

The *PVTx* properties of aqueous electrolyte solutions containing Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- and SO_4^{2-} under conditions of CO_2 capture and sequestration



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ABSTRACT

Based on the Pitzer electrolyte theory, an accurate density model of binary sulfate-water systems ($\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{K}_2\text{SO}_4\text{-H}_2\text{O}$ and $\text{MgSO}_4\text{-H}_2\text{O}$) has been established. Corresponding model parameters are obtained by the least square method. Compared with reliable experimental data of the $\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{K}_2\text{SO}_4\text{-H}_2\text{O}$ and $\text{MgSO}_4\text{-H}_2\text{O}$ systems, the average density deviations are 0.046%, 0.036%, 0.051%, 0.038%, respectively, which are within or close to experimental uncertainties. Combined a simple mixing rule with the density models of binary sulfate-water systems and previous chloride-water systems ($\text{LiCl}\text{-H}_2\text{O}$, $\text{NaCl}\text{-H}_2\text{O}$, $\text{KCl}\text{-H}_2\text{O}$, $\text{MgCl}_2\text{-H}_2\text{O}$ and $\text{CaCl}_2\text{-H}_2\text{O}$), a predictive density model is proposed for aqueous mixed electrolyte solutions containing Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- and SO_4^{2-} under conditions of CO_2 capture and sequestration (CCS) (generally less than 473 K and 300 bar). Compared to experimental density data of multi-component water-salt systems, the average density deviation of each system is usually less than 0.1%. The model can be used to calculate the apparent molar volume at infinite dilution and the volumetric properties of CO_2 -bearing multi-component electrolyte solutions under the CCS conditions. A computer code for the volumetric properties of multi-component aqueous electrolyte solutions can be obtained from the corresponding author.

1. Introduction

Thermodynamic modeling of aqueous electrolyte solutions has long been an endeavor for chemists (Anderko and Pitzer, 1993; Chou, 1987; Duan et al., 2008; Mao and Duan, 2008; Mao et al., 2015; Pitzer et al., 1984; Rogers and Pitzer, 1982). One of the most important thermodynamic properties is the density or volume (V) as a function of temperature (T), pressure (P), and composition (x) (*PVTx* properties). The *PVTx* properties of aqueous electrolyte solutions are widely used in geochemistry, such as the studies of fluid inclusions (Dugdale and Hagemann, 2001; Mao and Duan, 2008; Mao et al., 2010, 2015; Subias and Fernandez Nieto, 1995), fluid flow simulation (Henderson et al., 2005; Magueijo et al., 2005; Pruess and Garcia, 2002), and fluid-rock interactions (Hoshino et al., 2006; Huijzen et al., 2006; Mishra et al., 2003).

Recently, it was well accepted that CO_2 capture and sequestration (CCS) is a technically feasible and effective strategy to reduce the amount of worldwide CO_2 emissions to the atmosphere, and that

injecting CO_2 into deep saline formations (aquifers) is considered to be one of the best options for CCS (Bodnar et al., 2013). In order to simulate or predict the geochemical behavior (or dynamic mechanism) of formation water and water-rock interactions before and after the injection of CO_2 into deep saline formations, we must know the *PVTx* properties of CO_2 -free and CO_2 -bearing aqueous electrolyte solutions (Duan et al., 2008; Hu et al., 2007). However, the densities of CO_2 -bearing (or CO_2 -free) deep formation water (mainly containing Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- and SO_4^{2-}) are often unknown.

Since the beginning of last century, thousands of measurements from numerous laboratories have been reported for the densities or molar volumes of aqueous electrolyte solutions containing Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- and SO_4^{2-} , but most of volumetric data are for the binary water-salt systems. The density or volumetric data of the $\text{LiCl}\text{-H}_2\text{O}$, $\text{NaCl}\text{-H}_2\text{O}$, $\text{KCl}\text{-H}_2\text{O}$, $\text{MgCl}_2\text{-H}_2\text{O}$ and $\text{CaCl}_2\text{-H}_2\text{O}$ systems were reviewed in our previous work (Mao and Duan, 2008). The density or volumetric data of the $\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{K}_2\text{SO}_4\text{-H}_2\text{O}$ and $\text{MgSO}_4\text{-H}_2\text{O}$ systems are summarized in Table 1, and the $T\text{-}P\text{-}x$ range of

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Table 1
Literature data for the density (volume) of binary aqueous sulfate solutions.

References	T/K	P/bar	$m_{\text{salt}}/(\text{mol}\cdot\text{kg}^{-1})$	N	Quantity measured
The Li₂SO₄-H₂O system					
Pearce and Eckstrom (1937)	298.15	1.01	0.1 to 3.0944	10	ρ
Marks (1959)	293.15	1.01	0.100 to 2.500	7 (4)	ρ
Wirth and LoSurdo (1968)	273.150 to 318.272	1.01	1.3334	11	ρ
Cartón et al. (1994a)	282.75 to 323.15	1.01	2.9981 to 3.2009	6	ρ
Cartón et al. (1994b)	283.15 to 313.15	1.01	3.0272 to 3.1926	5	ρ
Cartón et al. (1995)	278.15 to 338.15	1.01	0.4057 to 3.1992	83	ρ
Abdulagatov and Azizov (2003)	295.35 to 573.15	0.123 to 396.5	0.0944 to 0.8850	251	ρ
Hervello and Sánchez (2007)	283.15 to 298.15	1.01	0.2142 to 3.0903	36	ρ
Silva et al. (2007)	278.15 to 318.15	1.01	0.4787 to 2.2740	16 (8)	ρ
Hu et al. (2016)	293.15 to 343.15	1.01	0.05 to 2.681	143 (143)	$\rho\cdot\rho_w$
The Na₂SO₄-H₂O system					
Trimble (1922)	298.15	1.01	0.06251 to 1.96269	8	ρ
Gibson (1927)	298.15, 303.15	1.01	0.06931 to 2.73366	17	ρ
Gibson (1934)	298.15	1.01	0.07112 to 2.73796	9	$\rho\cdot\rho_w$
Pearce and Eckstrom (1937)	298.15	1.01	0.1 to 1.9641	8	ρ
Vener and Thompson (1949)	298.15 to 373.15	1.01	1.95579 to 3.51021	17 (5)	ρ
Vener and Thompson (1950)	305.53	1.01	3.51021	1 (1)	ρ
Marks (1959)	293.15	1.01	0.100 to 1.000	5 (2)	ρ
Dunn (1966)	298.15	1.01	0.84236 to 0.19690	2	ρ
Fabuss et al. (1966)	298.15 to 448.15	1.01	0.01 to 0.15	32	ρ
Ellis (1968)	323.15 to 473.15	20	0.05 to 1	35	ρ
Korosi and Fabuss (1968)	298.15 to 423.15	1.01	0.0333 to 1.2026	28	ρ
Wirth and LoSurdo (1968)	273.15 to 318.407	1.01	1.3334	12	ρ
Millero and Knox (1973)	273.15 to 323.15	1.01	0.002226 to 1.00476	52	$\rho\cdot\rho_w$
Chen et al. (1977)	273.15 to 323.15	99.90 to 901.70	0.00899 to 0.3335	115	V_ϕ
Millero et al. (1977b)	298.15	1.01	0.09962 to 1.00034	10	$\rho\cdot\rho_w$
Chen et al. (1980)	273.15 to 308.15	1.01	0.00259 to 0.72018	81	$\rho\cdot\rho_w$
Chen and Millero (1981)	273.15, 298.15	100 to 1000	0.0671 to 0.2411	40	$\rho\cdot\rho_w$
Lo Surdo et al. (1982)	288.15 to 318.15	1.01	0.05203 to 1.62488	65	$\rho\cdot\rho_w$
Fleischmann and Mersmann (1984)	313.15	1.01	0.03520 to 3.39280	15	ρ
Isono (1984)	288.15 to 328.15	1.01	0.050 to 1.500	44	ρ
Connaughton et al. (1986)	308.15 to 368.15	1.01	0.10100 to 2.06783	67	$\rho\cdot\rho_w$
Phutela and Pitzer (1986a)	273.15 to 475.81	1.0 to 102.5	0.01 to 1.00	460	ρ, V_ϕ
Quintana et al. (1986)	288.15 to 308.15	1.01	0.00100 to 0.05359	15	ρ
Saluja et al. (1992)	297.19 to 371.82	6	0.00969 to 1.53238	43	ρ
Sánchez et al. (1994)	288.15 to 308.15	1.01325	0.00100 to 0.20308	42	ρ
Obšil et al. (1996)	298.15 to 573.15	100, 300	0.025 to 0.50	80	V_ϕ
Obšil et al. (1997)	298.18 to 572.73	98.7 to 307.0	0.004882 to 1.0032	134	$\rho\cdot\rho_w$
Okorafor (1999)	283.15 to 323.15	1.01	0.63558 to 3.26014	5 (3)	ρ
Azizov and Akhundov (2000)	291.31 to 573.15	24.4 to 397.9	0.088 to 1.116	200	ρ
Magalhães et al. (2002)	298.15	1.01	0.01008 to 1.8871	13	ρ
Kiepe et al. (2003)	283.15 to 343.15	1.01	0.500 to 2.254	17	ρ, V_ϕ
Hervello and Sánchez (2007)	283.15 to 298.15	1.01	0.1002 to 1.8476	24	ρ
Banipal et al. (2008)	288.15 to 318.15	1.01	0.49850, 0.99705	8	ρ
Iulian et al. (2008)	298.15	1.01	0.14368 to 1.76007	11	ρ
Zhuo et al. (2008)	298.15	1.01	0.09205 to 0.50013	5	ρ
Apelblat et al. (2009)	278.15 to 333.15	1.01	0.10 to 1.00	168	ρ
Liu and Ren (2009)	298.15	1.01	0.2000 to 1.2001	9	ρ
Urrjola et al. (2011)	298.15	1.01	0.450 to 1.954	3	ρ
Ghafri et al. (2013)	298.11 to 473.02	11 to 686	0.783 to 1.502	126	ρ
Mazurek and Drużyński (2014)	293.15 to 323.15	1	1.37 to 3.42	4 (1)	ρ
Zezin et al. (2015)	298.15 to 523.15	1 to 700	0.09999 to 1.21083	98	$\rho\cdot\rho_w$
The K₂SO₄-H₂O system					
Trimble (1922)	298.15	1.01	0.04395 to 0.69123	6	ρ
Adams (1932)	298.15	1.01	0.02881 to 0.63792	12	ρ
Jones and Ray (1937)	298.15	1.01	0.00020 to 1.12592	12 (4)	ρ
Pearce and Eckstrom (1937)	298.15	1.01	0.1 to 0.6889	5	ρ
Wirth (1937)	298.15	1.01	0.01488 to 0.36112	10	$\rho\cdot\rho_w$
Jones and Colvin (1940)	273.15, 298.15	1.01	0.00050 to 0.51191	24	ρ
Marks (1959)	293.15	1.01	0.100 to 0.507	4 (1)	ρ
Dunn (1966)	298.15	1.01	0.21060 to 0.51175	3	ρ
Ellis (1968)	323.15 to 473.15	20	0.05 to 0.5	28	ρ
Millero and Knox (1973)	273.15, 323.15	1.01	0.001994 to 0.70706	42	$\rho\cdot\rho_w$
Millero et al. (1977b)	298.15	1.01	0.09954 to 0.50094	5	$\rho\cdot\rho_w$
Ishii and Fujita (1978)	303.15 to 333.37	1.01	0.71437 to 1.02467	6 (6)	ρ
Hovey et al. (1988)	298.15	1.01	0.03623 to 0.49662	9	V_ϕ
Mydlarz et al. (1989)	293.15 to 323.15	1.01	0.64217 to 0.94805	4	ρ
Dedick et al. (1990)	278.15 to 368.15	1.01	0.01015 to 0.65018	103 (6)	$\rho\cdot\rho_w$
Mydlarz and Jones (1990)	288.15 to 308.15	1.01	0.58651 to 0.79884	3	ρ
Saluja et al. (1992)	297.19 to 371.82	6	0.01042 to 0.40209	23	ρ
Obšil et al. (1996)	298.15 to 573.15	100, 300	0.025 to 0.50	80	V_ϕ
Obšil et al. (1997)	298.20 to 572.75	98.8 to 306.6	0.004834 to 0.5052	127	$\rho\cdot\rho_w$

(continued on next page)

Table 1 (continued)

References	T/K	P/bar	$m_{\text{salt}}/(\text{mol}\cdot\text{kg}^{-1})$	N	Quantity measured
Azizov (1998)	293.61 to 573.15	22.3 to 389.2	0.0658 to 0.4070	200	ρ
Nikam et al. (1999)	298.15 to 313.15	1.01	0.00803 to 0.10144	28 (28)	ρ
Taboada et al. (2002)	298.15 to 318.15	1.01	0.69784 to 0.90239	3	ρ
Hervello and Sánchez (2007)	283.15 to 298.15	1.01	0.0427 to 0.7110	32	ρ
Jimenez et al. (2009)	298.15 to 303.15	1.01	0.6980 to 0.6982	5	ρ
The $\text{MgSO}_4\text{-H}_2\text{O}$ system					
Jones and Ray (1942)	298.15	1.01	0.00010 to 2.03793	14	ρ
Marks (1959)	293.15	1.01	0.100 to 1.792	6 (1)	ρ
Fabuss et al. (1966)	298.15 to 448.15	1.01	0.00972 to 0.29165	32	ρ
Korosi and Fabuss (1968)	298.15 to 423.15	1.01	0.0250 to 0.9032	28	ρ
Millero and Knox (1973)	273.15, 323.15	1.01	0.002439 to 0.89033	37	$\rho\cdot\rho_w$
Chen et al. (1977)	273.15 to 323.15	196.62 to 995.33	0.01985 to 0.2503	68	V_ϕ
Millero et al. (1977b)	298.15	1.01	0.053890 to 1.001120	12	$\rho\cdot\rho_w$
Chen et al. (1980)	273.15 to 308.15	1.01	0.00099 to 1.48251	79	$\rho\cdot\rho_w$
Chen and Millero (1981)	273.15, 298.15	100 to 1000	0.0504, 0.1808	40	$\rho\cdot\rho_w$
Lo Surdo et al. (1982)	278.15 to 318.15	1.01	0.03775 to 2.39917	113	$\rho\cdot\rho_w$
Connaughton et al. (1986)	308.15 to 368.15	1.01	0.20699 to 2.83834	63	$\rho\cdot\rho_w$
Phutela and Pitzer (1986a)	273.15 to 475.77	1.0 to 104.1	0.01 to 0.2503	369	ρ, V_ϕ
Phutela and Pitzer (1986b)	298.15	20	0.1679 to 2.1860	10	ρ/ρ_w
Quintana et al. (1986)	288.15 to 308.15	1.01	0.00100 to 0.04965	15	ρ
Sánchez et al. (1994)	288.15 to 308.15	1.01	0.00100 to 0.20242	42	ρ
Motin (2004)	308.15 to 323.15	1.01	0.0625 to 1.0000	15(15)	V_ϕ
Abdulagatov et al. (2007)	288.57 to 398.19	1.01 to 305.00	0.084 to 2.5350	69	ρ
Hervello and Sánchez (2007)	283.15 to 298.15	1.01	0.1933 to 3.0440	31	ρ
Zhuo et al. (2008)	298.15	1.01	0.05000 to 0.50000	6	ρ

Notes: T is temperature; P is pressure; m_{salt} is the molality of sulfate; N is the number of datum points; ρ is the density of aqueous sulfate solution; ρ_w is the density of pure water; V_ϕ is the apparent molar volume of sulfate. The number in the parentheses after N are the number of datum points not used in the parameterization.

these experimental data for each sulfate-water system is shown in Fig. 1S (Supporting Material). However, these experimental data are still scattered and only cover a limited $T\text{-}P\text{-}x$ space, inconvenient to use. Hence theorists have devoted extensive efforts to modeling the volumetric properties of these aqueous electrolyte solutions so as to interpolate between the data points or extrapolate beyond the data range.

Over the last several decades, quite a few models have been reported to calculate the densities (or volumes) of aqueous sulfate solutions. Some competitive models of binary sulfate-water systems ($\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{K}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{MgSO}_4\text{-H}_2\text{O}$) (Abdulagatov and Azizov, 2003; Connaughton et al., 1986; Dedick et al., 1990; Obšil et al., 1996; Phutela and Pitzer, 1986a) are commented here. Abdulagatov and Azizov (2003) presented an empirical model with thirty-six parameters to calculate the density of $\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$ system up to 573 K and 400 bar with an average deviation of 0.02% from experimental data, which is within experimental uncertainties, but the valid salinity of that model is limited to 1 $\text{mol}\cdot\text{kg}^{-1}$. Dedick et al. (1990) and Obšil et al. (1996) developed respectively a volumetric model based on the Pitzer electrolyte theory for aqueous K_2SO_4 solution. However, Dedick et al. (1990) did not take into account the effect of pressure on the solution density. The apparent molar volumes at infinite dilution calculated from the model of Obšil et al. (1996) deviate significantly from experimental data at high temperatures, e.g., its maximum deviation of apparent molar volume are high up to 10 $\text{cm}^3\cdot\text{mol}^{-1}$ at 573 K. Connaughton et al. (1986) developed a volumetric model based on the Pitzer electrolyte theory for the $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ and $\text{MgSO}_4\text{-H}_2\text{O}$ systems, respectively, but equations of the Pitzer parameters involve no pressure terms, so the model cannot calculate the densities at higher pressures as the model of Dedick et al. (1990). Phutela and Pitzer (1986a) established a $PVTx$ model based on the Pitzer theory for the $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ and $\text{MgSO}_4\text{-H}_2\text{O}$ systems, but the maximal valid temperature and pressure of the model are limited to 473 K and 100 bar, and the volumetric deviations are also big in the entire $P\text{-}T$ range.

In order to overcome the deficiencies of the previous models, here we first present an improved and universal model to calculate the $PVTx$ properties (or densities) of the binary systems ($\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{K}_2\text{SO}_4\text{-H}_2\text{O}$ and $\text{MgSO}_4\text{-H}_2\text{O}$) within or close to experimental

uncertainties under conditions of CCS (generally less than 473 K and 300 bar). Then combined a simple mixing rule with the density models of binary sulfate-water systems and previous chloride-water systems ($\text{LiCl}\text{-H}_2\text{O}$, $\text{NaCl}\text{-H}_2\text{O}$, $\text{KCl}\text{-H}_2\text{O}$, $\text{MgCl}_2\text{-H}_2\text{O}$ and $\text{CaCl}_2\text{-H}_2\text{O}$) of Mao and Duan (2008), a predictive density model is proposed for aqueous mixed electrolyte solutions containing Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- and SO_4^{2-} . Finally, the density model is used to calculate the apparent molar volumes of sulfate in water at infinite dilution and the densities of CO_2 -bearing aqueous electrolyte solutions with the approach of Mao et al. (2010).

2. Density model of binary aqueous sulfate solutions as a function of temperature, pressure and composition

Based on the excess Gibbs theory of aqueous electrolyte solutions of Pitzer (1973), we found that the following model can accurately correlate the $PVTx$ properties of binary aqueous sulfate solutions:

$$\rho_{\text{sol}} = \frac{(1000 + mM_s)\rho_{\text{H}_2\text{O}}}{1000 + mV_\phi\rho_{\text{H}_2\text{O}}} \quad (1)$$

$$V_\phi = V_\phi^0 + v|z_+z_-|A_V h(I) + 2v_+v_-mRT(B_{\text{MX}}^V + v_+z_+mC_{\text{MX}}^V) \quad (2)$$

$$h(I) = \frac{\ln(1 + bI^{0.5})}{2b} \quad (3)$$

$$I = \frac{1}{2} \sum_i m_i z_i^2 \quad (4)$$

where ρ_{sol} and $\rho_{\text{H}_2\text{O}}$ are the density of solution and pure water in $\text{g}\cdot\text{cm}^{-3}$, respectively. m is the molality of salt (Li_2SO_4 , Na_2SO_4 , K_2SO_4 , or MgSO_4) in $\text{mol}\cdot\text{kg}^{-1}$. M_s is the molar mass of salt in $\text{g}\cdot\text{mol}^{-1}$. V_ϕ^0 is the apparent molar volume in $\text{cm}^3\cdot\text{mol}^{-1}$ and V_ϕ^0 is the apparent molar volume of sulfate at infinite dilution in the same unit. z_+ and z_- are the charge of cation and anion, respectively. v_+ and v_- are the number of cation and anion charge, respectively, and $v = v_+ + v_-$. A_V is the volumetric Debye-Hückel limiting law slope. I is the ionic strength. B_{MX}^V and C_{MX}^V are the second and third virial coefficients of salt MX (where M and X denote cation and anion, respectively). $R = 83.14472$

$\text{cm}^3 \cdot \text{bar} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ and $b = 1.2 \text{ kg}^{0.5} \cdot \text{mol}^{-0.5}$. In this work, $\rho_{\text{H}_2\text{O}}$ is calculated from the Gibbs free energy model of IAPWS97 (Wagner et al., 2000), and A_V is calculated from the model of Bradley and Pitzer (1979) (see Appendix A).

According to Krumgalz et al. (1996), B_{MX}^V has a general form as

$$B_{\text{MX}}^V = \beta_{\text{MX}}^{(0)V} + \beta_{\text{MX}}^{(1)V} g(\alpha_1 I^{0.5}) + \beta_{\text{MX}}^{(2)V} g(\alpha_2 I^{0.5}) \quad (5)$$

$$g(\alpha_i I^{0.5}) = \frac{2}{(\alpha_i I^{0.5})^2} [1 - (1 + \alpha_i I^{0.5}) \exp(-\alpha_i I^{0.5})] \quad (6)$$

where $\alpha_1 = 2.0 \text{ kg}^{0.5} \cdot \text{mol}^{-0.5}$ and $\beta_{\text{MX}}^{(2)V} = 0$ are for the 1:1, 1:2 and 2:1 electrolytes, and $\alpha_1 = 2.0 \text{ kg}^{0.5} \cdot \text{mol}^{-0.5}$ and $\alpha_2 = 12 \text{ kg}^{0.5} \cdot \text{mol}^{-0.5}$ are for the 2:2 electrolytes. For binary chloride-water systems (Mao and Duan, 2008), $\beta_{\text{MX}}^{(1)V}$ can be set as zero. However, for binary $\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{K}_2\text{SO}_4\text{-H}_2\text{O}$ and $\text{MgSO}_4\text{-H}_2\text{O}$ systems, $\beta_{\text{MX}}^{(1)V}$ cannot be omitted and should be added to reduce the volumetric deviation. $\beta_{\text{MX}}^{(2)V}$ here is set as zero because it has little effect on the density of $\text{MgSO}_4\text{-H}_2\text{O}$ system within the $T\text{-}P$ range of experimental data available.

V_ϕ^0 , $\beta_{\text{MX}}^{(0)V}$, $\beta_{\text{MX}}^{(1)V}$ and C_{MX}^V in above equations are a function of T and/or P , and corresponding parameters can be obtained by fitting to experimental volumetric data with a least square approach. However, because V_ϕ^0 changes rapidly at high temperature and displays a complex behavior with considerable curvature at low temperature, an indirect fitting method similar to that of Rogers and Pitzer (1982) is adopted in this work.

Assuming 1 kg water contains m mole sulfate, the solution volume is $V(m)$, then

$$V_\phi = \frac{V(m) - 1000/\rho_{\text{H}_2\text{O}}}{m} \quad (7)$$

$$\begin{aligned} \frac{V(m)}{m} - \frac{1000}{m\rho_{\text{H}_2\text{O}}} &= V_\phi^0 + v|z_+z_-|A_V h(I_m) \\ &+ 2v_+v_-mRT [\beta_{\text{MX}}^{(0)V} + \beta_{\text{MX}}^{(1)V} g(\alpha_1 I_m^{0.5})] \\ &+ 2v_+^2v_-z_+m^2RTC_{\text{MX}}^V \end{aligned} \quad (8)$$

Assuming 1 kg water contains m_r (reference molality) mole sulfate, the solution volume is $V(m_r)$, then

$$\begin{aligned} \frac{V(m_r)}{m_r} - \frac{1000}{m_r\rho_{\text{H}_2\text{O}}} &= V_\phi^0 + v|z_+z_-|A_V h(I_m) \\ &+ 2v_+v_-m_rRT [\beta_{\text{MX}}^{(0)V} + \beta_{\text{MX}}^{(1)V} g(\alpha_1 I_{m_r}^{0.5})] \\ &+ 2v_+^2v_-z_+m_r^2RTC_{\text{MX}}^V \end{aligned} \quad (9)$$

Eq. (8) subtracts Eq. (9), and the following equation can be obtained:

$$\begin{aligned} \frac{V(m)}{m} &= \frac{V(m_r)}{m_r} + \frac{1000}{\rho_{\text{H}_2\text{O}}} \left(\frac{1}{m} - \frac{1}{m_r} \right) \\ &+ v|z_+z_-|A_V [h(I_m) - h(I_{m_r})] \\ &+ 2v_+v_-RT \{ \beta_{\text{MX}}^{(0)V} (m - m_r) + \beta_{\text{MX}}^{(1)V} [mg(\alpha_1 I_m^{0.5}) - m_r g(\alpha_1 I_{m_r}^{0.5})] \} \\ &+ 2v_+^2v_-z_+RTC_{\text{MX}}^V (m^2 - m_r^2) \end{aligned} \quad (10)$$

Combining Eqs. (5), (6) and (10) with $V(m) = (1000 + mM_s)/\rho_{\text{sol}}$, then the following equation is acquired:

$$\begin{aligned} \frac{1000 + mM_s}{m\rho_{\text{sol}}} &= \frac{V(m_r)}{m_r} + \frac{1000}{\rho_{\text{H}_2\text{O}}} \left(\frac{1}{m} - \frac{1}{m_r} \right) + v|z_+z_-|A_V [h(I_m) - h(I_{m_r})] \\ &+ 2v_+v_-RT (m - m_r) \beta_{\text{MX}}^{(0)V} \\ &+ 4v_+v_-RT \{ m[1 - (1 + \alpha_1 I_m^{0.5}) \exp(-\alpha_1 I_m^{0.5})]/(\alpha_1^2 I_m^2) \\ &- m_r[1 - (1 + \alpha_1 I_{m_r}^{1/2}) \exp(-\alpha_1 I_{m_r}^{1/2})]/(\alpha_1^2 I_{m_r}) \} \beta_{\text{MX}}^{(1)V} \\ &+ 2v_+^2v_-z_+RT (m^2 - m_r^2) C_{\text{MX}}^V \end{aligned} \quad (11)$$

Eqs. (1)–(11) form the density model, which correlates temperature, pressure, density and molality of salts. The density is a reciprocal of volume, thus Eqs. (1)–(11) can be called the $PVTx$ model of binary water-salt solutions. Since $V(m_r)$ is a function of T and P as $\beta_{\text{MX}}^{(0)V}$ and

$\beta_{\text{MX}}^{(1)V}$, the work left is to find the optimal m_r and a universal function for $V(m_r)$, $\beta_{\text{MX}}^{(0)V}$, $\beta_{\text{MX}}^{(1)V}$ and C_{MX}^V . After numerous tries, the following equations are found to satisfy the requirement.

$$V(m_r) = c_1 + c_2 T + c_3 T^2 + c_4 T^3 + c_5 P \quad (12)$$

$$\begin{aligned} \beta_{\text{MX}}^{(0)V} &= c_6 + c_7 T + \frac{c_8}{647 - T} + \frac{c_9}{T - 227} \\ &+ P \left(c_{10} + c_{11} T + c_{12} T^2 + \frac{c_{13}}{647 - T} + \frac{c_{14}}{T - 227} \right) \end{aligned} \quad (13)$$

$$\begin{aligned} \beta_{\text{MX}}^{(1)V} &= c_{15} + c_{16} T + c_{17} T^2 + \frac{c_{18}}{647 - T} \\ &+ P \left(c_{19} + c_{20} T + \frac{c_{21}}{647 - T} + \frac{c_{22}}{T - 227} \right) \end{aligned} \quad (14)$$

$$C_{\text{MX}}^V = c_{23} + \frac{c_{24}}{647 - T} \quad (15)$$

The parameters (c_1 – c_{24}) are evaluated from a large number of experimental data as will be discussed later.

3. Review of density data of binary aqueous sulfate solutions

The densities (or volumes) of the $\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{K}_2\text{SO}_4\text{-H}_2\text{O}$ and $\text{MgSO}_4\text{-H}_2\text{O}$ systems were measured over a wide $T\text{-}P\text{-}m_{\text{salt}}$ range, and thousands of data have been reported (Table 1). In this study, we focus our interest in the temperature range below 573 K.

The $\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$ system: 9 datum sets (568 density measurements in total) have been reported for this system, covering a $T\text{-}P\text{-}m_{\text{salt}}$ range of 273–573 K, 1–400 bar and 0–3.2 mol·kg⁻¹. Abdulagatov and Azizov (2003) made the extensive density measurements for this system. Most of data are consistent with each other except some data of Silva et al. (2007) (Fig. 1a). Therefore, 413 datum points are included in the parameterization. The newly density data of Hu et al. (2016) (143 datum points) are not used in the fitting but to verify the validity of this model.

The $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ system: The density (volume) measurements of aqueous Na_2SO_4 solution are the most extensive of the four systems. 41 datum sets (2128 datum points in total) have been found for this system, covering a $T\text{-}P\text{-}m_{\text{salt}}$ range of 273–573 K, 1–1000 bar and 0–3.5 mol·kg⁻¹. Part data of Marks (1959) and Mazurek and Drużyński (2014) (Fig. 1b) deviate obviously from others in the same $T\text{-}P\text{-}m_{\text{salt}}$ range. So apart from some data of Marks (1959) and Mazurek and Drużyński (2014), 2116 data are used in the parameterization.

The $\text{K}_2\text{SO}_4\text{-H}_2\text{O}$ system: The density (volume) measurements of aqueous K_2SO_4 solutions are not as extensive as those of the $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ system. 24 datum sets (774 datum points in total) have been found for this system, which cover a $T\text{-}P\text{-}m_{\text{salt}}$ range of 273–573 K, 1–400 bar and 0–1 mol·kg⁻¹. Some data of Jones and Ray (1937) (Fig. 1c) deviate obviously from other data at the same conditions. Therefore, apart from data of Jones and Ray (1937), 729 data are used to optimize the model parameters.

The $\text{MgSO}_4\text{-H}_2\text{O}$ system: In total 19 datum sets (1049 datum points) have been found for this system, covering a $T\text{-}P\text{-}m_{\text{salt}}$ range of 273–475 K, 1–300 bar and 0–3 mol·kg⁻¹. Most data are consistent with each other except for some data of Motin (2004) (Fig. 1d). Therefore, all experimental data but those of Motin (2004) are used in the parameterization (1033 datum points).

4. Parameterization and comparison with experimental data of binary aqueous sulfate solutions

The parameters (c_1 – c_{24}) of Eqs. (12)–(15) are fitted directly to the experimental density data mentioned above by the least-square regression with the same weight. Table 2 lists the optimized parameters. For the $\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{K}_2\text{SO}_4\text{-H}_2\text{O}$ and $\text{MgSO}_4\text{-H}_2\text{O}$ systems, number of parameters is 18, 15, 9 and 12, respectively (Table 3). The

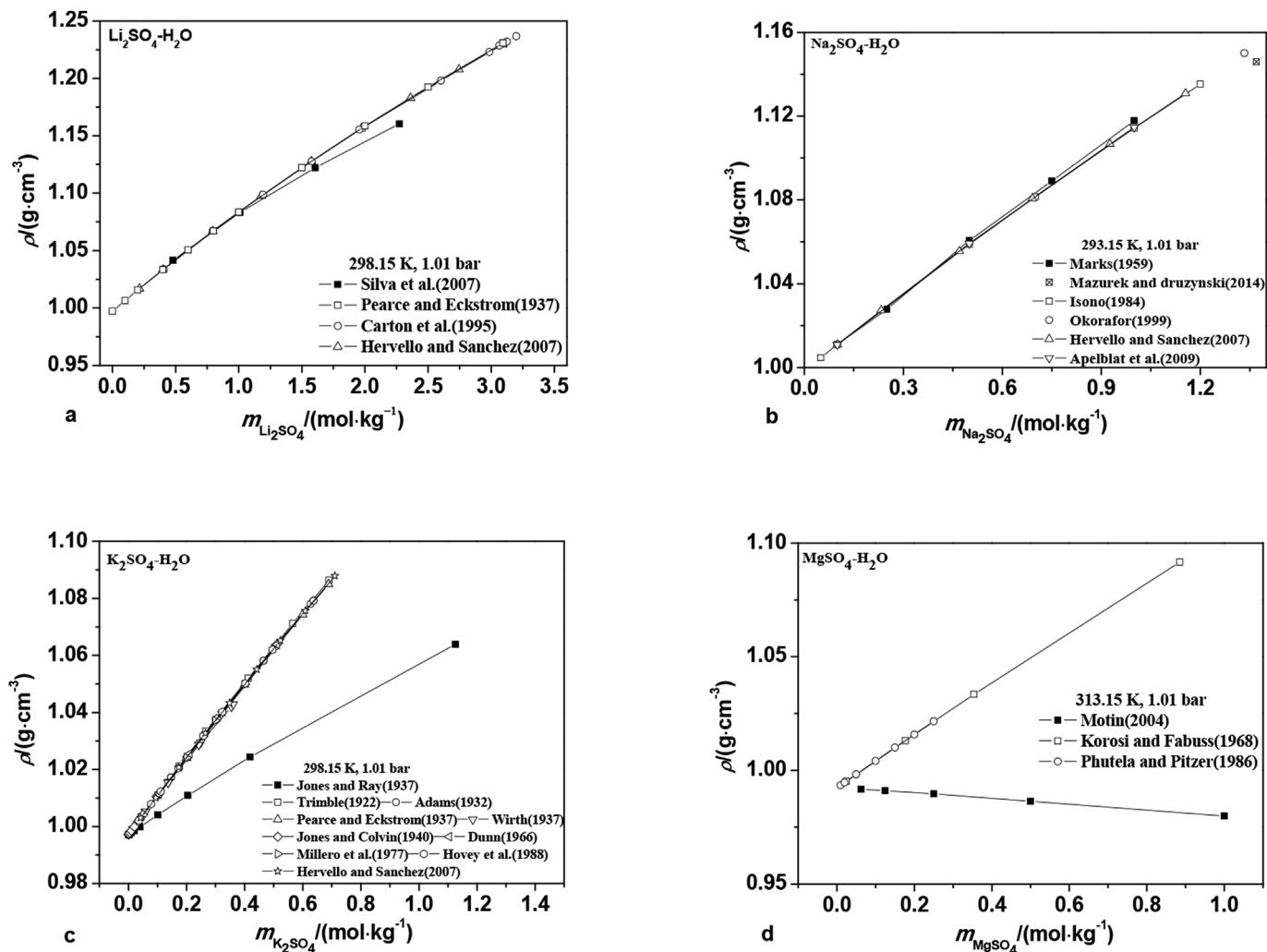


Fig. 1. Some experimental data at the same temperature and pressure: ρ is density and m is molality.

Table 2
Parameters (c_1 – c_{24}) in Eqs. (12)–(15).

Parameters	Systems			
	$\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$	$\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$	$\text{K}_2\text{SO}_4\text{-H}_2\text{O}$	$\text{MgSO}_4\text{-H}_2\text{O}$
c_1	1.5418532E+03	9.9663759E+02	9.3045852E+02	9.5835279E+02
c_2	-3.5636643E+00	4.2091252E-01	5.0138960E-01	3.1204276E-01
c_3	8.3761250E-03	-	-	-
c_4	-4.5369216E-06	-	-	-
c_5	-4.7575936E-02	-4.7932011E-02	-3.1984451E-02	-4.4367886E-02
c_6	-3.0902907E-04	-2.3358147E-05	3.2169705E-04	-3.8269517E-05
c_7	8.6575960E-07	2.9258506E-07	-	1.2604162E-06
c_8	-	-	-7.2720305E-02	-1.3437478E-01
c_9	5.1686731E-03	-2.8689383E-02	-8.4771983E-04	5.9556710E-03
c_{10}	1.3883660E-07	3.5276676E-03	-3.2587919E-07	1.3261864E-06
c_{11}	-8.8907364E-10	1.6737932E-07	-	-6.4960244E-09
c_{12}	-	-1.0034145E-09	-	-
c_{13}	4.4917335E-05	-	8.8588004E-05	2.8500877E-04
c_{14}	-	5.6700614E-05	-	-2.0109244E-05
c_{15}	1.3801983E-03	-4.8130211E-06	-	9.3289922E-04
c_{26}	4.0626490E-06	-1.8982471E-03	-	-
c_{17}	-	8.4674743E-06	-	-
c_{18}	-8.6340605E-01	-	-	-
c_{19}	-	-3.4496965E-01	-	-
c_{20}	-	4.4402252E-02	-	-
c_{21}	4.2499248E-04	-	-	-
c_{22}	-2.3850383E-04	-	-	-
c_{23}	7.4102690E-06	-	-	-
c_{24}	-2.7360538E-03	-	-1.4759992E-03	-

Table 3
T, P, m range and number of parameters for the model.

Systems	T	P	m_{salt}	N	Salt	M_s	m_r
	K	bar	$\text{mol}\cdot\text{kg}^{-1}$			$\text{g}\cdot\text{mol}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$
$\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$	273 to 573	1 to 300	0 to 1.5	18	Li_2SO_4	109.938	3.5
$\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$	273 to 573	1 to 500	0 to 2.0	15	Na_2SO_4	142.036	3.5
$\text{K}_2\text{SO}_4\text{-H}_2\text{O}$	273 to 573	1 to 400	0 to 1.0	9	K_2SO_4	174.252	1.5
$\text{MgSO}_4\text{-H}_2\text{O}$	273 to 475	1 to 300	0 to 2.5	12	MgSO_4	120.361	3.3

Notes: T is temperature; P is pressure; m_{salt} is the molality of sulfates; N is the number of parameters; M_s is the molar mass of salt; m_r is the reference molality.

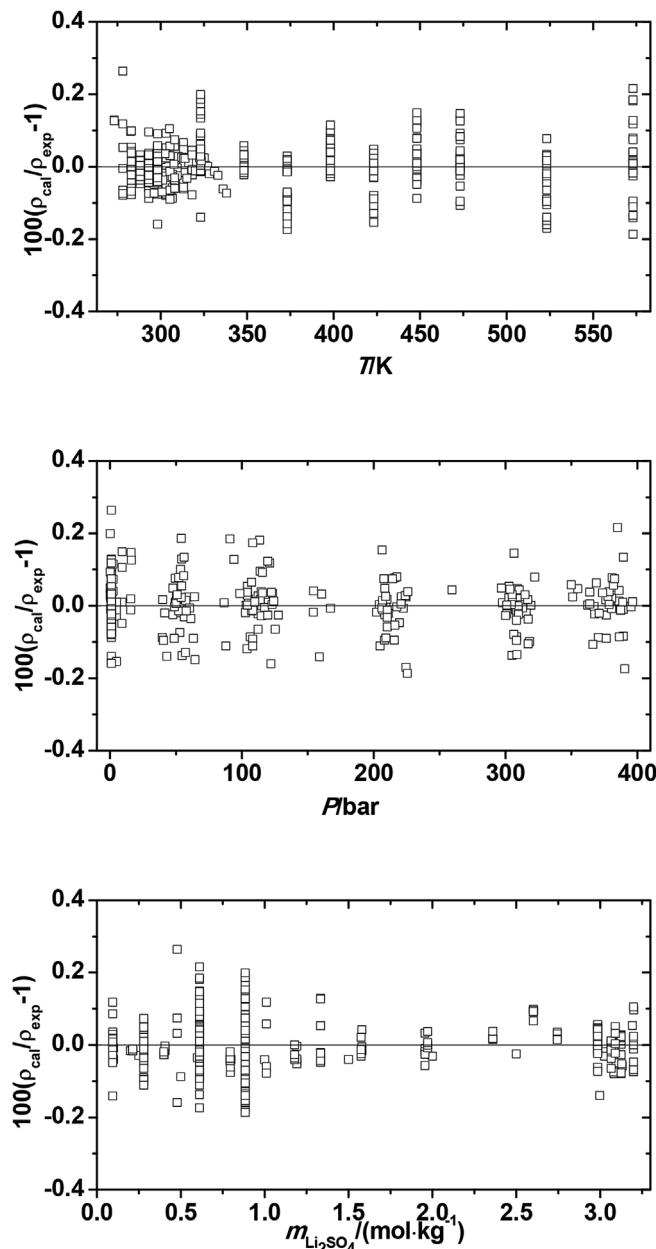


Fig. 2. Density deviations of this model from experimental data of the $\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$ system: Experimental data are from Table 1S (Supporting Material), and T , P , m , ρ_{cal} and ρ_{exp} denote temperature, pressure, molality, calculated density, and experimental density, respectively, which denote the same meanings in the following figures.

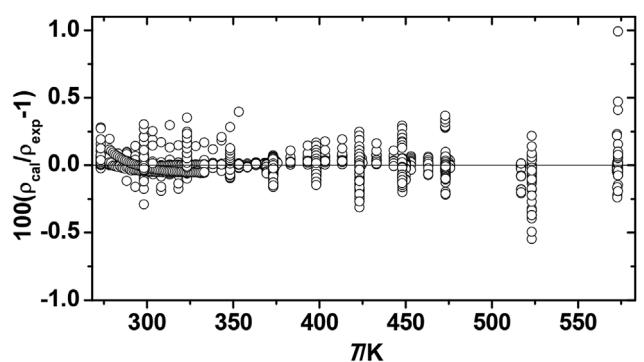


Fig. 3. Density deviations of this model from experimental data of the $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ system: Experimental data are from Table 1S (Supporting Material).

optimal m_r and valid T - P - m_{salt} range for each binary system are also listed in Table 3. The average density deviations from extensive experimental data in the above T - P - m_{salt} range for the $\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{K}_2\text{SO}_4\text{-H}_2\text{O}$ and $\text{MgSO}_4\text{-H}_2\text{O}$ systems are 0.046%, 0.036%, 0.051% and 0.038%, respectively.

The average and maximal deviations of calculated densities from each set of data are compiled in Table 1S (Supporting Material) in the **Supplementary data.docx** file (see Appendix B). Figs. 2–5 show the density deviations between experimental and predicted results for the $\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{K}_2\text{SO}_4\text{-H}_2\text{O}$ and $\text{MgSO}_4\text{-H}_2\text{O}$ systems, respectively. As can be seen from Figs. 2–5, most experimental data are reproduced by this model with deviations of less than 0.1%. It should be noted that the PVT_x data of the $\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$ system from Hu et al. (2016), which are not used in the parameterization, are in good agreement with this model, with an average density deviation of 0.022% (Table 1S). Figs. 2S–3S (Supporting Material) indicate that the calculated apparent molar volumes of Li_2SO_4 , Na_2SO_4 , K_2SO_4 and MgSO_4 in water are also in agreement with experimental data.

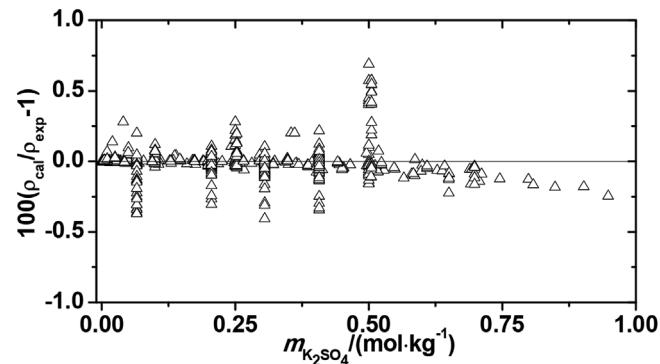
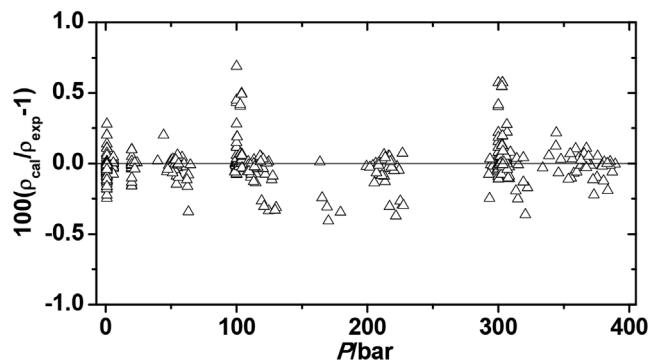
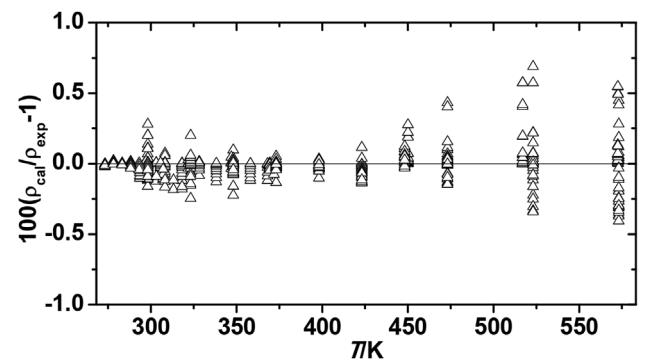


Fig. 4. Density deviations of this model from experimental data of the $\text{K}_2\text{SO}_4\text{-H}_2\text{O}$ system: Experimental data are from Table 1S (Supporting Material).

5. Prediction of the densities of multi-component aqueous electrolyte solutions containing Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- and SO_4^{2-}

Although experimental measurements began from the early last century, the $PVTx$ data of the multi-component aqueous electrolyte solutions containing Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- and SO_4^{2-} are still insufficient. The sources of volumetric data of each ternary water-salt system involving the above ions are listed in Table 4, from which it can be seen that quite a few ternary systems have no volumetric data, and most data are of 298.15 K and atmospheric pressure. Densities of ternary systems at high temperatures and pressures were only measured in recent years (Ghafri et al., 2012; Zezin et al., 2014a, 2014b, 2015). Density data of the multi-component (higher than ternary) aqueous electrolyte solutions are rare. According to the Pitzer electrolyte theory,

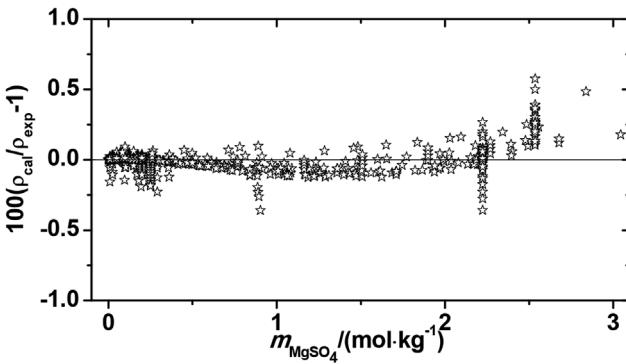
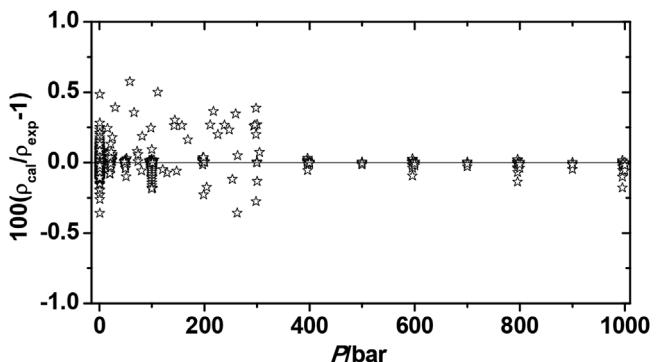
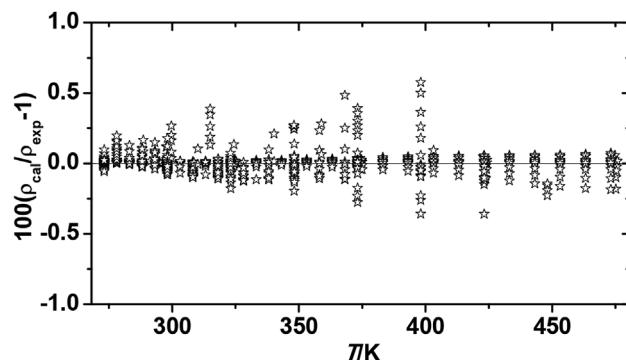


Fig. 5. Density deviations of this model from experimental data of the $\text{MgSO}_4\text{-H}_2\text{O}$ system: Experimental data are from Table 1S (Supporting Material).

the $PVTx$ properties of the multi-component aqueous electrolyte solutions can be calculated if the interaction parameters between different ions are known. However, the interaction parameters between different ions must be obtained from experimental volumetric data, which are insufficient and cannot meet the requirement. Therefore, a predictive density model should be the optimal option. According to Young and Smith (1954), the mean apparent molar volume of a multi-component aqueous electrolyte solution has the following relation to that of the single-salt solution:

$$V_{\text{mean}}^\phi = \sum_j \frac{m_j V_{\phi j}}{\sum_j m_j} \quad (16)$$

where V_{mean}^ϕ is the mean apparent molar volume of multi-component aqueous electrolyte solution, m_j is the molality of salt j , and $V_{\phi j}$ is the apparent molar volume of binary aqueous electrolyte solution at the

Table 4

Literature data for the density (volume) of ternary systems.

References	T/K	P/bar	$m_2/(\text{mol}\cdot\text{kg}^{-1})$	$m_3/(\text{mol}\cdot\text{kg}^{-1})$	Quantity measured
The LiCl(2)-NaCl(3)-H₂O system					
Campbell and Kartzmark (1956)	298.15	1.01	0.49050 to 1.97743	0.35860 to 1.42322	ρ
The LiCl(2)-KCl(3)-H₂O system					
Campbell and Kartzmark (1956)	298.15	1.01	0.49307 to 1.97971	0.28144 to 1.12154	ρ
Kapustinskii et al. (1960)	298.15	1.01	0.24980 to 2.34130	0.25123 to 2.34301	ρ
The LiCl(2)-MgCl₂(3)-H₂O system					
None					
The LiCl(2)-CaCl₂(3)-H₂O system					
None					
The NaCl(2)-KCl(3)-H₂O system					
Ruby and Kawai (1926)	298.15	1.01	0.2 to 3.2	0.2 to 3.2	ρ
Wirth (1937)	298.15	1.01	0.03799 to 1.03242	0.03960 to 0.67464	$\rho\cdot\rho_{\text{NaCl}}$
Campbell and Kartzmark (1956)	298.15	1.01	0.35677 to 1.42125	0.27858 to 1.12874	ρ
Fabuss et al. (1969)	298.15	1.01	0.4807 to 3.2448	0.0707 to 1.1536	ρ
Goldsack and Franchetto (1977)	298.15	1.01	0.50 to 2.50	0.50 to 2.50	ρ
Nowlan et al. (1980)	298.2	1.01	0.125 to 3.000	0.125 to 3.000	ρ
Millero and Sotolongo (1986)	298.15	1.01	0.30330 to 1.20420	0.29580 to 1.19670	$\rho\cdot\rho_w$
Kumar (1988)	298.15	1.01	0.02330 to 4.10940	0.06345 to 3.33270	$\rho\cdot\rho_w$
Dedick et al. (1990)	278.15 to 368.15	1.01	0.20415 to 1.76243	0.18757 to 1.74585	$\rho\cdot\rho_w$
Mahapatra et al. (1991)	298.15	1.01	0.0077 to 0.9926	0.0074 to 0.6499	$\rho\cdot\rho_w$
Redman and Rohani (1994)	299.2 to 321.2	1.01	0.34221 to 5.15887	0.26827 to 3.97044	ρ
Miller et al. (1996)	298.15	1.01	0.370416 to 0.657637	0.368180 to 0.660337	ρ
Zhang and Han (1996)	298.15	1.01	0.01211 to 4.25624	0.01470 to 3.83190	ρ
Ghafri et al. (2012)	283.15 to 472.96	9.2 to 684.2	0.90720 to 4.27680	0.14280 to 0.67320	ρ
Zezin et al. (2014a)	298.09 to 523.22	1 to 400	0.01064 to 3.58656	0.03171 to 3.58550	$\rho\cdot\rho_w$
The NaCl(2)-MgCl₂(3)-H₂O system					
Millero et al. (1985)	298.15	1.01	0.10597 to 2.69307	0.03701 to 0.89648	$\rho\cdot\rho_w$
Millero and Lampreia (1985)	298.15	1.01	0.30396 to 2.67609	0.10064 to 0.89135	$\rho\cdot\rho_w$
Connaughton and Millero (1987)	278.15 to 368.15	1.01	0.30027 to 2.69655	0.10115 to 0.89991	$\rho\cdot\rho_w$
Saluja et al. (1995)	296.02 to 371.82	6	0.27673 to 4.43890	0.10483 to 1.28240	$\rho\cdot\rho_w$
Iulian et al. (2008)	298.15	1.01	0.1060 to 2.6931	0.0370 to 0.8965	ρ
Qiblawey and Abu-Jdayil (2010)	298.15 to 318.15	1.01	0.0982 to 3.6311	0.0717 to 2.7076	ρ
Zezin et al. (2014b)	298.14 to 523.16	1 to 700	0.10006 to 3.00012	0.0998 to 3.0101	$\rho\cdot\rho_w$
The NaCl(2)-CaCl₂(3)-H₂O system					
Nowlan et al. (1980)	298.2	1.01	0.125 to 3.000	0.375 to 2.250	ρ
Kumar et al. (1982)	298.15	1.01	0.01653 to 4.72850	0.00501 to 6.62333	$\rho\cdot\rho_w$
Kumar and Atkinson (1983)	278.15 to 308.15	1.01	0.19900 to 3.94750	0.06750 to 1.35533	$\rho\cdot\rho_w$
Oakes et al. (1990)	298.154 to 308.138	1.01	0.01672 to 4.54513	0.01187 to 2.87545	ρ
Saluja et al. (1995)	296.02 to 371.82	6	0.2879 to 4.4528	0.0995 to 1.4612	$\rho\cdot\rho_w$
Zhang et al. (1997)	298.15	1.01	0.00363 to 3.54204	0.01087 to 3.35323	ρ
Hu (2000)	298.15	1.01	0.1000 to 4.600	0.0275 to 2.6692	ρ
Qiblawey et al. (2014)	293.15 to 323.15	1	0.5 to 4.5	0.5 to 4.5	ρ
Zezin et al. (2014b)	298.14 to 523.17	1 to 700	0.09998 to 3.35813	0.010 to 6.004	$\rho\cdot\rho_w$
The KCl(2)-MgCl₂(3)-H₂O system					
Kumar (1989)	298.15	1.01	0.05740 to 3.85425	0.03095 to 1.37820	$\rho\cdot\rho_w$
The KCl(2)-CaCl₂(3)-H₂O system					
Kumar (1986)	298.15	1.01	0.04810 to 4.24125	0.02397 to 1.41660	$\rho\cdot\rho_w$
Zhang et al. (1997)	298.15	1.01	0.00178 to 3.23568	0.00107 to 3.56574	ρ
The MgCl₂(2)-CaCl₂(3)-H₂O system					
Saluja et al. (1995)	296.02 to 371.82	6	0.0963 to 1.3075	0.0920 to 1.4451	$\rho\cdot\rho_w$
The LiCl(2)-Li₂SO₄(3)-H₂O system					
Wirth and LoSurdo (1968)	273.15 to 318.222	1.01	1.00000 to 3.00000	0.33333 to 1.00000	ρ
The LiCl(2)-Na₂SO₄(3)-H₂O system					
None					
The LiCl(2)-K₂SO₄(3)-H₂O system					
None					
The LiCl(2)-MgSO₄(3)-H₂O system					
None					
The NaCl(2)-Li₂SO₄(3)-H₂O system					
None					
The NaCl(2)-Na₂SO₄(3)-H₂O system					
Fabuss et al. (1966)	298.15 to 448.15	1.01	0.1 to 2.5	0.01 to 0.15	ρ
Wirth and LoSurdo (1968)	273.150 to 318.212	1.01	1.26600 to 3.22600	0.25800 to 0.91133	ρ
Fabuss et al. (1969)	298.15 to 423.15	1.01	0.5514 to 3.4219	0.0118 to 0.2644	ρ
Millero et al. (1985)	298.15	1.01	0.19627 to 2.67618	0.03498 to 0.89598	$\rho\cdot\rho_w$
Millero and Lampreia (1985)	298.15	1.01	0.28597 to 2.63515	0.11602 to 0.89908	$\rho\cdot\rho_w$
Millero and Sotolongo (1986)	298.15	1.01	0.14880 to 1.34685	0.05105 to 0.45040	$\rho\cdot\rho_w$
Connaughton and Millero (1987)	278.15 to 368.15	1.01	0.28212 to 2.63019	0.12327 to 0.90596	$\rho\cdot\rho_w$
Dedick et al. (1990)	278.15 to 368.15	1.01	0.19163 to 1.92531	0.00823 to 0.58612	$\rho\cdot\rho_w$
Hu (2000)	298.15	1.01	0.0640 to 0.8357	0.05 to 0.50	ρ
Iulian et al. (2008)	298.15	1.01	0.1049 to 2.6880	0.06543 to 0.89210	ρ
Zezin et al. (2015)	298.15 to 523.16	1 to 700	0.09995 to 5.00004	0.09980 to 1.00075	$\rho\cdot\rho_w$
The NaCl(2)-K₂SO₄(3)-H₂O system					
Wirth (1937)	298.15	1.01	0.03880 to 1.03502	0.01471 to 0.24817	$\rho\cdot\rho_{\text{NaCl}}$

(continued on next page)

Table 4 (continued)

References	T/K	P/bar	$m_2/(\text{mol}\cdot\text{kg}^{-1})$	$m_3/(\text{mol}\cdot\text{kg}^{-1})$	Quantity measured
Millero and Sotolongo (1986) Dedick et al. (1990)	298.15 278.15 to 368.15	1.01 1.01	0.14850 to 1.34850 0.19599 to 1.74515	0.05050 to 0.45050 0.06828 to 0.58467	$\rho\cdot\rho_w$ $\rho\cdot\rho_w$
The NaCl(2)-MgSO₄(3)-H₂O system					
Fabuss et al. (1966)	298.15 to 448.15	1.01	0.1 to 2.5	0.00972 to 0.29165	ρ
Fabuss et al. (1969)	298.15 to 423.15	1.01	0.4813 to 3.2484	0.0177 to 0.2888	ρ
Nowlan et al. (1980)	298.2	1.01	0.125 to 1.500	0.125 to 1.500	ρ
Millero et al. (1985)	298.15	1.01	0.10478 to 2.68398	0.02554 to 0.67936	$\rho\cdot\rho_w$
Millero and Lampreia (1985)	298.15	1.01	0.28094 to 2.67736	0.07648 to 0.60596	$\rho\cdot\rho_w$
Connaughton and Millero (1987)	278.15 to 368.15	1.01	0.27462 to 2.72793	0.06802 to 0.68135	$\rho\cdot\rho_w$
The KCl(2)-Li₂SO₄(3)-H₂O system					
None					
The KCl(2)-Na₂SO₄(3)-H₂O system					
Dedick et al. (1990) Iulian et al. (2008)	278.15 to 368.15 298.15	1.01 1.01	0.17973 to 1.75200 0.15585 to 1.35600	0.06600 to 0.59009 0.04800 to 0.44805	$\rho\cdot\rho_w$ ρ
The KCl(2)-K₂SO₄(3)-H₂O system					
Millero and Sotolongo (1986)	298.15	1.01	0.14685 to 1.34715	0.05095 to 0.45105	$\rho\cdot\rho_w$
The KCl(2)-MgSO₄(3)-H₂O system					
None					
The MgCl₂(2)-Li₂SO₄(3)-H₂O system					
None					
The MgCl₂(2)-Na₂SO₄(3)-H₂O system					
Millero et al. (1985) Millero and Lampreia (1985) Connaughton and Millero (1987) Iulian et al. (2008)	298.15 298.15 278.15 to 368.15 298.15	1.01 1.01 1.01 1.01	0.03577 to 0.89071 0.09889 to 0.79441 0.10334 to 0.89433 0.03577 to 0.89070	0.03214 to 0.89569 0.10059 to 0.89545 0.10567 to 0.89666 0.03213 to 0.89570	$\rho\cdot\rho_w$ $\rho\cdot\rho_w$ $\rho\cdot\rho_w$ ρ
The MgCl₂(2)-K₂SO₄(3)-H₂O system					
None					
The MgCl₂(2)-MgSO₄(3)-H₂O system					
Millero et al. (1985) Millero and Lampreia (1985) Connaughton and Millero (1987)	298.15 298.15 278.15 to 368.15	1.01 1.01 1.01	0.03293 to 0.89952 0.10311 to 0.89687 0.09762 to 0.90548	0.02822 to 0.67741 0.07405 to 0.66936 0.07089 to 0.67679	$\rho\cdot\rho_w$ $\rho\cdot\rho_w$ $\rho\cdot\rho_w$
The CaCl₂(2)-Li₂SO₄(3)-H₂O system					
None					
The CaCl₂(2)-Na₂SO₄(3)-H₂O system					
None					
The CaCl₂(2)-K₂SO₄(3)-H₂O system					
None					
The CaCl₂(2)-MgSO₄(3)-H₂O system					
None					
The Li₂SO₄(2)-Na₂SO₄(3)-H₂O system					
Wirth and LoSurdo (1968)	273.15 to 318.779	1.01	0.32973 to 0.99627	0.33707 to 1.00360	ρ
The Li₂SO₄(2)-K₂SO₄(3)-H₂O system					
None					
The Li₂SO₄(2)-MgSO₄(3)-H₂O system					
None					
The Na₂SO₄(2)-K₂SO₄(3)-H₂O system					
Millero and Sotolongo (1986) Dedick et al. (1990)	298.15 298.15 to 368.15	1.01 1.01	0.05080 to 0.45035 0.01193 to 0.58859	0.04965 to 0.44920 0.06141 to 0.63807	$\rho\cdot\rho_w$ $\rho\cdot\rho_w$
The Na₂SO₄(2)-MgSO₄(3)-H₂O system					
Fabuss et al. (1966)	298.15 to 448.15	1.01	0.01 to 0.15	0.01 to 0.30	ρ
Millero et al. (1985)	298.15	1.01	0.06798 to 0.89582	0.05115 to 0.67645	$\rho\cdot\rho_w$
Millero and Lampreia (1985)	298.15	1.01	0.10319 to 0.89632	0.07356 to 0.66841	$\rho\cdot\rho_w$
Connaughton and Millero (1987)	278.15 to 368.15	1.01	0.09352 to 0.88322	0.08759 to 0.67986	$\rho\cdot\rho_w$
The K₂SO₄(2)-MgSO₄(3)-H₂O system					
None					

Notes: T is temperature; P is pressure; m_i is the molality of salt i; ρ is the density of aqueous electrolyte solution; ρ_w is the density of pure water; ρ_{NaCl} is the density of aqueous NaCl solution.

same ionic strength of total solution. $V_{\phi j}$ for the Li₂SO₄-H₂O, Na₂SO₄-H₂O, K₂SO₄-H₂O and MgSO₄-H₂O systems can be calculated from the density model developed here, and $V_{\phi j}$ for the LiCl-H₂O, NaCl-H₂O, KCl-H₂O, MgCl₂-H₂O and CaCl₂-H₂O systems can be calculated from the density model of Mao and Duan (2008). So the following equations can be used to calculate the density or volume of the multi-component aqueous electrolyte solutions:

$$V_{\text{mean}}^{\phi} = \frac{V(m) - 1000/\rho_{\text{H}_2\text{O}}}{m} \quad (17)$$

$$V(m) = \frac{1000 + \sum_j m_j M_{sj}}{\rho_{\text{sol}}} \quad (18)$$

where M_{sj} is the molar mass of salt j. The average and maximal density deviations of this predictive method for each ternary water-salt system are listed in Table 2S (Supporting Material) in the **Supplementary data.docx** file (Appendix B), where most of experimental data are accurately reproduced with deviations less than 0.1% (Fig. 6). Fig. 7 shows that the predictive model agrees very well with the experimental density data of the NaCl-KCl-MgCl₂-CaCl₂-H₂O system at 1.01 bar, with

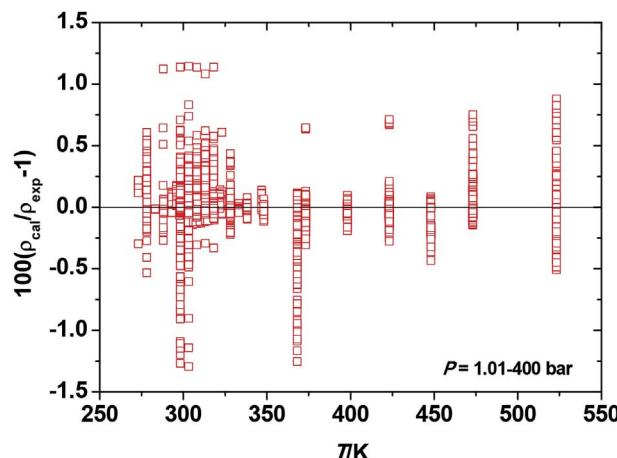


Fig. 6. Density deviations of this model from experimental data of ternary aqueous electrolyte solutions: Detailed comparisons see Table 2S (Supporting Material).

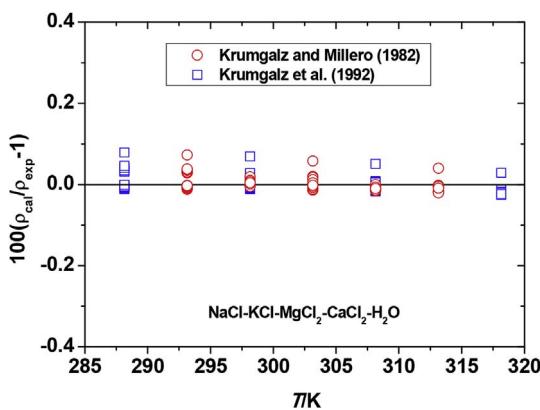


Fig. 7. Density deviations of this model from experimental data of the NaCl-KCl-MgCl₂-CaCl₂-H₂O system.

ionic strength up to 9.6 mol·kg⁻¹ (Krumgalz et al., 1992; Krumgalz and Millero, 1982).

6. Applications of the density model

6.1. Calculating infinite dilution apparent molar volume (V_ϕ^0)

Infinite dilution apparent molar volume (V_ϕ^0) (or infinite dilution partial molar volume) for aqueous electrolyte solution is of fundamental interest to study the ion-solvent interactions. The values of the infinite dilution apparent molar volume at various temperatures and pressures can be calculated from above density model. From Eq. (9), V_ϕ^0 can be obtained:

$$V_\phi^0 = \frac{V(m_r)}{m_r} - \frac{1000}{m_r \rho_{H_2O}} - v|z_+z_-|A_V h(I_{m_r}) - 2v_-v_-m_r RT [\beta_{MX}^{(0)V} + \beta_{MX}^{(1)V} g(\alpha_1 I_{m_r}^{0.5}) + v_+z_+m_r C_{MX}^V] \quad (19)$$

Table 5 lists the experimental and calculated V_ϕ^0 from this model and other models at 298.15 K and 1.01 bar. Figs. 8 and 9 show the infinite dilution apparent molar volume as a function of temperature at constant pressure. It can be seen that V_ϕ^0 gradually increases with temperature at low temperatures, and decreases with temperature at high temperatures. It can be very negative at high temperatures.

Table 5

Comparisons of infinite dilution apparent molar volume (V_ϕ^0) at $T = 298.15 \text{ K}$ and $P = 1.01 \text{ bar}$.

The Li ₂ SO ₄ -H ₂ O system		
References		$V_\phi^0/(\text{cm}^3 \cdot \text{mol}^{-1})$
Exp.	Abdulagatov and Azizov (2003)	13.00
Calculated	This model	12.96
	Pearce and Eckstrom (1937)	12.91
	Mukerjee (1961)	14.40
	Millero (1971)	12.22
	Millero (1972)	13.10
	Krumgalz et al. (1996)	12.58
	Abdulagatov and Azizov (2003)	12.68
	Hu et al. (2016)	12.61

The Na₂SO₄-H₂O system

References		$V_\phi^0/(\text{cm}^3 \cdot \text{mol}^{-1})$
Exp.	Pearce and Eckstrom (1937)	12.09
	Ellis (1968)	11.60
	Lo Surdo et al. (1982)	11.72
	Phutela and Pitzer (1986a)	11.22
	Zhuo et al. (2008)	11.46
Calculated	This model	11.50
	Redlich (1940)	11.64
	Millero (1971)	11.56
	Millero (1972)	11.56
	Perron et al. (1975)	11.76
	Chen et al. (1977)	11.62
	Millero et al. (1977a)	11.56
	Connaughton et al. (1986)	11.48
	Monnin (1989)	11.79
	Mahapatra et al. (1991)	11.40
	Sánchez et al. (1994)	10.60
	Krumgalz et al. (1996)	11.78

The K₂SO₄-H₂O system

References		$V_\phi^0/(\text{cm}^3 \cdot \text{mol}^{-1})$
Exp.	Pearce and Eckstrom (1937)	33.70
	Wirth (1937)	32.28
	Ellis (1968)	31.70
Calculated	This model	32.20
	Adams (1932)	32.30
	Jones and Ray (1937)	32.36
	Wirth (1937)	31.94
	Redlich (1940)	33.44
	Dunn (1968)	31.99
	Millero (1971)	32.02
	Millero (1972)	32.04
	Perron et al. (1975)	32.00
	Millero et al. (1977a)	32.02
	Monnin (1989)	32.17
	Dedick et al. (1990) ^①	32.41
	Dedick et al. (1990) ^②	32.36
	Mahapatra et al. (1991)	32.26
	Krumgalz et al. (1996)	32.05

The MgSO₄-H₂O system

References		$V_\phi^0/(\text{cm}^3 \cdot \text{mol}^{-1})$
Exp.	Lo Surdo et al. (1982)	-7.39
	Phutela and Pitzer (1986a)	-7.87
	Abdulagatov et al. (2007)	-7.29
	Zhuo et al. (2008)	-6.89

(continued on next page)

Table 5 (continued)

The Li ₂ SO ₄ -H ₂ O system		
References		$V_{\phi}^0/\text{cm}^3\cdot\text{mol}^{-1}$
Calculated	This model	-7.47
	Millero (1972)	-7.19
	Chen et al. (1977)	-7.18
	Leyendeckers and Hunter (1977)	-7.18
	Millero et al. (1977a)	-7.20
	Connaughton et al. (1986)	-7.49
	Monnin (1989)	-7.84
	Sánchez et al. (1994)	-5.90
	Krumgalz et al. (1996)	-7.38

Notes: ① is calculated from the entire data set, and ② is calculated at each individual temperature.

6.2. Calculating the densities of CO₂-bearing aqueous electrolyte solutions under the CCS conditions

When CO₂ is dissolved into deep saline formations, no volumetric models available can accurately calculate the density of CO₂-bearing saline formations under the conditions of CCS. The PVTx model in this work can be used to predict the densities of aqueous electrolyte solutions containing Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻ and SO₄²⁻. If CO₂ is dissolved into aqueous electrolyte solution, the molar volume V of CO₂-bearing solution is

$$V = x_{\text{water-salt}} V_{\text{water-salt}} + x_{\text{CO}_2} V_{\text{CO}_2,\phi}^{\text{water-salt}} \quad (20)$$

where $V_{\text{water-salt}}$ is the molar volume of aqueous electrolyte solution which can be calculated from the PVTx model proposed in Section 5, $x_{\text{water-salt}}$ is the mole fraction of water-salt components, x_{CO_2} is the mole fraction of CO₂ in aqueous electrolyte solution, and $V_{\text{CO}_2,\phi}^{\text{water-salt}}$ is the

apparent molar volume of CO₂ in aqueous electrolyte solution.

Usually, CO₂ solubility in water is not big under the conditions of CCS. If salts are added, CO₂ solubility will decrease obviously with increasing salinity. Therefore, the possibilities of CO₂-cation and CO₂-anion pairs appearing in solutions are very small. In this case, the effect CO₂-salt interactions on $V_{\text{CO}_2,\phi}^{\text{water-salt}}$ can be neglected. That is, $V_{\text{CO}_2,\phi}^{\text{water-salt}}$ can be approximated as the apparent molar volume of CO₂ in water ($V_{\text{CO}_2,\phi}^{\text{water}}$). Eq. (20) is then changed into

$$V = x_{\text{water-salt}} V_{\text{water-salt}} + x_{\text{CO}_2} V_{\text{CO}_2,\phi}^{\text{water}} \quad (21)$$

where $V_{\text{CO}_2,\phi}^{\text{water}}$ can be calculated from the PVTx model of the CO₂-H₂O system (Mao et al., 2010). In order to test the validity of Eq. (21), experimental volumetric data of the CO₂-H₂O-NaCl solutions under the conditions of CCS are compared with the model. Table 6 lists the average and maximum density deviations, and Fig. 10 shows the density deviations of Eq. (21) from experimental data of the CO₂-H₂O-NaCl solutions. These results show that the agreement is good. Because the experimental volumetric data of other CO₂-water-salt solutions were not found, future experimental work for those solutions is needed to further validate Eq. (21).

7. Conclusions

An accurate density model is developed for the Li₂SO₄-H₂O, Na₂SO₄-H₂O, K₂SO₄-H₂O and MgSO₄-H₂O systems over a wide T-P-m_{salt} range within or close to experimental uncertainties. The average density deviations from extensive experimental data for the Li₂SO₄-H₂O, Na₂SO₄-H₂O, K₂SO₄-H₂O, and MgSO₄-H₂O systems are 0.046%, 0.036%, 0.051%, 0.038%, respectively. The density models of binary sulfate-water and chloride-water systems (Mao and Duan, 2008) can be combined by a simple mixing rule to predict the densities or molar volumes of aqueous mixed electrolyte solutions containing Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻ and SO₄²⁻. The PVTx model here can be used to

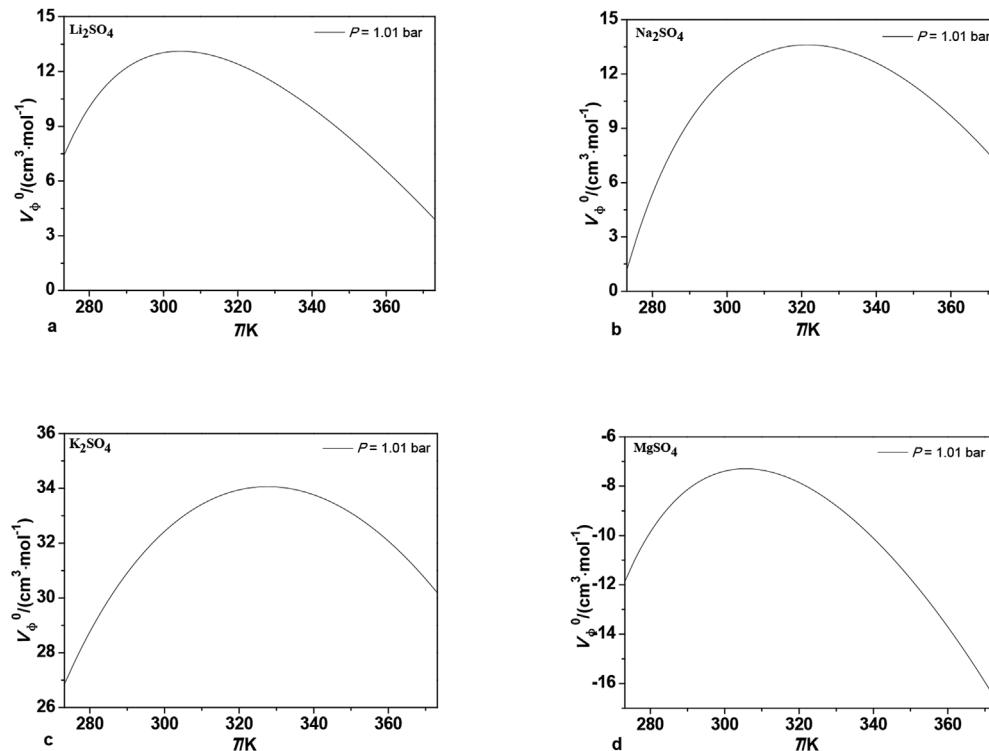


Fig. 8. Apparent molar volume of Li₂SO₄, Na₂SO₄, K₂SO₄ and MgSO₄ at infinite dilution (V_{ϕ}^0) as a function of temperature at 1.01 bar.

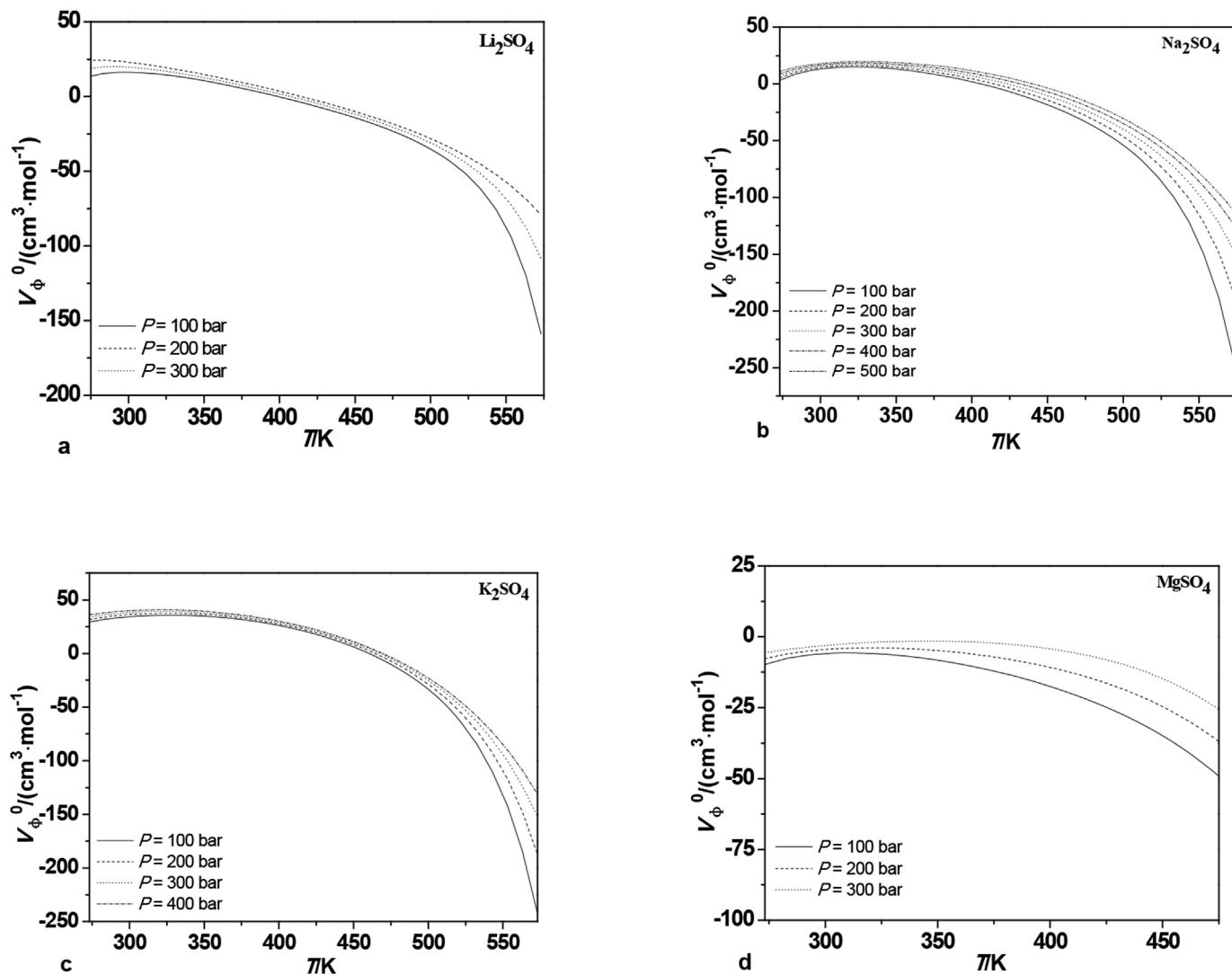


Fig. 9. Apparent molar volume of Li_2SO_4 , Na_2SO_4 , K_2SO_4 and MgSO_4 at infinite dilution (V_ϕ^0) as a function of temperature at higher pressures.

Table 6

The deviations of the model from experimental data of the $\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}$ solutions under the CCS conditions.

References	T/K	P/bar	$x_{\text{CO}_2}/(-)$	$x_{\text{NaCl}}/(-)$	N	AAD/%	MAD/%
Nighswander et al. (1989)	353.35 to 473.65	21.1 to 100.3	0.0028 to 0.0154	0.003058 to 0.03095	34	0.914	2.912
Teng and Yamasaki (1998)	278 to 293	64.4 to 294.9	0.0232 to 0.0322	0.010514 to 0.010656	24	0.137	0.349
Li et al. (2004)	332.15	2.4 to 289.3	0.006689 to 0.017993	0.028987 to 0.029871	29	0.276	0.471
Song et al. (2005)	276.15 to 283.15	40 to 130	0.00422 to 0.03289	0.01069 to 0.01101	90	0.101	0.169
Yan et al. (2011)	323.2 to 413.2	50 to 400	0.003130 to 0.022217	0.01730 to 0.08237	36	0.197	0.399
Zhang et al. (2011)	313.04 to 353.25	100 to 180.2	0.004121 to 0.016784	0.000379 to 0.000384	97	0.167	0.226
Song et al. (2013)	332.26 to 414.36	99.45 to 180.14	0.004453 to 0.014458	0.017468 to 0.066892	300	0.179	0.488

Notes: T is temperature; P is pressure; x_{CO_2} is the mole fraction of CO_2 ; x_{NaCl} is the mole fraction of NaCl ; N is the number of measurements; $\text{AAD} = \frac{1}{N} \sum_i^N |\rho_{\text{cal},i} - \rho_{\text{exp},i}| / \rho_{\text{exp},i} \times 100$, where ρ_{cal} and ρ_{exp} are the calculated and experimental densities, respectively; MAD is the maximal absolute deviation calculated with this model.

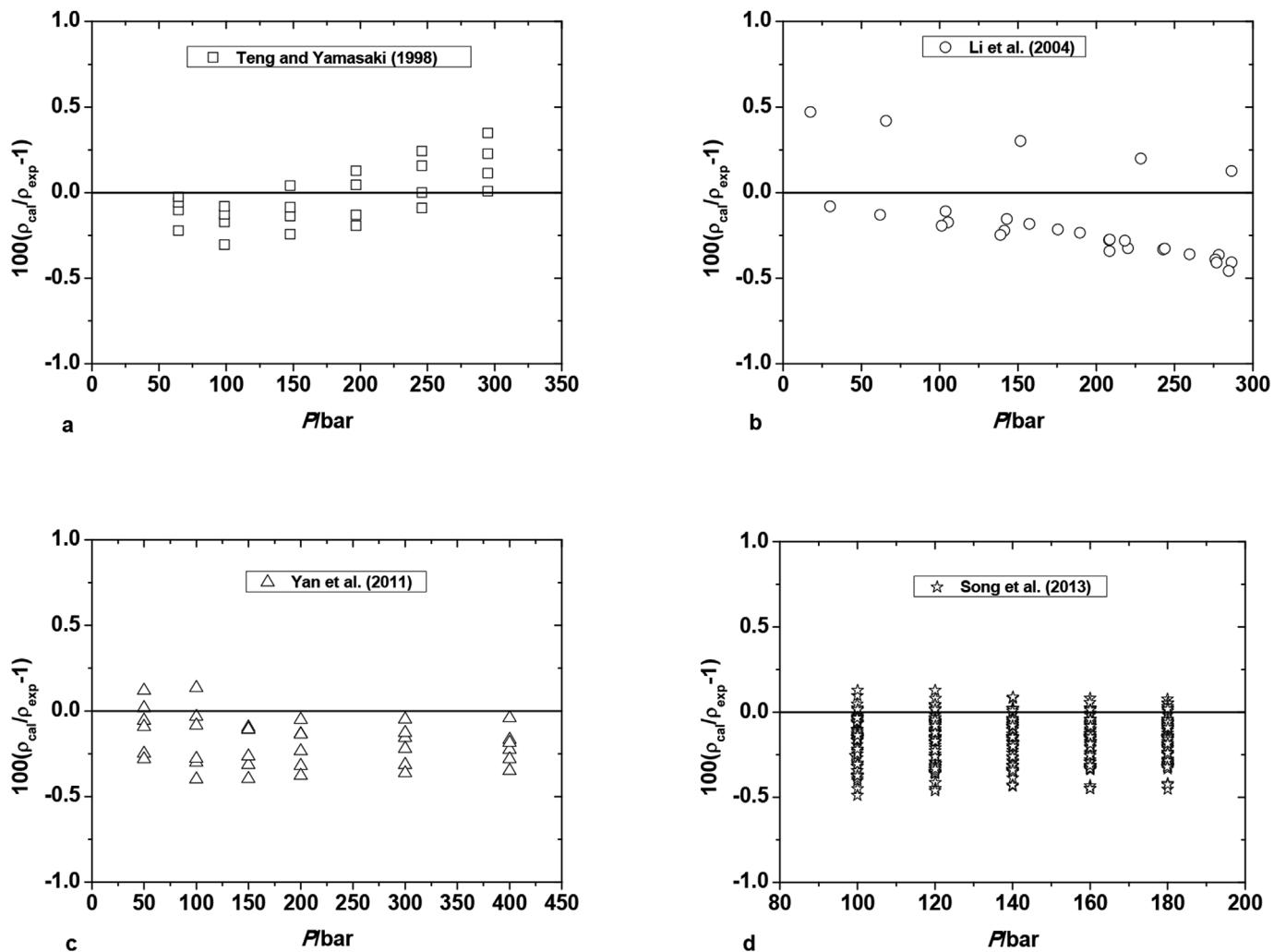


Fig. 10. Density deviations of this model from experimental data of the $\text{CO}_2\text{-H}_2\text{O}\text{-NaCl}$ solutions.

predict the infinite dilution apparent molar volume of sulfate in water and the volumetric properties of CO_2 -bearing deep saline formations. Although the importance of aqueous electrolyte solutions is well known, experimental volumetric data of the multi-component mixed electrolyte solutions are still lacking, and future experimental work should be focused on these systems or the CO_2 -bearing mixed electrolyte solutions over a much wider $T\text{-}P\text{-}x$ range.

Appendix A

The volumetric Debye-Hückel limiting law slope A_V is defined as Bradley and Pitzer (1979), which takes the following form:

$$A_V = -4RT \left(\frac{\partial A_\phi}{\partial P} \right)_T \quad (\text{A1})$$

$$A_\phi = \frac{1}{3} \left(\frac{2\pi N_0 \rho_w}{1000} \right)^{\frac{1}{2}} \left(\frac{e^2}{DkT} \right)^{\frac{3}{2}} \quad (\text{A2})$$

where ρ_w is the density of pure water calculated from the Gibbs free energy model of Wagner et al. (2000), and D is the dielectric constant of pure water calculated from Eq. (1) of Bradley and Pitzer (1979). The other parameters are: $N_0 = 6.0221415 \times 10^{23} \text{ mol}^{-1}$, $e = 1.60217733 \times 10^{-19} \text{ C}$, $k = 1.3806505 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$.

Appendix B. Supplementary data

Supplementary data related to this article can be found in the **Supplementary data.docx** file, where two tables show the density deviations of this model from experimental data of binary aqueous sulfate solutions (Table 1S) and ternary aqueous electrolyte solutions (Table 2S), and three

figures show the temperature-composition-pressure range that literature data cover for the PVTx properties of binary aqueous sulfate solutions (Fig. 1S), and the apparent molar volume of Li_2SO_4 , Na_2SO_4 , K_2SO_4 and MgSO_4 as a function of temperature (Fig. 2S) and molality (Fig. 3S), respectively.

Appendix C. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.apgeochem.2017.10.002>.

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