

Solution Structure of Alkaline NaBH₄ Solution: A sight From X-ray Scattering

YongquanZhou^a, ChunhuiFang^b, Yan Fang^c, Song Tao^d

¹Qinghai Institutes of Salt Lake, Chinese Academy of Sciences, Xining 810008, China

^ayongqzhu@163.com^bfangch@isl.ac.cn^cfangy8@isl.ac.cn^dtaosong521@163.com

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Abstract. The time and space-averaged structure of alkaline aqueous NaBH₄ solution were given by X-ray scattering with a five-circle goniometer in Beijing Synchrotron radiation facility. Then the hydration structure of BH₄⁻ were presented through geometrical model calculation, the characteristic distance and the hydration number of BH₄⁻(B-O(w)) in higher concentration solutions were determined to be 0.34 nm and 2~3. There are three kinds of ion associating structure of BH₄⁻ and Na⁺ in higher concentration solutions. The [(H₂O)₄Na(H₂O)₂Na(H₂O)₄]²⁺ (with Na-Na distance of 0.363 nm), the [(H₂O)₄Na(BH₄)₂Na(H₂O)₄]⁰ (with Na-Na distance of 0.421 nm), and the [BH₄Na(H₂O)₄]⁰ with the Na-B distance of 0.30 nm

1. Introduction

Sodium tetrahydroborate (NaBH₄) is a versatile reducing agents in various organic and inorganic processes[1,2]. The percentage of hydrogen present in NaBH₄ and released by hydrolysis are 10.6 and 10.8%, respectively, therefore NaBH₄ is the most attractive chemical hydride materials for H₂ generation and storage in automotive fuel cell applications[3,4]. Direct borohydride fuel cell (DBFC) technology is being actively investigated by many research groups. Although the DBFC was first proposed in the early 1960s[5], further progresses suffered a hiatus of about 40 years due to lack of research on the understanding of the complex electrode mechanism and electrode kinetics of the BH₄⁻ oxidation reaction[6]. The BH₄⁻ hydration especially the dihydrogen bonding in those clusters and the ion association may play an important in the BH₄⁻ electrode oxidation process.

In the present work, the time and space averaged structure of basic NaBH₄ solutions with sat/water of 1:4 and 1:8 were studied by the X-ray flat specimen cell reflectometry in Beijing Synchrotron Radiation Facility (BSRF II) at 298 K. Their structural functions and difference radial distribution functions and were obtained, and the hydration structures were given through model calculation.

2. Experiments

2.1 Sample Preparation

Commercially available NaOH (GR) and NaBH₄ (AR) were used without further purification. The NaBH₄·2H₂O was synthesized according the ternary phase diagram of NaBH₄-NaOH-H₂O[7] and examined by both element analysis and X-ray powder diffraction. Density, *d*, of all the solutions was measured using a graduated pycnometer (≈15cm³) with a reproducibility of (0.05%) in a thermostat (GDH-1015W, safe, China, ±0.01K). The compositions (*c*₁, the concentration of NaBH₄, *c*₂ the concentration of NaOH); salt/water molar ratio, *R*; density, *d*; temperature, *T*; linear absorption coefficient, *μ*; stoichiometric volume, *V* of the sample solutions are listed in Table 1.

Table 1. Composition and properties of solution samples

No	<i>c</i> ₁ /(mol·L ⁻¹)	<i>c</i> ₂ /(mol·L ⁻¹)	<i>d</i> /(g·cm ⁻³)	<i>μ</i> /cm ⁻¹	<i>V</i> /nm ³	<i>R</i>	<i>T</i> /K
B1H425	9.15	1.84	1.0785	1.7021	181.48	4	298
B1H425	5.50	2.19	1.0879	1.0812	301.91	8	298

2.1 X-ray Scattering measurements

X-ray scattering experiments were carried out on a Huber five-circle diffractometer at 4WLC beam line of BSRF II. Detector is equipped with the solid fluorescence detector and NaI scintillation crystal detector. The energy of photon is 13.9 keV with a wavelength of 0.0892 nm. A self-designed thermostatic liquid sample cell was used to maintain the temperature at 298 ± 0.5 K. The diffraction angle range of measurements spanned over $2^\circ \leq 2\theta \leq 110^\circ$, corresponding to a scattering vector range of $2.5 \text{ nm}^{-1} \leq s \leq 132 \text{ nm}^{-1}$ ($s = 4\pi \sin\theta/\lambda$). The sample solutions were scanned with the accumulated count was large than 10^4 photons with the statistical error $< 1\%$. In order to eliminate the concentration change during the experiment, the samples were covered by a Mylar foil of 6 μm in order to prevent composition change from evaporation of the solutions. The goniometer must be aligned in the standard procedures for every diffraction measurement. Detailed descriptions of measurement skills and intensity collections had been described elsewhere [8].

2.2 Data Treatment

After background radiation subtraction and the solution absorption correction^[9], Then, polarization, incoherent scattering, multiple scattering corrections and geometric correction were performed, respectively. The corrected intensity was normalized to an electron unit by comparing the asymptote of the experimental data with calculated coherent intensity at large scattering vector ($s > 100 \text{ nm}^{-1}$). The structural function $i(s)$ of solution was calculated by subtracting the normalized intensity and the independent scatterings from all atoms in the solution as

$$i(s) = KI_p(s) - \sum_{i=1}^{N_{\text{atom}}} x_i [f_i^2(s) + (\Delta f_i'')^2 + \text{del}(s) \cdot I_i^{\text{incoh}}(s)] \quad (1)$$

The s -weighted structure function $s \cdot i(s)$ was Fourier-transformed into the radial distribution function (RDF)

$$D(r) = 4\pi r^2 \rho_0 + (2r/\pi) \int_0^{\text{max}} s \cdot i(s) \cdot M(s) \cdot \sin(sr) ds \quad (2)$$

where ρ_0 indicates average electron density of the sample ($\rho_0 = [\sum x_i f_i(0)]^2/V$). The modification function $M(s)$

$$M(s) = \sum x_i [f_i^2(0) + (\Delta f_i'')^2] / \sum x_i [f_i^2(s) + (\Delta f_i'')^2] \cdot \exp(-ks^2) \quad (3)$$

was used for the calculation of RDF. The constant k is a damping factor chosen arbitrarily. The spurious ripples were removed from RDF by calculating the peak shape and performing Fourier transformation again. The model structure function was computed by

$$i_{\text{calcd}}(s) = \sum \sum x_i n_{ij} [f_i(s) \cdot f_j(s) \cdot \sin(sr_{ij}) / (sr_{ij}) \cdot \exp(-b_{ij}s^2)] \quad (4)$$

All treatments of the diffraction data were performed with an Origin and the FORTRAN programs KURVLR 2009 [8].

3. Results and Discussion

3.1 Structure Functions

Experimental structural functions $i(s)$, which represent the extent of interference between atoms i and j , contain a lot of structural information. The s -weighted structural functions $s \cdot i(s)$ are presented in Fig.1. The $s \cdot i(s)$ curves remain oscillated near the zero axis, showing that the diffraction experiments and data treatment processes are reliable.

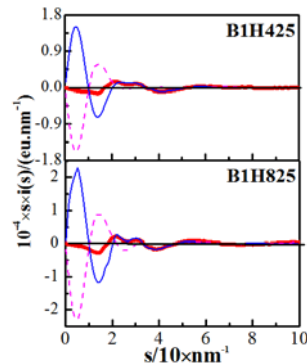


Fig.1. Comparison among experimental (thick solid line), model calculated (thin solid line) structural function and their differences (dashed line)

3.2 Radial Distribution Functions.

Fig.2 shows the difference radial distribution functions in the form of $D(r)-4\pi r^2\rho_0$ for the sample solutions investigated. We can easily find that there are no spurious peaks where $r < 0.1$ nm from the figure, which means the statistical and systematic errors are reduced to the minimum. Peaks are observed in the DRDF at 0.12, 0.24, 0.29, 0.320, 0.350, 0.4 and 0.470 nm for all samples. As shown in Fig. 5, the first peak at about 0.10 nm can be assigned to intramolecular O-H interactions in H_2O molecules. The peak at 0.125 nm is the intra-ionic B-H (BH_4) distance within BH_4^- , and this assignment is suggested by the crystal structure data[10]; The peak at 0.24 nm is ascribed to the Na^+-H_2O interactions within the first hydration shell of hydrated Na^+ ions on the basis of the crystal structure of $NaBH_4 \cdot 2H_2O$ [10], the previous findings from X-ray diffraction[11,12], computer simulation[13] and *ab initio*[14], and the sum of the ionic radius of Na^+ (0.102 nm) and the size of a water molecule (0.14 nm); The peak at about 0.29 nm can be ascribed to the H-Bonding of bulk water[15]; The second peak at 0.34 nm arises mainly from the octahedral vertexes of hydrated Na^+ (cis O- O_{Na^+}) according to $(2)^{1/2} r_{Na-O(1)} = 0.340$ nm; The peak at 0.35 nm may be assigned to B-W(I) the interaction of the hydrated BH_4^- and the interaction of the contact ion pair (CIP) of Na^+ and BH_4^- , Na-Na interaction with a hydrated dimer sodium ions; the peak at 0.396 nm is due to the interaction between octahedral vertexes and $O_B-H_2O(I)$ interaction in the hydrated $B(OH)_4^-$ ion. The peak around 0.43 and 0.47 nm is due to the interactions of Na-O(2) and trans O-O(Na^+), respectively. However, the interactions above 0.50 nm are so intricate and are usually the overlapping of several bands that it is difficult to make qualitative descriptions.

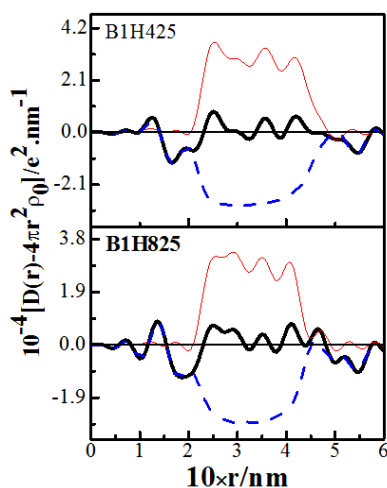


Fig. 2. Radial distribution functions in the form of $D(r)-4\pi r^2\rho_0$ of the $NaBH_4$ solutions:

Experimental (the thick solid line), calculated (the thin solid line) and difference (the dashed line)

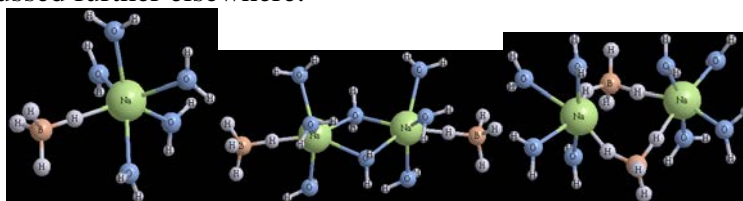
3.3 Structure Model Fitting.

The theoretical DRDFs of the alkaline $NaBH_4$ solution are gained by inputting the structural parameters (c , r_{ij} , n_{ij} , b_{ij}) obtained from the preliminary analysis above and previous studies of Na^+ and OH^- ions in water, and the interatomic distances, computed by atomic coordinates, crystal cell parameters and space-group of $NaBH_4$, $NaBH_4 \cdot 2H_2O$ [10]. The structural parameters were allowed to vary until the experimental and calculated structural function curves coincide after 20 nm^{-1} , and the model-calculated $D(r)-4\pi r^2\rho_0$ curve presented in Fig.2 from Equ. (2) is in good agreement with the experimental curve in the form and that every peak corresponds with each other, which demonstrates a satisfactory model calculation. The optimized structure parameters from geometrical model calculated were summarized in Table 2. Schematic diagrams of the possible ion association were given as Fig.3.

Table 2 Structure parameters of alkaline NaBH₄ solution from geometrical model calculation

Interactions	r/nm	B1H425		r/nm	B1H825	
		b/ 10 ² nm ⁻²	n		b/ 10 ² nm ⁻²	n
B-H	0.119	0.012	4.0	0.0116	0.010	4.0
Na-O(1)	0.242	0.007	5.0	0.245	0.002	5.3
O-O(OH)	0.265	0.009	3.50	0.265	0.028	3.0
H-Bonding	0.294	0.015	2.0	0.293	0.0098	2.0
Na-B	0.301	0.009	1.0	0.30	0.009	1.0
B-O(W)	0.342	0.023	2.0	0.343	0.002	3.0
cis-O-O(Na)	0.354	0.019	8.0	0.348	0.008	8.2
Na-Na	0.363	0.023	0.8	0.361	0.029	0.9
B-O(Na)	0.406	0.015	4.0	0.400	0.008	4.0
Na-O (Na)	0.42	0.01	2.0	0.41	0.008	2.0
Na-B(W)	0.46	0.0012	2.0	0.46	0.012	2.0
Na-Na (B)	0.421	0.011	0.5	0.425	0.028	0.4

The finally refined results especially the information of dihydrogen bonds in alkaline NaBH₄ solution will be discussed further elsewhere.



(a) (b) (c)

Fig.3 Schematic diagrams of the ion association in alkaline aqueous NaBH₄ solution (a), [(BH₄)Na(H₂O)₅]⁺; (b), (H₂O)₄Na(H₂O)₂Na(H₂O)₄; and (c), (H₂O)₄Na(BH₄)₂Na(H₂O)₄

4. Summary

The time-averaged and space-averaged structure of alkaline aqueous NaBH₄ solution at 298 K were given by X-ray scattering in Beijing Synchrotron radiation facility. Their structural functions and difference radial distribution functions were obtained through data processing. Then the hydration structure were given through geometrical model calculation.

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