An Experimental and PM3 Semiempirical Quantum-chemical Investigation of Anomalous Aluminium Dissolution in Proton-donor Solvents Containing HCl

Naum M. Gontmakher,* Olga I. Barteneva, Igor' V. Dorogan and Ruslan M. Minyaev

Institute of Physical and Organic Chemistry, Rostov State University, 344104 Rostov-on-Don, Russian Federation. Fax: +7 8632 285667

An anomalous chemical mechanism of aluminium dissolution has been experimentally determined in electrolytes containing HCl based on proton-donor solvents (methanol, ethanol, propanol, water), and this mechanism has been explained by a new theoretical approach based on the comparison of the work function of aluminium with the electron affinity of oxidizing complexes.

The chemical mechanism of metal dissolution in contrast to the usual electrochemical one has been experimentally discovered in aprotic solvents (tetrahydrofuran and its mixtures).[1–2] Earlier,[3] by quantum-chemical methods, reasons for the high rate of metal dissolution in an HCl–THF mixture were explained by the presence of a highly active oxidizing component $(C_4H_8O)_2H^+$. The present paper is devoted to an experimental investigation of the chemical mechanism of aluminium dissolution in an HCl solution of proton-donor solvents (methanol, ethanol, propanol, water) and to a theoretical explanation of this mechanism.

The electrodes (Al, 99.99%) were firstly treated according to the technique already discussed.[1–2] Purification of the organic solvents was performed according to the technique described in ref. 4. The total aluminium dissolution rate (i_Σ) was determined using a gravimetric and photocolorimetric technique with Eriochrome cyanine as a reagent and recalculating to current density units taking into account trivalent ions. The electrode potential (E) was kept constant using a P-5827M potentiostat and was measured in relation to a silver chloride electrode and recalculated to the normal hydrogen electrode (NHE).

In the media under study, the character of the (i_Σ, E) dependence is determined by the nature of the solvent. In methanol and ethanol solutions containing HCl, aluminium dissolution is characterized by quite a few anomalies. The rate of aluminium dissolution does not depend on the electrode potential (see Fig. 1, curve 1). The magnitude of i_Σ is essentially more than the electrochemical current of self-dissolution, estimated by the extrapolation of polarization curves (see Fig. 1, curves 2, 3) to the corrosion potential. These facts, in particular the independence of the rate of dissolution on the electrode potential during cathodic polarization, have allowed us to assume the possibility of a chemical mechanism of aluminium dissolution which essentially predominates over the electrochemical one. In aqueous solution the rate of aluminium dissolution during cathodic polarization is insignificant at room temperature and is

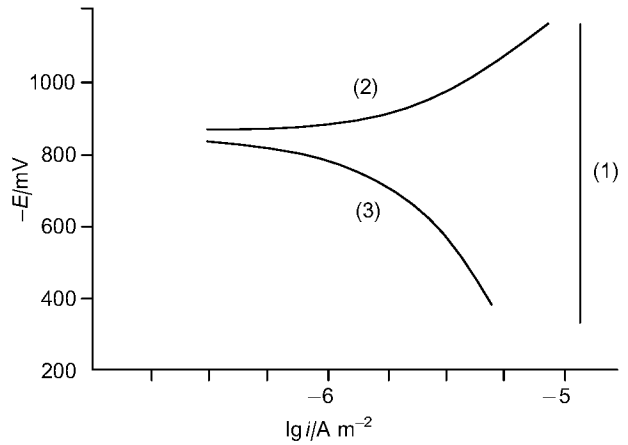

Fig. 1 Dependence of the summary dissolution rate on potential (1), cathodic (2), anodic (3) polarization curves for 2 M HCl solution in ethanol ($T = 25\,^\circ C$).

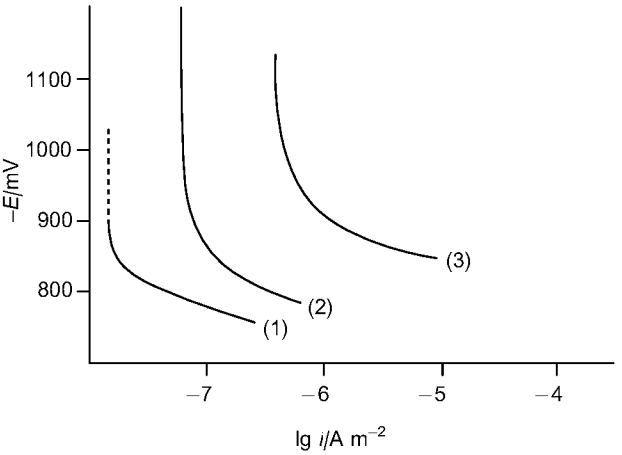

Fig. 2 Summary aluminium dissolution rate *versus* potential at different temperatures in 1 M HCl aqueous solution: (1), 20 °C; (2), 60 °C; (3), 90 °C.

comparable with the experimental error (see Fig. 2, curve 1). At the highest temperatures (more than 60 °C) the rate of aluminium dissolution increases and becomes independent of electrode potential during cathodic polarization (see Fig. 2, curves 2,3). This fact also evidently testifies to the possibility of chemical dissolution of aluminium in aqueous solution. The rate of chemical dissolution decreases in the following order of solvent: MeOH, EtOH, PrOH, H_2O (see Fig. 3).

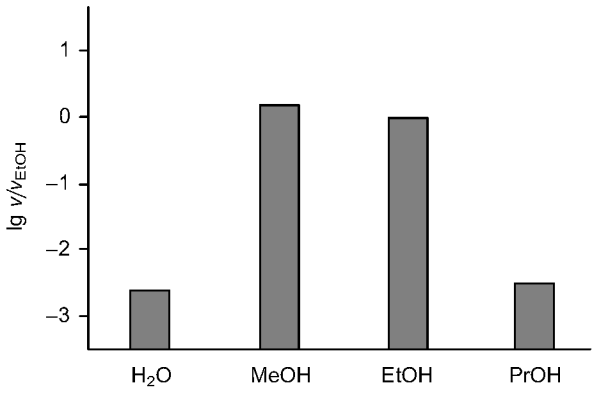

Fig. 3 Ratio of the experimental chemical dissolution rate in the solution under consideration to that in ethanol.

In order to explain the influence of solvent nature on the chemical dissolution rate we tried to analyse the electrolyte bulk characteristics, for example, changes in the acid dissolution constants (see Fig. 4). The order of change of the aluminium dissolution rate and the dissociation constant of HCl coincide with each other in the sequence: methanol, ethanol, propanol. However, the increase in the chemical dissolution rate on going from water to methanol cannot be explained simply by the dissociation factors.

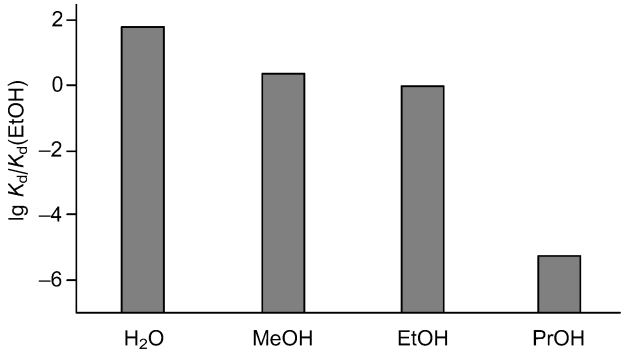

Fig. 4 Ratio of the HCl dissociation constant in the solution under consideration to that in ethanol.

The present work is based on the assumption stated previously by Frumkin,[6] *i.e.* metal dissolution may be facilitated when in the vicinity of a 'dissolved' atom, hydrogen ion discharge occurs. He predicted that the chemical mechanism would be preferable in non-aqueous solutions where the constant of acid dissociation is essentially lower than that in water.

There is an important difference between the electrochemical and chemical mechanisms. The electrochemical mechanism includes two electrode reactions as a first stage: metal ionization and the reduction of depolarizer[6] which are connected only statistically by the number of electrons. The chemical mechanism, assumed, is caused by one-electron transfer from metal to oxidant. Not considering all kinetic processes, the one-step electron transfer from molecule A to oxidant B is possible when the ionization potential of A is either equal to or lower than the electron affinity of the oxidant B. For the chemical dissolution of the metal, this implies that the work function of the metal is equal to or lower than the electron affinity of an active particle (oxidant) in solution. In the present paper the work function of aluminium is taken to be equal to 4.2 eV [7] and considered to be constant.

In order to find an active particle with an electron affinity close to the value of 4.2 eV we have performed a semi-empirical PM3 [8] calculation of possible stable protonated particles coordinated by n ($n = 1$–3) solvent molecules. The calculations revealed that there exist two types of stable molecular structures **1** and **2**, corresponding to minima on the potential energy surface. The heats of formation (ΔH_f) and electron affinity (A^e) of **1** and **2** surrounded by two solvent molecules in the gas phase and in solution are presented in Table 1. Methanol structures **1** and **2**, predicted by calculations, are given in Fig. 5.

According to the calculations, increasing the number of solvent molecules (from two to three) in the solvation shell of the active particles in solution does not essentially change the electron affinity. Therefore, we will only consider complexes including two solvent molecules.

The proton in the structure **1** is located midway between the oxygen atoms, whereas the proton in **2** binds only to one oxygen atom. Since structure **1** is thermodynamically less stable than **2**, the form **1** has not been taken into account in further considerations. The electron affinity of **2** in the gas phase and solution, where solvation effects were calculated using a polarizable continuum model,[9] increases in the order: water < methanol < ethanol < propanol (see Table 1). Taking into account the change of electron affinity in the above series, results obtained by the PM3 method allow us to explain the increase in the chemical dissolution rate on going from H_2O to MeOH (see Fig. 3). This increase is caused by enlarging the electron affinity of **2** in the same row. A further decrease in the chemical dissolution rate on going from methanol to ethanol and propanol is explained by a decrease in the HCl dissolution constant in the series rather than electron affinity changes. At the same time, chemical dissolution is not observed in water at room temperature at all, because the electron affinity of **2** is considerably lower than the work function of aluminium.

Table 1 Heat of formation in the gas phase (ΔH_f/kcal mol^{-1}) and solution (ΔH_f^s/kcal mol^{-1}) and electron affinity in the gas phase (A_V^e/eV) and solution (A_S^e/eV) of structures **1** and **2** of water, methanol, ethanol and propanol complexes.

Structure	ΔH_f	ΔH_f^s	A_V^e	A_S^e
$(H_2O)_2H^+$ **1**	86.4	4.2	6.48	2.94
$(H_2O)_2H^+$ **2**	82.1	−4.4	6.22	2.54
$(MeOH)_2H^+$ **1**	92.6	29.9	7.47	4.88
$(MeOH)_2H^+$ **2**	84.3	16.6	7.11	4.31
$(EtOH)_2H^+$ **1**	73.6	13.5	7.66	5.19
$(EtOH)_2H^+$ **2**	63.6	3.2	7.35	4.86
$(PrOH)_2H^+$ **1**	63.2	10.4	7.45	5.30
$(PrOH)_2H^+$ **2**	54.8	2.9	7.09	4.77

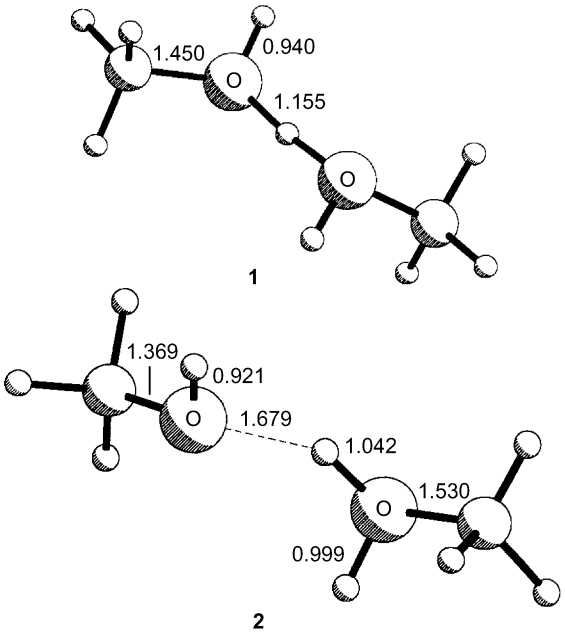

Fig. 5 Structures **1** and **2** of methanol complexes calculated by the PM3 method. Bond lengths are given in Å. Analogous structures were calculated for water, ethanol and propanol complexes.

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