ADSORPTION BEHAVIOUR OF ISOMERIC COMPOUNDS AT MERCURY/AQUEOUS 0.1 M KCl INTERFACE AT 25°C

B.V. Apparao

Department of Chemistry, Gandhigram Rural University, Gandhigram - 624 302.

Adsorption of 1,4 - butane diol and ethyl cellosolve (isomers) at mercury/0.10 m KCl aq. interface has been studied through double layer capacity measurements. Surface excess, standard free energy of adsorption and the anodic shift of E_{pzc} are greater while the charge corresponding to maximum adsorption (σ^m_{max}) is more negative, for ethyl cellosolve than for the diol. Nevertheless, both the compounds obeyed 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.

Dyatkina and Damaskin [1] have found differences in the adsorption behaviour of certain aromatic isomers at mercury/aqueous solution interface. They have attributed the differences in dipolemoment values and intramolecular hydrogen bonding. Nevertheless, such studies are scanty in literature. 1,4-butane diol and ethyl cellosolve are a set of isomers with the dipolemoments of 2.24 and 2.08 respectively, the hydrogen bonding of 1,4-butane diol with water molecules being relatively higher. Studies on adsorption behaviour of 1,4-butane diol and ethyl cellosolve at mercury/solution interface have been made through differential capacitance measurements and the results are presented in this paper.

EXPERIMENTAL

Differential capacities were measured by Grahame's a.c. bridge method [2,3] using a dropping mercury electrode at different frequencies from 200 to 10000 H_z. All the experimental details were essentially the same as described in the earlier paper [4]. In the presence of the adsorbates, the capacities were found to be frequency dependent and the data reported here are equilibrium double layer capacities (extrapolated zero frequency values). The measurements were made in the potential range -0.10 V to -1.8 V vs NCE in an air thermostat controlled at 25 ± 0.1°C.

Charge density on the electrode surface (σ^M) and surface excess of the adsorbate (Γ_A) have been computed employing the capacity data, as explained in the earlier paper [4].

RESULTS AND DISCUSSION

The differential capacity-potential curves for ethyl cellosolve (cf. Fig. 1) exhibit cathodic as well as anodic desorption peaks whereas in case of 1,4-butane diol (cf. Fig. 2), no such peaks exist; there is only a characteristic cross over of the curves at extreme cathodic and anodic polarizations. With the increase in concentration of ethyl cellosolve, the anodic desorption peak is found to shift towards more anodic potentials and the cathodic peak, towards more cathodic potentials.

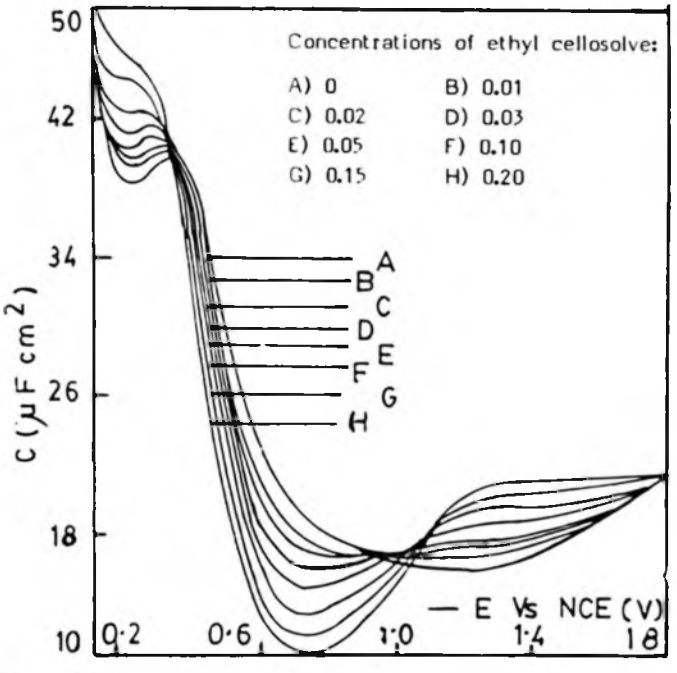


Fig. 1 Differential capacity-potential curves for Hg in 0.10 m KCl solution containing ethyl cellosolve.

0013 466 × 34 (36) 237-240

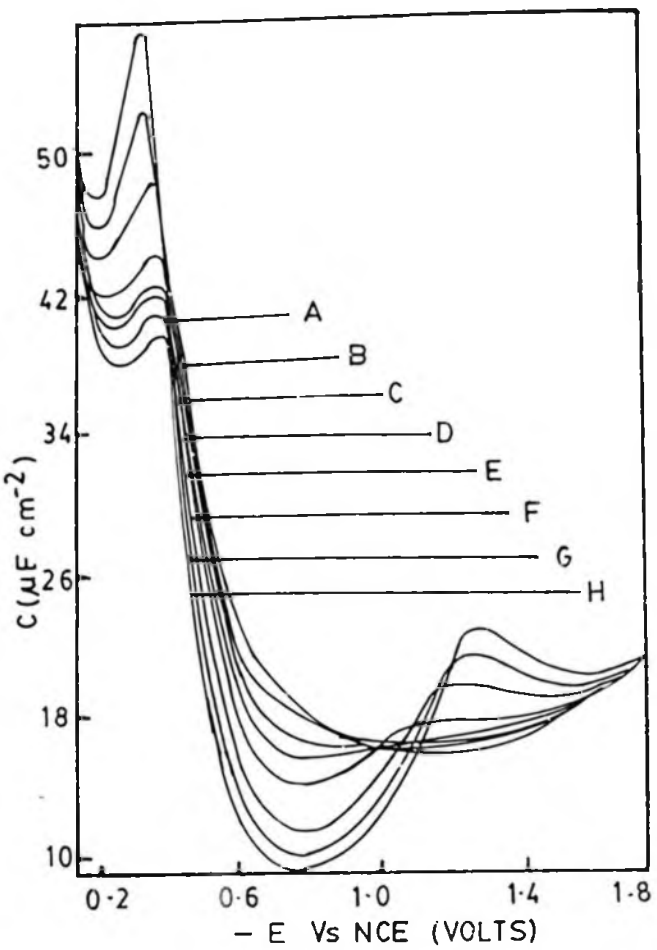


Fig. 2 Differential capacity-potential curves for Hg in 0.10 m KCl solution containing 1,4-butane diol at concentrations: (A) 0 (B) 0.02 (C) 0.03 (D) 0.05 (E) 0.07 (F) 0.10 (G) 0.15 (H) 0.20 m

A comparison of surface excess - potential curves (cf.Fig.3) shows that at a given potential and bulk concentration, surface excess of ethyl cellosolve is much more than that of 1,4-butane diol except at extreme anodic and cathodic polarizations. Ethyl cellosolve is more strongly adsorbed on mercury surface than the diol isomer when the electrode is not strongly polarized and more readily desorbed than the diol at extreme polarizations. Desorption is incomplete in both cases at anodic polarizations in the potential range studied.

Adsorption isotherms for both the compounds are found to be congruent with respect to potential as well as charge (plots not shown here) and within the concentration range studied the saturation value of surface excess Γ_s is not reached in case of both. Γ_s

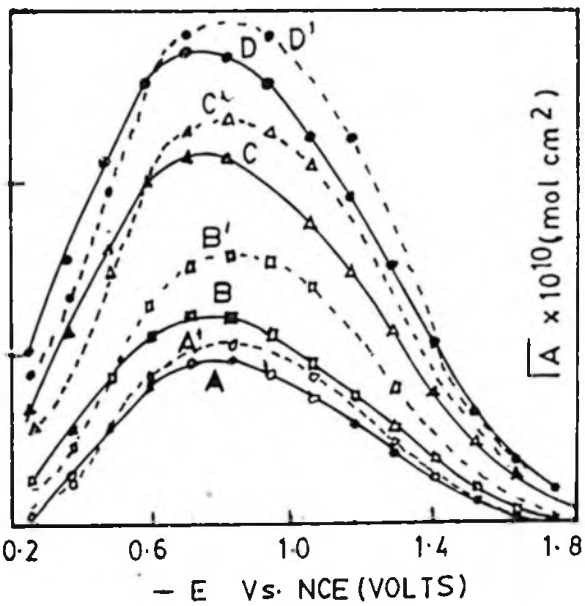


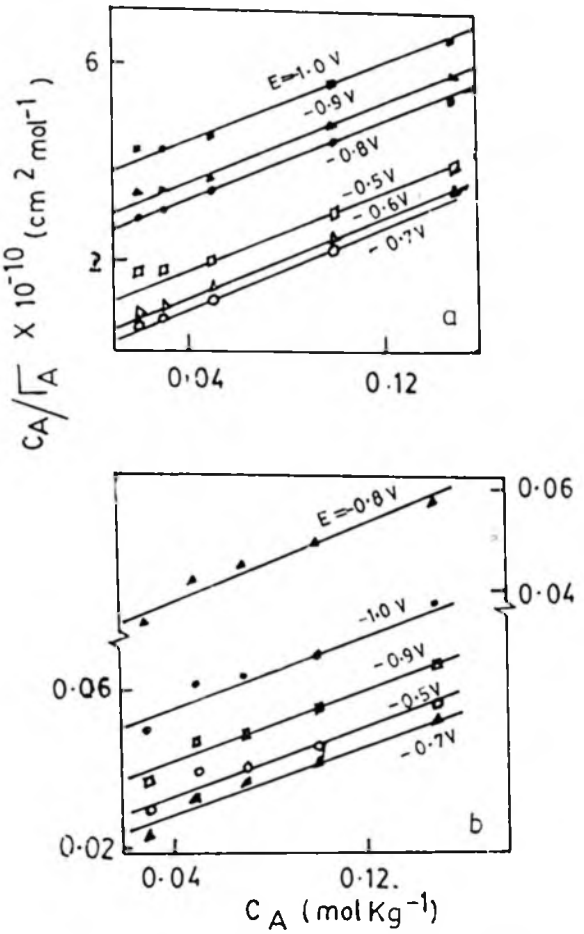
Fig. 3 Surface excess of the absorbate as a function of electrode potential. (A) 0.03 (B) 0.05 (C) 0.10 (D) 0.15 m of 1,4-butane diol. A', B', C', D' for ethyl cellosolve at the same molalities

is obtained indirectly as follows. Plots of C_A/Γ_A vs C_A at constant E are linear and parallel for both the compounds (cf. Figs. 4a and b) showing thereby that their adsorption behaviour obeys Langmuir's adsorption isotherms with a slope equivalent to $1/\Gamma_s$. The values of Γ_s thus obtained are 4.67 and 4.86 for 1,4-butane diol and ethyl cellosolve respectively.

Standard free energy of adsorption ($\Delta\bar{G}^\circ$), has been computed according to the equation of Conway and Barradas [5] when the adsorption isotherm is of Langmuir's type.

$$\ln\left[\left(\frac{55.5}{C_A}\right)\left(\frac{\theta}{1-\theta}\right)\right] = -\frac{\Delta\bar{G}^\circ}{RT} \qquad \ldots(1)$$

The dependence of $\Delta\bar{G}^\circ$ on E (cf. Fig. 5) is quadratic for both the compounds as expected for simple neutral organic substances. The magnitude of $\Delta\bar{G}^\circ$ is higher for cellosolve than for diol at potentials between -0.45 V and -1.0 V vs NCE and lower than that of diol at more anodic potentials. This can be attributed to the relatively weaker hydrogen bonding of ethyl cellosolve molecules with water molecules than those of 1,4-butane diol and also to more readiness for desorption of cellosolve at higher polarization.



Figs. 4a&b a) Test for Langmuir's isotherm for ethyl cellosolve.
b) Test for Langmuir's isotherm for 1,4-butane diol potential (V vs NCE) indicated on each line

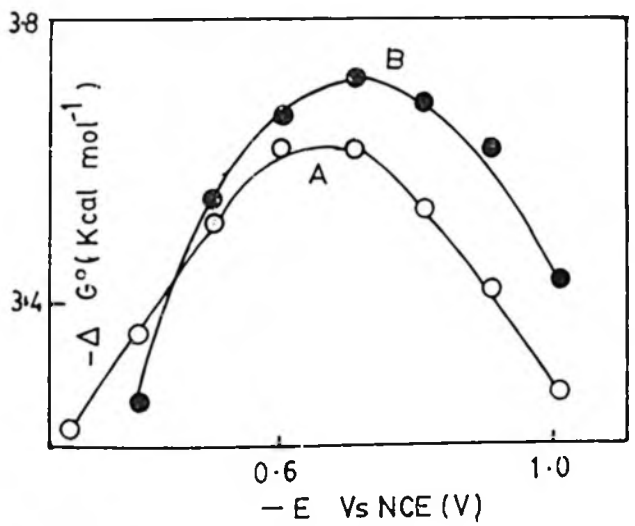


Fig. 5 Standard free energy of adsorption ($\Delta \bar{G}°$) as a function of electrode potential (E) (A) 1,4-butane diol (B) ethyl cellosolve

Anodic shift of potential of zero charge (E_{pzc}) with the increase in concentration of the adsorbates in both cases (Fig. 6) indicates their orientation with the positive end towards the electrode and functional group in solution. Linear shift of E_{pzc} with surface coverage (θ) of the adsorbates (cf. Fig. 7) suggests single and stable orientation [6] throughout the coverage region. The magnitude of $(\partial E_{pzc}/\partial \theta)_{\theta \to 0}$ (which accounts for the contribution due to normal components of the permanent organic dipoles) [7] is greater for ethyl cellosolve than 1,4-butane diol. For identical 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 (σ^M_{max}) is -2.9 μc cm^{-2} for 1,4-butane diol and -4.7 μc cm^{-2} for ethyl cellosolve. Damaskin and Frumkin [8] have expressed σ^M_{max} as:

$$\sigma^M_{max} = -(\partial E_{pzc}/\partial \theta)_{\theta \to 0} [C_0^2/(C_0 - C_1)] \qquad ...(2)$$

$C°$ and C_1 are the capacities at $\theta = 0$ and $\theta = 1$ respectively. The first term on the right hand

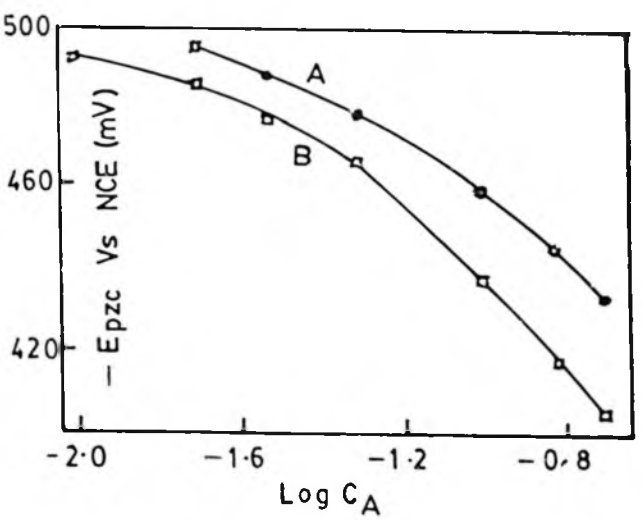


Fig. 6 Epzc as a function of log C_A of the adsorbates

(A) 1,4 - butane diol
(B) ethyl cellosolve

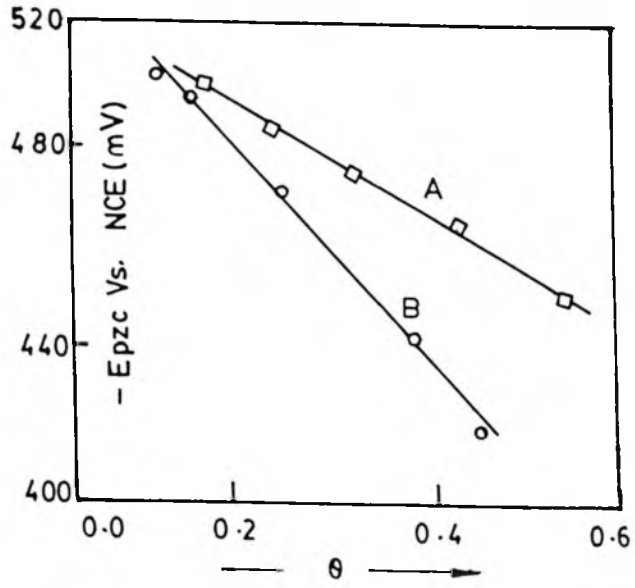


Fig. 7 Epzc as a function of surface coverage of the adsorbates (A) 1,4 - butane diol (B) ethyl cellosolve

side of the above equation accounts for the permanent dipoles and the second term, due to induced dipoles. It appears that contribution due to permanant dipoles (ethyl cellosolve >1,4-butane diol) controls the value of σ^{M}_{max} in these two compounds and hence more negative σ^{M}_{max} for ethyl cellosolve.

REFERENCES

1. S.L. Dyatkina and B.B. Damaskin, *Electrokhimiya*, 5 (1969) 438.

2. D.C. Grahame, *J. Am. Chem. Soc.*, 63 (1941) 207.

3. D.C. Grahame, *J. Am. Chem. Soc.*, 71 (1949) 2975.

4. B.V. Apparao and M.V. Ramanamurti, *J. Chem. Soc. Faraday Trans.* 1, 75 (1979) 2576.

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

6. S. Trasatti, *J. Electroanal. Chem.*, 53 (1974) 335.

7. B.A. Abd-El-Nabey and S. Trasatti, *J. Chem. Soc., Faraday Trans. 1*, 71 (1975) 2130.

8. B.B. Damaskin and A.N. Frumkin, *J. Electroanal. Chem.*, 34 (1972) 191.

Back volumes and individual issues of the Journal of Electrochemical Society of India are available at concessional rates.

Limited number of copies of the proceedings of the Annual Technical Meetings are also available for sale.

The Following publications of the Electrochemical Society of India are available at the original price

1. DIRECTORY OF ALLUMINIUM, 1955, pages 65 Price 15/-
2. REFRESHER COURSE IN METAL FINISHING, 1974 edited by Prof. K. I. Vasu, 14 articles 128 pages, Price Rs. 40/-
3. ELECTRODEPOSITION & METAL FINISHING, Proceedings of the Symposium held at Karaikudi on Dec. 27-28, 1957-Price: Rs. 20/-
4. MATERIALS FOR MACHINE TOOLS, 1976 Rs. 50/-
5. PROCEEDINGS OF THE ANNUAL TECHNICAL MEETINGS, 1979-1984, Rs. 100/- Per copy of each year.