THE ORIENTATION OF SOLVENT-DIPOLES AT THE SURFACE OF THE PURE SOLVENT

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INTRODUCTION

Over the past few years in our laboratory a method has been developed for the estimation of the standard chemical potentials of single ions in nonaqueous solvents relative to water[1], $\Delta\mu^0$. For methanol[2] and ethanol[3] the values of $\Delta\mu^0$ thus found agreed very well with those estimated by Popovych *et al.*[4] and Padova[5] using different methods. Therefore it can be concluded that for these solvents a reliable set of $\Delta\mu^0$ values is available.

From these data and the corresponding values of the standard real potentials, $\Delta\alpha^0$, the difference between the surface potentials of the solvents and water, $\Delta\chi$, can be calculated according to eqn. (1):

$$\Delta\chi = (\Delta\alpha_i^0 - \Delta\mu_i^0)/zF \tag{1}$$

Where z is the valency of the ion i, and F is Faraday's constant.

The surface potentials of the solvents can be calculated by combining these data with the value of the surface potential of water. The latter value, however, is rather uncertain. Case and Parsons[6] estimated $-0.1 \text{ V} \leqslant \chi_{H_2O} \leqslant 0.1 \text{ V}$. De Ligny *et al.*[7] made an estimate of the standard chemical potential of the hydrogen ion in water, which gave (in combination with the value of the standard real potential of the hydrogen ion in water, derived by Randles[8]) the value $\chi_{H_2O} = -0.3 \text{ V}$. A revised calculation based on more recent data yields a value[9] of χ_{H_2O} of $0.04 \pm 0.1 \text{ V}$ which fits very well in the range of values proposed by Case and Parsons.

In addition to values of χ, values are reported in the literature for the temperature coefficient of χ, for water[10], methanol[11] and ethanol[12]. $d\chi/dT$ can be determined, provided that some assumptions are made about the concentration and temperature dependence of the activity coefficients of single ions.

In the following, we shall try to deduce the orientation of solvent molecules at the surface from the values of χ and $d\chi/dT$. Since we only have data on these two quantities, we are obliged to use a rather simple physical model of the surface layer, involving a limited number of parameters. The two state orientation model developed by Levine *et al.*[13] for the Stern inner region at the mercury–water interface serves as this simple model.

THEORY

According to the model of Levine *et al.* the surface region is a plane monolayer of polarisable solvent molecules, situated *in vacuo* between two continuous media: the solvent and air phases respectively. The distribution of the permanent charges in the molecules is approximated by a point dipole. These dipoles are situated at the sites of a two-dimensional hexagonal lattice. It has been assumed that every site of the lattice is occupied. Only the component of the permanent dipole moment of the solvent molecules normal to the surface is considered. This component can have only two values, *i.e.* in the direction solvent to air $p_{s \to a}$ and in the opposite (negative) direction $p_{a \to s}$.

It has been assumed that the two orientation states are distributed randomly over the lattice sites. So, the mean field in the normal direction is the same at all sites, and there is no resulting horizontal field.

The mean dipole moment in the normal direction, per lattice site, is made up of a term representing the mean permanent dipole moment, m_p, and of a term representing the mean induced dipole-moment, m_i. Thus, we can write for χ:

$$\chi = -4\pi N(m_p + m_i) = -4\pi N \frac{p(\lambda - \delta)}{1 + \alpha C_e / d^3} \tag{2}$$

where N is the number of solvent molecules per unit area, $p(\lambda - \delta)$ is the mean permanent dipole moment in the normal direction m_p, p and δ are functions of $p_{s \to a}$ and $p_{a \to s}$:

$$p = \tfrac{1}{2}(p_{a \to s} + p_{s \to a}) \tag{3}$$

$$\delta = (p_{a \to s} - p_{s \to a})/2p \tag{4}$$

and λ is the difference between the fractions of the number of dipoles per unit area in either of the orientation states:

$$\lambda = (N_{s \to a} - N_{a \to s})/N \tag{5}$$

The denominator in eqn. (2) is a measure of the extent to which the mean permanent dipole moment is reduced by the mean induced dipole moment. α is the polarizability of a solvent molecule, d is the distance between the lattice sites and C_e is an effective coordination number which accounts for the interactions with solvent-dipoles at neighbouring sites and with one array of image dipoles in the solvent phase[13,14]:

$$C_e = 11.0 \left\{ 1 + 0.1612 \frac{\varepsilon - 1}{\varepsilon + 1} \right\} \tag{6}$$

where ε is the bulk dielectric constant of the solvent. It is assumed that the monolayer plane is at a distance $\tfrac{1}{2}d$ from the air and liquid interfaces.

If the temperature dependence of all quantities except λ is ignored, it follows from eqn. (2) that:

$$d\chi/dT = -4\pi Np \frac{d\lambda/dT}{1 + \alpha C_e / d^3} \tag{7}$$

In their article Levine *et al.* derived an equilibrium expression for λ by minimizing

the free energy of the surface layer with respect to λ, since the free energy should be constant with respect to changes in the fractions $N_{s \to a}$ and $N_{a \to s}$, i.e., in λ.

From this equilibrium expression the following eqn. can be found for $d\lambda/dT$:

$$\frac{d\lambda}{dT} = \frac{-(1-\lambda^2)\ln(1+\lambda)/(1-\lambda)}{2T\{(1-\lambda^2)C_e p^2/(d^3 kT(1+\alpha C_e/d^3))+1\}} \tag{8}$$

Combination with eqn. (7) gives:

$$d\chi/dT = \frac{2\pi Np(1-\lambda^2)\ln(1+\lambda)/(1-\lambda)}{T\{(1-\lambda^2)C_e p^2/d^3 kT + \alpha C_e/d^3 + 1\}} \tag{9}$$

Eqns. (2) and (9) contain three unknown quantities: λ, p and δ, or λ, $p_{s \to a}$ and $p_{a \to s}$, or, instead of $p_{s \to a}$ and $p_{a \to s}$, the angles $\theta_{s \to a}$ and $\theta_{a \to s}$ between the dipole vector and the normal to the surface in the two orientation states. As there are only two known quantities, χ and $d\chi/dT$, a range of possible combinations of $\theta_{s \to a}$ with $\theta_{a \to s}$ and with λ, can be found.

RESULTS AND DISCUSSION

The obvious way of solving eqns. (2) and (9) is the elimination of λ. However, this yields a very complicated equation in $\theta_{s \to a}$ and $\theta_{a \to s}$. Therefore, we calculated $d\chi/dT$ for a range of assumed combinations of $\theta_{s \to a}$ and $\theta_{a \to s}$. Comparison with the literature values of $d\chi/dT$ then gives a set of possible combinations of $\theta_{s \to a}$ and $\theta_{a \to s}$.

TABLE 1

VALUES OF THE DIFFERENCE BETWEEN THE SURFACE POTENTIALS OF THE SOLVENT S AND WATER, $\Delta\chi$, AND OF THE TEMPERATURE COEFFICIENT OF THE SURFACE POTENTIAL, $d\chi/dT$

S	$\Delta\chi_{(S-H_2O)}/V$	$(d\chi/dT)/mVK^{-1}$
H_2O		-0.39 ± 0.04
CH_3OH	-0.28	1.84
C_2H_5OH	-0.32	1

The calculations were made for the two extreme values of χ_{H_2O} considered by Case and Parsons, i.e. -0.1 and $+0.1$ V, and the corresponding values of χ_{MeOH} and χ_{EtOH}. The values of $d\chi/dT$ and of $\Delta\chi$ are tabulated in Table 1. Values of μ, ε and α were taken from the literature[15]. The choice of a value of d is rather arbitrary. We used the van der Waals diameter of the solvent molecules[2,3]. As an alternative a value of d can be estimated from the density of the liquids. Assuming a hexagonal close packing this gave for water a value of d 25% larger than the van der Waals diameter. However, the results for the two values of d were practically the same.

Water

In Fig. 1a the combinations of $\theta_{s \to a}$ and $\theta_{a \to s}$ which gave values of $d\chi/dT$

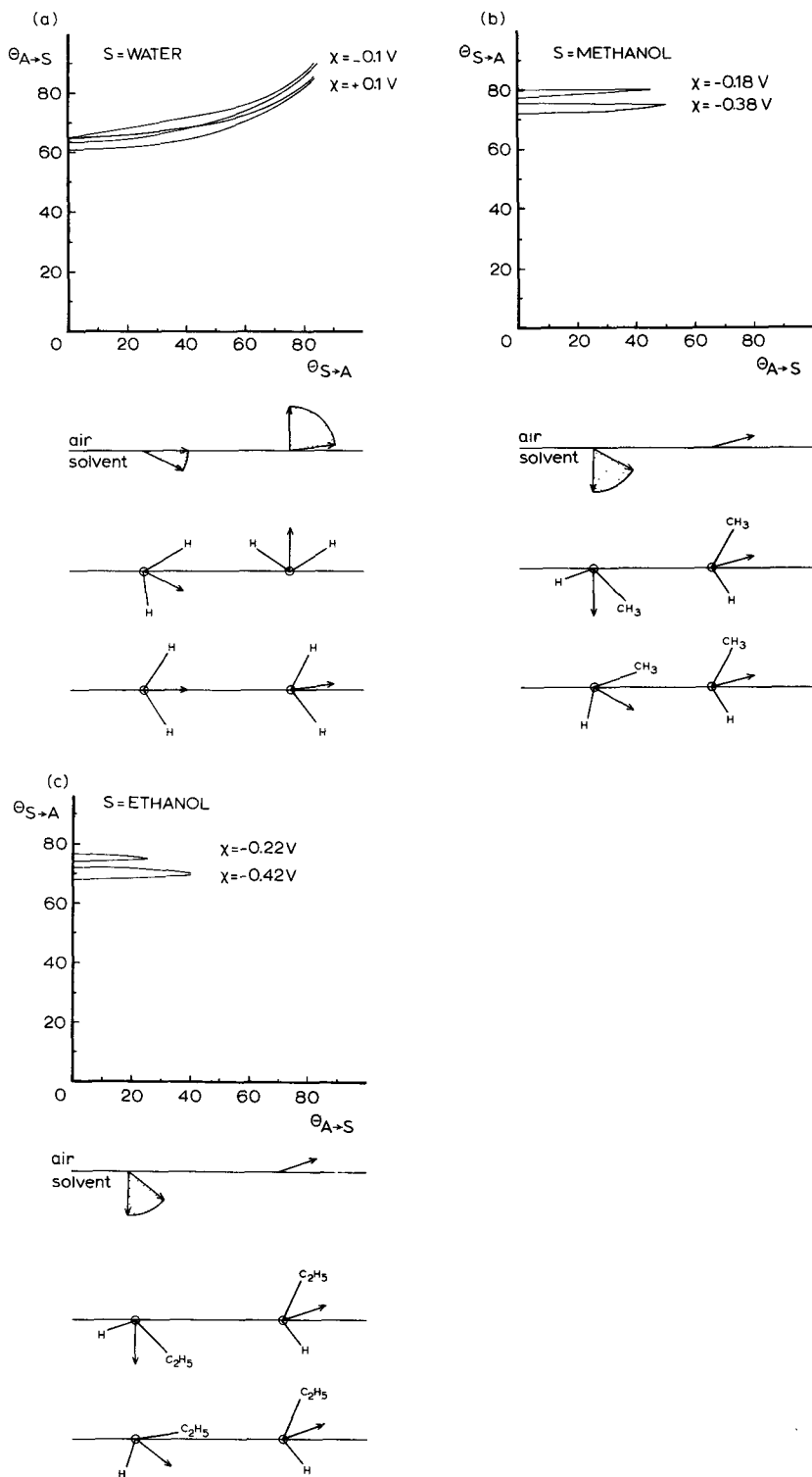Fig. 1. The possible combinations of $\theta_{a \to s}$ and $\theta_{s \to a}$ for the extreme values of χ and the orientations of the solvent-dipoles and -molecules corresponding with the extreme combinations of $\theta_{a \to s}$ and $\theta_{s \to a}$. (a) Water, (b) methanol, (c) ethanol.

from -0.35 to -0.43 mV K^{-1} are plotted. Also the range of possible directions of the dipole vector in the two orientation states and the proposed orientation of the solvent molecules corresponding with the extreme directions of the dipole vector are indicated. As Fig. 1a shows, $\theta_{a \rightarrow s}$ may vary over a range of only $25°$ while simultaneously $\theta_{s \rightarrow a}$ may vary over a range of $85°$. So, only one of the orientation states is reasonably well fixed. However, the negative sign of $d\chi/dT$ indicates that the larger fraction of dipoles will be in the latter state, since according to Boltzmann's law the ratio of the fractions goes to unity with increasing temperature. (As a matter of fact eqn. (9) shows that the sign of λ is fixed by the sign of $d\chi/dT$.)
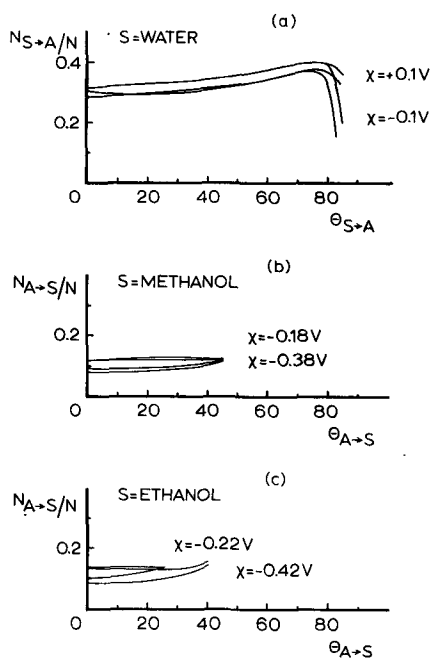

Fig. 2. The fraction of solvent-dipoles in one of the orientation states as a function of $\theta_{s \rightarrow a}$ for water (a) and $\theta_{a \rightarrow s}$ for methanol (b) and ethanol (c) for the extreme values of χ.

In Fig. 2a the smaller fraction $N_{s \rightarrow a}/N$, is plotted *vs.* $\theta_{s \rightarrow a}$. It can be seen that the magnitudes of the two fractions do not change very much over the range of possible combinations of $\theta_{s \rightarrow a}$. Therefore we can conclude that for the larger fraction of the solvent dipoles in the surface layer both the direction of the dipole vector and the magnitude of this fraction are rather well fixed.

From Figs. 1a and 2a it will be clear that the sign of χ is not a sound criterion for the determination of the magnitude of the fractions in either orientation state, or of the precise directions of the dipole vector of the solvent molecules at the surface[10,12]. Even if χ is negative the larger fraction of solvent molecules is oriented with the dipole vector pointing to the water phase.

In Fig. 3a calculated values of $d\chi/dT$ are plotted *vs.* $\theta_{a \rightarrow s}$ for some specified values of $\theta_{s \rightarrow a}$. This figure shows that the value of $d\chi/dT$ is a very good criterion
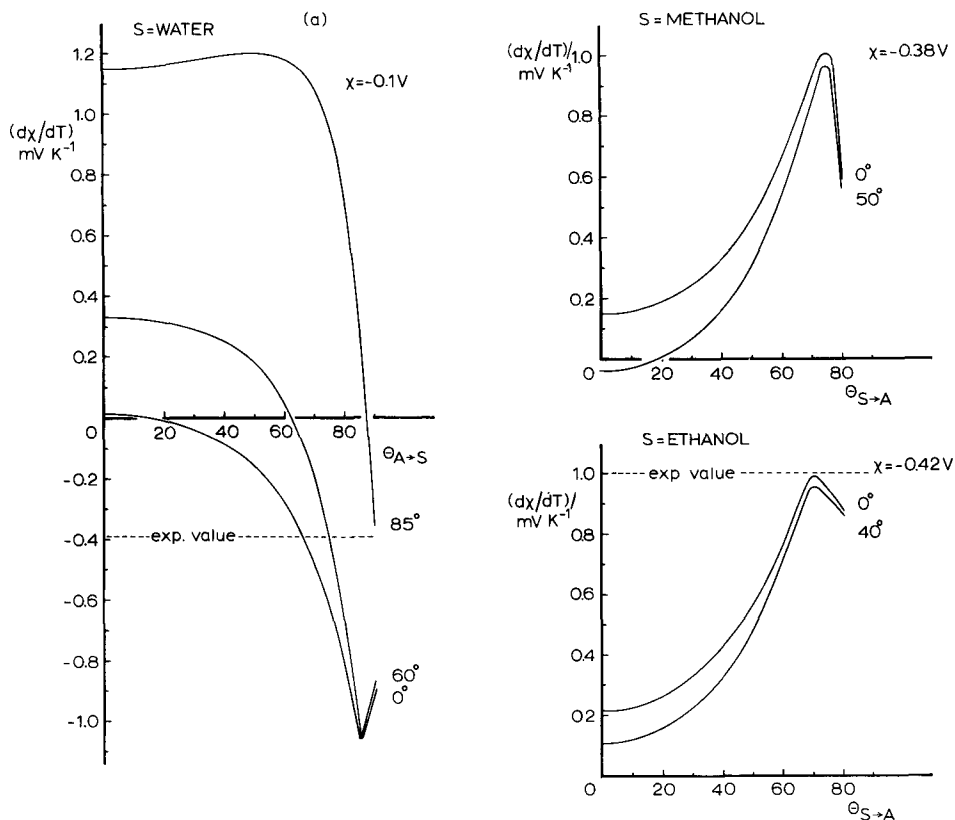
Fig. 3. Calculated values of $d\chi/dT$ as a function of $\theta_{a \to s}$ for water (a) and $\theta_{s \to a}$ for methanol (b) and ethanol (c) for some specified values of $\theta_{s \to a}$ and $\theta_{a \to s}$ respectively.

for the determination of the direction of the solvent dipoles: near the experimental value of $d\chi/dT$ the curves run very steep and are close together.

The negative sign of $d\chi/dT$ is often used as an argument in favour of a positive sign of χ[6,12]. However, also the opposite view is held[7].

According to the model of Levine et al., no conclusions about the sign of χ can be drawn from the sign of $d\chi/dT$: the sign of $d\chi/dT$ corresponds with the sign of λ (see eqn. (9)), the sign of χ with the sign of $\delta - \lambda$ (see eqn. (2)). From a mathematical point of view, λ and δ can be considered as independent variables (χ and $d\chi/dT$ being the dependent variables). If $|\delta| < |\lambda|$, χ and $d\chi/dT$ have opposite signs, but if $|\delta| > |\lambda|$ and δ and λ have opposite signs, the signs of χ and $d\chi/dT$ are equal.

Methanol and ethanol

The results for methanol and ethanol are shown in Figs. 1b, 2b, 3b, and Figs. 1c, 2c, 3c respectively. As can be seen from Figs. 3b and 3c for both solvents the calculated values of $d\chi/dT$ reach a sharp maximum of about 1 mVK^{-1}. Since for methanol this value is closest to the experimental value of 1.84 mVK^{-1}, in Fig. 1b combinations of $\theta_{s \to a}$ and $\theta_{a \to s}$ are plotted which give values of $d\chi/dT$

larger than 0.95 mVK^{-1}. We have no explanation for the large discrepancy between the calculated and the experimental value of dχ/dT. For ethanol the calculated maximum value agrees very well with the experimental value. In Fig. 1c combinations of $\theta_{s \to a}$ and $\theta_{a \to s}$ are plotted which give values of dχ/dT larger than 0.95 mVK^{-1}.

Figs. 1b and 1c show $\theta_{s \to a}$ to be almost constant for methanol and ethanol. $\theta_{a \to s}$ may vary over a range of 0–50° for methanol and over a range of 0–25° ($\chi = -0.22$ V) and 0–40° ($\chi = -0.42$ V) for ethanol.

It follows from the positive sign of dχ/dT that for both solvents the fraction $N_{s \to a}/N$ is the larger one. The preference for a particular orientation appears to be extremely large, as compared with water (Fig. 2). The solvent molecules at the surface belonging to the fraction $N_{s \to a}/N$ are probably oriented with the alkyl groups pointed to the air phase, as shown in Figs. 1b and 1c.

As was the case for water, the results do not depend much on the value of χ within the range chosen, although for ethanol the range of possible values of $\theta_{a \to s}$ distinctly decreases with increasing values of χ.

It can be concluded that for methanol and ethanol the direction of the solvent-dipoles at the surface is very well established, since for 9/10 of the solvent-dipoles the angle between the dipole vector and the normal to the surface is narrowly fixed.

The "residual" energies of the solvent molecules in the two orientation states

The interaction energies of individual solvent molecules with the bulk solvent phase are different in the two orientation states on account of, *e.g.*, hydrogen bonding with the second layer of solvent molecules, terms due to images of dipole and higher moments and nonelectrostatic adsorption energies. The difference between these residual energies, $\Delta E_r = E_{r_{s \to a}} - E_{r_{a \to s}}$, can be calculated from the equilibrium expression for λ mentioned before, *i.e.* eqn. (2.19i) in ref. 13. The values of ΔE_r found for water range from 0.5 to 3.6 kJmol^{-1} depending on the values adopted for χ, $\theta_{s \to a}$ and $\theta_{a \to s}$, for methanol and ethanol from -9 to -6 kJmol^{-1}. These values are of the same order of magnitude as the energy of hydrogen bonding.

SUMMARY

A method is described for the assessment of the preferential orientation of solvent-dipoles at the surface of the solvent from the surface potential χ and its temperature coefficient, dχ/dT. The method is based on the model of Levine *et al.* of the Stern inner region at the mercury–water interface in the absence of ionic adsorption. In this model two possible orientation states are assigned to the solvent-dipoles (in the "up" and "down" directions, respectively), with the magnitudes

of the components of the dipole moment normal to the surface differing in the two states.

According to the described method a range of possible combinations of the orientation states and of the magnitudes of the fractions of the solvent-dipoles in each state can be outlined.

For the three solvents studied, *i.e.* water, methanol and ethanol, a range of possible combinations is found in which one orientation state, corresponding with the larger fraction, is quite well fixed while simultaneously in the other orientation state the angle between the dipole vector and the normal to the surface may vary over a large range. The fractions of the solvent dipoles in either state are relatively constant. In water, 60–80% of the surface molecules are oriented with their dipoles pointing to the water phase. The angle between the dipole vector and the normal to the surface is 60–90°. Probably, one of the hydrogen atoms is pointing to the air phase.

In methanol and ethanol, 90% of the surface molecules are oriented with their dipoles pointing to the air phase. The angle between the dipole vector and the normal to the surface is 70–80°. Probably, the alkyl groups are pointing to the air phase.

It appears that the orientation of the solvent-dipoles at the surface of the solvent is more strongly reflected in $d\chi/dT$ than in χ.

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