

Study of Electron transfer kinetics on Self-assembled monolayers of alkanethiols in non-aqueous solvents

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We find from literature that relatively less attention has been paid to the study of blocking properties of alkanethiol SAMs in non-aqueous solvents primarily due to their perceived instability in these solvents. In this study we investigate by cyclic voltammetry and Electrochemical Impedance Spectroscopy the barrier properties of alkanethiol SAMs to the ferrocene electron transfer reaction in different non-aqueous solvents. We find that the electron transfer through the monolayer is facilitated by the ability of the solvent molecules to interact with the alkanethiol molecule and disorganize the monolayer. We have also evaluated the barrier properties of alkanethiol SAMs formed in different non-aqueous solvents. Our impedance results show that the barrier properties of the SAMs depend to a large extent on the solvent used as adsorption medium.

Experimental

A gold disk electrode of geometric area of 0.002 cm^2 was used as the working electrode for study of ferrocene redox reaction in acetonitrile, propylene carbonate, ethanol, DMF, DMSO and formamide. The SAMs were formed in neat dodecanethiol (DDT) and hexadecanethiol (HDT) by keeping the Au electrode previously treated with dilute aqua regia. Impedance studies in presence of redox species were carried out at formal potential of ferrocene redox system as derived from cyclic voltammetry.

Results and discussion

Cyclic voltammograms of ferrocene redox reaction on bare and neat dodecanethiol coated gold electrode in acetonitrile and propylene carbonate show that the first cycle CV of neat thiol coated electrode exhibits initial blocking behavior. However as scanning continues we obtain a CV similar to bare gold electrode with larger peak separation than a fully reversible redox reaction. Our results show that the alkanethiol monolayer is stable in acetonitrile and propylene carbonate and the thiol monolayer undergoes some kind of disorganization which results in significant faradaic current during ferrocene redox reaction¹.

From the electrochemical impedance data we find that the charge transfer resistance (R_{ct}) values for ferrocene reaction are found to be $113 \Omega \text{ cm}^2$ and $2650 \Omega \text{ cm}^2$ respectively for neat DDT and HDT coated electrodes. These values correspond to apparent rate constants (k_{app}) of $2.35 \times 10^{-3} \text{ cm s}^{-1}$ and $1.0 \times 10^{-4} \text{ cm s}^{-1}$ respectively. Our results indicate that in the case of acetonitrile and propylene carbonate, the solvent molecules disorganise the alkanethiol SAMs and in the process allow the ferrocene molecules to get a closer access to the electrode surface. Subsequently the electron transfer process occurs by tunneling from an average distance corresponding to half the thickness of the monolayer. The solvent molecules of acetonitrile and propylene carbonate are free and are not bound to each other a situation contrary to what exists in the case of water which has an extensive H-bonded network in the bulk. Our results also show that the neat thiol monolayers resist the disorganization by non-aqueous electrolytes much better than the SAMs prepared in ethanol as solvent.

However the situation is reversed in the case of a solvent such as formamide which has an extensive two dimensional H-bonded network^{2, 3}. In this case the ferrocene electron transfer reaction is almost totally blocked as shown by our CV and impedance results. This is because formamide due its two dimensional hydrogen bonded network in the bulk does not solvate the monolayer. Since the monolayer is undisturbed, it is well organized and better blocking in this solvent.

The situation is intermediate between the two cases mentioned above in other non-aqueous solvents like ethanol, DMF, DMSO which possess some degree of internal bulk order due to hydrogen bonding. They exhibit much less tendency to disorganise the monolayer formed by thiol molecules than acetonitrile and propylene carbonate. However, the electron transfer process in these SAMs is facilitated when compared to that of much better ordered solvent such as formamide. Our results therefore establish a clear correlation between the bulk structure of some non-aqueous solvents and their ability to influence the blocking behaviour of SAMs formed by alkanethiol molecules on gold.

We also find that the blocking behaviour of alkanethiol monolayer to ferrocyanide redox reaction is also very much dependent on the solvent medium used for adsorption. Thus we find that the blocking properties of the monolayer varies in the order: chloroform \approx hexane $>$ ethanol $>$ DMF $>$ toluene $>$ acetonitrile $>$ hexadecane when they are used as adsorbing medium. This behaviour is also reflected from the impedance values obtained in 1M NaF in water without any redox species. It is not entirely understood why such trend is exhibited in these cases. However, various factors such as the size, bulk order, viscosity, dielectric constant and polarity of adsorption solvents seem to play a role in varying degree. The permeability of the monolayer to redox species is also quite often influenced by the intercalation of solvent molecules during adsorption process.

Our results show that keeping the substrate in the adsorbing medium of alkanethiol in ethanol for prolonged duration does not in any way help in the formation of more blocking and compact monolayer. On the other hand the monolayer has better blocking properties if the thiol molecules are adsorbed for 1 hour in ethanol medium followed by keeping the substrate in Millipore water for 6 hours. The extensive 3-D hydrogen bonding in water contributes to strong hydrophobic interaction among terminal methyl groups of alkanethiol and this in turn helps in the formation of well ordered structure that blocks the electron transfer process more effectively.

References :

1. U.K.Sur and V.Lakshminarayanan, *J.Electroanal.Chem.*, 516 (2001) 31
2. C.Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, 2nd Edition, VCH, New York, 1990, p.14
3. Israelachvili, *Intermolecular and surface forces*, Academic Press, London, 1997 p.122,124