Association Constant of Acetic Acid in 1.02 m NaCl Aqueous Medium at Elevated Temperatures and Pressures

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The association constant of acetic acid in 1.02 m (NaCl) aqueous solution has been determined potentiometrically at temperatures up to 260 °C and pressures up to 1005 bar. A high-temperature high-pressure concentration cell having two hydrogen electrodes has been used for the measurement. The apparent association constant Q'_{HAC} increases with increasing temperature but decreases with increasing pressure:

$(Q'_{\mathrm{HAC}})_{25\,°\mathrm{C},\,108\,\mathrm{bar}} = 2.86 \cdot 10^4$, $(Q_{\mathrm{HAC}})_{25\,°\mathrm{C},\,500\,\mathrm{bar}} = 2.7 \cdot 10^4$,
$(Q'_{\mathrm{HAC}})_{200\,°\mathrm{C},\,500\,\mathrm{bar}} = 4.65 \cdot 10^4$, $(Q'_{\mathrm{HAC}})_{260\,°\mathrm{C},\,1005\,\mathrm{bar}} = 6.57 \cdot 10^4\ \mathrm{m}^{-1}$.

The knowledge of the association constant of acetic acid at elevated temperatures and pressures is necessary for the calculation of acetate/acetic acid buffer systems under the corresponding conditions.

Only data from conductivity measurements for diluted acetic acid in water are found in the literature for high temperatures and pressures [1–3] as well as data for high ionic strength media at atmospheric pressure and normal temperatures [4–6].

We have determined the acetic acid association constant at temperatures up to 260 °C and argon gas pressures up to 1005 bar in a 1.02 m NaCl medium by means of potential measurements on the cell

$$\mathrm{Pt,\ H_2} \left| \begin{array}{c} \mathrm{solu}_2: \\ [\mathrm{Ac^-}],\ [\mathrm{H^+}]_2 \\ \mathrm{NaCl} \\ \text{(sample)} \end{array} \right\| \begin{array}{c} \text{intermediate} \\ \text{electrolyte} \\ \mathrm{NaCl} \end{array} \left\| \begin{array}{c} \mathrm{solu}_1: \\ [\mathrm{H^+}]_1 \\ \mathrm{NaCl} \\ \text{(reference)} \end{array} \right| \mathrm{H_2,\ Pt} \qquad (1)$$

1. Experimental

The apparatus and the general experimental conditions and procedures have been described previously [7–9]. Suprapure grade NaCl (MERCK) has been used along with p.a. grade HCl, CH_3COOH (HAC), and $NaCH_3COO$ (NaAc) for the preparation of the solutions.

The reference compartement was filled with 0.01019 m HCl and 1.00981 m NaCl solution in all cases.

Sample solutions of two different compositions have been used to investigate the association equilibrium of acetic acid, containing 0.01019 m HAc and 1.00981 m NaCl in one case (see Table 2) and an analytical ratio of acetate to hydrogen ions of 2 : 1 in the other case (see Table 1) represented by 0.01019 m NaAc and 0.005095 m HCl as well as 1.003715 m NaCl to establish the desired ionic strength.

1.02 m NaCl was used as intermediate electrolyte as in the former experiments.

The air in the high pressure cell was replaced by repeated pressurization with pure hydrogen to 40 bar, and argon gas (special Argon, Linde; 0.1 vpm oxygen) was used to establish the desired higher pressures. Measurements were made by continuously increasing the temperature (0.5 °C min^{-1}) after initial stabilization of the electrode potentials (overnight).

2. Results and Discussion

The experimental results are listed in Tables 1–2. Making the same assumptions as before [8] and considering complete dissociation of HCl and NaAc

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Table 1. EMF of Cell (1) and the apparent Association Constants of HAc.

T (°C)	P [a] (bar)	ΔE [b] (mV)	E_j (mV)	[HAc] (10^{-3} m)	$10^{-3}\,Q'_{\mathrm{HAc}}$ (m^{-1})	P [a] (bar)	ΔE [b,d] (mV)	[HAc] (10^{-3} m)	$10^{-3}\,Q'_{\mathrm{HAc}}$ [c] (m^{-1})
25	108	145.54	0.639	5.0604	28.60	199	145.32	5.0601	28.36
30	109	147.96	0.622	5.0604	28.55	201	147.29	5.0595	27.82
40	111	152.17	0.593	5.0594	27.79	207	151.42	5.0584	27.02
50	114	156.55	0.576	5.0588	27.27	213	155.79	5.0578	26.53
60	116	161.33	0.542	5.0586	27.16	219	160.52	5.0576	26.39
70	119	166.60	0.518	5.0591	27.52	224	165.60	5.0579	26.60
80	122	172.18	0.499	5.0599	28.16	230	171.00	5.0585	27.08
90	125	178.08	0.481	5.0610	29.08	233	176.52	5.0593	27.65
100	128	184.27	0.468	5.0623	30.26	242	182.54	5.0605	28.66
110	131	190.47	0.454	5.0635	31.43	249	188.56	5.0616	29.64
120	133	197.05	0.441	5.0649	32.95	255	194.83	5.0629	30.84
130	137	203.99	0.430	5.0665	34.83	262	201.50	5.0644	32.40
140	140	210.99	0.420	5.0680	36.78	268	208.60	5.0662	34.37
150	143	218.37	0.410	5.0696	39.15	275	215.81	5.0678	36.47
160	148	226.06	0.400	5.0713	41.90	282	223.13	5.0694	38.71
170	151	233.90	0.391	5.0729	44.88	289	230.93	5.0711	41.49
180	155	242.10	0.383	5.0744	48.38	297	238.75	5.0733	44.37
190	160	249.50	0.374	5.0755	50.93				
200	164	257.85	0.365	5.0768	54.78				
210	169	266.13	0.355	5.0780	58.63				
220	174	275.13	0.346	5.0794	63.66				
230	180	284.60	0.337	5.0807	69.65				

[a] $p\,(H_2+Ar)$. Probable error ± 3 bar.
[b] Probable error ± 0.1 mV.
[c] Probable error ± 3%.
[d] E_j values are the same as in the left data series.

Table 2. EMF of Cell (1) and Apparent Association Constants of HAc.

T (°C)	p [a] (bar)	ΔE [b] (mV)	E_j (mV)	[HAc] (10^{-3} m)	$10^{-3}\,Q'_{\mathrm{HAc}}$ [c] (m^{-1})	p [a] (bar)	ΔE (mV)	E_j (mV)	[HAc] (10^{-3} m)	$10^{-3}\,Q'_{\mathrm{HAc}}$ (m^{-1})
20	202	72.18	0.624	9.619	29.5	499	72.33	0.614	9.594	27.0
25	205	72.94	0.614	9.608	28.3	507	73.26	0.598	9.587	26.3
30	208	73.87	0.599	9.600	27.6	523	75.23	0.575	9.575	25.4
40	214	75.99	0.575	9.593	26.9	541	77.40	0.585	9.570	24.9
50	220	78.21	0.562	9.587	26.4	558	79.68	0.534	9.566	24.6
60	226	80.47	0.534	9.583	26.0	576	82.18	0.516	9.568	24.7
70	232	83.03	0.516	9.585	26.2	594	84.71	0.501	9.570	24.9
80	239	85.66	0.502	9.589	26.6	613	87.32	0.487	9.574	25.2
90	245	88.60	0.488	9.598	27.4	632	90.06	0.477	9.579	25.7
100	252	91.51	0.479	9.606	28.2	651	92.78	0.468	9.585	26.2
110	258	94.60	0.470	9.617	29.3	669	95.73	0.460	9.594	27.0
120	265	97.62	0.461	9.626	30.3	688	98.93	0.453	9.606	28.2
130	271	101.17	0.455	9.643	32.2	707	102.09	0.446	9.618	29.4
140	278	104.57	0.448	9.656	33.9	727	105.32	0.441	9.629	30.6
150	285	108.32	0.442	9.673	36.3	747	108.78	0.433	9.643	32.3
160	291	111.96	0.435	9.688	38.4	768	112.42	0.428	9.659	34.3
170	299	115.62	0.430	9.702	40.7	790	115.76	0.423	9.670	35.7
180	306	119.40	0.425	9.716	43.2	811	119.02	0.416	9.678	37.0
190	314	123.45	0.419	9.732	46.5	835	122.90	0.411	9.694	39.5
200	321	127.29	0.413	9.745	49.2	860	126.57	0.404	9.707	41.6
210	329	131.37	0.407	9.759	52.7	886	130.75	0.399	9.724	44.8
220	338	135.71	0.401	9.775	56.9	911	135.06	0.394	9.74	48.5
230	347	140.78	0.396	9.797	63.4	940	139.94	0.391	9.76	53.6
240						971	145.06	0.387	9.78	59.7
250						1005	149.99	0.384	9.80	65.7
260										

[a] $p\,(H_2+Ar)$. Probable error ± 3 bar. [b] Probable error ± 0.1 mV. [c] Probable error ± 6%.

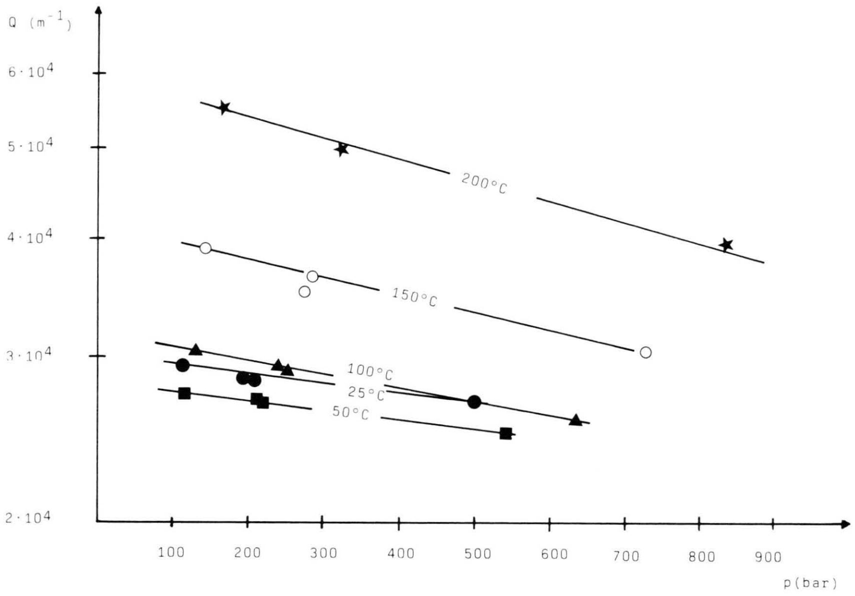

Fig. 1. The association constant of acetic acid as a function of pressure at different temperatures.

the following equations apply to the acetate/acetic acid system:

$$\Delta E = \frac{RT}{f} \ln \frac{[\mathrm{H}^+]_1}{[\mathrm{H}^+]_2} - E_j \,. \tag{2}$$

The concentration of undissociated acetic acid is given by

$$[\mathrm{HAc}] = m_{\mathrm{HCl},2} - [\mathrm{H}^+]_2 \,. \tag{3}$$

The correction of $[\mathrm{H}^+]_2$ by subtracting the amount of the free hydrogen ions generated from the dissociation of water could be neglected for the same reasons as before in both experimental series [8–11].

Mass balance then yields for the concentration of free acetate ions

$$\begin{aligned}[\mathrm{Ac}^-] &= m_{\mathrm{NaAc}} - [\mathrm{HAc}] \\ &= m_{\mathrm{NaAc}} - m_{\mathrm{HCl},2} + [\mathrm{H}^+]_2 \,. \end{aligned} \tag{4}$$

The acetic acid association constant

$$Q'_{\mathrm{HAc}} = \frac{[\mathrm{HAc}]}{[\mathrm{Ac}^-]\,[\mathrm{H}^+]_2} \tag{5}$$

may therefore be calculated from the measured potentials by the equation

$$Q'_{\mathrm{HAc}} = \frac{m_{\mathrm{HCl},2} - m_{\mathrm{HCl},1} \cdot \exp\left[-(\Delta E + E_j) \cdot f/RT\right]}{m_{\mathrm{HCl},1} \cdot \exp\left[-(\Delta E + E_j) \cdot f/RT\right] \{m_{\mathrm{NaAc}} - m_{\mathrm{HCl},2} + m_{\mathrm{HCl},1} \cdot \exp\left[-(\Delta E + E_j) \cdot f/RT\right]\}} \,, \tag{6}$$

where: f = Faraday's Constant, 96,485 C mol^{-1} and
R = Gas Constant, 8.315 J mol^{-1} K^{-1}.

The junction potentials E_j were calculated from the Henderson equation as described before [8], using stoichiometric concentrations (molalities) and limiting equivalent conductances $\lambda^0(\mathrm{i})$ as given by Quist and Marshall [12]. $\lambda^0(\mathrm{Ac}^-)$ values were extrapolated from the literature data at 18 °C and 25 °C. The error expected from such an extrapolation is negligible because the contribution of acetate ion to E_j is small [8, 9].

A Q'_{HAc} value of $3 \cdot 10^4$ m^{-1} is obtained from the extrapolation of the graph at 25 °C in Fig. 1 to 1 bar. This value is about 10% lower than that given by Ellilä [6] for 1 m NaCl medium ($3.3 \cdot 10^4$). Patterson and Mesmer [13] determined the dissociation quotient of acetic acid in 1 molal NaCl medium up to 300 °C but only at pressures along the saturation curves at the corresponding temperatures. Their work yields the values $3.1 \cdot 10^4$, $3.3 \cdot 10^4$, $4.3 \cdot 10^4$ and $6.3 \cdot 10^4$ m^{-1} for the apparent association constants at 25, 100, 150 and 200 °C respectively. The extrapolation of our plots to the corresponding saturation pressures yields values which are 3 to 5% lower than those of Patterson and Mesmer. This small deviation towards lower values may be related to the use of argon as pressurizing medium in our experiments. This may change slightly the dielectric constant ε of the solvent, where a small increase of ε has to be expected. Such relative increase may be due to the moderation of the ε lowering electrostatic interaction between the Na^+ and Cl^- ions and the water dipols resulting from the dissolved inert gas.

Figure 1 shows that Q'_{HAc} increases with rising temperature but decreases with increasing pressure. That is quite in agreement with the expected behaviour considering an electrostatical model of the association, since the dielectric constant ε varies in the opposite direction and electrolyte systems tend to generate more charged species with increasing pressure and so to increase the electrostriction as a contribution to volume reduction.

However, this simple electrostatical model does not apply alone for the protonation of the acetate anion. This is underlined by the fact that the Q'_{HAc} values at 50 °C are lower than those at 25 °C and the graph for 25 °C intersects that for 100 °C at $p = 500$ bar. Also the values of the association constant of acetic acid as a function of temperature (0–50 °C) at atmospheric pressure and infinite dilution show a minimum at 25 °C [14]. Unfortunately there are no values in the work of Patterson and Mesmer [13] between 25 and 100 °C. Also the measurements of Ellilä [6] did not exceed 40 °C. However, a plot of his values (calculated as association constants) vs. temperature shows a decrease with rising temperature and a zero slope at 40 °C, so that a minimum around 50 °C is probable.

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