The Adsorption of Amino Acids at the Mercury—Water Interphase. II: Glycyl-glycine*

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The adsorption of glycyl-glycine from 0.1 mol 1^{-1} aqueous KPF_6 solutions has been studied by electrocapillary and capacity methods. In contrast to glycine, glycyl-glycine behaves as a typical organic adsorbate. Its adsorption isotherm is congruent when potential is used as the electrical variable and not when charge is used. The large repulsive effects between adsorbed species are ascribed to solvation rather than electrostatic effects.

INTRODUCTION

In the previous paper[1] the adsorption of glycine was studied in acid, neutral, and basic solutions. The glycinium ion and the glycinate ion are adsorbed weakly but behave in a way to be expected for a cation and an anion. The adsorption of the zwitterion is in some ways characteristic of a highly polar molecule carrying no net charge and yet the very small potential shifts accompanying adsorption at constant electrode charge lead to the supposition that the main component of the large dipole moment[2] 5.2×10^{-29} Cm (15.5 D) is oriented parallel to the electrode surface. It was therefore of interest to study a similar molecule with an even higher dipole moment. Glycyl-glycine is also a zwitterion and has a dipole moment[2] of 9.2×10^{-29} Cm (27.6 D).

EXPERIMENTAL

Double layer capacity and electrocapillary measurements were made at 25 °C as described previously[3] using the same methods for preparing the base electrolytes[1]. Technical grade glycyl-glycine was twice recrystallized from water at 50—60 °C and dried at 110 °C.

RESULTS

Differential capacity curves for glycyl-glycine in 0.1 mol 1^{-1} KPF_6 were measured at 25 °C at eleven concentrations. Some of the results are shown in Fig. 1. It is apparent from these curves that glycyl-glycine adsorbs preferentially near the point of zero charge and therefore behaves like a typical organic adsorbent. Some form of desorption process must occur in the region around — 1.15 V where there is an inversion in the concentration dependence of the capacity. However, no frequency dispersion of the capacity was observed here. Frequency effects were observed in dilute solution (< 0.04 mol 1^{-1}) on the positive side of the point of zero charge. The capacity was plotted against the square root of the frequency and the capacity extrapolated linearly to zero

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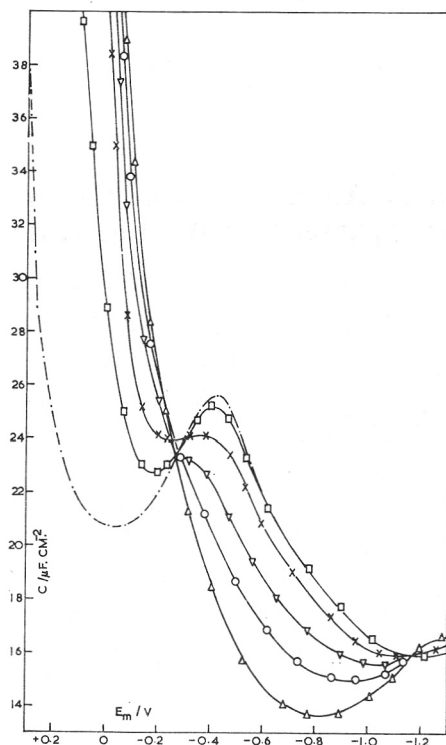Fig. 1. Capacity potential curves for a mercury electrode in solutions of glycyl-glycine in 0.1 mol 1^{-1} aqueous KPF_6.
— · — base solution; □ — 0.01; x — 0.10; ∇ — 0.25; 0 — 0.40; △ — 0.65, mol 1^{-1} glycyl-glycine. Potential with respect to a 0.1 mol 1^{-1} KCl calomel electrode.

frequency was used in the further analysis[4]. The error on these was rather large owing to the poor low frequency response of the bridge as a result of its transformer input and output.

Electrocapillary curves were measured for four concentrations. They agreed well with the twice integrated capacity curves on the negative branch except at concentrations above 0.4 mol 1^{-1}. These high concentrations were therefore not used in the analysis. Discrepancies on the positive branches appeared at the low concentrations as with glycine and were ascribed to contact angle changes[5,6]. The integrated capacity curves were used in the subsequent analysis. Coordinates of the point of zero charge are given in Table I. The potential of zero charge was determined using the streaming electrode method.

Analysis of Results

Surface excesses of glycyl-glycine were determined using a third order polynomial fit of the ξ — log c data. The results are shown in Fig. 2. They confirm the conclusion derived from the capacity curves that the adsorption behaviour is typical of an organic compound. Maximum adsorption occurs when the charge on the electrode is zero. Desorption occurs rather more rapidly with negative charges than with positive. Apart from this slightly stronger adsorption

TABLE I

Coordinates of the Point of Zero Charge of Mercury in Contact with 0.10 mol l⁻¹ KPF₆
Containing Glycyl-glycine at 25 °C

$c/$mmol 1^{-1}	$-E^z/$mV	$\gamma^z/$mN m^{-1}	C^z/μF cm^{-2}
10.0	539.5	424.1	22.96
16.0	539.0		22.85
25.0	538.5		22.92
40.0	537.5	423.5	22.89
63.0	537.0		22.63
100	536.0		22.07
160	535.0	422.0	21.13
250	534.0		19.92
400	532.5		18.20
630	530.0	418.0	15.59
1000	523.5		12.16

Potentials with respect to a 0.1 mol 1⁻¹ KCl calomel electrode in contact with a 0.1 mol 1⁻¹ solution of KPF₆ (not containing glycyl-glycine).

on positive charges the form of these curves is quite different from that of the glycine curves. The adsorption isotherms shown in Fig. 3 are logarithmic with slopes strongly dependent upon charge. At the adsorption maximum the
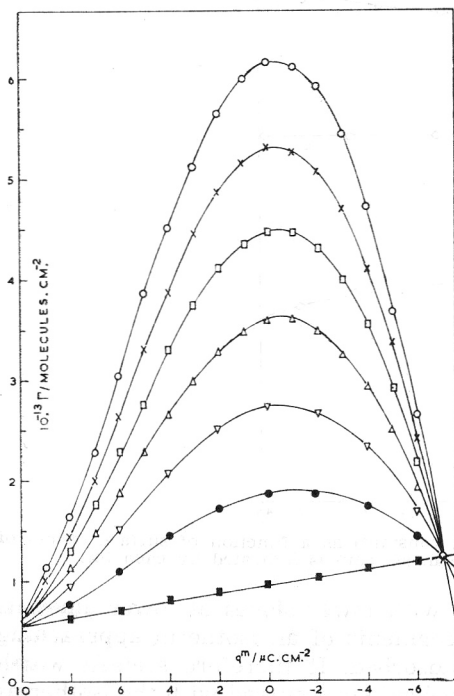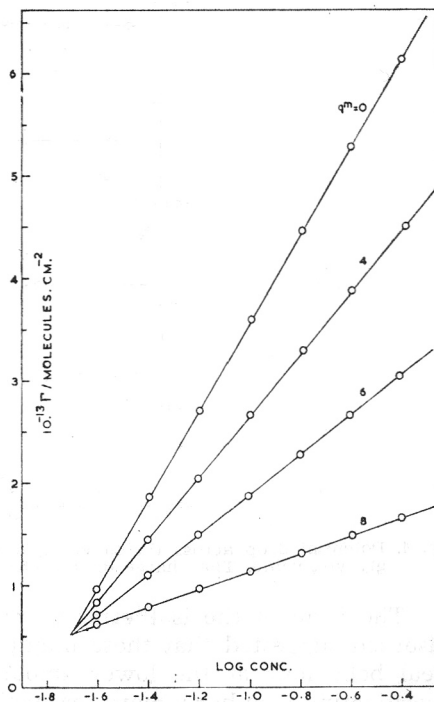

Fig. 2. Surface excess of glycyl-glycine as a function of charge on the electrode.
— 0.025; ● — 0.040; ▽ — 0.063; △ — 0.10; □ — 0.16; x — 0.25; ○ — 0.40 mol 1⁻¹ glycyl-glycine

3. Surface excess of glycyl-glycine as a function of logarithm of its concentration in solution. The charge on the electrode in μC cm⁻² is indicated by each line.

slope corresponds to a two-dimensional second virial coefficient of 2.7 nm²
per molecule (270 A²) with correspondingly larger values at larger charges.
The projection of a molecular model lying flat on a plane has an area of 0.45
nm² so that the value of the second virial coefficient indicates the existence
of strong repulsive forces. The apparent change in these with charge means
that the adsorption isotherms are not congruent in the charge. This is con-
firmed from surface pressure plots although the surface pressures are very
small, the highest value for the 0.4 mol l⁻¹ solution being 4.3 mN m⁻¹.
Consequently this conclusion relies on the assumption that very small dif-
ferences are not artefacts.

A similar conclusion is reached from the plot of the potential drop across
the inner layer against the amount adsorbed (Fig. 4) which is not linear except
at the point of maximum adsorption. The fact that this occurs at zero charge
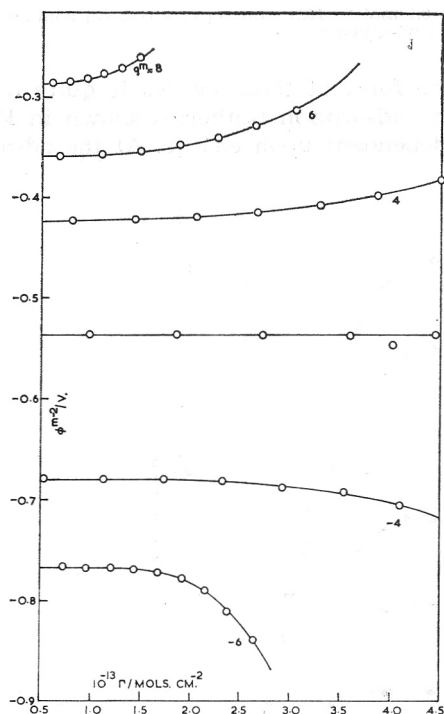on the electrode suggests that the dipole is essentially parallel to the electrode
surface.

Fig. 4. Potential drop across the inner layer (+ a constant) as a function of surface excess of
glycyl-glycine. The charge on the electrode in μC cm⁻² is indicated by each line.

The form of the isotherms in Fig. 3 with lower slopes at lower amounts
adsorbed suggested that these might be segments of an isotherm approaching
ideal behaviour at the lower amounts adsorbed. It therefore seemed worth
investigating whether a more reasonable behaviour occurred with the isotherms
at constant potential[7,8]. These are plotted in Fig. 5 and it is at once evident that
these are more nearly congruent. In fact they superpose quite closely except
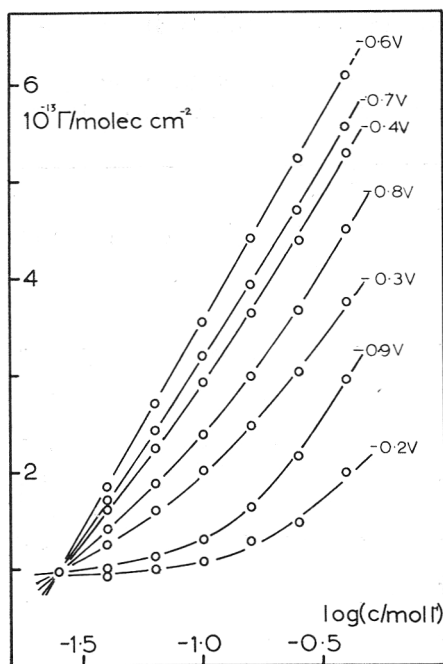at the smallest amounts adsorbed where experimental inaccuracies become

Fig. 5. Surface excess of glycyl-glycine as a function of logarithm of its concentration in solution. The potential of the electrode in indicated by each line.
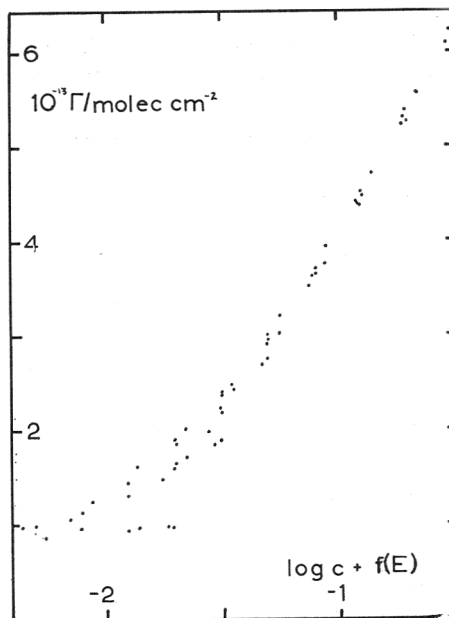
Fig. 6. The data of Fig. 5 superposed by adding a potential-dependent quantity to the log concentration scale.

significant (Fig. 6). The amount by which the isotherm must be shifted along the log c axis for coincidence is closely proportional to $(E - E^m)^2$ where E^m is the potential corresponding to maximum adsorption, Fig. 7. Thus the free
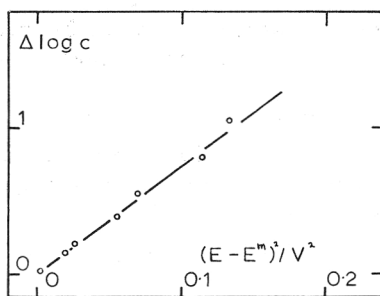
Fig. 7. The shift of the isotherm along the concentration axis required for superposition in Fig. 6. plotted against the square of the potential with respect to the potential of maximum adsorption.

energy of adsorption is a parabolic function of the potential. The congruence of the isotherm with respect to potential is confirmed by plotting according to the 'virial' equation (Fig. 8). Although there are some deviations which may be ascribed to experimental error, the lines at the different potentials are essentially parallel and their slope corresponds to a two-dimensional second virial coefficient of 2.3 nm² per molecule. This is in fairly close agreement with

the value derived from the line at $q = 0$ in Fig. 3 since this is also a line at constant potential.

Further confirmation of these conclusions is obtained by plotting the electrode charge against the amount adsorbed at constant potential (Fig. 9).
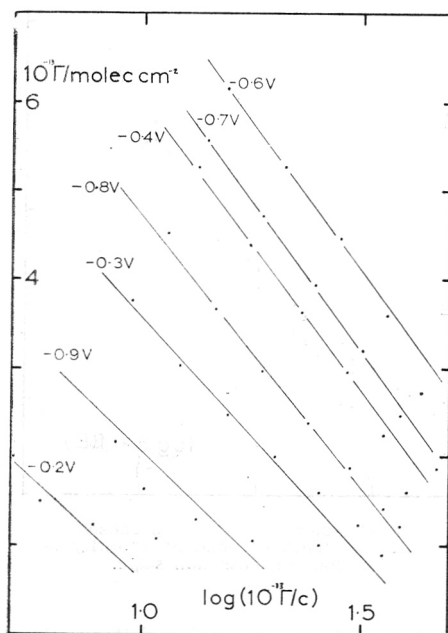

Fig. 8. The data of Fig. 5 plotted as a 'virial' adsorption isotherm. The potential of the electrode is indicated by each line.
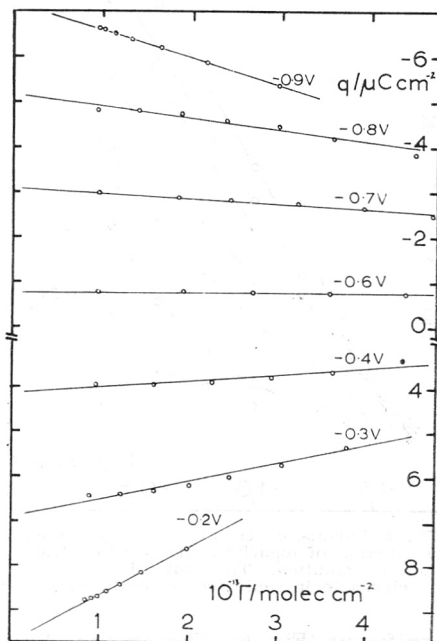
Fig. 9. The charge on the electrode as a function of the surface excess of glycyl--glycine. The potential of the electrode is indicated by each line.

Straight lines are obtained in agreement with Frumkin's postulate[7]. For an isotherm which is congruent in the potential these lines are described by the equation[9]

$$q - q^b = kT\, \Gamma\, (\partial \ln \beta / \partial E) \tag{1}$$

where q^b is the value of q in the base solution and β is the adsorption coefficient. When the standard free energy of adsorption is a quadratic function of the potential, this may be expresseed

$$\ln \beta = \ln \beta^m - (b/2)\, \Delta^2 \tag{2}$$

and

$$\partial \ln \beta / \partial E = -b\, \Delta \tag{3}$$

where

$$\Delta = E - E^m$$

and the superscript m indicates the potential at which the adsorption is a maximum.

Thus equation (1) may be written as

$$q - q^b = -b\, \Delta\, kT\, \Gamma \tag{4}$$

and the slopes of the lines in Fig. 9 should be given by

$$(\partial q/\partial \Gamma) = -b\,kT\,\Delta \qquad (5)$$

The slopes of the lines in Fig. 9 are plotted against the potential in Fig. 10 and these points are compared with the line calculated from the value of b obtained from Fig. 7 according to equation (2). The satisfactory agreement shows that this system of equations describes the adsorption of glycyl-glycine adequately.
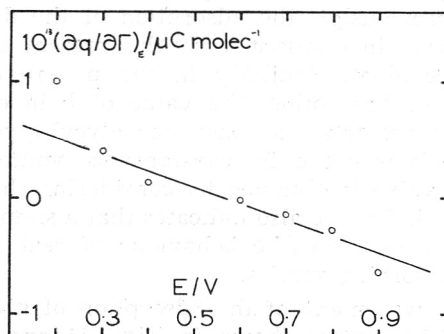

Fig. 10. The coefficient $(\partial q/\partial \Gamma)_E$ as a function of the potential of the electrode. Points are calculated from the slopes of the lines in Fig. 9. The line is calculated from the slope of the line in Fig. 7.

DISCUSSION

Adsorption of glycyl-glycine on mercury contrasts strongly with that of glycine in that the larger molecule behaves as a typical organic adsorbate although still being adsorbed rather weakly. This difference of behaviour is unlikely to be due to a difference in the energy of the two molecules in solution. The solubility of glycine[10] in water at 25 °C is 2.886 mol l^{-1} while that of glycyl-glycine[11] is 1.512 mol l^{-1}. This corresponds to a difference in solvation energy of less than 2 kJ mol^{-1}. If the adsorbed layer is assumed to be ideal, the difference of the free energy of adsorption at the potential of zero charge is about twice this value. Since both molecules are apparently oriented with their dipoles parallel to the interface the effect of the image force must be very similar for both. The effect of the larger number of water molecules displaced by glycyl-glycine must therefore be outweighed by some other factor in favour of its adsorption. This can be tentatively suggested to be that the larger molecule causes a smaller disruption of the structure of the interfacial water layer.

The most striking difference between glycine and glycyl-glycine is of course the charge-dependence of the adsorption. It is suggested that the reason for this is the greater difficulty in re-orienting the larger molecule. Thus at all accessible charges glycyl-glycine adsorbs parallel to the interface and consequently its large dipole moment has no effect on the adsorption characteristics, which are consequently in this respect closely similar to those of much less polar organic adsorbates. If this is correct then the behaviour of glycine can be ascribed to some reorientation at extreme charges and is consistent with theoretical expectations[7,12,13]. Some support for the relative degrees of interaction with interfacial solvent can be obtained from the values of two-dimensional second virial coefficient which at uncharged mercury is larger for glycine than for glycyl-glycine. It seems unlikely that these large repulsive interactions are due to electrostatic effects since dipoles rotating

in a plane should attract each other. They are more probably due to orientation of neighboring solvent molecules into a two-dimensional solvation shell.

The specific nature of the interaction between the solvent and the adsorbate is emphasized by comparing the behaviour of glycyl-glycine with that of butan-1:4-diol or butyne-1:4-diol. The projected area of these molecules is quite similar being 0.45 nm² for glycyl-glycine and 0.38 nm² for the diols. However, as shown previously[14] the adsorption of the diols conforms closely to a Langmuir isotherm in contrast with the present system where strong repulsive forces are evident. Similarly in the potential dependence of the standard free energy of adsorption, the value of b in equation (3) is found to be approximately three times as large for glycyl-glycine as for the diols (the value for the diols is not quite constant; as pointed out previously[14] a more nearly constant value is obtained by considering the free energy dependence on charge). This difference also indicates that a simple water-replacement model is inadequate to describe the behaviour of real systems with respect to the nature of the adsorbing species.

No detailed study was made of the adsorption of glycyl-glycine in acidic and basic solutions. The curves shown in Figs. 11 and 12 suggest that the 'organic' nature of glycyl-glycine remains quite strongly expressed in acid solutions but that in alkaline solutions it behaves more like an anion.
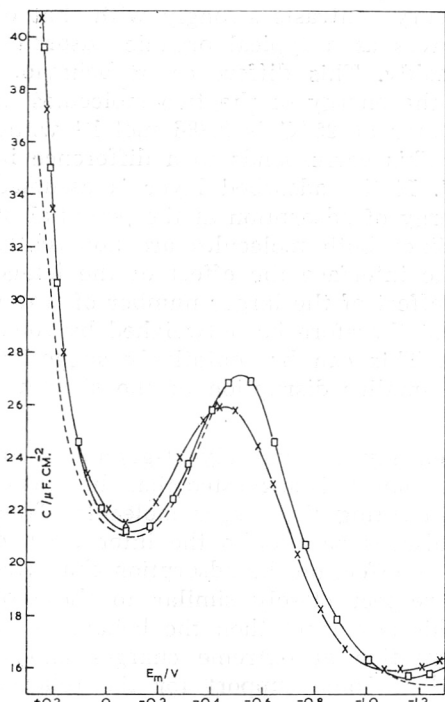

Fig. 11. Capacity-potential curves for a mercury electrode in 0.25 mol 1⁻¹ HPF₆ — — — , □ — containing 0.1 mol 1⁻¹ glycine; x — containing 0.1 mol 1⁻¹ glycyl- -glycine.
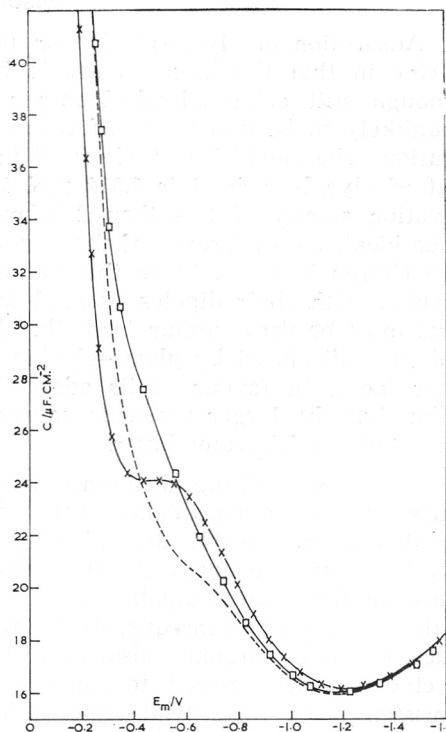
Fig. 12. Capacity-potential curves for a mercury electrode in 0.1 mol 1⁻¹ KOH ——— ; □ — containing 0.1 mol 1⁻¹ glycine; x — containing 0.1 mol 1⁻¹ glycyl-glycine.

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IZVOD

Adsorpcija amino kiselina na međufazi živa—voda

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Mjerenjem elektrokapilarnih krivulja i diferencijalnog kapaciteta na živinim elektrodama u elektrolitu KPF_6 proučavana je adsorpcija glicil-glicina. Za razliku od glicina, glicil-glicin se ponašanja poput organskog adsorbata, tj. biva preferencijalno adsorbiran blizu točke nula naboja. Adsorpciona izoterma glicil-glicina kongruentna je samo ako se kao električna varijabla uzima potencijal, a ne naboj elektrode. Veliki repulzivni efekti između adsorbiranih molekula pripisuju se efektima solvatacije, a ne elektrostatskim silama. Ipak je pokazano da jednostavni model zamjene vode ne objašnjava dovoljno dobro opažene fenomene. Izlaz iz nejasne situacije predlaže se prihvaćanjem modela u kojem susjedne molekule otapala tvore dvodimenzionalni solvatacioni sloj oko molekula glicil-glicina.

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