

Potentials of Zero Charge and the Nature of the Solvent

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With 2 figures

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The comparison of the charge—potential dependences for *Hg*, *Ga* and *In + Ga* in water, acetonitrile and dimethyl sulfoxide shows that the influence of the orientation of the dipole molecules of the solvent affects the electric double layer structure much less at a negative surface charge than at the zero charge.

Ein Vergleich des Zusammenhangs von Ladung und Potential für *Hg*, *Ga* und *In + Ga* (eutektische Legierung) in Wasser, Acetonitril und Dimethylsulfoxid zeigt, daß der Einfluß der Orientierung der Lösungsmitteldipole die Struktur der elektrischen Doppelschicht bei einer negativen Oberflächenladung viel weniger beeinflusst als am elektrokapillaren Nullpunkt.

The comparison of the dependence of the charge density of an electrode on its potential E for mercury and gallium has shown that markedly different results are obtained if we compare the potentials of zero charge (pzc) $E_{\sigma=0}$ and the potentials of an equal negative charge $E_{\sigma=q}$, where q has a sufficiently large negative value ($q = -15 \div -18 \mu\text{C}/\text{cm}^2$)^{1,2}. While $\Delta(E_{\sigma=0})_{Ga}^{Hg} = (E_{\sigma=0})_{Hg} - (E_{\sigma=0})_{Ga}$ is equal to 0.50 v, the distance between the negative branches of the σ , E curves in the range of the potentials E in which they become parallel is only 0.17 v. This difference was explained by the fact that when the negative charge of the electrode decreases and approaches the pzc, water molecules undergo reorientation, so that the negative, i.e.

¹ A. FRUMKIN, N. POLIANOVSKAYA, N. GRIGORYEV and I. BAGOTSKAYA, *Electrochim. Acta* **10** (1965) 793.

² A. FRUMKIN, N. POLIANOVSKAYA and N. GRIGORYEV, *Dokl. Akad. Nauk SSSR* **157** (1964) 957.

oxygen, ends of water dipoles are oriented towards the electrode. This process is much more pronounced for more hydrophilic *Ga*, than for relatively hydrophobic *Hg*³. This phenomenon was considered in a more sophisticated way in ^{4,5} assuming that the surface layer contains both clusters of water molecules with a relatively small dipole moment, whose orientation is determined entirely by the electric field of the double layer, and single dipole molecules whose orientation is determined not only by the magnitude and direction of the field, but also by the chemical (specific) interaction of the oxygen end of the dipole⁴, or of both its ends⁵ with the metal surface.

It was pointed out in ¹ that in comparing the quantity $E_{\sigma=0}$ with the difference of the work functions ΔW_e or the Volta potential between two metals in vacuum $\psi^{Me_2 Me_1}$ ⁶, in many cases it is more reasonable to use the quantity $\Delta E_{\sigma=q}$ rather than $\Delta E_{\sigma=0}$, since at negative surface charges the influence of the difference in the orientation of water molecules is not so pronounced. The experimental data for a number of metals which support this conclusion, as well as the earlier history of the problem are given in ⁷. Recently TRASATTI⁸ approached the problem of the relationship between the pzc and the electron work function from a somewhat different point of view.

The influence of the orientation of the solvent molecules on the relationship between the quantities $\Delta E_{\sigma=0}$ and ΔW_e can be considered without increasing the number of metals to be compared, as was done in ^{7,8}, but by varying the solvent nature for a given pair of metals^{9,10}. The first attempts in this direction were made already in¹, where the data obtained in molten salts were given for the pair *Hg*—*Ga*. These data, however, are not sufficiently accurate and besides in this case the influence of the solvent nature is superimposed by that of the temperature variation. Later the behaviour of mercury, gallium and the eutectic indium-gallium alloy in water and acetonitrile was compared⁹⁻¹¹. Just as in water, in acetonitrile the value of

³ A. FRUMKIN, B. DAMASKIN, N. GRIGORYEV and I. BAGOTSKAYA, *Electrochim. Acta* **19** (1974) 69.

⁴ B. DAMASKIN and A. FRUMKIN, *Electrochim. Acta* **19** (1974) 173.

⁵ R. PARSONS, *J. electroanalyt. Chem.* **59** (1975) 229.

⁶ A. FRUMKIN and A. GORODETZKAYA, *Z. physik. Chem.* **136** (1928) 451.

⁷ A. FRUMKIN, B. DAMASKIN, I. BAGOTSKAYA and N. GRIGORYEV, *Electrochim. Acta* **19** (1974) 75.

⁸ S. TRASATTI, *J. electroanalyt. Chem.* **33** (1971) 351.

⁹ A. FRUMKIN, I. BAGOTSKAYA and N. GRIGORYEV, *Denki Kagaku* **43** (1975) 2.

$\Delta(E_{\sigma=0})_{Ga}^{Hg} = 0.29$ exceeds that of $\Delta(E_{\sigma=q})_{Ga}^{Hg} = 0.24$ (Fig. 1), but here the difference is less than in aqueous solutions. Moreover, the value of $\Delta(E_{\sigma=0})_{Ga}^{Hg}$ in acetonitrile is less than in water*.

More interesting results were obtained in comparing the behavior of mercury and the eutectic indium-gallium alloy (16.4 at.-% *In*) in acetonitrile and dimethyl sulfoxide (DMSO)¹² (Fig. 2). In choosing

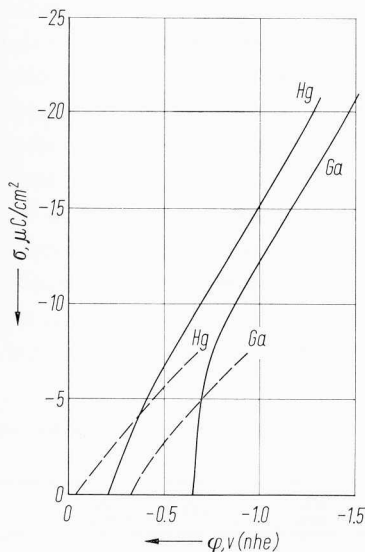


Fig. 1

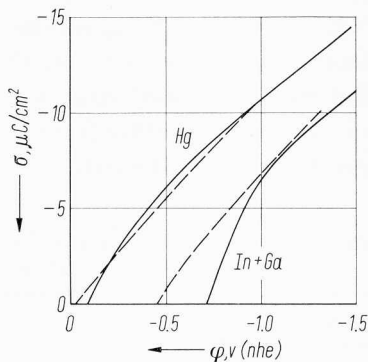


Fig. 2

Fig. 1. The σ , φ dependences for mercury and gallium. — water, --- acetonitrile

Fig. 2. The σ , φ dependences for mercury and *In* + *Ga* eutectic alloy. — dimethyl sulfoxide, --- acetonitrile

* All potentials in Figs. 1 and 2 are referred to the standard hydrogen electrode in water. No attempts were made to make any corrections for the potential difference at the interface between aqueous and nonaqueous solutions. This is of no importance, however for comparison of the values of $\Delta(E_{\sigma=0})_{Me_2}^{Me_1}$ and $\Delta(E_{\sigma=q})_{Me_2}^{Me_1}$ in different solvents since the value of this unknown correction was the same in experiments with each solvent. We desisted, however, from a confrontation of the values of $E_{\sigma=0}$ and $E_{\sigma=q}$ obtained for the same metal in different solvents.

¹⁰ I. BAGOTSKAYA, S. FATEEV, N. GRIGORYEV and A. FRUMKIN, *Elektrokhimiya* **9** (1973) 1676.

¹¹ I. BAGOTSKAYA and A. KALYUJNAYA, *Elektrokhimiya* (in press).

¹² I. BAGOTSKAYA and L. DUBOVA, unpublished data.

dimethyl sulfoxide as solvent, we proceeded from the assumption that the presence of a chemically active oxygen atom in the $S=O$ group may lead to a well-defined orientation of adsorbed molecules. In the case of dimethyl sulfoxide we were obliged to use the indium—gallium alloy instead of Ga , since at negative potentials at the DMSO/ Ga interface the capacity shows an appreciable dependence on frequency, which points to the presence of a chemical reaction*.

It is difficult to compare the data obtained in organic solvents for the indium-gallium alloy with those for water because the differential capacity of the indium-gallium alloy (just as that of indium) in water at the most negative accessible potentials for yet unknown reasons is by about 10% higher than that of mercury⁷, so that the σ , φ curves of mercury and indium-gallium have no parallel sections. Therefore, the value of $\Delta(E_{\sigma=q})_{In+Ga}^{Hg}$ can be only approximately estimated in the case of aqueous solutions. In the nonaqueous solutions investigated so far the differential capacity of $In+Ga$ at sufficiently negative potentials does not differ from that of the other metals studied by us. Tables 1 and 2 list the data on Ga and $In+Ga$ obtained up till now.

Table 1. ΔE -values at $\sigma = 0$ and $\sigma = q$ of Ga and Hg or $In+Ga$ and Hg in different solvents

Me_1-Me_2	Solvent	$\Delta(E_{\sigma=0})_{Me_1}^{Me_2}$	$\Delta(E_{\sigma=q})_{Me_1}^{Me_2}$
$Ga-Hg$	CH_3CN	0.29	0.23
	H_2O	0.50	0.17
	$(CH_3)_2SO$	0.71	—
$In+Ga-Hg$	CH_3CN	0.42	0.37
	H_2O	0.48	(0.34)
	$(CH_3)_2SO$	0.63	0.43

Table 2. Capacities of the dense layer, C_H , in $\mu F/cm^2$ for $In+Ga$ and Hg with charges $\sigma = 0$ and $\sigma = q$ in different solvents

	CH_3CN		H_2O		$(CH_3)_2SO$	
	$\sigma = 0$	$\sigma = q$	$\sigma = 0$	$\sigma = q$	$\sigma = 0$	$\sigma = q$
$In+Ga$	28.5	10	60.5	18	54	8.5
Hg	16	10	29	17	24	8.5

* The value of $\Delta(E_{\sigma=0})_{Ga}^{Hg}$ could be determined, however, by the dropping electrode method.

The measurements on $In+Ga$ in dimethyl sulfoxide were carried out in $LiClO_4$ solutions whose concentration varied within 0.01–0.1 M. The value of pzc was determined from the position of the differential capacity minimum in dilute solutions and by means of a dropping electrode. The experimental details will be published elsewhere.

As can be seen from Table 2, the data on pzc agree well with the results of the comparison of the capacity of the dense layer C_H of $In+Ga$ and of Hg at constant σ in different solvents.

The examination of Tables 1 and 2 shows that the difference in the double layer structure between Ga and Hg and between $In+Ga$ and Hg smooth down when passing from zero to negative surface charges and that the solvent nature affects the potential difference between different metals at the same negative charge much less than that at the zero charge. It should be noted that the value of $\Delta(E_{\sigma=0})_{Me_1}^{Me_2}$ in DMSO, both for Ga and $In+Ga$, is not less, but much higher, than in water. The value of W_e for $In+Ga$ has not yet been determined.