ORTHO-PARA-HYDROGEN AND *PARA-ORTHO*-DEUTERIUM SEPARATION FACTORS ON LiX ZEOLITE AT 50-112 K

Vladislav P. BYSTROV[2)], Evgenii B. IVANOV[1)], Victor S. PARBUZIN[1)*]

[1)]Department of Chemistry, M.V. Lomonosov Moscow State University,
Vorob'evy Gory, 119899, Moscow, Russia
e-mail: vsp@phys.chem.msu.ru
[2)]A.M. Prokhorov General Physics Institute RAS
Vavilov str. 38, 117942, Moscow, Russia

ABSTRACT

The paper reports on a comprehensive set of experimentally measured *ortho-para*-H_2 and *para-ortho*-D_2 separation factors at low temperature adsorption on an especially prepared sample of X type zeolite. The zeolite was investigated in its lithium cationic form by a new version of the gas solid chromatographic technique ECMA (Elution Chromatography with Modifying Adsorbates). Six types of eluents were used: four pure gases He, Ne, H_2, D_2, and two mixed eluents – He-H_2 and He-D_2 various compositions. The new ECMA version gives results of high precision. At easily attainable temperatures 77-50 K and practically suitable fractional coverages 0.6-0.8, the selectivity of adsorbent LiX ranges from 1.45 to 2.0 for *ortho-para*-H_2, and 1.108 - 1.254 for *para-ortho*-D_2. A low *ortho-para*-conversion catalytic activity and high selectivity of new sorbent LiX allow separation of *ortho-para*-isomers of dihydrogens by Moving Temperature Gradient Adsorption technique.

Keywords: *Ortho-para*- H_2, *Ortho-para*-D_2, Adsorptive separation coefficients, Zeolite LiX

INTRODUCTION

Last years witness a new wave of interest to the problem of nuclear-spin modifications of the hydrogenic diatomic molecules (homonuclear dihydrogens *ortho*-H_2, *para*-H_2, *ortho*-D_2, *para*-D_2[1,2]). The reasons can be found in remarkable quantum properties of molecular dihydrogens due to

their small molecular mass, moments of inertia, weak attractive forces and nonzero nuclear spin (s=1/2 for proton and s=1 for deuteron [3]). More and more experiments in fundamental and applied sciences demand spin-isomeric dihydrogens of higher purities and in bigger quantities [4-6]. The known methods of obtaining highly enriched *para*-H_2 (*ortho*-D_2) by ortho-para catalytic conversion at the temperature of liquid hydrogen (20 K) [7,8], as well as enrichment of *ortho*-H_2 (*para*-D2) by preferential physisorption on gamma-alumina, also at 20 K [9,10], do not satisfy these new requirements. Firstly, as we are aware, working at this temperature can bear certain consequences, i.e. a high risk of explosion for liquid hydrogen, or necessity to use complex and cumbersome refrigerating equipment, or high price of deficient liquid helium and suitable cryostats [11]. In fact, only a few laboratories are capable of performing such experiments. Secondly, there are experiments requiring very pure spin-dihydrogens while working *on-line*. Such an operating mode is very difficult to implement using adsorption at 20 K; for example, in the case when one needs to supply the experiment with pure *ortho*-H_2 (*para*-D_2) for many hours. Equilibrium concentration of *para*-D_2 at 20 K is 98 %, so it is theoretically impossible to obtain the more concentrated product [12] by catalysis at this temperature.

In our opinion, the best solution for such kind of tasks is to use the quasi-counter-current adsorption technique based on the MTGA (Moving Temperature Gradient Adsorption) mode. This approach is implemented on a gas separating cascade, MGU DETRA, working at easily attainable "nitrogen" temperatures 77-50 K [2]. The transition from hydrogenic to nitrogenic temperatures was made possible by choosing a new adsorbent – specially synthesized ultra pure zeolite of the X type in its lithium cationic form. The choice of the Li-form was stimulated by its successful application for air separation at room temperature [13]. Besides, we have found good isotopic selectivity on a LiX sample, earlier [14]. The new adsorbent surpasses the «classical» gamma-alumina and modern adsorbents of allegedly comparable selectivity [15] in two major respects: (i) practical selectivity; (ii) low concentration of detrimental paramagnetic admixtures (heavy metal cations). Our experiments with modern sorbents (commercial zeolites) showed very low real separation efficiency while attempting to enrich *ortho*-H2 (*para*-D_2) by the MTGA technique. This inefficiency is explained by high catalytic ortho-para-conversion activity of commercial zeolites which preclude their use for spin isomer separation.

EXPERIMENTAL

The details of the experimental apparatus and methods for studying physico-chemical adsorption parameters by gas solid chromatography were published earlier [16,17]. The present version of a cryogenic chromatograph was essentially upgraded by connecting it to a personal computer with a corresponding data acquisition system. The key feature of our ECMA (Eluent Chromatography with Modifying Adsorbates) technique is a

possibility to use one of the studied mixture components as a carrier gas either in its pure form (e.g. H_2, HD, D_2) or in a mixture with an inert gas (He-H_2, He-D_2). In fact, six types of eluents were used: (i) four pure gases, He, Ne, H_2, D_2, from commercial 40 L steel cylinders; and two types of mixed eluents were prepared in 10L steel cylinders: He – H_2 – mixtures; He – D_2 gas mixtures. All the eluents were additionally purified by flowing through three forecolumns filled up with zeolite NaX (300 K), activated charcoal (77 K), and ortho-para converter with $Fe(OH)_3$ on the silica catalyst (77 K). Not only does this approach significantly accelerate collections data, but it also improves the experimental precision and expands the accessible limits of cryogenic temperature and coverage [18].

As far as the adsorbent is concerned, the pressed powder of air-dried LiX was crushed in an agate mortar and sieved to the size of 0.25 – 0.50 mm. The sorbent with the mass of 0.85 g was used to fill up a 80x0.20 cm copper column. The column was soldered to stainless steel tubes connecting with a cryogenic chromatographic apparatus equipped with a vacuum glass system for gas sample introduction and two cryostats bridging the temperature gap from 50 to 200 K [16,17]. Before experiments, the sorbent in the column was pretreated for 12 hours at 63 K in the purified helium at the flow 40 - 45 mL/min. The samples of four homonuclear H_2 and D_2 spin isomers with addition of HD approx. 1% were prepared and stored in glass balloons. The sample loop of 4.5 ml volume allowed us to adjust the sample quantity by pressure regulation. The fundamental relation of a gas solid chromatography method for the adsorption separation factor S_{ij} [17]:

$$S_{ij} = (t_i - t_o)/(t_j - t_o)$$

where t denotes retention time, or time of peak maximum, read from a chromatogram; lower index i refers to a preferentially adsorbed component, j – to a less adsorbed component, and "0" - the nonadsorbed gas (marker).

EXPERIMENTAL RESULTS

The experimentally measured values of *ortho-para*-H_2 and *para-ortho*-D_2 separation factors are given in Table 1 and in Figure 1. These data demonstrate two main parameters determining the selectivity of low temperature adsorptive nuclear spin isomers separation:
(i) temperature, (ii) value of absolute adsorption *a* (or fractional coverage $\Theta = a/a_0$, where limiting adsorption a_0 is about 220 cm^3/g for LiX [14]). The data for *o-p*-H_2 and *p-o*-D_2 will be discussed separately.

Ortho-para-H_2 separation

Selectivity of LiX changes from 1.24 to 1.95 in the temperature range 104-52 K, which is more than enough for further effective *ortho-para*-hydrogen separation on MGU-DETRA cascade by exploiting our moving temperature gradient adsorption techniques [2].

Table 1. Experimental values of *ortho-para*-H_2 (*para-ortho*-D_2) separation factors S_{ij} versus temperature on high purity LiX zeolite. Values of H_2 (D_2) adsorptions are given as *a*, Ncm^3/g of dehydrated adsorbent.

	o-p-H_2 separation factors				*p-o*-D_2 separation factors	
T, K	S_{ij} (a=0)	S_{ij}	a, cm^3/g	T, K	S_{ij}	a, cm^3/g
104.1	1.285±0.013[*]	1.242±0.012	81	82.5	1.067±0.011	130
100	1.327	1.266	92	77.4	1.130	90
95.0	1.386±0.014	1.301	104	77.4	1.124	112
90.6		1.334	120	77.4	1.119	124
84.2		1.391	136	77.4	1.108	145
77.4		1.450±0.015	164	70.0	1.193±0.012	140
71.5		1.516	172	70.0	1.192	149
63.2		1.656	178	70.0	1.176	164
56.8		1.79	180	63.5	1.264	155
55.0		1.84	182	63.5	1.268	163
51.7		1.95±0.02	190	63.5	1.254±0.013	176

[*] Precomputed maximum error of separation factors is 1.5 to 2.0 %, while mean error estimated in duplicate and triplicate experiments does not exceed ±1.0 %.
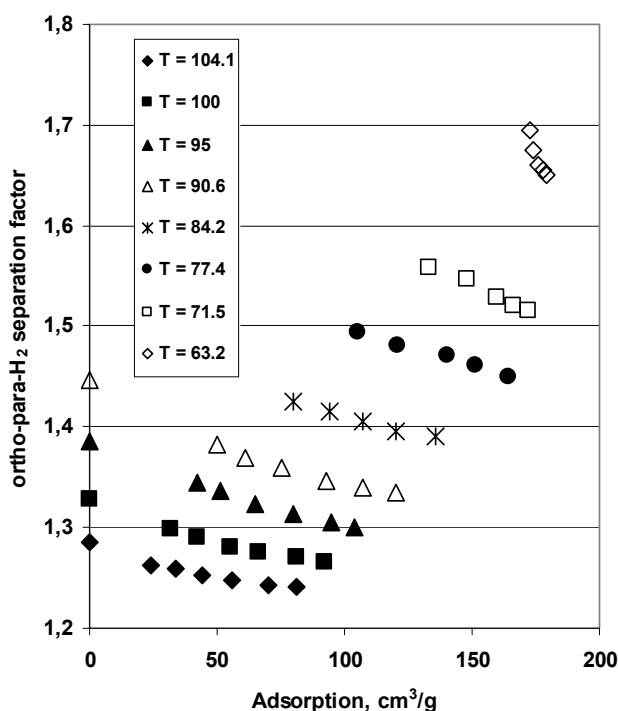

Fig. 1. *Ortho-para*-H_2 separation factors vs adsorption on ultrapure LiX zeolite at different temperatures.

The best solution for the problem is working at easily attainable temperatures of liquid N_2 (77 K) or at N_2 triple point (63 K) when LiX reaches the adsorption level of 160-180 cm^3/g which means high throughput.

A decrease in the selectivity with coverage at constant temperature is demonstrated by three lower curves in Figure 1. For example, the selectivity changes from 1.3 to 1.39 at 77 K. The same tendency is observed at lower temperatures, e.g. at T=95 K from 1.39 at zero coverage to 1.30 at a=104 cm^3/g.

Para-ortho-D_2 separation

The data analysis for D_2 and H_2 nuclear spin forms shows lower selectivity for deuterium in comparable conditions of temperature and coverage. For example, S_{ij} for D_2 equals 1.19 at 77 K and 1.27 at 63 K. Nevertheless, even these lower selectivities are sufficient to separate para-ortho-D_2 by an additional separation column in MGU-DETRA cascade.

The presented vast set of data is especially interesting when applied for testing and further development of the microscopic theory of quantum adsorbates in restricted geometries with voids of nano- and subnanometer dimensions [19]. This problem, as well as the thermodynamic treatment of homonuclear dihydrogens physisorption, will be discussed in respective publications.

CONCLUSION

Ortho-para-H_2 and *para-ortho*-D_2 separation factors on very pure LiX zeolite were thoroughly studied in the temperature range 50-112 K at fractional coverages ranging from 0 to ~0.8. The adsorbent reaches optimum parameters for practical separation of *ortho-para*-modifications of H_2 and D_2 on the sorbent fixed bed by applying the moving temperature gradient adsorption mode.

ACKNOWLEDGEMENT

REFERENCES

[1] A. Farkas, *Orthohydrogen, parahydrogen and heavy hydrogen*, Cambridge University Press, 1935.

[2] V.S. Parbuzin, V.A. Yakovlev, A.A. Lukyanov, Y.A. Leshchev, *Ars Separatoria Acta,* 2003, *2*, 84-96.

[3] J. Van Kranendonk, *Solid Hydrogen: Theory of the Properties of Solid H_2, HD, and D_2*, Plenum Press, New York, 1983.

[4] A.P. Serebrov, *Uspekhi Fizicheskih Nauk*, 2005, *175*, 905-924.

[5] T. Oka, http://fermi.uchicago.edu/publications/

[6] a) T. Momose, *Vibr. Spectroscopy*, 2004, *34*, 95-108; b) J. Natterer, T. Greve, J. Bargon, *Chem. Phys. Lett.*, 1998, *293*, 455-460.

[7] N.S. Sullivan, D. Zhou, C.M. Edwards, *Cryogenics,* 1990**,** *30*, 734-735.

[8]   S. Tam, M.E. Fajardo, *Rev. Sci. Instr.,* 1999**,** *70*, 1926-1932.
[9]   C.M.Cunningham, D.S.Chapin, H.L.Johnston, *J.Amer.Chem.Soc*., 1958, *80*, 2382-2384.
[10] B.N. Zimoglyad, Y.P. Blagoi, G.G. Zhun. *Zh. Fiz. Khim.*, 1966, *40*, 2871-2875.
[11] M.J. Clouter, *J. Phys. E: Sci. Instrum.*, 1972, *5*, 1099-1102.
[12] A. Honig, M. Lewis, Z.-Z. Yu, S. Yucel. *Phys. Rev. Lett.*, 1986, *56*, 1866-1871.
[13] F.R. Fitch, M. Bulow, A.F. Ojo, US Pat. No. 5464467 (1995).
[14] V.S. Parbuzin, Thesis, Moscow State University, 1966.
[15] B.N. Zimoglyad, Y.P. Blagoi, G.G. Zhun, S.N. Doshina, *Dokl. AN SSSR*, 1970, *194*, 606-609.
[16] V.S. Parbuzin, Y.A. Leshchev, A.A. Lukyanov, K.D. Scherbakova, *Zh. Fiz. Khim.,* 1987*, 61*, 3077-3078.
[17] V.S. Parbuzin, V.V. Guliants, *Chromatographia*, 1990, *30*, 283-286.
[18] E.B. Ivanov, V.S. Parbuzin, Manuscript in preparation.
[19] A.V. Larin, V.S. Parbuzin, *Mol. Phys*., 1992, *77*, 869-891.