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Adsorption of 1,2-Propanediol and Methyl Cellosolve at Mercury–0.10 m KCl aq Interface at 25 °C

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Adsorption of 1,2-propanediol and methyl cellosolve (isomeric compounds) at Hg–0.10 m KCl (aq) solution interface evaluated through equilibrium double layer capacity measurements indicated congruency of adsorption isotherms with respect to both potential (E) and charge density (σ^M); applicability of Langmuir's adsorption isotherm; quadratic dependence of $\Delta\bar{G}^\circ$ on E and single stable orientation with the hydrocarbon chain facing the electrode and functional group in solution throughout the coverage region, for both the compounds. Surface excess, standard free energy of adsorption and the anodic shift of E_{pzc}, are greater while the charge corresponding to maximum adsorption is more negative, for methyl cellosolve than for the diol.

The differences in the adsorption behaviour of some aromatic isomeric compounds[1] at the mercury-solution interface were attributed to differences in dipole moment and intramolecular hydrogen bonding. However, such studies are scanty in the literature.

Diols have been shown to behave in a different way[2,3] from monohydric alcohols at the mercury-aq solution interface. Adsorption of glycol has been thoroughly studied by electrocapillary[3] and differential capacity measurements.[4] 1,2-Propanediol (methyl glycol) and 2-methoxy ethanol (glycol monomethyl ether also known as methyl cellosolve) are two isomeric compounds with dipole moments 2.25 and 2.04 respectively, the hydrogen bonding of the former with water molecules being relatively higher. The present communication describes their adsorption behaviour at Hg–0.10 m KCl (aq) solution interface through equilibrium double layer capacity measurements.

Experimental

Differential capacities were measured by Grahame's a.c. bridge method[5,6] using a dropping mercury electrode. A variable signal generator (Marconi TF 1370) facilitated variation of a.c. frequency from 200 to 10000 Hz. Observed frequency independent capacity data with Hg–0.10 m KCl aq agreed with Grahame's data.[6] In the presence of the adsorbates, the capacity was frequency dependent and the data reported in this paper are equilibrium double layer capacities (extrapolated zero frequency values). Mercury drops knocked off periodically at a prefixed interval by a locally made electromagnetic drop detacher were perfectly spherical at the instant of bridge balance. Interval of two successive knocks of the detacher was measured accurate to 0.005 s. The bridge was balanced at the instant of the detachment of the drop from the capillary tip. The bridge output signal amplified by a multistage transistor preamplifier (Marconi TM 6591A) was displayed on a Dumont oscillograph (type 274). A large mercury pool electrode and 1 M KCl calomel electrode (NCE) were used as the auxiliary and reference electrodes respectively. The potential between the test electrode and the reference electrode was measured on a portable potentiometer (Pye-Cambridge; accuracy one mV). Differential capacities were measured in the potential range −0.10 to −1.80 V *vs.* NCE. The measurements were carried out in an air thermostat controlled at 25±0.1 °C.

Mercury was purified following Trasatti's method.[3] KCl (BDH-AnalaR) twice recrystallized from conductivity water was used. Methyl cellosolve (Riedel) was treated with lithium hydride until the evolution of hydrogen gas ceased and then distilled twice. 1,2-Propanediol (BDH-AnalaR) was twice distilled under reduced pressure and the middle cut was collected. Solutions at required molalities of the adsorbates in 0.10 m KCl (aq) were deoxygenated with purified and presaturated nitrogen before carrying out the experiments.

The differential capacitance measured was independent of the drop time even at the desorption peaks indicating universal attainment of adsorption equilibrium.

Results and Discussion

The differential capacity-potential curves for both 1,2-propanediol (Fig. 1) and methyl cellosolve (Fig. 2) follow the same shape typical for an aliphatic organic compound. The capacity curves for methyl cellosolve exhibit small cathodic and anodic desorption peaks whereas these peaks are totally absent in the curves for 1,2-propanediol; there is only a characteristic cross-over of the curves at extreme cathodic and anodic polarizations. With the increase in concentration of

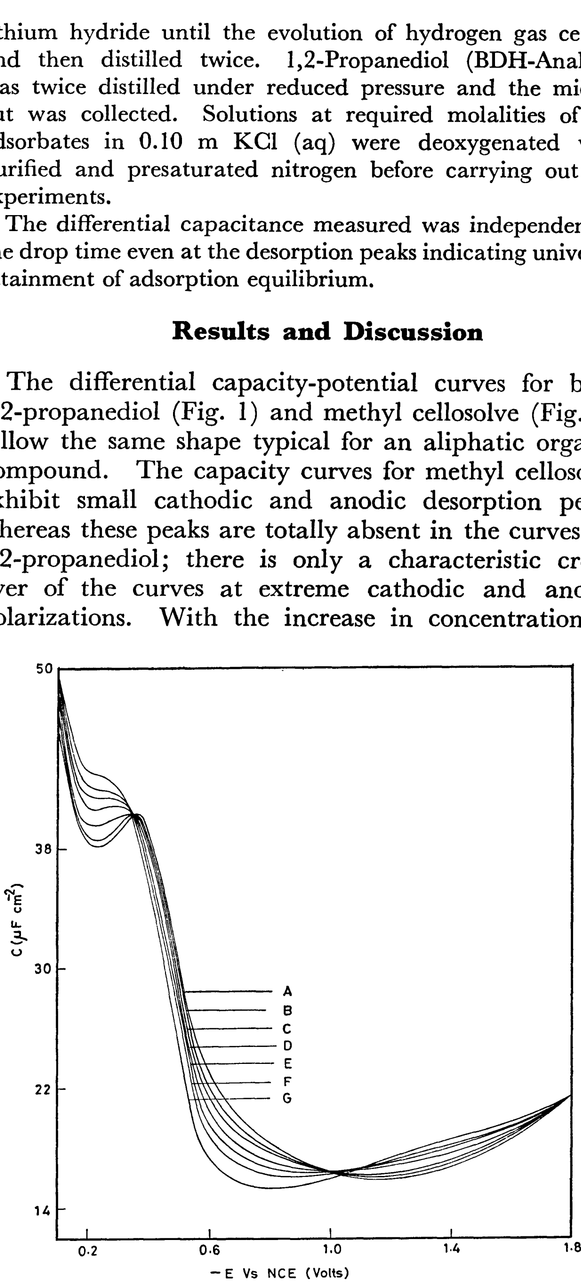

Fig. 1. Differential capacity-potential curves for Hg in 0.10 m KCl solution containing 1,2-propanediol at concentrations: (A) 0, (B) 0.05, (C) 0.10, (D) 0.20, (E) 0.30, (F) 0.40, (G) 0.60 m.

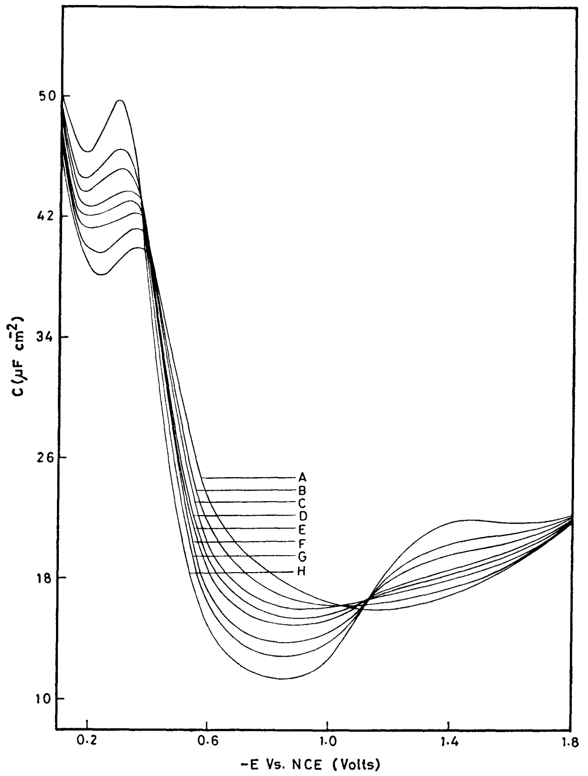

Fig. 2. Differential capacity-potential curves for Hg in 0.10 m KCl solution containing methyl cellosolve at concentrations: (A) 0, (B) 0.05, (C) 0.10, (D) 0.15, (E) 0.20, (F) 0.30, (G) 0.40, (H) 0.60 m.

methyl cellosolve, the cathodic desorption peak shifts towards more cathodic potentials and the anodic peak, towards more anodic potentials.

Evaluation of σ^M *and* Γ_A. Charge density on the electrode surface (σ^M) has been computed according to the equation:

$$\sigma^M = \int C\mathrm{d}E + K_1, \tag{1}$$

and surface excess of the organic adsorbate (Γ_A), with the help of the equation:

$$\Gamma_A = \frac{1}{2.303RT}\left(\frac{\partial\sigma^M}{\partial \log c}\right)_E \mathrm{d}E + K_2, \tag{2}$$

where R and T have their usual thermodynamic meaning.

Both the integrations have been performed numerically at the intervals of 10 mV starting at extreme cathodic potential *viz.*, -1.8 V *vs.* NCE at which the capacity curves at all concentrations of the adsorbates coincided with the corresponding one of the base electrolyte. K_1 was the charge density on the electrode in pure base electrolyte solution (K_2 being equal to zero) at -1.8 V. The differential term in Eq. 2 is obtained from σ^M *vs.* log c plots; these adsorbates are knwon to behave ideally especially in the concentration range studied and hence the activity is replaced by concentration.

Surface Excess of the Organic Adsorbates. The surface excess-potential curves (*cf.* Fig. 3) show complete desorption of both the compounds at extreme cathodic polarizations; desorption is, however, incomplete at anodic polarizations in the potential range studied. At a given bulk concentration and potential, the surface excess of methyl cellosolve is found to be more than that of 1,2-propanediol.

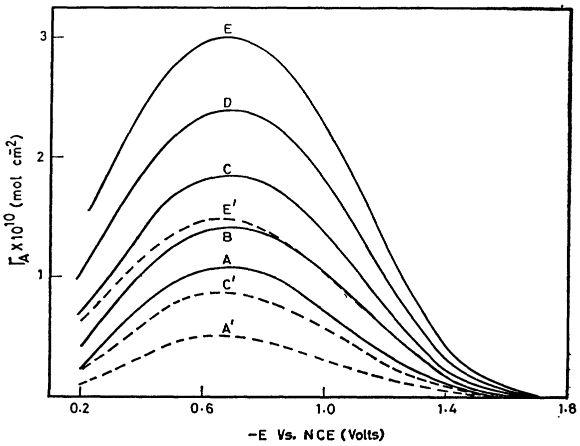

Fig. 3. Surface excess of the adsorbate as a function of electrode potential. (A) 0.10, (B) 0.15, (C) 0.20, (D) 0.30, (E) 0.40 m methyl cellosolve. (A′) 0.10, (C′) 0.20, (E′) 0.40 m 1,2-propanediol.

Linear plots observed in the variation of (i) electrode charge *vs.* surface excess at constant potential and (ii) electrode potential *vs.* surface excess at constant charge suggest that the adsorption isotherms for both the compounds are congruent with respect to both electrode potential and charge.[7,8] Such plots for methyl cellosolve are shown in Figs. 4a and 4b.

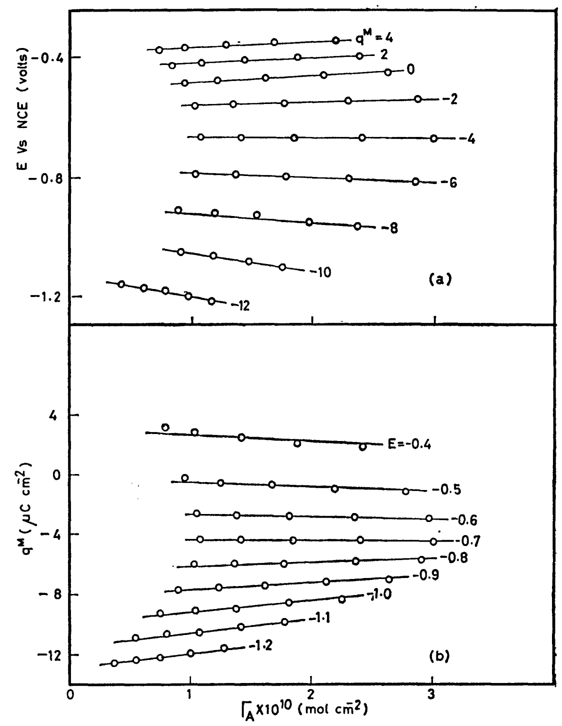

Fig. 4. (a) Electrode potential as a function of surface excess of methyl cellosolve at constant charge. Charge (μC cm^{-2}) indicated on each line.

(b) Electrode charge as a function of surface excess of methyl cellosolve at constant potential. Potential (V *vs.* NCE) indicated on each line.

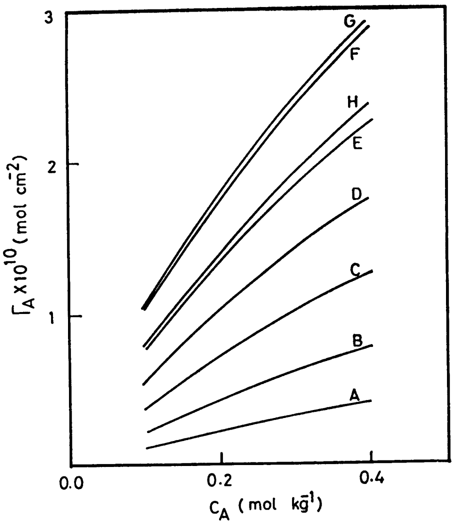

Fig. 5. Surface excess as a function of bulk concentration of methyl cellosolve at constant potential. (A) $E=-1.4$, (B) -1.3, (C) -1.2, (D) -1.1, (E) -1.0, (F) -0.8, (G) -0.6, (H) -0.4 V *vs.* NCE.

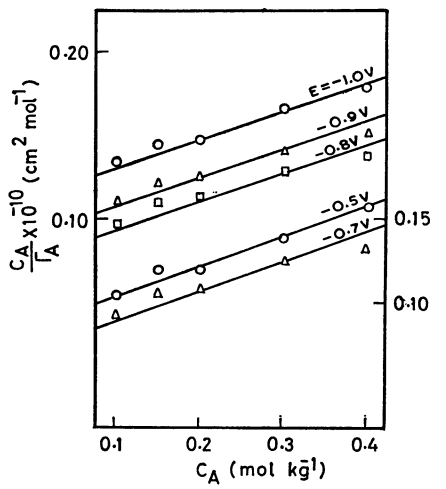

Fig. 6. Test for Langmuir's isotherm for methyl cellosolve at various potentials. Potential (V *vs.* NCE) indicated on each line.

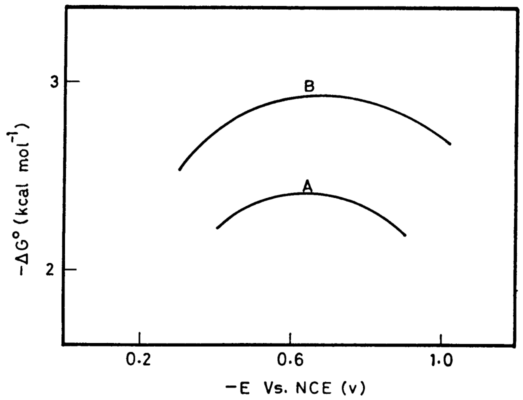

Fig. 7. Standard free energy of adsorption ($\Delta\bar{G}^\circ$) as a function of electrode potential (E). (A) 1,2-propanediol, (B) methyl cellosolve.

The plots of surface excess *vs.* bulk concentration at constant electrode potential for both the compounds do not yield saturation value of surface excess (Γ_S) within the concentration range studied (*cf.* Fig. 5 for methyl cellosolve). The value of Γ_S is therefore obtained by an indirect method as given below. The plots of c_A/Γ_S *vs.* c_A at constant E are linear and parallel for both the compounds showing thereby that their adsorption behaviour obeys Langmuir's adsorption isotherm with a slope equivalent to $1/\Gamma_S$. These plots for methyl cellosolve are shown in Fig. 6. The values of Γ_S thus obtained are 5.00 and 5.26 for 1,2-propanediol and methyl cellosolve respectively.

Standard Free Energy of Adsorption. The standard free energy of adsorption ($\Delta\bar{G}^\circ$) has been calculated according to the equation given by Conway and Barradas[9] when the adsorption isotherm is of Langmuir's type.

$$\ln\left(\frac{55.5}{c_A}\cdot\frac{\theta}{1-\theta}\right) = \frac{-\Delta\bar{G}^\circ}{RT}. \tag{3}$$

The values of $\Delta\bar{G}^\circ$ have been obtained at constant coverage, $\theta=0.3$ ($\theta=\Gamma_A/\Gamma_S$) and at various electrode potentials. The dependence of $\Delta\bar{G}^\circ$ on E (*cf.* Fig. 7) is found to be quadratic for both the compounds as expected for simple neutral organic substances. The magnitude of $\Delta\bar{G}^\circ$ at any potential is higher for cellosolve than for diol. This can be attributed to the relatively weaker hydrogen bonding of cellosolve molecules with water molecules than that of diol.

E_{pzc} vs. $\log c_A$ and θ. Anodic shift of E_{pzc} with the increase in concentration of both the adsorbates

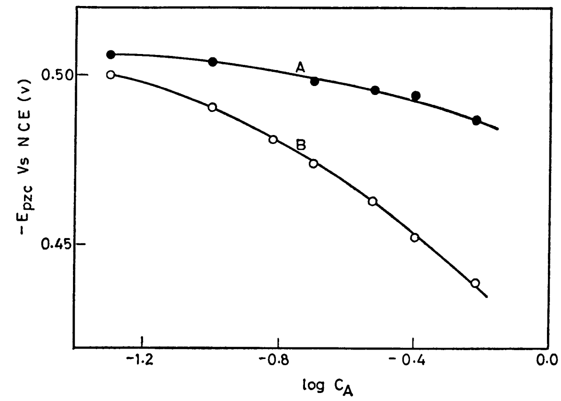

Fig. 8. E_{pzc} as a function of log c_A of the adsorbates. (A) 1,2-propanediol, (B) methyl cellosolve.

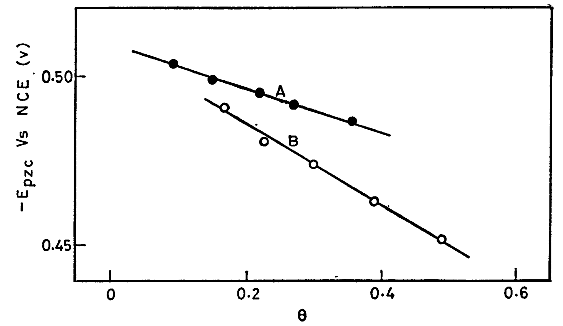

Fig. 9. E_{pzc} as a function of surface coverage of the adsorbates. (A) 1,2-propanediol, (B) methyl cellosolve.

indicates their orientation with the positive end towards the electrode and functional group in solution (*cf.* Fig. 8). Linear shift of E_{pzc} with surface coverage (θ) of the adsorbates (*cf.* Fig. 9) suggests single and stable orientation[10] throughout the coverage region. The magnitude of $(\partial E_{\text{pzc}}/\partial\theta)_{\theta\to 0}$ which accounts for the contribution due to normal components of the permanent organic dipoles[11] is greater for methyl cellosolve than for 1,2-propanediol. For equivalent concentrations, the magnitude of ΔE_{pzc} is more for cellosolve than for diol. This can be explained on the basis of (i) the normal component of the cellosolve dipoles being higher than that of diol dipoles and (ii) more number of negatively oriented water dipoles being replaced, due to relatively stronger adsorption of cellosolve dipoles than diol dipoles.

The electrode charge corresponding to maximum adsorption ($\sigma^{\text{M}}_{\text{max}}$) is $-3.2\,\mu\text{C cm}^{-2}$ for 1,2-propanediol and $-4.2\,\mu\text{C cm}^{-2}$ for methyl cellosolve. Damaskin and Frumkin[12] have expressed $\sigma^{\text{M}}_{\text{max}}$ as

$$\sigma^{\text{M}}_{\text{max}} = -\left(\frac{\partial E_{\text{pzc}}}{\partial\theta}\right)_{\theta\to 0}\left(\frac{C_0{}^2}{C_0-C_1}\right). \qquad (4)$$

The first term on the right hand side accounts for the contribution due to permanent dipoles and the second term, due to induced dipoles where C_0 and C_1 are the capacities at $\theta=0$ and $\theta=1$ respectively. It appears that the contribution due to permanent dipoles (Methyl cellosolve>1,2-propanediol) controls the value of $\sigma^{\text{M}}_{\text{max}}$ in these two compounds and hence more negative $\sigma^{\text{M}}_{\text{max}}$ for methyl cellosolve.

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