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The P,V,T,x properties of binary aqueous chloride solutions up to $T = 573$ K and 100 MPa

Shide Mao [a], Zhenhao Duan [b,*]

[a] School of Earth Sciences and Resources, China University of Geosciences, Beijing 100083, China
[b] Key Laboratory of the Study of Earth's Deep Interior, Institute of Geology and Geophysics, Chinese Academy of Sciences, P.O. Box 9825, Beijing 100029, China

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ABSTRACT

A highly accurate P,V,T,x model is developed for aqueous chloride solutions of the binary systems, *viz.* (LiCl + H_2O), (NaCl + H_2O), (KCl + H_2O), ($MgCl_2$ + H_2O), ($CaCl_2$ + H_2O), ($SrCl_2$ + H_2O), and ($BaCl_2$ + H_2O). The applied ranges of temperature, pressure, and concentrations for the systems (LiCl + H_2O), (NaCl + H_2O), (KCl + H_2O), ($MgCl_2$ + H_2O), ($CaCl_2$ + H_2O), ($SrCl_2$ + H_2O), and ($BaCl_2$ + H_2O) are (273 K to 564 K, 0.1 MPa to 40 MPa, and 0 to 10 molal), (273 K to 573 K, 0.1 MPa to 100 MPa, and 0 to 6.0 molal), (273 K to 543 K, 0.1 MPa to 50 MPa, and 0 to 4.5 molal), (273 K to 543 K, 0.1 MPa to 40 MPa, and 0 to 3.0 molal), (273 K to 523 K, 0.1 MPa to 60 MPa, and 0 to 6.0 molal), (298 K to 473 K, 0.1 MPa to 2 MPa, and 0 to 2.0 molal) and (273 K to 473 K, 0.1 MPa to 20 MPa, and 0 to 1.6 molal), respectively. Comparison of the model with thousands of experimental data points concludes that the average deviation over the above T,P,m range is 0.020% to 0.066% in density (or volume) for these systems, which indicates high accuracy. From this model, various volumetric properties, such as the apparent molar volume at infinite dilution and isochores of fluid inclusions, can be calculated, thus having a wide range of geological applications, such as reservoir fluid flow simulation and fluid-inclusion study. A computer code is developed for this model and can be downloaded from the website: www.geochem-model.org/programs.htm and online calculations is made available on: www.geochem-model.org/models.htm

1. Introduction

Thermodynamic modelling of aqueous salt fluids (brine) has long been an endeavour for geochemists [1–9]. One of the most important thermodynamic properties is the density as a function of temperature, pressure, and salt content (or P,V,T,x properties). The P,V,T,x properties have been widely used for geochemical applications, such as fluid-inclusion studies [10–12], fluid flow simulation [13–15], fluid–rock interactions [16–18], CO_2 sequestrations [19,20] and unit conversion from molarity to molality.

Experimentalists have done a lot of work measuring the density or volume of these aqueous salt solutions since the beginning of last century. Thousands of measurements have been reported from numerous laboratories. We have collected the density or volumetric data for the (LiCl + H_2O), (NaCl + H_2O), (KCl + H_2O), ($MgCl_2$ + H_2O), and ($CaCl_2$ + H_2O) systems in table 1. However, these experimental data are still scattered and they cover only a limited T,P,m space and are inconvenient to use. Hence theorists have devoted extensive efforts to the modelling of the volumetric properties of these aqueous electrolyte solutions so as to interpolate between the data points or extrapolate beyond the data range. However, all of the published models, including the models of Pitzer and his co-workers [2,3], are found to possess intolerable deficiencies, which lead to the motivation of this study.

Over the last 20 years, more than 10 models have been reported to calculate the density (volume) of these aqueous chloride solutions [1–3,9,21–36]. Each model has its strength and weakness and here we mainly comment on the most competitive models for these binary aqueous chloride systems.

Abdulagatov and Azizov [21] presented an empirical model (Abdulagatov model) to calculate the density of the (LiCl + H_2O) system using 48 parameters, covering the T,P,m range of (291 to 608) K, (0.1 to 30) MPa, and (0 to 15.5) molal with an average deviation 0.065% from their experimental data. However, the model cannot reduce to the density of pure water when the LiCl concentration approaches zero, which means it cannot calculate properties of dilute solutions. The density of water can be accurately calculated by the equations of IAPWS97 [37] or IAPWS95 [38] with an accuracy of about ±0.01%. The density of water calculated from their model by setting the molality of LiCl to zero is compared with the results from IAPWS97 (figure 1). It can be seen that the calculated densities of pure water from their model deviate substantially from those of IAPWS97 for temperatures above 500 K. The substantial deviation for pure water suggests that their model is unreliable for calculating the density of dilute LiCl solutions.

* Corresponding author. Tel.: +86 10 82998377.
E-mail address: duanzhenhao@yahoo.com (Z. Duan).

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TABLE 1
Literature data for density (volume) of binary aqueous chloride solutions

Reference	T/K	P/(0.1 MPa)	m_{salt}/(mol · kg^{-1})	Quantity measured
		(LiCl + H_2O) system		
[62]	298.15 to 473.15	20.27	0.1 to 1.0	ρ
[63]	298.15	1.01	0 to 3.84	V_ϕ
[64]	293.15 to 313.15	1.01	0.1172	V_ϕ
[65]	273.15 to 318.16	1.01	3.999	ρ
[66]	298.15	1.01	0.0817 to 0.7641	$\rho - \rho_w$
[67]	298.15	1.01	0.95 to 5.62	ρ
[68]	278.15 to 308.15	1.01	0.05 to 3.50	V_ϕ
[69]	298.15	1.01	0.1078 to 1.0879	$\rho - \rho_w$
[70]	278.15 to 368.15	1.01	0.1189 to 1.2128	ρ
[29]	298.15	1.01 to 404.20	0.25 to 4.97	$\rho - \rho_w$
[71]	321.63 to 549.77	7.6 to 325.7	0.0515 to 2.989	$\rho - \rho_w$
[47]	298.14 to 363.31	1.01	2.63 to 19.61	ρ
[72]	278.15 to 338.15	1.01	0.1009 to 1.0009	ρ
[73]	288.15 to 318.15	1.01	1.13 to 12.13	ρ
[74,75]	278.15 to 368.15	3.5	0.0249 to 1.0036	V_ϕ
[21]	291.25 to 607.71	1.01 to 305.52	0.13 to 15.50	ρ
		(NaCl + H_2O) system		
[76]	298.15	1 to 2000	0.0 to 5.7	V/V_0
[77]	293.15	1.01	0.17 to 5.4	C_V
[78]	298.15 to 358.15	1 to 1000	0.9 to 5.7	V
[62]	298.15 to 473.15	20.27	0.1 to 1.0	ρ
[50]	298.15 to 448.15	1.01	0.1 to 2.5	ρ
[63]	298.15	1.01	0.03 to 3.7	V_ϕ
[79]	273.2 to 338.15	1.01	0.21 to 1.01	ρ
[48]	298.15 to 423.15	P_s	0.1 to 3.6	ρ
[64]	293.15 to 313.15	1.01	0.11425	V_ϕ
[65]	273.15 to 318.21	1.01	4	ρ
[67]	298.15	1.01	1.02 to 5.60	ρ
[68]	278.15	1.01	0.05 to 3.5	V_ϕ
[80]	273.15 to 328.15	1.01	0.01 to 1.0	$\rho - \rho_w$
[81]	295.15 to 448.15	1 to 300	0.0 to 5.7	C_V
[82]	323.15	1.01	0.005 to 1.0	V_ϕ
[83]	274.65 to 318.15	1.01	0.027 to 3.014	V_ϕ
[49]	373 to 623	98 to 981	0.35 to 5.40	ρ
[42]	273 to 323	100 to 1000	0.03 to 2.0	V_ϕ
[84]	298.15 to 323.15	1.01	0.01 to 5.82	ρ
[69]	298.15	1.01	0.01 to 1.00	$\rho - \rho_w$
[85]	373 to 573	100 to 1000	0.02 to 5.7	V
[86]	298.15	1.01	0.063 to 2.812	V_ϕ
[87]	273.15 to 308.15	1.01	0.01 to 1.5	$\rho - \rho_w$
[88]	288.15 to 318.15	1.01	0.06 to 5.9	$\rho - \rho_w$
[70]	278.15 to 368.15	1.01	0.1 to 1.2	ρ
[89]	348.15 to 473.15	20	0 to 4.4	ρ
[33]	278.15 to 318.15	1.01	0.37 to 6.00	$\rho - \rho_w$
[90–92]	366.15 to 405.15	60 to 1380	0 to 3.67	V/V_0
[44]	573.15 to 873.15	100 to 3000	1.09 to 4.28	V
[39]	298.15 to 318.15	1.01	0 to 6.1	ρ
[93]	298.15 to 673.15	1.01 to 385	0.10 to 4.99	$\rho - \rho_w$
[29]	298.15	1.01 to 406.8	0.058 to 4.991	$\rho - \rho_w$
[31]	308.15 to 368.15	1.01	0.256 to 6.198	$\rho - \rho_w$
[94]	323 to 597	1 to 400	0 to 5.0	$\rho - \rho_w$
[40]	298.23 to 308.12	1	0.08 to 6.04	ρ
[43]	573.15 to 773.15	58 to 581.8	0 to 26.43	ρ
[52]	623.15	153 to 167	0.25 to 3	ρ
[57]	298.15 to 413.15	1 to 20	0.5 to 4.5	$\rho - \rho_w$
[41]	298.05 to 522.98	70.5 to 415	0.165 to 5.484	V_ϕ
[51]	277.15 to 343.15	1.01	0.1 to 1	ρ
[95]	253 to 293	1.01	0.009 to 6.0	ρ
[96]	308.15 to 323.15	1.01	0.0625 to 1	V_ϕ
		(KCl + H_2O) system		
[97]	308 to 318	1	0.05 to 4.6	ρ
[98]	298 to 613	P_s	0.25 to 3.0	$1/\rho$
[62]	298.15 to 473.15	20.27	0.1 to 1.00	ρ
[99]	298.15	1	0.27 to 4.0	ρ
[100]	373 to 653	P_s	0.14 to 3.4	ρ
[53]	298.15	1.01	0.007 to 0.424	ρ
[63]	298.15	1.01	0 to 2.93	V_ϕ
[79]	273.2 to 338.15	1.01	0.21 to 0.83	ρ
[48]	298.15 to 423.15	P_s	0.10 to 3.61	ρ
[64]	293.15 to 313.15	1.01	0.115	V_ϕ
[67]	298.15	1.01	0.50 to 4.00	ρ
[101]	298 to 623	98 to 1471	0.27 to 4.5	ρ
[42]	273.15 to 323.15	196.62 to 995.33	0.17 to 1.00	V_ϕ

TABLE 1 (*continued*)

Reference	T/K	P/(0.1 MPa)	m_{salt}/(mol · kg^{-1})	Quantity measured
[84]	293.15 to 323.15	1.01	0.33 to 4.55	ρ
[69]	298.15	1.01	0.10 to 1.00	$\rho - \rho_w$
[86]	298.15	1.01	0.046 to 2.009	V_ϕ
[102]	288 to 328	1	0.05 to 4.0	ρ
[70]	278.15 to 368.15	1.01	0.04 to 1.00	ρ
[39]	298.15 to 318.15	1.01	0 to 4.5	ρ
[29]	298.15	1.01 to 406.4	0.0585 to 3.012	$\rho - \rho_w$
[54]	298.15	1.01	0.5 to 4.5	$\rho - \rho_w$
[52]	623	148.5 to 167.6	0.25 to 3.0	ρ
[51]	277.15 to 343.15	1.01	0.1 to 1	ρ
		($MgCl_2 + H_2O$) system		
[103]	298.15	1.01	0.04 to 0.23	ρ
[104]	298.15	1.01	0.19 to 0.70	ρ
[105]	323.15 to 473.15	20.27	0.1 to 1.0	ρ
[106]	298.15	1.01	0.004 to 0.341	$\rho - \rho_w$
[42]	273.15 to 323.15	99.9 to 1001.2	0.009 to 0.315	V_ϕ
[69]	298.15	1.01	0.05 to 0.97	$\rho - \rho_w$
[87]	273.15 to 308.15	1.01	0.005 to 1.475	$\rho - \rho_w$
[33]	278.15 to 318.15	1.01	0.01 to 5.43	$\rho - \rho_w$
[39]	298.15 to 318.15	1.01	0 to 3.31	ρ
[55]	288.15 to 328.15	1.01	0.05 to 5.00	ρ
[29]	298.15	1.01 to 406.4	0.03 to 2.95	$\rho - \rho_w$
[31]	308.15 to 368.15	1.01	0.35 to 4.61	$\rho - \rho_w$
[107]	297.18 to 371.82	6	0 to 0.53	ρ
[27]	369 to 627	102 to 303	0.03 to 3.04	$\rho - \rho_w$
		($CaCl_2 + H_2O$) system		
[108]	268.15 to 413.15	1.01	0.0034 to 0.0687	ρ
[103]	298.15	1.01	0.04 to 0.13	ρ
[109]	298.15	1.01	2.71 to 6.05	ρ
[104]	298.15	1.01	0.18 to 0.79	ρ
[105]	323.15 to 473.15	20.27	0.05 to 1.00	ρ
[79]	273.2 to 338.15	1.01	0.22 to 1.00	ρ
[106]	298.15	1.01	0.01 to 0.33	$\rho - \rho_w$
[69]	298.15	1.01	0.01 to 0.98	$\rho - \rho_w$
[110]	298.15	1.01	0.02 to 0.41	V_ϕ
[111]	298.15	1.01	0.0 to 5.0	$\rho - \rho_w$
[39]	298.15 to 318.15	1.01	0 to 5.05	ρ
[55]	288.15 to 328.15	1.01	0.05 to 6	ρ
[29]	298.15	1.01 to 407.1	0.05 to 4.98	$\rho - \rho_w$
[112]	323.15 to 473.15	20.27	0 to 5.07	ρ
[54]	298.15	1.01	0.5 to 4.5	$\rho - \rho_w$
[107]	297.19 to 371.96	6	0 to 0.98	ρ
[113]	323.05 to 597.45	1.01 to 374	0.05 to 5.01	$\rho - \rho_w$
[40]	298 to 308	1	0.28 to 19.24	ρ
[52]	623	158 to 220	0.225 to 3.234	ρ
[47]	298.15 to 363.27	1.01	0.99 to 9.5	ρ
[25]	298 to 523	70.3 to 415	0.24 to 6.15	$\rho - \rho_w$
[24]	298.15 to 398.15	1 to 599.9	0.18 to 6.01	ρ
		($SrCl_2 + H_2O$) system		
[103]	298.15	1.01	0.05 to 0.26	ρ
[105]	323.15 to 473.15	20.27	0.1 to 1.0	ρ
[106]	298.15	1.01	0.004 to 0.329	$\rho - \rho_w$
[69]	298.15	1.01	0.20 to 0.40	$\rho - \rho_w$
[55]	288.15 to 328.15	1.01	0.05 to 2.5	ρ
[32]	323.15 to 473.15	20.27	0 to 2.72	ρ
[107]	297.19 to 371.96	6	0 to 1	ρ
[56]	298.15	1.01	0.10 to 3.63	ρ
		($BaCl_2 + H_2O$) system		
[103]	298.15	1.01	0.54	ρ
[104]	298.15	1.01	0.19 to 0.75	ρ
[105]	323.15 to 473.15	20.27	0.1 to 1	ρ
[79]	273.2 to 338.2	1.01	0.19 to 0.64	ρ
[106]	298.15	1.01	0.004 to 0.387	$\rho - \rho_w$
[69]	298.15	1.01	0.10 to 0.96	$\rho - \rho_w$
[55]	288.15 to 328.15	1.01	0.05 to 1.5	ρ
[45]	288.15 to 423.15	0.987 to 200	0.1 to 1.22	$\rho - \rho_w$
[57]	298.15 to 413.15	1 to 20	0.5 to 4.5	$\rho - \rho_w$

Note: ρ denotes the density of aqueous chloride solutions; ρ_w is the density of pure water; V_ϕ is the apparent molar volume of the chlorides; V is the volume of aqueous chloride solutions; V_0 denotes the volume of pure water; C_W is sound velocity of the chloride solutions; P_s is the saturation pressure of solutions.

Rogers and Pitzer [2] developed an extensively used but complicated model covering a wide T,P,m range, respectively (273 K to 573 K, 0.1 MPa to 100 MPa, and 0 to 5.5 molal) based on experimental data before 1980. However, the reliable range is limited below 2 m NaCl for temperatures below 298.15 K. Comparisons with the later data [29,31,33,39–41] covering the range of T = (273–308) K and molality above 2.0 m, the experimental data of Chen *et al.* [42] over the range of temperature (273 to 298) K with

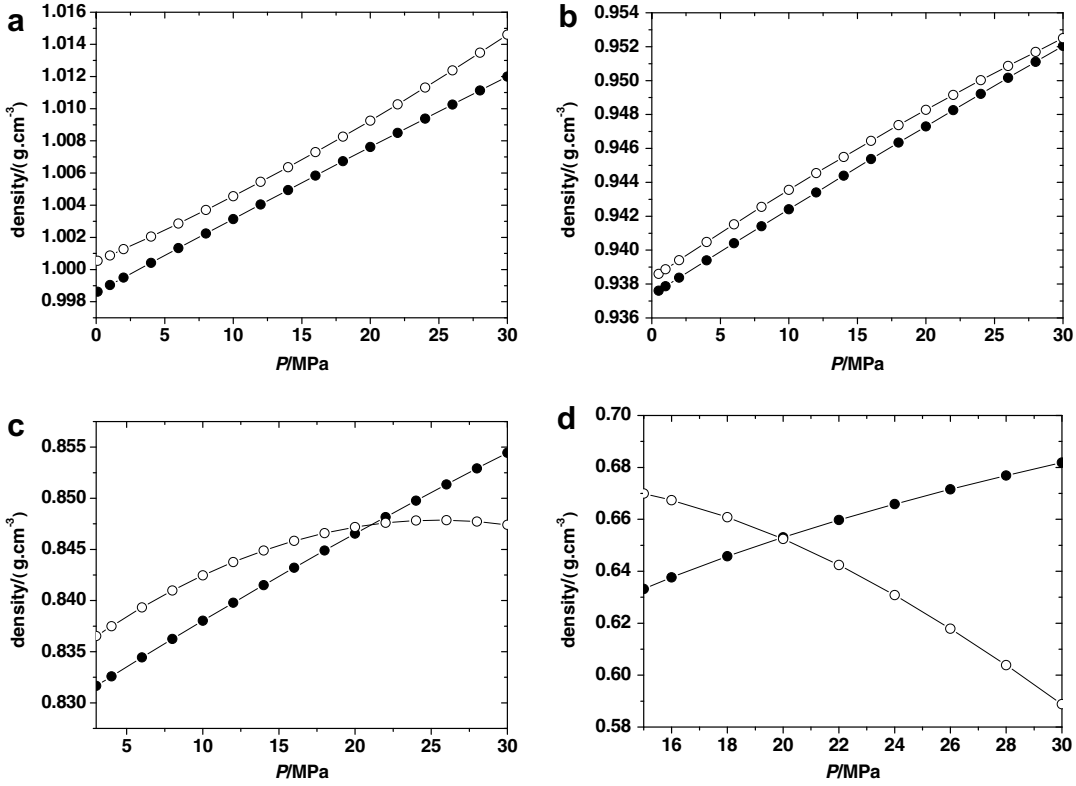

FIGURE 1. Plot of density against pressure for water (Abdulagatov model *versus* IAPWS97) –●– IAPWS97 [37]; –○– Abdulagatov and Azizov [21]; T = 291 K (a), 400 K (b), 500 K (c), 608 K (d).

molality above 0.78 m indicate that the deviations are more than 0.1%, much beyond the experimental uncertainties (about 0.01%). In addition, the model is unreliable at temperatures close to 573 K, where the deviations are over 1% as compared with experimental data [43,44]. As for the density models for the ($KCl + H_2O$) system, the most competitive model is developed by Pabalan and Pitzer [3], covering a wide T,P,m range, respectively (273 K to 573 K, 0.1 MPa to 50 MPa, and 0 to 4.5 molal). This model can reproduce experimental data with experimental precision except at T = 573 K and molality above 4.0 m, where the density decreases with pressure above 30 MPa (figure 2), which is thermodynamically incorrect. For the ($MgCl_2 + H_2O$) system, the best model is proposed by Wang *et al.* [23] covering a wide T,P,m range, respectively (273 K to 627 K, 0.1 MPa to 100 MPa, and 0 to 5.4 molal). They modelled the apparent molar volume of ($MgCl_2 + H_2O$) solutions and claimed that the standard deviation of fit is 1.58 $cm^3 \cdot mol^{-1}$, which is much larger than the experimental uncertainty. For the ($CaCl_2 + H_2O$) system, there are two density models that cover a wide T,P,m region. One was developed by Safarov *et al.* [24] with 54 parameters. This model has three flaws: (i) it cannot reduce to pure water density by setting molality of $CaCl_2$ to zero and therefore it cannot yield correct prediction for dilute $CaCl_2$ solutions; (ii) too many parameters give rise to over fitting so that the results calculated from the model contradict the actual density trend (figure 3), which is thermodynamically incorrect; (iii) the model adopts an iterative method and is time consuming for calculations. Another density model for the ($CaCl_2 + H_2O$) system was presented by Oakes *et al.* [25] covering a wide T,P,m range, respectively (273 K to 523 K, 0.1 MPa to 40 MPa, and 0 to 6.15 molal). The model is accurate over most of the stated range, but the standard deviations exceed (0.1–2.0)% at temperatures between (473 and 523) K as compared with their fitting data [25]. For the ($SrCl_2 + H_2O$) and ($BaCl_2 + H_2O$) systems, few density models are presented due to limitation of experimental data. Phutela *et al.* [26] modelled the density of aqueous $SrCl_2$ solutions (273 K to 473 K, 0.1 MPa to 2 MPa, and 0 m to 1.0 molal) with accuracy close to experimental results. Puchalska and Atkinson [45] calculated the apparent molar volume of aqueous $BaCl_2$ solutions (273 K to 473 K, 0.1 MPa to 20 MPa, and 0 to1.6 molal) without giving equations as a function of temperature and pressure, but it can yield apparent molar volumes at infinite dilutions.

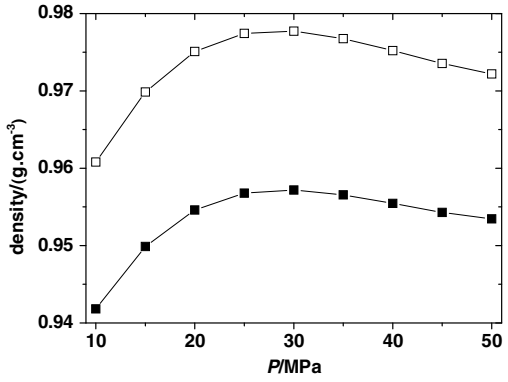

FIGURE 2. Plot of density for ($KCl + H_2O$) solutions from the model of Pabalan and Pitzer [3]: T = 573 K, m_{KCl} = 4.0 m (–■–), m_{KCl} = 4.5 m (–□–).

In order to overcome the deficiencies of the previous models, here we present an improved and universal model to calculate the P,V,T,x properties (or densities) of the binary systems, ($LiCl + H_2O$), ($NaCl + H_2O$), ($KCl + H_2O$), ($MgCl_2 + H_2O$), ($CaCl_2 + H_2O$), ($SrCl_2 + H_2O$), and ($BaCl_2 + H_2O$), with experimental accuracy over a wide T,P,m range. The framework of the model is presented in

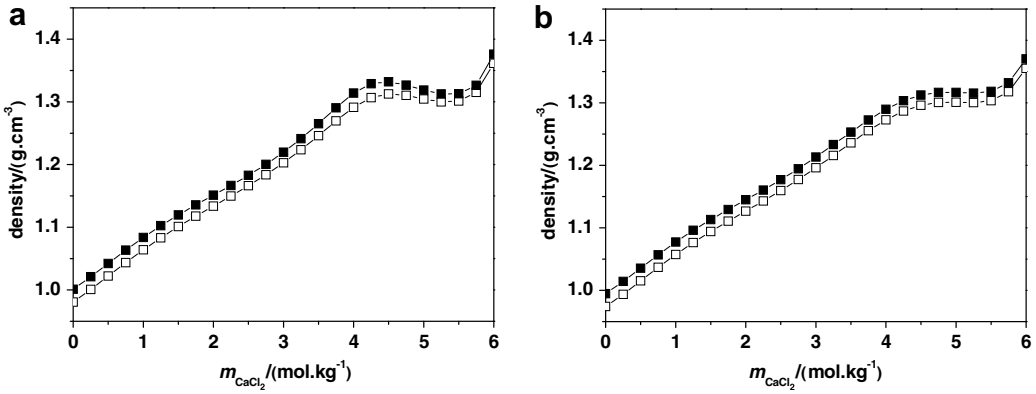

FIGURE 3. Plot of density against molality for ($CaCl_2 + H_2O$) solutions from the model of Safarov et al. [24]: P = 10 MPa (-□-), 60 MPa (–■–); T = 348.15 K (a), 360 K (b).

Section 2 and the experimental data are reviewed in Section 3. Parameterization and comparison with experimental data are shown in Section 4. Then in Section 5, the density model is applied to derive the infinite dilute apparent molar volume of aqueous chloride solutions and to calculate the density and isochores of fluid inclusions.

2. Density model as a function of temperature, pressure and composition

After extensive search and try, we found the following model that can accurately correlate the P,V,T,x properties of binary aqueous chloride solutions:

TABLE 2
Parameters ($c_1 - c_{23}$) for equations (10)–(12)

Parameters	Systems						
	($LiCl + H_2O$)	($NaCl + H_2O$)	($KCl + H_2O$)	($MgCl_2 + H_2O$)	($CaCl_2 + H_2O$)	($SrCl_2 + H_2O$)	($BaCl_2 + H_2O$)
c_1	1.17271480E + 03	1.06607098E + 03	2.90812061E + 02	1.18880927E + 03	1.12080057E + 03	1.11894213E + 03	1.10229139E + 03
c_2	1.40527916E−01	−8.39622456E−03	6.54111195E + 00	−1.43194546E + 00	−2.61669538E−01	−7.37321458E−01	−7.53497776E−01
c_3	−5.53962649E−04	5.35429127E−04	−1.61831978E−02	3.87973220E−03	1.52042960E−03	1.77908655E−03	1.92829036E−03
c_4	1.72402126E−06	7.55373789E−07	1.46280384E−05	−2.20330377E−06	−6.89131095E−07	0	0
c_5	−1.57184556E + 00	−4.19512335E−01	1.41397987E + 01	6.38745038E + 00	−5.11802652E−01	0	0
c_6	8.89959461E−03	1.45082899E−03	−1.07266230E−01	−5.51728055E−02	2.22234857E−03	0	−1.15406910E−03
c_7	−1.52090064E−05	−3.47807732E−06	2.64506021E−04	1.50231562E−04	−5.66464544E−06	0	0
c_8	0	0	−2.19789708E−07	−1.35757912E−07	2.92950266E−09	0	0
c_9	7.33553879E−03	1.10913788E−02	3.02182158E−02	8.43627549E−03	2.43934633E−02	2.21225680E−02	2.57437715E−02
c_{10}	4.06701494E−04	1.14498252E−03	−2.15621394E−03	5.25365072E−03	−1.42746873E−03	6.62517291E−04	1.64541676E−04
c_{11}	−2.38873863E−06	−5.51181270E−06	9.24163206E−06	−1.87204100E−05	7.35840529E−06	−2.37296050E−06	−9.30035886E−07
c_{12}	3.94900863E−09	7.05483955E−09	−1.10089434E−08	4.20263897E−08	−9.43615480E−09	0	0
c_{13}	−3.56131664E−02	−5.05734723E−02	2.87018859E−02	−1.18062548E + 00	−5.18606814E−02	0	0
c_{14}	−6.18472877E−05	−1.32747828E−04	−6.73119697E−04	6.07424747E−04	−6.16536928E−05	0	0
c_{15}	3.00484214E−06	4.77261581E−06	1.68332473E−04	−1.20268210E−04	−1.04523561E−05	0	0
c_{16}	−1.02229075E−08	−1.76888377E−08	−7.99645640E−07	5.23784551E−07	4.52637296E−08	0	0
c_{17}	0	0	1.11881560E−09	−8.23940319E−10	−1.05076158E−10	0	0
c_{18}	2.35592818E−04	6.40541237E−04	−6.59292385E−03	9.75167613E−03	2.31544709E−03	0	0
c_{19}	−2.68117086E−04	3.07698827E−04	−2.02369103E−03	−4.92959181E−04	−1.09663211E−03	−4.21300430E−03	0
c_{20}	−2.17228726E−05	−1.64042763E−04	−1.70609099E−04	−2.73642775E−04	1.90836111E−04	0	0
c_{21}	1.19732313E−07	7.06784935E−07	1.00510108E−06	5.42602386E−07	−9.25997994E−07	9.46738388E−08	0
c_{22}	−1.51104808E−10	−6.50338372E−10	−1.86624642E−09	−1.95602825E−09	1.54388261E−09	0	0
c_{23}	3.83403994E−04	−4.50906014E−04	1.91919166E−02	1.00921935E−01	−1.29354832E−02	0	0

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

System	T/K	P/MPa	m_{salt}/(mol · kg^{-1})	N	Salt	M_s/(g · mol^{-1})	m_r/(mol · kg^{-1})
($LiCl + H_2O$)	273 to 564	0.1 to 40	0 to 10	21	LiCl	42.394	10
($NaCl + H_2O$)	273 to 573	0.1 to 100	0 to 6.0	21	NaCl	58.443	6
($KCl + H_2O$)	273 to 543	0.1 to 50	0 to 4.5	23	KCl	74.551	6
($MgCl_2 + H_2O$)	273 to 543	0.1 to 30	0 to 3.0	23	$MgCl_2$	95.236	2
($CaCl_2 + H_2O$)	273 to 523	0.1 to 60	0 to 6.0	23	$CaCl_2$	110.986	5
($SrCl_2 + H_2O$)	298 to 473	0.1 to 2	0 to 2.0	8	$SrCl_2$	158.536	2
($BaCl_2 + H_2O$)	273 to 473	0.1 to 20	0 to 1.6	7	$BaCl_2$	206.286	1.5

N, numbers of parameters; M_s, molar mass of salt; m_r, the reference molality.

TABLE 4
The model deviations from experimental data of aqueous chloride solutions

References	T/K	P(/0.1 MPa)	m_{LiCl}/(mol · kg^{-1})	N[a]	AAD/%	MAD/%
			(LiCl + H_2O) system			
[62]	298.15 to 473.15	20.27	0.1 to 1.0	32	0.025	0.054
[63]	298.15	1.01	0 to 3.84	48	0.008	0.082
[64]	293.15 to 313.15	1.01	0.1172	21	0.001	0.003
[65]	273.15 to 318.16	1.01	3.999	12	0.047	0.086
[66]	298.15	1.01	0.0817 to 0.7641	8	0.006	0.010
[67]	298.15	1.01	0.95 to 5.62	9	0.111	0.227
[68]	278.15 to 308.15	1.01	0.05 to 3.50	35	0.012	0.051
[69]	298.15	1.01	0.1078 to 1.0879	9	0.006	0.008
[70]	278.15 to 368.15	1.01	0.1189 to 1.2128	59	0.013	0.044
[29]	298.15	1.01 to 404.20	0.25 to 4.97	38	0.019	0.124
[71]	321.63 to 549.77	7.6 to 325.7	0.0515 to 2.989	172	0.027	0.182
[47]	298.14 to 363.31	1.01	2.63 to 16.77	107	0.092	0.493
[72]	278.15 to 338.15	1.01	0.1009 to 1.0009	183	0.007	0.031
[73]	288.15 to 318.15	1.01	1.13 to 12.13	36	0.054	0.138
[74,75]	278.15 to 368.15	3.5	0.0249 to 1.0036	77	0.016	0.082
[21]	291.25 to 564.24	1.01 to 305.52	0.13 to 15.50	277	0.132	0.992
			NaCl + H_2O system			
			m_{NaCl}/(mol · kg^{-1})			
[104]	273.2 to 338.15	1.01	0.21 to 1.01	17	0.007	0.017
[62]	298.15 to 473.15	20.27	0.1 to 1	32	0.009	0.046
[50]	298.15 to 448.15	1.01	0.1 to 2.5	32	0.044	0.233
[63]	298.15	1.01	0 to 3.66	21	0.005	0.009
[79]	273.2 to 338.15	1.01	0.21 to 1.01	17	0.007	0.017
[64]	293.15 to 313.15	1.01	0.11425	21	0.002	0.005
[65]	273.15 to 318.21	1.01	4	9	0.062	0.115
[67]	298.15	1.01	1.02 to 5.60	5	0.097	0.146
[68]	278.15	1.01	0.05 to 3.5	19	0.020	0.045
[80]	273.15 to 328.15	1.01	0.01 to 0.965	83	0.004	0.043
[83]	274.65 to 318.15	1.01	0.027 to 3.014	69	0.008	0.047
[42]	273.15 to 323.15	99.9 to 1001.2	0.03 to 2.01	179	0.017	0.042
[84]	298.15 to 323.15	1.01	0.01 to 5.82	44	0.010	0.028
[69]	298.15	1.01	0.01 to 1.00	12	0.006	0.011
[86]	298.15	1.01	0.063 to 2.812	40	0.005	0.014
[87]	273.15 to 308.15	1.01	0.01 to 1.50	57	0.007	0.029
[88]	288.15 to 318.15	1.01	0.062 to 5.924	58	0.007	0.024
[70]	278.15 to 368.15	1.01	0.1 to 1.2	60	0.008	0.084
[89]	303.15 to 473.15	20.27	0 to 4.39	63	0.038	0.236
[33]	278.15 to 318.15	1.01	0.37 to 6.00	46	0.015	0.076
[44]	573.15	100 to 1000	1.09 to 4.28	24	0.330	0.803
[39]	298.15 to 318.15	1.01	0 to 6.1	45	0.007	0.026
[93]	298.15 to 498.1	1.01 to 144	0.10 to 4.99	12	0.015	0.045
[29]	298.15	1.01 to 406.8	0.058 to 4.991	40	0.011	0.052
[31]	308.15 to 368.15	1.01	0.256 to 6.198	141	0.011	0.033
[94]	323.05 to 549.79	1 to 401.6	0.0026 to 5.0464	413	0.028	0.213
[40]	298.23 to 308.12	1	0.08 to 6.04	23	0.009	0.032
[43]	573.15	70 to 85.8	0 to 5.46	7	0.351	0.533
[57]	298.15 to 413.15	1 to 20	0.5 to 4.5	32	0.018	0.066
[41]	298.05 to 522.98	70.5 to 415	0.165 to 5.484	179	0.045	0.305
[51]	277.15 to 343.15	1.01	0.1 to 1	201	0.004	0.009
[95]	273 to 293	1.01	0.009 to 6.014	90	0.016	0.075
[96]	308.15 to 323.15	1.01	0.0625 to 1	15	0.047	0.207
			(KCl + H_2O) system			
			m_{KCl}/(mol · kg^{-1})			
[62]	298.15 to 473.15	20.27	0.1 to 1	31	0.028	0.087
[63]	298.15	1.01	0 to 2.93	19	0.006	0.018
[79]	273.2 to 338.15	1.01	0.21 to 0.83	16	0.012	0.059
[64]	293.15 to 313.15	1.01	0.115	21	0.001	0.002
[67]	298.15	1.01	0.50 to 4.00	8	0.027	0.041
[42]	273.15 to 323.15	196.62 to 995.33	0.17 to 1.00	75	0.035	0.105
[84]	293.15 to 323.15	1.01	0.33 to 4.55	45	0.032	0.166
[69]	298.15	1.01	0.10 to 1.00	10	0.008	0.012
[86]	298.15	1.01	0.046 to 2.009	21	0.005	0.019
[70]	278.15 to 368.15	1.01	0.04 to 1	70	0.011	0.068
[39]	298.15 to 318.15	1.01	0 to 4.5	50	0.026	0.083
[29]	298.15	1.01 to 406.4	0.0585 to 3.012	35	0.013	0.041
[54]	298.15	1.01	0.5 to 4.5	4	0.040	0.120
[51]	277.15 to 343.15	1.01	0.1 to 1	201	0.009	0.044
			($MgCl_2$ + H_2O) system			
			m_{MgCl_2}/(mol · kg^{-1})			
[103]	298.15	1.01	0.04 to 0.23	4	0.002	0.003
[104]	298.15	1.01	0.19 to 0.70	2	0.003	0.003
[105]	323.15 to 473.15	20.27	0.1 to 1.0	28	0.034	0.136

(*continued on next page*)

TABLE 4 (*continued*)

References	T/K	P(/0.1 MPa)	m_{LiCl}/(mol · kg^{-1})	N[a]	AAD/%	MAD/%
[106]	298.15	1.01	0.004 to 0.341	9	0.002	0.003
[42]	273.15 to 323.15	99.9 to 1001.2	0.009 to 0.315	123	0.006	0.026
[69]	298.15	1.01	0.05 to 0.97	10	0.002	0.006
[87]	273.15 to 308.15	1.01	0.005 to 1.475	78	0.005	0.024
[33]	278.15 to 318.15	1.01	0.01 to 5.43	144	0.029	0.238
[39]	298.15 to 318.15	1.01	0 to 3.31	35	0.017	0.028
[55]	288.15 to 328.15	1.01	0.05 to 5.00	56	0.091	0.311
[29]	298.15	1.01 to 406.4	0.03 to 2.95	34	0.011	0.067
[31]	308.15 to 368.15	1.01	0.35 to 4.61	66	0.051	0.634
[107]	297.18 to 371.82	6	0 to 0.53	24	0.012	0.042
[27]	369 to 517	102 to 303	0.03 to 3.04	85	0.087	0.603
			($CaCl_2 + H_2O$) system m_{CaCl_2}/(mol · kg^{-1})			
[103]	298.15	1.01	0.04 to 0.13	4	0.003	0.007
[109]	298.15	1.01	2.71 to 6.05	7	0.132	0.193
[104]	298.15	1.01	0.18 to 0.79	6	0.008	0.013
[105]	323.15 to 473.15	20.27	0.05 to 1.00	35	0.042	0.119
[79]	273.2 to 338.15	1.01	0.22 to 1.00	15	0.015	0.037
[106]	298.15	1.01	0.01 to 0.33	8	0.002	0.005
[69]	298.15	1.01	0.01 to 0.98	12	0.009	0.015
[110]	298.15	1.01	0.02 to 0.41	10	0.021	0.052
[111]	298.15	1.01	0.0 to 5.0	16	0.046	0.162
[55]	288.15 to 328.15	1.01	0.05 to 6	56	0.066	0.354
[29]	298.15	1.01 to 407.1	0.05 to 4.98	39	0.022	0.122
[112]	323.15 to 473.15	20.27	0 to 5.07	49	0.132	0.323
[107]	297.19 to 371.96	6	0 to 0.98	38	0.028	0.146
[113]	323.05 to 450.13	1.01 to 407.1	0.05 to 5.01	167	0.087	0.644
[47]	298.15 to 363.27	1.01	0.99 to 5.90	24	0.063	0.211
[25]	298 to 523	70.3 to 415	0.24 to 4.96	120	0.091	0.558
[24]	298.15 to 398.15	1 to 599.9	0.18 to 6.01	240	0.064	0.481
			($SrCl_2 + H_2O$) system m_{SrCl_2}/(mol · kg^{-1})			
[103]	298.15	1.01	0.05 to 0.26	5	0.004	0.008
[105]	323.15 to 473.15	20.27	0.1 to 1.0	28	0.023	0.118
[106]	298.15	1.01	0.004 to 0.329	9	0.003	0.007
[69]	298.15	1.01	0.20 to 1.0	9	0.008	0.011
[32]	323.15 to 473.15	20.27	0 to 2.72	61	0.060	0.569
[107]	297.19 to 371.96	6	0 to 1	24	0.107	0.566
			($BaCl_2 + H_2O$) system m_{BaCl_2}/(mol · kg^{-1})			
[104]	298.15	1.01	0.19 to 0.75	6	0.013	0.032
[105]	323.15 to 473.15	20.27	0.1 to 1	28	0.035	0.141
[79]	273.2 to 338.2	1.01	0.19 to 0.64	14	0.014	0.039
[106]	298.15	1.01	0.004 to 0.387	9	0.001	0.003
[69]	298.15	1.01	0.10 to 0.96	10	0.009	0.028
[55]	288.15 to 328.15	1.01	0.05 to 1.5	49	0.033	0.106
[45]	288.15 to 423.15	0.987 to 200	0.1 to 1.22	214	0.019	0.152

[a] N, number of measurements; AAD, average absolute deviations calculated from this model; MAD, maximal absolute deviations calculated from this model.

$$\rho_{sol} = \frac{(1000 + mM_s)\rho_{H_2O}}{1000 + mV_\phi\rho_{H_2O}}, \quad (1)$$

$$V_\phi = V_\phi^\circ + v|z_+z_-|A_V h(I) + 2v_+v_-mRT(B_V + v_+z_+mC_V), \quad (2)$$

where ρ_{sol} and ρ_{H_2O} are the density of solutions and pure water in g · cm^{-3}, respectively. The values of ρ_{H_2O} used here are calculated from the equations of IAPWS97 [37] and m is the molality of salts (LiCl, NaCl, KCl, $MgCl_2$, $CaCl_2$, $SrCl_2$, or $BaCl_2$) in mol · kg^{-1}. The M_s is the molar mass of chlorides in g · mol^{-1}. The V_ϕ is the apparent molar volume in cm^3 · mol^{-1} and V_ϕ° is the apparent molar volume of the chlorides at infinite dilution in the same unit. The z_+ and z_- are the charge of cation and anion, respectively, while v_+ and v_- are the number of cation and anion charges, respectively, and $v = v_+ + v_-$. The A_V is the volumetric Debye–Hückel limiting law slope as defined by [46] (see Appendix A). The I is ion strength:

$$I = \frac{1}{2}\sum_i m_i z_i^2, \quad (3)$$

$$h(I) = \frac{\lg(1 + bI^{0.5})}{2b}, \quad (4)$$

where b = 1.2 kg$^{0.5}$ · mol$^{-0.5}$. The B_V and C_V of equation (2) are the second and third virial coefficients, and R = 8.314472 cm^3 · MPa · mol^{-1} · K^{-1}. The V_ϕ°, B_V and C_V are a function of temperature T (in K) and pressure P (in MPa) by fitting to experimental data with a least squares algorithm. However, because V_ϕ° changes rapidly at high temperatures and displays a complex behaviour with considerable curvature at low temperatures, we adopt an indirect fitting method similar to the method of Rogers and Pitzer [2].

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

$$V_\phi = \frac{V(m) - \frac{1000}{\rho_{H_2O}}}{m}, \quad (5)$$

$$\frac{V(m)}{m} - \frac{1000}{m\rho_{H_2O}} = V_\phi^\circ + v|z_+z_-|A_V h(I_m) + 2v_+v_-mRT(B_V + v_+z_+mC_V). \quad (6)$$

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

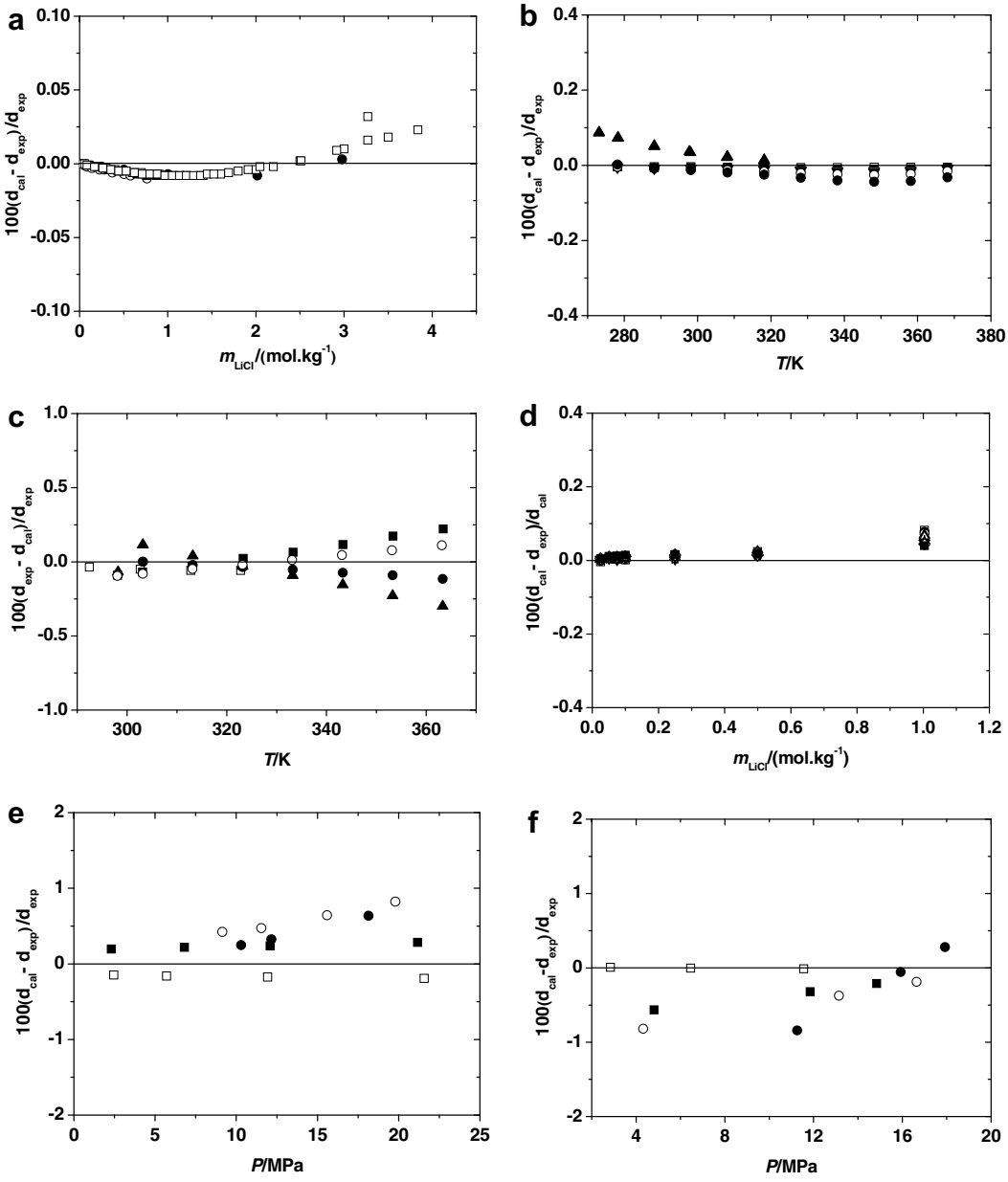

FIGURE 4. Plot of density deviations against temperature, molality, and pressure for our model from experimental data for (LiCl + H_2O) solutions: d_{cal} is the density calculated from this model and d_{exp} is the experimental density data (dots in figure), as are the same in figures 5 to 10. (a) T = 298.15 K, P = 0.1 MPa, ● Gates and Wood [29], ○ Desnoyers *et al.* [66], ■ Millero *et al.* [69], □ Vaslow [63]. (b) P = 0.1 MPa, Out and Los [70]: m_{LiCl} = 0.1189 m (□), 0.2383 m (■), 0.3581 m (▽), 0.4786 m (▼), 0.7210 m (○), 1.2128 m (●); Wirth and Losurdo [65]: m_{LiCl} = 0.1189 m (▲). (c) P = 0.1 MPa, Wimby and Berntsson [47], m_{LiCl} = 2.6297 m (□), 10.707 m (■), 14.4389 m (●), 12.4408 m (○), 15.647 m (▲). (d) P = 0.35 MPa, Brown *et al.* [74,75], T = 278.15 K (□), 283.15 K (●), 288.15 K (○), 298.15 K (▲), 308.15 K (△), 318.15 K (★), 328.15 K (▼), 338.15 K (☆), 348.15 K (♦), 358.15 K (◇), 368.15 K (■). (e) m_{LiCl} = 10.062 m, Abdulagatov and Azizov [21], T = 291.25 K (□), 373.59 K (■), 533.15 K (○), 564.24 K (●). (f) m_{LiCl} = 15.498 m, Abdulagatov and Azizov [21], T = 306.39 K (□), 418.62 K (■), 449.61 K (○), 557.08 K (●).

$$\frac{V(m_r)}{m_r} - \frac{1000}{m_r \rho_{H_2O}} = V^{\circ}_{\phi} + \nu|z_+z_-|A_V h(I_{m_r}) + 2\nu_+\nu_- m_r RT(B_V + \nu_+ z_+ m_r C_V). \quad (7)$$

Subtracting equation (7) from equation (6), the following equation is obtained

$$\frac{V(m)}{m} = \frac{V(m_r)}{m_r} + \frac{1000}{\rho_{H_2O}}\left(\frac{1}{m} - \frac{1}{m_r}\right) + \nu|z_+z_-|A_V[h(I_m) - h(I_{m_r})] + 2\nu_+\nu_- RT[B_V(m - m_r) + \nu_+ z_+ C_V(m^2 - m_r^2)]. \quad (8)$$

Combining equation (8) with the equation $V(m) = \frac{1000 + mM_s}{\rho_{sol}}$, where M_s is molar mass of chloride in g · mol^{-1}, then equation (9) results:

$$\frac{1000 + mM_s}{m\rho_{sol}} = \frac{V(m_r)}{m_r} + \frac{1000}{\rho_{H_2O}}\left(\frac{1}{m} - \frac{1}{m_r}\right) + \nu|z_+z_-|A_V[h(I_m) - h(I_{m_r})] + 2\nu_+\nu_- RT[B_V(m - m_r) + \nu_+ z_+ C_V(m^2 - m_r^2)]. \quad (9)$$

Equations of (1)–(9) form the basis of our density model, which correlates temperature, pressure, density, and molality of salts. The density is reciprocal volume, thus equations (1)–(9) can be called the P,V,T,x model of (water + salt) solution. The $V(m_r)$ is a function of temperature and pressure as B_V and C_V in this study. Therefore, the problem remaining is to find the optimal m_r and a universal function form for calculating $V(m_r)$, B_V and C_V. After numerous tries, we find that the following equations can satisfy the requirement

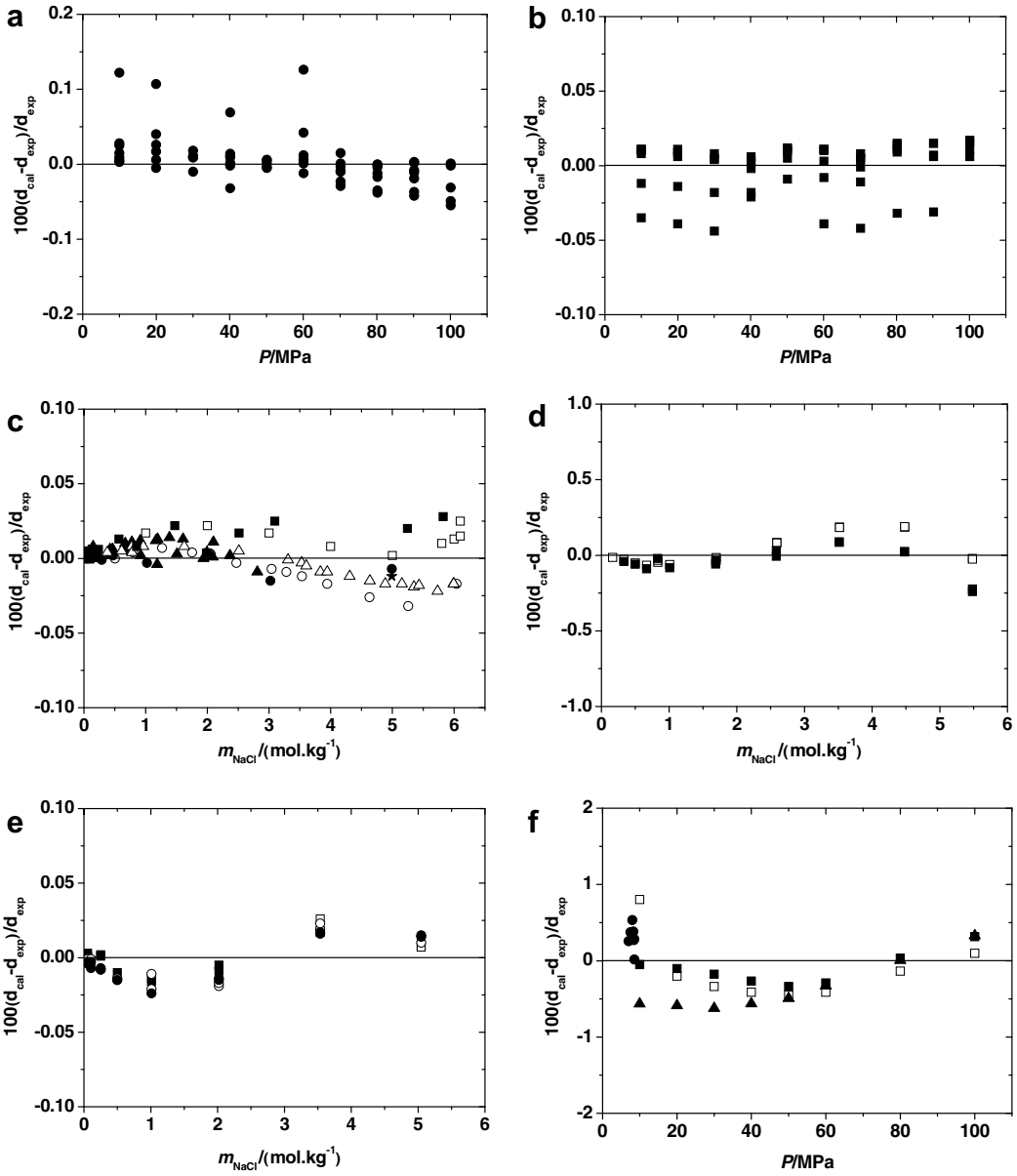

FIGURE 5. Plot of density deviations against molality and pressure for our model from experimental data for (NaCl+H_2O) solutions: (a) T = 273.15 K, Chen *et al.* [42], m_{NaCl} = 0.0303-2.008 m (●). (b) T = 323.15 K, Chen *et al.* [42], m_{NaCl} = 0.1299–1.307 m (■). (c) T = 298.15 K, P = 0.1 MPa, □ Romanklw and Chou [39], ○ Oakes *et al.* [40], ♦ Gates and Wood [29], ▲ Olofsson [86], △ Surdo *et al.* [33], ★ Albert and Wood [93], ■ Goncalves and Kestin [84]. (d) T = 523 K, Simonson [41], P = 7.1 MPa (□), 40.9 MPa (■). (e) T = 349.16 K, Majer *et al.* [94], P = 0.1 MPa (□), 0.65 MPa (■), 20.3 MPa (○), 39.9 MPa (●). (f) T = 573.15 K, Gehrig *et al.* [44]: m_{NaCl} = 1.09 m (□), 1.90 m (■), 4.28 m (▲); Bischoff [43]: ●P = 7 to 8.58 MPa, m_{NaCl} = 0 to 5.46 m.

$$V(m_r) = c_1 + c_2T + c_3T^2 + c_4T^3 + P(c_5 + c_6T + c_7T^2 + c_8T^3), \quad (10)$$

$$B_V = \frac{c_9}{T-227} + c_{10} + c_{11}T + c_{12}T^2 + \frac{c_{13}}{647-T} + P\left(\frac{c_{14}}{T-227} + c_{15} + c_{16}T + c_{17}T^2 + \frac{c_{18}}{647-T}\right), \quad (11)$$

$$C_V = \frac{c_{19}}{T-227} + c_{20} + c_{21}T + c_{22}T^2 + \frac{c_{23}}{647-T}. \quad (12)$$

The parameters ($c_1 - c_{23}$) are evaluated from a large number of experimental data as discussed below.

3. Review of the density data of binary aqueous chloride solutions

The densities (or volumes) of binary aqueous chloride solutions have been measured over a wide T,P,m range with thousands of measurements (table 1) for (LiCl + H_2O), (NaCl + H_2O), (KCl + H_2O), ($MgCl_2$ + H_2O), ($CaCl_2$ + H_2O), ($SrCl_2$ + H_2O), and ($BaCl_2$ + H_2O) systems. In this study, we focus our interest in the temperature range below 573 K.

The (LiCl + H_2O) system: over 1000 measurements of the density of aqueous LiCl solutions have been reported for this system, covering a T,P,m range, respectively 273 K to 564 K, 0.1 MPa to 40 MPa, and 0 to16.8 molal. Most of these data are consistent with each other. Above 16.8 m only Wimby and Berntsson [47] measured the density of LiCl + H_2O solutions between T = (293 and 340) K at l atm.

The (NaCl + H_2O) system: the density (volume) measurements of aqueous NaCl solutions are the most extensive in all aqueous electrolyte solutions. In total, more than 3000 data points have been reported. Rogers and Pitzer [2] reviewed in detail the

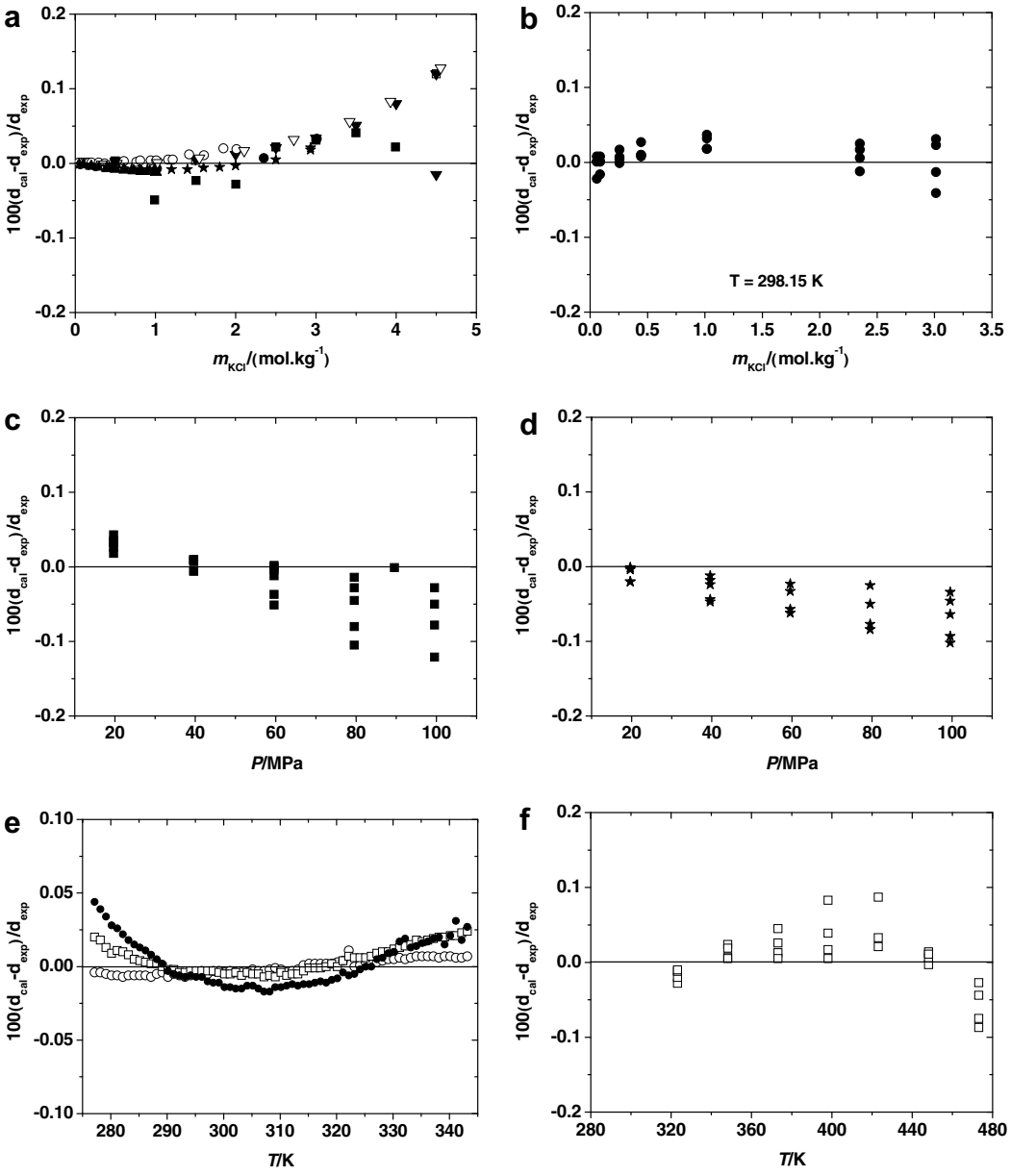

FIGURE 6. Plot of density deviations against pressure and temperature for our model from experimental data for (KCl + H_2O) solutions: (a) T = 298.15 K, P = 0.1 MPa, □ Kumar [54], ▼ Romanklw and Chou [39], ● Gates and Wood [29], ○ Olofsson [86], ▲ Millero *et al.* [69], ▽ Goncalves and Kestin [84], ★ Vaslow [63], ■ Ostroff *et al.* [67]. (b) T = 298.15 K, Gates and Wood [29], P = 10.38 to 40.64 MPa (●). (c) T = 273.15 K, Chen *et al.* [42], m_{KCl} = 0.1655 to 1.004 m (■). (d) T = 323.15 K, Chen *et al.* [42], m_{KCl} = 0.3331 to 1.004 m (★). (e) P = 0.1 MPa, Apelblat and Manzurola [51], m_{KCl} = 0.1 m (○), 0.5 m (□), 1.0 m (●). (f) P = 2.027 MPa, Ellis [62], m_{KCl} = 0.1 to 1.0 m (□).

experimental data prior to 1982. In all, over 40 data sets are found for the density (volume) of (NaCl + H_2O) system with a wide T,P,m range and experimental precision of 0.0001% to 0.1%. Most of the experimental data between T = (273 and 573) K are consistent with each other except for the small number of data points [48–50], whose density (volume) data apparently deviate from other data sets over the same T,P,m range. Therefore, all data points but those of [48–50] are included in the parameterization that cover a wide T,P,m range, respectively (273 K to 573 K, 0.1 MPa to 100 MPa, and 0 to 6 molal) for the (NaCl + H_2O) system.

The (KCl + H_2O) system: the density (volume) measurements of aqueous KCl solutions are also extensive. Pabalan and Pitzer [3] made a critical review of these density data before 1988. After 1988, Apelblat and Manzurola [51] and Crovetto *et al.* [52] undertook experimental studies on the density of aqueous KCl solutions. Most of experimental data below T = 543 K are consistent with one another except for the data from [48,53]. All data points but these [48,53] are taken for parameterization to provide a wide range of values (273 K to 543 K, 0.1 MPa to 50 MPa and 0 to 4.5 molal) for the (KCl + H_2O) system.

The ($MgCl_2$ + H_2O) system: the experimental studies on the density (volume) of aqueous $MgCl_2$ solutions are not as extensive as those for the (NaCl + H_2O) system. Wang *et al.* [23] carried out a detailed study of the thermodynamic properties of aqueous $MgCl_2$ solutions, including the review of the volumetric properties. By comparison, we find that all data sets available are consistent each other, hence all these data points are used in the parameterization covering a large T,P,m range, respectively of 273 K to 543 K, 0.1 MPa to 30 MPa, and 0 to 3.0 molal.

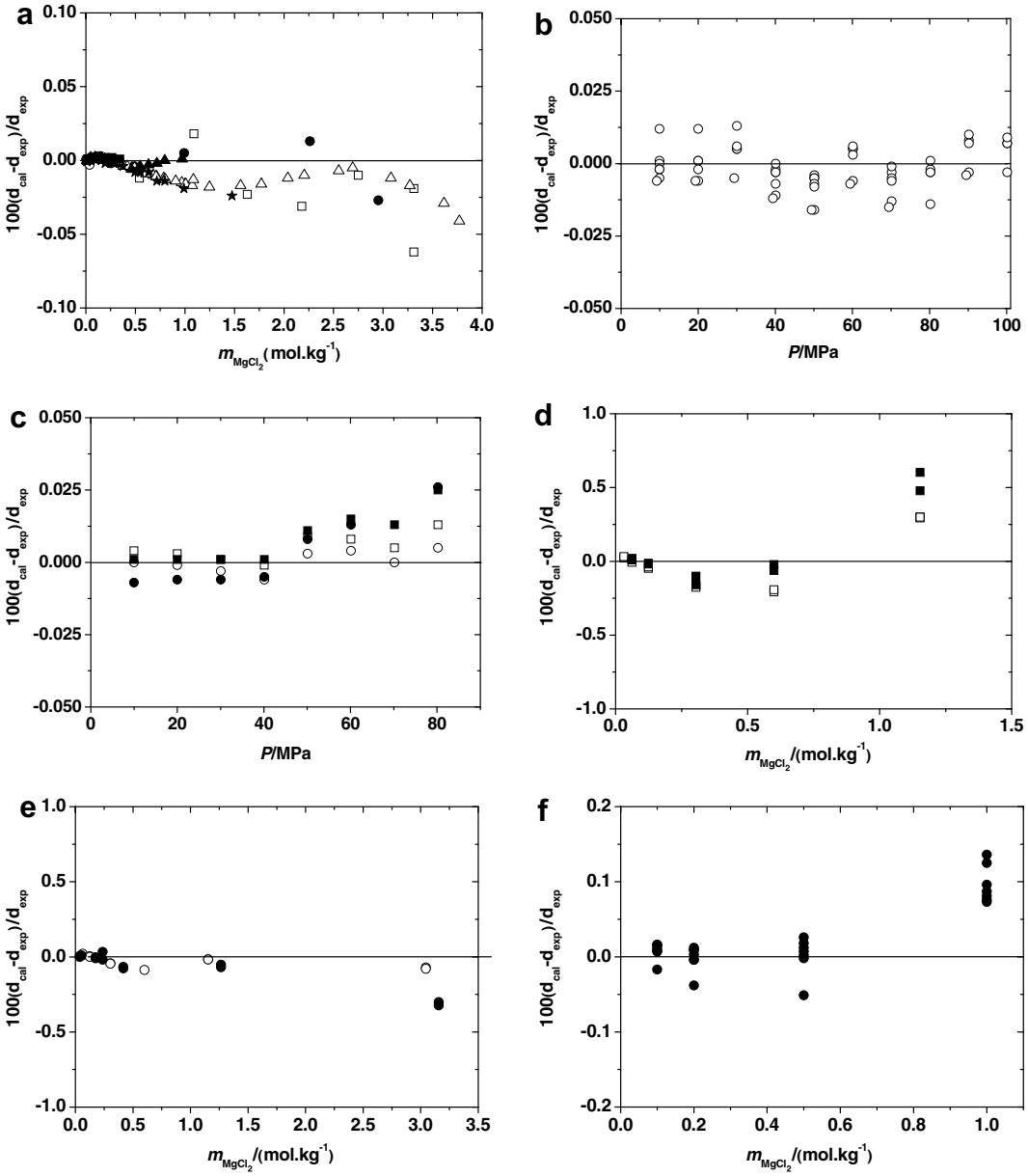

FIGURE 7. Plot of density deviations against pressure and molality for our model from experimental data for ($MgCl_2 + H_2O$) solutions: (a) $T = 298.15$ K, $P = 0.1$ MPa, □ Romanklw and Chou [39], ■ Perron *et al.* [106], ○ Shedlovsky [103], ● Gates and Wood [29], △ Surdo *et al.* [33], ▲ Millero *et al.* [69], ★ Chen *et al.* [87]. (b) $T = 273.15$ K, Chen *et al.* [42], $m_{MgCl_2} = 0.00876$ to 0.3150 m (○). (c) $T = 323.15$ K, Chen *et al.* [42], $m_{MgCl_2} = 0.0794$ m (○), 0.1395 m (□), 0.2184 m (■), 0.3150 m (●). (d) $T = 517$ K, Obsil *et al.* [27], $P = 10.3$ MPa (□), 30.3 MPa (■). (e) $T = 450$ K, Obsil *et al.* [27], $P = 10.1$ MPa (○), 30.5 MPa (●). (f) Ellis *et al.* [105], $T = 323.15$ to 473.15 K, $P = 2.027$ MPa (●).

The ($CaCl_2 + H_2O$) system: there is a large number of experimental data for the density of aqueous $CaCl_2$ solutions, covering a T,P,m range, respectively, of 273 K to 523 K, 0.1 MPa to 60 MPa, and 0 to 6.0 molal. Most data points are consistent with each other except for the data points in [39,40,54]. Therefore, all experimental data but those from [39,40,54] are used in the parameterization of the model.

The ($SrCl_2 + H_2O$) and ($BaCl_2 + H_2O$) systems: the density (volume) measurements of aqueous $SrCl_2$ and $BaCl_2$ solutions are not extensive. For the ($SrCl_2 + H_2O$) system, the range of experimental data is limited over the T,P,m range of (273 K to 473 K, 0.1 MPa to 2 MPa, and 0 to 3.6 molal), and the experimental data [55,56] are inconsistent with the results of the other workers. For the ($BaCl_2 + H_2O$) system, the experimental data [57] are inconsistent with those from the other studies. Therefore, all data points listed in table 1 for the ($SrCl_2 + H_2O$) and ($BaCl_2 + H_2O$) systems but those [55–57] are included in the parameterization. For the ($SrCl_2 + H_2O$) system, the valid T,P,m range is, respectively (298 K to 473 K, 0.1 MPa to 2 MPa, and 0 to 2.0 molal); and for the ($BaCl_2 + H_2O$) system, the valid T,P,m range is, respectively (273 K to 473 K, 0.1 MPa to 20 MPa, and 0 to 1.6 molal).

4. Parameterization and comparison with experimental data

The parameters ($c_1 - c_{23}$) of equations (10)–(12) are fitted directly to the experimental density data discussed above by least-squares regression. Table 2 lists the optimized parameters. For the binary $LiCl + H_2O$, $NaCl + H_2O$, $KCl + H_2O$, $MgCl_2 + H_2O$, $CaCl_2 + H_2O$, $SrCl_2 + H_2O$, and $BaCl_2 + H_2O$ systems, the number

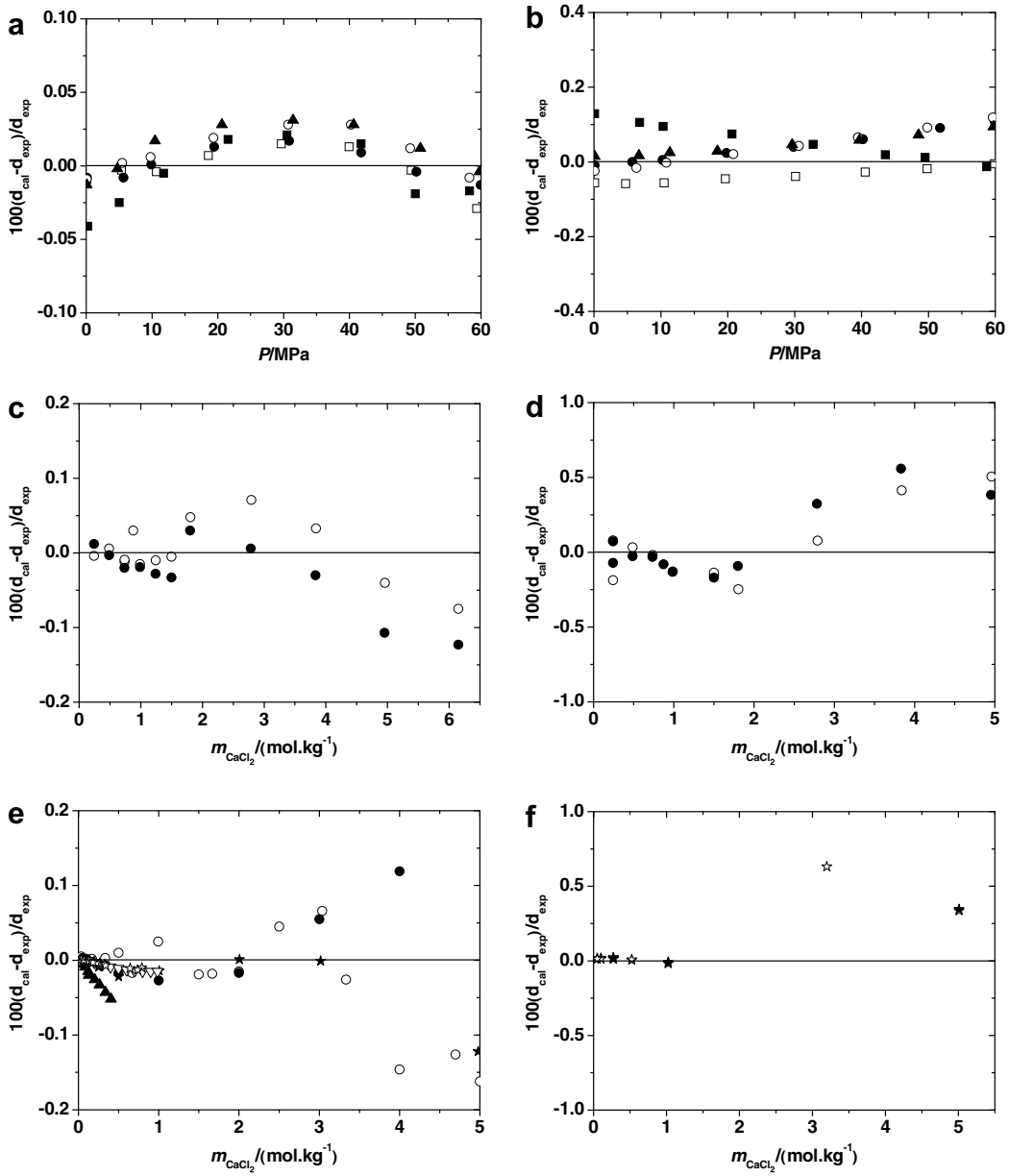

FIGURE 8. Plot of density deviations against molality for our model from experimental data for ($CaCl_2 + H_2O$) solutions: (a) Safarov *et al.* [24], m_{CaCl_2} = 0.184 m, T = 298.15 K (□), 323.15 K (●), 348.15 K (○), 373.15 K (▲), 398.15 K (■). (b) Safarov *et al.* [24], m_{CaCl2} = 4.852 m, T = 298.15 K (□), 323.15 K (●), 348.15 K (○), 373.15 K (▲), 398.15 K (■). (c) T = 298 K, Oakes et al. [25], P = 7.3 MPa (○), 41.7 MPa (●). (d) T = 523 K, Oakes *et al.* [25], P = 7.2 MPa (○), 40.7 MPa (●). (e) T = 298.15 K, P = 0.1 MPa, ○ Kumar *et al.* [111], ▲ Spitzer *et al.* [110], ● Isono [55], ★ Gates and Wood [29], ▽ Millero *et al.* [69], ☆ Perron *et al.* [106]. (f) T = 449.75 K, Gates and Wood [113], P = 20.4 MPa (☆), 29.1 MPa (★).

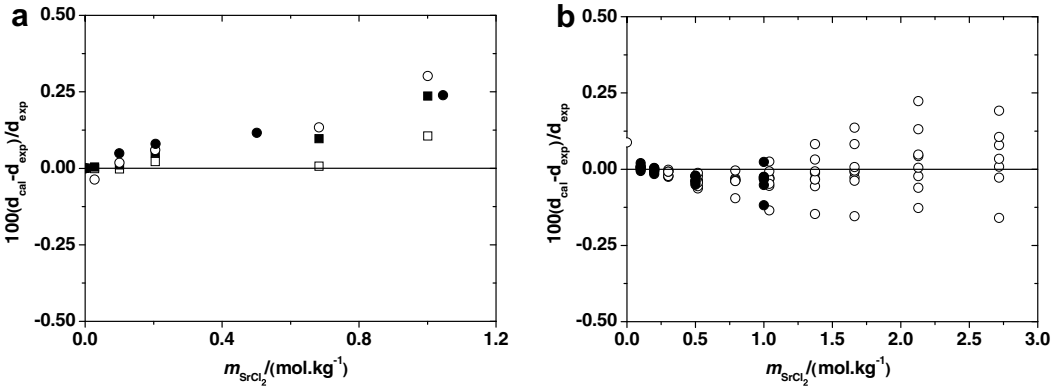

FIGURE 9. Plot of density deviations against molality for our model from experimental data for ($SrCl_2 + H_2O$) solutions: (a) P = 0.6 MPa, Saluja and Leblanc [107], T = 297.19 K (□), 321.9 K (■), 346.92 K (○), 371.96 K (●). (b) P = 2.027 MPa, Kumar [32], T = 298.15 to 473.15 K (○); Ellis *et al.* [105], T = 323.15 to 473.15 K (●).

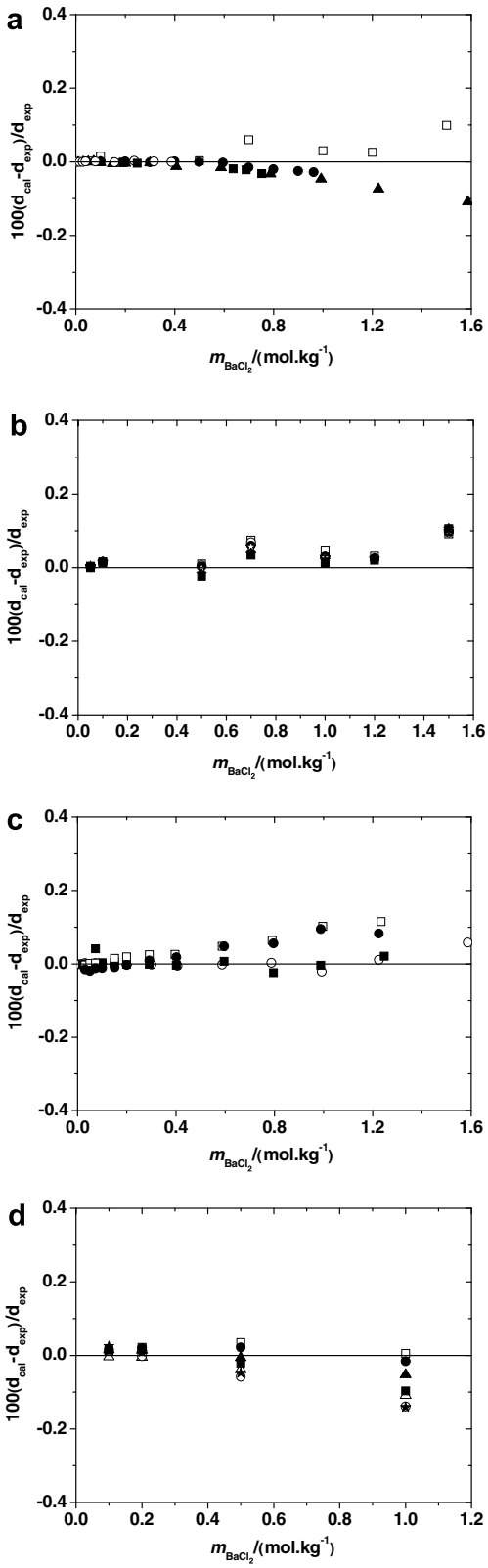

FIGURE 10. Plot of density deviations against molality for our model from experimental data for ($BaCl_2 + H_2O$) solutions: (a) $T = 298.15$ K, $P = 0.1$ MPa, □ Isono [55], ●Millero *et al.* [69], ▲ Puchalska and Atkinson [45], ○ Perron *et al.* [106], ■ Dunn [104]. (b) $P = 0.1$ MPa, Isono [55], $T = 288.15$ K (□), 293.15 K (○), 298.15 K (●), 303.15 K (☆), 318.15 K (★), 328.15 K (■). (c) $P = 20$ MPa, Puchalska and Atkinson [45], $T = 353.15$ K (○), 373.15 K (■), 393.15 K (□), 413.15 K (●). (d) $P = 2.027$ MPa, Ellis *et al.* [105], $T = 323.15$ K (□), 348.15 K (●), 373.15 K (▲), 398.15 K (△), 423.15 K (○), 448.15 K (★), 473.15 K (■).

of parameters is 21, 21, 23, 23, 23, 8, and 7, respectively (table 3). The optimal m_r and valid T,P,m range for the seven binary systems are also listed in table 3. The average deviation from extensive and reliable experimental density data over the above T,P,m range for ($LiCl + H_2O$), ($NaCl + H_2O$), ($KCl + H_2O$), ($MgCl_2 + H_2O$), ($CaCl_2 + H_2O$), ($SrCl_2 + H_2O$), and ($BaCl_2 + H_2O$) systems is 0.054%, 0.025%, 0.020%, 0.034%, 0.066%, 0.045%, and 0.021%, respectively.

The average and maximal deviations calculated from this model are compiled in table 4. Figures 4–10 show the density deviations between the experimental results and model predictions for every binary aqueous chloride solution. As can be seen from table 4 and figures 4–10, most experimental data are accurately reproduced by this model with deviations of less than 0.1%.

TABLE 5
Comparisons of infinite dilution apparent molar volume (V°_ϕ) at $T = 298.15$ K and 0.1 MPa

$LiCl + H_2O$		$NaCl + H_2O$		$KCl + H_2O$	
Reference	V°_ϕ/($cm^3 \cdot mol^{-1}$)	Reference	V°_ϕ/($cm^3 \cdot mol^{-1}$)	Reference	V°_ϕ/($cm^3 \cdot mol^{-1}$)
This model	17.10	This model	16.51	This model	27.09
[114]	17.06	[115]	16.67	[62]	26.50
[116]	17.00	[62]	16.80	[63]	26.89
[117]	17.06	[63]	16.63	[79]	26.81
[118]	17.10	[119]	16.65	[120]	26.85
[121]	16.85	[79]	16.61	[54]	26.91
[62]	16.60	[68]	16.64	[3]	26.98
[63]	16.99	[80]	16.62	[122]	26.87
[64]	16.96	[82]	16.62	[123]	26.84
[66]	16.91	[124]	16.61	[125]	26.85
[68]	16.99	[83]	16.62		
[126]	17.03	[120]	16.62		
[127]	17.13	[69]	16.61		
[70]	16.81	[128]	16.71		
[129]	18.20	[111]	16.72		
[71]	16.73	[130]	16.68		
[131]	16.87	[2]	16.68		
[72]	16.45	[33]	16.62		
[73]	17.59	[132]	16.58		
[74]	16.20	[31]	16.68		
[21]	17.17	[94]	16.30		
		[40]	16.63		
		[125]	16.62		
		[41]	16.66		
$MgCl_2 + H_2O$		$CaCl_2 + H_2O$		$BaCl_2 + H_2O$	
This model	13.70	This model	17.43	This model	21.06
[104]	14.49	[104]	17.78	[104]	23.24
[105]	15.60	[105]	17.00	[105]	25.90
[133]	14.49	[79]	17.83	[79]	23.14
[124]	14.52	[133]	17.81	[106]	22.98
[106]	14.02	[106]	17.65	[134]	23.18
[120]	14.08	[110]	16.10	[45]	22.53
[69]	14.52	[135]	17.20		
[136]	14.51	[134]	17.86	$SrCl_2 + H_2O$	
[134]	14.52	[137]	18.05	Reference	V°_ϕ/($cm^3 \cdot mol^{-1}$)
[128]	15.00	[128]	18.35	This model	17.90
[33]	14.14	[111]	18.86	[133]	17.50
[29]	13.76	[132]	18.53	[106]	18.26
[31]	14.40	[54]	18.53	[110]	16.10
[138]	14.16	[28]	17.42	[111]	18.86
[28]	13.67	[122]	17.42		
[122]	13.73	[40]	17.53		
[125]	14.08	[125]	17.61		
[23]	13.72	[25]	16.83		
		[24]	16.68		

5. Applications of this model

5.1. Calculating the infinite dilution apparent molar volume (V_ϕ°)

The infinite dilution apparent molar volume (V_ϕ°) (or infinite dilution partial molar volume) for aqueous electrolyte solutions is of fundamental interest to study ion–solvent interactions. The values of the infinite dilution apparent molar volume at various temperatures and pressures can be calculated from above density model. Subtracting equation (9) from equation (6), the V_ϕ° results as

$$V_\phi^\circ = \frac{V(m_r)}{m_r} - \frac{1000}{m_r \rho_{H_2O}} - \nu|z_+ z_-|A_V h(I_{m_r}) - 2\nu_+\nu_- RT(B_V m_r + \nu_+ z_+ C_V m_r^2). \quad (13)$$

Table 5 shows the comparison between the values of V_ϕ° derived from this model and from other methods at $T = 298.15$ K and 0.1 MPa. Figures 11 and 12 show the infinite dilution apparent molar volume as a function of temperature at constant pressure. It can be seen that the infinite dilution apparent molar volume gradually increases with temperature at low temperatures, and decreases with temperature at high temperatures. It can be very negative at very high temperatures.

5.2. Calculating density and isochores of fluid inclusions

Density and isochores are very important for the study of fluid inclusions. The water + chloride fluid inclusions have often been found in geological regions, *e.g.* the second type of inclusions of the bronze wing lode-gold deposit in western Australia [10]; the magamtic fluid in the Harney Peak Granite and associated

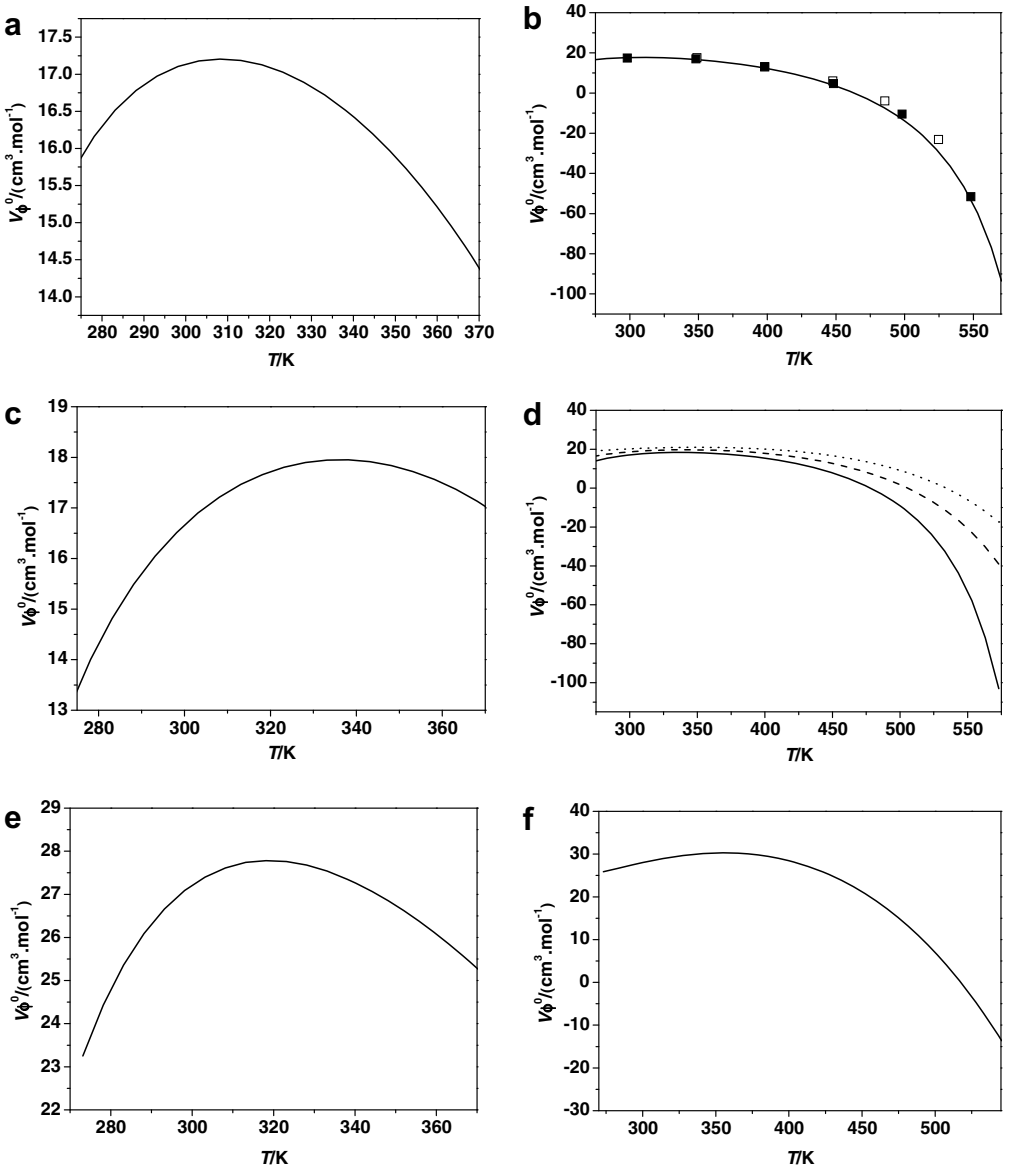

FIGURE 11. Plot of apparent molar volumes against temperature for LiCl, NaCl and KCl at infinite dilution (V_ϕ°) a and b are for the (LiCl + H_2O) system; c and d are for the (NaCl + H_2O) system; e and f are for the (KCl + H_2O) system; the line is calculated from this model. (a) $P = 0.1$ MPa. (b) $P = 16$ MPa, ■ Majer *et al.* [71], □ Abdulagatov and Azizov [21]. (c) $P = 0.1$ MPa. (d) $P = 10$ MPa (solid line), 50 MPa (dashed line), 100 MPa (dotted line). (e) $P = 0.1$ MPa. (f) $P = 40$ MPa.

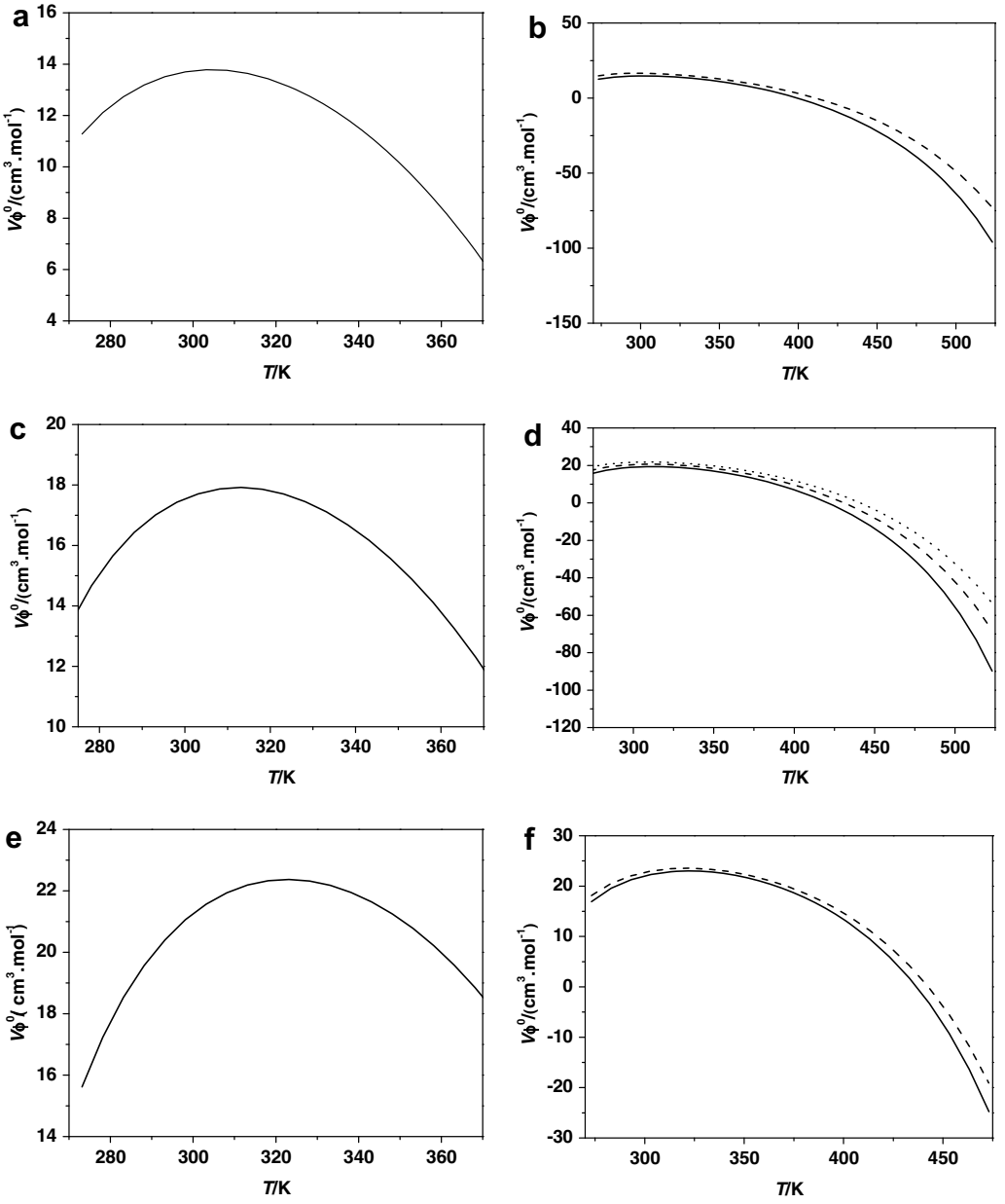

FIGURE 12. Plot of apparent molar volumes against temperature for $MgCl_2$, $CaCl_2$ and $BaCl_2$ at infinite dilution (V°_ϕ) a and b are for the ($MgCl_2 + H_2O$) system; c and d are for the ($CaCl_2 + H_2O$) system; e and f are for the ($BaCl_2 + H_2O$) system; the line is calculated from this model. (a) $P = 0.1$ MPa. (b) $P = 10$ MPa (solid line), 30 MPa (dashed line). (c) $P = 0.1$ MPa. (d) $P = 20$ MPa (solid line), 40 MPa (dashed line), 60 MPa (dotted line). (e) $P = 0.1$ MPa. (f) $P = 10$ MPa (solid line), 20 MPa (dashed line).

pegmatites of the Black Hills, South Dakota, USA [58]; some inclusions of the As + (Ag) sulfide veins in the Spanish Central System [59] and the Satluj Valley NW Himalayas, India [60]. Usually, temperature and composition of the fluid inclusions can be obtained from microthermometric observations, but density, pressure at the homogenization temperature and isochores must be acquired from thermodynamic models. Combining the model of Shibue [61] used to calculate homogenization pressure, we calculate the density of the ($NaCl + H_2O$) system at homogenization temperature and pressure (figure 13). In addition, isochores of the ($NaCl + H_2O$) system over the range of $T = (273$ to $573)$ K are also calculated in terms of the density model (figure 14), from which it can be seen that isochores are a somewhat curved below $T = 373$ K but are almost linear with temperature above 400 K. Since the isochores above $T = 400$ K are approximately linear, the model should be able to extrapolate beyond the T,P range of experiment.

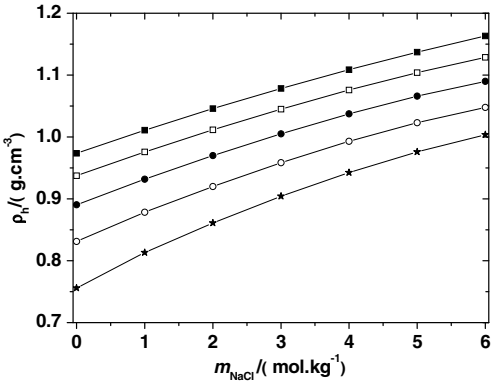

FIGURE 13. Plot of density against molality for the ($NaCl + H_2O$) system at homogenization temperature and pressure: ρ_h is homogenization density. $T = 350$ K (–■–), 400 K (–□–), 450 K (–●–), 500 K (–○–), 550 K (–★–).

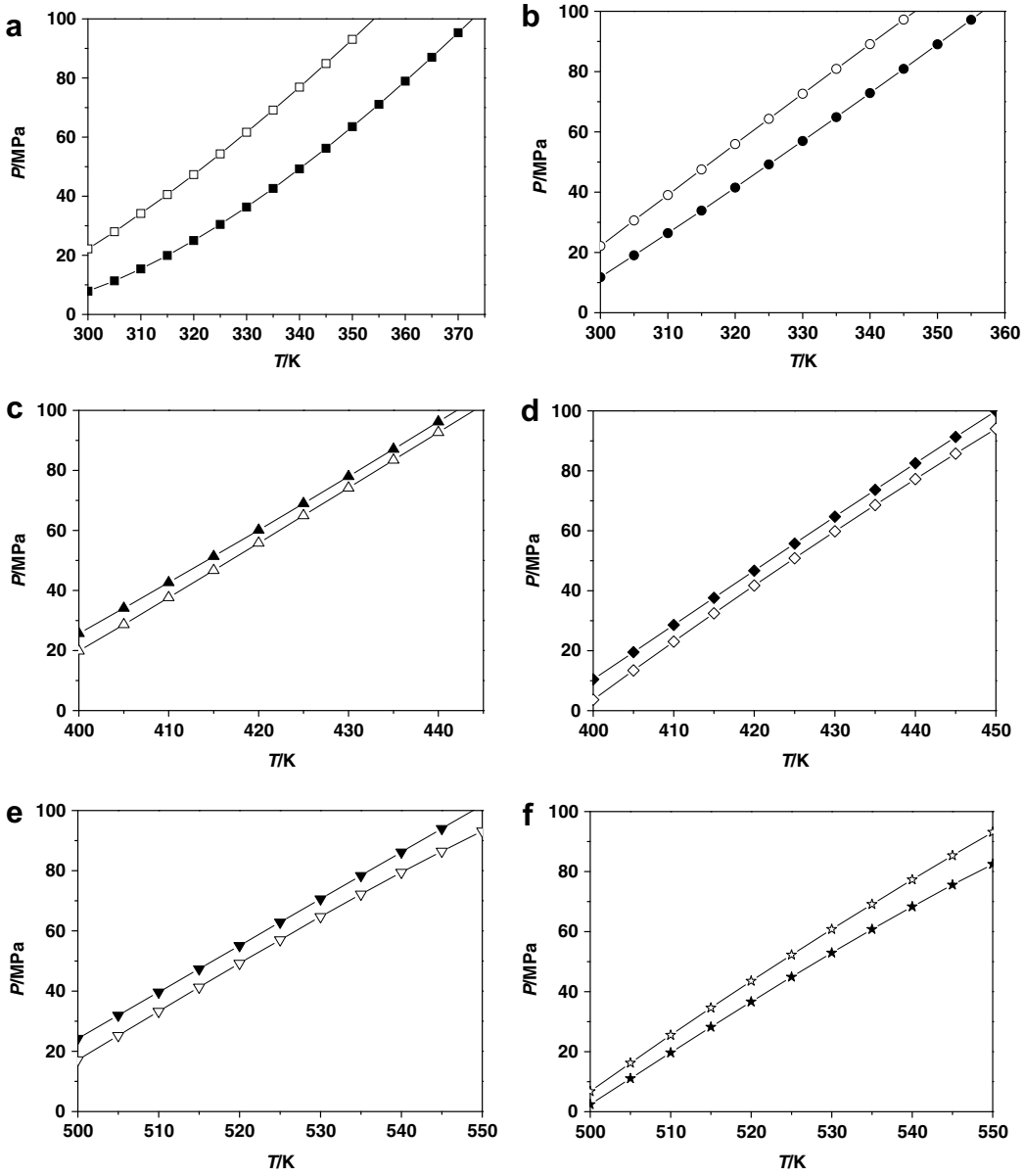

FIGURE 14. Plot of pressure against temperature to illustrate the isochores for the ($NaCl + H_2O$) system: unit of molar volume (V_m) is $cm^3 \cdot mol^{-1}$. (a) –■– $V_m = 18.02$, $m_{NaCl} = 0$ m; –□– $V_m = 17.98$, $m_{NaCl} = 2$ m. (b) –●– $V_m = 18.19$, $m_{NaCl} = 4$ m; –○– $V_m = 18.30$, $m_{NaCl} = 6$ m. (c) –▲– $V_m = 18.96$, $m_{NaCl} = 0$ m; –△– $V_m = 19.04$, $m_{NaCl} = 2$ m. (d) –♦– $V_m = 19.20$, $m_{NaCl} = 4$ m; –◇– $V_m = 19.43$, $m_{NaCl} = 6$ m. (e) –▼– $V_m = 21.19$, $m_{NaCl} = 0$ m; –▽– $V_m = 20.88$, $m_{NaCl} = 2$ m. (f) –★– $V_m = 20.88$, $m_{NaCl} = 4$ m; –☆– $V_m = 20.91$, $m_{NaCl} = 6$ m.

Unit conversion from molarity (c) to molality (m) can also be obtained from the density model. Detailed see Appendix B.

6. Conclusions

An accurate density model over a wide range of temperature, pressure, and concentration is developed for the binary ($LiCl + H_2O$), ($NaCl + H_2O$), ($KCl + H_2O$), ($MgCl_2 + H_2O$), ($CaCl_2 + H_2O$), ($SrCl_2 + H_2O$), and ($BaCl_2 + H_2O$) systems that produces results approximately equal to the experimental accuracy. The average deviation from extensive experimental density data for the systems $LiCl + H_2O$ (273 K to 564 K, 0.1 MPa to 40 MPa, and 0 to10 molal), $NaCl + H_2O$ (273 K to 573 K, 0.1 MPa to 100 MPa, and 0 to 6.0 molal), $KCl + H_2O$ (273 K to 543 K, 0.1 MPa to 50 MPa, and 0 to 4.5 molal), $MgCl_2 + H_2O$ (273 K to 543 K, 0.1 MPa to 40 MPa, and 0 to 3.0 molal), $CaCl_2 + H_2O$ (273 K to 523 K, 0.1 MPa to 60 MPa, and 0 to 6.0 molal), $SrCl_2 + H_2O$ (298 K to 473 K, 0.1 MPa to 2 MPa, and 0 to 2.0 molal) and $BaCl_2 + H_2O$ (273 K to 473 K, 0.1 MPa to 20 MPa, and 0 to 1.6 molal), with the range of temperature, pressure and molality shown respectively, is 0.054%, 0.025%, 0.020%, 0.034%, 0.066%, 0.045%, and 0.021%, respectively. The infinite dilution apparent molar volume V°_{ϕ}, density and isochores of the fluid inclusions can be calculated from this density model. A computer code is developed for this model and can be downloaded from the website: www.geochem-model.org/programs.htm.

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Appendix A

The volumetric Debye–Hückel limiting law slope A_V is as defined by Bradley and Pitzer [46], which takes the following form:

$$A_v = -4RT\left(\frac{\partial A_\phi}{\partial P}\right)_T, \tag{A.1}$$

$$A_\phi = \frac{1}{3}\left(\frac{2\pi N_0 \rho_w}{1000}\right)^{\frac{1}{2}}\left(\frac{e^2}{DkT}\right)^{\frac{3}{2}}, \tag{A.2}$$

where ρ_w is the density from equations of IAPWS97 [37] and D is the dielectric constant of pure water calculated from original equation (1) of Bradley and Pitzer [46]. The parameters are $N_0 = 6.0221415 \times 10^{23}\ \mathrm{mol^{-1}}$, $e = 1.60217733 \times 10^{-19}\ \mathrm{C}$, $k = 1.3806505 \times 10^{-23}\ \mathrm{J \cdot K^{-1}}$.

Appendix B

Unit conversion from molarity (c) to molality (m) can be obtained from the density model. Molarity reported in many experimental measurements is dependent on temperature and pressure, but is inconvenient to use when temperature and pressure change. However, molality does not change with temperature and pressure and is widely used in geochemical and chemical engineering fields. Therefore, in many applications, one needs to convert molarity (c) to molality (m). With the highly accurate model of this study and an iterative method, the conversion is simple:

$$m = \frac{1000c}{1000\rho_{sol} - cM_s}, \tag{B.1}$$

where c is in $\mathrm{mol \cdot dm^{-3}}$, m is in $\mathrm{mol \cdot kg^{-1}}$, M_s is in $\mathrm{g \cdot mol^{-1}}$, and ρ_{sol} (in $\mathrm{g \cdot cm^{-3}}$) is calculated from above density model.

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