The Structure of Water in Mixed Solvents E. Gileadi School of Chemistry Tel-Aviv University Tel-Aviv 69978 ISRAEL

It is well known that water is a complex liquid, comprising aggregates of molecules, even at its boiling point. This is commonly attributed to hydrogen bonding, and leads to an anomalously high boiling point and dielectric constant. However, this structure is not maintained in mixed solvents. Using the excess proton conductivity as a probe, one finds that in mixtures of acetonitrile and water, no excess conductivity of the proton is observed until the mole fraction of water has reached about 0.1, and even when it is 0.5, the excess conductivity is much less than in pure water, even though at any moment in time, each water molecule must be in contact with several other water molecules. [1-6]. We define this state as mono-water, in contrast to bulk water, which can be named aggregate water

The corrosion of metals in such mixed solvents must depend on the structure of water. Question regarding the dielectric constant of mono water, which can have a strong influence on the solubility of salt, the tendency to form passive films and even the standard potentials of various reaction involved directly in the corrosion process have not been studied.

It should be added that this is not a purely academic question. Thus, wide use of methanol as a fuel, or even oil and liquid natural gas, which will have to be transported by pipelines or vehicles and stored, may lead to corrosion, the rate of which depends on small amounts of water mixed with the fuel.

Another question that is still open is the thickness of a layer of water adsorbed at the interface between a metal and moist air, that would allow solvation of salts, electrolytic conductivity and involvement in the corrosion reaction proper (i.e. hydrogen evolution or oxygen reduction).

The roughness of the surface will also play a role in this respect. Thus, it is the common wisdom that a rough surface would corrode faster than a highly polished one, but this does not take into account the structure of water at such an interface. Assuming, for simplicity, a sinusoidal roughness, the vapor pressure of water at the peaks will be higher than that in the valleys, because of the different curvature. This could lead to microscopic or nano sized pools of water in the recessed regions, with no continuity in the two directions parallel to the surface.

References

- Z. Stein and E. Gileadi J. Electrochem. Soc. 132 (1985) 2166
- [2] R.G. Kelly, P. J. Moran, J. Kruger, C.Zollman and E. Gileadi, J. Electrochem.Soc., 136, (1989) 3262
- [3] C.S. Brossia, E. Gileadi, R. G. Kelly, Corr.Sci. 37 (1995) 1455
- [4] E. Gileadi, E. Kirowa-Eisner, Electrochim. Acta, 51 (2006) 6003.
- [5] E. Gileadi and E. Kirowa-Eisner, Electrochim. Acta, **51** (2006) 6003
- [6] E Gileadi, J Solid-State Electrochem. **15** (2011) 1359