References

1 G. N. La Mar, *J. Chem. Phys., 41,* 2992 (1964).
2 G. N. La Mar, *J. Chem. Phys., 43,* 235 (1965).
3 D. G. Brown and R. S. Drago, *J. Am. Chem. Soc., 92,* 1871 (1970).
4 H. P. Fritz, W. Gretner, H. J. Keller and K. E. Schwarzhans, *Z. Naturforsch., 25b,* 174 (1970).
5 H. M. McConnell and R. E. Robertson, *J. Chem. Phys., 29,* 1361 (1958).
6 I. Solomon, *Phys. Rev., 99,* 559 (1955).
7 N. Bloembergen, *J. Chem. Phys., 27,* 572, 595 (1957).

The Temperature Dependence of the Dielectric Properties of Unassociated Organic Solvents at Polarizable Interfaces

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As it was shown previously [1, 2], the three state model for solvent dipoles can be used successfully to describe the differential capacity at Hg/nonaqueous interface in the case of unassociated or weakly associated organic solvents.

The model may be tested further by examining the temperature dependence of the surface potential and the adsorption entropy as was done previously for Hg/aqueous interface [3, 4]. The temperature coefficient of the surface potential for a number of organic solvents with the exception for methanol is positive [5]. However the interpretation of this quantity in terms of solvent dipole orientation and the sign of the surface potential depends on the molecular model used to describe the dielectric properties of the solvent monolayer. Another quantity which is accessible experimentally is the solvent adsorption entropy. The only data available for nonaqueous solvents are those for Hg/propylene carbonate interface [6]. It is evident that the accepted interpretation based on a two state model is not valid in this case. The molar adsorption entropy has a maximum at a negative charge density which would suggest a preferred orientation at the uncharged mercury with the negative end of the propylene carbonate dipole pointing towards the metal and consequently, a negative surface potential. However the occurrence of the solvent capacity 'hump' at a high positive charge density would imply just the opposite.

The purpose of this paper is to discuss the temperature dependence of the dielectric properties of the Hg/solution interface in the case of N,N-dimethylformamide, methanol and acetone including also the literature data for propylene carbonate [5]. The adsorption entropy has been calculated on the basis of the temperature dependence of the double layer differential capacity following the thermodynamic arguments of Harrison *et al.* [7]. The results have been compared with the prediction of three state model.

References

1 W. R. Fawcett, *Israel J. Chem., 18,* 3 (1979).
2 Z. Borkowska and W. R. Fawcett, *Electrokhimiya,* accepted.
3 R. M. Reeves, *Mod. Aspects Electrochem., 2,* 239 (1974).
4 R. Parsons, *Electrochim. Acta, 21,* 681 (1976).
5 Z. Borkowska, W. R. Fawcett and S. Anatawan, *J. Phys. Chem.,* submitted.
6 Nguyen Huu Chong, A. Jenard and H. D. Hurwitz, *J. Electroanal. Chem.,* in press.
7 J. A. Harrison, J. E. B. Randles and D. J. Shiffrin, *J. Electroanal. Chem., 48,* 359 (1973).

Solvent Effect on N-Methylthiourea. A ^{1}H-NMR Study

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The solvent influence on the spectroscopic properties of the solute can be used to obtain information about its configuration in solution. With this objective the influence of the temperature on the ^{1}H-nmr spectra of N-methylthiourea was studied in the following solvents 1,2-propanodiolcarbonate, trimethylphosphate, tributylphosphate and dimethylsulfoxide mixed with CCl_4 in a ratio 1:1 in volume. At low temperature the methyl group signals of thiourea split showing the signals corresponding to *cis* and *trans* positions of methyl protons. These results agree with the behaviour reported for other solvents.

However, the low field spectra corresponding to N–H and $N–H_2$ protons show a higher complexity as is shown in Fig. 1.

The splitting of the $N-H_2$ signal in two signals with different intensities, A and B, indicates the presence of two non equivalent configurations of