



## RESEARCH REPOSITORY

*This is the author's final version of the work, as accepted for publication following peer review but without the publisher's layout or pagination.  
The definitive version is available at:*

<http://dx.doi.org/10.1016/j.jct.2016.12.001>

Hnědkovský, L., May, P.M. and Hefter, G. (2017) Apparent molar volumes of aqueous solutions of sodium acetate and sodium benzoate at temperatures from 323K to 573K and pressure 10MPa.  
The Journal of Chemical Thermodynamics, 109 . pp. 100-108.

<http://researchrepository.murdoch.edu.au/id/eprint/35099/>

Copyright: © 2016 Elsevier Ltd.  
It is posted here for your personal use. No further distribution is permitted.

## Accepted Manuscript

Apparent molar volumes of aqueous solutions of sodium acetate and sodium benzoate at temperatures from 323 K to 573 K and pressure 10 MPa

Lubomir HnedkovsWky, Peter M. May, Glenn Hefter

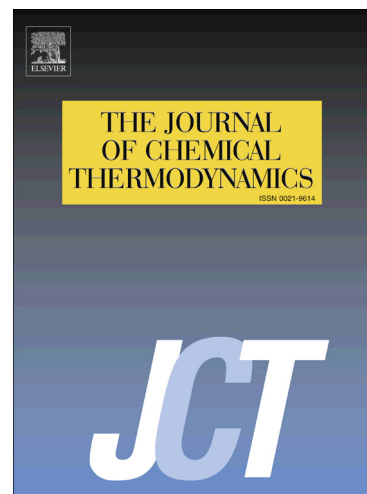
PII: S0021-9614(16)30398-6  
DOI: <http://dx.doi.org/10.1016/j.jct.2016.12.001>  
Reference: YJCHT 4912

To appear in: *J. Chem. Thermodynamics*

Received Date: 24 June 2016  
Revised Date: 10 November 2016  
Accepted Date: 1 December 2016

Please cite this article as: L. HnedkovsWky, P.M. May, G. Hefter, Apparent molar volumes of aqueous solutions of sodium acetate and sodium benzoate at temperatures from 323 K to 573 K and pressure 10 MPa, *J. Chem. Thermodynamics* (2016), doi: <http://dx.doi.org/10.1016/j.jct.2016.12.001>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



**Apparent molar volumes of aqueous solutions of sodium acetate and sodium benzoate at temperatures from 323 K to 573 K and pressure 10 MPa.**

**Lubomir Hnedkovsky\*, Peter M. May and Glenn Hefter#**

*School of Engineering & Information Technology, Murdoch University, Murdoch, WA 6150, Australia*

*# Chemistry Department, Murdoch University, Murdoch, WA 6150, Australia*

*\*Corresponding author, l.hnedkovsky@murdoch.edu.au*

**ABSTRACT**

Densities of aqueous solutions of sodium acetate and sodium benzoate have been measured at 50 K intervals in the temperature range 323.15 K to 573.15 K at constant pressure  $p = 10.0$  MPa by vibrating tube densimetry. The solute molalities ranged from 0.05 to 4.0 mol·kg<sup>-1</sup> (for sodium acetate) or 1.0 mol·kg<sup>-1</sup> (for sodium benzoate). The observed densities were used to calculate apparent molar volumes, which were fitted with an extended Redlich-Rosenfeld-Meyer-type equation to yield standard partial molar volumes of the solutes at infinite dilution. No direct comparisons with literature data were possible but the present results are broadly consistent with previous studies. This work greatly expands the database for the volumetric behaviour of both solutes at high temperatures. Despite the probable presence of anion hydrolysis the volumes of both salts show the steep decrease at high temperatures typical of simple 1:1 electrolytes. As expected, the acetate ion has a smaller volume than benzoate, with the difference increasing markedly with temperature, possibly reflecting the greater hydrophobicity of the benzoate ion. Combination of the present results with appropriate literature data enabled calculation of the volume change for the neutralization reaction:  $\text{HX(aq)} + \text{NaOH(aq)} \rightarrow \text{NaX(aq)} + \text{H}_2\text{O}$ . The values were similar for the two solutes and show a complex dependence on temperature.

**Keywords :** Density, apparent molar volume, acetate, benzoate, aqueous solutions, high temperature

## 1. Introduction

The volumetric behaviour of aqueous solutions of electrolytes at high temperatures, pressures and concentrations provides important insights into the nature of the solute-solute-solvent interactions in such solutions [1–3]. Such information is particularly valuable for salts involving organic ions because they can be used as model systems for the development of functional group additivity models. [4] Such data also have practical applications, for example, in understanding the high temperature degradation of organic wastes [3,5], and the corrosion of materials in geothermal power stations [6].

While some studies have been reported of the volumetric properties of aqueous solutions of simple electrolytes (mostly those with monatomic ions) [7,8], some strong acids or bases [9,10] and neutral/organic molecules [11,12], rather little is known about salts containing organic anions. The properties of sodium acetate and sodium benzoate solutions are of specific interest in relation to the well-known Bayer process, used to produce purified alumina from bauxitic ores [13]. Most bauxite ores contain significant amounts of organic matter, which is degraded to relatively simple sodium carboxylates by the hot (up to *ca.* 573 K) concentrated NaOH(aq) used to digest the ore [14,15]. These compounds have many industrial consequences, including the inhibition of precipitation and product discoloration [14]. Furthermore, the cyclic nature of the Bayer process creates a significant carbon ‘load’ in the process solutions, which impacts on their density [16] and thus on engineering design.

Considerable success has been achieved in recent years modelling the densities of Bayer solutions using simple linear mixing rules [16–18]. The application of such rules requires knowledge of the properties (volumes in this context) of the individual components up to high ionic strengths over the temperature range of interest. In real process solutions there are far too many species to model in this way. However, good results have been obtained by using sodium acetate ( $\text{NaOOCCH}_3$ , NaOAc) and sodium benzoate ( $\text{NaOOC}_6\text{H}_5$ , NaOBz) as proxies to model the effects of the plethora of aliphatic and aromatic compounds [14,15], respectively, that are known to form in real Bayer solutions.

Accordingly, this paper reports high precision vibrating-tube density measurements on aqueous solutions of sodium acetate and sodium benzoate up to 573 K and to reasonably high solute concentrations at 10 MPa (100 bar). This pressure is always greater than system pressure under the conditions of interest thereby avoiding complications from vaporization.

## 2. Experimental

### 2.1. Sample description and preparation

Specifications of the samples used in this work are summarized in table 1. Sodium acetate (anhydrous; “Analytical Reagent” grade) and sodium benzoate (“BioUltra” grade) were

**Table 1**

Specification of chemical samples.

Chemical name	Formula	CASRN	Supplier	Mass fraction purity <sup>a</sup>
Sodium acetate	CH <sub>3</sub> CO <sub>2</sub> Na	127-09-3	Chem-Supply	>0.990
Sodium benzoate	C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> Na	532-32-1	Sigma	>0.995

<sup>a</sup> As stated by the supplier

dried under vacuum ( $p \approx 20$  Pa) at 130 °C for 24 hours. The free-flowing salts so obtained were used, without further purification, to prepare individual test solutions. Ten solutions of sodium acetate with molalities ( $m$ ) ranging from 0.05 to 4.00 mol·kg<sup>-1</sup> and eight sodium benzoate solutions at  $0.05 \leq m/\text{mol}\cdot\text{kg}^{-1} \leq 1.00$  were prepared by weight using buoyancy corrections. All solutions were prepared with high purity water (Millipore Milli-Q system) which had been freshly degassed under vacuum. The mass of each solution was ~1 kg and the estimated uncertainty in the reported molality was  $\pm 2 \times 10^{-5}$  mol·kg<sup>-1</sup> (excluding the effects of impurities).

## 2.2. Density measurements

The custom-built vibrating-tube densimeter described in detail previously [19] was used to determine the density differences between the solutions and water. The densimeter was calibrated at each experimental temperature with high purity water and dry nitrogen (Linde, mole fraction purity 0.9999) using densities taken from the literature [20,21]. Experimental temperatures were measured with a secondary-standard platinum-resistance thermometer (Burns Engineering, USA, model 12001-A-15-10-1-A) calibrated by the manufacturer. The estimated uncertainty of the temperature is 0.03 K at the lowest experimental temperature (323 K) gradually increasing to about 0.1 K at the highest experimental temperature (573 K). Pressure was measured with an uncertainty of 0.1 % by a digital pressure transducer (Druck, UK, model PDCR 4071) calibrated by manufacturer. The period of oscillation of the vibrating tube (typically ~9 ms for water) was measured by a digital counter (Agilent, USA, model 53131A) with an uncertainty of 1 ns. This ensured that the resolution of the density measurements was at least 0.007 kg·m<sup>-3</sup>. Combining all the uncertainties in the input quantities (temperature, pressure, oscillation period) the overall uncertainty in the calibration constant of the vibrating tube was about 0.1 % and the overall uncertainty in the measured density difference was estimated to be:  $U(\Delta\rho) = (0.001\Delta\rho + 0.007)$  kg·m<sup>-3</sup>. Solutions at the highest experimental temperature (573 K) were checked for possible thermal decomposition by varying the flow rate thereby prolonging the residence time of the sample in the hot zone of the densimeter; no signs of decomposition were detected.

### 3. Results and discussion

#### 3.1. Densities and apparent volumes

The measured differences between the solution densities and that of pure water at the same temperature and pressure are recorded in tables 2 and 3 for each solution at the experimental temperatures. It is noteworthy that measurements on NaOBz(aq) were obtained without complication up to  $T = 573$  K, given that benzoic acid decomposes in aqueous solutions at  $T > 498$  K [22].

Also presented in tables 2 and 3 are the corresponding apparent molar volumes for NaOAc(aq) and NaOBz(aq) which were calculated using the usual relationship:

$$V_{\phi} = M / \rho - \Delta\rho / (m \cdot \rho \cdot \rho_w) \quad (1)$$

where  $M$  is the molar mass of the solute ( $M = 82.034$  g·mol<sup>-1</sup> and 144.103 g·mol<sup>-1</sup> for NaOAc and NaOBz, respectively),  $m$  is the molality of the solute (mol-solute/kg-solvent),  $\rho$  and  $\rho_w$  are the density of the solution and of pure water, and  $\Delta\rho = \rho - \rho_w$ .

**Table 2**

Experimental density differences,  $\Delta\rho$ , and apparent molar volumes,  $V_{\phi}$ , of aqueous solutions of sodium acetate at various temperatures,  $T$ , and molality,  $m$ , at pressure  $p = 10$  MPa).<sup>a</sup>

$T/K$	$p/\text{MPa}$	$m/\text{mol}\cdot\text{kg}^{-1}$	$\Delta\rho/\text{kg}\cdot\text{m}^{-3}$	$U(\Delta\rho)/\text{kg}\cdot\text{m}^{-3}$	$V_{\phi}/\text{cm}^3\cdot\text{mol}^{-1}$	$U(V_{\phi})/\text{cm}^3\cdot\text{mol}^{-1}$
323.16	10.02	0.0500	2.025	0.009	41.45	0.18
323.16	10.02	0.1001	4.031	0.011	41.60	0.11
323.16	10.02	0.2001	7.979	0.015	41.83	0.07
323.16	10.02	0.3998	15.678	0.023	42.17	0.05
323.15	10.02	0.6503	25.053	0.032	42.47	0.05
323.15	10.02	1.0071	37.899	0.045	42.81	0.04
323.15	10.02	2.0382	72.000	0.079	43.62	0.03
323.15	10.00	2.8061	94.76	0.10	44.15	0.03
323.15	10.02	2.9990	100.20	0.11	44.26	0.03
323.15	10.02	4.0044	126.61	0.13	44.83	0.03
373.30	10.01	0.0500	2.042	0.009	41.05	0.19
373.31	10.01	0.1001	4.059	0.011	41.28	0.11
373.33	10.01	0.2001	8.005	0.015	41.70	0.08
373.34	10.00	0.3998	15.708	0.023	42.13	0.06

373.35	10.00	0.6503	25.019	0.032	42.59	0.05
373.35	10.00	1.0071	37.699	0.045	43.13	0.05
373.35	10.00	2.0382	71.215	0.078	44.23	0.03
373.35	9.99	2.9990	98.71	0.11	45.07	0.03
373.36	9.99	4.0044	124.28	0.13	45.80	0.03
423.17	10.01	0.1001	4.280	0.011	38.50	0.13
423.17	10.02	0.2001	8.415	0.015	39.14	0.08
423.16	10.04	0.3998	16.392	0.023	40.03	0.06
423.15	10.06	0.6503	26.017	0.033	40.76	0.06
423.15	10.05	1.0071	38.995	0.046	41.66	0.05
423.15	10.03	2.0382	73.030	0.080	43.38	0.04
423.15	10.04	2.9990	100.74	0.11	44.58	0.04
423.14	10.03	4.0044	126.27	0.13	45.62	0.03
473.15	10.01	0.1001	4.735	0.012	31.66	0.15
473.15	10.02	0.2001	9.252	0.016	32.88	0.10
473.15	10.01	0.3998	17.891	0.025	34.48	0.07
473.15	9.99	0.6503	28.189	0.035	35.88	0.07
473.15	10.00	1.0071	42.002	0.049	37.40	0.06
473.15	9.99	2.0382	77.787	0.085	40.27	0.04
473.15	9.97	2.9990	106.56	0.11	42.18	0.04
473.15	9.97	4.0044	132.85	0.14	43.77	0.04
523.17	10.01	0.1001	5.637	0.013	14.96	0.19
523.17	10.01	0.2001	10.888	0.018	17.75	0.13
523.17	10.01	0.3998	20.750	0.028	21.31	0.10
523.17	10.01	0.6503	32.298	0.039	24.33	0.09
523.18	10.01	1.0071	47.598	0.055	27.39	0.08
523.18	10.03	2.0382	86.550	0.094	32.87	0.07
523.18	10.03	2.9990	117.47	0.12	36.20	0.06
523.18	10.04	4.0044	145.36	0.15	38.88	0.05
573.12	10.00	0.1001	7.741	0.015	-36.06	0.28
573.12	10.00	0.2001	14.631	0.022	-27.65	0.20
573.12	10.00	0.3998	27.198	0.034	-17.60	0.16
573.12	10.00	0.6503	41.580	0.049	-9.71	0.13
573.13	10.00	1.0071	60.210	0.067	-2.00	0.11
573.14	10.01	2.0382	106.18	0.11	11.20	0.09
573.14	10.01	2.9990	141.48	0.15	18.77	0.08
573.14	10.00	4.0044	172.93	0.18	24.38	0.07

<sup>a</sup> Standard uncertainties are:  $u(T) = \{0.0003T - 0.06\}$  K,  $u(p) = 0.01$  MPa,  $u(m) = 2 \times 10^{-5}$  mol·kg<sup>-1</sup>. Expanded uncertainties  $U(\Delta\rho)$  and  $U(V_\phi)$  are at the 0.95 confidence level.

$\Delta\rho = \rho - \rho_w$  is the difference between the density of the solution and pure water at the same temperature and pressure.

**Table 3**

Experimental density differences,  $\Delta\rho$ , and apparent molar volumes,  $V_\phi$ , of aqueous solutions of sodium benzoate at various temperatures,  $T$ , and molality,  $m$ , at pressure  $p = 10$  MPa).<sup>a</sup>

$T/K$	$p/\text{MPa}$	$m/\text{mol}\cdot\text{kg}^{-1}$	$\Delta\rho/\text{kg}\cdot\text{m}^{-3}$	$U(\Delta\rho)/\text{kg}\cdot\text{m}^{-3}$	$V_\phi/\text{cm}^3\cdot\text{mol}^{-1}$	$U(V_\phi)/\text{cm}^3\cdot\text{mol}^{-1}$
323.16	10.02	0.0514	2.787	0.010	89.90	0.19
323.15	10.02	0.1011	5.440	0.012	90.08	0.13
323.15	10.02	0.1501	8.025	0.015	90.19	0.10
323.14	10.02	0.2008	10.664	0.018	90.31	0.09
323.15	10.01	0.3052	16.006	0.023	90.50	0.08
323.15	9.99	0.4011	20.807	0.028	90.64	0.07
323.15	9.99	0.6503	32.822	0.040	90.95	0.06
323.15	10.00	1.0002	48.649	0.056	91.35	0.06
373.15	10.01	0.0514	2.680	0.010	93.16	0.20
373.16	10.00	0.1011	5.230	0.012	93.35	0.13
373.16	10.00	0.1501	7.709	0.015	93.51	0.11
373.17	10.01	0.2008	10.230	0.017	93.71	0.09
373.19	10.01	0.3052	15.332	0.022	93.98	0.08
373.20	10.01	0.4011	19.896	0.027	94.21	0.07
373.21	10.01	0.6503	31.312	0.038	94.65	0.07
373.22	10.02	1.0002	46.287	0.053	95.17	0.06
423.14	10.01	0.1011	5.286	0.012	94.24	0.14
423.15	10.01	0.1501	7.775	0.015	94.55	0.12
423.16	10.02	0.2008	10.324	0.017	94.74	0.10
423.16	10.01	0.3052	15.437	0.022	95.19	0.09
423.16	10.01	0.4011	20.004	0.027	95.54	0.08
423.17	10.00	0.6503	31.348	0.038	96.30	0.07
423.16	10.00	1.0002	46.281	0.053	96.98	0.06
473.15	10.02	0.1011	5.650	0.013	91.19	0.17
473.15	10.03	0.1501	8.281	0.015	91.85	0.13
473.15	10.03	0.2008	10.961	0.018	92.33	0.12
473.15	9.99	0.3052	16.337	0.023	93.14	0.10
473.15	10.01	0.4011	21.095	0.028	93.85	0.09
473.15	10.01	0.6503	32.933	0.040	95.10	0.08



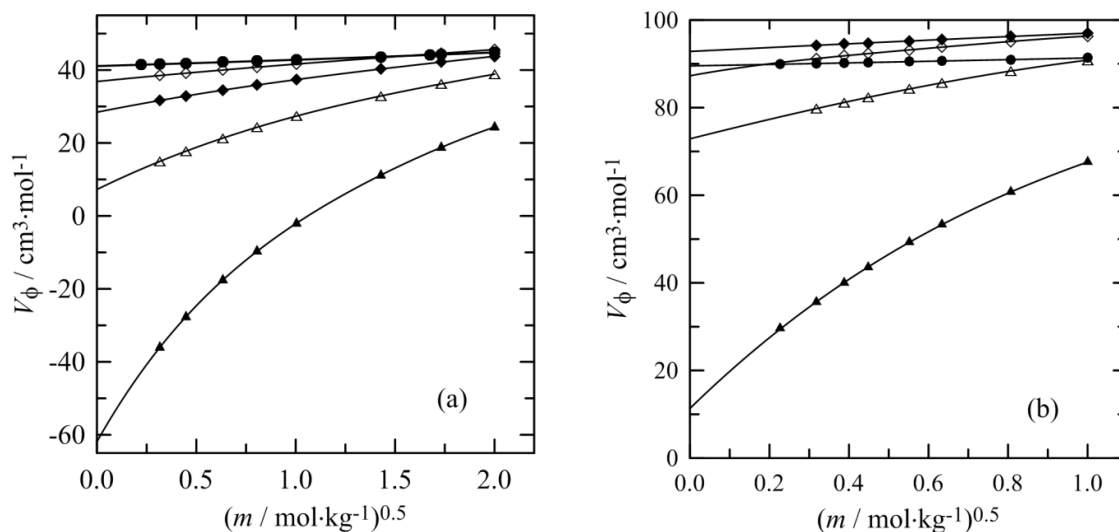
473.15	10.01	1.0002	48.376	0.055	96.34	0.07
523.16	10.01	0.1011	6.458	0.013	79.81	0.20
523.16	10.01	0.1501	9.428	0.016	81.15	0.17
523.16	10.01	0.2008	12.417	0.019	82.33	0.15
523.16	10.02	0.3052	18.358	0.025	84.27	0.13
523.16	10.03	0.4011	23.599	0.031	85.71	0.12
523.16	10.04	0.6503	36.527	0.044	88.32	0.10
523.16	10.04	1.0002	53.241	0.060	90.85	0.09
573.13	9.99	0.0514	4.514	0.012	29.63	0.44
573.13	9.99	0.1011	8.558	0.016	35.59	0.30
573.14	9.99	0.1501	12.346	0.019	40.01	0.25
573.14	9.99	0.2008	16.129	0.023	43.49	0.22
573.16	10.00	0.3052	23.508	0.031	49.29	0.19
573.15	10.01	0.4011	29.940	0.037	53.34	0.18
573.15	10.01	0.6503	45.527	0.053	60.76	0.15
573.14	10.01	1.0002	65.369	0.072	67.55	0.14

<sup>a</sup> Standard uncertainties are:  $u(T) = \{0.0003T - 0.06\}$  K,  $u(p) = 0.01$  MPa,  $u(m) = 2 \times 10^{-5}$  mol·kg<sup>-1</sup>. Expanded uncertainties  $U(\Delta\rho)$  and  $U(V_\phi)$  are at the 0.95 confidence level.

$\Delta\rho = \rho - \rho_w$  is the difference between the density of the solution and pure water at the same temperature and pressure

### 3.2. Data fitting and standard molar volumes

Figure 1 plots the apparent molar volumes,  $V_\phi$ , against concentration (as  $\sqrt{m}$ ) at various temperatures. Note that the  $V_\phi$  values in tables 2 and 3 are uncorrected for the hydrolysis of the anions and for ion pairing of the salt. The extent of hydrolysis is relatively small for the present range of concentrations but becomes significant at lower concentrations and especially at higher temperatures. Reliable correction for hydrolysis requires accurate knowledge of properties of the (unhydrolysed) acetate or benzoate ions, which is not currently available. Similar considerations apply to ion pairing. Further details regarding the hydrolysis equilibria are given in Appendix A.

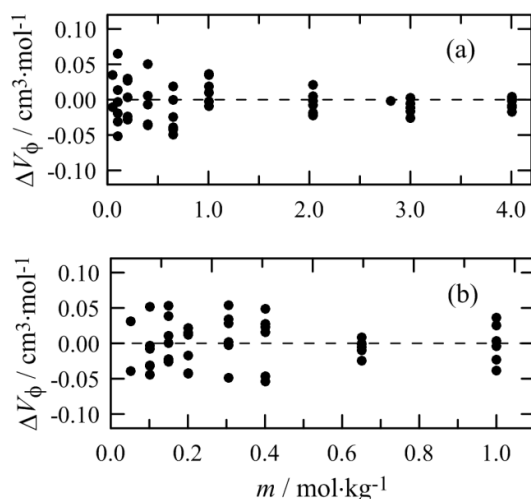


**Fig. 1.** Apparent molar volumes as a function of concentration ( $\sqrt{m}$ ) for aqueous solutions of: (a) sodium acetate and (b) sodium benzoate, at temperatures  $T/K = 323.15, 423.15, 473.15, 523$  and  $573.15$  (top to bottom) and  $p = 10$  MPa.

The apparent molar volumes of the sodium acetate and benzoate solutions over the whole temperature and concentration ranges were fitted using an extended Redlich-Rosenfeld-Meyer-type equation of the form:

$$V_{\phi} = V^{\circ} + A_v \left\{ \sqrt{m} + \sum_i a_i \rho_w^{j_i} \tau^{k_i} (\ln \tau)^{l_i} m^{n_i} \right\} \quad (2)$$

where  $V^{\circ}$  is the standard molar volume (the partial molar volume at infinite dilution) of the solute in aqueous solution,  $A_v$  is the theoretical Debye-Hückel slope for volumes [23],  $a_i$  are adjustable parameters of the fit,  $\rho_w$  is the density of pure water at a given temperature and pressure and  $\tau = T/1000$ . The pure water density and the Debye-Hückel slopes were calculated by means of the IAPWS-95 formulation of the properties of pure water [21]. The parameters of the fitting equations are given in Table 4. The number of adjustable parameters was kept to a minimum using a variety of common numerical-analysis criteria. The ability of equation (2) to fit the data in tables 2 and 3 is illustrated in figure 2 which plots the distribution of deviations of the experimental points from the fitting equation. Maximum deviations were  $\pm 0.06 \text{ cm}^3 \cdot \text{mol}^{-1}$  while the average deviations were  $\pm 0.03 \text{ cm}^3 \cdot \text{mol}^{-1}$  for both systems.



**Fig. 2.** Deviation plots of  $\Delta V_{\phi} = V_{\phi, \text{exp}} - V_{\phi, \text{fit}}$  as a function of concentration ( $m$ ) at the studied temperatures for aqueous solutions of: (a) sodium acetate and (b) sodium benzoate.

Equation (2) is sufficiently flexible to provide a close fit of the experimental data without over-fitting but it has the disadvantage that it needs the density of pure water and the Debye-Hückel slope as input variables. It is important that these two quantities should be taken from the same source(s) so as to minimise inconsistencies in the predicted apparent molar volumes. All the numerical values reported in this paper were obtained via equation (2); however, for the convenience of interested users, the experimental data were also fitted with functions of temperature and concentration only. These fits do not yield the proper Debye-Hückel slopes, require more fitting parameters, and are not suitable for extrapolation outside the experimental matrix. Nevertheless, such equations have the advantage of being easier and more straightforward for data manipulation. The details of these working equations are given in Appendix B.

**Table 4**  
Fitting parameters of equation (2)<sup>a</sup>

$i$	$j_i$	$k_i$	$l_i$	$n_i$	$a_i$	$\sigma(a_i)^b$
Sodium acetate						
1	2	-1	0	0	-14.28	0.39
2	4	2	0	0	-41.5	1.2
3	1	2	0	0	12.00	0.22
4	3	0	0	0	33.45	0.98
5	1	-3	0	0	-0.144	0.012

6	2	3	0	1	10.76	0.61
7	0	-1	0	1	-0.981	0.047
8	3	-1	0	1	0.873	0.037
9	2	1	0	1.5	-1.43	0.11
10	2	-3	0	1.5	-0.213	0.017
11	1	3	0	1.5	-1.42	0.15
12	0	-3	0	1.5	0.231	0.018
13	4	2	0	3	-0.0493	0.0097
14	1	0	-1	3	0.0171	0.0025
15	2	2	0	3	0.153	0.024

Sodium benzoate						
1	2	3	0	0	-273.59	0.70
2	3	0	-1	0	-162.2	1.4
3	2	1	0	0	-310.0	3.3
4	0	-1	0	0	-27.254	0.076
5	0	0	-1	0	-31.30	0.15
6	2	0	0	1	-0.835	0.030
7	0	0	0	1.5	3.06	0.15
8	0	1	0	1.5	-5.21	0.26
9	3	2	0	1.5	5.71	0.34
10	4	1	0	2	-3.83	0.28
11	3	1	0	3	0.553	0.057

<sup>a</sup> The units used in equation (2) are  $V_\phi, V^0/\text{cm}^3 \cdot \text{mol}^{-1}$ ,  $A_V/\text{cm}^3 \cdot \text{mol}^{-1.5} \cdot \text{kg}^{0.5}$ ,  $\rho_1/\text{g} \cdot \text{cm}^{-3}$ ,  $T/\text{K}$ ,  $m/\text{mol} \cdot \text{kg}^{-1}$ . <sup>b</sup> Standard error (95% confidential interval).

Equation (2) was used to generate smoothed values of  $V_\phi$  and to obtain the standard partial molar volumes of both solutes as functions of temperature. For convenience, the values of  $V^0$  for the two salts and the  $A_V$  values are listed at rounded temperatures in Table 5.

**Table 5**

Theoretical Debye-Hückel slopes,  $A_V$ , and standard (infinite dilution) partial molar volumes<sup>a</sup>,  $V^0$ , at rounded temperatures and  $p = 10$  MPa, calculated via equation (2).

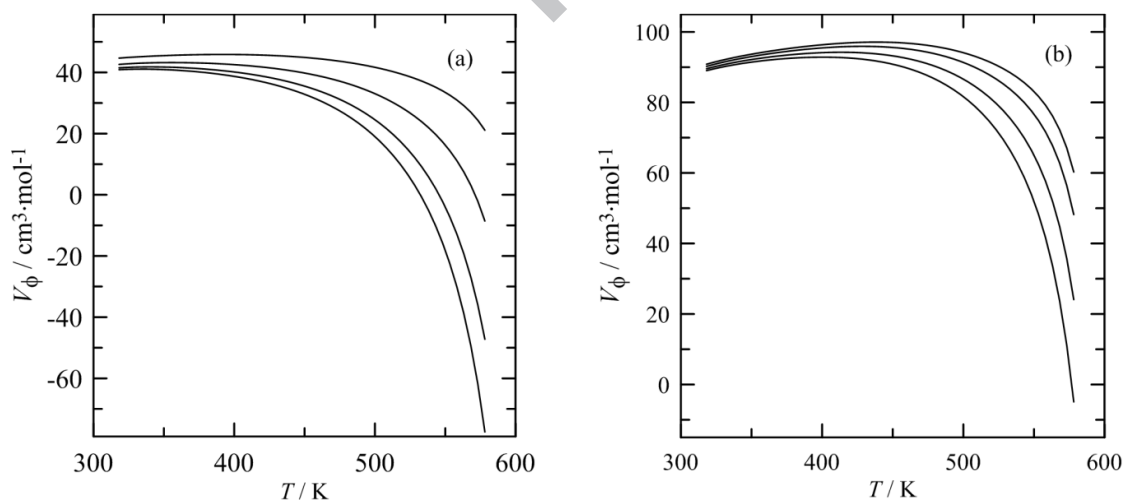
$T / \text{K}$	$A_V / \text{cm}^3 \cdot \text{mol}^{-1.5} \cdot \text{kg}^{0.5}$	$V^0 / \text{cm}^3 \cdot \text{mol}^{-1}$	
		NaOAc	NaOBz
323.15	2.314	40.99	89.51
348.15	2.962	40.96	91.34
373.15	3.862	40.24	92.42
398.15	5.113	38.85	92.84
423.15	6.879	36.61	92.48
448.15	9.439	33.17	91.01
473.15	13.298	27.92	87.88

498.15	19.433	19.78	82.20
523.15	29.949	6.73	72.29
548.15	50.194	-15.86	53.92
573.15	98.007	-61.94	11.27

<sup>a</sup> Uncorrected for hydrolysis or ion pairing

### 3.3. Effects of temperature and concentration on $V_\phi$

The pattern of behaviour of  $V_\phi$  for both salts with respect to temperature and concentration (Figure 3) is similar to that of many 1:1 electrolytes [7,8]. Thus, at constant  $m$ , there is an initial small increase in  $V_\phi$  with increasing  $T$  followed by a dramatic decrease in  $V_\phi$  at higher  $T$ . This decrease is undoubtedly due to the greater electrostriction by the ions of the increasingly compressible solvent. For NaOAc(aq) the initial rise in  $V_\phi$  is barely discernible (or even, at lower  $m$ , absent, Figure 3(a)) but is clearly observable for NaOBz(aq), with  $T_{\max}$  decreasing considerably with decreasing  $m$  (Figure 3(b)). The rapid decrease in  $V_\phi$  at higher  $T$  for both salt systems is interesting because it occurs in spite of the hydrolysis of the anions that produces the uncharged acid molecules  $\text{CH}_3\text{COOH}(\text{aq})$  and  $\text{C}_6\text{H}_5\text{COOH}(\text{aq})$ . Such species typically show a rapid *increase* in  $V_\phi$  as  $T \rightarrow T_{\text{critical}}$  [11]. This phenomenon is further discussed below.



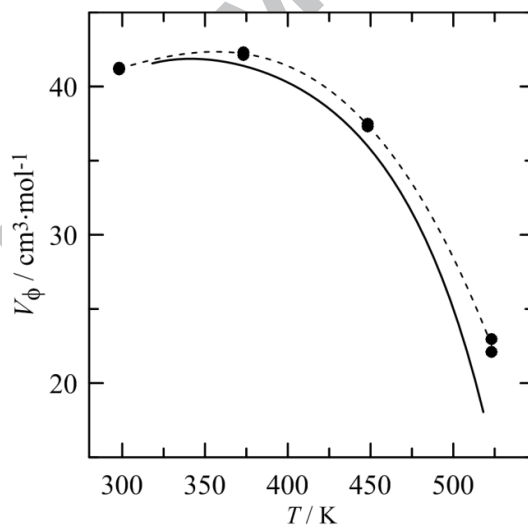
**Fig. 3.** Apparent molar volumes as a function of temperature at  $p = 10$  MPa for aqueous solutions of: (a) sodium acetate and (b) sodium benzoate, at concentrations (bottom to top),  $m/\text{mol}\cdot\text{kg}^{-1} = 0, 0.1, 1.0, 4.0$  and  $0, 0.1, 0.5, 1.0$ , respectively.

### 3.4. Comparisons with literature data

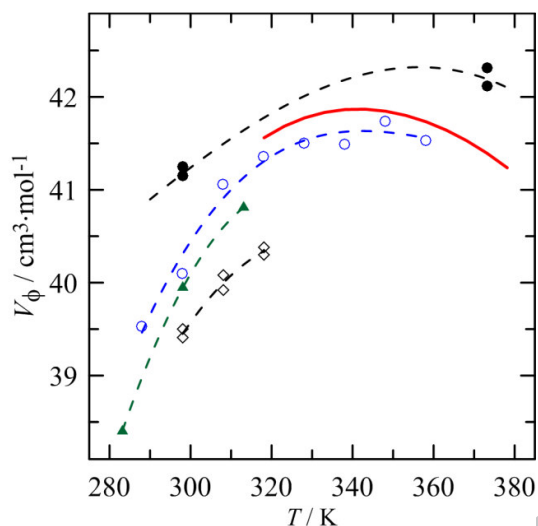
To the best of our knowledge, the only closely comparable volumetric data available for these two systems at high temperatures are those of Criss and Wood [24] for sodium acetate

at  $p = 28$  MPa and  $298 \leq T/K \leq 573$ , albeit at just one concentration ( $m = 0.1209$  mol·kg<sup>-1</sup>). Their  $V_\phi$  values are plotted in Figure 4 along with those calculated from the present data for NaOAc(aq) at  $p = 10$  MPa via equation (2) at the same concentration. The two isobars exhibit closely similar shapes but, as expected [8,11], show an increase in  $V_\phi$  with increasing pressure and temperature.

All other published experimental volumetric data for these two systems were measured at or near atmospheric pressure and are clustered around temperatures near or below 323 K (the lowest temperature studied in the present work). Nevertheless, semi-quantitative comparisons can still be made. Figure 5 illustrates the temperature and pressure dependences of  $V_\phi$  for 0.1209 mol·kg<sup>-1</sup> NaOAc(aq) at  $283 \leq T/K \leq 383$  and  $0.1 \leq p/\text{MPa} \leq 28$ . To construct this diagram the available literature data at 0.1 MPa were interpolated (using polynomial fits) to  $m = 0.1209$  mol·kg<sup>-1</sup>. Whilst the overlap with the current work is limited, all the data are broadly consistent, with the present  $V_\phi$  values at  $p = 10$  MPa lying above those of Ballerat-Busserolles *et al.* [25] at  $p = 0.35$  MPa, which in turn are larger than the values at  $p = 0.1$  MPa [26,27].

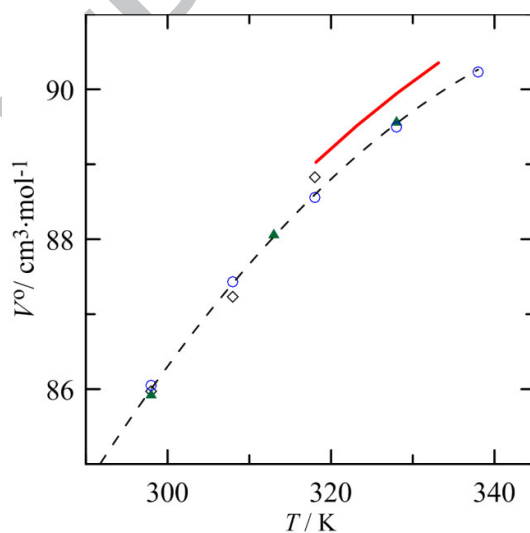


**Fig. 4.** Comparison of present and literature values of the apparent molar volumes of 0.1029 mol·kg<sup>-1</sup> sodium acetate solution over a wide temperature range: full line, present work at  $p = 10$  MPa; ●, Criss and Wood [24] at  $p = 28$  MPa (the dashed line is a visual aid only).



**Fig. 5.** Comparison of the present and literature values of the apparent molar volumes of sodium acetate solution (at  $m = 0.1029 \text{ mol}\cdot\text{kg}^{-1}$ ) at lower temperatures: full red line, this work at  $p = 10 \text{ MPa}$ ; ●, Criss and Wood [24] at  $p = 28 \text{ MPa}$ ; ○, Ballerat-Busserolles *et al.* [25] at  $p = 0.35 \text{ MPa}$ ; ▲, Allred and Woolley [26] at  $p = 0.1 \text{ MPa}$ ; ◇, Banipal *et al.* [27] at  $p = 0.1 \text{ MPa}$ ; the dashed lines are visual aids only.

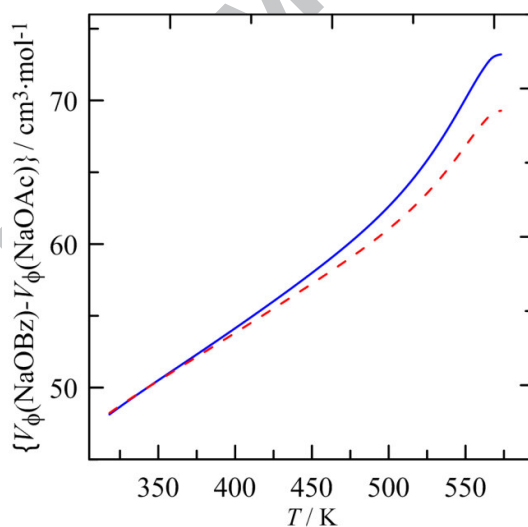
For NaOBz solutions comparisons with previous studies are most conveniently made using the standard molar volumes. Figure 6 compares the  $V^{\circ}$  values at low temperatures and atmospheric pressure to present results at  $p = 10 \text{ MPa}$ ; again there is good consistency.



**Fig. 6.** Standard partial molar volume of sodium benzoate in aqueous solution as a function of temperature: full red line, this work at  $p = 10 \text{ MPa}$ ; ○, Strong *et al.* [28] at  $p = 0.1 \text{ MPa}$ ; ▲, Ostiguy *et al.* [29] at  $p = 0.1 \text{ MPa}$ ; ◇, Banipal *et al.* [30] at  $p = 0.1 \text{ MPa}$ ; the dashed line is a visual aid only.

### 3.5. Comparison of $\text{OAc}^{-}(\text{aq})$ and $\text{OBz}^{-}(\text{aq})$ volumes

Figure 7 contains the plots of the differences,  $\Delta V$ , between the standard molar volumes of NaOBz(aq) and NaOAc(aq) as a function of temperature. At infinite dilution, assuming the ionic contributions are additive (*i.e.*, ignoring the possible effects of hydrolysis), the contribution of  $\text{Na}^+(\text{aq})$  is eliminated by the subtraction and the curve reflects the difference in the standard molar volumes of  $\text{OBz}^-(\text{aq})$  and  $\text{OAc}^-(\text{aq})$ . However, it is notable that there is little change in the differences even at  $m = 1.0 \text{ mol}\cdot\text{kg}^{-1}$  (figure 7) where ionic additivity no longer applies. Similar curves (not shown) are obtained at other concentrations. The difference in volume between the two anions is a reflection of the larger geometric size and the more hydrophobic character of  $\text{OBz}^-(\text{aq})$  *cf.*  $\text{OAc}^-(\text{aq})$ . The rather strong increase in  $\Delta V$  with rising temperature (figure 7) is probably a reflection of the hydrophobic character of  $\text{OBz}^-$  since the geometric size of ions is little affected by temperature [31]. This inference is consistent with the positive changes in molar volumes that occur [32,33] for small neutral hydrophobic organic molecules as  $T \rightarrow T_{\text{critical}}$ , which contrast markedly with the negative decreases that are usually observed for electrolyte solutions [7,8].



**Fig. 7.** The difference between the standard molar volumes of aqueous solutions of sodium benzoate and sodium acetate as a function of temperature: solid line,  $m = 0 \text{ mol}\cdot\text{kg}^{-1}$ ; dashed line,  $m = 1.0 \text{ mol}\cdot\text{kg}^{-1}$ .

### 3.5. Neutralization volumes

The present standard molar volumes can be combined with literature data for aqueous solutions of NaOH [19], acetic acid [32] and benzoic acid [33] to calculate  $\Delta_r V^\circ$ , the standard molar volume change for the neutralization reaction:





where  $X^- = \text{OAc}^-$  or  $\text{OBz}^-$ . The magnitude of  $\Delta_r V^\circ$  is then calculated as:

$$\Delta_r V^\circ = V^\circ(\text{NaX}(\text{aq})) + V^\circ(\text{H}_2\text{O}) - V^\circ(\text{HX}(\text{aq})) - V^\circ(\text{NaOH}(\text{aq})) \quad (4)$$

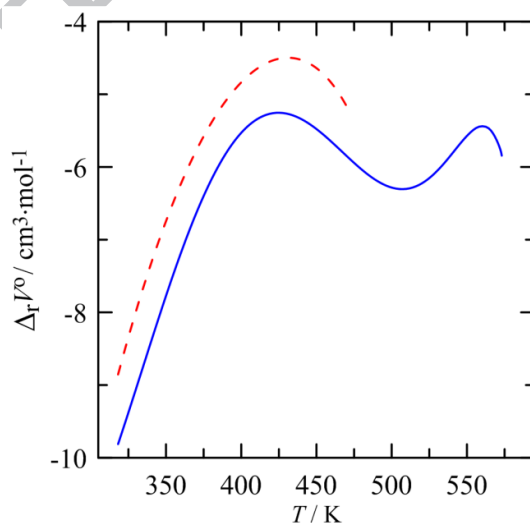
The values of  $\Delta_r V^\circ$  so obtained are shown in Figure 8 as a function of temperature at  $p = 10$  MPa. Applying ionic additivity but recognising the partial hydrolysis of the anions, equation (4) reduces to:

$$\Delta_r V^\circ = \alpha^\circ \Delta_{\text{dis}} V^\circ(\text{HX}) - \Delta_{\text{dis}} V^\circ(\text{H}_2\text{O}) \quad (5)$$

with  $\alpha^\circ$  representing the limiting ( $m \rightarrow 0$ ) fraction of undissociated acid and  $\Delta_{\text{dis}} V^\circ$  corresponding respectively to the standard molar volume changes of the reactions:



As would be expected, where comparison is possible (benzoic acid is not stable in aqueous solution at  $T \geq 498$  K [22]), the shape and magnitude of the  $\Delta_r V^\circ(T)$  curves for both solutes are very similar.



**Fig. 8.** Standard molar volume change for the neutralization of weak acids by sodium hydroxide as a function of temperature: full blue line, acetic acid; dashed red line, benzoic acid (data available only to 473 K).

It should be mentioned that the similarity of the (sodium) acetate and benzoate curves in figures 7 and 8 suggests (but doesn't prove) a similar level of ion pairing for these two systems over the whole temperature range. While both salts are fully dissociated at ambient  $T$ , like most electrolytes in aqueous solution they are expected to show significant ion pairing at higher  $T$ . It is possible to estimate ion pairing constants, *e.g.* via the SUPCRT92 program, however, the reliability of such calculations is, in our experience, dubious and they are not included here. It is however interesting to note that the effects of ion pairing on the observed volumes would be opposite to those of hydrolysis.

#### 4. Conclusions

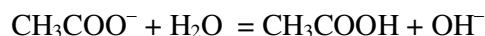
The densities of aqueous solutions of sodium acetate and sodium benzoate have been characterized by vibrating-tube densimetry at  $323 \leq T/K \leq 573$  and  $0.05 \leq m/\text{mol}\cdot\text{kg}^{-1} \leq 4$  (NaOAc) or 1 (NaOBz) at  $p = 10$  MPa. The  $V_\phi$  values calculated from these data for both salts are well behaved over the investigated ranges and are broadly comparable to those of typical strong electrolytes despite the partial hydrolysis of the organic anions and possible countervailing effects from ion pairing at higher  $T$ . Detailed consideration of the data show, as expected, that the volume of  $\text{OAc}^-(\text{aq})$  is smaller than that of  $\text{OBz}^-(\text{aq})$  but that this difference increases significantly with increasing  $T$ , possibly because of the greater hydrophobicity of  $\text{OBz}^-(\text{aq})$ . The volume changes for the neutralization process (equations (3) & (4)) are closely parallel over the whole temperature range.

#### Acknowledgement

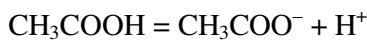
This work was funded through AMIRA International Limited, Project P507B, by the Australian alumina industry (Alcoa World Alumina, Rio Tinto Alcan, and BHP-Billiton /Worsley Alumina), and the Australian Government through two Linkage Grants (Nos. LP0349107 and LP0560477) from the Australian Research Council.

#### Appendix A. Ionic equilibrium

The hydrolysis of sodium acetate in solution at an overall concentration of  $m$  mol·kg<sup>-1</sup>:



or the related ionization equilibrium:



were analysed using the following set of equations:

$$\begin{aligned} [\text{CH}_3\text{COO}^-] + [\text{CH}_3\text{COOH}] &= m \\ [\text{Na}^+] &= m \\ [\text{H}^+] + [\text{Na}^+] &= [\text{OH}^-] + [\text{CH}_3\text{COO}^-] \\ K_a &= \frac{\gamma_{\pm}^2 [\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \\ K_w &= [\text{H}^+][\text{OH}^-] \end{aligned} \quad (\text{A1} - \text{A5})$$

where the terms in square brackets represent molalities of ionic or molecular species in the solution,  $m$  is the bulk molality (analytical concentration) of the sodium acetate. The mean activity coefficient ( $\gamma_{\pm}$ ) was approximated by an extended Debye-Hückel expression [23]

$$\ln \gamma_{\pm} = \frac{-A\sqrt{m}}{1+B\sqrt{m}} + 0.055m \quad (\text{A6})$$

with parameters A and B calculated from the properties of water [20]. The activity coefficient of undissociated acetic acid was assumed to be unity. The dissociation constant of acetic acid,  $K_a$ , and the ionic product of water,  $K_w$ , were taken from the literature [34,35]. Generally, the concentration of undissociated acetic acid increased with increasing temperature and with increasing sodium acetate concentration. In the limit of infinite dilution the highest possible degree of hydrolysis can be calculated as

$$\alpha^{\circ} = \frac{[\text{CH}_3\text{COOH}]}{m} = \frac{\sqrt{K_w}}{K_a + \sqrt{K_w}} \quad (\text{A7})$$

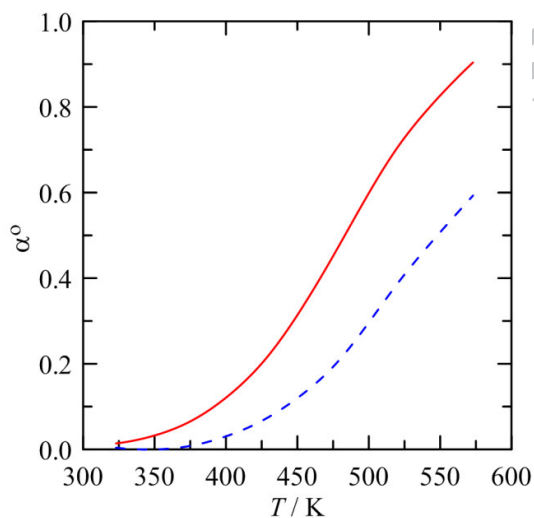
At  $T = 323$  K the maximum number of undissociated acetic acid molecules will account for 1.4 % of the total concentration; at  $T = 573$  K this fraction rises to 90.4 %. Thus the correction of the standard molar volume, calculated from

$$V_{\text{exp}}^{\circ} = V^{\circ} + \Delta_{\text{corr}} V^{\circ} = (V_{\text{Na}^+}^{\circ} + V_{\text{CH}_3\text{COO}^-}^{\circ}) + \alpha^{\circ} (V_{\text{CH}_3\text{COOH}}^{\circ} - V_{\text{CH}_3\text{COO}^-}^{\circ}) \quad (\text{A8})$$

will be extremely sensitive to the difference between the standard molar volume of undissociated acid and the acetate ion. Any inaccuracy in  $(V_{\text{CH}_3\text{COOH}}^{\circ} - V_{\text{CH}_3\text{COO}^-}^{\circ})$  will be magnified by the large value of  $\alpha$  at high temperatures.

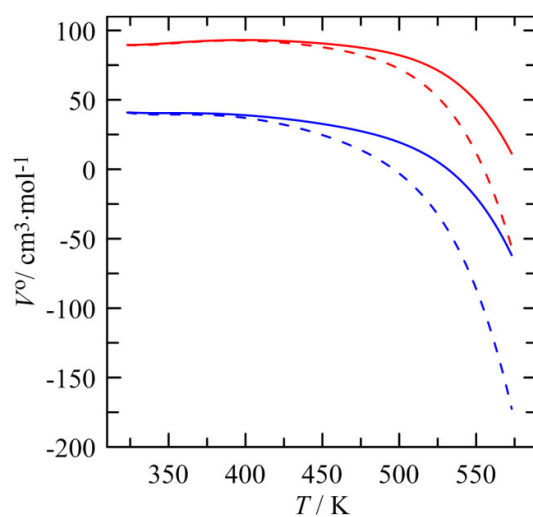
The hydrolysis of benzoate was treated in exactly the same way as acetate. Benzoic acid is slightly stronger than acetic acid [36], even so, at high  $T$  the degree of dissociation drops substantially, leaving about 60% of benzoic acid molecules undissociated.

Figure 1A shows that, with increasing  $T$ , the limiting fraction of molecular acetic or benzoic acid,  $\alpha^0$ , present in NaOAc(aq) and NaOBz(aq) respectively, changes from almost zero (corresponding to complete dissociation) to values corresponding to high levels of association.



**Fig. 1A.** Fraction of undissociated acid molecules in infinitely dilute aqueous solution of sodium salts as a function of temperature: solid red line, acetic acid; dashed blue line, benzoic acid.

To illustrate the qualitative effect of hydrolysis on  $V^0$  the ionization volumes of the acids were estimated using the SUPCRT92 software package [37]. At low  $T$  the corrections for hydrolysis are small but become larger at higher  $T$  (figure 2A). At 573 K the differences between the uncorrected and corrected standard partial molar volumes are  $-111 \text{ cm}^3 \cdot \text{mol}^{-1}$  and  $-68 \text{ cm}^3 \cdot \text{mol}^{-1}$  for NaOAc(aq) and NaOBz(aq), respectively.



**Fig. 2A.** Approximate effects of anion hydrolysis on the standard molar volumes of sodium acetate (bottom, blue) and sodium benzoate ion (top, red): solid lines – uncorrected for hydrolysis; dashed lines – corrected for hydrolysis using volumes of ionization calculated from SUPCRT92.

**Appendix B. Alternative fitting equation**

To avoid the rather tedious pre-calculations of water density and Debye-Hückel slopes necessary in fitting equation (2), the experimental  $V_\phi$  values can alternatively be fitted with an interpolating function using only temperature and molality as input variables. The alternative fitting function took the form:

$$V_\phi = \sum_i a_i \varphi_i(\tau, \mu) \quad (\text{B1})$$

where  $a_i$  are fitting parameters and  $\varphi_i(\tau, \mu)$  are the base functions of reduced temperature,  $\tau = T/1000$ , and the square root of molality  $\mu = \sqrt{m}$ . The fitting parameters (together with their standard errors) and the corresponding base functions are listed in Table B1. Apparent molar volumes (uncorrected for hydrolysis) for both NaOAc(aq) and NaOBz(aq) are represented within  $\pm 0.08 \text{ cm}^3 \cdot \text{mol}^{-1}$  (standard deviation  $\sigma(V_\phi) = 0.04 \text{ cm}^3 \cdot \text{mol}^{-1}$ ), without the formation of artificial local extrema.

**Table 1B.**

Fitting parameters and base function of equation (B1).

$a_i$	$\alpha(a_i)$	$\varphi_i$
<b>Sodium acetate</b>		
11616	386	$\tau^2 \ln \tau$
-6787	140	$1/\tau^2$
6258.3	96.7	$1/(\tau^3 \ln \tau)$
63841	1085	$\tau^2$
-13439	224	$\ln \tau/\tau^2$
-69523	1220	$\ln \tau$
1256	115	$\mu/(t \ln \tau)$
-76.58	8.23	$\mu/\tau^3$
-150.9	15.7	$\mu/(\tau^3 \ln \tau)$
1710	121	$\mu \tau^2/\ln \tau$
-2155	180	$\mu/\ln \tau$
-0.1317	0.0478	$\mu \ln \tau/\tau^2$
33.49	7.95	$\mu \tau^2/\ln \tau$
-67.6	14.3	$\mu \tau^3/\ln \tau$
-34690	999	$\tau \ln(1+\mu)/\ln \tau$
-2825	108	$\ln(1+\mu) \ln \tau/\tau^2$
35807	1042	$\ln(1+\mu)/\tau$

-69861	2454	$\tau^2 \ln(1+\mu) \ln \tau$
28671	838	$\ln(1+\mu)/(\tau \ln \tau)$
-8457	291	$\ln(1+\mu)/\tau^2$

**Sodium benzoate**

-45860	2499	$1/\ln \tau$
-29882	3066	1
57244	2817	$\tau^2/\ln \tau$
-7551	824	$\ln \tau$
151068	5438	$\tau^3 \ln \tau$
22201	1153	$\tau \ln \tau$
-638.2	80.5	$\mu \tau^3 \ln \tau$
7.95	1.50	$\mu^3 \ln \tau$
70.92	5.86	$\mu^3 \tau^3/\ln \tau$
0.1457	0.0337	$\mu^4/\tau^3$
58.07	6.20	$\mu^4 \tau^3$
-63157	3479	$\tau \ln(1+\mu) \ln \tau$
52087	2979	$\ln(1+\mu)/\ln \tau$
-52.27	5.08	$\ln(1+\mu)/\tau^3$
-98170	6319	$\tau^3 \ln(1+\mu) \ln \tau$
368.2	31.5	$\ln(1+\mu)/\tau^2$
-60506	3411	$\tau \ln(1+\mu)/\ln \tau$

**References**

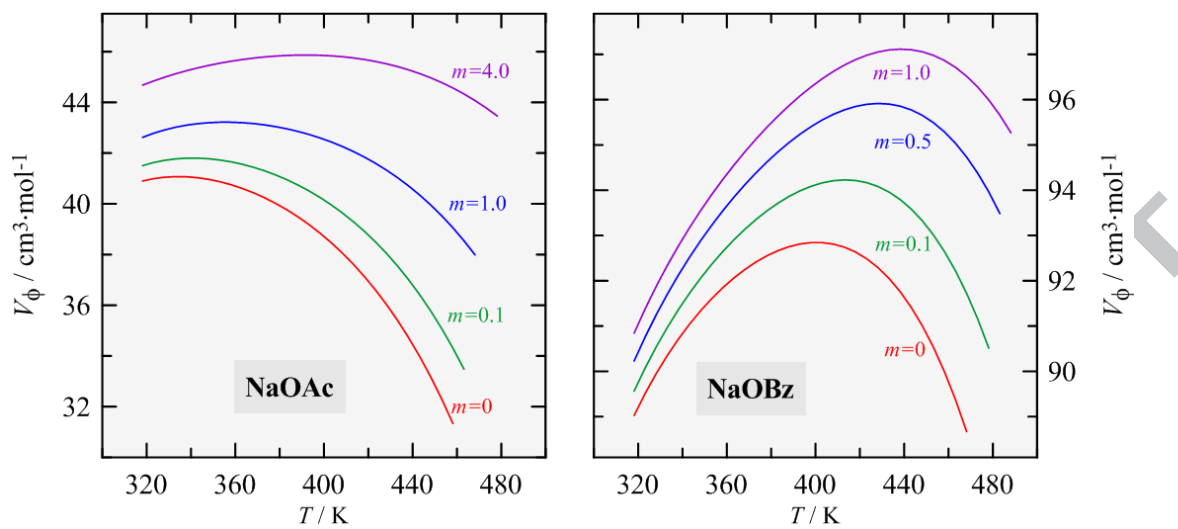
- [1] D.A. Palmer, R. Fernández-Prini, A.H. Harvey (Eds.), *Aqueous Systems at Elevated Temperatures*, Elsevier, Amsterdam, 2004.
- [2] G.T. Hefter, *Molar volumes of electrolyte solutions*, in: E. Wilhelm, T.M. Letcher (Eds.), *Volume Properties: Liquids, Solutions and Vapours*, RSC Publishing, Cambridge, UK, 2015, pp 493–511.
- [3] V. Majer (Ed), *Physicochemical Properties of Water and Aqueous Solutions for Industrial Applications; Extended Abstracts of the IAPWS Annual Symposium*, Paris, 1995.
- [4] L. Hnědkovský, I. Cibulka, *Int. J. Thermophys.* 25 (2004) 387-395.
- [5] N. Sato, A.T. Quitain, K. Kang, H. Daimon, K. Fujie, *Ind. Eng. Chem. Res.* 43 (2004) 3217-3222.
- [6] P. Kritzer, *J. Supercrit. Fluids* 29 (2004) 1-29.
- [7] R.H. Wood, R.W. Carter, J.R. Quint, V. Majer, P.T. Thompson, J.R. Boccio, *J. Chem. Thermodyn.* 26 (1994) 225-249.
- [8] M. Obšil, V. Majer, G.T. Hefter, V. Hynek, *J. Chem. Thermodyn.* 29 (1997) 575-593.
- [9] A.V. Sharygin, R.H. Wood, *J. Chem. Thermodyn.* 29 (1997) 125-148.

- [10] H.R. Corti, J.M. Simonson, *J. Solution Chem.* 35 (2006) 1057-1074.
- [11] L. Hnedkovsky, R.H. Wood, V. Majer, *J. Chem. Thermodyn.* 28 (1996) 125-142.
- [12] I. Cibulka, L. Hnedkovsky, P. Hynčica, *J. Mol. Liq.* 131-132 (2007) 206-215.
- [13] L.K. Hudson, Alumina Production, in: A. R. Burkin (Ed.) *Production of Aluminium and Alumina, Critical Reports on Applied Chemistry*, Wiley, New York, 1987, vol. 20, pp. 11-46.
- [14] T. Machold, E. Macedi, D.W. Laird, P. M. May, G. T. Hefter, *Hydrometallurgy* 99 (2009) 51-57.
- [15] T. Machold, D.W. Laird, C.C. Rowen, P.M. May, G.T. Hefter, *Hydrometallurgy* 107 (2011) 68-73.
- [16] E. Königsberger, G. Eriksson, P.M. May, G.T. Hefter, *Ind. Eng. Chem. Res.* 44 (2005) 5805-5814.
- [17] E. Königsberger, S. Bevis, G.T. Hefter, P.M. May, *J. Chem. Eng. Data* 50 (2005) 1270-1276.
- [18] L. Hnědkovský, E. Königsberger, L.-C. Königsberger, I. Cibulka, S. Schrödle, P.M. May, G.T. Hefter, *J. Chem. Eng. Data* 55 (2010) 1173-1178.
- [19] L. Hnědkovský, E. Königsberger, I. Cibulka, L. Königsberger, S. Schrödle, P.M. May, G. Hefter, *J. Chem. Eng. Data* 52 (2007) 2237-2244.
- [20] A.H. Harvey, E.W. Lemmon, *NIST/ASME Steam Properties, Formulation for General and Scientific Use. NIST Standard Reference Database 10, Version 3.0*, 2013.
- [21] R. Span, E.W. Lemmon, R.T. Jacobsen, W. Wagner, A. Yokozeki, *J. Phys. Chem. Ref. Data* 29 (2000) 1361-1433.
- [22] I. Cibulka, L. Hnedkovsky, P. Hynčica, *J. Mol. Liq.* 131-132 (2007) 206-215.
- [23] J. Koryta, J. Dvořák, L. Kavan, *Principles of Electrochemistry*, Wiley, Chichester, 1993, pp.34-41.
- [24] C.M. Criss, R.H. Wood, *J. Chem. Thermodyn.* 28 (1996) 723-741.
- [25] K. Ballerat-Busserolles, T.D. Ford, T.G. Call, E.M. Woolley, *J. Chem. Thermodyn.* 31 (1999) 741-762.
- [26] G.C. Alfred, E.M. Woolley, *J. Chem. Thermodyn.* 13 (1981) 155-164.
- [27] T.S. Banipal, K. Singh, P.K. Banipal, A.K. Sood, P. Singh, G. Singh, *J. Chem. Eng. Data* 53 (2008) 2758-2765.
- [28] L.E. Strong, M. Bowe, J. White, K. Abi-Selah, *J. Solution Chem.* 23 (1994) 541-560.
- [29] C. Ostiguy, J.C. Ahluwalia, G. Perron, J.E. Desnoyers, *Can. J. Chem.* 55 (1977) 3368-3370.
- [30] T.S. Banipal, N. Guleriaa, B.S. Lark, P.K. Banipal, G. Singh, *Indian J. Chem.* 40A (2001) 275-282.
- [31] G.A. Krestov, N.P. Novosyolov, I.S. Perelygen, A.M. Kolker, L.P. Safonova, V.D. Ovchinnikova, V.N. Trostin, *Ionic Solvation*, Ellis Horwood, New York, 1994.
- [32] L. Hnedkovsky, R.H. Wood, V. Majer, *J. Chem. Thermodyn.* 28 (1996) 125-142.
- [33] J. Jedelský, L. Hnedkovsky, P. Hynčica, I. Cibulka, *J. Chem. Thermodyn.* 32 (2000) 1299-1310.
- [34] R.E. Mesmer, C.S. Patterson, R.H. Busey, and H.F. Holmes, *J. Phys. Chem.* 93 (1989) 7483-7490.



- [35] A.V. Bandura, S. N. Lvov, J. Phys. Chem. Ref. Data 35 (2006) 15-30.
- [36] R. Kettler, D.J. Wesolowski, D.A. Palmer, J. Solution Chem. 24 (1995) 385-406.
- [37] J.W. Johnson, E.H. Oelkers, H.C. Helgeson, Comput. Geosci. 18 (1992) 899-947.

ACCEPTED MANUSCRIPT



**Highlights**

- First measurements on volumes of NaOBz(aq) at high temperatures
- Greatly expanded measurements on volumes of NaOAc(aq) at high temperatures
- Evaluation of standard volumes on NaOAc(aq) and NaOBz(aq)
- Estimation of the standard volumes of neutralization of weak acids with NaOH

ACCEPTED MANUSCRIPT