Calculation of Concentration and Electrostatic Potential Profiles at Liquid-Membrane/Water and Liquid/Liquid Interfaces

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A method based on statistical thermodynamics has been used to describe concentration distributions of neutral and charged molecules in the vicinity of liquid-liquid or polymer membrane–liquid interfaces. The model is outlined and various applications are shown. One of these is a study of the transition region at the interface of two immiscible liquids. The results show that this transition is not sharp. The width of the interfacial region (where the concentration varies gradually) depends on the mutual solubility of the two liquids and on the size of the molecules. In another application the potential drop across the interfacial region has been calculated as a function of composition of the bulk phases. This type of calculation allowed the numerical simulation of the potentiometric behavior of a recently developed ion-selective electrode which employs negatively charged ion carrier.

Keywords   Statistical thermodynamics, concentration distribution, charged molecule, interface, immiscible liquids

The electrochemistry of the interface of two immiscible electrolytes (ITIES) has been widely studied in recent years. In contrast to the classical electrochemical interfaces like the metal/electrolyte interface the charge transfer process may be either electron transfer or ion transfer. Thus studying the rate of ion transfer at ITIES became a rich new field for scientific investigation. There has been, however, another independently developing field of electrochemistry where ion transfer between two immiscible phases is the main phenomenon: the field of ion-selective electrodes. These electrodes are usually prepared in the membrane form, *i.e.*, a sensitive membrane separates a reference solution from the sample solution. A potential drop develops across the membrane which depends on the sample composition according to the Nernst equation (in simple cases at least). Generally (but not always) the potential drop is concentrated at the two sides of the membrane, *i.e.*, at the membrane/solution interfaces. This interfacial potential drop is established by the distribution of ions between the membrane and the aqueous phase. The stability of the potential drop is assured by the usually very high rate of equilibrium exchange rate (exchange current density) of some ions in the system. The membrane may consist of a solid ion conductor (salt, glass) or a water-immiscible electrolyte confined in the membrane by pore filling or forming a membrane by gelation.

We have been most interested in understanding ion-selective electrode membranes made from plasticized PVC which can be considered as a gelled organic solvent immiscible with water. Such membranes are cast from solution. They may incorporate various compounds besides PVC and plasticizer, *e.g.*, lipophilic salts or molecules capable of complexing simple ions like potassium very strongly (crown ethers, valinomycin, *etc.*). We wanted to understand at the molecular level the potentiometric behavior of such membranes, particularly the formation of the potential drop at the interface, the causes of the sometimes peculiar potentiometric behavior and the role of ion transfer kinetics in potentiometry. We have used statistical thermodynamic models to describe the structure of the interface and the distribution of ions across the interface. The results included also the potential drop across the interface. This has been shown to depend on the composition of the electrolyte and the membrane. Thus we could calculate potential drop values for many series of compositions and could reconstruct the potentiometric behavior of the interfaces. Since our model treated the organic phase as a liquid, our results relate to ITIES as well.

In the present paper we shall first present an overview of the model used, then we show results about the structure of liquid/liquid interface as calculated from the model. In the subsequent sections we summarize some of our earlier results related to ion-selective electrodes, such as
* calibration characteristics of ion-selective electrodes (ISEs),
* interference by salt additives and
* effect of surfactants
and finally we present a new result for ion-selective electrodes with charged carriers.

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Statistical Thermodynamic Model

Different models have recently described the molecular structure of the liquid/liquid interface. These include a molecularly sharp interface between two phases[1], an interfacial range with gradual concentration change of two solvents[2], an interface as an "elastic" inner layer[3] and a dynamic interface with capillary waves superimposed on a molecularly sharp interfacial region.[4] The most detailed models of the interface are Monte Carlo (MC) and molecular dynamics (MD) computer simulations.[5–7] Although, the power of the computers increasing steadily, the calculation of large and complex systems is still very difficult to realize. Since exact treatment of complex systems is not yet practicable, approximate methods applied to model systems should be considered as alternatives.

A very successful approach to describe complex fluids has been originally developed by Scheutjens and Fleer[8] (SF-theory), subsequently extended to model self-assembling systems by Leermakers *et al.*[9] and to compute interfacial properties of liquid-liquid interfaces by Barneveld *et al.*[10] The theory is based on the following approximations:

1. The "many particle" problem of MC and MD is reduced to a "single particle" problem. This means, that for a test molecule, the full set of conformations (relative positions of molecule segments) of the molecule is generated by a propagator method.[8] The statistical weight of the conformations is determined by the molecular field (segment potentials) that is generated by the molecules themselves. Ensemble averaging leads to an overall density distribution of the molecule segments. The equilibrium distribution is characterized by the consistency of the density distribution and the molecular fields. This point is reached by using a Newton-type algorithm, which determines simultaneously, both the potential fields and the segment density profiles.

2. The second simplification is the discretization of the space by using a lattice. This means that all molecules, which are composed of one or more molecule segments have their segments on lattice sites only. The lattice may have different geometry, such as flat, cylindrical and spherical. In our studies we always used the flat lattice, in which there are parallel layers. The density and potential gradients are only allowed perpendicular to these layers (direction *z*) and consequently we have a mean field approximation in the other directions (*i.e.* the layers are assumed to be homogeneous).

3. Generally a segment's potential should depend on all possible types of interaction with its surroundings. The theory takes into account three types of interactions: (i) the short-range nearest neighbor interaction, which is characterized by the Flory–Huggins-type pair interaction parameter[11], (ii) the long-range electrostatic interaction and (iii) the hard-core interaction. If there are charges in the system, they are assumed to be located on the planes in the center of each lattice layer, forming a multi-plate capacitor system. In this way the electrostatic potential is calculated applying the discrete form of the Poisson–Boltzmann equation.[12]

A computer model of the interface may provide a detailed and pictorial view of the interfacial distribution of different species and of the potential drop at the interface. Making model calculations at different compositions of the system we can obtain the respective electrostatic potential drop at the interface and use these values to set up what would be a potentiometric calibration line in real experiment. In this way it is possible to study the potentiometric behavior of different membrane systems, the effect of various interfering ions and the adsorption of different species at the interface.

Applications of the Model

Calculation of interfacial density profiles

As an illustration of the SF-theory, we present an analysis of a binary mixture of simple molecules A_n and W. A_n represents a molecule that is composed of *n* molecule segments of type A while W represents a water molecule. The chemical meaning of segment A is not specified in the present analysis, it is simply any molecule segment chemically different from water but having (approximately) the same size as water. It is assumed, that the segments A and W fit each one site of the lattice used for the discretization of the space. Here we chose a flat lattice with 20 layers and the width of each layer is 0.3 nm, which is roughly the diameter of a water molecule.

The Flory–Huggins interaction parameter for the molecule segments A and W (χ_{AW}) is defined as the energy change (in units of k_BT) associated with the exchange of a segment A from pure A phase with a water molecule from pure water.[13] Thus $\chi_{WA}=\chi_{AW}$ and from the analogous definitions $\chi_{AA}=\chi_{WW}=0$. If the Flory–Huggins interaction parameter is greater than a critical value ($\chi_{AW}>\chi_{AW}^C$), the binary mixture of A and W separates into two phases, which gives rise to the appearance of an interface.

The mean-field solution of the segment density profiles of the components in a system composed of W and A_1 for different values of χ_{AW} is shown in Fig. 1. It can be seen that for $\chi_{AW}>2$ two phases are formed. The thickness of the interface depends on the interaction parameter. If this parameter is close to the critical value (in this case, *i.e.*, for simple molecules of equal size, to 2), the interface becomes very wide and the composition of the two coexisting phases is close to each other. At the critical value of 2 the interface disappears and there is only one phase. These results of our model are in agreement with classical statistical calculations.

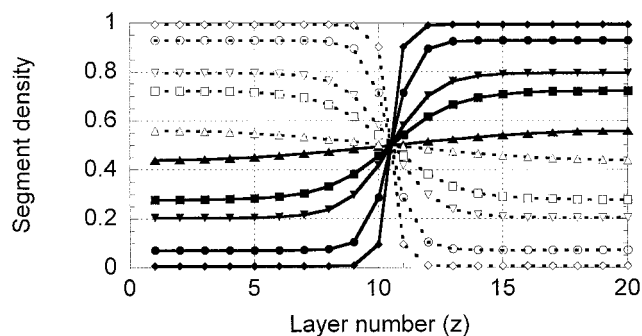The next stage of our investigation was to study the structure of the interface between water and a liquid

Fig. 1   Segment density profiles of the components in a system composed of W and A_1 for different values of χ_{AW}. Full lines show the segment density of W, broken lines that of A. Differently shaped symbols represent different values of Flory–Huggins interaction parameter χ_{AW}: $\triangle \blacktriangle$, 2.02; $\square \blacksquare$, 2.15; $\triangledown \blacktriangledown$, 2.30; $\bigcirc \bullet$, 3.0; $\diamondsuit \blacklozenge$, 5.0.

Fig. 2   Dependence of the thickness of the interface between water (W) and A_n molecule on the interaction parameter χ_{AW} and the length of the molecule A_n (the value of n).

consisting of A_n molecules. One may think of A_n like a straight chain alkane or an oligomer some other repeating units. The dependence of the thickness of the interface on the interaction parameter χ_{AW} and the length of the molecule A_n (the value of n) is presented in Fig. 2.

It is clear, that the thickness of the interface and the critical value of the interaction parameter both depend on the parameter n. For any given value of χ_{AW} a longer molecule forms a sharper (narrower) interface. This is not surprising since the longer molecule is also more hydrophobic (the transfer of one molecule A_n means transfer of n segments A). We also see that for any given n the interface becomes sharper as χ_{AW} increases, *i.e.*, as the molecule becomes more hydrophobic. The critical value of χ_{AW} is known to depend on n as

$$\chi_{AW}^C = 0.5(1 + \frac{1}{\sqrt{n}})^2$$

This formula gives $\chi_{AW}^C = 2$ for $n=1$ and $\chi_{AW}^C = 1.05$ for $n=5$. These values agree well with the simulation results. For the limit of $n=$infinite the theory gives $\chi_{AW}^C = 0.5$.[14] One may note by inspecting Fig. 2 that χ_{AW} has to be quite close to χ_{AW}^C to observe any broadening of the interface.

These results are interesting despite the approximations used in the model. The structure of the interfacial layer may be very important in the kinetics of ion transfer. Our results show that—in contrast to many earlier models—the liquid-liquid interface cannot be considered a sharp plane. These results do not exclude, however, the possibility of a relatively sharp but rough interface, since our density (concentration) data for any layer are values obtained by averaging within the layer. To our knowledge no experimental results exist which accurately describe the structure of the liquid/liquid interface. Therefore only model calculations can be
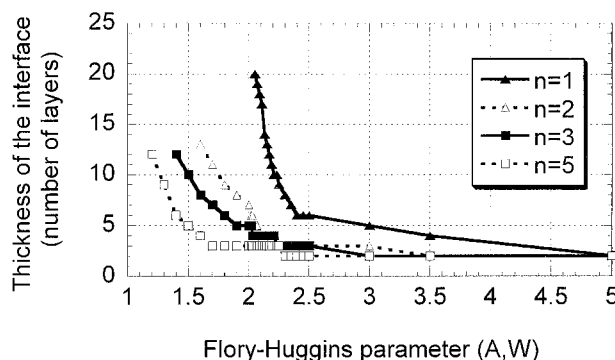
used and compared at present. From the work presented here one may conclude that the more hydrophobic the water-immiscible phase the sharper the interface.

Potentiometry with cation-sensitive liquid ion-exchange membranes

Using the SF-theory, we studied a system that consists of a cation-exchange liquid membrane in contact with the aqueous solution of a salt consisting of two monovalent ions. This theory was chosen because it enables the modeling of spontaneous formation of the interface without the presumption of the exact place and thickness of the interface.

In the cation sensitive liquid ion-exchange system the predominant components are the water molecules, the organic solvent molecules (*e.g.* polyvinyl chains together with plasticizer molecules in PVC based membranes), free ionic sites within the membrane (strongly hydrophobic anions such as tetraphenylborate), hydrophilic cation (counterion) and anion (coion).

As stated before, the diffusion potential across the membrane is assumed to be approximates zero or at least independent of sample composition and thus the change of the membrane potential is due to the change of boundary potential at the membrane–water interface.

First we studied the dependence of the electrostatic potential developed at the water–organic interface on the hydrophilicity of the countercation. Then we proceeded to investigate the coanion influence on the potential response (electrostatic potential drop at the interface *versus* logarithm of the concentration of cation in the bulk of the water phase) by varying the hydrophilicity of the coion. This way the experimentally observable features of this type of electrodes could be simulated. Results of this analysis have been published.[15]

Potentiometry using liquid ion exchange membranes with complexing agents (carriers)

As stated in the previous section the statistical thermodynamic approach was suitable for describing the

most important potentiometric characteristics of ion-exchange type liquid membrane ISEs. An even more important kind of these electrodes uses some neutral complexing agent like valinomycin or crown ethers beside the ion exchanger in the membrane. The original SF-theory, however, could not take local complexation equilibrium between different species into account. Therefore an extension of the SF-theory, a multistate self-consistent field theory has been developed and published.[16] This new theory accounts for the complexation reaction between carrier and one or more complexing ions by introducing complex-stability constants as additional parameters.

Using this new approach the potentiometric behavior of liquid membrane ion-selective electrodes with neutral carriers (complexing agents) has been qualitatively reproduced.[17] Molecular interpretation of phenomena like Nernstian response, interference, detection limits and the effect of liphophilic salt additives could be given.

A new development in ion-selective potentiometry has been that not only neutral but also charged complexing molecules may be used in the membranes.[18] The trick was to use suitable type and quantity of ionic additives. Our model calculations succeeded in reproducing this experimental observation.[19] Moreover the nonideal behavior of such electrodes at higher analyte concentrations was also correctly reproduced. This is shown in Fig. 3.
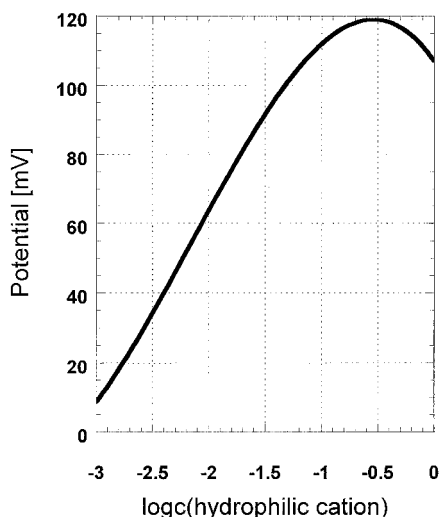
In conclusion, statistical thermodynamic model which was originally developed to describe surfactant systems could be efficiently used to reproduce the potentiometric behavior of ion-selective membrane electrodes of various types. Beyond this one could obtain pictorial insight into the distribution of species at interfaces of immiscible electrolytes. Such pictures may provide more accurate description of electrochemical phenomena at ITIES than the classical sharp plane interface. While direct confirmation of the model by experiment is not yet possible some of its consequences like the effect of varying hydrophobicity may be verified.

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Fig. 3 Potential response of an ion-selective electrode based on negatively charged carrier.