Fig. 5) are strikingly different from those for pyrazine (Fig. 2): beyond a given value of Γ, dependent on q, the $\Delta E - \Gamma$ relations suddenly change slope to lines having approximately the *same* slopes independent of q. This effect is evidently related to the changes of slope with increasing Γ also seen in the $\Phi - \Gamma$ plots to be discussed below. Qualitatively, these sudden changes of slope of the EM plots are probably the result of orientation of the pyridine molecules themselves, as indicated in other ways in previous thermodynamic work[26,27].

If a sudden and complete change of orientation of adsorbed pyridine occurred at a critical Γ, with continuing further orientation at higher Γ, an EM relation would result having the form of Fig. 6a which is *not* similar to the experimental behavior (Fig. 6c). A progressive effect involving two *parallel* orientation processes 1, 2 as in Fig. 6b, is required to account for the experimental results (Fig. 5) with pyridine. Process 2 originates at a critical value of Γ (which experimentally depends on q). The behavior exhibited in Fig. 5 can now be understood in relation to that of Figs. 1 and 2 and equations (2) and (4) in the following way.

At low positive, and all negative q values, adsorption of pyridine appears to behave like that of pyrazine where the molecule probably lies *flat* in the interphase producing $\Delta\chi$ change only by displacement of previously oriented solvent dipoles. Thus, the initial regions of the EM relations of Fig. 5 for various temperatures are similar to the whole series of lines of Fig. 2 for pyrazine and correspond to progressive replacement of $\uparrow$ and $\downarrow$ dipoles distributed according to the value of q, the surface charge.

Beyond a critical coverage, and dependent on q, pyridine molecules reorient from a flat to an upright position and then contribute a relatively large ΔE having a dependence on Γ characterized by a slope m′ independent of q. Thus, the total ΔE will then be related** to q and Γ by a »free« solute dipole orientation term plus a term similar to than in equation (2) for pyrazine.

The total EM effect for oriented dipoles in substitutional adsorption will then be

$$\Delta E_q = 4\pi\Gamma\,\mu_{py}/\varepsilon_s + \frac{x\,\Gamma\,(N\uparrow - N\downarrow)}{N_T}\,4\pi\,\mu_s/\varepsilon_s \tag{5}$$

where $\bar{\mu}_{py}$ is the effective normal moment* of pyridine and μ_s that of the solvent, water. The slope m' of the EM line will now be

$$m' = \delta\,\Delta E_q/\delta\,\Gamma = \frac{4\pi}{\varepsilon_s}\,[\bar{\mu}_{py} + \frac{x\,(N\uparrow - N\downarrow)}{N_T}\,\mu_s] \tag{6}$$

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* For free dipole orientation $\bar{\mu}_{py}$ can be $f(q)$, as in low field dielectric theory. However, in the double-layer, for $|q| > ca.\ 2\,\mu\,C\,cm^{-2}$ high field conditions obtain. Also, previous experimental results[26,27] indicate that the onset of orientation of pyridine at the Hg electrode is rather sharp.

** Damaskin *et al.* (p. 132 in ref. 32) considered 2-position adsorption and treated the contributions from flat and oriented adsorbate molecules to the adsorption potential difference in relation to the dependence of free energy of adsorption on coverage using a model of the double-layer involving 2 or 3 parallel condenser components.

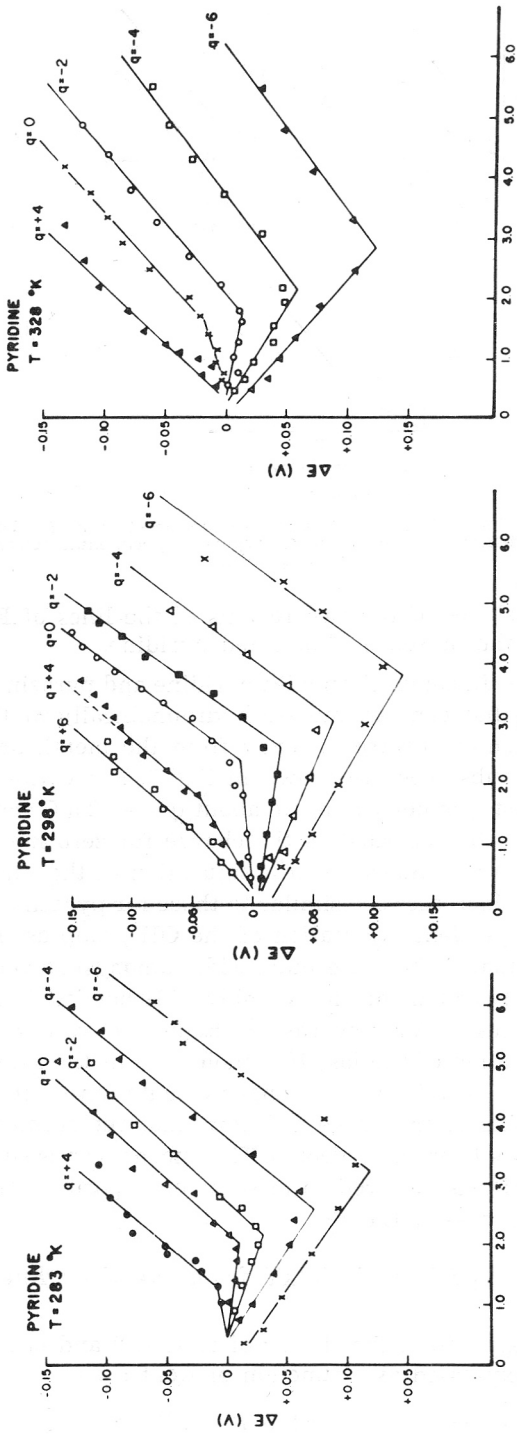

Fig. 5. Esin and Markov plots for pyridine adsoption at Hg as a function of Γ at various q values in 0.03 M aq. $NaClO_4$. *a*) 283 °K; *b*) 298 °K; *c*) 328 °K.

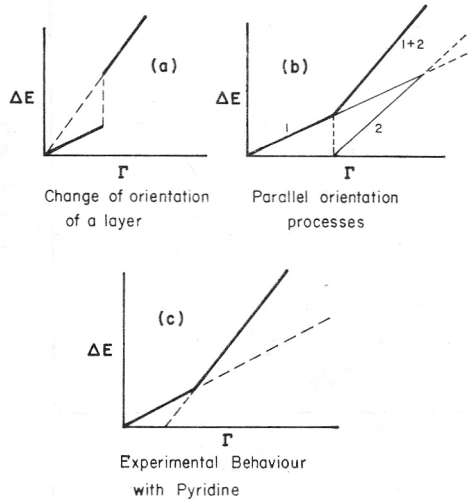

Fig. 6. Schematic representation[25] of $\Delta E - \Gamma$ plots for *(a)* sudden change of orientation of a layer of dipoles; *(b)* a parallel orientation process and *(c)* typical experimental behavior with pyridine at negative q values.

The difference of the slopes of the two regions of the lines of Fig. 5 could be used to estimate ε_s in the presence of oriented pyridine.

(c) Amyl alcohol. — In comparison with pyridine and pyrazine, amyl alcohol is a flexible molecule that can accumulate hydrophobically at the Hg surface with its OH group oriented toward or away from the metal, depending on q. The EM plots for this substance are shown in Fig. 7. For various q values the $\Delta E - \Gamma$ lines are almost symmetrical again about $q = -2\ \mu\ C\ cm^{-2}$ which, $\pm$ 0.5 $\mu\ C\ cm^{-2}$, is probably to be regarded as the charge for zero net solvent orientation. Apart from the ΔE changes towards saturation of the surface layer, the magnitudes of ΔE as Γ increases are similar to those for pyrazine (Fig. 2). There is no evidence for independent orientation of the OH group as there is for the pyridine dipoles; presumably the OH group resides amongst solvent water molecules and behaves simply as part of the assembly of H-bonded water OH groups. The rather rapid changes of ΔE towards the highest Γ values are of interest and may be due to isolation of the last H_2O molecules at the interface amongst C_5H_{11}-chains giving rise to relatively stronger orientation of these H_2O molecules by the field arising from charge q. Their final replacement then occurs with a larger ΔE as $\Theta \rightarrow 1$ for amyl alcohol. This mechanism is supported by the fact (Fig. 7) that the effects referred to arise at both positive and negative q, symmetrically about $q = -2\ \mu\ C\ cm^{-2}$.

Evaluation of $(N\uparrow - N\downarrow)/N_T$ *and* Uc/kT *from the Free Energy of Adsorption*

As shown previously[10] from the theory of refs. 1, 2 and 6, the free energy of adsorption can be expressed as a function of field F as

$$\Delta G_q^o = \Delta G_{max}^o + x R [\mu F - R U c]/kT$$

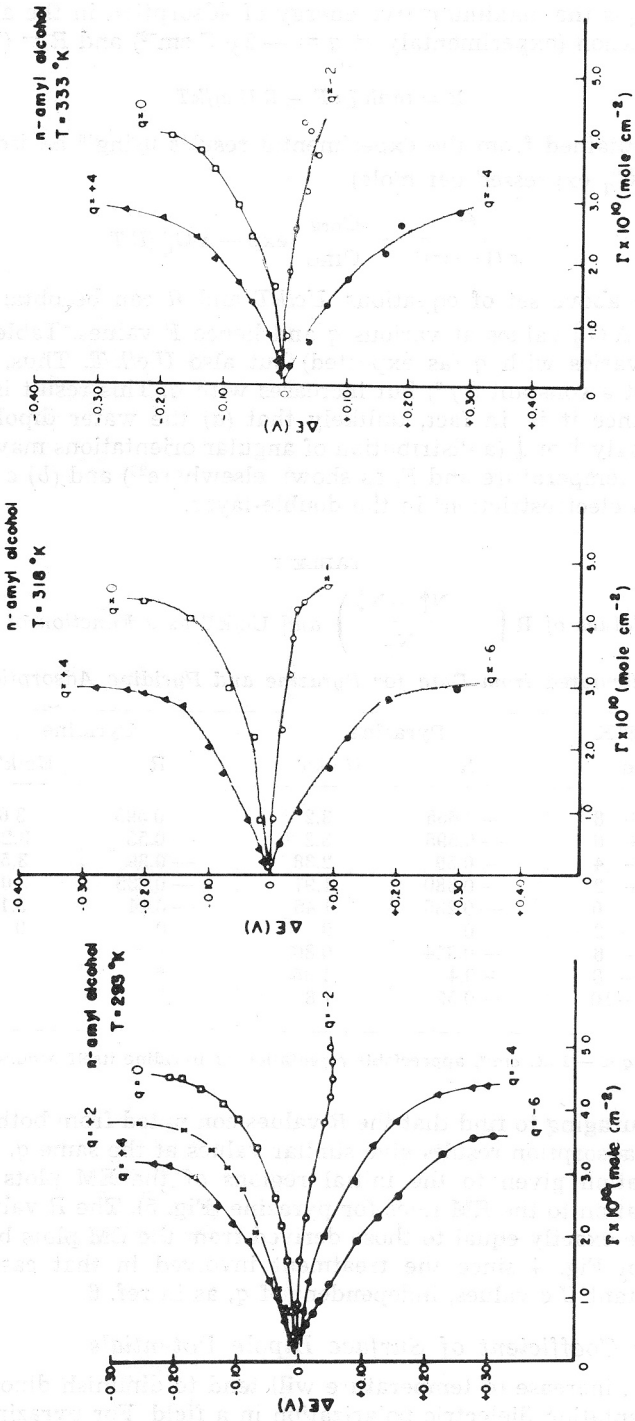

Fig. 7. Esin and Markov plots for *n*-amyl alcohol adsorption at Hg at various q values in 0.3 M aq. $NaClO_4$ *a*) 293 °K; *b*) 318 °K; *c*) 333 °K.

where ΔG^{o}_{max} is the maximum free energy of adsorption in the absence of net solvent orientation (experimentaly at $q = -2\,\mu\,C\,cm^{-2}$) and $R = (N\uparrow - N\downarrow)/N_T$. Also

$$R = tanh\,[\mu F - R\,U\,c]/kT$$

and ΔG^{o}_{q} is obtained from the experimental results using[10] an isotherm of the form (with ΔG^{o}_{q} expressed per mole)

$$\frac{\Theta}{x\,(1-\Theta)^{x}} = \frac{C_{org}}{C_{H_2O}}\,\exp - \Delta G^{o}_{q}/R\,T$$

From the above set of equations, Uc/kT and R can be obtained from the experimental ΔG^{o}_{q} values at various q and hence F values. Table I shows not only that R varies with q (as expected) but also $U\,c/k\,T$. Thus, it is evident that $U\,c$ is not a constant (*cf.*[6]) but increases with q. This result is perhaps not unexpected since it is, in fact, unlikely that *(a)* the water dipole orientation will be limitingly ↑ or ↓ (a distribution of angular orientations may be expected, depending on temperature and F, as shown elsewhere[28]) and *(b)* c may increase with q due to electrostriction[3] in the double-layer.

TABLE I

Values of $R\left(=\frac{N\uparrow - N\downarrow}{N_T}\right)$ *and* Uc/kT *as a Function of* q

Calculated from Data for Pyrazine and Pyridine Adsorption

293° K	Pyrazine		Pyridine	
q	R	Uc/kT	R	Uc/kT
+ 8	— 0.655	3.2	— 0.595	3.65
+ 6	— 0.595	3.2	— 0.53	3.25
+ 4	— 0.50	2.38	— 0.39	3.5
+ 2	— 0.380	1.97	— 0.235	2.0
0	— 0.235	1.45	— 0.14	3.1
— 2	0	0	0	0
— 6	+ 0.324	0.80	*	
— 8	+ 0.47	1.35	*	
— 10	+ 0.59	1.8	*	

* For $q < -2\,\mu C\,cm^{-2}$, appreciable orientation of pyridine itself occurs.

It is encouraging to find that the R values computed from both the pyrazine and pyridine adsorption results give similar values at the same q. This supports the interpretation given to the initial regions of the EM plots for pyridine (Fig. 2) in relation to the EM lines for pyrazine (Fig. 5). The R values cannot be expected to be exactly equal to those derived from the EM plots by the method exemplified in Fig. 4 since the treatment involved in that case empirically assumed constant $U\,c$ values, independent of q, as in ref. 6.

Temperature Coefficient of Surface Dipole Potentials

Generally, increase of temperature will tend to diminish dipole orientation as it does orientation dielectric polarization in a field. For pyrazine adsorption,

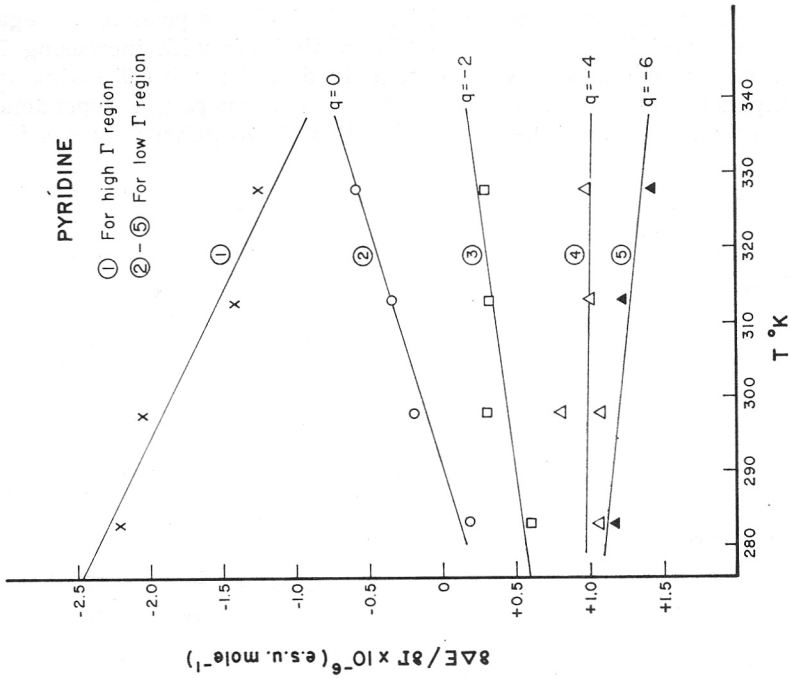

Fig. 8b. Temperature dependence of slopes dΔE/dΓ in the two regions of the Esin and Markov plots of Fig. 5. for pyridine adsorption.

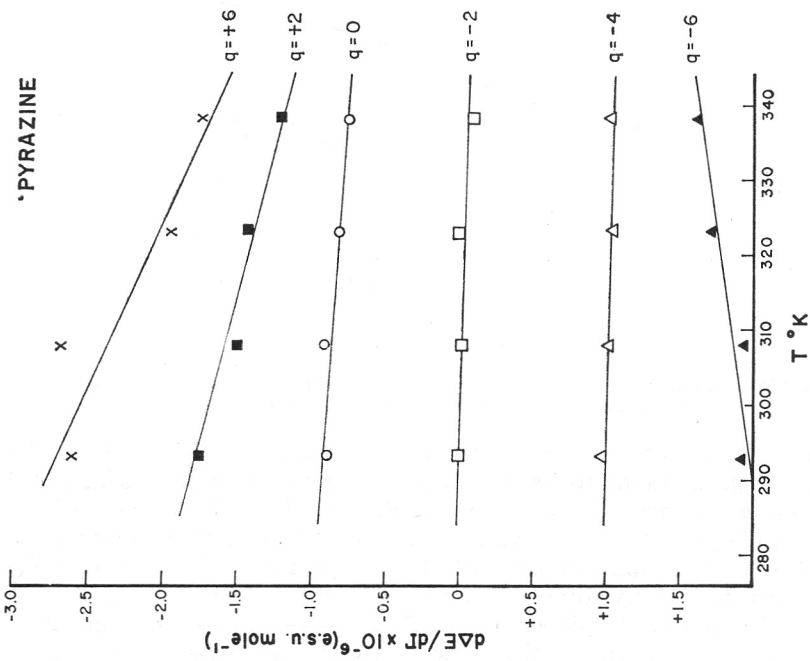

Fig. 8a. Temperature dependence of slopes dΔE/dΓ of Esin and Markov plots for pyrazine adsorption.

this is borne out by the general trend of the results in Fig. 8a for pyrazine where the tendency is for the slopes $d\Delta E/d\Gamma$ which are positive or negative, depending on q and the sign of $N\uparrow - N\downarrow$, to diminish with increasing T. Of course, for either orientation, N_T will tend to diminish with T owing to the thermal expansion of the interphase water. The temperature dependence of χ_d will depend on the magnitude of $U\,c$, (Fig. 9), and for higher values of $U\,c/k\,T$

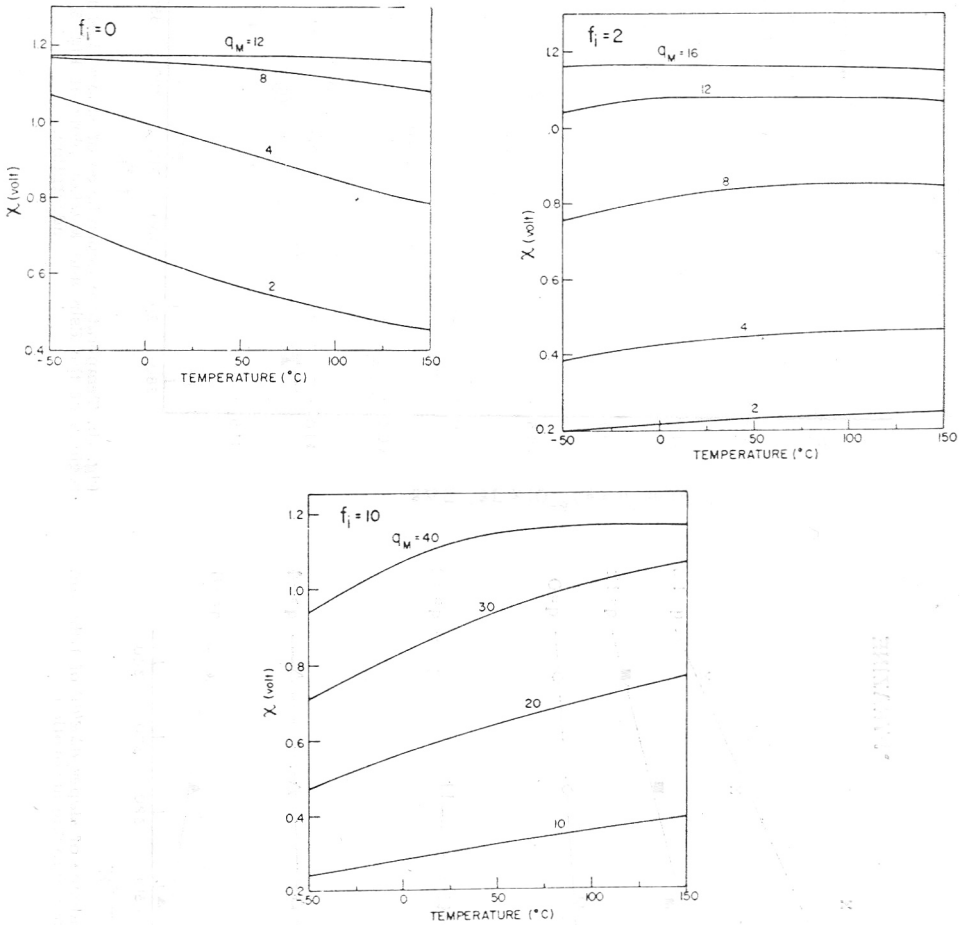

Fig. 9. Calculated values of χ_d as a function of temperature for various values of the dipole interaction term Uc/kT ($= f_i$), based on refs. 6 and 31.

the sign of the temperature dependence of χ_d and hence $d\Delta E/d\Gamma$ can become changed[31], *e. g.* as seems to be the case for the pyridine results in Fig. 8b, in comparison with those for pyrazine in Fig. 8a. For the sections of the EM plots for pyridine at high Γ values beyond the inflection points in Fig. 5, $d\Delta E/d\Gamma$ decreases appreciably with T as expected if this region of the EM plots corresponds to pyridine molecule orientation. Also, in Fig. 8a, the fact that $d\Delta E/d\Gamma$ is almost independent of T at $q = -2$ to -4 μ C cm^{-2} but is not zero at 0 μ C cm^{-2} confirms the view that zero net water dipole orientation obtains at such a charge but not at $q = 0$.

Surface Pressure Relations

Surface pressures Φ were obtained from the surface tension values at various q's by previously described methods[33]. Figs. 10 and 11 show the relations of Φ to Γ at various surface charges for pyrazine and pyridine respectively. It is clear that the $\Phi - \Gamma$ relations are almost independent of q for pyridine. This suggests that changes of surface charge cause little or no change of orientation of pyrazine while pyridine becomes progressively more oriented by the field arising from the charged interface as $-q$ increases, and this causes lower Φ as orientation becomes greater at more negative q. This effect is consistent with more negative ΔG^{o}_{ads}, also evaluated in this work, as q becomes more negative and Θ becomes larger. These observations are consistent with *attractive* interactions[10,22,26] between oriented pyridine molecules at high coverages.

Comparison of Figs. 2 and 5 for ΔE with Figs. 10, 11 and 12 for Φ shows clearly that there is a close relation between the Γ values at which a change of slope of the $\Delta E - \Gamma$ lines occurs in the EM plots and the Γ values at which the change of slope for $\Phi - \Gamma$ lines occurs. Evidently the more oriented state

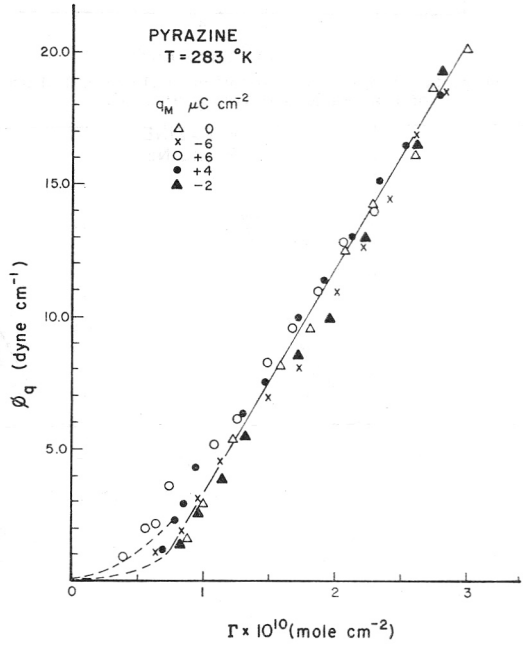

Fig. 10. Surface pressure (Φ) plots for pyrazine adsorption at Hg in 0.03 M aq. $NaClO_4$ as a function of Γ at various q values at 25 °C.

of pyridine adsorption exhibits, perhaps surprisingly[27], a lower Φ and this must arise from attractive effects as mentioned above. Perhaps, in the oriented state at negative q values, the N-centres which when $q < 0$ are oriented outward to the solvent, become intermolecularly H-bonded *via* H_2O bridges[34]. This will promote lower Φ and more negative ΔG^{o}_{ads} values.

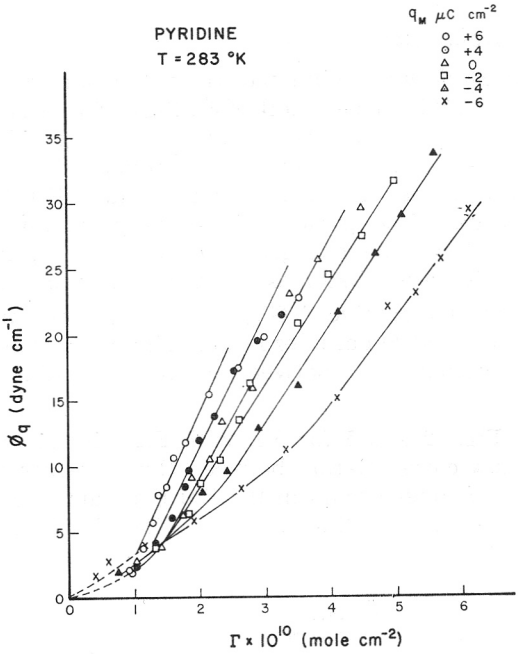

Fig. 11. Surface pressure (Φ) plots for pyridine adsorption at Hg in 0.03 M aq. $NaClO_4$ as a function of Γ at various q values at 25 °C.

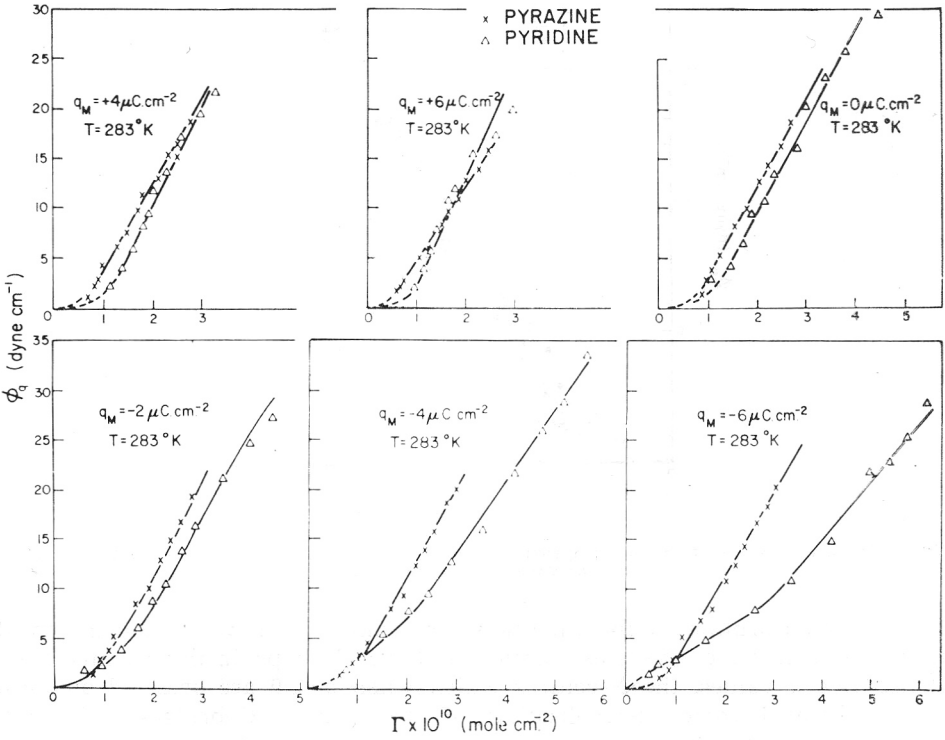

Fig. 12. Comparison of Φ — Γ plots for pyrazine and pyridine at various q values (0.03 M aq. $NaClO_4$, 25 °C).

Evidently pyridine requires greater coverage for onset of orientation, the more negative is q. This seems consistent with the orientation of water at negatively charged Hg since H bonding between the oriented water and the N centre will be facilitated with the H-end of the water dipole in the surface layer where flat-lying pyridine molecules can optimally H-bond with such water molecules.

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IZVOD

Struktura otapala i orijentacija molekula u dvosloju na granici faza živa—voda

B. E. Conway i H. P. Dhar

Na primjerima adsorpcije pirazina, piridina i amil-alkohola proučavani su efekti dipol-dipol interakcije i orijentacije molekula u elektrokemijskom dvosloju. Pokazano je, da je promjena površinskog dipolnog potencijala jednaka nuli tek kad je naboj na elektrodi — 2 $\mu C/cm^2$, i da se taj podatak slaže s modelom u kojem je kisik vodene molekule na površini okrenut prema metalu. Promatrane promjene dipolnog potencijala χ_d (Esin-Markov efekt) do oko $\pm$ 0,3 V u skladu su s očekivanjima teorije, na osnovu modela zamjene orijentiranih molekula vode adsorbatom. Temperaturna ovisnost χ_d posljedica je veličine energije za dipol-dipol interakciju, kao i koordinacionog broja. Površinski tlak ponajviše je linearna funkcija površinske koncentracije adsorbata te je neovisan o naboju na elektrodi za pirazin, ali znatno ovisan za piridin.

CHEMISTRY DEPARTMENT
UNIVERSITY OF OTTAWA

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