



DEUTERIUM ISOTOPE SEPARATION IN THE CHEMICAL REACTION OF ALUMINIUM AMALGAM AND WATER

László Kótai^{[a]*}, József Lippart^[a] and István Gács^[a]

Keywords: aluminium amalgam; deuterium-depleted hydrogen; deuterium isotope separation

Deuterium isotope separation process takes place in the reaction of the amalgamated aluminium metal surface and water. The reaction produces hydrogen gas with ~40 ppm deuterium content and the formed aluminium hydroxide gel is enriched in deuterium. The theoretical separation factor is $s=3.9$. Besides the kinetic isotope effect, the key factor in the separation process is the $H_2O+HD=HDO+H_2$ exchange reaction. Since only a low amount of amalgam forms on the aluminium surface, the overvoltage difference of the deuterium and the hydrogen on the mercury does not play key role in the process. The main role of the amalgam formation is embodied in the decomposition of the stable oxide layer on the aluminium surface, thus ensuring free metallic surfaces for the reaction with the water.

* Corresponding Authors

Fax: +36-23-376-456

E-Mail: kotai.laszlo@ttk.mta.hu

[a] Institute of Materials and Environmental Chemistry,
Research Centre for Natural Sciences, Hungarian Academy
of Sciences, H-1025, Pusztaszeri. u. 59-67, Budapest,
Hungary

Results and Discussions

The enrichment of the deuterium in natural waters by electrolysis has been known for a long time⁶. The isotope separation factor (s) can be defined as:

$$s = \frac{(H/D)_{gas}}{(H/D)_{liquid}} \quad (1)$$

Introduction

Deuterium-depleted water (DDW) has been a very promising antitumor agent used in human therapy¹. The increasing demand has induced intensive research for new manufacturing methods². Although the reaction of sodium amalgam with water resulted deuterium-depleted hydrogen with ~50 ppm deuterium content³ which can easily be transformed into DDW, the availability of the sodium amalgam is limited (the only source is the mercury cathodic rock salt electrolysis process). Thus, other sources for deuterium-poor hydrogen and DDW respectively, is needed. Dissolution of metallic aluminium in aqueous NaOH and sulphuric acid⁴ has resulted deuterium-depleted hydrogen evolution. Since the reactivity of aluminium toward water can be initiated by amalgamation of its surface with mercury(II) chloride solutions⁵, the reactions of aluminium or aluminium amalgam with water are potential candidates for deuterium poor hydrogen production.

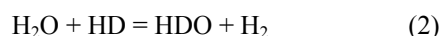
Experimental parts

A metallic aluminium rod (99,99 % aluminium content, ALCOA KÖFÉM, Hungary) was immersed into 20 % aq. NaOH and after washing with water was immediately immersed into an 5 wt. % aq. mercury(II)chloride solution when intensive hydrogen gas evolution and aluminium hydroxide precipitate formation could be observed. The deuterium content of the hydrogen was determined by IR spectroscopy of the water condensed in a liq. trap and obtained by the reaction of the hydrogen gas with CuO at 600°C.

The numerical value of the separation factor is depends on some key factors such as the nature of the electrode materials. The factor is generally higher if the electrode metal has hydrogenating activity⁷ or the metals are alloyed with other metals⁸. The amalgams are a special kind of alloys, and the separation factor in the reaction of sodium amalgam with water is considerably higher⁹ than the separation factor obtained by pure metallic sodium and water¹⁰. The hydrogen and deuterium overvoltage and their differences on metallic mercury are also key factors in the isotope separation processes in the presence of metal amalgams⁹. Although, in the case of amalgams this difference may also be attributed to the presence and effect of metals dissolved in the mercury or the presence of intermetallic compounds as NaHg_x alloys¹¹.

Preparation of hydrogen by the electrolysis of water is a simple reduction of the hydrated proton (deuterium cation)¹². Consequently, reduction of H⁺ and D⁺ cations with electrons originating from chemical reducing agents like metals, the same isotope separation effects can be expected. Since the dissolution rates of metals in deuterated acids are slower than in normal acids¹³, isotope separation can be expected in these reactions. E.g. in case of alkali metals, zink, calcium or aluminium⁴ the deuterium content of the evolved hydrogen gas has decreased. Other factors affecting isotope separation in the electrolytic hydrogen generation can also be occurred.

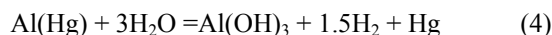
Isotope exchange reaction between the formed deuterium containing hydrogen gas and the water has also occurred:



Using natural water in these processes, no D₂O or D₂ are present due to the low absolute value of deuterium content in the system, so only the HD content has to be taken into consideration. The reaction (3) is an equilibrium reaction, and the equilibrium constant is about 3 at 20 °C¹⁴.

$$K = \frac{[\text{HDO}][\text{H}_2]}{[\text{H}_2\text{O}][\text{HD}]} \quad (3)$$

Aluminium is an amphoteric element and its reaction with 0.1 N sulphuric acid¹⁵ or sodium hydroxide⁴ showed deuterium isotope separation with 2.0 and 4.3 separation factor, respectively. Aluminium does not react directly with water due to the surface oxide layer which prevent the contact with water. Decomposing this layer with mercury(II) chloride which simultaneously amalgamates the aluminium surface, an amalgam covered reactive aluminium layer is formed which easily decomposes the water without adding acids or bases¹⁶:



For water samples containing deuterium at natural abundance level the experimentally found separation factor was proved to be ~3.9 which is slightly higher than the values obtained for sodium amalgams (Table 1).

Table 1.

Isotope separation factors in the reactions of metals and their amalgams with hydrated H⁺(D⁺) ions

Metal	Reactant	s value	Ref.
Na	H ₂ SO ₄	1.2	15
Na	H ₂ O	1.7-2.8	4
Na(Hg)	H ₂ O	3.3-3.5	4,9
Al	H ₂ SO ₄	2.0	15
Al(Hg)	H ₂ O	3.9	Our work
Al	NaOH	4.3	4

Either the pH or the presence of mercury plays important role in the deuterium isotope separation factors. Topley and Eyring have concluded¹⁷ that the separation factors during electrolysis are generally lower in acidic than in alkaline solutions independently from the nature of the electrode metal. The same tendency could be observed in case of alkali metals, calcium and aluminium by Hughes et al.⁴ If the water reacts with sodium, the formed NaOH is a strong base which initiates the deuterium isotope exchange reactions between the water and the HD gas⁹. The main reason for this behaviour is the difference between the activation energies of NaOD and NaOH formation due to the lower zero point energy of the NaOD which leads to the preferred NaOD formation¹⁸.

In case of aluminium hydroxide precipitate¹⁹ there is no considerable concentration of free OH⁻ or OD⁻ ions. It is correlated with the facts that in sulphuric acid solutions the separation factor is much smaller (2.0) than in neutral water (s=3.90). In the presence of NaOH, however, only a slight

increase could be observed since the sodium hydroxide dissolves the aluminium hydroxide precipitate and the free hydroxide ion concentration is controlled by the dissociation equilibria of the formed hydroxyaluminate complexes. Not only the hydroxide ions but other monovalent anions can initiate the isotope separation processes, because using sodium chloride to prevent the passivation of aluminium in sulphuric acid solutions, the presence of sodium chloride increases the deuterium isotope separation factor from 2.0 to 4.0⁴.

References

- Somlyai, G., Kovács, A., Guller, I., Gyöngyi, Z., Krempels, K., Somlyai, I., Szabó, M., Berkényi, T., Molnár, M., *Eur. J. Cancer*, **2010**, *8*, 208.; Cong, F.-S.; Zhang, Y.-R.; Sheng, H.-C.; Ao, Z.-H.; Zhang, S.-Y.; Wang, J.-Y., *Exp. Therap. Med.* **2010**, *1*, 277.; Ioan, S.; Manolescu, N.; Comisel, V.; Tamaian, R.; Titeacu, G., *Bull. Univ. Agric. Sci. and Veter. Med. Cluj-Napoca, Veter. Med.* **2008**, *65*, 443.; Mirica, R. E., *Env. Eng. Manag. J.*, **2010**, *9*, 1543.; Kovacs, A., Guller, I., Krempels, K., Somlyai, I., Janosi, I., Gyongyi, Z., Szabo, I., Ember, I., Somlyai, G., *J. Cancer Therapy* **2011**, *2*, 548.
- Huang, F., Meng, C., *Ind. Eng. Chem. Res.*, **2011**, *50*, 378; Zhang, L.-Y., Kong, Z., Chen, D.-C., *Huaxue Shijie* **2009**, *50*, 748-750, 765.
- Kótai, L., Lippart, J., Gacs, I., Kazinczy, B., Vidra, L., *Ind. Eng. Chem. Res.* **1999**, *38*, 2425. Kótai, L., WO 9633129 A1; HU 2008000528 A1
- Hughes, E. D.; Ingold, C. K.; Wilson, C. L., *Nature (London, United Kingdom)*, **1934**, *133*, 291.; Hughes, E. D., Ingold, C. K., Wilson, C. L., *J. Chem. Soc.*, **1934**, 493;
- Wislicenus, H., Kaufmann, L., *Ber. Deutsch. Chem. Gesell.*, **1895**, *28*, 1323.
- Washburn, E. W., Urey, H. C., *Proc. Natl. Acad. Sci.* **1932**, *18*, 496.
- Reshetnikov, S. M.; Sokol'skaya, A. M.; Sokol'skii, D. V., *Dokl. Akad. Nauk SSSR*, **1966**, *168*, 629.
- Brun, J.; Varberg, Th.; Gundersen, W.; Solli, R. *Forhandlinger - det Kongelige Norske Videnskabers Selskab*, **1956**, *29*, 5.
- Kótai, L., Vidra, L., Kaziczy, B., Gács, I., *Acta Chem. Scand.*, **1999**, *53*, 155.
- Davis, C. O., Johnston, H. L., *J. Am. Chem. Soc.*, **1934**, *56*, 493.
- Inoue, Y., Osugi, A., *J. Electroanal. Soc. Jpn.*, **1952**, *20*, 502; Inoue, Y., Osugi, A., Amawa, T., Asafuji, T., Adachi, K., Takai, A., *J. Electroanal. Soc. Jpn.*, **1952**, *20*, 504.
- Tunold, R., Johansen, B., Jaksic, M., *Adv. Hydrogen Energy*, **1990**, *8*(Hydrogen Energy Prog., Vol. 2), 711.
- Brun, J., *Forhandlinger - det Kongelige Norske Videnskabers Selskab*, **1951**, *24*, 114.; Brun, J. *Acta Chem. Scand.*, **1951**, *5*, 1402.; Bellobono, I. R.; Mazza, F., *J. Phys. Chem.* **1971**, *75*, 2112.
- Bonhoeffer, K. F., Rummel, K. W., *Naturwiss.*, **1934**, *22*, 45.; Farkas, L., Farkas, A., *Trans. Faraday Soc.* **1934**, *30*, 1071; *Proc. Roy. Soc.* **1934**, *146A*, 623.
- Farkas, A., Farkas, L., *Nature*, **1934**, *133*, 139,
- Huang, X.-N; Lu, C.-ju; Huang, Y.-X; Liu, S; Wang, C; Chen, D., *Int. J. Hydrogen Energy*, **2011**, *36*, 15119.
- Topley, B., Eyring, H., *Nature*, **1934**, *133*, 292.
- Horiuti, J., Szabo, A. L., *Nature*, **1934**, *133*, 327.