

Short Communication

## Evidence of Isotope Separation During Chemical Reaction of Sodium Amalgams and Natural Water

László Kótai,\* László Vidra, Béla Kazinczy and István Gács

Institute of Chemistry, Chemical Research Center, Hungarian Academy of Sciences, Pusztaszeri út 59–67, H-1025, Budapest, Hungary

Kótai, L., Vidra, L., Kazinczy, B. and Gács, I., 1999. Evidence of Isotope Separation During Chemical Reaction of Sodium Amalgams and Natural Water. – Acta Chem. Scand. 53: 155–156. © Acta Chemica Scandinavica 1999.

The role of deuterium in the nuclear (power) industry is well known, and numerous methods have been developed for the separation of deuterium-enriched compounds, including heavy water. Nevertheless, improvement of isotope separation is still an important and challenging task.<sup>1,2</sup> Since deuterium-poor light water and its derivatives (also obtainable in this process) have provided new perspectives both in cancer research and therapy,<sup>3</sup> the development of efficient methods for the production of light water in large quantities is particularly important.<sup>4</sup>

It has been known that the deuterium content of the hydrogen obtained in the reaction of metals with acidic or alkaline aqueous solutions or water is lower than in the original reactant solutions.<sup>5,6</sup> As a general rule, it can be stated that the presence of alloys increases the value of the separation factor. However, mercury, having no contact with the metals in the system, has no effect on the separation factor.<sup>6</sup> At the same time, it has been stated that hydrogen and deuterium can be separated via mercury-pool cathode electrolysis of aqueous solutions.<sup>7</sup> In this process the separation factor can be increased by substances which increase the rate of hydrogen deposition (e.g. CoS). Therefore, our efforts were directed to the development of such a separation method which eliminates the drawbacks of the electrolysis (e.g. polarization); at the same time the benefit of alloys providing increased separation factor is realized.

This paper presents isotope separation under *in-situ* generation of hydrogen gas by chemical reaction between a sodium-amalgam reagent and natural water. Our efforts were directed to obtain deuterium-depleted hydrogen gas and water.

### Experimental

The sodium amalgam containing 0.3% of sodium was obtained by mercury-pool cathode electrolysis of a satur-

ated sodium chloride solution (current density 1 A cm<sup>-2</sup>; decomposition potential 4.5 V; temperature 90 °C). A chloride-selective Ti/RuO<sub>2</sub> electrode was used as anode. The sodium content of the amalgam was calculated from the sodium chloride content of the residual brine (260 g dm<sup>-3</sup>) and from the amount of mercury consumed in the reaction.

The sodium amalgam containing 3.0% sodium was prepared by the amalgamation of metallic sodium and mercury in a sand bath at 110 °C under an inert gas atmosphere. The sodium amalgam was allowed to react with water at 90 °C until the sodium content of the amalgam decreased to 0.01% simultaneously with the formation of sodium hydroxide solution (10 or 50% NaOH). At lower temperatures the reaction of the sodium amalgam was very slow.

We also made an attempt to react metallic sodium with water at 90 °C. In the presence of a large excess of water the reaction ran without problems. However, owing to the interference of air humidity and to small changes in the deuterium content of the water, these experiments could not be carried out.

A determination of the deuterium content of the gas obtained was performed by IR spectroscopy of the water formed either via the direct combustion of hydrogen in oxygen or air, or by catalytic conversion by means of a copper oxide catalyst. The measurement of the deuterium content of the hydrogen was also checked via the measurement of the amount of deuterium in the residual solution. The oxidation techniques used (direct/catalytic, oxygen/air) did not have a significant influence on the deuterium content of the water. It should be noted, however, that the water vapor in the air may influence the analytical results owing to its higher deuterium content (154 ppm of HDO in the condensed water). For similar reasons, the hydrogen gas also had to be dried carefully before combustion.

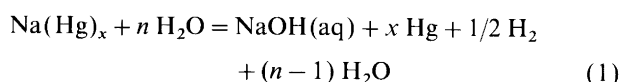
\*To whom correspondence should be addressed.

Table 1. Isotope separation factors of sodium and sodium–amalgam water systems.

Reagent	Temperature, $t/^{\circ}\text{C}$	Separation factor, $s$	Refs.
Na	40	2.60	6
3.0% Na(Hg) <sub>x</sub>	90	3.31	This work
0.3% Na(Hg) <sub>x</sub>	90	3.47	This work

## Results and discussion

The *in situ* formation of the hydrogen is presented in eqn. (1):



The sodium hydroxide formed in this exothermic reaction remains in the solution. The experimental isotope separation factors defined in eqn. (2) are illustrated in Table 1.

$$s = (\text{H/D})_{\text{gas phase}} / (\text{H/D})_{\text{liquid phase}} \quad (2)$$

Under the experimental conditions described the isotope separation factor (at 90 °C) for the reaction of the amalgam obtained by electrolysis (0.3% sodium) was found to be 3.47. This value was calculated on the basis of eqns. (1) and (2). The isotope separation factor is independent of the amount of water decomposed. Conversion of this sodium amalgam into 50% sodium hydroxide solution provided hydrogen with 50 ppm of deuterium. Since in the course of the industrial production of sodium hydroxide a sodium amalgam (0.3–0.4% sodium) decomposes at 90–100 °C, this phenomenon allows the introduction of an industrial technology for the production of deuterium-poor hydrogen gas and water.<sup>4</sup>

Table 1 shows that a decreasing content of mercury in the sodium amalgam leads to decreasing values of the separation factor. Although above 40 °C the reaction between metallic sodium and water could not be carried out successfully, in the reaction of a sodium mirror with water vapor the separation factors at 23 and 80 °C were found to be the same.<sup>8</sup>

Further, it is known that on mercury<sup>9</sup> and on other metals<sup>10,11</sup> the values of the hydrogen and deuterium over-potentials depend on temperature.<sup>12</sup> However, the deviation between the hydrogen and deuterium over-potentials on mercury remains constant as a function of temperature. Thus eqn. (3) is valid.

$$d(\eta_{\text{H}} - \eta_{\text{D}})/dt = 0 \quad (3)$$

Since the separation factor is proportional to the difference in the over-potentials of two isotopes,<sup>13</sup> the separation factor can be also considered to be independent of temperature in a sodium amalgam–water system. In this way, the separation factors obtained for sodium metal at 40 °C and for sodium amalgam at 90 °C, in the first approximation, are comparable.

Considering that the separation factor for the reaction

of sodium with water (0% amalgam) has a lower value ( $s=2.60$ ) in comparison with that obtained for the amalgam containing 0.3% sodium ( $s=3.47$ ), it may be assumed that the sodium in the other amalgam (3.0% sodium) partly reacts as the pure metal. This may explain the lower than expected value ( $s=3.31$ ) obtained at the higher sodium content (3.0%). The presence of sodium–mercury compounds as loose associates may also have an effect on the separation factor.<sup>14,15</sup>

It may be established that the degree of separation may be influenced primarily by differences in the over-potentials of hydrogen and deuterium on mercury and/or sodium amalgams, and secondarily by isotope exchange between the liquid and gas phase and by catalytic effects in simultaneous processes, primarily due to the materials formed.

Isotopic exchange between hydrogen and water is catalyzed by several metals. However, mercury does not have such an effect.<sup>6,12</sup> At the same time, various acids and bases also have catalytic effects on this type of isotopic exchange reaction.<sup>16</sup> In the isotopic exchange reaction between hydroxide and deuterioxide ions in sodium hydroxide solutions, the role of a hydroxide-ion cluster with three water molecules is of considerable importance.<sup>17</sup>

*Acknowledgments.* We express our thanks to Dr György Jáklí for the determination of the deuterium content.

## References

- Willms, R. S., Konishi, S. and Okuno, K. *Fusion Technol.* 26 (3, Pt. 2) (1994) 659.
- Morozov, A. V., Rozenkevich, M. B. and Sakharovsky, Yu. A. In: Veziroglu, T. N., Ed. *Hydrogen Energy Prog. XI, Proc. 11th World Hydrogen Energy Conf.*, Int. Assoc. Hydrogen Energy, Coral Gables, FL 1996, Vol. 3, p. 2657.
- Somlyai, G., Jancso, G., Jakli, Gy, Vass, K., Barna, B., Lakics, V. and Gaal, T. *FEBS Lett.* 1 (1993) 317.
- Kótai L. *PCT Int. Pat. Appl.* WO 96,33,129 (1995). [Chem. Abstr. 125 (1996) P333389s].
- Davis, C. O. and Johnston, H. L. *J. Am. Chem. Soc.* 56 (1934) 492.
- Johnston, H. L. and Davis, C. O. *J. Am. Chem. Soc.* 64 (1942) 2613.
- Shinagawa, M., Tsuruno, H., Saito, H., Muzusaki, H., Muromatsu, A. and Nezu, H. *J. Nucl. Sci. Technol.* 10 (1973) 719.
- Bemmer, R. O. and Volman, D. H. *J. Phys. Chem.* 77 (1973) 1844.
- Christov, St. G. *Electrochim. Acta* 4 (1961) 306.
- Hammerli, M., Mislan, J. P. and Olmstead, W. J. *J. Electrochem. Soc.* 116 (1969) 779.
- Hammerli, M., Mislan, J. P. and Olmstead, W. J. *J. Electrochem. Soc.* 117 (1970) 751.
- Hirota, K. and Horiuti, J. *Sci. Pap. Inst. Tokyo* 30 (1936) 151.
- Post, B. and Hiskey, C. F. *J. Am. Chem. Soc.* 72 (1950) 4205.
- Inoue, Y. and Osugi, A. *J. Electroanal. Soc. Jpn.* 20 (1952) 502.
- Inoue, Y., Osugi, A., Amawa, T., Asafuji, T., Adachi, K. and Takai, A. *J. Electroanal. Soc. Jpn.* 20 (1952) 504.
- Wirtz, K. and Bonhoeffer, K. F. *Z. Phys. Chem., Teil A* 177 (1936) 1.
- Taylor, C. E. and Tomlinson, C. *Trans. Faraday Soc.* 70 (1974) 1132.

Received July 29, 1998.