

# Thermodynamics of aqueous acetic and propionic acids and their anions over a wide range of temperatures and pressures†

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The apparent molar volumes of aqueous acetic acid were determined *via* density measurements at 298 K <  $T$  < 573 K and 10 MPa <  $p$  < 38 MPa. The results were corrected for acid ionization and extrapolated to the standard state of infinite dilution. The new data have been combined with literature values of the standard molar volumes and standard molar heat capacities of acetic and propionic acids, and of acetate and propionate ions. Three correlation models were tested in the description of the standard thermodynamic properties at superambient conditions for the two acids and their anions. The most dependable model, inspired by the fluctuation solution theory, has been selected for generation of the recommended data. Adjustable parameters of the model were obtained by simultaneous correlation of the volumes and heat capacities together with experimental dissociation constants of the acid. It is shown that this model can be used for precise and consistent calculations of standard thermodynamic properties of the two acids and their conjugate ions over a wide range of temperatures and pressures.

## Introduction

Calculations of chemical or phase equilibria in hydrothermal systems or in boiler plant chemistry require reliable standard chemical potentials of aqueous solutes in a wide range of temperatures and pressures. On the other hand, determining thermodynamic functions from experiments for every solute of interest, at a variety of conditions, is largely uneconomical, especially in the case of organic compounds. This is why methods for predicting thermodynamic properties of aqueous solutes from a limited number of measured data are highly needed. Several different approaches allowing correlation and/or prediction of the standard thermodynamic properties at superambient conditions have been proposed.

The main goal of this study was to compare correlation and prediction qualities of several models in a case study, focusing on two typical volatile aliphatic carboxylic acids and their anions. Beside the fundamental aspects, information on this class of compounds at superambient conditions is of particular interest for organic geochemistry since volatile carboxylic acids are present at sizeable concentrations in oil-field brines, hot springs and different sedimentary basin fluids.<sup>1</sup> Tests were performed with acetic and propionic acids, because there is a considerable amount of experimental information available for these species, both on the derivative level (standard molar volumes and standard molar heat capacities) and on the integral level (equilibrium constants for acid dissociation reactions).

Another objective was to expand the data set of experimental results on carboxylic acids by new volumetric measurements of aqueous acetic acid at temperatures up to 573 K and pressures to 38 MPa. The first part of the paper is devoted to the presentation of these measurements and to the treatment of experimental results for obtaining data for the undissociated acetic acid at the standard state of infinite dilution. In the second part we test three correlation models for the simultaneous description of the standard molar volume and standard molar heat capacity data and for predictions of acid dissociation constants. The three approaches tested are: (a) the model of Helgeson, Kirkham and Flowers (HKF, refs. 2–4), using the dielectric properties of solvent, (b) an analogue of the HKF model (DEN, refs. 5–8) where the dielectric constant and its derivatives are replaced by the  $pVT$  properties of water and (c) the model inspired by the fluctuation solution theory proposed recently by Sedlbauer *et al.*<sup>9</sup> (SOCW). Based on the results of the tests, the SOCW model was used in the third part of the paper for precise representation of the standard thermodynamic properties of the aqueous species included in this study. It is also shown that standard chemical potentials of the studied species can be predicted with a reasonable accuracy using the group contribution scheme proposed recently.<sup>10</sup>

## Experimental and data treatment

### Instrument and method

The solutions of CH<sub>3</sub>COOH(aq) were prepared by weight from analytical grade acetic acid at three target concentrations of 0.2, 0.75 and 1.5 molal. The exact composition was

† Electronic Supplementary Information available. See <http://www.rsc.org/suppdata/cp/b0/b000593m/>

determined by titration using commercial solutions of NaOH(aq) for quantitative analysis with concentrations close to those for acetic acid. The molalities of acetic acid (aq) are expected to be accurate to 0.2%.

Experiments were performed using the vibrating tube flow densimeter described by Majer *et al.*,<sup>11</sup> which allows working at high temperatures with highly corrosive solutions. Since the instrument was described thoroughly in the above literature, only the most salient features will be mentioned here. The instrument was equipped with the 1.6 mm od Pt/Rh(20%) “U” tube vibrating in a magnetic field of two permanent magnets. The “drive” and “pick-up” bars were cemented to the upper flattened part of the tube, which allowed use of pole pieces for focusing the magnetic field to the bars. The drive and pick-up circuits were coupled electronically in a phase locked loop allowing sustained vibration of the tube at the resonance frequency.<sup>12</sup> The instrument operated in a flow mode with an HPLC Constametric II pump introducing water to the system at a flow rate near 0.5 cm<sup>3</sup> mol<sup>-1</sup> and a Circle Seal back pressure regulator maintaining pressure with stability to better than 0.02 MPa. Use of a sample loop connected to a six-port valve allowed continuous switching between water and solution. The density difference  $\Delta\rho$  between solution and water can be calculated from the change in the period of vibration  $\tau$  as follows:

$$\Delta\rho = \rho - \rho_w = K(\tau^2 - \tau_w^2), \quad (1)$$

where the subscript w relates to water. The calibration constant  $K$  was obtained from three or four repeated measurements with two fluids of well-known densities. We used several pairs of calibrating fluids; the results are shown in Table 1, which lists the average calibration constants, the expected error limits  $\sigma K$  and the pairs of calibration fluids used. Calibration was usually performed at the beginning of measurements at a given  $T$  and  $p$  and repeated at the end of experiments. The value of calibration constant generally does not evolve significantly with time and remains constant within its accuracy limits over the whole period of measurements at one temperature and pressure. The pressure dependence of the calibration constant was not finally considered as it was within the error margins of the determination of  $K$ . The random error in  $\Delta\rho$  was estimated from equation  $\sigma_{\text{ran}}\Delta\rho = 0.05 + 0.002\Delta\rho$  ( $[\Delta\rho]/\text{kg m}^{-3}$ ), obtained by fitting together the differences in multiple data points for all temperatures and pressures. The temperature was measured using a Burns industrial thermometer which was calibrated against the Rosemount primary standard. The stability in temperature readings was better than 0.02 K and the uncertainty in determination of temperatures was expected to be below 0.05 K. The pressure was read with a Heisse Bourdon gauge with a precision of 0.01 MPa and an uncertainty below 0.05 MPa, corresponding to accuracy warranted by the producer (0.1% of the full range of the gauge 40 MPa). It is not expected that the propagation of errors in concentration, temperature and pressure could significantly increase uncertainty of experimental  $\Delta\rho$  in the temperature range of our measurements.

**Table 1** Calibration constants of the densimeter at experimental temperatures

$T/\text{K}$	$K/\text{kg m}^{-3} \text{ms}^{-2}$	$\sigma K$ (%)	Calibration fluids <sup>a</sup>
298	623.3	0.20	D <sub>2</sub> O/H <sub>2</sub> O, NaCl(aq, 3M)/H <sub>2</sub> O
373	612.0	0.25	D <sub>2</sub> O/H <sub>2</sub> O, NaCl(aq, 3M)/H <sub>2</sub> O
448	598.5	0.30	He/H <sub>2</sub> O, D <sub>2</sub> O/H <sub>2</sub> O
523	589.5	0.30	He/H <sub>2</sub> O, D <sub>2</sub> O/H <sub>2</sub> O
573	578.9	0.30	N <sub>2</sub> /H <sub>2</sub> O

<sup>a</sup> Literature sources for calculating density of calibration fluids: H<sub>2</sub>O—ref. 13, D<sub>2</sub>O—ref. 14, NaCl(aq)—ref. 15, N<sub>2</sub>—ref. 16.

The first six columns of Table 2 list the experimental results obtained at five experimental temperatures and three pressures. The experimental values of the apparent molar volumes,  $V_{\Phi}^{\text{exp}}$ , were calculated from eqn. (2):

$$V_{\Phi}^{\text{exp}} = \frac{M_s}{\rho} + \frac{\Delta\rho}{m\rho\rho_w}, \quad (2)$$

where  $M_s$  is the molar mass of solute. The error in the apparent molar volume  $\sigma V_{\Phi}^{\text{exp}}$  was calculated approximately from the statistical estimate of uncertainty in the density difference  $\Delta\rho$  based on the random experimental error  $\sigma_{\text{ran}}\Delta\rho$  and the relative error of the calibration constant,  $\sigma K/K$ :

$$\sigma V_{\Phi}^{\text{exp}} = \frac{1}{m\rho\rho_w} \left[ \left( \frac{\sigma K \Delta\rho}{K} \right)^2 + (\sigma_{\text{ran}} \Delta\rho)^2 \right]^{0.5}. \quad (3)$$

### Corrections for dissociation

Acetic acid as a weak electrolyte undergoes partial ionization in aqueous solutions:



for which the balance is:

$$m(\text{H}^+) = m(\text{A}^-) = \alpha m, \quad (5)$$

$$m(\text{HA}) = (1 - \alpha)m, \quad (6)$$

where  $m$  is stoichiometric molality and  $\alpha$  is the degree of dissociation of electrolyte in the solution. The parameter  $\alpha$  can be calculated from the equation for equilibrium constant of reaction (4):

$$K_{\text{dis}} = \frac{\alpha^2 m \gamma_{\pm}^2}{(1 - \alpha) \gamma_{\text{u}}}. \quad (7)$$

At all experimental conditions we considered the activity coefficient of uncharged acid,  $\gamma_{\text{u}}$ , to be equal to unity. Because the degree of ionization is generally small, ionic concentrations are also low, and Pitzer's form<sup>17</sup> of the extended Debye–Hückel limiting law can be used for estimating the activity coefficient of the ions:<sup>18</sup>

$$\ln \gamma_{\pm} = -A_{\Phi} \left[ \frac{(\alpha m)^{1/2}}{1 + 1.2(\alpha m)^{1/2}} + (2/1.2) \ln(1 + 1.2(\alpha m)^{1/2}) \right], \quad (8)$$

where  $A_{\Phi}$  is the concentration slope of the osmotic coefficient in the Debye–Hückel limiting law, which we have calculated from the formulations of Archer and Wang<sup>19</sup> and Hill.<sup>13</sup> The nominal apparent molar volume  $V_{\Phi}^{\text{exp}}$  resulting from experiments is a sum of contributions of undissociated and ionized species:

$$V_{\Phi}^{\text{exp}} = (1 - \alpha)V_{\Phi}(\text{HA}) + \alpha[V_{\Phi}(\text{H}^+) + V_{\Phi}(\text{A}^-)], \quad (9)$$

where the contributions of ionized parts were estimated from:

$$V_{\Phi}(\text{H}^+) + V_{\Phi}(\text{A}^-) = V_s^{\circ}(\text{H}^+) + V_s^{\circ}(\text{A}^-) + (A_v/1.2) \ln[1 + 1.2(\alpha m)^{1/2}], \quad (10)$$

$A_v$  being the volumetric slope in the Debye–Hückel limiting law. In agreement with the approximations made for activity coefficients, the last term on the right-hand side of eqn. (10) expresses deviation from ideality and is consistent with eqn. (8).

For calculation of the corrected values of apparent molar volumes of acetic acid,  $V_{\Phi}(\text{HA})$  in eqn. (9), we had to evaluate the degree of dissociation  $\alpha$  from the dissociation constant, using eqns. (7) and (8), and volumetric contributions of ionic species from the standard molar volumes of aqueous ions,  $V_s^{\circ}(\text{H}^+)$  and  $V_s^{\circ}(\text{A}^-)$ , in eqn. (10). All required properties ( $K_{\text{dis}}$

**Table 2** Experimental values of the apparent molar volumes of acetic acid in aqueous solutions and corrections for dissociation;  $m^0 = 1 \text{ mol kg}^{-1}$ 

$T/\text{K}$	$p/\text{MPa}$	$m/m^0$	$\Delta\rho/\text{kg m}^{-3}$	$V_{\Phi}^{\text{exp}}/\text{cm}^3 \text{ mol}^{-1}$	$\sigma V_{\Phi}^{\text{exp}}/\text{cm}^3 \text{ mol}^{-1}$	$\alpha$	$\Delta V_{\Phi}^{\text{corr}}/\text{cm}^3 \text{ mol}^{-1}$	$V_{\Phi}/\text{cm}^3 \text{ mol}^{-1}$
298.13	20.04	1.5300	11.270	51.84	0.05	0.0039	0.04	51.88
298.16	20.04	1.5300	11.294	51.83	0.05	0.0039	0.04	51.87
298.14	20.03	0.7429	5.778	51.72	0.08	0.0054	0.06	51.78
298.14	20.02	0.7429	5.759	51.75	0.08	0.0054	0.06	51.81
298.14	20.02	0.1991	1.638	51.49	0.26	0.0100	0.12	51.61
298.13	20.02	0.1991	1.583	51.76	0.26	0.0100	0.12	51.88
298.15	20.02	0.1991	1.624	51.56	0.26	0.0100	0.12	51.68
298.15	37.09	1.5300	11.072	51.66	0.05	0.0040	0.05	51.71
298.15	37.09	1.5300	11.213	51.57	0.05	0.0040	0.05	51.62
298.15	37.09	0.7429	5.633	51.6	0.08	0.0057	0.07	51.67
298.15	37.09	0.7429	5.559	51.7	0.08	0.0057	0.07	51.77
298.15	37.09	0.1991	1.483	51.94	0.26	0.0110	0.13	52.07
298.15	37.09	0.1991	1.577	51.48	0.26	0.0110	0.13	51.6
298.15	37.09	0.1991	1.592	51.41	0.26	0.0110	0.12	51.53
373.15	10.05	1.5300	6.202	57.62	0.05	0.0031	0.06	57.68
373.15	10.05	1.5300	6.312	57.54	0.05	0.0031	0.06	57.6
373.15	10.05	0.7429	3.266	57.43	0.08	0.0043	0.08	57.51
373.15	10.06	0.7429	3.291	57.39	0.08	0.0043	0.08	57.47
373.15	10.06	0.1991	0.912	57.37	0.28	0.0082	0.15	57.52
373.15	10.06	0.1991	0.899	57.44	0.28	0.0082	0.15	57.59
373.15	34.97	1.5300	6.714	56.64	0.04	0.0033	0.06	56.7
373.15	34.97	1.5300	6.811	56.57	0.05	0.0033	0.06	56.63
373.15	34.97	0.7429	3.381	56.66	0.08	0.0046	0.08	56.74
373.15	34.97	0.7429	3.456	56.55	0.08	0.0046	0.08	56.63
373.15	35.07	0.1991	1.006	56.27	0.28	0.0087	0.16	56.43
373.15	35.04	0.1991	0.960	56.52	0.27	0.0087	0.16	56.68
448.25	10.00	1.5300	2.940	64.28	0.05	0.0019	0.06	64.34
448.25	10.00	1.5300	2.957	64.26	0.05	0.0019	0.06	64.32
448.25	10.00	0.7429	1.567	64.14	0.09	0.0027	0.09	64.23
448.25	10.00	0.7429	1.535	64.2	0.09	0.0027	0.09	64.29
448.25	10.00	0.1991	0.414	64.26	0.32	0.0051	0.17	64.43
448.25	10.00	0.1991	0.420	64.23	0.32	0.0051	0.17	64.4
448.28	35.13	1.5300	3.899	62.47	0.05	0.0021	0.06	62.53
448.28	35.13	1.5300	3.901	62.47	0.05	0.0021	0.06	62.53
448.27	35.16	0.7429	2.016	62.40	0.09	0.0029	0.09	62.49
448.27	35.16	0.7429	2.039	62.36	0.09	0.0029	0.09	62.45
448.27	35.09	0.1991	0.549	62.45	0.31	0.0056	0.17	62.62
448.27	35.09	0.1991	0.566	62.35	0.31	0.0056	0.17	62.52
523.17	10.02	1.5300	-0.233	74.78	0.05	0.0010	0.07	74.85
523.17	10.01	1.5300	-0.185	74.73	0.05	0.0010	0.07	74.8
523.17	10.00	0.7429	-0.039	74.61	0.10	0.0013	0.09	74.7
523.17	10.00	0.7429	0.008	74.51	0.10	0.0013	0.09	74.6
523.16	10.00	0.1991	0.048	74.15	0.39	0.0026	0.18	74.33
523.17	10.00	0.1991	-0.001	74.53	0.39	0.0026	0.18	74.71
523.16	35.10	1.5300	1.847	70.43	0.05	0.0011	0.06	70.49
523.16	35.12	1.5300	1.734	70.55	0.05	0.0011	0.06	70.61
523.16	35.12	0.7429	0.934	70.44	0.10	0.0015	0.09	70.53
523.16	35.12	0.7429	0.912	70.48	0.10	0.0015	0.09	70.57
523.16	35.13	0.1991	0.271	70.35	0.37	0.0029	0.17	70.52
523.16	35.13	0.1991	0.285	70.24	0.37	0.0029	0.17	70.41
573.28	10.00	1.5300	-4.107	89.74	0.06	0.0006	0.10	89.84
573.29	10.00	1.5300	-4.132	89.78	0.06	0.0006	0.10	89.88
573.28	10.00	0.7429	-2.252	90.19	0.12	0.0007	0.12	90.31
573.29	9.98	0.7429	-2.225	90.13	0.12	0.0007	0.12	90.25
573.29	9.98	0.1991	-0.938	93.32	0.47	0.0015	0.26	93.58
573.30	9.98	0.1991	-0.854	92.50	0.48	0.0015	0.26	92.76
573.33	9.99	0.1991	-0.779	91.75	0.48	0.0015	0.26	92.01
573.28	35.09	1.5300	0.239	78.96	0.06	0.0007	0.07	79.03
573.31	35.09	1.5300	0.242	78.96	0.06	0.0007	0.07	79.03
573.29	35.09	0.7429	-0.008	79.28	0.12	0.0009	0.09	79.37
573.27	35.09	0.7429	0.047	79.14	0.12	0.0009	0.09	79.23
573.28	35.09	0.1991	-0.203	81.05	0.43	0.0018	0.19	81.24
573.27	35.09	0.1991	-0.175	80.80	0.43	0.0018	0.19	80.99

and  $V_{\Phi}^{\circ}(\text{A}^-)$ ) at all experimental conditions were estimated from the SUPCRT92 package<sup>20</sup> using the revised HKF equation of state<sup>3</sup> with parameters for acetic acid and acetate ion given by Shock.<sup>1</sup> Setting  $V_{\Phi}^{\circ}(\text{H}^+) = 0$  at all conditions follows the standard hydrogen convention. Degrees of dissociation  $\alpha$ , calculated corrections  $\Delta V_{\Phi}^{\text{corr}} = V_{\Phi}(\text{HA}) - V_{\Phi}^{\text{exp}}$  and the corrected standard molar volumes  $V_{\Phi}^{\circ}(\text{HA})$  are listed in last three columns of Table 2. The absolute values of corrections were quite small and increase with temperature ( $0.26 \text{ cm}^3 \text{ mol}^{-1}$  being the largest correction).

To check the accuracy of our corrections we applied the same calculation method to the values of apparent molar volumes of propionic acid reported by Criss and Wood<sup>21</sup> at the pressure of 28 MPa and temperatures up to 523 K. Comparison of our corrections for ionization with those of Criss and Wood (which were obtained by a different method and using different data) showed very close agreement of the two sets of corrections at higher temperatures and only small differences of  $0.02 \text{ cm}^3 \text{ mol}^{-1}$  and  $0.03 \text{ cm}^3 \text{ mol}^{-1}$  at temperatures  $T = 298 \text{ K}$  and  $T = 373 \text{ K}$ , respectively.

## Extrapolations

Corrected values of the apparent molar volumes  $V_{\Phi}(\text{HA})$  were extrapolated to infinite dilution using weighted regression and the equation:

$$V_{\Phi}(\text{HA}) = V_{\text{s}}^{\circ}(\text{HA}) + b(1 - \alpha)m. \quad (11)$$

where  $V_{\text{s}}^{\circ}(\text{HA})$  is the standard molar volume of undissociated acid. The weights of  $V_{\Phi}(\text{HA})$  were set to  $1/\sigma^2 V_{\Phi}^{\text{exp}}$  (see eqn. (3)). A linear relationship was found to be sufficient for extrapolations in the limits of experimental uncertainties at all conditions except at  $T = 573$  K and both pressures, where eqn. (11) was not able to fit the data satisfactorily. It is possible that the more concentrated solutions of acetic acid at this highest temperature were subject to chemical decomposition to some extent, therefore in this case we have approximated the values of  $V_{\text{s}}^{\circ}(\text{HA})$  with experimental values of  $V_{\Phi}(\text{HA})$  at the lowest experimental molality. The values of standard molar volumes  $V_{\text{s}}^{\circ}(\text{HA})$  of acetic acid are listed in the first part of the supplementary information† to this paper (available in electronic format†) together with estimated uncertainties, which are based on the expected error of  $V_{\Phi}(\text{HA})$  at the lowest experimental molality. The uncertainties at  $T = 573$  K were increased by the difference between  $V_{\Phi}^{\text{exp}}$  values at the highest and the lowest molalities due to the unknown character of these differences.

## Results and discussion

### Data base of standard thermodynamic properties

Acetic acid is often present in appreciable amounts in hydrothermal systems, reservoir fluids and biological solutions.<sup>1</sup> Due to its importance this acid belongs among the best

studied aqueous organic solutes with data covering a wide range of temperatures and pressures. Experimental data for propionic acid are less abundant, but still several literature sources report data at superambient conditions. Thus, the two acids constitute a natural choice for testing the models for correlation/prediction of the standard thermodynamic properties of aqueous carboxylic acids. Beside results at derivative level resulting from calorimetric and densimetric measurements (standard molar heat capacities and standard molar volumes), a considerable amount of experimental information is available for dissociation constants of the acids. To be able to utilize this source of data we also included in this study the standard thermodynamic properties for acetate and propionate ions, which are needed for modelling dissociation constants of acids. Most data for the two anions could be retrieved from the experimental results for sodium salts of acetic and propionic acids, reported in literature, in combination with the standard thermodynamic properties of the sodium ion which are well known in a wide range of conditions. A summary of literature values of standard molar volumes and standard molar heat capacities of aqueous acetic and propionic acids and aqueous sodium acetate and sodium propionate is given in the supplementary information;† a concise overview of data sources can be found in Table 3. The data and their estimated uncertainties have been used as reported in original sources with a few exceptions as follows.

Ackermann and Schreiner<sup>28</sup> presented specific heat capacities of solutions of acetic and propionic acids to 373.15 K. We have converted their experimental data into apparent molar heat capacities, calculated the corrections for ionization and for chemical relaxation effect and extrapolated the data to infinite dilution (for details of calculating the corrections to apparent molar heat capacities see, *e.g.*, Inglese *et al.*<sup>27</sup>). Estimated uncertainties of the resulting standard molar heat

**Table 3** Literature sources of experimental results on standard molar volumes and standard molar heat capacities of acetic and propionic acids and sodium acetate and sodium propionate

Ref.	Property	$T/\text{K}$	$p/\text{MPa}$	No. exp. points
<i>Acetic acid</i>				
This work	$V_{\text{s}}^{\circ}$	298–573	10–37	10
Allred and Woolley <sup>22</sup>	$V_{\text{s}}^{\circ}, C_{\text{p},\text{s}}^{\circ}$	283–313	0.1	3, 3
King <sup>23</sup>	$V_{\text{s}}^{\circ}$	298	0.1	1
Konicek and Wadso <sup>24</sup>	$C_{\text{p},\text{s}}^{\circ}$	298	0.1	1
Makhatadze <i>et al.</i> <sup>25</sup>	$V_{\text{s}}^{\circ}$	278–348	0.1	4
Makhatadze and Privalov <sup>26</sup>	$C_{\text{p},\text{s}}^{\circ}$	278–348	0.1	4
Inglese <i>et al.</i> <sup>27</sup>	$C_{\text{p},\text{s}}^{\circ}$	303–523	28	4
Ackermann and Schreiner <sup>28</sup>	$C_{\text{p},\text{s}}^{\circ}$	273–373	0.1	11
Riedl and Jolicoeur <sup>29</sup>	$V_{\text{s}}^{\circ}, C_{\text{p},\text{s}}^{\circ}$	298	0.1	1, 1
Ballerat-Busserolles <i>et al.</i> <sup>30</sup>	$V_{\text{s}}^{\circ}, C_{\text{p},\text{s}}^{\circ}$	278–393	0.35	10, 24
<i>Propionic acid</i>				
Palma and Morel <sup>31</sup>	$V_{\text{s}}^{\circ}$	298	0.1	1
Konicek and Wadso <sup>24</sup>	$C_{\text{p},\text{s}}^{\circ}$	298	0.1	1
Makhatadze <i>et al.</i> <sup>25</sup>	$V_{\text{s}}^{\circ}$	278–348	0.1	4
Makhatadze and Privalov <sup>26</sup>	$C_{\text{p},\text{s}}^{\circ}$	278–348	0.1	4
Criss and Wood <sup>21</sup>	$V_{\text{s}}^{\circ}$	298–523	28	4
Inglese <i>et al.</i> <sup>27</sup>	$C_{\text{p},\text{s}}^{\circ}$	303–523	28	4
Ackermann and Schreiner <sup>28</sup>	$C_{\text{p},\text{s}}^{\circ}$	273–373	0.1	11
<i>Sodium acetate</i>				
Sakurai <sup>32</sup>	$V_{\text{s}}^{\circ}$	298	0.1	1
King <sup>23</sup>	$V_{\text{s}}^{\circ}$	298	0.1	1
Watson and Felsing <sup>33</sup>	$V_{\text{s}}^{\circ}$	298–313	0.1	4
Criss and Wood <sup>21</sup>	$V_{\text{s}}^{\circ}$	298–523	28	4
Inglese <i>et al.</i> <sup>27</sup>	$C_{\text{p},\text{s}}^{\circ}$	303–523	28	4
Riedl and Jolicoeur <sup>29</sup>	$V_{\text{s}}^{\circ}, C_{\text{p},\text{s}}^{\circ}$	298	0.1	1, 1
Ballerat-Busserolles <i>et al.</i> <sup>30</sup>	$V_{\text{s}}^{\circ}, C_{\text{p},\text{s}}^{\circ}$	278–393	0.35	10, 24
<i>Sodium propionate</i>				
Rosenholm and Hepler <sup>34</sup>	$V_{\text{s}}^{\circ}, C_{\text{p},\text{s}}^{\circ}$	298	0.1	1, 1
Watson and Felsing <sup>33</sup>	$V_{\text{s}}^{\circ}$	298–313	0.1	4
Sakurai <sup>32</sup>	$V_{\text{s}}^{\circ}$	278–318	0.1	3
Criss and Wood <sup>21</sup>	$V_{\text{s}}^{\circ}$	298–523	28	4
Inglese <i>et al.</i> <sup>27</sup>	$C_{\text{p},\text{s}}^{\circ}$	303–523	28	4

capacities refer to 95% confident limits of extrapolation of apparent molar heat capacities to infinite dilution.

Most included experimental results at  $T = 298.15$  K and  $p = 0.1$  MPa have been taken over from the review presented by Cabani *et al.*<sup>35</sup> We have checked the original papers for the data treatment and for uncertainty of measurements. If not available, estimated uncertainties of the volumetric results have been set as for the results of our measurements for acetic acid at the closest experimental conditions (which in this case was at  $T = 298.15$  K and  $p = 20$  MPa). The same method of estimating the experimental uncertainties was applied for the experimental results of Criss and Wood<sup>21</sup> and Allred and Woolley.<sup>22</sup>

From the set of standard molar heat capacities by Inglese *et al.*<sup>27</sup> the dubious value of  $C_{p,s}^\circ$  at  $T = 448$  K for propionic acid has been omitted.

Corrections for dissociation were not considered by Makhatadze *et al.*<sup>25</sup> and Makhatadze and Privalov.<sup>26</sup> Their values of  $V_s^\circ$  have therefore been increased by  $0.1 \text{ cm}^3$  at all conditions, based on comparison with corrections calculated in this paper and in the paper of Criss and Wood.<sup>21</sup> The values of  $C_{p,s}^\circ$  at temperatures 278, 298, 323 and 348 K were increased by 1.4, 1.3, 1.2 and  $1.1 \text{ J K}^{-1} \text{ mol}^{-1}$  for acetic acid, and by 1.1, 1.0, 0.9 and  $0.8 \text{ J K}^{-1} \text{ mol}^{-1}$  for propionic acid, respectively. These estimates were made with respect to calculations of Inglese *et al.*<sup>27</sup> at closest experimental conditions.

Experimental results on apparent molar volumes and apparent molar heat capacities of acetic acid and sodium acetate presented recently by Ballerat-Busserolles *et al.*<sup>30</sup> were corrected for ionization and hydrolysis reactions, respectively, and extrapolated to infinite dilution. Our corrections for ionization of acetic acid are very close to the estimates of Ballerat-Busserolles and collaborators; they differ, however, significantly in the case of sodium acetate hydrolysis. The degree of hydrolysis calculated with data and parameters from SUPCRT92 software package<sup>20</sup> is about an order of magnitude higher than estimated in this source. However, all calculated corrections are small and typically comparable or smaller than expected experimental error. For extrapolated results the uncertainties were set to 95% confident limits of extrapolation, but at least to  $0.3 \text{ cm}^3 \text{ mol}^{-1}$  for  $V_s^\circ$  and  $3 \text{ J K}^{-1} \text{ mol}^{-1}$  for  $C_{p,s}^\circ$ .

Table 4 presents the literature sources of experimental dissociation constants for the two investigated acids available as a function of temperature. Literature sources which provide only one experimental result at 298.15 K and 0.1 MPa were not considered. Our selection was guided by the review published by Shock;<sup>1</sup> the results were used as presented in the original papers without any changes. Due to this fact and because of their large total number we considered it unnecessary to present all the data again in this paper. Also it was not possible to determine unambiguously what are the errors limits of the experimental values. Therefore estimated uncertainties of  $\log K_{\text{dis}}$  in the calculations were set according to

**Table 4** Literature sources of experimental results on dissociation constants of acetic and propionic acids

Ref.	$T/\text{K}$	$p/\text{MPa}$	No. exp. points
Lown <i>et al.</i> <sup>36a</sup>	298–498	0.1–300	49
Mesmer <i>et al.</i> <sup>37a</sup>	298–523	$p_{\text{sat}}$	8
Harned and Ehlers <sup>38a</sup>	273–323	0.1	13
Harned and Ehlers <sup>39b</sup>	273–323	0.1	13
Ellis <sup>40ab</sup>	298–498	$p_{\text{sat}}$	12
Fisher and Barnes <sup>41a</sup>	298–623	$p_{\text{sat}}$	7
Oscarson <i>et al.</i> <sup>42a</sup>	548–593	$p_{\text{sat}}$	3
Noyes <i>et al.</i> <sup>43a</sup>	291–579	$p_{\text{sat}}$	5
Hamann and Strauss <sup>44ab</sup>	298	0.1–300	8

<sup>a</sup> Acetic acid. <sup>b</sup> Propionic acid.

simple rules supposing a decrease of accuracy with increasing temperature. An estimated error was set to 0.01 units of  $\log K_{\text{dis}}$  at  $T < 373$  K, 0.02 units of  $\log K_{\text{dis}}$  at  $373 < T < 473$  K, and 0.03 units of  $\log K_{\text{dis}}$  at  $T > 473$  K, with adjustment of an additional 0.02  $\log K_{\text{dis}}$  units for experimental results at pressures over 100 MPa.

### Correlation models

The standard chemical potential of a solute<sup>‡</sup>  $\mu_s^\circ$  at a temperature  $T$  and pressure  $p$  can be calculated by integration from a reference value of the standard chemical potential at  $T_r$  and  $p_r$  (usually 298.15 K and 0.1 MPa):

$$\mu_s^\circ[T, p] = \mu_s^\circ[T_r, p_r] + (T_r - T)S_s^\circ[T_r, p_r] + \int_{T_r}^T C_{p,s}^\circ dT - T \int_{T_r}^T C_{p,s}^\circ \frac{dT}{T} + \int_{p_r}^p V_s^\circ dp \quad (12)$$

where  $S_s^\circ[T_r, p_r]$  and  $\mu_s^\circ[T_r, p_r]$  is the entropy and potential of an aqueous solute in the reference state, respectively. Temperature integration is carried out at a reference pressure  $p_r$  and pressure integration at a temperature  $T$ . To evaluate the integrals, expressions for the standard molar volume  $V_s^\circ = V_s^\circ(T, p)$  and for the standard molar heat capacity  $C_{p,s}^\circ = C_{p,s}^\circ(T, p_r)$  are needed. Some models which appeared in the literature may only be used for calculating the pressure dependence of the standard chemical potentials (only a volumetric equation is reported) or may be applied only to a specific type of solutes, ionic or nonelectrolyte. Three thermodynamic models of different theoretical backgrounds have been chosen in this study for the purpose of tests. The employed models are quite general in character and should be able to describe a wide variety of aqueous solutes. In the HFK model<sup>2,3</sup> the changes of thermodynamic properties during the process of solvation are expressed from the Born equation and nonsolvation terms (empirical functions of temperature and pressure) are used to reconcile the model with reality:

$$V_s^\circ = a_1 + \frac{a_2}{\psi + p} + \left( a_3 + \frac{a_4}{\psi + p} \right) \left( \frac{1}{T - \Theta} \right) - \frac{\omega}{\epsilon_w^2} \left( \frac{\partial \epsilon_w}{\partial p} \right)_T + \left( \frac{1}{\epsilon_w} - 1 \right) \left( \frac{\partial \omega}{\partial T} \right)_p, \quad (13)$$

$$C_{p,s}^\circ = c_1 + \frac{c_2}{(T - \Theta)^2} + \omega T \left[ \frac{\partial}{\partial T} \frac{1}{\epsilon_w^2} \left( \frac{\partial \epsilon_w}{\partial T} \right)_p \right] + 2T \frac{1}{\epsilon_w^2} \left( \frac{\partial \epsilon_w}{\partial T} \right)_p \left( \frac{\partial \omega}{\partial T} \right)_p - T \left( \frac{1}{\epsilon_w} - 1 \right) \left( \frac{\partial^2 \omega}{\partial T^2} \right)_p \quad (14)$$

where the heat capacity equation is stated at the reference pressure  $p_r = 0.1$  MPa. The symbols  $a$  and  $c$  stand for six adjustable parameters in the nonsolvation part of equation,  $\omega$  is related to the ionic radius (for nonelectrolytes this is another adjustable parameter independent of  $T$  and  $p$ ),  $\epsilon_w$  is the dielectric constant (relative permittivity) of water,  $\Theta = 228$  K and  $\Psi = 260$  MPa. The model was originally proposed for aqueous electrolytes and it has been used by analogy also for nonelectrolytes, although theoretical foundation for this extension is missing. This approach was reported to have difficulties in the description of derivative properties of aqueous nonelectrolyte solutes and when extrapolating towards the critical point of water.<sup>9,45</sup>

An effort has been made recently to keep the concept of the HKF model, but to modify the equations to make them compatible with the theories of near-critical phenomena.<sup>5,6</sup> These theories suggest that the thermodynamic quantities of a solute

<sup>‡</sup> The standard state adopted for aqueous species is unit activity in a hypothetical one molal solution referenced to infinite dilution.

scale with the solvent density and its derivatives, when the critical point of water is approached, rather than with the solvent dielectric properties. For a “density” model<sup>7,8</sup> (DEN) tested recently the analogues to eqns. (13) and (14) are:

$$V_s^\circ = a + a_T T - (\omega + \omega_T T) \left( \frac{\partial \rho_w}{\partial p} \right)_T, \quad (15)$$

$$C_{p,s}^\circ = c + \frac{c_T}{T - \Theta} + (\omega + \omega_T) T \left( \frac{\partial^2 \rho_w}{\partial T^2} \right)_p + 2\omega_T T \left( \frac{\partial \rho_w}{\partial T} \right)_p \quad (16)$$

where both equations are valid at any  $T$  and  $p$  and  $a$ ,  $c$  and  $\omega$  are six adjustable parameters. Since the experimental data considered in this study did not reach above 573 K it was sufficient to use a five-parameter form where  $\omega_T = 0$ .

The approach proposed by Sedlbauer *et al.*<sup>9</sup> (SOCW) is based on the results of the fluctuation solution theory<sup>46</sup> (FST); the equation for the standard molar volume of a neutral molecule or an ion can be written as:

$$V_s^\circ = (1 - z)\kappa_w RT + d(V_w - \kappa_w RT) + \kappa_w RT \rho_w \{a + c \exp(\theta/T) + b[\exp(\rho_w) - 1] + \delta[\exp(\lambda \rho_w) - 1]\} \quad (17)$$

where  $V_w$ ,  $\rho_w$  and  $\kappa_w$  are molar volume, specific density and molar compressibility of water,  $\vartheta = 0.005 \text{ m}^3 \text{ kg}^{-1}$ ,  $\lambda = -0.01 \text{ m}^3 \text{ kg}^{-1}$  and  $\theta = 1500 \text{ K}$  are general constants,  $a$ ,  $b$ ,  $c$ , and  $d$  are four adjustable parameters,  $\delta$  is a parameter which is determined depending on the charge of the solute. The parameter  $z$  is zero for neutral molecules and  $z$  is equal to the charge of an ion (*i.e.*  $z \geq 1$  for cations and  $z \leq 1$  for anions) for electrolyte species. The term with the  $(1 - z)$  multiplication factor assures that the hydrogen convention for ions, which requires  $V_s^\circ(\text{H}^+) = 0$ , is fulfilled. Since eqn. (17) reduces to the virial equation limited to the second virial coefficient when the ideal gas limit is approached it allows, in principle, one to obtain by integration the heat capacity of hydration  $\Delta_{\text{hyd}} C_{p,s}^\circ$  expressing the difference between  $C_{p,s}^\circ$  and the heat capacity of a solute in an ideal gas state,  $C_{p,s}^{\text{ig}}$ . The heat capacity equation can be then written as

$$C_{p,s}^\circ = \Delta_{\text{hyd}} C_{p,s}^\circ + C_{p,s}^{\text{ig}} = -T \int_0^p \left( \frac{\partial^2 V_s^\circ}{\partial T^2} \right)_p + C_{p,s}^{\text{corr}} + C_{p,s}^{\text{ig}} \quad (18)$$

The correction term  $C_{p,s}^{\text{corr}}$  with one or two adjustable parameters has to be used at temperatures below the critical point of water since eqn. (17) is not able to provide a quantitative description of hydration properties when integrating across the vapour–liquid equilibrium curve for pure water. The importance of this correction decreases with increasing temperature and it is equal to zero at the critical temperature of water. A detailed account of equations for  $\Delta_{\text{hyd}} C_{p,s}^\circ$  and other thermodynamic properties from the SOCW model is given in the Appendix.

### Tests of models and recommendations

In the first test the three models were used for simultaneous correlation of the standard molar volume and standard molar heat capacity data from the supplementary information<sup>†</sup> for each solute (acid or ion). The expected uncertainty  $\sigma x$  ( $x = V_s^\circ$  or  $C_{p,s}^\circ$ ) served for estimating the reciprocal of the variance  $1/\sigma^2 x = 1/(\sigma x)^2$  used as weighting factor in the correlation. The experimental results for  $V_s^\circ$  and  $C_{p,s}^\circ$  of sodium salts were used to obtain the properties of anions by subtracting  $V_s^\circ$  or  $C_{p,s}^\circ$  of sodium ion at given conditions, calculated from the SOCW model with the parameters given in ref. 9. Results of

the correlation are reported in Table 5 in terms of the average absolute deviations

$$s_a = \frac{1}{n} \sum_i (|\Delta X|/\sigma X)_i, \quad (19)$$

$X$  being the difference between calculated and experimental data points ( $V_s^\circ$  and/or  $C_{p,s}^\circ$ ). The average absolute deviation has a meaning close to the standard weighted deviation, but it is somewhat more appealing, since its value equal to unity or lower indicates directly description of experimental data in the limits of estimated uncertainties (without considering the number of adjustable parameters). It is apparent from Table 5 that the HKF equation was not quite satisfactory for precise description of nonelectrolyte species, while DEN and SOCW models give better results for this type of solute. The quality of correlation of ionic species is comparable for all three models, the experimental values being fitted within the limits of expected data errors. Most correlations of the ions showed signs of overfitting, which was particularly the case for the HKF model.

In the second test we compared experimental values of  $\log K_{\text{dis}}$  from the literature with the dissociation constants of acids calculated at elevated temperatures from different models using parameters obtained in the previous step (simultaneous correlation of  $V_s^\circ$  and  $C_{p,s}^\circ$  data). For this purpose the equations for standard molar volumes and standard molar heat capacities were integrated (eqn. (12)) to obtain the chemical potentials of all species and dissociation constants were calculated using the equation:

$$\log K_{\text{dis}} = \frac{-(\mu_s^\circ(\text{anion}) - \mu_s^\circ(\text{acid}))}{2.303RT} \quad (20)$$

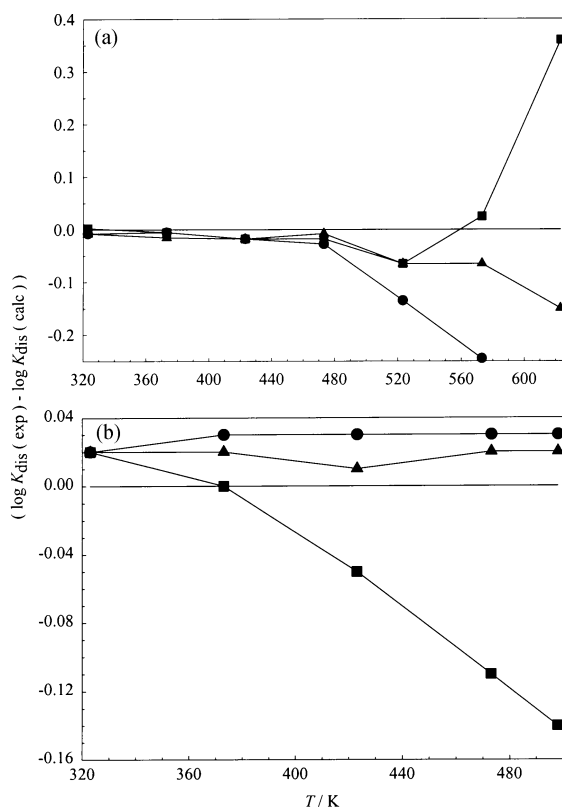
The value of  $\mu_s^\circ[T_r, p_r]$  was assimilated to the standard molar Gibbs free energy of formation of aqueous species  $G_{f,s}^\circ[T_r, p_r]$  at 298.15 K and 0.1 MPa. The results are summarized in Table 6 and the deviation plots (Figs. 1(a) and 1(b)) indicate the ability of all three models to predict dissociation constants with reasonable accuracy. This was the case also for the HKF model, despite the fact that the description of the derivative properties of undissociated acids was not satisfactory and the  $V_s^\circ$  and  $C_{p,s}^\circ$  data were in most cases overfitted. The highest accuracy of predictions was achieved by the SOCW model, which also corresponds with the good description of derivative data as shown in Table 5. Since the correct model should exhibit both qualities, correlation flexibility for all included properties and predictive capability for chemical potentials, the SOCW model was chosen for the final representation of standard thermodynamic properties of aqueous species covered in this study.

Table 6 also includes calculations of  $\log K_{\text{dis}}$  from SUPCRT92 software package<sup>20</sup> and from a group contribu-

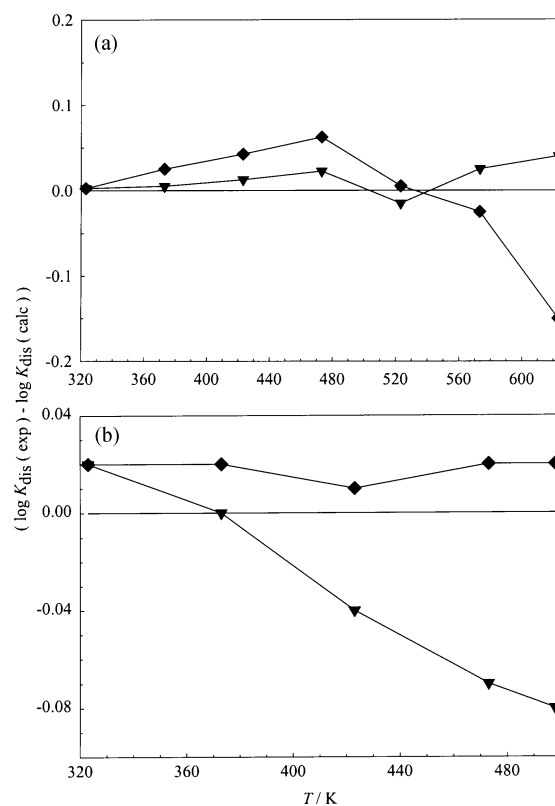
**Table 5** Test of models in the correlation of  $V_s^\circ$  and  $C_{p,s}^\circ$  for acetic and propionic acids and their anions in terms of the average absolute deviations  $s_a$  (numbers of ill-conditioned parameters are in parenthesis)

Model	Acetic acid	Propionic acid	Acetate ion	Propionate ion
HKF	1.34(0) <sup>a</sup>	2.47(1)	0.86(3)	0.79(3)
	2.02 <sup>b</sup> 0.93 <sup>c</sup>	3.10 2.18	0.53 1.15	0.56 1.56
SOCW	1.17(0)	0.73(0)	0.87(2)	0.83(2)
	1.08 1.22	0.36 0.91	0.76 0.96	0.63 1.58
DEN	0.77(0)	0.80(0)	1.21(0)	0.94(1)
	1.22 0.49	0.83 0.79	0.83 1.53	0.70 1.75

<sup>a</sup> Parameter is considered as ill-conditioned if its absolute value is lower than its 95% confidence interval. <sup>b</sup> Average absolute deviation for the set of  $V_s^\circ$  only,  $s_{aV} = (1/n_V) \sum_i (|\Delta V_s^\circ|/\sigma V_s^\circ)_i$ . <sup>c</sup> Average absolute deviation for the set of  $C_{p,s}^\circ$  only,  $s_{aC} = (1/n_C) \sum_i (|\Delta C_{p,s}^\circ|/\sigma C_{p,s}^\circ)_i$ .



**Fig. 1** Comparison of the HKF (■), DEN (●) and SOCW (▲) models in calculation of the dissociation constants for (a) acetic and (b) propionic acid; plots of the differences between calculated and experimental values along the saturation curve of water.



**Fig. 2** Comparison of the SUPCRT92 (▼) and GROUP (◆) prediction schemes in the calculation of the dissociation constants for (a) acetic and (b) propionic acid; plots of the differences between calculated and experimental values along the saturation curve of water.

tion scheme (GROUP), proposed recently on the basis of the SOCW model for aqueous organic solutes by Yezdimer *et al.*,<sup>10</sup> a graphic comparison of the two prediction schemes is in deviation plots (Figs. 2(a) and 2(b)). The parameters of the HKF model for acids used in SUPCRT92 were obtained by Shock<sup>1</sup> from a different type of regression of a similar set of volumetric and heat capacity data as used in this study with one parameter,  $\omega$  adjusted using the data on the dissociation constant. This explains better the relative success of the pre-

dictions from the SUPCRT92 package compared with our calculations with the HKF model adjusted with the use of the  $V_s^\circ$  and  $C_{p,s}^\circ$  data only. The GROUP method has been recently developed as a parameterization of the SOCW equations for selected functional groups of organic compounds (hydrocarbons, alcohols, amines, amides, carboxylic acids, carboxylates, ammonium ions, amino acids). Calculations performed with the GROUP scheme are truly predictive since they are based on regressions of a large database of mainly

**Table 6** Comparison of dissociation constants for acids ( $\log K_{\text{dis}}$ ) calculated from different models with literature values along the saturation curves of water

	T/K							
	323	373	423	473	498	523	573	623
<i>Acetic acid</i>								
SOCW	-4.78	-4.93	-5.18	-5.51		-5.92	-6.46	-7.31
GROUP	-4.79	-4.97	-5.24	-5.58		-5.99	-6.50	-7.31
HKF	-4.79	-4.94	-5.18	-5.50		-5.92	-6.55	-7.82
SUPCRT92	-4.79	-4.95	-5.21	-5.54		-5.97	-6.55	-7.50
DEN	-4.78	-4.94	-5.18	-5.49		-5.85	-6.28	-6.90
EXP	-4.79 <sup>a</sup>	-4.94 <sup>a</sup>	-5.18 <sup>a</sup>	-5.48 <sup>a</sup>		-5.99 <sup>b</sup>	-6.53 <sup>b</sup>	-7.46 <sup>b</sup>
	-4.79 <sup>c</sup>	-4.95 <sup>b</sup>	-5.21 <sup>b</sup>	-5.54 <sup>b</sup>		-5.98 <sup>c</sup>	-6.52 <sup>d</sup>	
	-4.79 <sup>e</sup>	-4.94 <sup>c</sup>	-5.18 <sup>c</sup>	-5.52 <sup>c</sup>				
	-4.78 <sup>f</sup>	-4.95 <sup>f</sup>	-5.22 <sup>f</sup>	-5.53 <sup>f</sup>				
<i>Propionic acid</i>								
SOCW	-4.92	-5.08	-5.33	-5.66	-5.85		-6.58	-7.40
GROUP <sup>g</sup>	-4.92	-5.08	-5.33	-5.66	-5.85		-6.56	-7.37
HKF	-4.92	-5.06	-5.27	-5.53	-5.69		-6.40	-7.48
SUPCRT92 <sup>h</sup>	-4.92	-5.06	-5.28	-5.57	-5.75		-6.46	-7.35
DEN	-4.92	-5.09	-5.35	-5.67	-5.86		-6.52	-7.17
EXP	-4.91 <sup>i</sup>	-5.06 <sup>f</sup>	-5.32 <sup>f</sup>	-5.64 <sup>f</sup>	-5.83 <sup>f</sup>			
	-4.90 <sup>f</sup>							

<sup>a</sup> Ref. 36. <sup>b</sup> Ref. 41. <sup>c</sup> Ref. 37. <sup>d</sup> Ref. 42. <sup>e</sup> Ref. 38. <sup>f</sup> Ref. 40. <sup>g</sup> GROUP—ref. 10. <sup>h</sup> SUPCRT92—ref. 20. <sup>i</sup> Ref. 39.

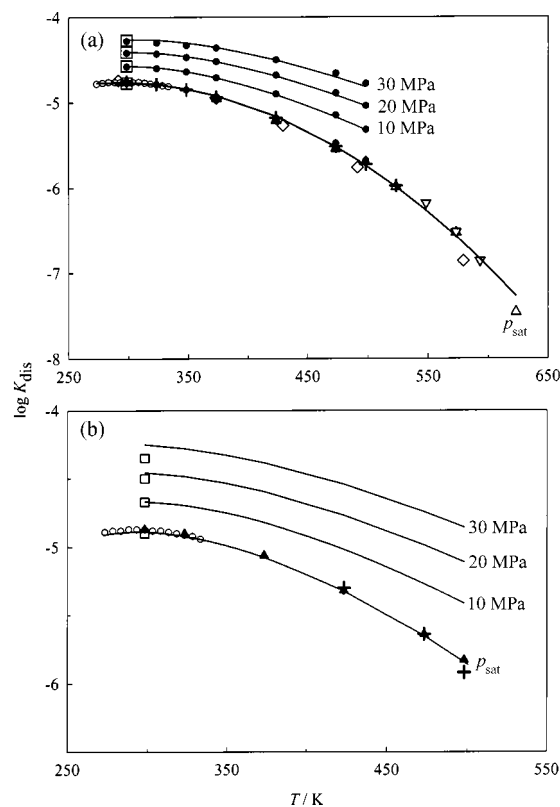
volumetric and heat capacity results for a variety of organic compounds without use of the  $K_{\text{dis}}$  data. The accuracy of dissociation constants predicted by the group contribution scheme is good, which suggests the probability of reasonable redictions of the chemical potential for other polar organic compounds by this method. With respect to consistent comparison of the results, the values of  $S_{\text{s}}^{\circ}[T_{\text{r}}, p_{\text{r}}]$  and  $G_{\text{f},\text{s}}^{\circ}[T_{\text{r}}, p_{\text{r}}]$  in eqn. (12) were used as recommended by Shock<sup>1</sup> in calculations of chemical potentials of our solutes for all models reported in Table 6.

In the final step the SOCW model was used for simultaneous weighted regression of all experimental results,  $V_{\text{s}}^{\circ}$ ,  $C_{\text{p},\text{s}}^{\circ}$  and  $\log K_{\text{dis}}$  presented in Tables 3 and 4, respectively, to obtain a consistent and stable set of parameters of the model for the acids and their corresponding anions. The average absolute deviation  $s_{\text{a}}$  was 0.65 for regression of the acetic acid and acetate ion data set, and 0.99 for the propionic acid and propionate ion data set. Resulting parameters are reported in Table 7. Parameter  $a$  for the undissociated acids was set to zero, because its values were ill-conditioned in the preliminary regression.

All thermodynamic information needed for convenient calculations with the SOCW equations is summarized in Table 8; the Hill equation of state for water<sup>13</sup> was used in all calculations.

Table 9 provides a set of calculated standard thermodynamic properties of acetic and propionic acids and acetate and propionate ions as a function of temperature at saturation pressure and at the 100 MPa isobar. Enthalpies  $H_{\text{s}}^{\circ}[T, p]$  were obtained from a relationship analogous to eqn. (12); similarly, as for the chemical potential,  $H_{\text{s}}^{\circ}[T_{\text{r}}, p_{\text{r}}]$  was assimilated to the standard molar enthalpy of formation of aqueous species  $H_{\text{f},\text{s}}^{\circ}[T_{\text{r}}, p_{\text{r}}]$  at 298.15 K and 0.1 MPa. The table serves as first-hand information on these properties and may also be used as a test when implementing the equations into a calculation procedure. The values of  $\log K_{\text{dis}}$  can be easily calculated from eqn. (20) using the tabulated chemical potentials.

§ Compilations of experimental results on  $V_{\text{s}}^{\circ}$  and  $C_{\text{p},\text{s}}^{\circ}$  (about 4000 data points) which served as a regression matrix<sup>10</sup> are available at the Internet address <http://www.kfy.vslib.cz/aqueous/download.htm>



**Fig. 3** Experimental and calculated (SOCW model)  $\log K_{\text{dis}}$  for (a) acetic and (b) propionic acid. ( $\square$ ) Hamann and Strauss,<sup>44</sup> ( $\bullet$ ) Lown *et al.*,<sup>36</sup> ( $\blacktriangle$ ) Ellis,<sup>40</sup> ( $\triangle$ ) Fisher and Barnes<sup>41</sup>, (+) Mesmer *et al.*,<sup>37</sup> ( $\nabla$ ) Oscarson *et al.*,<sup>42</sup> ( $\circ$ ) Harned and Ehlers,<sup>38,39</sup> and ( $\diamond$ ) Noyes *et al.*<sup>43</sup>

These values are plotted in Fig. 3(a) and 3(b) together with the data points from major literature sources.

When calculating the corrections for ionization of acids the standard thermodynamic properties of undissociated acid and conjugate ion are needed. In principle, the process of calculating the corrections to apparent molar volumes of acetic acid, which was described above, and the subsequent corre-

**Table 7** Parameters of the SOCW model for acetic and propionic acids and acetate, propionate and sodium ions

	$a/\text{m}^3 \text{kg}^{-1}$	$b \times 10^4/\text{m}^3 \text{kg}^{-1}$	$c \times 10^5/\text{m}^3 \text{kg}^{-1}$	$d$	$e \times 10^{-2}/\text{J K}^{-1} \text{mol}^{-1}$	$g/\text{J K}^{-2} \text{mol}^{-1}$
Acetic acid	0	1.6526	-2.5053	1.6786	2.3543	-0.623 82
Propionic acid	0	2.4387	-3.7102	1.9689	3.4383	-0.933 43
Acetate	-0.659 74	1.2786	-0.017 832	2.0193	0.195 40	0.164 93
Propionate	-0.657 31	1.0390	-1.3302	3.0517	1.2510	-0.211 74
$\text{Na}^+$ <sup>a</sup>	-0.007 113 6	2.3126	-3.0289	-1.5203	2.9492	-1.145 65

<sup>a</sup> The parameters are taken over from ref. 9.

**Table 8** Supplementary thermodynamic data for calculations with the SOCW model

	$G_{\text{f},\text{s}}^{\circ}[T_{\text{r}}, p_{\text{r}}]/\text{kJ mol}^{-1}$	$H_{\text{f},\text{s}}^{\circ}[T_{\text{r}}, p_{\text{r}}]/\text{kJ mol}^{-1}$	$S_{\text{s}}^{\circ}[T_{\text{r}}, p_{\text{r}}]/\text{J K}^{-1} \text{mol}^{-1}$
Standard molar thermodynamic functions of aqueous species at $T_{\text{r}} = 298.15$ and $p_{\text{r}} = 0.101$ MPa (ref. 1)			
Acetic acid	-396.5	-485.8	178.7
Propionic acid	-391.0	-512.4	206.7
Acetate	-369.3	-486.0	86.2
Propionate	-363.1	-513.1	110.9
$\text{Na}^+$ (ref. 4)	-261.9	-240.1	59.0

Ideal gas heat capacities ( $\text{J K}^{-1} \text{mol}^{-1}$ ) (polynomial fits of the data recommended in ref. 47)

Acetic acid and acetate ion:  $C_{\text{p},\text{s}}^{\text{ig}} = 14.619 + 0.16392 T + 3.7274 \times 10^{-5} T^2 - 1.2163 \times 10^{-7} T^3 + 4.5138 \times 10^{-11} T^4$ .

Propionic acid and propionate ion:  $C_{\text{p},\text{s}}^{\text{ig}} = 4.0608 + 0.38122 T - 32.963 \times 10^{-5} T^2 + 1.666 \times 10^{-7} T^3 - 3.743 \times 10^{-11} T^4$ .



**Table 9** Calculated standard thermodynamic properties of acetic acid, propionic acid, and their ions at saturation pressure and at the 100 MPa isobar as a function of temperature from the SOCW model, using parameters from Tables 6 and 7

$T/K$	$p/\text{MPa}$	$V_s^\circ/\text{cm}^3 \text{ mol}^{-1}$	$C_{p,s}^\circ/\text{J K}^{-1} \text{ mol}^{-1}$	$H_s^\circ/\text{kJ mol}^{-1}$	$\mu_s^\circ/\text{kJ mol}^{-1}$
<i>Acetic acid</i>					
298.15	0.1	52.10	171.3	-485.8	-396.5
373.15	$p_{\text{sat}}$	57.26	195.6	-472.4	-411.4
473.15	$p_{\text{sat}}$	67.69	231.9	-450.7	-435.8
573.15	$p_{\text{sat}}$	89.62	255.9	-427.1	-464.5
298.15	100	52.13	170.1	-482.0	-391.3
373.15	100	55.75	186.6	-469.2	-405.8
473.15	100	62.05	213.3	-448.7	-429.4
573.15	100	69.29	185.1	-428.4	-457.5
<i>Propionic acid</i>					
298.15	0.1	67.72	256.2	-512.4	-391.0
373.15	$p_{\text{sat}}$	74.99	275.6	-493.1	-408.7
473.15	$p_{\text{sat}}$	89.41	318.2	-463.0	-438.6
573.15	$p_{\text{sat}}$	119.88	340.5	-431.2	-474.5
298.15	100	68.12	256.5	-507.7	-384.2
373.15	100	73.15	263.9	-489.2	-401.3
473.15	100	81.72	293.6	-460.6	-430.3
573.15	100	91.27	243.6	-433.1	-465.4
<i>Acetate ion</i>					
298.15	0.1	40.65	26.2	-486.0	-369.3
373.15	$p_{\text{sat}}$	38.61	38.0	-482.9	-376.1
473.15	$p_{\text{sat}}$	25.98	-99.4	-484.0	-385.8
573.15	$p_{\text{sat}}$	-66.99	-1325.8	-524.0	-392.8
298.15	100	42.39	23.5	-481.3	-365.2
373.15	100	40.98	58.7	-477.6	-372.1
473.15	100	35.51	10.6	-473.6	-382.6
573.15	100	17.38	-107.8	-477.7	-393.3
<i>Propionate ion</i>					
298.15	0.1	54.71	114.1	-513.1	-363.1
373.15	$p_{\text{sat}}$	54.73	119.8	-504.1	-372.4
473.15	$p_{\text{sat}}$	44.89	18.2	-495.2	-387.4
573.15	$p_{\text{sat}}$	-41.10	-1155.4	-521.4	-402.1
298.15	100	55.83	139.8	-508.3	-357.6
373.15	100	56.28	140.7	-498.0	-366.9
473.15	100	52.93	118.2	-484.5	-382.5
573.15	100	38.30	15.1	-477.0	-400.6

The value of the standard molar enthalpies and chemical potentials at  $T_r = 298.15 \text{ K}$  and  $p_r = 0.101 \text{ MPa}$  were set equal to  $H_{r,s}^\circ[T_r, p_r]$  and  $G_{r,s}^\circ[T_r, p_r]$ , respectively.

lation of the standard thermodynamic properties, should be iterative. Because the corrections for acetic acid are typically smaller or comparable with the values of estimated experimental uncertainties and because the method of calculating the corrections does not seem to be of crucial importance in case of carboxylic acids, we did not attempt to recalculate the corrections using the new correlations.

## Conclusions

The apparent molar volumes of acetic acid reported in this paper increase with increasing temperatures, confirming hydrophobic character of this nonelectrolyte. The new experimental results are in good agreement with literature data and rank acetic acid among the most thoroughly studied aqueous organic species. The experimental results of acetic and propionic acids and their conjugate anions have been used for testing several models for description of standard thermodynamic properties of aqueous solutes. It was found that the widely used HKF model provides reasonable predictions of dissociation constants for these acids, but fails in accurate description of nonelectrolyte derivative properties. The simple "density" model showed also satisfactory predictive capabilities and the correlation of derivative properties of nonelectrolyte solutes was much better than in the case of the HKF model. The best results were achieved in correlations and predictions when using the SOCW model, which was also used for precise representation of the standard thermodynamic

properties of the acids and their anions. Also, the reliability of predictions from the group contribution scheme for organic compounds has been proved.

The tests and results presented in this paper are a part of a continuing effort to explore predictive methods for thermodynamic properties of aqueous species in a wide range of temperatures and pressures, which are of interest for geochemical and chemical engineering purposes.

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## Appendix

The process of hydration as it is understood in this paper consists of a transfer of a solute molecule from an ideal gas standard state at pressure  $p_r = 0.1 \text{ MPa}$  and temperature  $T$  to the hypothetical ideal aqueous solution of unit molality at temperature  $T$  and pressure  $p$  referenced to infinite dilution. The SOCW model<sup>9</sup> is based on the equation for the standard

molar volume:

$$V_s^\circ = (1-z)\kappa_w RT + d(V_w - \kappa_w RT) + \kappa_w RT \rho_w \{a + c \exp(\theta/T) + b[\exp(\mathcal{G}\rho_w) - 1] + \delta[\exp(\lambda\rho_w) - 1]\}. \quad (\text{A1})$$

The pressure integration of eqn. (A1) from an ideal gas standard state to the aqueous standard state provides an equation for the Gibbs free energy of hydration:

$$\Delta_{\text{hyd}} G_s^\circ = (1-z)RT \ln \left[ \frac{\rho_w RT}{p_r} \right] + d \left( G_w - G_w^{\text{ig}} - RT \ln \left[ \frac{\rho_w RT}{M_w p_r} \right] \right) + RT \{ [a + c \exp(\theta/T) - b - \delta] \rho_w + (b/\mathcal{G}) [\exp(\mathcal{G}\rho_w) - 1] + (\delta/\lambda) [\exp(\lambda\rho_w) - 1] \} + G_s^{\text{corr}} \quad (\text{A2})$$

where the last term  $G_s^{\text{corr}}$  is an empirical correction for integration through a phase boundary ( $T < T_c$ ) when passing between ideal gas and liquid states. The other standard thermodynamic properties are calculated by simple differentiation of eqn. (A2):

$$\begin{aligned} \Delta_{\text{hyd}} S_s^\circ &= -(\partial \Delta_{\text{hyd}} G_s^\circ / \partial T)_p \\ &= -(1-z)R \left( \ln \left[ \frac{\rho_w RT}{p_r} \right] + 1 - T\alpha_w \right) \\ &+ d \left\{ S_w - S_w^{\text{ig}} + R \left( \ln \left[ \frac{\rho_w RT}{M_w p_r} \right] + 1 - T\alpha_w \right) \right\} \\ &+ R\theta c \exp(\theta/T) \frac{\rho_w}{T} \\ &- R \{ [a + c \exp(\theta/T) - b - \delta] \rho_w \\ &+ \frac{b}{\mathcal{G}} [\exp(\mathcal{G}\rho_w) - 1] + \frac{\delta}{\lambda} [\exp(\lambda\rho_w) - 1] \} \\ &- RT \left( \frac{\partial \rho_w}{\partial T} \right)_p \{ a + b[\exp(\mathcal{G}\rho_w) - 1] \\ &+ c \exp(\theta/T) + \delta[\exp(\lambda\rho_w) - 1] \} + S_s^{\text{corr}}, \end{aligned} \quad (\text{A3})$$

$$\begin{aligned} \Delta_{\text{hyd}} H_s^\circ &= \Delta_{\text{hyd}} G_s^\circ + T \Delta_{\text{hyd}} S_s^\circ \\ &= (1-z)RT(T\alpha - 1) \\ &+ d[H_w - H_w^{\text{ig}} - RT(T\alpha - 1)] \\ &+ RT\theta c \exp(\theta/T) \frac{\rho_w}{T} - RT^2 \left( \frac{\partial \rho_w}{\partial T} \right)_p \\ &\times \{ a + b[\exp(\mathcal{G}\rho_w) - 1] + c \exp(\theta/T) \\ &+ \delta[\exp(\lambda\rho_w) - 1] \} + H_s^{\text{corr}}, \end{aligned} \quad (\text{A4})$$

$$\begin{aligned} \Delta_{\text{hyd}} C_{p,s}^\circ &= (\partial \Delta_{\text{hyd}} H_s^\circ / \partial T)_p \\ &= (1-z) \left[ 2RT\alpha_w + RT^2 \left( \frac{\partial \alpha_w}{\partial T} \right)_p - R \right] \\ &+ d \left\{ C_{p,w} - C_{p,w}^{\text{ig}} \right. \\ &- 2RT\alpha_w - RT^2 \left( \frac{\partial \alpha_w}{\partial T} \right)_p \left. + R \right\} \\ &- T \left( Rc \exp(\theta/T) \theta^2 \frac{\rho_w}{T^3} + 2R \left( \frac{\partial \rho_w}{\partial T} \right)_p \right) \\ &\times \left\{ a + b[\exp(\mathcal{G}\rho_w) - 1] + c \exp(\theta/T) \right. \\ &\left. + \delta[\exp(\lambda\rho_w) - 1] - c \exp(\theta/T) \frac{\theta}{T} \right\} \end{aligned}$$

$$\begin{aligned} &+ RT \left( \frac{\partial \rho_w}{\partial T} \right)_p^2 [\mathcal{G}b \exp(\mathcal{G}\rho_w) + \lambda\delta \exp(\lambda\rho_w)] \\ &+ RT \left( \frac{\partial^2 \rho_w}{\partial T^2} \right)_p \left\{ a + b[\exp(\mathcal{G}\rho_w) - 1] \right. \\ &\left. + c \exp(\theta/T) + \delta[\exp(\lambda\rho_w) - 1] \right\} + C_{p,s}^{\text{corr}} \end{aligned} \quad (\text{A5})$$

$V_w$ ,  $G_w$ ,  $S_w$ ,  $H_w$ ,  $C_{p,w}$  are the molar volume, Gibbs free energy, entropy, enthalpy and heat capacity of water,  $V_w^{\text{ig}}$ ,  $G_w^{\text{ig}}$ ,  $S_w^{\text{ig}}$ ,  $H_w^{\text{ig}}$ ,  $C_{p,w}^{\text{ig}}$  are the same properties of water in an ideal gas standard state at temperature  $T$  and pressure  $p_r = 0.1$  MPa;  $\rho_w$  and  $M_w$  are the specific density and molar mass of water,  $\kappa_w = (1/\rho_w)(\partial \rho_w / \partial p)_p$  is isothermal compressibility,  $\alpha_w = -(1/\rho_w)(\partial \rho_w / \partial T)_p$  is the coefficient of thermal expansion and  $R$  is the ideal gas constant. General coefficients are  $\nu = 0.005$  m<sup>3</sup> kg<sup>-1</sup>,  $\lambda = -0.01$  m<sup>3</sup> kg<sup>-1</sup> and  $\theta = 1500$  K;  $a$ ,  $b$ ,  $c$  and  $d$  are adjustable parameters and the parameter  $\delta$  is determined depending on the charge of a particle ( $\delta = 0.35a$  for neutral molecules,  $\delta = 0$  for positive monovalent cations and  $\delta = -0.645$  for monovalent anions).

Correction terms in eqns. (A2) to (A5) have their origin in the difficulties in using a relatively simple volumetric equation, eqn. (1), in the subcritical region for obtaining by integration the thermodynamic functions of hydration. For compatibility and simplification the same correction function was used for ionic and nonelectrolyte solutes defined on the basis of heat capacity as:

$$C_{p,s}^{\text{corr}} = \begin{cases} (T - T_c)[e/(T - \Theta) + g]; & T < T_c, \\ 0; & T \geq T_c \end{cases} \quad (\text{A6})$$

By integration of (A7) we obtain:

$$S_s^{\text{corr}} = \begin{cases} IC_S + g(T - T_c) + \ln \left( \frac{T}{T_c} \right) (e - g\Theta) \\ \times \frac{T_c}{\Theta} + e(\Theta - T_c) \ln \left( \frac{T - \Theta}{T_c - \Theta} \right) / \Theta; & T < T_c \\ IC_S; & T \geq T_c \end{cases} \quad (\text{A7})$$

$$H_s^{\text{corr}} = \begin{cases} IC_H + g(T^2 - T_c^2)/2 + (T - T_c) \\ \times (e - gT_c) + e(\Theta - T_c) \ln \left( \frac{T - \Theta}{T_c - \Theta} \right); & T < T_c \\ IC_H; & T \geq T_c \end{cases} \quad (\text{A8})$$

$$G_s^{\text{corr}} = H_s^{\text{corr}} - TS_s^{\text{corr}} \quad (\text{A9})$$

$T_c = 647.126$  K is the critical temperature of water,  $\Theta = 228$  K is a general constant,  $e$  and  $g$  are two additional adjustable parameters and additivity constants  $IC_H$  and  $IC_S$  are adjusted using the literature data on thermodynamic functions of hydration ( $\Delta_{\text{hyd}} G_s^\circ$  and  $\Delta_{\text{hyd}} H_s^\circ$ ) at  $T_r = 298.15$  K and  $p_r = 0.101$  MPa.

The differences between the standard molar entropy, standard molar enthalpy and chemical potential of aqueous solutes at a state of  $T$  and  $p$  and the reference state of  $T_r = 298.15$  K,  $p_r = 0.101$  MPa are related to the thermodynamic functions of hydration as follows:

$$S_s^\circ[T, p] - S_s^\circ[T_r, p_r] = \int_{T_r}^T C_{p,s}^{\text{ig}}/T \, dT + \Delta_{\text{hyd}} S_s^\circ[T, p] - \Delta_{\text{hyd}} S_s^\circ[T_r, p_r], \quad (\text{A10})$$

$$H_s^\circ(T, p) - H_s^\circ(T_r, p_r) = \int_{T_r}^T C_{p,s}^{\text{ig}} \, dT + \Delta_{\text{hyd}} H_s^\circ[T, p] - \Delta_{\text{hyd}} H_s^\circ[T_r, p_r], \quad (\text{A11})$$

$$\begin{aligned} & \mu_s^\circ[T, p] - \mu_s^\circ[T_r, p_r] \\ &= -S_s^{\text{ig}}[T_r, p_r](T - T_r) + \int_{T_r}^T C_{p,s}^{\text{ig}} dT - T \\ & \quad \times \int_{T_r}^T C_{p,s}^{\text{ig}}/T dT + \Delta_{\text{hyd}} G_s^\circ[T, p] - \Delta_{\text{hyd}} G_s^\circ[T_r, p_r] \quad (\text{A12}) \end{aligned}$$

where  $C_{p,s}^{\text{ig}}$  is the solute's ideal gas heat capacity function. In eqns. (A10) to (A12) functions  $\Delta_{\text{hyd}} S_s^\circ$ ,  $\Delta_{\text{hyd}} H_s^\circ$  and  $\Delta_{\text{hyd}} G_s^\circ$  can be used without integration constants  $IC_H$  and  $IC_S$  which cancel out by subtracting  $\Delta_{\text{hyd}} X_s^\circ[T_r, p]$  and  $\Delta_{\text{hyd}} X_s^\circ[T_r, p_r]$  terms.

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