Standard Partial Molar Volumes of Aqueous Glycolic Acid and Tartaric Acid from 25 to 350 °C: Evidence of a Negative Krichevskii Parameter for a Neutral Organic Solute

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Apparent molar volumes have been determined using a high-pressure vibrating-tube densimeter for aqueous solutions of glycolic acid (HGly = HOCH$_2$COOH) and tartaric acid (H$_2$Tar = HOOCCH(OH)CH(OH)-COOH) at temperatures from 25 °C to 350 °C and pressures as high as 20 MPa. The resulting standard partial molar volumes V_2^o(HGly,aq) are relatively independent of temperature until 315 °C, at which point V_2^o(HGly,aq) deviates sharply toward negative values. This suggests that the Krichevskii parameter, $A_{Kr} = \lim(x_2 \rightarrow 0)\ (\partial p/\partial x_2)_{T,V}^c$, which describes the discontinuities in standard partial molar properties at the critical point of water, is negative. Almost all aqueous nonelectrolytes are characterized by positive Krichevskii parameters. This is the first negative value reported for any organic molecule that is not an ion or zwitterion and only the third ever observed directly for a neutral species (the others are B(OH)$_3$ and H$_3$PO$_4$). The standard partial molar volumes for H$_2$Tar(aq) are also relatively independent of temperature until 275 °C, suggesting a similar behavior. However, the onset of thermal decomposition prevented measurements at temperatures above 300 °C.

1. Introduction

Under ambient conditions, the hydration of neutral organic solutes and organic electrolytes reflects a balance between energetic, entropic, and volumetric hydrogen-bonding effects whose subtleties have occupied researchers for more than 100 years. At temperatures above about 200 °C, however, long-range solute−water interactions begin to dominate as a result of the decreased hydrogen bonding in water itself and the resulting increased compressibility of liquid water. Ions attract more and more water around them as the temperature is raised toward the critical point, resulting in a net decrease in their standard partial molar volume and a decrease in entropy, while neutral molecules usually repel water more effectively through hydrophobic interactions, resulting in a net increase in both their standard partial molar volumes and their entropies.[1−3] Typical behavior is illustrated in Figure 1, which plots the standard partial molar volumes of morpholine and its chloride salt, morpholinium chloride, up to 300 °C.[4] These are thought to approach +∞ and −∞, respectively, at the critical point of water.

The approach to the discontinuities in standard partial molar properties at the critical point of water is described by the Krichevskii parameter[5−8]

$$A_{Kr} = \lim(x_2 \rightarrow 0)\ (\partial p/\partial x_2)_{T,V}^c \qquad (1)$$

The Krichevskii parameter is related to the standard partial molar volume of the solute, V_2^o, through the relationship

$$A_{Kr} = \lim(T \rightarrow T_c, \rho \rightarrow \rho_c)\ [V_2^o/(\kappa_1^* V_1^*)]. \qquad (2)$$

Here, T_c and ρ_c are the critical temperature and density of water, respectively, x_2 is the mole fraction of solute, V_1^* is the molar

volume of water, and $\kappa_1^* = (V_1^*)^{-1}(\partial V_1^*/\partial p)_T$ is the isothermal compressibility of water. A_{Kr} is a finite constant with units of MPa. The increasingly large, negative values of the standard partial molar volumes V_2^o and heat capacities $C_{p,2}^o$ of simple electrolytes at temperatures approaching the critical point of water are now understood to arise from long-range solvent polarization effects arising from the infinite value of κ_1^* at the critical point. In contrast to electrolytes, V_2^o and $C_{p,2}^o$ of nonelectrolyte solutions become more and more positive as the temperatures increase, as a result of increasingly large hydrophobic interactions with water. Only two exceptions have been found to date. Both B(OH)$_3$ and H$_3$PO$_4$ are sufficiently polar that they exhibit almost constant values of V_2^o and $C_{p,2}^o$ at temperatures from 25 to about 330 °C at steam saturation, p_{sat}. These values plunge toward a negative discontinuity as the temperature is raised above 330 °C.[9,10] The behavior of V_2^o for B(OH)$_3$ is plotted in Figure 2. Similar behavior has been postulated for Si(OH)$_4$, based on high-temperature solubility data.[8]

Several workers have recently reported functional group additivity models that can be used to predict the standard partial molar properties of organic solutes under hydrothermal conditions, with varying degrees of success.[11−13] It is not generally recognized that at least one of these models,[13] which is based on solution fluctuation theory,[14] predicts that, with enough sufficiently polar groups, some neutral organic molecules can display negative Krichevskii behavior. Glycolic acid (HGly), HOCH$_2$COOH, and tartaric acid (H$_2$Tar), HOOCCH(OH)CH-(OH)COOH, are of interest in this context because they are small molecules with extreme hydrogen bonding, having one −OH group and one −COOH group on each alkyl carbon. In earlier papers,[15,16] we reported the ionization constant of glycolic acid and the apparent molar volumes of tartaric acid and its sodium salt at temperatures up to 250 °C, as part of a larger study to examine the effect of hydrogen-bonding functional groups on

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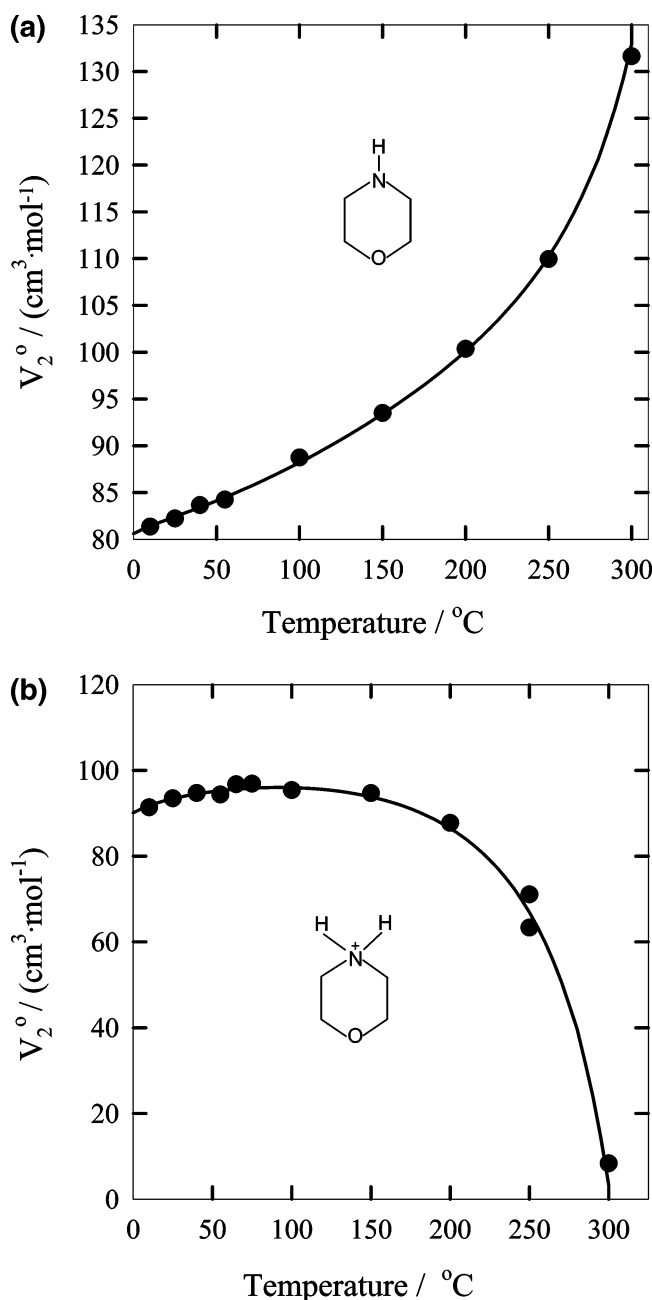
(a)

(b)

Figure 1. Standard partial molar volumes, V_2^o, for morpholine and morpholinium chloride from Tremaine et al.[4] showing typical positive and negative discontinuities of nonelectrolytes and electrolytes, respectively, with increasing temperature.

the standard partial molar volumes of organic acids, bases, and zwitterions at elevated temperatures. In this work, the measurements have been extended to temperatures of 350 °C and pressures of 20 MPa in an attempt to observe whether these hydroxy-carboxylic acids display positive or negative Krichevskii behavior.

2. Experimental Section

The sources of chemicals and methods of preparing solutions were discussed in our previous papers.[15,16] High-temperature volumetric measurements were made in a vibrating-tube densitometer, constructed according to the design of Albert and Wood,[17] as modified by Corti et al.[18] A detailed description of the densitometer and the experimental procedures has been given by Xiao et al.[19] and Clarke and Tremaine.[20] The densitometer
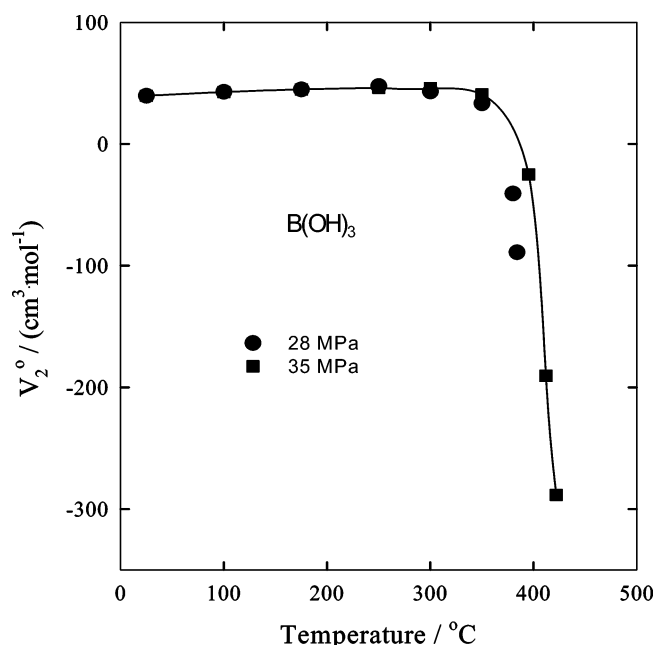

Figure 2. Standard partial molar volumes, V_2^o, of boric acid as a function of temperature, from Hnĕdkovský et al.,[9] showing a negative discontinuity at the critical end point, consistent with a negative Krichevskii parameter.

was calibrated daily with pure water and standard solutions of 1.0000 mol·kg^{-1} NaCl(aq), using the reference values compiled by Hill[21] and Archer,[22] respectively. The combined uncertainty in the measured relative densities, $(\rho - \rho_1^*)$, due to the sensitivity limits of the instrument itself and the accuracy of the reference data, is estimated to be ±0.0002 g·cm^{-3}. The precision of each measurement is ±0.00002 g·cm^{-3}.

At high temperatures, it was expected that aqueous solutions of glycolic acid and tartaric acid may decompose. As a precaution, all solutions and water were degassed to remove oxygen before use. At the highest temperatures, samples which had passed through the densitometer were collected by means of a sample loop in the exit stream and analyzed for decomposition products. Analyses by ^{13}C NMR indicated no decomposition products for glycolic acid samples taken at the highest temperatures, 335 and 350 °C, within detection limits of better than 2%, although we note that volatile decomposition products would be lost by evaporation when the sample was depressurized. In our experience,[19,20] thermal decomposition is usually accompanied by a sharp increase in the molality dependence of the measured apparent molar volumes with increasing dilution relative to those at lower temperatures. No such effects were observed for glycolic acid. At temperatures above 320 °C, the ^{13}C and ^{1}H NMR spectra of a 1 mol·kg^{-1} tartaric acid solution displayed a rich variety of peaks, corresponding to carbonyl, carboxyl, alkyne, and hydroxyl functional groups, which indicated that thermal decomposition had taken place during the course of the measurement. The apparent molar volumes displayed erratic behavior at these temperatures, consistent with thermal decomposition.

3. Results

Standard Partial Molar Volumes. The density of solutions in the vibrating-tube densitometer was determined from the expression

$$\rho = \rho_1^* + K(\tau^2 - \tau_1^2) \tag{3}$$

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where ρ and ρ_1^* are the densities of the solution and the water in g·cm^{-3}, respectively, τ and τ_1 are the resonance periods of the vibrating tube containing the solution and water, respectively, and K is a characteristic constant determined by calibration with the solvent water[21] and the standard NaCl solution.[22] The experimental apparent molar volumes V_ϕ were calculated through the usual expression

$$V_\phi^{exp} = 1000(\rho_1^* - \rho)/(m\rho\rho_1^*) + M/\rho \qquad (4)$$

where ρ_1^*, and ρ are the densities of pure water and solution (g·cm^{-3}), respectively, M is the molar mass of solute (g·mol^{-1}), and m is the solution molality (mol·kg^{-1}). Estimated uncertainties in V_ϕ for glycolic and tartaric acids were within ± 1 and ± 2 cm^3·mol^{-1}, respectively, at all temperatures. The statistical uncertainty in molality is the main contributor. The experimentally determined relative densities $(\rho - \rho_1^*)$ and apparent molar volumes for aqueous glycolic and tartaric acid are listed in Tables 1 and 2.

Because the neutral species of carboxylic acids ionize in water, a small correction to remove the contribution of the ionized species was made using Young's rule[4,16]

$$V_\phi^{exp} = (1 - \alpha)V_\phi(RCOOH,aq) +$$
$$\alpha V_\phi(RCOO^-,aq + H^+,aq) \quad (5)$$

The degree of ionization, α, for glycolic and tartaric acids was calculated from extrapolated ionization constants reported by Shock[23] and Xie and Tremaine,[16] respectively. Shock's values have been confirmed in our laboratory by direct measurements up to 250 °C.[15] Values for $V_\phi(RCOO^-,aq + H^+,aq)$ were calculated from recently measured values of $V_\phi(RCOO^-,aq + Na^+,aq)$ for both acids.[16,24] The magnitude of the correction is less than 0.5 cm^3·mol^{-1} for HGly(aq) and 1.1 cm^3·mol^{-1} for H$_2$Tar(aq) at the highest temperature studied. The magnitude of the correction is important because ionic contributions could override positive contributions of a neutral acid to cause the Krichevskii behavior of the stoichiometric mixture to be negative.

The standard partial molar volumes were determined by fitting linear equations to the molality-dependent experimental results for $V_\phi(RCOOH,aq)$ and extrapolating to infinite dilution according to the expression

$$V_{\phi,2} = V_2^o + B_V m \qquad (6)$$

The molality dependence is not large and in no case was the inclusion of the B_V term statistically significant. When the B_V was included, the extrapolated value of V_2^o differed from the simple average of $V_{\phi,2}$ at all molalities by less than 1 cm^3·mol^{-1}. The values of V_2^o, taken from the simple averages after correction for the effects of ionization, are listed in Tables 3 and 4.

The experimental values for V_2^o are plotted in Figures 3 and 4, along with the values predicted by the functional group additivity model of Yezdimer et al.[13] The plots for V_2^o(H$_2$Tar,aq) and V_2^o(HGly,aq) in Figures 3 and 4, respectively, include values below 100 °C reported by Høiland and Vikingstad[25] and Patterson and Woolley,[26] as well as high-temperature values from our own earlier work.[16] The temperature dependence of V_2^o for both acids is quite flat over most of the range, unlike the "typical" behavior for neutral solutes illustrated in Figure 1. Above 275 °C, tartaric acid shows a positive discontinuity in V_2^o, while the discontinuity for gly-

colic acid is negative. The group additivity model correctly predicts the values of V_2^o up to 250 °C. At higher temperatures, the predicted values are too negative and a negative discontinuity at the critical point is predicted for both acids.

The thermal decomposition of organic alcohols and carboxylic acids has been reviewed by Brill and Savage.[27] The major decomposition reactions at these temperatures are decarboxylation and dehydration. In the absence of oxygen, glycolic acid decomposes to CO$_2$ and methanol. The decomposition of tartaric acid is more complex, yielding CO$_2$, 2-butynedioic acid, 2-ketosuccinic acid, pyruvic acid, and possibly lactone, consistent with the NMR results. The volatile products remain in solution during measurements at high pressure but are lost from the samples before analysis. Since CO$_2$ and methanol have positive Krichevskii parameters, the negative divergence observed for glycolic acid must be real. The positive divergence of V_2^o for tartaric acid at 300 °C may be real, or it may be an artifact, reflecting positive contributions to V_2^o from dissolved CO$_2$ and other volatile decomposition products that are lost from the sample of effluent solution before analysis.

Krichevskii Parameters. The approach to the discontinuities in standard partial molar properties at the critical point of water is described by the dimensionless "generalized" Krichevskii parameter

$$A_{12} = V_2^o/(\kappa_1^* RT) = \lim(n_2 \to 0) \ [\partial(pV/RT)/\partial n_2]_{T,V,N1} \quad (7)$$

which is a smooth, continuous, and finite function, even at temperatures well below the critical point. The generalized A_{12} parameter is consistent with solution fluctuation theory, in which $A_{12} = (1 - C_{ij})$ where C_{ij} is the dimensionless spatial integral of the solute−solvent direct correlation function at infinite dilution.[5−7] The Krichevskii parameter, A_{Kr}, is related to A_{12} through the expression

$$A_{Kr} = A_{12}(T_c, p_c)[RT_c/V_1^c] \qquad (8)$$

where V_1^c represents the critical value of the molar volume of water ($V_1^c = 55.96$ cm^3·mol^{-1}), and $A_{12}(T_c, p_c)$ is the value of the parameter A_{12} at the critical point of pure water. Values of A_{12} for glycolic acid and tartaric acid, corresponding to our experimental values for V_2^o, are included in Tables 3 and 4, respectively, and plotted in Figure 5.

Several equations of state for standard partial molar properties are based on expressions for the density and temperature dependence of A_{12}.[5,14,28] One of the simplest, proposed by O'Connell et al.,[6] takes the form

$$A_{12} = V_1^*/(\kappa_1^* RT) + \{a + b[\exp(\vartheta\rho_1^*) - 1]\}\rho_1^* \qquad (9)$$

Here, V_1^* is the molar volume of water, and $\vartheta = 0.005$ m^3·kg^{-1} = 5 cm^3·g^{-1} is a constant derived by fitting the expression to data for a number of simple solutes. The constants a and b are solute-specific adjustable fitting parameters. The Krichevskii parameter for glycolic acid, A_{Kr}(HGly,aq), was estimated by fitting eq 9 to the data in Table 3 and extrapolating the fitted function for A_{12} to the critical density and temperature. Equation 9 was chosen, in preference to more complex expressions reported by Sedlbauer et al.[14] and Plyasunov et al.,[28] because the extra terms used to describe the low-temperature and low-density regions are not required for our analysis. The temperature range of data used in the fit was limited to 275−350 °C, due to the fact that the sign of near critical divergence is obvious only at temperatures above 275 °C. The inclusion of lower

TABLE 1: Apparent Molar Volume $V_{\phi,2}$ for Glycolic Acid after the Degree of Dissociation Correction

t/°C	p/MPa	m_2/mol·kg⁻¹	$10^2(\rho-\rho_1^*)$	V_ϕ^{exp}	α	$V_{\phi,2}$/cm³·mol⁻¹
$t = 24.96 \pm 0.01$ °C, $p = 0.10 \pm 0.01$ MPa						
24.96	0.10	0.9336	2.1676	51.79	0.0125	51.93 ± 0.33
24.96	0.10	0.7632	1.7904	51.75	0.0138	51.90 ± 0.28
24.96	0.10	0.5960	1.4124	51.70	0.0156	51.88 ± 0.29
24.96	0.10	0.3869	0.9296	51.62	0.0193	51.84 ± 0.37
24.96	0.10	0.1832	0.4465	51.53	0.0279	51.84 ± 0.39
24.96	0.10	0.1587	0.3892	51.40	0.0300	51.73 ± 0.22
$t = 25.36 \pm 0.01$ °C, $p = 0.10 \pm 0.01$ MPa						
25.36	0.10	0.6104	1.4431	51.75	0.0154	51.92 ± 0.19
25.36	0.10	0.5019	1.1982	51.64	0.0170	51.83 ± 0.19
25.36	0.10	0.4067	0.9788	51.56	0.0188	51.77 ± 0.17
25.36	0.10	0.3140	0.7603	51.53	0.0214	51.77 ± 0.17
25.36	0.10	0.1802	0.4371	51.65	0.0282	51.97 ± 0.26
25.36	0.10	0.1327	0.3275	51.28	0.0328	51.64 ± 0.16
$t = 29.88 \pm 0.01$ °C, $p = 0.10 \pm 0.01$ MPa						
29.88	0.10	0.9336	2.1257	52.30	0.0125	52.44 ± 0.33
29.88	0.10	0.7632	1.7618	52.17	0.0139	52.33 ± 0.27
29.88	0.10	0.5960	1.3918	52.10	0.0157	52.28 ± 0.28
29.88	0.10	0.3869	0.9142	52.06	0.0194	52.29 ± 0.37
29.88	0.10	0.1832	0.4404	51.90	0.0281	52.22 ± 0.39
29.88	0.10	0.1587	0.3836	51.80	0.0302	52.14 ± 0.22
$t = 34.87 \pm 0.01$ °C, $p = 0.10 \pm 0.01$ MPa						
34.86	0.10	0.9336	2.1043	52.58	0.0125	52.73 ± 0.33
34.87	0.10	0.7632	1.7384	52.53	0.0138	52.69 ± 0.28
34.87	0.10	0.5960	1.3671	52.57	0.0156	52.75 ± 0.28
34.87	0.10	0.3869	0.9020	52.43	0.0194	52.66 ± 0.36
34.87	0.10	0.1832	0.4352	52.24	0.0280	52.55 ± 0.38
34.87	0.10	0.1587	0.3758	52.34	0.0301	52.69 ± 0.22
$t = 39.89 \pm 0.02$ °C, $p = 0.10 \pm 0.01$ MPa						
39.87	0.10	0.9336	2.0730	52.98	0.0124	53.13 ± 0.32
39.91	0.10	0.7632	1.7149	52.91	0.0137	53.07 ± 0.27
39.89	0.10	0.5960	1.3521	52.88	0.0155	53.06 ± 0.28
39.90	0.10	0.3869	0.8900	52.80	0.0192	53.03 ± 0.36
39.91	0.10	0.1832	0.4271	52.74	0.0278	53.07 ± 0.38
39.88	0.10	0.1587	0.3720	52.64	0.0298	52.98 ± 0.21
$t = 100.24 \pm 0.02$ °C, $p = 11.06 \pm 0.02$ MPa						
100.24	11.09	0.6104	1.2375	56.38	0.0116	56.53 ± 0.18
100.23	11.05	0.5019	1.0384	56.05	0.0128	56.22 ± 0.16
100.26	11.07	0.4067	0.8040	57.17	0.0142	57.38 ± 0.20
100.27	11.03	0.3140	0.6980	54.60	0.0161	54.79 ± 0.16
100.21	11.06	0.1802	0.3565	57.41	0.0212	57.73 ± 0.30
100.22	11.04	0.1327	0.2773	56.27	0.0247	56.61 ± 0.15
$t = 150.65 \pm 0.02$ °C; $p = 11.13 \pm 0.01$ MPa						
150.66	11.13	0.8785	1.6672	59.08	0.0083	59.25 ± 0.35
150.64	11.14	0.6937	1.3360	58.96	0.0093	59.15 ± 0.29
150.61	11.15	0.5046	0.9826	58.93	0.0109	59.16 ± 0.32
150.63	11.13	0.3472	0.6901	58.65	0.0131	58.92 ± 0.27
150.66	11.13	0.2177	0.4373	58.56	0.0165	58.90 ± 0.24
150.68	11.13	0.1744	0.3504	58.62	0.0184	59.00 ± 0.13
$t = 149.94 \pm 0.06$ °C, $p = 10.94 \pm 0.02$ MPa						
150.01	10.93	0.8974	1.6868	59.25	0.0082	59.43 ± 0.32
149.92	10.92	0.7159	1.3711	59.04	0.0091	59.23 ± 0.28
150.00	10.98	0.5393	1.0384	59.13	0.0105	59.35 ± 0.30
149.90	10.95	0.3690	0.7289	58.75	0.0127	59.01 ± 0.28
149.90	10.92	0.1737	0.3385	59.30	0.0185	59.69 ± 0.37
149.88	10.93	0.1423	0.2905	58.25	0.0204	58.66 ± 0.19
$t = 200.34 \pm 0.02$ °C, $p = 11.04 \pm 0.04$ MPa						
200.36	11.03	0.9007	1.6380	62.16	0.0051	62.31 ± 0.36
200.36	11.01	0.7033	1.2951	62.10	0.0057	62.27 ± 0.34
200.35	11.00	0.5323	1.0240	61.22	0.0066	61.41 ± 0.27
200.32	11.07	0.3498	0.6707	61.55	0.0081	61.78 ± 0.36
200.32	11.02	0.1855	0.3537	61.91	0.0111	62.24 ± 0.34
200.32	11.11	0.1341	0.2698	60.58	0.0131	60.96 ± 0.21
$t = 201.17 \pm 0.02$ °C, $p = 10.92 \pm 0.01$ MPa						
201.15	10.92	0.8659	1.6081	61.72	0.0051	61.87 ± 0.34
201.19	10.92	0.6939	1.2979	61.77	0.0058	61.94 ± 0.31
201.16	10.91	0.5218	1.0016	61.33	0.0066	61.53 ± 0.30
201.17	10.91	0.3484	0.6792	61.17	0.0081	61.40 ± 0.33
201.15	10.91	0.1748	0.3637	59.66	0.0114	59.98 ± 0.34
201.19	10.92	0.1310	0.2625	60.74	0.0132	61.13 ± 0.22
$t = 250.22 \pm 0.02$ °C, $p = 10.98 \pm 0.06$ MPa						
250.23	10.93	0.8974	1.6302	65.05	0.0030	65.20 ± 0.42
250.23	10.92	0.7159	1.3032	65.26	0.0033	65.41 ± 0.38
250.23	10.95	0.5393	0.9951	65.12	0.0038	65.30 ± 0.36
250.19	11.06	0.3690	0.6781	65.49	0.0046	65.71 ± 0.38
250.23	11.06	0.1737	0.3280	64.99	0.0068	65.31 ± 0.44
250.20	10.96	0.1423	0.2755	64.31	0.0075	64.66 ± 0.24
$t = 251.18 \pm 0.04$ °C, $p = 10.91 \pm 0.01$ MPa						
251.16	10.91	0.8659	1.6299	64.12	0.0030	64.27 ± 0.38
251.16	10.92	0.6939	1.2986	64.55	0.0034	64.72 ± 0.38
251.24	10.94	0.5218	0.9828	64.62	0.0039	64.82 ± 0.37
251.16	10.92	0.3484	0.6841	63.62	0.0048	63.86 ± 0.36
$t = 275.39 \pm 0.06$ °C, $p = 14.46 \pm 0.04$ MPa						
275.33	14.47	0.9007	1.6918	65.60	0.0022	65.76 ± 0.43
275.35	14.45	0.7033	1.3210	65.91	0.0025	66.09 ± 0.47
275.43	14.41	0.5323	1.0412	64.87	0.0029	65.07 ± 0.36
275.44	14.51	0.1855	0.7197	64.60	0.0049	64.94 ± 0.44
$t = 275.13 \pm 0.03$ °C, $p = 15.33 \pm 0.01$ MPa						
275.17	15.33	0.8785	1.6114	66.33	0.0023	66.49 ± 0.37
275.17	15.32	0.6937	1.3064	65.78	0.0025	65.96 ± 0.38
275.12	15.33	0.5046	0.9163	67.22	0.0030	67.43 ± 0.50
275.11	15.33	0.3908	0.7355	66.28	0.0034	66.52 ± 0.23
275.11	15.33	0.1744	0.7345	64.89	0.0050	65.24 ± 0.34
275.09	15.34	0.1463	0.3037	65.69	0.0055	66.08 ± 0.59
$t = 300.02 \pm 0.05$ °C, $p = 14.45 \pm 0.02$ MPa						
300.08	14.42	0.9007	1.7902	65.49	0.0015	65.66 ± 0.57
299.99	14.45	0.7033	1.3968	65.86	0.0017	66.04 ± 0.56
299.93	14.44	0.5323	1.0909	64.94	0.0020	65.15 ± 0.44
300.05	14.47	0.3498	0.7120	65.54	0.0024	65.81 ± 0.56
300.03	14.46	0.1855	0.3827	65.31	0.0033	65.67 ± 0.51
300.06	14.44	0.1341	0.2823	64.60	0.0039	65.02 ± 0.32
$t = 300.18 \pm 0.02$ °C, $p = 15.35 \pm 0.01$ MPa						
300.17	15.35	0.8785	1.6929	66.64	0.0015	66.81 ± 0.49
300.18	15.34	0.6937	1.3674	66.11	0.0017	66.30 ± 0.46
300.20	15.34	0.5046	1.0099	65.87	0.0020	66.09 ± 0.51
300.15	15.35	0.3908	0.7783	66.26	0.0023	66.51 ± 0.34
300.16	15.35	0.3472	0.6960	66.09	0.0024	66.35 ± 0.31
300.21	15.35	0.2177	0.4374	66.23	0.0031	66.57 ± 0.39
$t = 300.40 \pm 0.09$ °C, $p = 19.59 \pm 0.031$ MPa						
300.52	19.60	1.0244	1.9531	66.49	0.0014	66.62 ± 0.52
300.41	19.60	0.7981	1.5402	66.43	0.0016	66.57 ± 0.57
300.35	19.58	0.6133	1.2257	65.44	0.0018	65.61 ± 0.44
300.32	19.59	0.4231	0.8233	66.77	0.0022	66.97 ± 0.57
$t = 315.16 \pm 0.05$ °C, $p = 15.35 \pm 0.01$ MPa						
315.23	15.35	0.8785	1.7861	65.74	0.0014	65.95 ± 0.60
315.14	15.36	0.6937	1.3985	66.45	0.0015	66.68 ± 0.60
315.10	15.36	0.5046	1.0570	65.15	0.0018	65.42 ± 0.54
315.18	15.34	0.3908	0.8275	64.90	0.0020	65.21 ± 0.37
315.17	15.35	0.3472	0.7201	65.90	0.0022	66.23 ± 0.33
$t = 325.35 \pm 0.01$ °C, $p = 14.44 \pm 0.03$ MPa						
325.34	14.40	0.9007	2.0784	60.33	0.0011	60.55 ± 0.78
325.35	14.45	0.7033	1.5306	63.74	0.0012	63.99 ± 0.92
325.34	14.45	0.5323	1.2679	59.39	0.0014	59.67 ± 0.73
325.35	14.45	0.3498	0.7895	62.62	0.0017	62.97 ± 0.84
$t = 325.11 \pm 0.01$ °C, $p = 15.35 \pm 0.00$ MPa						
325.10	15.36	0.8785	1.9259	62.95	0.0011	63.17 ± 0.73
325.11	15.35	0.6937	1.5083	63.73	0.0012	63.98 ± 0.74
325.10	15.35	0.5046	1.0997	64.00	0.0014	64.30 ± 0.70
325.12	15.35	0.3908	0.8558	64.01	0.0016	64.34 ± 0.48
$t = 325.37 \pm 0.02$ °C, $p = 19.60 \pm 0.01$ MPa						
325.39	19.59	1.0244	2.0944	65.67	0.0008	65.79 ± 0.70
325.38	19.60	0.7981	1.6459	65.71	0.0010	65.85 ± 0.72
325.36	19.61	0.6133	1.2852	65.34	0.0011	65.49 ± 0.59
325.38	19.61	0.4231	0.9112	64.46	0.0013	64.64 ± 0.62
325.33	19.61	0.2890	0.6261	64.45	0.0016	64.67 ± 0.48
$t = 335.56 \pm 0.02$ °C, $p = 15.31 \pm 0.00$ MPa						
335.55	15.31	0.9007	2.2760	55.09	0.0008	55.33 ± 0.91
335.54	15.31	0.7033	1.6715	59.26	0.0009	59.53 ± 1.11
335.55	15.30	0.5323	1.3619	55.09	0.0010	55.40 ± 0.89
335.56	15.31	0.3313	0.8853	52.70	0.0013	53.09 ± 0.92
335.59	15.31	0.1855	0.4381	60.77	0.0017	61.31 ± 0.90
$t = 335.14 \pm 0.04$ °C, $p = 15.36 \pm 0.01$ MPa						
335.14	15.36	0.8785	2.0971	58.62	0.0008	58.87 ± 0.90
335.09	15.36	0.6937	1.6766	58.28	0.0009	58.55 ± 0.91
335.21	15.36	0.5046	1.1963	59.84	0.0010	60.16 ± 0.90
335.15	15.35	0.3908	0.9175	60.67	0.0012	61.04 ± 0.53
335.13	15.35	0.3472	0.8457	58.57	0.0012	58.96 ± 0.33
$t = 350.28 \pm 0.02$ °C, $p = 19.61 \pm 0.01$ MPa						
350.26	19.60	1.0244	2.2845	62.43	0.0004	62.56 ± 0.92
350.30	19.60	0.7981	1.9073	58.47	0.0005	58.61 ± 0.77
350.27	19.61	0.6133	1.4269	60.66	0.0005	60.82 ± 1.00
350.29	19.63	0.4231	0.9881	60.86	0.0006	61.05 ± 0.93

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TABLE 2: Apparent Molar Volume $V_{\phi,2}$ for Tartaric Acid after the Degree of Dissociation Correction

t °C	p MPa	m_2 mol·kg^{-1}	$10^2(\rho - \rho_1^*)$ g·cm^{-3}	$V_\phi^{\exp}$ cm^3·mol^{-1}	α	$V_{\phi,2}$ cm^3·mol^{-1}
$t = 200.14 \pm 0.16$ °C, $p = 11.11 \pm 0.03$ MPa
200.06	11.11	0.8652	4.7278	95.11	0.0220	94.83 ± 0.90
200.06	11.12	0.6783	3.7466	95.39	0.0248	95.08 ± 0.96
200.01	11.06	0.5254	2.9797	94.31	0.0281	93.93 ± 0.79
200.07	11.13	0.3872	2.2141	94.53	0.0327	94.09 ± 0.81
200.17	11.13	0.3505	2.0082	94.60	0.0343	94.14 ± 0.79
200.44	11.12	0.2237	1.2874	95.04	0.0428	94.49 ± 0.79
$t = 200.30 \pm 0.03$ °C, $p = 10.99 \pm 0.01$ MPa
200.27	10.98	0.8843	4.7902	95.64	0.0218	95.38 ± 0.97
200.25	10.99	0.7412	4.0684	95.50	0.0237	95.21 ± 0.69
200.31	10.99	0.5155	2.9032	94.92	0.0284	94.55 ± 1.11
200.32	10.99	0.3425	1.9534	95.01	0.0347	94.56 ± 0.94
200.33	10.99	0.1784	1.0447	94.02	0.0478	93.34 ± 0.94
200.33	10.98	0.1446	0.8508	93.83	0.0530	93.07 ± 0.59
200.30	10.99	0.0950	0.5630	94.77	0.0649	93.88 ± 0.75
$t = 249.73 \pm 0.01$ °C, $p = 14.56 \pm 0.01$ MPa
249.74	14.56	1.0033	5.3921	96.91	0.0149	96.54 ± 1.10
249.75	14.56	0.8216	4.4961	96.52	0.0165	96.10 ± 0.93
249.74	14.57	0.5835	3.2730	95.91	0.0195	95.40 ± 1.30
249.73	14.56	0.4078	2.3087	96.25	0.0233	95.65 ± 1.06
249.71	14.55	0.3078	1.7497	96.54	0.0268	95.86 ± 1.25
$t = 275.14 \pm 0.04$ °C, $p = 10.99 \pm 0.01$ MPa
275.15	10.98	0.8843	4.6727	99.79	0.0130	99.36 ± 1.07
275.15	10.99	0.7412	3.9678	99.55	0.0142	99.08 ± 0.93
275.09	10.98	0.5155	2.8233	98.96	0.0170	98.39 ± 1.45
275.10	10.99	0.3425	1.9227	97.81	0.0208	97.09 ± 1.21
275.20	10.99	0.1784	1.0131	97.88	0.0287	96.88 ± 1.27
$t = 275.50 \pm 0.04$ °C, $p = 14.84 \pm 0.01$ MPa
275.51	14.85	1.0033	5.2302	100.18	0.0122	99.78 ± 1.32
275.50	14.85	0.8216	4.3298	100.38	0.0135	99.95 ± 1.18
275.57	14.85	0.5835	3.1668	99.29	0.0160	98.76 ± 1.49
275.46	14.84	0.4078	2.2421	99.29	0.0191	98.65 ± 1.27
275.46	14.84	0.3078	1.7063	99.20	0.0219	98.47 ± 0.91
275.52	14.84	0.1928	1.0810	98.94	0.0276	98.00 ± 1.02
$t = 300.07 \pm 0.04$ °C, $p = 10.99 \pm 0.01$ MPa
300.06	11.00	0.8843	4.1023	112.63	0.0103	112.27 ± 1.11
300.10	10.98	0.7412	3.4903	112.26	0.0112	111.86 ± 1.01
300.11	10.97	0.5155	2.4765	112.01	0.0134	111.53 ± 1.53
300.03	10.99	0.3425	1.6613	112.37	0.0164	111.78 ± 1.32
$t = 300.14 \pm 0.03$ °C, $p = 15.34 \pm 0.01$ MPa
300.13	15.34	0.8652	3.9012	115.01	0.0104	114.67 ± 1.02
300.18	15.34	0.6783	3.1680	113.20	0.0117	112.79 ± 1.01
300.15	15.33	0.5254	2.4696	113.69	0.0133	113.24 ± 0.99
300.15	15.35	0.3872	1.8266	114.36	0.0155	113.84 ± 0.94
300.11	15.34	0.3505	1.6587	114.33	0.0163	113.78 ± 0.78
300.11	15.34	0.2237	1.0723	114.10	0.0203	113.40 ± 0.89
$t = 300.41 \pm 0.04$ °C; $p = 15.06 \pm 0.01$ MPa
300.46	15.06	0.8216	3.7649	113.93	0.0106	113.57 ± 1.35
300.46	15.07	0.5835	2.7408	113.37	0.0126	112.93 ± 1.42
300.38	15.06	0.4078	1.9545	112.80	0.0151	112.26 ± 1.14
300.38	15.05	0.3078	1.4696	113.86	0.0173	113.27 ± 0.77
300.38	15.06	0.1928	0.9270	114.07	0.0219	113.32 ± 0.86

TABLE 3: Standard Partial Molar Volumes, V_2^o, and Generalized Krichevskii Parameter, A_{12}, for Aqueous Glycolic Acid

t °C	p MPa	V_2^o/(cm^3·mol^{-1})[a] experimental	A_{12}[a] experimental	V_2^o/(cm^3·mol^{-1}) eq 9	A_{12} eq 9
24.96	0.10	51.76 ± 0.08	46.15 ± 0.07	49.82[b]	44.42[b]
25.36	0.10	51.73 ± 0.29	46.12 ± 0.26	49.82[b]	44.42[b]
29.88	0.10	52.13 ± 0.09	46.19 ± 0.08	49.74[b]	44.08[b]
34.87	0.10	52.60 ± 0.12	46.19 ± 0.11	49.72[b]	43.66[b]
39.89	0.10	52.99 ± 0.07	46.01 ± 0.06	49.73[b]	43.18[b]
100.24	11.06	56.87 ± 2.65	38.78 ± 1.81	51.78[b]	35.30[b]
150.65	11.13	58.84 ± 0.16	28.31 ± 0.08	54.85[b]	26.39[b]
149.94	10.94	59.06 ± 0.76	28.41 ± 0.37	54.85[b]	26.39[b]
200.34	11.05	61.35 ± 1.01	18.89 ± 0.31	58.60[b]	18.05[b]
201.17	10.92	60.43 ± 0.99	18.42 ± 0.30	58.69[b]	17.89[b]
250.22	10.95	65.11 ± 0.74	11.17 ± 0.13	62.95[b]	10.80[b]
251.18	10.91	64.02 ± 1.67	10.83 ± 0.28	63.04[b]	10.67[b]
275.39	14.46	64.63 ± 1.00	8.02 ± 0.12	64.57	8.01
275.13	15.33	65.83 ± 1.53	8.28 ± 0.19	64.40	8.10
300.02	14.45	65.30 ± 0.79	5.08 ± 0.06	66.29	5.16
300.18	15.35	66.30 ± 0.67	5.28 ± 0.05	66.05	5.26
300.40	19.59	66.46 ± 2.40	5.84 ± 0.21	65.05	5.71
315.16	15.35	65.35 ± 1.93	3.58 ± 0.11	66.37	3.64
325.35	14.44	62.91 ± 7.77	2.47 ± 0.31	65.52	2.57
325.11	15.35	65.42 ± 0.77	2.69 ± 0.03	65.31	2.69
325.37	19.60	64.13 ± 0.74	3.17 ± 0.04	64.42	3.19
335.56	15.31	58.39 ± 8.75	1.54 ± 0.23	61.21	1.62
335.14	15.36	60.98 ± 3.04	1.69 ± 0.08	61.85	1.71
350.28	19.61	59.73 ± 6.53	1.10 ± 0.02	49.19	0.91

[a] Error limits correspond to standard deviations of the average V_ϕ. [b] Extrapolated values.

TABLE 4: Standard Partial Molar Volumes, V_2^o, and Generalized Krichevskii Parameter, A_{12}, for Aqueous Tartaric Acid

t/°C	p MPa	V_2^o/(cm^3·mol^{-1})[a] experimental	A_{12}[a] experimental	V_2^o/(cm^3·mol^{-1}) eq 9	A_{12} eq 9
200.14	11.11	93.85 ± 1.05	28.90 ± 0.32	76.45[b]	23.38[b]
200.30	10.99	93.20 ± 0.70	28.70 ± 0.32	76.45[b]	23.38[b]
249.73	14.56	95.21 ± 0.90	17.11 ± 0.15	89.81[b]	15.23[b]
275.14	10.99	96.10 ± 0.66	11.24 ± 0.08	100.23	11.73
275.50	14.84	97.64 ± 0.57	12.21 ± 0.07	97.64	12.21
300.07	10.99	111.26 ± 0.78	7.86 ± 0.06	118.56	8.38
300.14	15.34	113.19 ± 1.73	8.92 ± 0.14	113.01	8.91
300.41	15.06	112.86 ± 1.32	8.89 ± 0.10	113.04	8.91

[a] Error limits correspond to standard deviations of the average V_ϕ. [b] Extrapolated values.

temperature data resulted in a larger standard error and systematic, rather than random, deviations in the high-temperature region. The extrapolated value at the critical point, $\lim(T \rightarrow T_c, \rho \rightarrow \rho_c)A_{12} = -0.87 \pm 0.15$, corresponds to the negative Krichevskii parameter $A_{Kr}(\text{HGly,aq}) = (-84.01 \pm 14.03)$ MPa, according to eq 9. The stated uncertainties in A_{Kr}, here and below, are the standard errors in extrapolating eq 9 to the critical temperature and pressure.

A similar analysis for tartaric acid, based on the results at 275 and 300 °C, was inconclusive. The two-point extrapolation of eq 9 yields the value $A_{Kr}(\text{H}_2\text{Tar,aq}) = 71.98 \pm 8.02$ MPa that was obtained from $\lim(T \rightarrow T_c, \rho \rightarrow \rho_c)A_{12} = 0.75 \pm 0.08$. This result is suspect, because the data are far from the critical point and because of the possibility that undetected nonpolar decomposition products may have been present.

4. Discussion

To our knowledge, the results for glycolic acid provide the first experimental evidence of a negative Krichevskii parameter for any organic solute that is not a zwitterion. Plyasunov and Shock[8] have reported several algorithms for estimating A_{Kr} from thermodynamic data. In addition to the inorganic solutes boric acid, phosphoric acid, and silicic acid, only the alkanolcarboxylic acids and 2-amino-2-methyl-1-propanol (AMP) are identified as having $A_{Kr} < 0$. Recent measurements of V_2^o up to 300 °C in our laboratory[29] show a positive divergence for AMP, consistent with the "normal" behavior of neutral solutes and apparently disproving this prediction.

While not accurate above 250 °C, the group additivity model of Yezdimer et al.[13] suggests that the hydrophilic behavior of glycolic acid arises from the increasing negative contributions to V_2^o from the −OH and −COOH groups, which outweigh the increasing hydrophobicity of the −CH$_2$ group. After these measurements were complete, Plyasunov and Shock reported a group additivity model for predicting Krichevskii parameters, which is also consistent with this explanation.[30] Values of the group contributions to V_2^o and A_{12} predicted by Yezdimer et
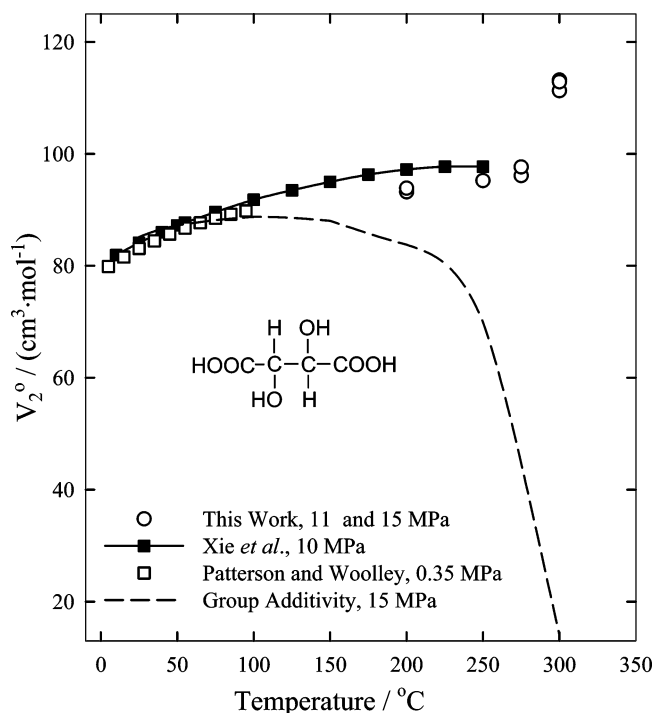
Figure 3. Standard partial molar volumes, V_2^o, of tartaric acid showing an apparent positive discontinuity at the critical end point. The dashed line shows the prediction made by extrapolating the functional group additivity model of Yezdimer et al.[13]
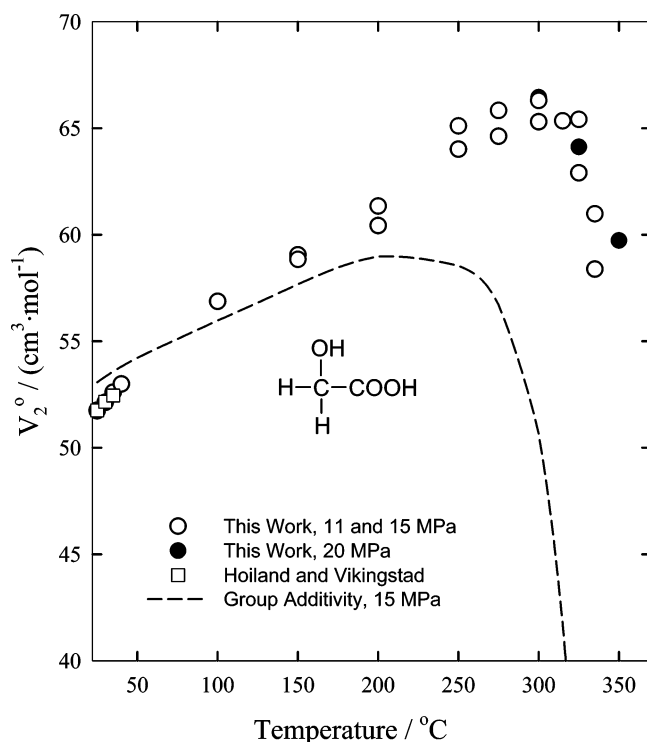

Figure 4. Standard partial molar volumes, V_2^o, of glycolic acid showing evidence for a negative discontinuity at the critical end point. The dashed line shows the prediction made by extrapolating the functional group additivity model of Yezdimer et al.[13]

al.[13] and the contributions to A_{Kr} postulated by Plyasunov and Shock[30] are tabulated in Table 5. The values predicted by Shock and Plyansunov's model, $A_{Kr}(HGly,aq) = -131$ MPa and $A_{Kr}(H_2Tar,aq) = -394$ MPa, differ substantially from our experimental results of $A_{Kr}(HGly,aq) = -84.01 \pm 14.03$ MPa and $A_{Kr}(H_2Tar,aq) = 71.98 \pm 8.02$ MPa, respectively.
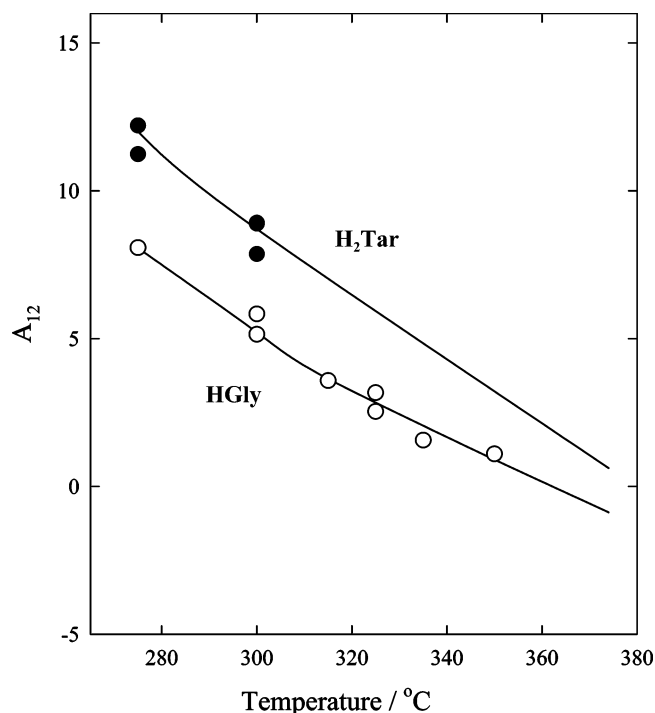

Figure 5. "Generalized" Krichevskii parameters, A_{12} for glycolic and tartaric acids, plotted as a function of temperature.

TABLE 5: Functional Group Contribution to V_2^o, A_{12}, and A_{Kr}

	Yezdimer et al.[13]				Plyasunov and Shock[30]	
	V_2^o/(cm^3·mol^{-1})		A_{12}		A_{12}	A_{Kr}/MPa
	250 °C	350 °C	250 °C	350 °C	374 °C	374 °C
$-CH_3$	45.5	125.8	7.8	2.3	0.3	29.3
$-CH_2$	24.8	42.4	4.3	0.8	0.04	3.6
$-CH$	4.2	-41.2	0.7	-0.8	-0.2	-14.9
$-OH$	4.0	-67.4	0.7	-1.2	-0.9	-90.1
$-COOH$	23.9	-60.1	4.1	-1.1	-1.5	-140.3

As shown in Figure 3, the near-critical divergence of tartaric acid is expected to be even more negative than glycolic acid because the $-CH$ group is thought to be less hydrophobic than the $-CH_2$ group. The group additivity models of both Yezdimer et al.[13] and Plyasunov and Shock[30] correspond to the following sequence for contributions to A_{Kr}

$$\text{(hydrophobic)} -CH_3 > -CH_2 > 0 > -CH > -OH >$$
$$-COOH \text{ (hydrophilic)}$$

It appears that the apparent positive divergence in V_2^o for tartaric acid may be an artifact of dissolved decomposition products, all of which have positive divergences according to the model.

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