Molecular Dynamic Simulations of Aqueous LiBr Solutions from Low Concentration to High Concentration

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Abstract: Molecular dynamic simulations of aqueous LiBr solutions from low concentration to high concentration with the molar ratio of LiBr: H_2O of 1:64, 1:32, 1:16, 1:8, 1:4, and 1 $: {}^{3}w$ ere carried out. The hydration number of Li ion decreases with increasing concentration, but this is compensated by the increasing number of Li⁺-Br⁻ contact ion pairs, and the coordination number of the first coordination shell of Li ion keeps approximately unchanged. The hydration shell of Br ion is well defined in highly concentrated LiBr solutions with the Br⁻O distance a little expanding and the shape of radial distribution function of Br⁻O more asymmetric. The contact ion pairs of Li⁺-Br⁻ appear even in more dilute solutions, and increase with the increasing of concentration. The Li⁺-Br⁻ distance is obviously shorter than the sum of ionic radii of Li ion and Br ion in aqueous solution, also shorter than that in LiBr crystals. The structure of water molecules in highly concentrated solutions is nearly destroyed, and the hydrogen bond among water molecules decreases markedly, but does not disappear. The calculated diffusion coefficients of Li⁺, Br⁻, and H₂O are comparable to the experimental values.

Key words: Molecular dynamic simulation; Aqueous LiBr solution; Radial distribution func₇ tion; Coordination number; Ion pair

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0 Introduction

Lots of chemical reactions and life phenomena occur in aqueous solutions. The knowledge of the structure and dynamics of ions in aqueous solutions is beneficial to the understanding of the nature of chemical reactions and life processes. The structures and dynamics of ions in aqueous solutions has been being an attractive field in chemistry. Thus, many publications, books, and monographs contribute to this field^[1-5]. Diffraction methods, spectroscopy, and computer simulations are the three main investigation tools. Molecular dynamic

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simulationprovide some unique information that other simulation method and experimental methods can not. These information include time-dependent properties and ultrafast ligand substitution reaction of simulated systems, typically, on the time scale of nanosecond.

Concentrated aqueous LiBr solutions are widely used in absorption refrigeration systems because of their very low vapor pressures. Structurally, the very low vapor pressure must be the results of interactions of species in aqueous LiBr solutions. Water molecules are bounded so tightly that they escape very hardly from solutions. The structures of aqueous LiBr solution at different concentrations have been studied by X-ray diffraction^[6], neutron diffraction with isotope substitution^[7,8], and Raman spectroscopy.^[9] No computer simulations have been carried out for aqueous LiBr solutions so far.

The hydration of alkali halides have been studied by many authors, especially for LiCl, using experimental and computer simulation methods^[1,2]. There are large differences among those results for the Li⁺-O distance and hydration number, but the tetrahedral coordination and the hydration number of 4 and Li⁺-O distance of about at 0. 2nm are widely accepted. The hydration of Br ion has been studied by X-ray diffraction^[1,2,6] and EXAFS and XAFS technique^[10-14] at room temperature and supercritical condition. Water molecules coordinate to Br ion mostly sixfold in aqueous solutions and the hydration shell of brion is of an octahedral structure. In this work, molecular dynamic simulations of aqueous LiBr solutions from low concentration numbers were obtained and analyzed. The diffusion coefficients of Li⁺, Br⁻, and H₂O at different concentrations were also calculated. Detailed comparisons with experimental results were made.

1 Methods

1.1 potential functions and parameters

In this work, the simple point charge (SPC) rigid water molecule model^[15] was used. This model includes a Lennard-Jones potential centered on the oxygen atom site, and assigns point charges of -0.82e at the oxygen center and +0.41e at each hydrogen site. The interactions between ions and water molecules were modeled by the effective Lennard-Jones pair potentials. Most computer simulations on the alkali halides have been made based on the set of effective pair potentials obtained by Tosi and Fumi^[16]. Fisher and Brickmann^[17] recalculated the Lennard-Jones potential parameters by fitting so-called Born-Mayer-Huggins form^[17], and demonstrated that these parameters worked very well to represent the non-electrostatic interactions of alkali halides. For ion-water interactions, the Lorentz-Berthelot mixing rules^[18] were used to calculate the cross-interaction terms. The overall potential parameters used in the simulations are given in Table 1.

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SPC water potentials						
Atom-Atom	¢∕A	$\not \in (kJ \cdot mol^1)$	q/e			
0-0	3.166	0.6502	-0.82			
Н-О	1.000	0.0000	+0.41			
Ion-Ion potentials						
Ion-Ion		9 'A	$\mathbf{F}(\mathbf{kJ} \cdot \mathbf{mol}^{1})$			
Li ⁺ -Li ⁺	4	2.75	0.00349			
Br ⁻ -Br ⁻	4.32		0.7106			
Li^+-Br^-	3.535		0.0498			
	Ion-Wate	er potentials				
Ion-Water		9 'A	$\mathbf{F}(\mathbf{kJ} \cdot \mathbf{mol}^1)$			
Li ⁺ -H ₂ O	2	. 958	0.0476			
Br^+ - $\operatorname{H}_2\operatorname{O}$	3.743		0.6797			

Table 1 Interaction potential parameters

1.2 **Details of simulations**

The simulations were made for six aqueous LiBr solutions from 0.867 molal to very highly concentrated 18.50 molal with the molar ratio of LiBr to H₂O of 1:64, 1:32, 1:16, 1:8, 1:4, and 1:3, respectively. The solution of 18.50 molal approaches to saturation according to the isotherm of LiBr-H₂O system at temperature $300 \text{ K}^{[19]}$. The densities of these solutions were interpolated from the tabular data set^[20]. The simulation box sizes were adjusted to the densities of solutions. In the simulations, the cubic periodical boundary condition and the minimum image convention were used. The details of simulations are listed in Table 2. The molecular dynamic simulation software package DL-POLY was employed. The equations of motion were integrated using Verlet leapfrog algorithm with a 0.5 fs time step and SHAKE technique for bond constraints^[18]. The NVT ensemble at temperature T = 300K was sampled with the Nose-Hoover thermostat^[21]. In order to improve efficiency, multiple timestep algorithm^[22] with the primary cutoff radii of 0.75nm and the Verlet neighbor list border of 0.000 mm. After 25 ps equilibration phase, the production phase started till 1000 ps.

Concentration $/(mol \cdot kg^{-1})$	Molar ratio LiBr:H2O	Density $/(\mathbf{g} \cdot \mathbf{cm}^{-3})$	Box size/nm	No•Of species in box
0.876	1:64	1.0482	1.9870	$4\mathrm{Li}^+$, $4\mathrm{Br}^-$, $256\mathrm{H}_2\mathrm{O}$
1.735	1:32	1.0971	2.0207	$8\mathrm{Li}^+$, $8\mathrm{Br}^-$, $256\mathrm{H}_2\mathrm{O}$
3.469	1:16	1.1884	2.0316	$16{ m Li}^+$, $16{ m Br}^-$, $256{ m H}_2{ m O}$
6.938	1:8	1.3482	2.0880	$32{ m Li}^+$, $32{ m Br}^-$, $256{ m H}_2{ m O}$
13.88	1:4	1.6174	2.1904	$64{ m Li}^+$, $64{ m Br}^-$, $256{ m H}_2{ m O}$
18.50	1:3	1.7549	2.0434	$64{\rm Li}^+$, $64{ m Br}^-$, $192{ m H}_2{ m O}$

 Table 2
 Details of simulations of various aqueous LiBr solutions at 300K

2 Results and discussion

The structural properties, i.e., radial distribution functions and running coordination numbers of six aqueous LiBr solutions are shown in Figure 1 to 10. We give detailed explanation and discussion in the following section.





Figure 2 Li⁺-H radial distribution functions and running coordination numbers of aqueous LiBr solutions at ³⁰⁰K.

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Before a detailed discussion, it is useful to distinguish the first coordination shell from

the first hydration shell. The first hydration shell means that only water molecules are coordinated to the central ions, while the first coordination shell includes water molecules and other ligands.



Figure 3 Br⁻-O radial distribution functions and running coordination numbers of aqueous LiBr solutions at 300K.



Figure 4 Br⁻-H radial distribution functions and running coordination numbers of aqueous LiBr solutions at ³⁰⁰K·

From Figures 1 to 4, we can see that the distance of Li^+ -O of 0. 202nm does not change with the variation of concentration, the hydration number changes from 4.5 to 1.85 with the increasing of solution concentration from 0.876mol to 18.50mol; whereas the distance of Br⁻-O is concentration dependent. This distance expands to 0.35nm from 0.326nm with the increasing of concentration. The profile of radial distribution function of Br⁻-O becomes more asymmetric, and the first minimum never reduce to zero. But surprisingly, the hydration number of Br ion keeps relatively constant, which means the hydration shell of Br ion keeps well defined and completely even at high concentrations. The Li^+ -H distance and Br⁻-H distance remain 0.274nm and 0.23nm respectively. The second hydration shells of Li ion and Br ion are pronounced, even the third hydration shell of Li ion can be seen. But the second hydration shell of Br ion shifts from about 0.515nm to 0.615nm with the increasing of concentration.

The distance of Li^+-Br^- of [0, 24nm is concentration independent. Such a short distance apparently means the forming of contact ion pairs of Li^+-Br^- , anymore, this distance is even (C)1994-2021 China Academic Journal Electronic Publishing House. All rights reserved, shorter than the sum of ionic radii of Li lon and Br ion in aqueous solutions^[1], as well as the distance of Li^+-Br^- in LiBr crystals^[23]. The number of contact ion pairs of Li^+-Br^- increases

with increasing concentration, even in dilute solution, the contaction pairs also occur. Carefully examined, it is found that the coordination number of Li ion in aqueous LiBr solution which is the sum of hydration number of Li ion and the running coordination number of Li^+ -Br⁻ contact ion pair in the first coordination shell keeps relatively constant. It should be pointed out that the running coordination number obtained by computer simulation methods is often larger than that from diffraction methods because of the concept and calculating method used in the computer simulations. The visualizations of the configurations for six aqueous LiBr solutions by MOLCAD^[24] show that the first coordination shells of Li ion is of tetrahedral structure, and the hydration shell of Br ion octahedral structure, respectively, even though the existence of Li⁺-Br⁻ contact ion pairs.



Figure 5 Li⁺-Br⁻ radial distribution functions and running coordination numbers of aqueous LiBr solutions at 300K.



The $\text{Li}^+\text{-}\text{Li}^+$ distance of about 0.408nm means the forming of solvent separation ion pair taking into account the $\text{Li}^+\text{-}O$ distance. Anymore, it seems that two Li ion share the same water molecule and keeps this structure linear. The $\text{Br}^-\text{-}\text{Br}^-$ distance of 0.41nm should be the distance of $\text{Br}^-\text{-}\text{Br}^-$ contact ion pair. It is understandable that the running coordination numbers of $\text{Li}^+\text{-}\text{Li}^+$ and $\text{Br}^-\text{-}\text{Br}^-$ increase with the increasing of concentration. At high concentration, the larger running coordination numbers of $\text{Li}^+\text{-}\text{Li}^+$ solvent separation ion pair and $\text{Br}^-\text{-}\text{Br}^-$ contact ion pair indicate the forming of large cluster structures which are ordered structure at short range compared with that in crystals (C)19.4-2021 China Academic Journal Electronic Publishing House. All rights reserved.

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Figure 7 Br⁻-Br⁻ radial distribution functions and running coordination numbers of aqueous LiBr solutions at 300K.

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Figure 8 O-O radial distribution functions and running coordination numbers of aqueous LiBr solutions at ³⁰⁰K.

Compared to experimental results, the distances of 0.202nm for Li⁺-O and average 0. 332nm for Br⁻-O are in well agreement with ones of 0. 196nm for Li⁺-O and 0. 338nm for Br⁻-O by X⁻ray and neutron diffraction on aqueous LiBr solutions, respectively^[6-8]. Recent *ab* initio calculation of Li ion hydration in aqueous solution shown the Li⁺-O distance is 0. 197nm and hydration number is 4^[9,25]. The EXAFS and XAFS studies on the hydration of Br ion gave the Br⁻-O distance from 0.319nm to 0.336nm and the hydration number ranged from 5.3 to 7.2^[10-14]. Moreover, these two distances obtained in this work are in well agreement with ones obtained by weighting the experimental values available^[1]. But surprisingly, the neutron diffraction of aqueous LiBr solution with the molar ratio of LiBr: H²O being 1: 4 shown that the well defined hydration shell around Li ion was kept in such a highly concentrated solution, which implied that the Li ion hydration occurred more preferentially compared wit that of Br ion, and no evidence was founded to confirm the existence of contact ion pairs of Li^+ -Br^{-[8]}. Our MD simulation results disagree with this conclusion. The hydration shell of Br ion keeps well defined and completely in aqueous solution with the Br⁻-O distance a little expanding with the increasing of concentration; the Li⁺-Br⁻ contact ion pairs in concentrated solutions present markedly. The Raman spectroscopic studies of aqueous LiBr solutions indicated the existence of Li⁺-Br⁻ contact ion pair at saturation and near saturation, the band for Li^+ -Br disappeared with dilution (LiBr:H₂O ≤ 1 : 4) ^[9]. The existence of Li⁺-(C)1994-2021 China Academic Journal Electronic Publishing House. All rights reserved Br contact ion pairs can also be supported by the facts that on average each Li ion was in contact with 1.5 Cl⁻ ion by neutron diffraction investigation of 27.5 molal LiCl(LiCl:H2O, 1 : 2) solution at temperature $T = 400 K^{[26]}$, as well as the existence of Li⁺-Cl⁻ contact ion pairs by MD simulations of highly concentrated LiCl solutions with different interaction potentials being used^[27-29]. The Li⁺-Br⁻ distance of 0.24nm is shorter than the sum of ionic radii of Li ion and Br ion in aqueous solutions, and also shorter than that in LiBr crystals. But this distance is close to that of 0.246nm in the structural study of LiBr in acetonitrile solution^[7].



Figure 9 O-H radial distribution functions and running coordination numbers of aqueous LiBr solutions at 300 K.

Figure 10 H-H radial distribution functions and running coordination numbers of aqueous LiBr solutions at ³⁰⁰K.

The Li⁺-H distance of 0.274nm is longer than that of 0.26nm by neutron diffraction^[7,8]. Because experimental values of Br⁺-H distance, Li⁺-Li⁺ distance, and Br⁻-Br⁻ distance are unavailable, no direct comparisons for these values were made. It should be mentioned that the radial distribution function Cl⁻-Cl⁻ in 14.9 mol aqueous LiCl solution (LiCl: H₂O, 1:4) was obviously resolved by neutron diffraction with chloride isotope substitution, a far ranging order of distribution of the Cl⁻ in solution appeared^[30]. The radial distribution function of Br-Br in highly LiBr solution are comparable to that of Cl⁻-Cl⁻ in highly concentrated LiCl solution except for the height of the first peak.

2.2 The structural properties of water molecules in aqueous solution

The structural properties of water molecules in aqueous LiBr solutions are displayed in Figures 8 to $^{10}_{1994-202}$ The O-O distance does not change, but the running coordination number. At and



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Figure 11 Concentration dependence of diffusion coefficients at 300K.

the profile of O-O radial distribution function change. In dilute LiBr solutions, water molecules keep the configuration like in pure water. With the increasing of concentration, the configuration destroyed seriously. A long tail appears in the first peak. The first minimum shifts to 0. 498nm from 0. 354nm. The second peak in radial distribution function becomes pronounced. The O-H distance is also kept unchanged. The number of hydrogen bonds among water molecules which is represented by the first peak in radial distribution function and running coordination number of O-H decreases obviously, but does not disappear \cdot The H-H distance of 0.242nm is shorter than that of 0. 265nm obtained by neutron diffraction for 13.88mol LiBr solution^[8].

2.3 **Diffusion coefficients**

The diffusion coefficients of Li^+ , Br^- , and H_2O at different concentrations were calculated from mean square displacement^[18]. The concentration dependencies of diffusion coefficients are displayed in Figure ¹¹ and listed in Table ³. The diffusion coefficients at low concentrations are comparable to the experimental results^[31]. At high concentrations, the diffusion coefficients of Li^+ and Br^- are almost the same, which gives the evidence that a large number of Li^+ -Br $^-$ contact ion pairs form.

Molar ratio of LiBr:H2O	${\rm Li}^+/({\rm cm}^2 \cdot {\rm s}^{-1} \cdot 10^4)$	${\rm Br}^{-}/({\rm cm}^{2} \cdot {\rm s}^{-1} \cdot 10^{4})$	H ₂ O/($cm^2 \cdot s^{-1} \cdot 10^4$)
1:64	0.407	0.231	1.026
1:32	0.447	0.531	1.025
1:16	0.208	0.431	0.792
1:8	0.100	0.126	0.369
1:4	0.032	0.032	0.168
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Table ³ Diffusion coefficients of aqueous LiBr solutions at ³⁰⁰K

³ Conclusions

Molecular dynamic simulations of aqueous LiBr solutions from low concentration to high concentration with the molar ratio of LiBr:H₂O of 1:64, 1:32, 1:16, 1:8, 1:4, and 1:3 were carried out. The hydration number of Li ion decreases with the increasing of concentration, but this is compensated by the increasing of the unmber of Li⁺-Br⁻ contact ion pairs, and the coordination shell of Li ion keeps unchanged. The hydration shell of Br ion is well defined in very highly concentrated LiBr solutions with the Br⁻-O distance a little expanding and the profile of radial distribution function more asymmetric. The contact ion pairs of Li⁺-Br⁻ appear even in more dilute solution, and increases with the increasing of concentration. The Li⁺-Br⁻ distance is obviously shorter than the sum of ionic radii of Li ion and Br ion in aqueous solution, also shorter than that in LiBr crystals. The structures of water molecules in highly concentrated solutions are nearly destroyed, and the hydrogen bond among water molecules decreases markedly, but does not disappear. At high concentration, the diffusion coefficients of Li⁺, and Br⁻ approach equal, which give an evidence that a large number of Li⁺-Br⁻ contact ion pairs form.

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LiBr 溶液从低浓度到高浓度的分子动力学模拟

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摘要: 在LiBr 与水的物质量比分别为1:64、1:32、1:16、1:8、1:4和1:3的情况下,对LiBr 溶液从低温到高温的分子动力学模拟进行了研究。随浓度增加,锂离子的水合数量呈减少趋势但 同时又从Li⁺-Br⁻接触离子对的数量增加中得到补偿,而Li离子的第一配位壳层的配位数量保持 不变。在高浓度LiBr 溶液中,Br-O之间的距离有所增加,Br⁻O的径向分布的形状更趋于非对称, 从而很好地确定了Br离子水合壳层Li⁺-Br⁻接触离子对可以在更稀的溶液中产生,但随浓度增加 而增加。Li⁺-Br⁻距离明显短于溶液中Li离子与Br离子的离子半径之和,也短于LiBr晶体中两者 离子半径之和。高浓度溶液中水分子的结构几乎被破坏,水分子间的氢键明显增加,但没有消失。 对Li⁺、Br⁻和水的扩数系数计算值与实验值进行了比较。

关键词:分子动力学模拟;LiBr 溶液;径向分布函数;配位数;离子对