

Thermodynamic Properties of the Glycine + H₂O System

Darren Rowland*

Fluid Science & Resources Division,

The University of Western Australia, Crawley, Western Australia 6009

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Abstract

New equations describing the thermodynamic properties of the glycine + H₂O system are obtained from previously published measurements. The measured values span a range of temperatures of approximately (273 to 473) K for glycine(aq) and (5 to 310) K for α -glycine(cr). This work provides critically-assessed values for the following properties: (1) thermal properties of α -glycine(cr) from (0 to 310) K, (2) the change in excess Gibbs energy for glycine(aq) solutions as a function of temperature, pressure, and molality, valid from (273 to 473) K, pressure up to 40 MPa, and the molality range (0 to 3.6) mol · kg⁻¹ (or the saturation molality if lower), and (3) standard-state properties for the aqueous solution process.

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1. INTRODUCTION

Efforts toward producing authoritative critical assessments of experimental data for important chemical systems are increasingly outpaced by the publication of new measurements. International expert collaboration of the kind fostered by the National Institute of Science and Technology (NIST), the OECD Nuclear Energy Agency (NEA) and the International Union of Pure and Applied Chemistry (IUPAC), which has led to vital critical evaluation and review of thermodynamic data,¹ seems unlikely to be sustained with the same intensity as in the past.² Investigators working outside the umbrella of these large institutions will accordingly become increasingly important for providing an alternative source of critical assessment.² However, without guidance, there is a tendency to re-visit particular chemical systems numerous times (e.g. KCl(aq)³⁻¹⁰ and LiCl(aq)¹¹⁻¹⁴) while many others remain

FIG. 1. Solubility values for α -glycine(cr) in H₂O tabulated by Yalkowsky *et al.*¹⁹

neglected.

The amino acids are perhaps the most important class of compounds whose thermodynamic properties have yet to be assessed critically in any comprehensive manner. Amino acids play critical roles as protein building blocks and biological precursors and are important industrial chemicals.^{15,16} As the simplest amino acid, glycine is often used as a model substance in a wide variety of studies aimed at understanding the physical and biochemical properties of amino acids, peptides, and proteins.^{17,18} Of more than 540 organic nonelectrolyte molecules | including pharmaceuticals, pollutants, nutrients, industrial and energy-related compounds | comprising five carbon atoms or fewer, glycine (CAS no. 56-40-6) ranks alongside urea (57-13-6), ethyl acetate (141-78-6), 1-butanol (71-36-3), and 1-pentanol (71-41-0) in the 'Handbook of Aqueous Solubility Data' as one of the substances whose solubility in H₂O has been reported most frequently.¹⁹ However, the values are widely scattered (Fig. 1).

Thermodynamic property data | such as osmotic coefficients, enthalpies, heat capacities and density/volumes | for the system glycine + H₂O are appearing in the literature with great frequency (more than seven new data sets published in 2017 alone). Although many experimental investigations have targeted the glycine + H₂O system, no comprehensive description of the thermodynamic properties has been presented. The primary aim of this work is to develop a thermodynamic equation of state (EOS) for glycine(aq) capable

TABLE 1. Knot locations and coefficients of the cubic spline for α -glycine(cr).

T_i (K)	a_i	b_i	c_i	d_i
0	5.4837×10^{-4}	-1.5876×10^{-2}	-2.2000×10^{-1}	16.899
20	-7.8919×10^{-5}	5.6025×10^{-3}	-1.9701×10^{-1}	10.536
40	-1.4418×10^{-5}	1.3655×10^{-3}	-6.7617×10^{-2}	8.2051
70	-1.6810×10^{-6}	2.7039×10^{-4}	-2.4615×10^{-2}	7.0163
100	-2.6712×10^{-8}	-1.1327×10^{-4}	-1.2930×10^{-2}	6.4758
200	5.3529×10^{-7}	-2.2095×10^{-4}	-3.6385×10^{-2}	4.0234
310	0	0	-6.5563×10^{-2}	-1.9400

of describing key measurements of the system's properties within their experimental uncertainty. A secondary aim is to determine the standard-state thermodynamic properties for the reaction



i.e. the dissolution of glycine in water.

2. THERMODYNAMIC PROPERTIES OF α -GLYCINE(CR)

A model for the thermodynamic properties of crystalline glycine is required to describe the phase equilibria and other data for α -glycine(cr) and glycine(aq). Three sources of experimental heat capacity measurements of α -glycine(cr) covering wide ranges of temperature are available: Parks *et al.*²⁰ from (93.2 to 299.5) K; Hutchens *et al.*²¹ from (11.6 to 301.7) K; and Drebuschak *et al.*²² from (6.5 to 304.2) K. The uncertainty in the values of Parks *et al.*²⁰ is large²¹ compared to more recent data so these were not used for fitting in the present work.

The present fitting procedure follows closely that of Archer.^{5,23,24} Briefly, a function $f(T)$ is used, where

$$f(T) = [T(C_{p,m}/C_p^o)^{-1/3} - bT] / T^o, \quad (2)$$

b was a constant chosen to be 0.22 for the present case (based on the approximate linear slope of the function $(T/T^o)(C_{p,m}/C_p^o)^{-1/3}$ between (60 and 120) K), C_p^o is $1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, and T^o is 1 K. The function $f(T)$ was fitted with a cubic spline in a least-squares regression of the experimental heat capacity values (see below). The 'knot' locations T_i are given in Table 1. For a specified T in the range T_i to T_{i+1} , $f(T)$ has the form

$$f(T) = a_i(T - T_i)^3 + b_i(T - T_i)^2 + c_i(T - T_i) + d_i. \quad (3)$$

TABLE 2. Derived thermodynamic properties of α -glycine(cr).

T (K)	$C_{p,m}$ (J · K ⁻¹ · mol ⁻¹)	$H_m(T) - H_m(0 \text{ K})$ (J · mol ⁻¹)	S_m (J · K ⁻¹ · mol ⁻¹)
25	4.47	28	1.498
50	19.27	318	8.940
75	32.93	978	19.446
100	43.31	1937	30.417
125	51.58	3126	40.989
150	58.94	4508	51.055
175	65.75	6068	60.658
200	72.23	7793	69.864
225	78.78	9680	78.747
250	85.63	11735	87.40
275	92.63	13963	95.89
300	99.64	16367	104.25
310	102.41	17377	107.56

At $T_i = 0 \text{ K}$, the first derivative was constrained to the value of b , i.e. -0.22 . At $T_i = 310 \text{ K}$, the second derivative with respect to temperature was set equal to zero (a 'natural spline' end condition). The coefficients a_i , b_i , c_i , and d_i were obtained by regressing the data of Hutchens *et al.*²¹ and Drebuschak *et al.*²² with equal weights applied to all points. The least squares problem is suited to Lawson and Hanson's 'Problem LSE' method²⁵ and was solved with the algorithm of Ref. 26 yielding the coefficients in Table 1. The number of digits given is not indicative of the statistical significance of the values but should be sufficient to calculate thermodynamic properties of α -glycine(cr), as shown in Table 2. Values of $H_m(T) - H_m(0 \text{ K}) = \int_0^T C_{p,m} dT'$ and $S_m = \int_0^T C_{p,m}/T dT'$ were obtained by numerical integration of $C_{p,m}$.

The deviations between the heat capacity of α -glycine(cr) and the model are of similar size to the differences between the experimental sources (Fig. 2). For example, deviations between the values of Drebuschak *et al.*²² and Eq. (2) are 2.3 % for $T < 20 \text{ K}$ and 0.15 % for $T > 20 \text{ K}$, which agree well with the stated experimental uncertainty (3 % from (6 to 20) K and within 0.5 % for $T > 20 \text{ K}$).

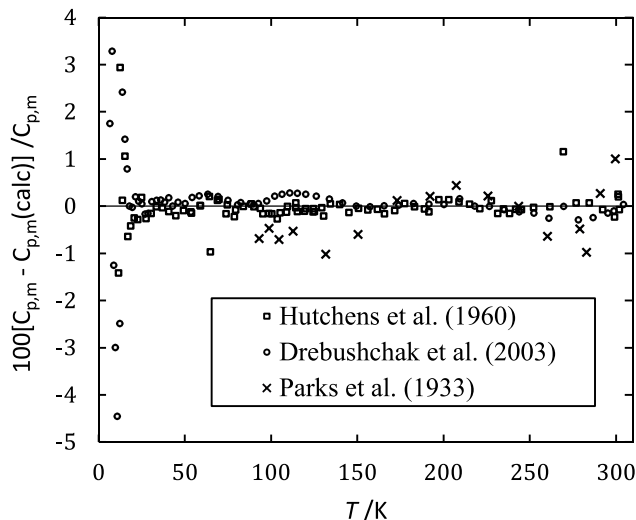


FIG. 2. Relative percent deviations between experimental heat capacity of α -glycine(cr) from Parks *et al.*²⁰, Hutchens *et al.*²¹, and Drebushchak *et al.*²² and calculations with equations (2) and (3).

3. THERMODYNAMIC PROPERTIES OF GLYCINE(AQ)

3.1. Description of the equation of state

The solubility of glycine(aq) increases by more than a factor of 10 from $3.33 \text{ mol} \cdot \text{kg}^{-1}$ at 298 K to around $34.5 \text{ mol} \cdot \text{kg}^{-1}$ at 463 K. Unfortunately, thermodynamic data for glycine(aq) including heat capacity and density are limited mostly to concentrations less than $3.6 \text{ mol} \cdot \text{kg}^{-1}$. The only data available for more highly concentrated solutions come from the study of water activity up to $45 \text{ mol} \cdot \text{kg}^{-1}$ by Na *et al.*²⁷; however, these data are restricted to 298.15 K and therefore have limited utility for constraining an EOS at high temperatures. For these reasons, the EOS developed here is valid only up to $3.6 \text{ mol} \cdot \text{kg}^{-1}$.

Treatment of the experimental data for glycine(aq) is based on the established assumption that the zwitterion form of glycine predominates in aqueous solution under the conditions of interest.^{18,28,29} The excess Gibbs energy of glycine(aq) can then be represented by

$$G^{\text{ex}}/(w_w RT) = m_G^2 \lambda_G + m_G^3 \nu_G + m_G^4 \chi_G, \quad (4)$$

where w_w is the mass of water in kg, m_G is the molality of glycine(aq), and λ_G , ν_G , and χ_G are adjustable parameters, dependent on temperature and pressure. The corresponding

equations for the osmotic coefficient ϕ and activity coefficient γ_G of glycine(aq) are

$$(\phi - 1) = m_G \lambda_G + 2m_G^2 v_G + 3m_G^3 \chi_G, \quad (5)$$

$$\ln \gamma_G = 2m_G \lambda_G + 3m_G^2 v_G + 4m_G^3 \chi_G. \quad (6)$$

These equations follow those of Pitzer³⁰ for nonelectrolyte substances but include additional terms cubic in glycine concentration.

The equation for the apparent molar relative enthalpy L_ϕ is

$$L_\phi = -RT^2[m_G \lambda_G^L + m_G^2 v_G^L + m_G^3 \chi_G^L], \quad (7)$$

where $\lambda_G^L = (\partial \lambda_G / \partial T)_p$, $v_G^L = (\partial v_G / \partial T)_p$, and $\chi_G^L = (\partial \chi_G / \partial T)_p$. The enthalpy corresponding to dilution from $m_1 \text{ mol} \cdot \text{kg}^{-1}$ to $m_2 \text{ mol} \cdot \text{kg}^{-1}$ is related to L_ϕ by

$$\text{dil}H = L_\phi(m_2) - L_\phi(m_1). \quad (8)$$

The isobaric apparent molar heat capacity $C_{p,\phi}$ is

$$C_{p,\phi} = C_{p,2}^o - RT^2[m_G \lambda_G^J + m_G^2 v_G^J + m_G^3 \chi_G^J], \quad (9)$$

where $\lambda_G^J = (\partial^2 \lambda_G / \partial T^2)_p + (2/T)(\partial \lambda_G / \partial T)_p$, $v_G^J = (\partial^2 v_G / \partial T^2)_p + (2/T)(\partial v_G / \partial T)_p$, $\chi_G^J = (\partial^2 \chi_G / \partial T^2)_p + (2/T)(\partial \chi_G / \partial T)_p$, and $C_{p,2}^o$ is the standard-state molar heat capacity of the solute. As in prior work,^{9,31} the apparent molar heat capacity was re-written in terms of a reference molality m_r (chosen as $3 \text{ mol} \cdot \text{kg}^{-1}$ in this work)

$$C_{p,\phi} + c_{p,w}^*/n_r = C_p(m_r)/n_r - RT^2[(m_G - m_r)\lambda_G^J + (m_G^2 - m_r^2)v_G^J + (m_G^3 - m_r^3)\chi_G^J], \quad (10)$$

where $c_{p,w}^*$ is the heat capacity of 1 kg of pure water, $C_p(m_r)$ is the heat capacity of a quantity of solution with reference molality and at the desired temperature and pressure, and n_r is the number of moles of solute in this quantity of solution.

The equation for the apparent molar volume V_ϕ is

$$V_\phi = V_2^o + RT[m_G \lambda_G^V + m_G^2 v_G^V + m_G^3 \chi_G^V], \quad (11)$$

where $\lambda_G^V = (\partial \lambda_G / \partial p)_T$, $v_G^V = (\partial v_G / \partial p)_T$, $\chi_G^V = (\partial \chi_G / \partial p)_T$, and V_2^o is the standard-state molar volume of the solute. As for $C_{p,\phi}$, V_ϕ can also be written in terms of the reference molality:

$$V_\phi + v_w^*/n_r = V(m_r)/n_r + RT[(m_G - m_r)\lambda_G^V + (m_G^2 - m_r^2)v_G^V + (m_G^3 - m_r^3)\chi_G^V], \quad (12)$$

where v_w^* is the volume of 1 kg of pure water and $V(m_r)$ is the volume of a quantity of solution of molality m_r .

The partial molar Gibbs energy of the solute in its standard state (the hypothetical ideal one mol · kg⁻¹ solution at the temperature and pressure of interest) is given in terms of the above equations as²⁴

$$\begin{aligned}
 G_{m,2,T,p}^o &= G_{m,2,T_r,p_r}^o + \frac{n_1 G_{m,1,T_r,p_r}^o - n_1 G_{m,1,T,p}^o}{n_r} \\
 &\quad + \frac{G_{T_r,p_r,m_r}^{\text{ex}} - G_{T,p,m_r}^{\text{ex}}}{n_r} \\
 &- (T - T_r) \left(S_{m,2,T_r,p_r}^o + \frac{n_1 S_{m,1,T_r,p_r}^o}{n_r} + \frac{S_{T_r,p_r,m_r}^{\text{ex}}}{n_r} \right) \\
 &\quad - T \int_{T_r}^T \frac{1}{T'^2} \int_{T_r}^{T'} \frac{C_{p,p_r}(m_r)}{n_r} dT' dT'',
 \end{aligned} \tag{13}$$

where

$$S_{T_r,p_r}^{\text{ex}} = -(\partial G_{T_r,p_r}^{\text{ex}} / \partial T)_p, \tag{14}$$

and where T_r and p_r were chosen as 298.15 K and 0.1 MPa, respectively.

The solubility of the anhydrous solid phase is given in terms of evaluable quantities by^{5,24}

$$\begin{aligned}
 {}_{\text{sol}}G_T^o &= {}_{\text{sol}}G_{T_r}^o + \{G_{m,2,T}^o - G_{m,2,T_r}^o\} \\
 &\quad - \{G_{m,\text{cr},T}^o - G_{m,\text{cr},T_r}^o\} \\
 &= -RT \ln(m_s \gamma_s / m^o),
 \end{aligned} \tag{15}$$

where m_s and γ_s are the saturation molality and activity coefficient at saturation, respectively, and m^o is 1 mol · kg⁻¹. The first term in braces (curly brackets) was obtained from Eq. (13) and the second term in curly braces was obtained from the equations for α -glycine(cr) developed in this work. To include solubility measurements in the global data fit, ${}_{\text{sol}}G_{T_r,p_r}^o$ and $S_{m,2,T_r,p_r}^o$ were treated as adjustable parameters.

The literature sources for data included in the fitting process are summarised in Tables 3 to 5. Each reference is shown along with the ranges of temperature, pressure, and concentration, the number of observations and type of data. Deviations from the EOS developed in this work are given by

$$\text{RMS} = \sqrt{\quad}$$

TABLE 3. Summary of literature sources for the activity and thermal properties of glycine(aq) included in fitting.

Reference	Temperature range (K)	Pressure range (MPa)	Concentration range (mol · kg ⁻¹)	<i>N</i>	Type	RMS	Bias
32	298.15	<i>p_s</i>	0.2{3.1	18	ϕ^a	0.0013	0.0006 ^b
33	298.15	<i>p_s</i>	0.98{3.3	9	ϕ^c	0.0021	-0.0019 ^b
34	298.15	<i>p_s</i>	0.77{1.4	2	ϕ^c	0.0031	0.0021 ^b
35	288.15{303.15	<i>p_s</i>	0.2{1.3	48 ^d	ϕ^a	0.0022	0.0018 ^b
36	298.15	<i>p_s</i>	0.59	1	<i>p_s - p_w</i>	0.0028	-0.0028 ^b
37	298.15	<i>p_s</i>	0.1{3.0	69	dil H	1.9	0.55 ^e
38	298.15	<i>p_s</i>	0.4{1.1	12	dil H	6.9	-5.7 ^e
39	298.15	<i>p_s</i>	0.4{3.0	7	dil H	3.5	-0.22 ^e
40,41	298.15	<i>p_s</i>	0.1{0.4	12	dil H	0.45	-0.006 ^e
42	278.15{313.15	<i>p_s</i>	0.1{3.1	24	$C_{p,\phi}$	2.7	0.06 ^f
43	288.15{328.15	<i>p_s</i>	0.01{0.46	45	$C_{p,\phi}$	2.8	0.05 ^f
44	323.17{499.10	0.1{30	0.1{2.3	118 ^g	$C_{p,\phi}$	1.7	-0.01 ^f
45	352.09{473.63	10	0.1{2.0	51	$C_{p,\phi}$	1.6	0.55 ^f
46	278.15{393.15	0.35	0.01{0.5	168 ^h	$C_{p,\phi}$	1.5	0.18 ^f

^a Based on isopiestic measurement with NaCl(aq) as reference substance.

^b RMS and Bias in terms of osmotic coefficient.

^c Based on isopiestic measurement with KCl(aq) as reference substance.

^d Raw isopiestic ratios were not reported; osmotic coefficients at (288.15, 293.15, and 303.15) K not in accord with enthalpy and heat capacity results and were rejected.

^e RMS and Bias have units of J · mol⁻¹.

^f RMS and Bias have units of J · K⁻¹ · mol⁻¹.

^g Data above 423 K rejected for unusual slope with respect to *T* (see Fig. 7).

^h All data below 0.1 mol · kg⁻¹ rejected.

and

$$\text{Bias} = \frac{1}{N} \sum_{n=1}^N (y_{\text{obs},n} - y_{\text{calc},n}). \quad (17)$$

The temperature and pressure dependence of the remaining adjustable parameters were given by the following relations

$$\lambda_G = \left[f(1, T) + 10^{-2} \left(\frac{p - p_r}{p^o} \right) f(2, T) + 10^{-4} \left(\frac{p^2 - p_r^2}{p^{o2}} \right) f(3, T) \right] / m^o, \quad (18)$$

TABLE 4. Summary of literature sources for the volumetric properties of glycine(aq) included in tting.

Reference	Temperature range (K)	Pressure range (MPa)	Concentration range (mol · kg ⁻¹)	<i>N</i>	Type	RMS ^a	Bias ^a
47	298.15	<i>p</i> _s	0.16{3.4	17	ρ	0.13	0.10
48	298.15	<i>p</i> _s	3.3	1	ρ	0.23	-0.23
49	298.15	<i>p</i> _s	0.25{2.5	10	ρV_ϕ	0.045	0.008
42	298.15	<i>p</i> _s	0.1{2.7	22	V_ϕ	0.15	0.065
50	288.15{298.15	<i>p</i> _s	0.1{0.5	8	ρ	0.047	0.013
51	298.15	3.3{112	1.0{3.0	31	ρV_ϕ	0.11	-0.057
52	298.15	<i>p</i> _s	0.03{0.9	9	$\rho - \rho_w$	0.081	-0.057
53	298.15	<i>p</i> _s	0.01{0.1	7	ρV_ϕ	0.056	-0.041
54	298.15{323.15	0.1{300	0.53{3.0	372	<i>v</i>	0.095	-0.018
43	288.15{328.15	<i>p</i> _s	0.01{0.46	98	ρV_ϕ	0.14	-0.01
55	278.15{318.15	<i>p</i> _s	0.01{0.1	51	$\rho - \rho_w$	0.20	-0.19
56	298.15	<i>p</i> _s	3.3	1	ρ	0.12	-0.12
57	288.15{308.15	<i>p</i> _s	0.1{1.1	28	$\rho - \rho_w$	0.11	-0.012
58	396.15{473.15	10{30	0.5{3.0	144	$\rho - \rho_w$	0.37	-0.09
59	298.15	<i>p</i> _s	0.5{2.9	6	ρ	0.064	0.001
60	298.15{318.15	<i>p</i> _s	0.05{0.4	33	ρV_ϕ	0.059	0.004
61	298.15	<i>p</i> _s	0.5{2.9	12	ρ	0.064	0.001
44	298.15	0.1{30.8	0.1{2.3	10	V_ϕ	0.17	-0.082
62	278.15{308.15	<i>p</i> _s	0.1{0.6	88	ρV_ϕ	0.073	-0.025
45	297.30	10	0.3{1.9	12	ρ	0.087	0.029
63	298.15	<i>p</i> _s	1.5{3.3	10	ρ	0.077	0.008
64	298.15	<i>p</i> _s	0.1{0.6	6	ρ	0.065	0.004
65	288.15{308.15	<i>p</i> _s	0.01{0.5	25	ρ	0.091	0.056
66	298.15	<i>p</i> _s	3.3	1	ρ	0.12	-0.12
67	298.15	<i>p</i> _s	0.1{0.45	8	ρ	0.091	-0.052
68	298.15	<i>p</i> _s	0.1{0.35	6	ρ	0.056	-0.052
29	298.16{443.16	0.3-30	0.16{0.85	195	ρV_ϕ	0.059	0.022
69	298.15	<i>p</i> _s	0.05{0.5	9	ρV_ϕ	0.081	-0.049
70	288.15{338.15	<i>p</i> _s	1.1{3.5	52	ρ	0.11	-0.061
71	293.15{308.15	<i>p</i> _s	0.05{0.3	24	V_ϕ	0.041	0.020
72	275.15{283.15	<i>p</i> _s	0.1{1.5	45	ρ	0.13	-0.001
73	283.15{313.15	0.1	0.05{1.0	63	ρV_ϕ	0.13	0.12
74	293.15{323.15	<i>p</i> _s	0.1{0.7	28	ρ	0.14	-0.087
75	278.15{308.15	<i>p</i> _s	0.1{0.5	24	ρ	0.11	-0.084
76	278.15{308.15	<i>p</i> _s	0.1{0.4	24	ρ	0.056	-0.042
77	293.15{323.15	<i>p</i> _s	0.1{0.7	28	ρV_ϕ	0.14	-0.13
78	288.15{308.15	<i>p</i> _s	0.1{1.0	50	ρV_ϕ	0.15	0.019
79	303.15{313.15	<i>p</i> _s	0.1{0.5	27	ρ	0.15	0.075
80	288.15{328.15	<i>p</i> _s	0.1{1.0	60	ρV_ϕ	0.20	0.19
81	288.15{318.15	<i>p</i> _s	0.1{0.45	32	ρV_ϕ	0.13	-0.007
82	278.15{308.15	0.1	0.05{0.5	44	ρV_ϕ	0.059	-0.023
83	293.15{323.15	0.1	0.1{0.7	28	V_ϕ	0.11	-0.079

^a RMS and Bias have units of cm³ · mol⁻¹.

TABLE 5. Summary of literature sources for solubility measurements of α -glycine(cr) in H₂O included in fitting.

Reference	Temperature range (K)	N^a	m_s at ≈ 298 K (mol · kg ⁻¹)	RMS	Bias ^b
47	273{343	15 (6)	3.329	0.004	0.0006
84	273.15{348.15	4 (1)	3.371	0.049	0.049
48,85	298.15	1	3.330	0.007	0.007
86	298.15	1	3.334	0.011	0.011
87	298.25	1	3.344	0.014	0.014
88	298.15	2	3.30 ^c	0.031	-0.023
89	298.25	1	3.342	0.013	0.013
90	298.25	1	3.342	0.013	0.013
91	298.25	1	3.352	0.022	0.022
92	303.15{313.15	2 (1)	N/A	0.004	0.004
93	273.15{373.15	11 (3)	3.278 ^d	0.004	0.0004
94,95	298.15	1	3.330	0.007	0.007
96	288.15{308.15	5 (4)	3.329	0.019	-0.005
97	298.15	1	3.41	0.087	0.087
56	298.15	1	3.344	0.021	0.021
98	298.2	1	3.329	0.003	0.03
99	298.15	1	3.330	0.007	0.007
28	298.2	1	3.333	0.01	0.01
100	298.2	1	3.335	0.012	0.012
101	298.2	1	3.333	0.010	0.010
102	288.15{308.15	3 (2)	3.333	0.008	0.002
103	281.9{345.0	5 (2)	3.300 ^d	0.055	0.006
63	298.15 ^e	15 (2)	3.345	0.022	0.022
104	288.15{308.15	3 (2)	3.333	0.008	0.002
105	281.9{461.6	22 (9)	3.300 ^d	0.044	0.011
106	288.15{308.15	5 (4)	3.340	0.017	0.008
107	296.05{318.65	6 (3)	3.28 ^d	0.054	-0.037
66	298.15	1	3.342	0.028	0.028
108	298.15	1	3.338	0.015	0.015
109	298.2{343.2	6 (2)	3.31	0.11	-0.085
110	288.15{308.15	5 (2)	3.389	0.096	-0.019
111	278.15{328.15	11 (7)	3.336	0.036	0.025
112	288.15{308.15	5 (4)	3.339	0.025	0.019
113	298.15	1	3.32	0.003	-0.003
114	283.2{353.2	9 (4)	3.244	0.060	-0.053
115	288.15{308.15	5 (3)	3.447	0.094	0.075
116	283.15{333.15	6 (3)	3.25 ^d	0.097	-0.079
117	288.15{308.15	5 (4)	3.339	0.037	0.032
118	283.15{343.15	7 (3)	3.253	0.047	-0.040
16	293.15{343.15	6 (2)	3.320	0.006	-0.006

^a Value in parentheses is number of data within range for fitting.

^b RMS and Bias have units of mol · kg⁻¹.

^c Average of two values.

^d Interpolation by present author.

^e Pressures ranging from (0.1 to 400) MPa.

$$v_G = \left[b_{4,1} + b_{4,2}10^3 \left(\frac{T^o}{T} - \frac{T^o}{T_r} \right) + b_{4,3} \ln \left(\frac{T}{T_r} \right) \right] / m^{o2}, \quad (19)$$

$$\chi_G = \left[b_{5,1} + b_{5,2}10^3 \left(\frac{T^o}{T} - \frac{T^o}{T_r} \right) \right] / m^{o3}, \quad (20)$$

$$C_p(m_r)/n_r = g(T) \times C_p^{o'}, \quad (21)$$

$$V(m_r)/n_r = h(T, p) \times V^{o'}, \quad (22)$$

where

$$\begin{aligned} f(i, T) = & b_{1,1} + b_{1,2}10^3 \left(\frac{T^o}{T} - \frac{T^o}{T_r} \right) \\ & + b_{1,3} \ln \left(\frac{T}{T_r} \right) + b_{1,4}10^{-2} \left(\frac{T - T_r}{T^o} \right) \\ & + b_{1,5}10^{-4} \left(\frac{T^2 - T_r^2}{T^{o2}} \right) \\ & + b_{1,6}10^3 \left(\frac{T^o}{T - 227\text{K}} - \frac{T^o}{T_r - 227\text{K}} \right), \end{aligned} \quad (23)$$

$$\begin{aligned} g(T) = & b_{6,1} + b_{6,2}10^{-2}T/T^o \\ & + b_{6,3}10^{-5}(T/T^o)^2 + b_{6,4}10^{-7}(T/T^o)^3, \end{aligned} \quad (24)$$

$$\begin{aligned} h(T, p) = & b_{7,1}10^2 + b_{7,2}T/T^o + b_{7,3}10^{-2}(T/T^o)^2 \\ & + b_{7,4}10^{-5}(T/T^o)^3 \\ & + p/p^o[b_{7,5} + b_{7,6}10^{-2}T/T^o \\ & + b_{7,7}10^{-4}(T/T^o)^2] \\ & + (p/p^o)^2[b_{7,8}10^{-2} + b_{7,9}10^{-4}T/T^o], \end{aligned} \quad (25)$$

and where $C_p^{o'}$ is $1.0 \text{ kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, $V^{o'}$ is $1.0 \text{ cm}^3 \cdot \text{mol}^{-1}$, and p^o is 1.0 MPa . The pressure dependence of $C_p(m_r)/n_r$ is expressed in $V(m_r)/n_r$.¹¹⁹ The least-squares estimated parameters are given in Table 6, where the absence of any value indicates that it was not required in the final fit. It is noteworthy that the apparent molar volumes of glycine(aq) are closely linear with respect to molality within the limits of agreement between independent experimental investigators so higher-order terms were unnecessary.

TABLE 6. Least-squares estimated parameters used in the EOS for glycine(aq).

Parameter	Value	Parameter	Value	Parameter	Value
$b_{1,1}$	-0.0910700	$b_{2,1}$	0.0281813	$b_{3,1}$	-0.0102214
$b_{1,2}$	-0.0865408	$b_{2,2}$	0.280470	$b_{3,2}$	-1.11271
$b_{1,3}$		$b_{2,3}$	-0.237372	$b_{3,3}$	-0.266590
$b_{1,4}$	-0.0335792	$b_{2,4}$	0.678425	$b_{3,4}$	-1.63480
$b_{1,5}$	-0.00789188	$b_{2,5}$	-0.0529803	$b_{3,5}$	0.132276
$b_{1,6}$	-0.00224372	$b_{2,6}$	0.000649611	$b_{3,6}$	0.0173487
$b_{4,1}$	0.0132700	$b_{6,1}$	6.87417	$b_{7,1}$	4.42157
$b_{4,2}$		$b_{6,2}$	56.5499	$b_{7,2}$	-0.604372
$b_{4,3}$	-0.0347660	$b_{6,3}$	-13.9442	$b_{7,3}$	0.151454
		$b_{6,4}$	128.131	$b_{7,4}$	-0.0636896
$b_{5,1}$	-0.00097550			$b_{7,5}$	-0.466825
$b_{5,2}$	-0.00118320			$b_{7,6}$	0.229698
		${}^{\text{sol}}G_{T_r}^o$	$-2.21131 \pm 0.006 \text{ kJ} \cdot \text{mol}^{-1}$	$b_{7,7}$	-0.0394257
		$S_{m,2,T_r}^o$	$155.698 \pm 0.03 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$b_{7,8}$	-0.177582
				$b_{7,9}$	0.0589028

4. AGREEMENT WITH EXPERIMENTAL RESULTS FOR GLYCINE(AQ)

4.1. Activity Results

All measurements of water vapour pressure, water activity, and isopiestic ratios were converted to osmotic coefficients for fitting. Properties of pure H₂O required in this work were calculated with the IAPWS 95 formulation.¹²⁰ Measured isopiestic ratios for glycine(aq) relative to NaCl(aq) or KCl(aq) were converted to osmotic coefficients with Pitzer parameters from the Joint Expert Speciation System (JESS).¹²¹ Smith and Smith¹²² reported isopiestic ratios at 298.15 K for glycine(aq) relative to sucrose(aq). These data were converted to osmotic coefficients by consideration of relevant literature data for sucrose(aq)^{123–130} contained in the JESS physicochemical property database¹²¹. The majority of the data for sucrose(aq) were in good accord and the osmotic coefficient, ϕ_S , could be described satisfactorily at 298.15 K up to sucrose concentration $m_S = 6 \text{ mol} \cdot \text{kg}^{-1}$ by the following cubic equation

$$\phi_S = 1 + 0.0799 \frac{m_S}{m^o} + 0.00904 \left(\frac{m_S}{m^o} \right)^2 - 0.00138 \left(\frac{m_S}{m^o} \right)^3. \quad (26)$$

Many of the available osmotic coefficient data for glycine(aq), especially those derived from direct measurements of vapour pressure or water activity, were subject to large scatter and were unsuitable for model regression (e.g.^{131–136}). The large dataset of Smith and Smith¹²² was also rejected as the resulting osmotic coefficients were systematically low by around 0.01 (in ϕ) compared to values from other sources.

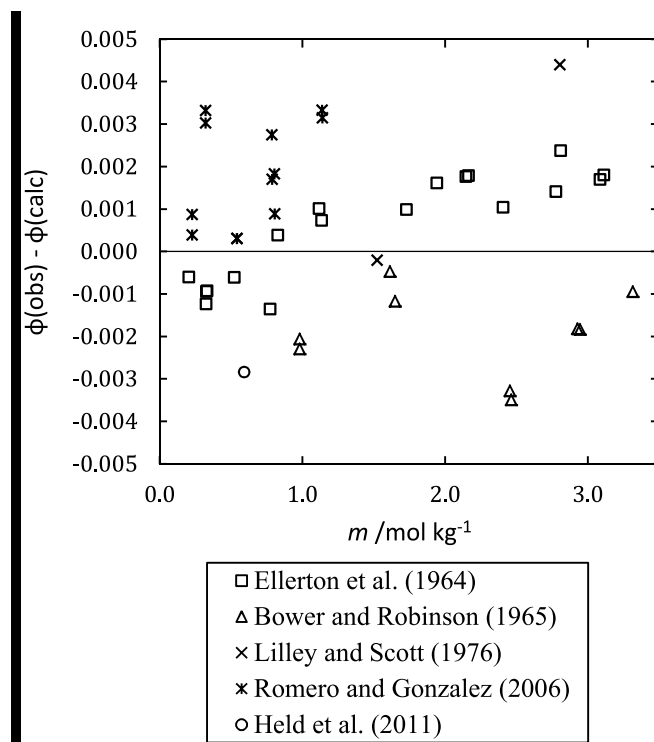


FIG. 3. Difference plot for the osmotic coefficients for glycine(aq) from the model at 298.15 K. Experimental results taken from Ellerton *et al.*³², Bower and Robinson³³, Lilley and Scott³⁴, Held *et al.*³⁶ and Romero and Gonzalez³⁵.

Figure 3 shows differences of the osmotic coefficients for glycine(aq) from the EOS at 298.15 K. The differences from the model are mostly within ± 0.003 , which is comparable with the best possible uncertainty based on typical isopiestic standards at 298.15 K¹³⁷.

Osmotic and activity coefficients for glycine(aq) at temperatures other than 298.15 K are rare in the literature. Values that are reported in the range (273.15 to 310.15) K^{35,122,133,138,139} tend to exhibit either unusual dependence on concentration, large scatter or poor agreement with other thermal properties. For these reasons, no activity data at temperatures other than 298.15 K were included in the fit. In spite of this deficiency in the data situation, osmotic coefficients near 273.15 K derived from freezing point measurements are represented quite well by the EOS (Fig. 4). The model predicts the osmotic coefficients as well as could be expected when considering the large scatter of values derived from different sources. The EOS even extends into the supersaturated glycine(aq) region with acceptable accuracy.

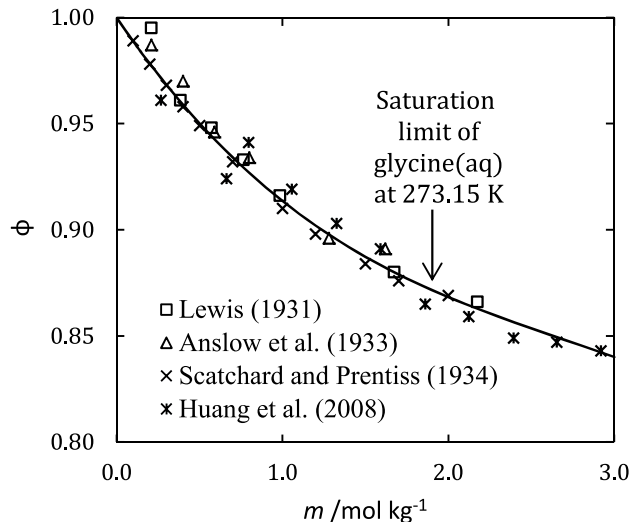


FIG. 4. Osmotic coefficients for glycine(aq) near 273.15 K derived from freezing point measurements. Experimental results taken from Lewis¹³⁸, Anslow *et al.*¹⁴⁰, Scatchard and Prentiss¹³⁹, and Huang *et al.*¹⁸. The curve was calculated with the model of this work.

4.2. Enthalpy and Heat Capacity Results

Several sources of molar enthalpy of dilution measurements are available at 298.15 K. The data sets of Gucker *et al.*,³⁷ Sturtevant,³⁸ Humphrey *et al.*,³⁹ and Wang *et al.*⁴⁰ are largely coherent and were all included in parameter fitting. Differences between the measured data and the EOS are within $15 \text{ J} \cdot \text{mol}^{-1}$ (Fig. 5). Data in Fig. 5 with the largest deviations are the long-chord dilutions (greater than 10-fold dilution with respect to glycine concentration) of Gucker *et al.*³⁷ and Sturtevant.³⁸ As these data correspond to large absolute values of enthalpy difference, the relative deviations from the model are mostly below 3 % for these long chords, which is comparable with the level of agreement between investigators.

Apparent molar isobaric heat capacities of glycine(aq) are available under ambient and non-ambient conditions, including results at high pressure and high temperature. Although most of the published data were included in the development of the EOS, it was necessary to reduce the relative weight of some datasets and to exclude others. For example, all measurement results of Ziemer *et al.*⁴⁶ having concentration less than $0.1 \text{ mol} \cdot \text{kg}^{-1}$ are subject to large uncertainty; they were therefore excluded from the fitting. The other data set from Ziemer *et al.*⁴⁶ was included in the optimisation with low weight, which was considered necessary because they cover a large range of temperature that would otherwise

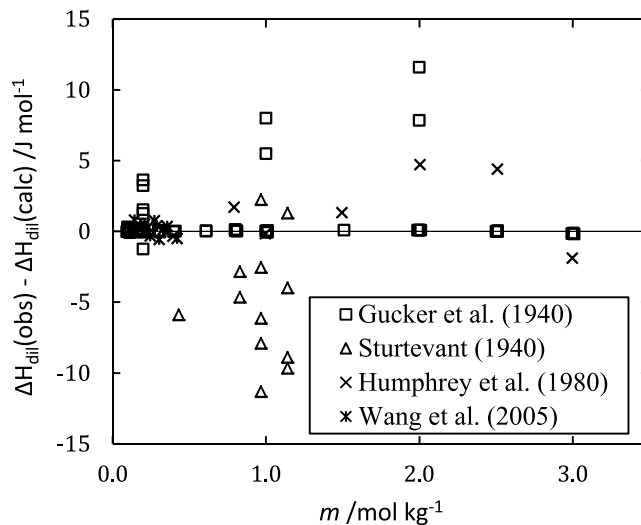


FIG. 5. Difference plot of measured enthalpies of dilution for glycine(aq) from the model at 298.15 K. Experimental results taken from Gucker *et al.*³⁷, Sturtevant³⁸, Humphrey *et al.*³⁹ and Wang *et al.*⁴⁰.

be inadequately represented.

Apparent molar heat capacity values at low concentration under near-ambient conditions are available from several sources. The agreement between the model and values reported in the literature is comparable with the differences between the independent investigations (Fig. 6).

The main sources of heat capacity data at high temperatures are Clarke *et al.*⁴⁴ and Downes *et al.*⁴⁵ Above 423 K, the data of Clarke *et al.*⁴⁴ exhibit unusual slope with respect to temperature (Fig. 7) and were excluded from fitting. However, their remaining data are in good agreement with the EOS. The data of Downes *et al.*⁴⁵ are reproduced within their uncertainty (Fig. 8).

4.3. Density Results

Densities and apparent molar volumes of glycine(aq) have been reported in more than 75 publications (Tables 4 and 9). Values of solution density, ρ , and density difference relative to pure H₂O, $\rho - \rho_w$, were converted to apparent molar volumes for fitting. Although wide ranges of temperature and pressure are covered in the literature, many data are restricted to near 298.15 K and 0.1 MPa and concentration less than 0.8 mol · kg⁻¹. A large number

FIG. 6. Apparent molar heat capacity of glycine(aq) at low pressure. Experimental results taken from Gucker *et al.*⁴², Hakin *et al.*⁴³ and Ziemer *et al.*⁴⁶. The curves were calculated with the model of this work.

FIG. 7. Apparent molar heat capacity of glycine(aq) near 30 MPa taken from Clarke *et al.*⁴⁴. Data at temperatures above 423 K were excluded from fitting. The curves were calculated with the model of this work.

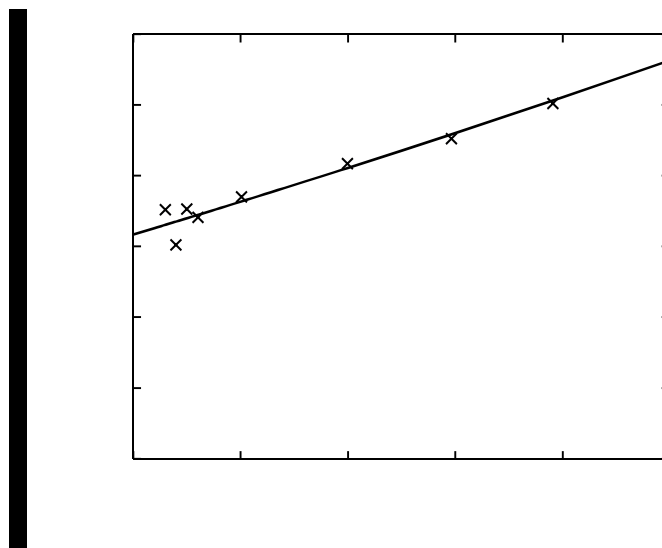


FIG. 8. Apparent molar heat capacity of glycine(aq) shown at 10 MPa from (401 to 471) K of Downes *et al.*⁴⁵. The curves were calculated with the model of this work.

FIG. 9. Apparent molar volume of glycine(aq) shown at 298.15 K. Nearly 300 data points from 32 references in Table 4 are shown. The curve was calculated with the model of this work.

of these data were rejected (i.e. not used in the fitting process) due to large internal scatter or unusual slope of apparent molar volume with respect to molal concentration.

Apparent molar volume data included in the fitting process are described mostly to within $0.1 \text{ cm}^3 \cdot \text{mol}^{-1}$, commensurate with the level of agreement between the most accurate independent literature sources (Fig. 9). The standard molar volume of glycine(aq) at 298.15 K calculated with the EOS is $43.29 \text{ cm}^3 \cdot \text{mol}^{-1}$, which compares favourably with the literature

FIG. 10. Apparent molar volume of glycine(aq) at high temperature and pressure from Hakin *et al.*⁵⁸. The curves were calculated with the model of this work.

values reviewed by Cibulka *et al.*²⁹ ranging from (43.01 to 43.50) $\text{cm}^3 \cdot \text{mol}^{-1}$.

The EOS also describes accurately the available apparent molar volume values at high temperatures and pressures. The data of Hakin *et al.*⁵⁸ are represented at a level consistent with their moderate internal scatter over a wide range of temperature and at pressures up to 30 MPa (Fig. 10). The data of Cibulka *et al.*²⁹ appear to highly reliable and are extremely well represented by the model (Fig. 11).

4.4. Phase Equilibria with α -Glycine(cr)

Measurements of the solubility of α -glycine(cr) in H_2O have been reported by more than 55 investigators (Tables 5 and 10). Solubility values included in the global fit are shown in Fig. 12, along with the results of the model developed in this work. The model describes the available data well within the scatter of the measurements. The recommended value for the solubility in H_2O of α -glycine(cr) at 298.15 K based on this work is $3.324 \text{ mol} \cdot \text{kg}^{-1}$.

The standard-state properties of the solution process represented by Eq. (1) are ${}_{\text{sol}}G_{T_r}^o = (-2.211 \pm 0.006) \text{ kJ} \cdot \text{mol}^{-1}$ (i.e. $\log_{10} K^o = 2.05$) and ${}_{\text{sol}}H_{T_r}^o = 14.15 \text{ kJ} \cdot \text{mol}^{-1}$. The

FIG. 11. Apparent molar volume of glycine(aq) at 2.1 MPa up to high temperature from Cibulka *et al.*²⁹. The curves were calculated with the model of this work.

FIG. 12. Solubility of glycine in H₂O. A total of 158 experimental results from literature sources in Table 5 are shown. The curve was calculated with the model of this work.

standard molar enthalpy of solution compares favourably with literature values (in kJ · mol⁻¹): 14.28 ± 0.35;⁸⁸ 14.16 ± 0.01;¹⁴¹ 14.08 ± 0.04;¹⁴² 14.20 ± 0.06;¹⁴³ 14.17 ± 0.05;^{144,145} 14.17 ± 0.02;¹⁴⁶ 14.2.¹⁴⁷

5. DISCUSSION AND CONCLUSIONS

The new equation for the heat capacity of α -glycine(cr) describes the available data to within their experimental uncertainty. Equation (2) is valid in the range (0 to 310) K. Additional experimental data (for regression) would be required to extend the equation to higher temperatures with confidence, allowing high-temperature solubility measurements to be included in the fitting process.

The EOS for glycine(aq) developed in this work covers the experimental range (0.1 to 40) MPa, (273.15 to 473.15 K) and (0 to 3.6) mol \cdot kg⁻¹. To aid in code checking and other purposes, various thermodynamic properties calculated with the EOS are presented in Table 7. Additional values can be obtained from the calculator provided on the JESS website (<http://jess.murdoch.edu.au/glycine.shtml>).

This study has identified some significant gaps in the data availability for glycine(aq). Isoopiestic properties at 298.15 K from multiple sources are highly coherent. On the other hand, osmotic coefficient values reported at other temperatures, e.g. Ref. 35, have large uncertainties and were considered unsuitable for inclusion in the fitting process. Highly-accurate isopiestic ratio measurements at temperatures other than 298.15 K would be useful for extending the EOS to higher concentrations and for increasing the confidence in solubility predictions.

Measurements of heat capacity and volumetric properties cover the full range of temperature and pressure but are limited to concentration below 3.6 mol \cdot kg⁻¹. A feature of the EOS in this work is that the apparent molar volume is a linear function of molality. There are not currently sufficient numbers of accurate data for volumetric properties of glycine(aq) to justify any higher-order terms. Additional experimental results at greater solute concentrations could allow such an extension, increasing the range of validity of the EOS. Extending the concentration range of the EOS into the supersaturated region would have benefits in glycine(cr) manufacturing, including the design of equipment and crystallizers.^{148,149} The supersaturated glycine(aq) region can be probed via modern contactless experimental techniques such as electrodynamic balance and acoustic levitation, giving insight into thermodynamic properties and crystal nucleation phenomena.

Although the valid range of the present EOS extends to 473 K, thermodynamic property measurements at high temperature may be unreliable: Cibulka *et al.*²⁹ report that thermal

TABLE 7. Predicted values of the activity coefficient, osmotic coefficient, apparent relative molar enthalpy, apparent molar heat capacity and apparent molar volume of glycine(aq) at selected values of pressure, temperature and concentration.

p (MPa)	T (K)	m_G (mol · kg ⁻¹)	γ_G	ϕ	L (J · mol ⁻¹)	C_p (J · K ⁻¹ · mol ⁻¹)	V (cm ³ · mol ⁻¹)
0.1	273.15	0.5	0.90169	0.95013	-430.14	-26.188	41.077
0.1	273.15	1.0	0.82985	0.91356	-828.18	-11.972	41.600
0.1	273.15	2.0	0.73545	0.86828	-1557.5	16.895	42.648
0.1	273.15	3.0	0.67408	0.84007	-2246.9	46.340	43.695
0.1	298.15	0.5	0.92164	0.96073	-205.25	46.563	43.637
0.1	298.15	1.0	0.86396	0.93254	-374.78	52.868	43.986
0.1	298.15	2.0	0.78958	0.90061	-636.22	65.910	44.684
0.1	298.15	3.0	0.74566	0.88663	-843.34	79.531	45.382
0.1	323.15	0.5	0.92909	0.96445	-75.809	72.870	44.715
0.1	323.15	1.0	0.87512	0.93787	-112.29	77.584	45.000
0.1	323.15	2.0	0.80251	0.90559	-96.788	87.446	45.570
0.1	323.15	3.0	0.75889	0.89112	-12.518	97.886	46.140
0.1	373.15	0.5	0.92547	0.96194	140.47	92.189	44.794
0.1	373.15	1.0	0.86309	0.92894	327.49	96.695	45.154
0.1	373.15	2.0	0.76650	0.87655	811.67	106.14	45.875
0.1	373.15	3.0	0.69744	0.83964	1393.5	116.16	46.595
10.0	273.15	0.5	0.90602	0.95253	-387.78	-7.8105	41.127
10.0	273.15	1.0	0.83784	0.91836	-743.46	4.8433	41.703
10.0	273.15	2.0	0.74969	0.87787	-1388.0	30.585	42.856
10.0	273.15	3.0	0.69376	0.85446	-1992.8	56.905	44.008
10.0	323.15	0.5	0.93096	0.96545	-70.872	76.789	44.955
10.0	323.15	1.0	0.87863	0.93987	-102.42	81.105	45.215
10.0	323.15	2.0	0.80897	0.90960	-77.041	90.171	45.734
10.0	323.15	3.0	0.76808	0.89714	17.104	99.815	46.253
10.0	373.15	0.5	0.92755	0.96306	131.97	94.745	44.998
10.0	373.15	1.0	0.86698	0.93119	310.48	99.091	45.343
10.0	373.15	2.0	0.77342	0.88105	777.67	108.22	46.031
10.0	373.15	3.0	0.70691	0.84639	1342.5	117.92	46.720
10.0	423.15	0.5	0.90994	0.95298	361.92	94.427	43.344
10.0	423.15	1.0	0.82985	0.90749	777.62	99.635	43.876
10.0	423.15	2.0	0.69649	0.82292	1740.8	110.48	44.940
10.0	423.15	3.0	0.59400	0.74981	2830.6	121.91	46.004
10.0	473.15	0.5	0.88263	0.93729	643.08	77.570	39.015
10.0	473.15	1.0	0.77693	0.87290	1347.2	83.935	39.721
10.0	473.15	2.0	0.60067	0.74351	2908.9	97.098	41.134
10.0	473.15	3.0	0.46762	0.62071	4626.0	110.84	42.546

decomposition of glycine(aq) occurs at 443 K. This may help to explain the aberrant behaviour above 423 K of the apparent molar heat capacity results of Clarke *et al.*,⁴⁴ as seen in Fig. 7.

Appendix: Methodology

Thermodynamic data, e.g. solubility values, are widespread in the chemical literature and need to be harmonised prior to extracting reliable thermodynamic parameters for modelling. An extensive search of the literature up to October 2017 was conducted to identify primary and secondary sources of thermophysical property values for the glycine(aq) system.

Approximately 13000 data points | some relating to solutions containing amounts of other solutes such as NaCl^{59,98,150} or KCl^{33,113,134} | were assembled and digitized into formatted text files according to the rules for the JESS solubility database (SOL). This database can store a vast range of properties including solubility, pH, density, mean activity coefficients and equilibrium constants. A key challenge for storing this information lies in providing a complete description of a large number of potentially complicated solutions { such as multicomponent mixtures { in a compact, and ultimately machine-processable, form.

A major issue with existing databases (e.g. Ref. 151) is that they only record the analytical concentrations of well-defined components, omitting information relating to the chemical behaviour of the solution components that is needed for processing experimental data. To the contrary, SOL data files require all of these details (e.g. pressure, temperature, composition and concentration of solution, measured property values, allowed chemical reactions and identities of solid phases) allowing the data to be processed in terms of the Gibbs energy EOS.

JESS facilities were used to inter-convert various thermodynamic properties, e.g. osmotic coefficients and water activity, and to unify data to SI units. Many types of solution property data were visualized to identify outliers. Rejected data are maintained in the database in accord with JESS strategies for physicochemical properties¹²¹ and thermodynamic parameters for chemical reactions^{2,152} but are omitted from all further processing such as parameter regression.

Literature sources for the solubility of α -glycine(cr) in H₂O are given in Tables 5 and 10. The sample purity (when reported) was always 99 % or greater. For each applicable source, the concentration of glycine(aq) at saturation, m_s , at or close to 298.15 K is shown. In most cases the values were obtained from the literature directly. In a few cases, where solubility values were reported at several temperatures above and below (but not at) 298.15 K, a value



FIG. 13. Experimental solubility results of α -glycine(cr) in H_2O^{103} plotted according to Eq. (A.1). The solid curve is the best-fitting straight line. The estimated solubility at 298.15 K is also shown (+).

at 298.15 K was estimated from a fit of solubility data with the following equation¹⁵³:

$$\ln \frac{m_s}{m^o} = a_s \left(\frac{T^o}{T} \right) + b_s. \quad (\text{A.1})$$

An example is shown in Fig. 13 for data from Mohan *et al.*¹⁰³ The best-fitting line in this case corresponds to $a_s = -1676.1$ and $b_s = 6.8148$.

The agreement between published and estimated values of m_s was one of the criteria used to determine whether particular solubility data sets were included in (Table 5) or excluded from (Table 10) the fitting process. Other data sets were excluded because their values were subject to large internal scatter. This criterion becomes especially important for bulk solution / solvent properties that are converted to more sensitive quantities for inclusion in the EOS. For example, osmotic coefficients obtained by conversion from water activity via

$$\phi = \frac{-55.51 \ln a_w}{m_G} \quad (\text{A.2})$$

will be highly scattered when a_w values are determined with uncertainty of ± 0.001 or more (as in Refs. 132 and 134). A similar problem can occur when solution densities are converted to apparent molar volumes. Many of the data in Tables 8 and 9 were rejected based on this criterion. Values were also excluded from fitting if they were only reported in the literature in graphical^{18,154} or equation^{27,155} form.

TABLE 8. Summary of literature sources for the activity and thermal properties of glycine(aq) excluded from fitting.

Reference	Temperature range (K)	Pressure range (MPa)	Concentration range (mol · kg ⁻¹)	<i>N</i>	Type
122	298.15	p_s	0.2{3.3	60	ϕ^a
133	298.15{310.15	p_s	0.005{3.15	28	$p_s - p_w$
27	298.15	p_s	3.4{45	^b	a_w
131	298.15	p_s	0.1{3.3	13	$p_s - p_w$
132	298.15	p_s	0.3{2.7	7	a_w
134	298.15	p_s	0.25{3.1	25	a_w
135	298.15	p_s	1.2{2.6	7	ϕ^c
136	298.15	p_s	0.1{1.2	10	a_w
138	< 273.15	p_s	0.2{2.2	7	fp
140	< 273.15	p_s	0.2{1.6	6	fp
122,139	< 273.15	p_s	0.1{2.0	11	fp
18	< 273.15	p_s	0.2{3.0	11	fp ^d
156	298.15	p_s	0.001{0.8	16	dil ^H
157	298.15	p_s	0.2{0.8	12	dil ^H
158,159	298.15	p_s	0.2{0.4	17	dil ^H
160	298.15	p_s	0.2{3.3	8	$C_{p,\phi}$
141	298.15	p_s	0.1{0.4	8	c_p
161	298.15	p_s	0.05{0.5	^b	$C_{p,\phi}$
155e	298.15	p_s	0.05{0.9	^b	$C_{p,\phi}$

^a Based on isopiestic measurement with sucrose(aq) as reference substance.

^b Values only given in form of equation.

^c Based on isopiestic measurement with NaCl(aq) as reference substance.

^d Values given in graphical form only.

^e Note added to proof in¹⁶² explains that these data are incorrect.

Overall, a significant fraction of the available data for glycine(aq) and α -glycine(cr) were rejected (over 1200 data points were omitted from a total of around 3750). Except for specific instances noted in Sections 4.4.1 to 4.4.3, almost all of the rejected data occurred in regions of the multidimensional (pressure, temperature, concentration) space where other data were available nearby for inclusion in the EOS. Therefore, rejecting such a large number of data did not severely impact the range of conditions over which the EOS is valid, as might be otherwise expected.

The parameters in the EOS were regressed by solving a linear least-squares problem via singular value decomposition of the fitting matrix, as described previously.^{31,121,206} This has

TABLE 9. Summary of literature sources for the volumetric properties of glycine(aq) excluded from fitting.

Reference	Temperature range (K)	Pressure range (MPa)	Concentration range (mol · kg ⁻¹)	<i>N</i>	Type
163	288.15{308.15	p_s	0.05{0.25	12	ρ/ρ_w
164	298.15	p_s	0.2{0.8	7	ρ
165	298.15	p_s	0.02{0.54	9	ρV_ϕ
166,167	298.15	p_s	0.02{0.2	7	ρV_ϕ
168	298.15{313.15	p_s	0.1{4.6	18	ρ
169	278.15{308.15	p_s	0.03{0.45	36	ρV_ϕ
170	298.15	p_s	0.1{0.5	7	ρV_ϕ
171,172	298.15	p_s	0.05{0.5	6	ρ
173	298.15	p_s	0.007{0.01	2	ρ
174	293.15{333.15	p_s	0.05{1.65	50	ρV_ϕ
46	278.15{368.15	0.35	0.01{1.0	88	V_ϕ
175	298	p_s	0.02{0.1	5	ρ
176	288.15{318.15	p_s	0.07{0.48	24	ρV_ϕ
177	298.15{308.13	p_s	1	3	ρ
135	288.15{313.15	p_s	0.06{0.27	96	ρ
178	308.15{318.15	p_s	0.1{0.95	28	ρV_ϕ
179	308.15{318.15	p_s	0.02{0.1	15	ρ
180	293.15{308.15	p_s	0.04{0.5	40	ρ
181,182	288.15{318.15	p_s	0.05{0.35	40	ρV_ϕ
183	298.15	p_s	0.01{0.1	6	ρ
184	288.15{318.15	0.1	0.01{0.8	40	ρV_ϕ
185	288.15{308.15	p_s	0.02{0.8	50	ρ
186	305.15{315.15	0.1	0.002{0.02	30	ρV_ϕ
187	298.15{308.15	p_s	0.06{0.27	12	ρV_ϕ
188	293.15{313.15	p_s	0.02{0.2	50	ρ
189	293.15{318.15	p_s	0.1	6	ρ
190	298.15	p_s	0.02{0.1	5	ρV_ϕ
191	275.63{278.65	0.075	0.03{0.1	56	ρ
192	288.15{318.15	p_s	0.02{0.21	36	ρV_ϕ
193	288.15{318.15	0.1	0.01{0.2	32	ρ
194	293.15{313.15	p_s	0.05{0.5	50	ρV_ϕ
195	298.15{313.15	0.1	0.02{0.12	24	ρV_ϕ
196	293.15{313.15	0.075	0.01{0.15	40	ρV_ϕ

been found to be a reliable and robust technique for obtaining Pitzer parameters and reduces some of the limitations of the Pitzer equations related to over-fitting of noisy experimental data.²⁰⁷

TABLE 10. Summary of literature sources for solubility measurements of α -glycine(cr) in H₂O excluded from fitting.

Reference	Temperature range (K)	N	m_s at ≈ 298 K (mol · kg ⁻¹)
197	room T	1	N/A
138	273.15	1	N/A
198	298.15	1	3.353
199	300.15	1	N/A
200	298.15	1	3.344
201	290.2{331.5	24	3.205 ^a
168	298.15{318.15	3	3.165
202	298.15	1	3.140
203	278.15{334.15	10	3.021,2.692 ^b
150	298.15	1	3.129 ^b
154	283.15{333.15	21	^c
204	293.15{323.15	7	4.077
205	298.15{323.15	2	3.332

^a Interpolation by present author.

^b Value reported for γ -glycine(cr) in H₂O.

^c Values given in graphical form only.

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* darren.rowland@uwa.edu.au; <http://jess.murdoch.edu.au>

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