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Thermodynamic Investigation of Electrolytes of the Vanadium Redox Flow Battery (III): Volumetric Properties of Aqueous $VOSO_4$

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ABSTRACT: This paper reports the densities of aqueous $VOSO_4$ that were measured gravimetrically at temperatures from (283.15 to 323.15) K. The apparent molar volume, ${}^{\varphi}V_B$, the partial molar volume of $VOSO_4$, $\overline{V}_B$, and coefficient of thermal expansion of the solution, α, were calculated. The values of the apparent molar volume, ${}^{\varphi}V_B$, were fitted to Pitzer's model for volumetric properties by the method of least-squares, which allowed the partial molar volume of the $VOSO_4$ at infinite dilution, $\overline{V}_B^0$, and Pitzer's parameters, $\beta_{MX}^{(0)V}$, $\beta_{MX}^{(1)V}$, and $\beta_{MX}^{(2)V}$, to be obtained. The small standard deviations of the fits show that Pitzer's model is also appropriate for representing the volumetric properties of aqueous solutions of $VOSO_4$.

1. INTRODUCTION

The all-vanadium redox flow battery (VRFB) as an effective energy-storage system proposed by Skyllas-Kazacos et al. has been investigated extensively.[1−3] In the VRFB, the electrolyte is one of the most important components. It is not only the conductor of the ions but also the energy-store medium. The cell employs the V(II)/V(III) and V(IV)/V(V) redox couples in the negative and positive half-cell electrolytes, respectively, with sulfuric acid as the supporting electrolyte. The chemistry of vanadium has recently attracted considerable attention from the industry and the academic community.[4−8] Particularly, reliable thermodynamic data are needed both to help in providing an adequate description of interactions between species in the VRFB electrolyte and to provide clues to optimize the overall performance of the VRFB. To our knowledge, so far no volumetric studies of VO^{2+} salts solution are available in literature. As a continuation of our previous investigation of vanadium electrolyte,[8−12] in the present paper, we report volumetric properties of aqueous solution of $VOSO_4$: the densities of aqueous solution of $VOSO_4$ were measured from (0.5 to 3) $mol\cdot kg^{-1}$ over the temperatures from range from (283.15 to 323.15) K. Values of apparent molar volume, ${}^{\varphi}V_B$, partial molar volume, $\overline{V}_B$, and the coefficient of thermal expansion of the solution, α, were calculated. The values of Pitzer's parameter for volumetric properties were obtained by fitting of the parameters of Pitzer's model equations to experimental data.

2. EXPERIMENTAL SECTION

2.1. Chemicals. $VOSO_4\cdot nH_2O(s)$ ($\geq$ 0.97 mass fraction, Shanghai Chemical Co., China) was recrystallized twice from water,[13] and $n = 3.06$ was determined by the gravimetric method.[14] Deionized water was prepared by an ultrapure water machine (WP-UPL-100C, Sichuan Woter Co., China); its conductivity was $\leq 2\cdot 10^{-5}\ S\cdot m^{-1}$.

2.2. Experimental Process. All aqueous $VOSO_4$ to be studied were freshly prepared by weight with corrections for air buoyancy. The molality of all studied solutions were known within ± 0.02 %. The densities were measured by a Westphal balance (PZ-B-5, Shanghai Jinke Trading Co., China) at 10 K intervals from (283.15 to 323.15) K. The solution to be measured was placed in a cell with a water jacket, agitated continuously, and thermostatted at each temperature with an accuracy ± 0.02 K. The criterion for the attainment of thermal equilibrium was taken to be a steady reading within $\pm\ 0.0001\ g\cdot cm^{-3}$ for density measurements successionally at intervals of 10 min. The density of pure water was also determined by the same method and in good agreement with the literature values[15] and within experimental error.

3. RESULTS AND DISCUSSION

3.1. Densities of the Aqueous Solution. The various values of densities measured with the Westphal balance at different temperatures are listed in Table 1. All values were the average of the three measured values.

3.2. Coefficient of Thermal Expansion. To obtain the values of the coefficient of thermal expansion of the solutions, α, the experimental values of $\ln \rho$ at a constant composition of solution were fit with the following linear equation: $\ln \rho = b - \alpha(T - 298.15)$, where b is the intercept in the equation and $-\alpha$ is the slope with all related coefficients, $r > 0.99$. According to the definition of the coefficient of thermal expansion of the solutions, α is written as:

$$\alpha \equiv (1/V)(\partial V/\partial T)_{p,m} = -(\partial \ln \rho/\partial T)_{p,m} \qquad (1)$$

the values of α at different molalities are listed in Table 1.

3.3. Apparent Molar Volume. The apparent molar volume, ${}^{\varphi}V_B$, was derived from the measured solution densities. Their values are calculated with the equation[16,17]

$${}^{\varphi}V_B = [1000(\rho_0 - \rho) + mM_B\rho_0]/m\rho\rho_0 \qquad (2)$$

where ρ_0 and ρ are the density of pure water and aqueous $VOSO_4$ solutions, respectively, m is the molality, and M_B the molar mass

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Table 1. Value of the Densities ($g\cdot cm^{-3}$) and the Coefficient of Thermal Expansion of Aqueous Solutions of $VOSO_4$ at (283.15 to 323.15) K

m	T/K						$\alpha\cdot 10^4$		
$mol\cdot kg^{-1}$	283.15	293.15	298.15	303.15	313.15	323.15	K^{-1}	$s\cdot 10^4$	r
0.5000	1.0746	1.0725	1.0707	1.0680	1.0650	1.0604	3.39	7.24	0.99
0.8000	1.1176	1.1148	1.1130	1.1107	1.1066	1.1017	3.63	6.11	0.99
1.0000	1.1449	1.1419	1.1398	1.1376	1.1333	1.1284	3.68	5.20	0.99
1.2000	1.1718	1.1695	1.1672	1.1646	1.1599	1.1547	3.75	6.85	0.99
1.5000	1.2113	1.2078	1.2053	1.2027	1.1983	1.1924	3.95	5.47	0.99
1.8000	1.2496	1.2456	1.2429	1.2404	1.2353	1.2299	4.03	3.68	0.99
2.0000	1.2741	1.2700	1.2674	1.2647	1.2596	1.2539	4.03	3.85	0.99
2.2000	1.2982	1.2939	1.2912	1.2888	1.2834	1.2776	4.02	3.72	0.99
2.5000	1.3337	1.3293	1.3265	1.3239	1.3185	1.3127	4.01	3.42	0.99
2.8000	1.3671	1.3628	1.3598	1.3572	1.3516	1.3456	4.00	3.81	0.99
3.0000	1.3895	1.3846	1.3813	1.3788	1.3734	1.3675	4.00	2.11	0.99

Table 2. Values of the Apparent Molar Volumes ${}^{\varphi}V_B$ ($cm^3\cdot mol^{-1}$) of $VOSO_4$ from (283.15 to 323.15) K

m	T/K					
$mol\cdot kg^{-1}$	283.15	293.15	298.15	303.15	313.15	323.15
0.5000	12.2 ± 0.2	13.2 ± 0.2	14.2 ± 0.2	14.9 ± 0.2	15.3 ± 0.2	15.5 ± 0.2
0.8000	13.9 ± 0.1	15.2 ± 0.1	15.8 ± 0.1	16.6 ± 0.1	17.1 ± 0.1	17.4 ± 0.1
1.0000	15.5 ± 0.1	16.7 ± 0.1	17.3 ± 0.1	17.9 ± 0.1	18.3 ± 0.1	18.5 ± 0.1
1.2000	16.7 ± 0.1	17.5 ± 0.1	18.0 ± 0.1	18.5 ± 0.1	19.1 ± 0.1	19.4 ± 0.1
1.5000	18.1 ± 0.1	19.1 ± 0.1	19.7 ± 0.1	20.2 ± 0.1	20.5 ± 0.1	20.8 ± 0.1
1.8000	19.3 ± 0.1	20.3 ± 0.1	20.9 ± 0.1	21.3 ± 0.1	21.8 ± 0.1	22.0 ± 0.1
2.0000	20.2 ± 0.1	21.1 ± 0.1	21.6 ± 0.1	22.0 ± 0.1	22.4 ± 0.1	22.7 ± 0.1
2.2000	21.0 ± 0.0	21.9 ± 0.0	22.4 ± 0.0	22.6 ± 0.0	23.1 ± 0.0	23.3 ± 0.0
2.5000	22.0 ± 0.0	22.8 ± 0.0	23.2 ± 0.0	23.5 ± 0.0	23.9 ± 0.0	24.1 ± 0.0
2.8000	23.2 ± 0.0	23.9 ± 0.0	24.3 ± 0.0	24.5 ± 0.0	24.9 ± 0.0	25.1 ± 0.0
3.0000	23.8 ± 0.0	24.5 ± 0.0	25.0 ± 0.0	25.2 ± 0.0	25.4 ± 0.0	25.6 ± 0.0

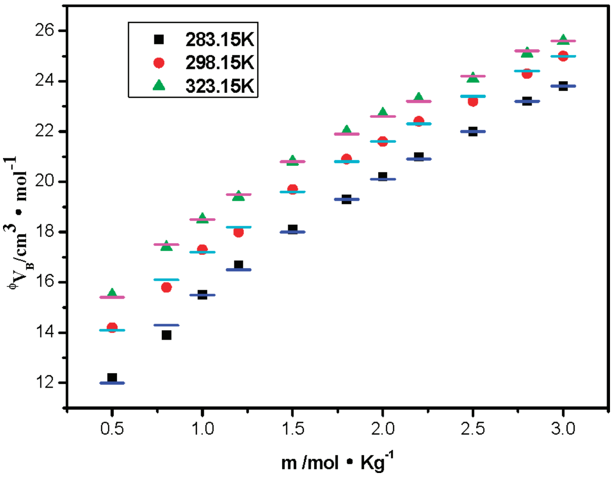

Figure 1. Plots of the apparent molar volume, ${}^{\varphi}V_B$, against the molality m. ▲, 283.15 K; ●, 298.15 K; ■, 323.15 K; —, values of fitting to Pitzer's equation.

of $VOSO_4$. The values of apparent molar volume calculated with eq 1 are listed in Table 2. Figure 1 is a plot of the apparent molar volume, ${}^{\varphi}V_B$, against the molality m. The apparent molar volume decreases as m increases.

3.4. Determination of $\bar{V}_B^0$. The apparent molar volume can be expressed in Pitzer's equation for volumetric properties:[18]

$$ {}^{\varphi}V_B = \bar{V}_B^0 + \nu|z_M z_X|(A_V/2b)\ln(1 + 1.2I^{1/2}) + 2\nu_M\nu_X RT\{mB_{MX}^V + (\nu_M z_M)m^2 C_{MX}^V\} \quad (3) $$

where Z_M and Z_X are the number of ionic charges of $VOSO_4$, for the positive and negative ions in electronic units, ν_M and ν_X are the numbers of ions of each type in the formula of the $VOSO_4$ and $\nu = \nu_M + \nu_X$, subscript M and X mean the cation and anion of $VOSO_4$, I is the total ionic strength given by $I = (1/2)\Sigma_i m_i z_i^2$, m is the molality of an ionic liquid, R is the gas constant, T are the thermodynamic temperatures, A_V has the same meaning as in literature,[16] and the parameter b is given the value 1.2 and taken as being temperature-independent. Pitzer's parameters B_{MX}^V account for short-range interactions between M and X; the third coefficient C_{MX}^V is for triple ion interactions and cannot be neglected at high concentrations ($m > 2.0$ $mol\cdot kg^{-1}$). Because aqueous solutions of $VOSO_4$ are 2−2 electrolytes and exit ionic association severely, Pitzer added the parameter $\beta_{MX}^{(2)V}$ to Pitzer's equation for a 2−2 type electrolyte. where B_{MX}^V is

Table 3. Values of Partial Molal Volume of $VOSO_4$ at Infinite Dilution $\overline{V}^0_B$ ($cm^3 \cdot mol^{-1}$), Pitzer's Parameters, Standard Deviations, and the Related Coefficients r for the Fitting to Equation 7 at (283.15 to 323.15) K

	T/K					
	283.15	293.15	298.15	303.15	313.15	323.15
$\overline{V}^0_B$	2.90	3.20	4.90	6.30	7.34	7.42
$10^4\ \beta^{(0)V}_{M,X}$	5.52	4.64	4.67	4.16	3.58	3.15
$10^3\ \beta^{(1)V}_{M,X}$	4.04	4.13	2.43	1.87	1.97	1.76
$10^2\ \beta^{(2)V}_{M,X}$	−2.85	−0.96	−0.0072	−2.73	−9.56	−11.32
10 s	1.72	1.11	1.82	1.53	1.04	0.79
r	0.99	0.99	0.99	0.99	0.99	0.99
A_V	1.643	1.793	1.875	1.962	2.153	2.372

Table 4. Values of the Partial Molar Volume $\overline{V}_B$ ($cm^3 \cdot mol^{-1}$) of $VOSO_4$ at Different Molalities and at Different Temperatures

m	T/K					
$mol \cdot kg^{-1}$	283.15	293.15	298.15	303.15	313.15	323.15
0.5000	12.2	14.1	15.6	14.8	14.1	14.2
0.8000	13.9	16.6	17.4	16.6	16.0	16.6
1.0000	15.6	18.5	19.2	18.1	17.5	18.1
1.2000	17.0	19.7	20.3	19.1	18.7	19.6
1.5000	18.7	22.0	22.7	21.3	20.8	22.0
1.8000	20.4	23.9	24.7	23.2	23.1	24.3
2.0000	21.8	25.3	26.1	24.5	24.4	25.9
2.2000	23.1	26.7	27.8	25.7	25.9	27.4
2.5000	24.9	28.6	29.9	27.7	28.1	29.7
2.8000	27.1	30.7	32.4	29.9	30.6	32.4
3.0000	28.5	32.1	34.3	31.5	32.2	33.9

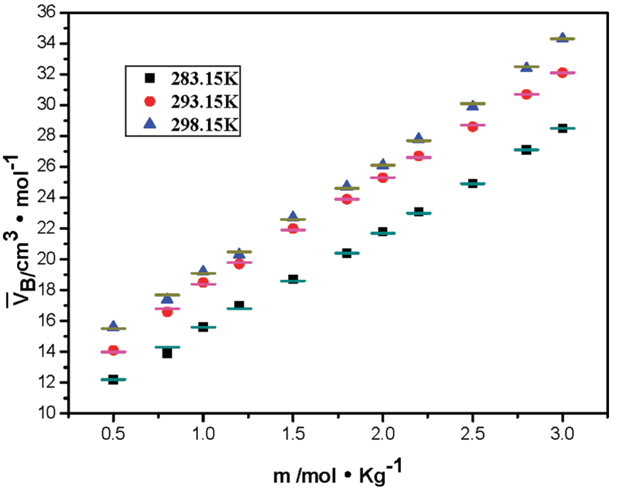

Figure 2. Plots of the partial molar volume, $\overline{V}_B$, against the molality m. ▲, 283.15 K; ●, 293.15 K; ■, 298.15 K; —, values of fitting to Pitzer's equation.

given by

$$B^V_{MX} = (\partial B^v_{MX}/\partial p)_{T,I} = \beta^{(0)V}_{MX} + g(x_1)\beta^{(1)V}_{MX} + g(x_2)\beta^{(2)V}_{MX} \qquad (4)$$

where $\beta^{(2)V}_{MX} = (\partial\beta^{(2)}{}_{MX}/\partial P)_{T,I}$, $\beta^{(2)}{}_{MX}$ is Pitzer's parameter for activity and osmotic coefficient and related to the association constant K by $\beta^{(2)}{}_{MX} = -K/2$. Therefore, $\beta^{(2)V}_{MX}$ is related to $-(\partial K/\partial P)_{T,I}$. In addition, the hydrolysis of $VO^{2+}(aq)$ in aqueous solution may occur: $VO^{2+}(aq) + H_2O \rightarrow VO(OH)^+(aq) + H^+(aq)$, but the hydrolysis constant (0.0000023) is too small compared with the association constant (300) of ion pair $[VOSO_4]^0$, so the effect of the hydrolysis on enthalpy of solution may be regardless.[11,19] In eq 4 $g(x)$ is defined by following eq 5, the parameter $\alpha_1 = 1.4$, and $\alpha_2 = 12$.

$$g(x) = 2[1 - (1 + x)\exp(-x)]/x^2$$
$$x = \alpha_1 I^{1/2} \text{ or } \alpha_2 I^{1/2} \qquad (5)$$

Therefore, rearranging eq 3 yields the working equation for aqueous solutions of $VOSO_4$:

$$Y = {}^{\varphi}V_B - 4(A_V/1.2)\ln(1 + 1.2I^{1/2}) \qquad (6)$$

$$Y = \overline{V}^0_B + 2RTm\beta^{(0)V}_{MX} + 2RTmg(\alpha_1 I^{1/2})\beta^{(1)V}_{MX} + 2RTmg(\alpha_2 I^{1/2})\beta^{(2)V}_{MX} \qquad (7)$$

The values of extrapolation function Y was calculated from ${}^{\varphi}V_B$ and other thermodynamic parameter by eq 6. Using the experimental fit of Y by eq 7, values of the Pitzer's parameters $\beta^{(0)V}_{MX}$, $\beta^{(1)V}_{MX}$, $\beta^{(2)V}_{MX}$, the standard deviation, s, and values of partial molal volume of $VOSO_4$ at infinite dilution, $\overline{V}^0_B$, were calculated and are also listed in Table 3. The very small standards deviations for the fitting to eq 7 implies that the volumetric properties of aqueous $VOSO_4$ can be predicted with Pitzer's model. In Figure 1 the line represents values of fitting to Pitzer's equation.

3.5. Partial Molal Volume. Partial molal volume, $\overline{V}_B$, is an important thermodynamic property of solution and is calculated conveniently from the apparent molal volume:

$$\overline{V}_B = {}^{\varphi}V_B + m(\partial {}^{\varphi}V_B/\partial m)_{P,T} \qquad (8)$$

where $m(\partial {}^{\varphi}V_B/\partial m)_{P,T}$ may be obtained by taking the partial derivative of eq 2 with respect to m at constant T and p. The values of thus calculated from eq 8 are listed in Table 4. Figure 2 is a plot of the partial molar volume, $\overline{V}_B$, against the molality m. From Figure 2, we can see that, at a given temperature, the partial molar volume of aqueous $VOSO_4$ follows a linear relation with m, and it increases with increasing molality.

4. CONCLUSIONS

The densities of aqueous solution of $VOSO_4$ were measured from (0.5 to 3) $mol \cdot kg^{-1}$ over the temperatures from (283.15 to 323.15) K. Values of apparent molar volume, partial molar volume, and the coefficient of thermal expansion of the solution were calculated based on the experimental data and Pitzer's model. The values of the apparent molar volume, ${}^{\varphi}V_B$, were fitted by the method of least-squares by Pitzer's equation for volumetric properties so that the partial molar volume of the solution at infinite dilution, $\overline{V}^0_B$, and Pitzer's parameters, were obtained. The small standard deviations of the fits, s, show that Pitzer's model is appropriate for representing the volumetric properties of aqueous solutions of $VOSO_4$.

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