

Research Article

Volumetric Properties in the $\text{NaAsO}_2 + \text{H}_2\text{O}$ System at Temperature from 283.15 to 363.15 K and Atmospheric Pressure

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Densities of sodium arsenite (NaAsO_2) aqueous solution with the molality varied from 0.19570 to 1.94236 mol·kg⁻¹ at temperature intervals of 5 K from 283.15 to 363.15 K and 101 ± 5 kPa were measured by a precise Anton Paar Digital vibrating-tube densimeter. Apparent molar volumes (V_ϕ) and thermal expansion coefficient (α) were obtained on the basis of experimental data. The 3D diagram of apparent molar volume against temperature and molality and the diagram of thermal expansion coefficient against molality were generated. According to the Pitzer ion-interaction equation of the apparent molar volume model, the Pitzer single-salt parameters ($\beta_{M,X}^{(0)v}$, $\beta_{M,X}^{(1)v}$, $\beta_{M,X}^{(2)v}$, and $C_{M,X}^{(v)}$, MX = NaAsO₂) and their temperature-dependent correlation $F(i, p, T) = a_1 + a_2 \ln(T/298.15) + a_3(T - 298.15) + a_4/(620 - T) + a_5/(T - 227)$ (where T is temperature in Kelvin and a_i are the correlation coefficients) for NaAsO₂ were obtained for the first time. The predictive apparent molar volumes agree well with the experimental values, and those results indicated that the single-salt parameters and the temperature-dependent formula are reliable.

1. Introduction

Arsenic (As) is a ubiquitously toxic, carcinogenic, and possibly teratogenic element [1, 2], and the toxicity of arsenite (As^{III}) is 60 times higher than that of arsenate (As^{V}) in the environment [3]. Many studies show that arsenic as a carcinogenic agent poses a high risk to human health if it is released into the environment, typically arsenicosis, a serious disease mainly caused by As-contaminated drinking groundwater [4–8]. Apparent molar volume reveals the volume change in solution caused by changes of temperature, concentration, and pressure and further provides some basic understanding of the structure and ion interaction in aqueous solution [9]. Accurate acknowledge of the thermodynamic properties of arsenic plays a vital role in solving environmental geochemistry of arsenic pollution [10].

As to arsenate compounds, the thermodynamic properties (ΔG_f^0 , ΔH_f^0 , S^0 , C_p^0 , V^0 , and ω) of arsenate and arsenite

aqueous systems were evaluated and the coefficients of the Helgeson–Kirkham–Flowers equations were revised [11]. Perfetti et al. measured the densities of arsenious and arsenic acid aqueous solution and obtained the standard partial molar volumes V^0 of the neutral aqueous As^{III} and As^{V} (oxy) hydroxide species [10]. Nordstrom et al. reviewed and updated thermodynamic data of arsenic minerals and aqueous species, focusing on internal consistency and the quality of the original measurements [12, 13]. Till now, the apparent molar volume properties on NaAsO₂ aqueous solution are not reported in the literature.

In this paper, the densities of the binary system NaAsO₂ + H₂O from 0.19570 to 1.94236 mol·kg⁻¹ at temperature from 283.15 to 363.15 K were measured. Apparent molar volumes and thermal expansion coefficients were obtained, and the Pitzer single-salt parameters and their temperature-dependent equation of NaAsO₂ were fitted on the basis of the Pitzer ion-interaction model for the first time.

TABLE 1: Source and purity of the chemical used in this work.

Reagents	CAS reg. no	Initial mass fraction purity	Purification method	Final mass fraction purity	Analysis method
NaAsO ₂ ^a	7784-46-5	0.99	Recrystallization	0.995	ICP-MS for AsO ₂ ^{-b}

^aXiya Reagent Co., Ltd. ^bStandard uncertainty u is $u(m) = 0.0063$ in mass fraction.

2. Experimental

2.1. Reagents. NaAsO₂ was obtained, with an analytical grade of 0.99 in mass fraction. The chemical was recrystallized after filtration, washing, and drying at 35°C before use in the glove box filled with nitrogen (UNilab Plus, MBraun, Germany). The purity of the recrystallized NaAsO₂ was 0.9950 in mass fraction, which was analyzed by inductively coupled plasma-mass (iCAP Q ICP-MS Thermo Scientific, Massachusetts, USA) with an uncertainty of ± 0.0063 in mass fraction, shown in Table 1. The characterization of the recrystallized NaAsO₂ by TG-DSC (Labsys, Setaram, France) is shown in Figure 1, and the weight loss of the sample was 0.0205 in mass fraction between 298 and 473 K, which was basically due to no loss of water within the range of the measured temperature. Double deionized water (DDW) was produced by an ultrapure water machine (Ulupure Technologies Co. Ltd., China) with conductivity less than $1 \times 10^{-4} \text{ S}\cdot\text{m}^{-1}$ and pH = 6.60 at 25°C, and it was used during the whole experiment.

2.2. Apparatus and Method. The stock solution was prepared with NaAsO₂ and fresh DDW in a glovebox filled with nitrogen by weight using a precision electronic balance (Mettler Toledo, Swiss) with an uncertainty of 0.2 mg. All other aqueous solutions were prepared by mass dilution from the stock solution with an uncertainty of 0.2 mmol·kg⁻¹ and stored in glass bottles at 4°C in the refrigerator.

Densities of sodium arsenite aqueous solution were measured by a precise Anton Paar Digital vibrating-tube densimeter (DMA4500, Anton Paar Co. Ltd., Austria), which was controlled within $\pm 0.01 \text{ K}$ by the automatically thermostat with an uncertainty of $1.4 \text{ mg}\cdot\text{cm}^{-3}$. Before the measurement, the apparatus was calibrated using dry air and fresh DDW at 293.15 K and $101 \pm 5 \text{ kPa}$. Density of pure water was measured with 10 K intervals from 279.15 to 369.15 K, and the results agree well with the literature [14], and the deviations between the experimental and reference data were within 0.003%, as shown in Table 2. Densities of the NaAsO₂ aqueous solutions were measured with molality from 0.19570 to 1.94236 mol·kg⁻¹ at temperature intervals of 5 K from 283.15 to 363.15 K and atmospheric pressure.

3. Results and Discussion

3.1. Densities of NaAsO₂ Aqueous Solution. The densities of NaAsO₂ aqueous solution were measured at different temperatures and molalities, and the results are listed in Table 3. It was clearly seen that the densities of NaAsO₂ aqueous solution are decreased with increasing of temperature at constant molality. Nevertheless, at the same temperature, the density values of NaAsO₂ aqueous solution are

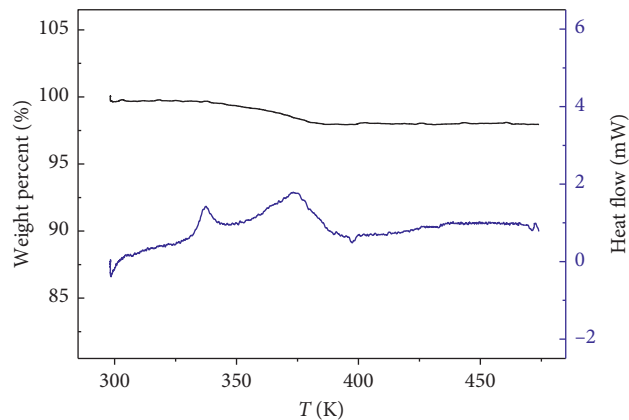


FIGURE 1: The TG-DSC curve of the recrystallized NaAsO₂.

TABLE 2: Comparison of densities of pure water at different temperatures between the experimental and the literature data.^a

T (K)	ρ^{exp} (g·cm ⁻³)	ρ^{lit} (g·cm ⁻³) ^b	$\Delta(\rho)\%$ ^c
279.15	0.99997	0.99994	0.0030
289.15	0.99896	0.99894	0.0020
299.15	0.99680	0.99678	0.0020
309.15	0.99369	0.99369	0.0000
319.15	0.98979	0.98979	0.0000
329.15	0.98520	0.98521	0.0010
339.15	0.97999	0.98001	0.0020
349.15	0.97422	0.97424	0.0021
359.15	0.96796	0.96796	0.0000
369.15	0.96119	0.96118	0.0010

^aStandard uncertainties u are $u(T) = 0.01 \text{ K}$ and $u(p) = 5 \text{ kPa}$, and $u(\rho)$ for ρ is $1.4 \text{ mg}\cdot\text{cm}^{-3}$. ^bLiterature [14]. ^c $\Delta(\rho)\% = 100 \times |\rho^{\text{exp}}/\rho^{\text{lit}} - 1|$.

increased indistinctively with the increasing of NaAsO₂ molality.

3.2. Thermal Expansion Coefficient of NaAsO₂ Aqueous Solution. Thermal expansion coefficient of NaAsO₂ aqueous solution, α , was defined as follows [15]:

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{p,m} = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_{p,m}. \quad (1)$$

An empirical equation can be obtained at constant molality and pressure as follows:

$$\rho = A_0 + A_1 (T - 273.15) + A_2 (T - 273.15)^2, \quad (2)$$

where ρ is the density of NaAsO₂ aqueous solution, T is the absolute temperature in Kelvin, and A_i are the empirical constants. The values of ρ obtained at different temperatures have been fitted by the least square method and are shown in

TABLE 3: Apparent molar volumes and densities of the NaAsO₂ + H₂O system at various temperatures and molalities at 101 ± 5 kPa.^a

$m(\text{NaAsO}_2)$ Mol·kg ⁻¹	ρ g·cm ⁻³	V_Φ cm ³ ·mol ⁻¹	ρ g·cm ⁻³	V_Φ cm ³ ·mol ⁻¹	ρ g·cm ⁻³	V_Φ cm ³ ·mol ⁻¹
$T = 283.15 \text{ K}$						
1.94236	1.54174	-96.8179	1.53826	-96.1708	1.53474	-95.6638
1.74671	1.47538	-96.6072	1.47215	-95.8962	1.46886	-95.3316
1.55298	1.41632	-97.7718	1.41333	-96.9925	1.41027	-96.3714
1.35720	1.35951	-99.5389	1.35679	-98.6871	1.35397	-98.0068
0.97105	1.25604	-106.8454	1.25389	-105.8578	1.25159	-105.0693
0.77617	1.20993	-116.6088	1.20801	-115.4939	1.20593	-114.6058
0.58372	1.16344	-129.5826	1.16181	-128.3595	1.15999	-127.3822
0.39237	1.12068	-159.3925	1.11935	-158.0320	1.11780	-156.9634
0.19570	1.07768	-249.5148	1.07670	-248.0568	1.07546	-246.9547
0.00000	0.99966	—	0.99908	—	0.99820	—
$T = 288.15 \text{ K}$						
1.94236	1.53116	-95.2661	1.52752	-94.9783	1.52383	-94.7832
1.74671	1.46549	-94.8841	1.46207	-94.5577	1.45857	-94.3245
1.55298	1.40712	-95.8741	1.40390	-95.5091	1.40060	-95.2448
1.35720	1.35105	-97.4614	1.34805	-97.0548	1.34494	-96.7549
0.97105	1.24917	-104.4410	1.24663	-103.9809	1.24397	-103.6459
0.77617	1.20370	-113.8897	1.20132	-113.3462	1.19881	-112.9440
0.58372	1.15800	-126.5968	1.15584	-126.0085	1.15354	-125.5718
0.39237	1.11605	-156.0997	1.11412	-155.4848	1.11201	-155.0170
0.19570	1.07399	-246.0876	1.07230	-245.5014	1.07041	-245.0817
0.00000	0.99707	—	0.99569	—	0.99410	—
$T = 293.15 \text{ K}$						
1.94236	1.53116	-95.2661	1.52752	-94.9783	1.52383	-94.7832
1.74671	1.46549	-94.8841	1.46207	-94.5577	1.45857	-94.3245
1.55298	1.40712	-95.8741	1.40390	-95.5091	1.40060	-95.2448
1.35720	1.35105	-97.4614	1.34805	-97.0548	1.34494	-96.7549
0.97105	1.24917	-104.4410	1.24663	-103.9809	1.24397	-103.6459
0.77617	1.20370	-113.8897	1.20132	-113.3462	1.19881	-112.9440
0.58372	1.15800	-126.5968	1.15584	-126.0085	1.15354	-125.5718
0.39237	1.11605	-156.0997	1.11412	-155.4848	1.11201	-155.0170
0.19570	1.07399	-246.0876	1.07230	-245.5014	1.07041	-245.0817
0.00000	0.99707	—	0.99569	—	0.99410	—
$T = 298.15 \text{ K}$						
1.94236	1.53116	-95.2661	1.52752	-94.9783	1.52383	-94.7832
1.74671	1.46549	-94.8841	1.46207	-94.5577	1.45857	-94.3245
1.55298	1.40712	-95.8741	1.40390	-95.5091	1.40060	-95.2448
1.35720	1.35105	-97.4614	1.34805	-97.0548	1.34494	-96.7549
0.97105	1.24917	-104.4410	1.24663	-103.9809	1.24397	-103.6459
0.77617	1.20370	-113.8897	1.20132	-113.3462	1.19881	-112.9440
0.58372	1.15800	-126.5968	1.15584	-126.0085	1.15354	-125.5718
0.39237	1.11605	-156.0997	1.11412	-155.4848	1.11201	-155.0170
0.19570	1.07399	-246.0876	1.07230	-245.5014	1.07041	-245.0817
0.00000	0.99707	—	0.99569	—	0.99410	—
$T = 303.15 \text{ K}$						
1.94236	1.53116	-95.2661	1.52752	-94.9783	1.52383	-94.7832
1.74671	1.46549	-94.8841	1.46207	-94.5577	1.45857	-94.3245
1.55298	1.40712	-95.8741	1.40390	-95.5091	1.40060	-95.2448
1.35720	1.35105	-97.4614	1.34805	-97.0548	1.34494	-96.7549
0.97105	1.24917	-104.4410	1.24663	-103.9809	1.24397	-103.6459
0.77617	1.20370	-113.8897	1.20132	-113.3462	1.19881	-112.9440
0.58372	1.15800	-126.5968	1.15584	-126.0085	1.15354	-125.5718
0.39237	1.11605	-156.0997	1.11412	-155.4848	1.11201	-155.0170
0.19570	1.07399	-246.0876	1.07230	-245.5014	1.07041	-245.0817
0.00000	0.99707	—	0.99569	—	0.99410	—
$T = 308.15 \text{ K}$						
1.94236	1.53116	-95.2661	1.52752	-94.9783	1.52383	-94.7832
1.74671	1.46549	-94.8841	1.46207	-94.5577	1.45857	-94.3245
1.55298	1.40712	-95.8741	1.40390	-95.5091	1.40060	-95.2448
1.35720	1.35105	-97.4614	1.34805	-97.0548	1.34494	-96.7549
0.97105	1.24917	-104.4410	1.24663	-103.9809	1.24397	-103.6459
0.77617	1.20370	-113.8897	1.20132	-113.3462	1.19881	-112.9440
0.58372	1.15800	-126.5968	1.15584	-126.0085	1.15354	-125.5718
0.39237	1.11605	-156.0997	1.11412	-155.4848	1.11201	-155.0170
0.19570	1.07399	-246.0876	1.07230	-245.5014	1.07041	-245.0817
0.00000	0.99707	—	0.99569	—	0.99410	—
$T = 313.15 \text{ K}$						
1.94236	1.52007	-94.6709	1.51626	-94.6424	1.51237	-94.6850
1.74671	1.45501	-94.1840	1.45137	-94.1289	1.44767	-94.1534
1.55298	1.39722	-95.0767	1.39376	-94.9992	1.39022	-95.0067
1.35720	1.34175	-96.5581	1.33847	-96.4597	1.33510	-96.4499
0.97105	1.24119	-103.4289	1.23831	-103.3333	1.23533	-103.3445
0.77617	1.19616	-112.6608	1.19340	-112.5145	1.19050	-112.4632
0.58372	1.15108	-125.2659	1.14848	-125.1021	1.14575	-125.0503
0.39237	1.10973	-154.6928	1.10731	-154.5528	1.10473	-154.5289
0.19570	1.06834	-244.8692	1.06609	-244.8135	1.06368	-244.9561
0.00000	0.99231	—	0.99033	—	0.98817	—
$T = 318.15 \text{ K}$						
1.94236	1.52007	-94.6709	1.51626	-94.6424	1.51237	-94.6850
1.74671	1.45501	-94.1840	1.45137	-94.1289	1.44767	-94.1534
1.55298	1.39722	-95.0767	1.39376	-94.9992	1.39022	-95.0067
1.35720	1.34175	-96.5581	1.33847	-96.4597	1.33510	-96.4499
0.97105	1.24119	-103.4289	1.23831	-103.3333	1.23533	-103.3445
0.77617	1.19616	-112.6608	1.19340	-112.5145	1.19050	-112.4632
0.58372	1.15108	-125.2659	1.14848	-125.1021	1.14575	-125.0503
0.39237	1.10973	-154.6928	1.10731	-154.5528	1.10473	-154.5289
0.19570	1.06834	-244.8692	1.06609	-244.8135	1.06368	-244.9561
0.00000	0.99231	—	0.99033	—	0.98817	—
$T = 323.15 \text{ K}$						
1.94236	1.52007	-94.6709	1.51626	-94.6424	1.51237	-94.6850
1.74671	1.45501	-94.1840	1.45137	-94.1289	1.44767	-94.1534
1.55298	1.39722	-95.0767	1.39376	-94.9992	1.39022	-95.0067
1.35720	1.34175	-96.5581	1.33847	-96.4597	1.33510	-96.4499
0.97105	1.24119	-103.4289	1.23831	-103.3333	1.23533	-103.3445
0.77617	1.19616	-112.6608	1.19340	-112.5145	1.19050	-112.4632
0.58372	1.15108	-125.2659	1.14848	-125.1021	1.14575	-125.0503
0.39237	1.10973	-154.6928	1.10731	-154.5528	1.10473	-154.5289
0.19570	1.06834	-244.8692	1.06609	-244.8135	1.06368	-244.9561
0.00000	0.99231	—	0.99033	—	0.98817	—
$T = 328.15 \text{ K}$						
1.94236	1.50842	-94.7894	1.50439	-94.9561	1.50025	-95.1719
1.74671	1.44388	-94.2384	1.44001	-94.3908	1.43604	-94.5963
1.55298	1.38660	-95.0791	1.38289	-95.2211	1.37907	-95.4202
1.35720	1.33163	-96.5086	1.32807	-96.6411	1.32440	-96.8342
0.97105	1.23224	-103.4322	1.22904	-103.6081	1.22574	-103.8600
0.77617	1.18749	-112.4984	1.18436	-112.6244	1.18111	-112.8292
0.58372	1.14289	-125.0870	1.13990	-125.2217	1.13678	-125.4425
0.39237	1.10201	-154.5877	1.09916	-154.7787	1.09617	-155.0549
0.19570	1.06111	-245.1416	1.05840	-245.5166	1.05554	-245.9837
0.00000	0.98586	—	0.98339	—	0.98077	—
$T = 333.15 \text{ K}$						
1.94236	1.50842	-94.7894	1.50439	-94.9561	1.50025	-95.1719
1.74671	1.44388	-94.2384	1.44001	-94.3908	1.43604	-94.5963
1.55298	1.38660	-95.0791	1.38289	-95.2211	1.37907	-95.4202
1.35720	1.33163	-96.5086	1.32807	-96.6411	1.32440	-96.8342
0.97105	1.23224	-103.4322	1.22904	-103.6081	1.22574	-103.8600
0.77617	1.18749	-112.4984	1.18436	-112.6244	1.18111	-112.8292
0.58372	1.14289	-125.0870	1.13990	-125.2217	1.13678	-125.4425
0.39237	1.10201	-154.5877	1.09916	-154.7787	1.09617	-155.0549
0.19570	1.06111	-245.1416	1.05840	-245.5166	1.05554	-245.9837
0.00000	0.98586	—	0.98339	—	0.98077	—
$T = 338.15 \text{ K}$						
1.94236	1.50842	-94.7894	1.50439	-94.9561	1.50025	-95.1719
1.74671	1.44388	-94.2384	1.44001	-94.3908	1.43604	-94.5963
1.55298	1.38660	-95.0791	1.38289	-95.2211	1.37907	-95.4202
1.35720	1.33163	-96.5086	1.32807	-96.6411	1.32440	-96.8342
0.97105	1.23224	-103.4322	1.22904	-103.6081	1.22574	-103.8600
0.77617	1.18749	-112.4984	1.18436	-112.6244	1.18111	-112.8292
0.58372	1.14289	-125.0870	1.13990	-125.2217	1.13678	-125.4425
0.39237	1.10201	-154.5877	1.09916	-154.7787	1.09617	-155.0549
0.19570	1.06111	-245.1416	1.05840	-245.5166	1.05554	-245.9837
0.00000	0.98586	—	0.98339	—	0.98077	—
$T = 343.15 \text{ K}$						
1.94236	1.49599	-95.4295	1.49156	-95.7097	1.48689	-95.9977
1.74671	1.43194	-94.8431	1.42768	-95.1155	1.42320	-95.3957
1.55298	1.37512	-95.6640	1.37102	-95.9411	1.36671	-96.2108
1.35720	1.32060	-97.0712	1.31666	-97.3367	1.31251	-97.6106
0.97105	1.22229	-104.1578	1.21869	-104.4757	1.21489	-104.7911
0.77617	1					

TABLE 3: Continued.

$m(\text{NaAsO}_2)$ Mol·kg ⁻¹	ρ g·cm ⁻³	V_Φ cm ³ ·mol ⁻¹	ρ g·cm ⁻³	V_Φ cm ³ ·mol ⁻¹	ρ g·cm ⁻³	V_Φ cm ³ ·mol ⁻¹
1.55298	1.36208	-96.4328	1.35689	-96.4935		
1.35720	1.30806	-97.8220	1.30308	-97.8506		
0.97105	1.21081	-105.0049	1.20629	-104.9954		
0.77617	1.16656	-113.8768	1.16227	-113.8641		
0.58372	1.12278	-126.5346	1.11867	-126.4490		
0.39237	1.08271	-156.3771	1.07877	-156.1936		
0.19570	1.04262	-248.0259	1.03890	-247.7787		
0.00000	0.96895	—	0.96570	—		

^aStandard uncertainties u are $u(T) = 0.01$ K and $u(p) = 5$ kPa. $u(m)$ for NaAsO₂ aqueous solution is 0.2 mmol·kg⁻¹, $u(\rho)$ for ρ is 1.4 mg·cm⁻³, and $u(V_\Phi)$ for V_Φ is 0.0030 cm³·mol⁻¹.

Table 4, with the correlation coefficients (R^2) and standard deviations of 0.9997 and 0.00007, respectively.

At constant molality and pressure, equation (3) was used to acquire partial derivatives of temperature ($\partial\rho/\partial T$) _{p} :

$$\left(\frac{\partial\rho}{\partial T}\right)_p = A_1 + 2A_2(T - 273.15). \quad (3)$$

Substituting equation (3) into equation (1), the thermal expansion coefficients of NaAsO₂ aqueous solution were calculated with various molalities at different temperatures. According to the calculated data, the relation of the thermal expansion coefficient and the molality at temperature intervals of 5 K from 283.15 to 363.15 K is plotted in Figure 2. It can be seen that the thermal expansion coefficient for NaAsO₂ aqueous solution increased with the increasing of temperature at the constant molality. Also, with the increasing of molality, the thermal expansion coefficient increased obviously at $T = 283.15$ to 333.15 K, almost unchanged at $T = 338.15$ to 348.15 K, and decreased lightly at $T = 353.15$ to 363.15 K.

3.3. Apparent Molar Volume and Pitzer Parameter of NaAsO₂.
The apparent molar volumes of NaAsO₂ aqueous solution were calculated using measured densities of pure water and the sample solutions by the following equation:

$$V_\phi = 1000 \frac{(\rho_w - \rho_s)}{m_i \cdot \rho_w \cdot \rho} + \frac{M_i}{\rho}, \quad (4)$$

where m_i is the molality (mol·kg⁻¹) of the solute in the aqueous solution, M_i is the molar mass (kg·mol⁻¹) of the solute, and ρ_w and ρ are the densities (g·cm⁻³) of pure water and sample solution, respectively. The calculated apparent molar volumes of NaAsO₂ with an uncertainty of 0.0030 cm³·mol⁻¹ are listed in Table 3, and the 3D surfaces (m_i , T , V_Φ) of apparent molar volume of NaAsO₂ versus temperature and molality are plotted in Figure 3. The results indicate that apparent molar volume of NaAsO₂ universally increased with increasing temperature at low molality, and it foremost increased and then decreased with the increasing temperature at high molality.

Pitzer's electrolyte solution theory is based on the model of ion interaction and statistical mechanics. It can accurately express the thermodynamic properties of electrolyte aqueous solution. The apparent molar volumes of NaAsO₂ were

calculated using the following Pitzer equation to construct the Pitzer model [16, 17]:

$$V_\Phi + \frac{v_w}{n_r} = \frac{V(m_r)}{n_r} + v|Z_M Z_X| \frac{A^V}{2b} \ln\left(\frac{1 + b\sqrt{I}}{1 + b\sqrt{I_r}}\right) + 2v_M v_X RT \left\{ m B_{MX}^v(m) - m_r B_{MX}^v(m_r) + v_M z_M C_{M,X}^v(m^2 - m_r^2) \right\}. \quad (5)$$

The relationship between $B_{M,X}^v(m)$ and ionic strength I of aqueous solution was employed as follows:

$$B_{M,X}^v = \beta_{M,X}^{(0)v} + \beta_{M,X}^{(1)v} g(\alpha_{B1} \sqrt{I}) + \beta_{M,X}^{(2)v} g(\alpha_{B2} \sqrt{I}), \quad (6)$$

$$g(t) = 2 \left[\frac{1 - (1 + t)\exp(-t)}{t^2} \right], \quad (7)$$

where m (mol·kg⁻¹) is the molality of NaAsO₂ aqueous solution, v_w is the volume of 1 kg pure water, $V(m_r)$ is the volume of a certain solution of reference molality $m_r = 1.5$ mol·kg⁻¹ containing 1 kg of water, $n_r = 1.5$ mol is the moles number of this certain solution, A^V is the Debye-Hückel limiting-law slope for the apparent molar volume, z_M and z_X are the charges of the cation and anion for NaAsO₂ ($z_M = 1$, $z_X = 1$), v_M and v_X are the stoichiometric numbers of M and X ions formed by stoichiometric dissociation of one molecule of MX, and $v = v_M + v_X$, as for NaAsO₂ ($v_M = 1$, $v_X = 1$, $v = 2$), $\alpha_{B1} = 1.4$ kg^{1/2} mol^{1/2}, $\alpha_{B2} = 9.3$ kg^{1/2} mol^{1/2}, $b = 1.2$ kg^{1/2} mol^{-1/2}, and I (mol·kg⁻¹) is the ionic strength of the aqueous solution calculated as $(1/2)\sum m_i z_i^2$, R (cm³·MPa·K⁻¹·mol⁻¹) is the gas constant, and T is the temperature. The temperature-dependent and pressure-dependent volumetric ion-interaction parameters are $B_{M,X}^v(m)$ and $C_{M,X}^v(m)$.

The Pitzer ion-interaction parameters of the volumetric properties are expressed as functions $F(i, p, T)$:

$$\beta_{M,X}^{(0)v} = F(0, p, T), \quad (8)$$

$$\beta_{M,X}^{(1)v} = F(1, p, T), \quad (9)$$

$$\beta_{M,X}^{(2)v} = F(2, p, T), \quad (10)$$

TABLE 4: The empirical constants (A_i) and standard deviations (SD) of NaAsO₂ aqueous solution at different temperatures and p at constant molality and pressure.

m (mol·kg ⁻¹)	A_0	$10^4 A_1$	$10^6 A_2$	R^2	SD
1.94236	1.5476	-5.9767	-2.0638	0.9997	0.00002
1.74671	1.4808	-5.5469	-2.1204	0.9998	0.00003
1.55298	1.4214	-5.1049	-2.2069	0.9998	0.00005
1.35720	1.3642	-4.6333	-2.3221	0.9998	0.00002
0.97105	1.2598	-3.5908	-2.5584	0.9999	0.00004
0.77617	1.2134	-3.2059	-2.7181	1.0000	0.00007
0.58372	1.1665	-2.6774	-2.9045	1.0000	0.00002
0.39237	1.1233	-2.1469	-3.0987	1.0000	0.00003
0.19570	1.0798	-1.5388	-3.3456	0.9999	0.00005

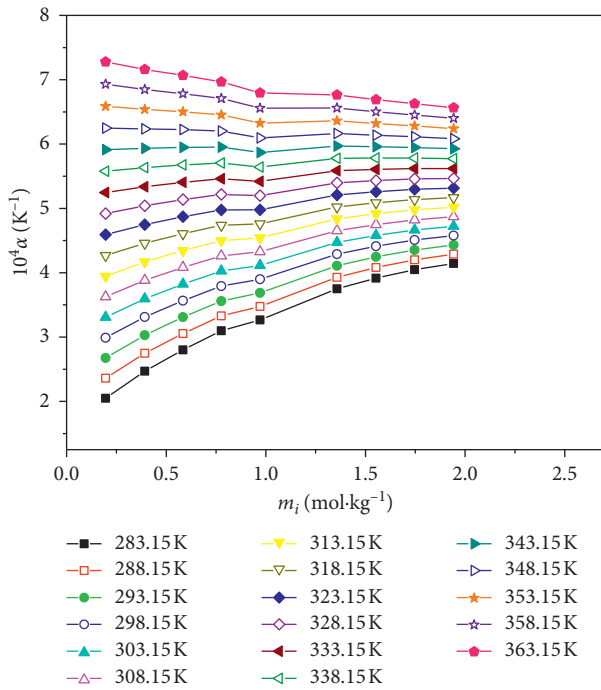


FIGURE 2: Thermal expansion coefficient (α) of NaAsO₂ (aq) against the molality (m) at different temperatures.

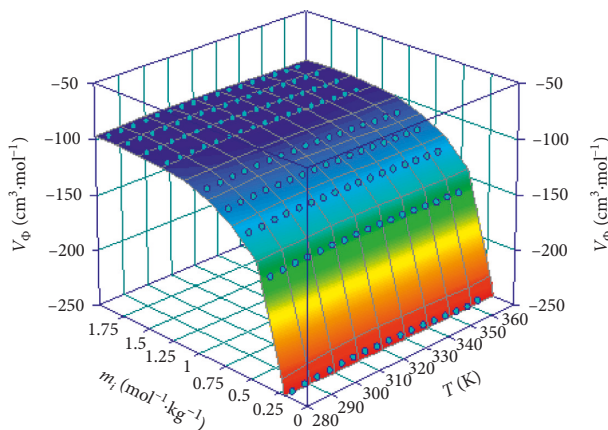


FIGURE 3: Apparent molar volumes of NaAsO₂ aqueous solution against temperature and molality at atmospheric pressure.

TABLE 5: The pitzer single-salt parameters of NaAsO₂ at different temperatures.

T (K)	$\beta^{(0)v}$	$\beta^{(1)v}$	$\beta^{(2)v}$	$C^{(0)v}$
283.15	-0.0252	0.1036	9.6726	0.0026
288.15	-0.0245	0.1008	9.5275	0.0025
293.15	-0.0239	0.0982	9.3899	0.0025
298.15	-0.0233	0.0956	9.2592	0.0024
303.15	-0.0229	0.0938	9.1245	0.0023
308.15	-0.0223	0.0916	9.0005	0.0023
313.15	-0.0217	0.0895	8.8891	0.0022
318.15	-0.0213	0.0878	8.7694	0.0021
323.15	-0.0209	0.0860	8.6669	0.0021
328.15	-0.0204	0.0841	8.5631	0.0020
333.15	-0.0200	0.0826	8.4661	0.0020
338.15	-0.0195	0.0809	8.3752	0.0019
343.15	-0.0191	0.0792	8.2921	0.0019
348.15	-0.0189	0.0781	8.2003	0.0019
353.15	-0.0186	0.0769	8.1137	0.0019
358.15	-0.0182	0.0755	8.0237	0.0018
363.15	-0.0174	0.0729	7.9326	0.0017

$$C_{M,X}^v = F(3, p, T), \quad (11)$$

with $F(i, p, T)$ represented as

$$F(i, P, T) = a_1 + a_2 \ln \frac{T}{298.15} + a_3 (T - 298.15) + \frac{a_4}{620 - T} + \frac{a_5}{T - 227}, \quad (12)$$

where T is the temperature in Kelvin, p is the pressure in MPa, and a_i are the polynomial coefficients. All the thermodynamic and dielectric properties involved were calculated by the IAPWS-95 equation from Ref. [18].

On the basis of equations (5) to (7), the single-salt parameters $\beta_{M,X}^{(0)v}$, $\beta_{M,X}^{(1)v}$, $\beta_{M,X}^{(2)v}$, and $C_{M,X}^v$ for NaAsO₂ at each temperature were fitted and are listed in Table 5. The temperature relation coefficients a_i in equations (8) to (12) were fitted and are listed in Table 6, and the fitted results of each single-salt parameter $\beta_{M,X}^{(0)v}$, $\beta_{M,X}^{(1)v}$, $\beta_{M,X}^{(2)v}$, and $C_{M,X}^v$ of NaAsO₂ were in good agreement with the experimental values, which indicated that the Pitzer model we constructed is suitable to describe the volumetric properties of the binary

TABLE 6: The temperature-dependent equation coefficients of Pitzer parameters of NaAsO₂.

Polynomial coefficient	Pitzer parameters			
	$\beta^{(0)v}$	$\beta^{(1)v}$	$\beta^{(2)v}$	$C^{(0)v}$
α_1	-1.6307×10^{-1}	4.8917×10^{-1}	3.2765×10^1	3.6363×10^{-2}
α_2	5.4520×10^{-1}	-1.5004×10^0	-1.0041×10^2	-1.3276×10^{-1}
α_3	-2.0407×10^{-3}	5.6413×10^{-3}	3.6187×10^1	5.0425×10^{-4}
α_4	4.2987×10^1	-1.2384×10^2	-7.1663×10^3	-1.0344×10^1
α_5	4.3834×10^{-1}	-6.0862×10^{-1}	-8.8443×10^1	-1.3035×10^{-1}

system NaAsO₂ + H₂O. On the basis of temperature-dependent coefficients and calculated Pitzer single-salt parameters, the apparent molar volume for NaAsO₂ aqueous solution at each temperature from 283.15 to 363.15 K could be predicted, not only for the experimental temperature, which are meaningful for the actual application.

4. Conclusion

The densities and apparent molar volumes of NaAsO₂ aqueous solution from 283.15 to 363.15 K at atmospheric pressure were obtained for the first time. Apparent molar volumes and thermal expansion coefficient were calculated, and the Pitzer single-salt parameters ($\beta_{M,X}^{(0)v}$, $\beta_{M,X}^{(1)v}$, $\beta_{M,X}^{(2)v}$, and $C_{M,X}^v$) were parameterized from the Pitzer ion-interaction model. The temperature-dependent equation coefficients were obtained on account of the least-squares method. It is essential to study the thermodynamic properties, especially apparent molar volume, and construct a model of thermodynamic for solving environmental geochemical arsenic pollution.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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