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PVT and Derived Thermodynamic Properties for the Glycine–Water System at Temperatures from 298 to 323 K and Pressures up to 300 MPa[1]

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The specific volumes for the glycine–water system have been measured in the temperature range 298–323 K and at pressures up to 300 MPa, using a glass piezometer. The uncertainties in the specific volume are estimated to be less than 0.03%. The *PVT* relations are correlated by the Tait equation. Good agreement was found with correlations by the Tait equation using a simple extension similar to that proposed by Dymond and Malhotra. The isothermal compressibility and apparent molar volume of glycine are calculated by the Tait equation. The apparent molar volume of glycine increases with increasing pressure.

KEY WORDS: glycine; high pressure; *PVT* relation; Tait equation; water.

1. INTRODUCTION

PVT relations and thermodynamic properties for amino acid–water systems have attracted considerable interest as a model system which incorporates some of the molecular features associated with biopolymers [1–3]. Although a number of measurements for the glycine–water system have been reported at atmospheric pressure and 298.15 K [3–5], systematic studies covering wide range of pressure and temperature are scarce [6]. The present investigation was undertaken to obtain accurate *PVTx* data for the glycine–water system and to investigate the pressure effect on the derived thermodynamic properties, such as the apparent molar volume of glycine.

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2. EXPERIMENTAL

The specific volumes for the glycine–water system were measured with a glass piezometer. The glass piezometer used in this study is similar to that of Kumagai and Takahashi [7] and is shown in Fig. 1. The piezometer (H) was made of borosilicate glass and consisted of a capillary (3-mm i.d. and 100-mm length) and a bulb (about 10.3-cm^3 volume). The volume of the piezometer was calibrated using mercury with an uncertainty of less than 0.01 %. The sample liquid introduced into the piezometer was sealed with mercury sandwiched between two stainless-steel pieces fixed to a hard steel rod (0.6-mm diameter). The upper end of the rod was connected to the core (C) of a linear variable differential transformer (B) mounted on the outside of the high-pressure guide (D). The guide had a 15-mm o.d., 5-mm i.d., and 290-mm length and was made of Cu–Be alloy. The mercury was displaced in accordance with the volume change of the sample liquid due to pressure. The displacement of the mercury was detected through the displacement of the core (C) by the use of the differential transformer and

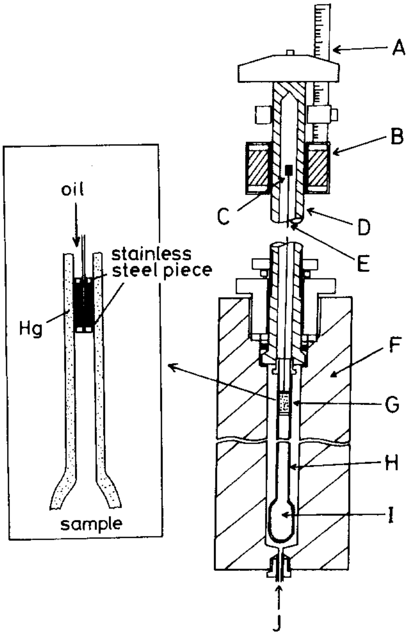

Fig. 1. Experimental apparatus. A, micrometer; B, differential transformer; C, core; D, high-pressure guide; E, hard steel rod; F, high-pressure vessel; G, separator; H, glass piezometer; I, sample solution; J, pressure inlet.

measured by the use of a micrometer (A) and a null detector. The uncertainty in the determination of displacement is 0.03 mm. The details of the procedure for the determination of the specific volume were described by Kumagai and Takahashi [7]. Pressure was generated by a plunger pump and transmitted to the heat-treated SK steel high-pressure vessel (F) containing the piezometer. The pressure was measured with a Heise bourdon gauge, which was calibrated against a pressure balance periodically. The uncertainty in the pressure measurements was estimated to be less than 0.1 MPa. The temperature of the liquid sample was controlled by immersing the pressure vessel in a water bath, which was thermostatically controlled to within ±5 mK. The temperature of the bath was measured with a standard mercury thermometer calibrated by the Leeds–Northrup platinum resistance thermometer. The uncertainty of the temperature measurements is within 10 mK.

The deionized distilled water and the glycine of special grade, 99+% purity, were used without further purification. The solution of the desired composition was prepared by mixing about 200 cm^3 of water and the desired amount of glycine in a flask. The composition was determined by weighing the sample before and after the evaporation of the water. At least four 10-cm^3 volumes of the solution were sampled for the determination of the composition. The accuracy of the composition determination is estimated to be 2×10^{-5} mole fraction.

The pH of the solution at the temperature range of this study and at atmospheric pressure was about 6.0, which corresponds to the isoelectric point of glycine. At this pH, most of the glycine is a dipolar ion in the solution.

3. RESULTS AND DISCUSSION

3.1. Experimental Results

The specific volume measurements were performed three times for each solution. The values shown in Table I are averages based on the three measurements. The difference between each experimental value and the average was less than 0.03%. To check the reliability of the present *PVT* apparatus, the present data for pure water were compared with the literature values. The present data agreed with those of Kell and Whalley [8], Chen et al. [9], Grindley and Lind [10], Kubota et al. [11], and Haar et al. [12] within 0.01, 0.01, 0.02, 0.03, and 0.02%, respectively. Ellerton et al. [13] measured the density for the glycine–water system at 298.15 K and atmospheric pressure. The present data agreed with those of Ellerton et al. within 0.2%.

Table I. Specific Volumes for the Glycine–Water System
(P in MPa; v in $cm^3 \cdot g^{-1}$)

	298.15 K			
	v			
P	$x(H_2O) = 1.0$	$x(H_2O) = 0.99050$	$x(H_2O) = 0.97048$	$x(H_2O) = 0.94821$
0.1	1.0030	0.9868	0.9570	0.9290
10	0.9985	0.9826	0.9534	0.9258
20	0.9943	0.9786	0.9498	0.9227
30	0.9900	0.9746	0.9462	0.9196
40	0.9858	0.9707	0.9428	0.9166
50	0.9819	0.9669	0.9394	0.9137
60	0.9780	0.9633	0.9362	0.9108
70	0.9742	0.9597	0.9330	0.9080
80	0.9706	0.9562	0.9299	0.9051
90	0.9670	0.9529	0.9269	0.9024
100	0.9635	0.9496	0.9240	0.8998
110	0.9602	0.9464	0.9211	0.8973
120	0.9568	0.9433	0.9182	0.8947
130	0.9536	0.9403	0.9155	0.8923
140	0.9504	0.9374	0.9129	0.8898
150	0.9475	0.9344	0.9102	0.8874
160	0.9443	0.9315	0.9077	0.8851
170	0.9414	0.9287	0.9052	0.8829
180	0.9385	0.9261	0.9028	0.8806
190	0.9358	0.9234	0.9004	0.8785
200	0.9330	0.9207	0.8980	0.8763
210	0.9303	0.9182	0.8957	0.8742
220	0.9277	0.9157	0.8934	0.8721
230	0.9253	0.9133	0.8912	0.8701
240	0.9226	0.9109	0.8890	0.8682
250	0.9202	0.9085	0.8869	0.8662
260	0.9179	0.9063	0.8848	0.8643
270	0.9154	0.9040	0.8828	0.8624
280	0.9132	0.9018	0.8808	0.8605
290	0.9109	0.8996	0.8789	0.8587
300	0.9087	0.8976	0.8768	0.8570

Table I. (*Continued*)

	303.15 K v			
P	$x(H_2O)=1.0$	$x(H_2O)=0.98726$	$x(H_2O)=0.97302$	$x(H_2O)=0.94435$
0.1	1.0044	0.9831	0.9620	0.9262
10	1.0000	0.9791	0.9583	0.9231
20	0.9957	0.9752	0.9547	0.9200
30	0.9915	0.9713	0.9511	0.9170
40	0.9873	0.9675	0.9475	0.9140
50	0.9835	0.9638	0.9442	0.9111
60	0.9796	0.9603	0.9409	0.9084
70	0.9760	0.9568	0.9377	0.9056
80	0.9722	0.9534	0.9345	0.9029
90	0.9687	0.9501	0.9315	0.9003
100	0.9652	0.9470	0.9286	0.8977
110	0.9619	0.9438	0.9257	0.8951
120	0.9586	0.9407	0.9228	0.8927
130	0.9554	0.9377	0.9200	0.8902
140	0.9522	0.9349	0.9173	0.8879
150	0.9491	0.9320	0.9147	0.8856
160	0.9461	0.9292	0.9121	0.8833
170	0.9432	0.9264	0.9095	0.8811
180	0.9403	0.9239	0.9071	0.8789
190	0.9376	0.9212	0.9047	0.8767
200	0.9348	0.9186	0.9022	0.8746
210	0.9322	0.9161	0.8999	0.8726
220	0.9296	0.9137	0.8977	0.8705
230	0.9270	0.9113	0.8955	0.8685
240	0.9245	0.9089	0.8932	0.8665
250	0.9220	0.9067	0.8911	0.8646
260	0.9197	0.9044	0.8890	0.8628
270	0.9173	0.9022	0.8869	0.8609
280	0.9150	0.9000	0.8849	0.8590
290	0.9127	0.8978	0.8829	0.8572
300	0.9106	0.8957	0.8809	0.8554

Table I. (*Continued*)

	313.15 K			
	v			
P	$x(H_2O) = 1.0$	$x(H_2O) = 0.98753$	$x(H_2O) = 0.97135$	$x(H_2O) = 0.95892$
0.1	1.0078	0.9870	0.9633	0.9471
10	1.0034	0.9830	0.9596	0.9437
20	0.9993	0.9791	0.9560	0.9404
30	0.9951	0.9751	0.9525	0.9371
40	0.9910	0.9713	0.9490	0.9339
50	0.9870	0.9677	0.9457	0.9308
60	0.9832	0.9642	0.9425	0.9278
70	0.9795	0.9608	0.9393	0.9248
80	0.9758	0.9574	0.9362	0.9218
90	0.9723	0.9541	0.9331	0.9190
100	0.9689	0.9509	0.9303	0.9163
110	0.9655	0.9478	0.9274	0.9136
120	0.9622	0.9446	0.9246	0.9109
130	0.9590	0.9417	0.9218	0.9084
140	0.9559	0.9388	0.9192	0.9059
150	0.9529	0.9359	0.9165	0.9034
160	0.9499	0.9331	0.9139	0.9010
170	0.9470	0.9304	0.9115	0.8986
180	0.9442	0.9278	0.9091	0.8963
190	0.9414	0.9251	0.9066	0.8940
200	0.9387	0.9226	0.9042	0.8917
210	0.9360	0.9200	0.9020	0.8895
220	0.9334	0.9176	0.8997	0.8873
230	0.9308	0.9152	0.8975	0.8852
240	0.9283	0.9128	0.8953	0.8831
250	0.9258	0.9105	0.8931	0.8811
260	0.9234	0.9083	0.8911	0.8792
270	0.9211	0.9061	0.8890	0.8773
280	0.9190	0.9039	0.8870	0.8753
290	0.9168	0.9017	0.8850	0.8734
300	0.9146	0.8996	0.8831	0.8716

Table I. (*Continued*)

	323.15 K v			
P	$x(H_2O) = 1.0$	$x(H_2O) = 0.98780$	$x(H_2O) = 0.97118$	$x(H_2O) = 0.94837$
0.1	1.0121	0.9917	0.9674	0.9385
10	1.0077	0.9876	0.9637	0.9352
20	1.0035	0.9837	0.9601	0.9320
30	0.9993	0.9798	0.9565	0.9289
40	0.9952	0.9760	0.9530	0.9257
50	0.9913	0.9724	0.9496	0.9227
60	0.9875	0.9689	0.9465	0.9198
70	0.9838	0.9654	0.9433	0.9169
80	0.9801	0.9619	0.9401	0.9142
90	0.9765	0.9586	0.9371	0.9115
100	0.9732	0.9555	0.9342	0.9089
110	0.9698	0.9523	0.9313	0.9064
120	0.9665	0.9492	0.9285	0.9039
130	0.9633	0.9462	0.9257	0.9013
140	0.9603	0.9433	0.9230	0.8989
150	0.9672	0.9405	0.9204	0.8965
160	0.9541	0.9377	0.9178	0.8941
170	0.9512	0.9350	0.9153	0.8918
180	0.9485	0.9323	0.9128	0.8896
190	0.9456	0.9297	0.9104	0.8874
200	0.9429	0.9272	0.9080	0.8852
210	0.9402	0.9246	0.9057	0.8832
220	0.9376	0.9222	0.9034	0.8811
230	0.9350	0.9197	0.9012	0.8790
240	0.9324	0.9173	0.8989	0.8770
250	0.9299	0.9151	0.8968	0.8750
260	0.9276	0.9129	0.8948	0.8731
270	0.9253	0.9106	0.8927	0.8712
280	0.9229	0.9084	0.8906	0.8693
290	0.9206	0.9063	0.8886	0.8675
300	0.9184	0.9041	0.8867	0.8657

The apparent molar volume, ϕ_v, of the glycine can be expressed as

$$\phi_v = M/d - 1000(d - d_w)/mdd_w \qquad (1)$$

where M is the molecular weight of the glycine, m the molality, d the density of the solution, and d_w the density of the water. The apparent molar volumes calculated from the present data are shown in Fig. 2. The result calculated from the equation proposed by Ellerton et al. at 298.15 K is given by the solid line. The results of the present study agreed with the calculated results to within 2%.

3.2. Tait Equation

The $PVTx$ relations for the glycine–water system were correlated with the Tait equation. The Tait equation can be expressed in the form

$$(V_0 - V)/V_0 = C \ln[(B + P)/(B + P_0)] \qquad (2)$$

where V and V_0 are specific volumes at the corresponding pressures, P and P_0, and B and C are parameters. The reference state was chosen to be 0.1 MPa. The parameters were optimized by minimizing the deviation of the calculated volume from the experimental one. For water, C was equal to 0.13196 and B was expressed by a linear function of temperature as

$$B = 2.0588 \times 10^2 + 0.2769\ T \qquad (3)$$

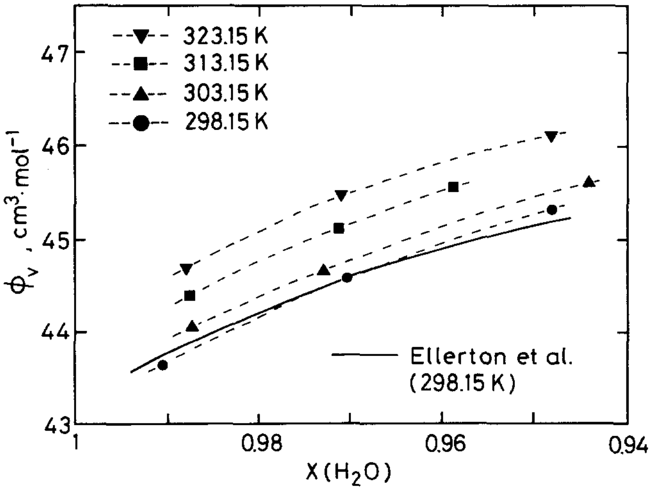

Fig. 2. The apparent molar volume of glycine at 0.1 MPa.

Table II. Deviations of the Experimental Specific Volume for the Glycine–Water System from the Tait Equation

Temperature (K)	$X(H_2O)$	Max. dev. (%)[a]	ADD (%)[a]	Bias (%)[a]
298.15	1.0	0.03	0.01	0.00
	0.99050	0.05	0.01	0.01
	0.97048	0.08	0.02	0.02
	0.94821	0.09	0.03	0.03
303.15	1.0	0.03	0.01	0.00
	0.98726	0.03	0.01	0.01
	0.97302	0.04	0.02	−0.00
	0.94435	0.05	0.02	0.02
313.15	1.0	0.02	0.01	−0.01
	0.98753	0.02	0.01	−0.01
	0.97135	0.04	0.02	−0.01
	0.95892	0.05	0.01	0.00
323.15	1.0	0.02	0.01	0.00
	0.98780	0.02	0.01	−0.01
	0.97118	0.05	0.03	−0.03
	0.94837	0.07	0.05	−0.05

[a] Maximum deviation (%) = max. of 100 $|(V_{\text{expt}} - V_{\text{calc}})|/V_{\text{calc}}$. ADD(%) = (100/ND) $\sum_1^{\text{ND}} |(V_{\text{expt}} - V_{\text{calc}})|/V_{\text{calc}}$ and bias(%) = (100/ND) $\sum_1^{\text{ND}} ((V_{\text{expt}} - V_{\text{calc}}))/V_{\text{calc}}$, where ND is the total number of data points.

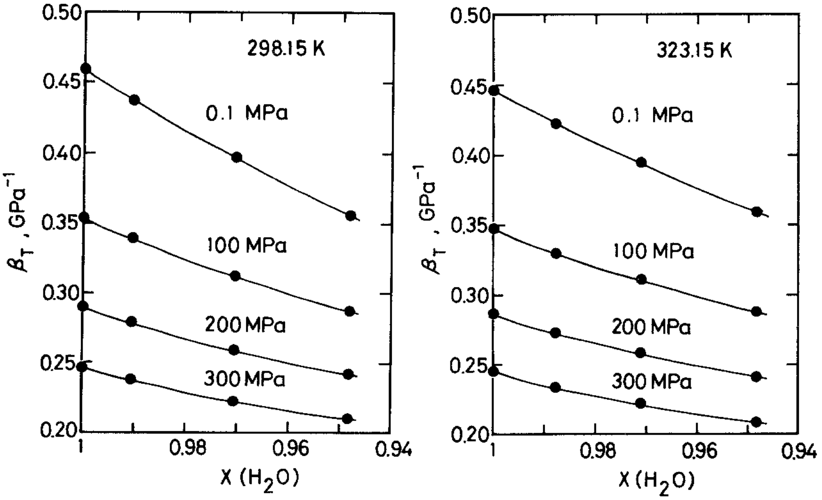

Fig. 3. The isothermal compressibility for the glycine–water system at 298.15 and 323.15 K.

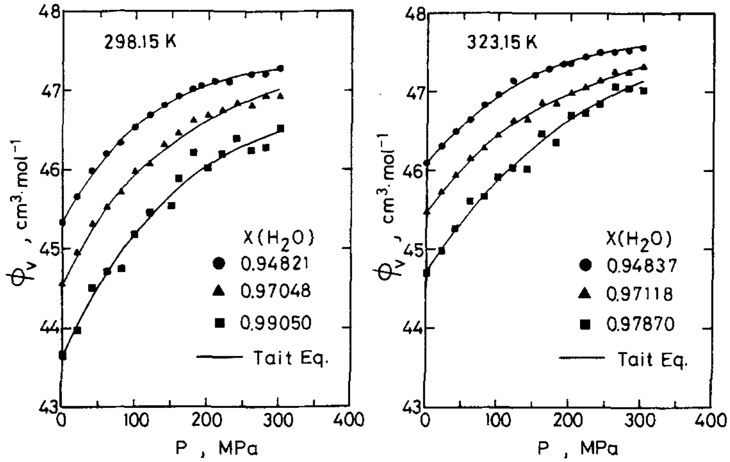

Fig. 4. The apparent molar volume of glycine at 298.15 and 323.15 K.

Dymond and Malhotra [14] proposed the one-fluid approximation for B for mixtures of *n*-alkanes, while C was considered to be constant.

For the glycine–water system, C could also be treated as a constant, 0.13196. The parameter B could be expressed by the following equation:

$$B = B_0 + 1.598 \times 10^3 X_G \tag{4}$$

where B_0 is the value of B calculated from Eq. (3), and X_G is the mole fraction of glycine. Comparison of the volumes calculated with the Tait equation and Eqs. (3) and (4) with the experimental values is given in Table II. The Tait equation can fit the data with an average absolute deviation of 0.015%. The isothermal compressibility β_T was calculated using the Tait equation as shown in Fig. 3. The compressibility decreased with pressure or the mole fraction of glycine. The apparent molar volumes of glycine were calculated with Eqs. (1) and (2) and are shown in Fig. 4. The apparent molar volume increased with pressure or the mole fraction of glycine. This behavior is the same as that observed by Yananos [4].

4. CONCLUSIONS

PVTx relations were obtained for the glycine–water system at 298–323 K and pressures up to 300 MPa. The data for the water in this study showed a good agreement with literature values.

The Tait equation, with the parameter $C = 0.13196$, gave a satisfactory correlation of the specific volumes of the glycine–water system. The parameter B of the Tait equation was found to depend on temperature and the mole fraction of glycine. The apparent molar volume of glycine under pressure was calculated with the Tait equation and was found to increase with pressure or the mole fraction of glycine.

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