

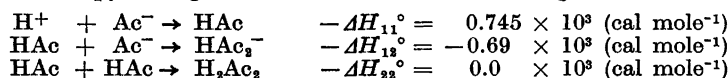
Thermochemical Studies on Metal Complexes

IV. Free Energy, Enthalpy, and Entropy Changes of Proton Acetate Complexes in Aqueous Solution

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The proton acetate system has been studied calorimetrically, and the enthalpy changes determined for the following reactions:



From these enthalpy changes and the changes in free energy, computed from reported stability constants, the entropy changes have been calculated. Only the first reaction investigated is found to be entropy stabilized. The investigation was performed in an aqueous sodium perchlorate medium of ionic strength 3.00 M and a temperature of 25.00°C, but a comparison with other ionic strengths and media is made.

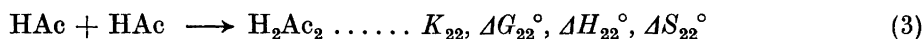
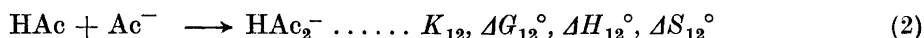
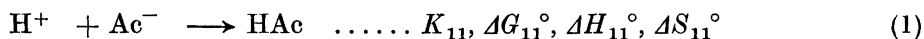
A very interesting problem when using acetate buffers in measurements of metal acetate complexes is the complex formation of the proton acetate system itself. The partial dimerization of acetic acid in aqueous solutions has been established by a variety of experimental investigations, using cryoscopic methods,¹ vapor pressure measurements,² distribution procedures,³ potentiometric measurements,⁴ and Raman spectra studies.⁵ The potentiometric method used by Rossotti *et al.*,^{6,7} Grenthe and Williams,⁸ and Persson⁹ on the proton acetate system indicated also association between HAc—Ac⁻. Three complex species, HAc, HAc₂⁻, and H₂Ac₂, are thus assumed, although variations in liquid junction potentials and activity coefficients complicate the interpretation of the experimental results.

As a complement to the equilibrium measurements calorimetric methods may be used. Schlyter and Martin¹⁰ report enthalpy values of formation for all three species* but Wadsö¹¹ could not find any effect caused by the dimeric

* For the proton acetate system Schlyter and Martin¹⁰ report the following enthalpy changes: $-\Delta H_{11}^\circ = 0.72 \times 10^3 \text{ (cal mole}^{-1}\text{)}$, $-\Delta H_{12}^\circ = -0.30 \times 10^3 \text{ (cal mole}^{-1}\text{)}$, and $-\Delta H_{22}^\circ = -0.43 \times 10^3 \text{ (cal mole}^{-1}\text{)}$.

form. In connection with calorimetric measurements of metal acetate systems¹² some results were obtained and are reported in this paper.

The symbols and equations used are mainly those defined in Ref. 13. For the three reactions studied the indices of the thermodynamic constants are following:



The following values of stability constants reported by Persson⁹ in an aqueous sodium perchlorate medium of ionic strength 3.00 M at 25.0°C are used in this investigation:

$$K_{11} = (1.035 \pm 0.015) \times 10^5 \text{ (M}^{-1}\text{)}$$

$$K_{12} = 0.28 \pm 0.04 \text{ (M}^{-1}\text{)}$$

$$K_{22} = 0.05 \pm 0.02 \text{ (M}^{-1}\text{)}$$

EXPERIMENTAL

Chemicals

Sodium perchlorate was prepared according to Ref. 13 and the dried salt was analyzed by a cation exchange procedure. Tests showed no chloride or chlorate ions. Titrations with acid gave a total concentration of weak protolytes less than 5×10^{-5} moles per mole sodium perchlorate. This impurity was neglected. The ionic medium was maintained in all solutions used by adding weighed amounts of this salt.

The acetate buffers used were prepared from sodium acetate, NaAc·3H₂O (Merck, *p.a.*) and 99.5 % acetic acid (Merck, *p.a.*) and analyzed by potentiometric titrations on acetic acid and acetate with sodium hydroxide and perchloric acid, respectively.

Procedure

The calorimeter used was that described in a previous paper.¹⁴ The measurements of the reaction heats were performed by titration series on a calorimeter solution, S, of 100.0 ml with additions of known amounts of a titration solution, T. The heat evolved at each addition was measured and each series was repeated at least once. To determine the dilution heats series with only one of the two reacting components present were performed.

All measurements were carried out at a temperature of 25.00°C and, except some dilution experiments, in an aqueous sodium perchlorate medium of ionic strength 3.00 M, which was chosen as the standard state for these measurements.

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MEASUREMENTS AND RESULTS

The electrical calibrations¹⁴ gave a linear dependence of the heat equivalent upon the total amount of titrant added, the relations being given by the eqns.:

$$- \varepsilon_v = 2.084 + 0.0197 v \quad (4)$$

$$- \varepsilon_v = 2.129 + 0.0198 v \quad (5)$$

Eqns. (4) and (5) are valid for additions with a 2 ml and a 5 ml pipette, respectively. The accuracy is better than $\pm 5 \times 10^{-3}$ cal ohm⁻¹ in the range $0 < v < 30$. No differences were observed between systems with various buffers.

$H^+ + Ac^- \rightarrow HAc$. For this reaction the enthalpy change was determined from titration series of solutions with the compositions:



The dilution heats of the acid were determined by adding T into 3.000 M NaClO₄ while the dilution heats of the acetate were neglected. The experimental data of v , Q_x , and Q_{dil} are given in Table 1 together with calculated values of

Table 1. The reaction heats, Q_x , and the dilution heats, Q_{dil} , obtained at the titrations of Ac^- with H^+ tabulated together with the corrected values, Q_{react} , the calculated values of total amount HAc formed at each addition, a , and the formation heats, $-\Delta H_{11}^\circ$. The given values of Q_x and Q_{dil} are averages of two series.

Series type	v (ml)	Q_x (cal)	Q_{dil} (cal)	Q_{react} (cal)	$a \times 10^3$ (mole)	$-\Delta H_{11}^\circ \times 10^{-3}$ (cal mole ⁻¹)
I	2.009	1.568	0.074	1.517	2.009	0.755
	4.018	1.544	0.045	1.519	2.009	0.756
	6.027	1.532	0.040	1.497	2.008	0.745
	8.036	1.510	0.036	1.466	2.007	0.730
II	5.023	0.963	0.033	0.930	1.255	0.741
	10.045	0.962	0.033	0.929	1.251	0.743

$-\Delta H_{11}^\circ$. Titrations of type I were carried out with $C_A = 0.120$ (M), $C_H = 1.000$ (M), and the additions 2.009 ml. The effect of the formation of HAc_2^- and H_2Ac_2 could not be neglected if the equilibrium constants reported ^{6,7,9} are reliable, and corrections were performed for this as for the hydrolysis of Ac^- . Q_{react} is the heat obtained after all corrections mentioned. From Q_{react} and a , the total amount of HAc formed at each addition, $-\Delta H_{11}^\circ$ is calculated. In titrations of type II, $C_A = 0.030$ (M), $C_H = 0.250$ (M), and the additions 5.023 ml, and in this instance all corrections, except for the dilution heats of the acid, could be neglected. The enthalpy values obtained at the different concentrations agreed within the calculated errors (see Table 1).

The found average value of $-\Delta H_{11}^\circ$, $(0.745 \pm 0.009) \times 10^3$ (cal mole⁻¹), is 3 % larger than that of Schlyter and Martin ¹⁰ and 3 % smaller than a value found by Hansson ¹⁵ (see Table 7), but the first one may be affected by a systematic error in the calibration ¹⁶ and the second by random errors due to small reaction heats. ¹⁵

$HAc + Ac^- \rightarrow HAc_2^-$. The formation of HAc_2^- , if it exists, is favoured by high concentrations of acetic acid and acetate ions. By diluting following buffers, T, of different compositions into 3 M NaClO₄



Table 2. The reaction heats, Q_X , for the additions of 2.009 ml acetate buffer into 100.0 ml 3.000 M NaClO_4 . The given values of Q_X are averages of two series. $C_A = 1.500$ (M) and $C_{\text{NaClO}_4} = 1.500$ (M) in the T solutions.

v (ml)	Q_X (cal)				
	$C_{\text{HA}} = 0$	$C_{\text{HA}} = 0.15$	$C_{\text{HA}} = 0.5$	$C_{\text{HA}} = 1.5$	$C_{\text{HA}} = 3$
2.009	-0.156	-0.066	0.068	0.545	1.470
4.018	-0.162	-0.069	0.064	0.527	1.412
6.027	-0.153	-0.058	0.053	0.518	1.343
8.036	-0.152	-0.073	0.052	0.495	1.297
10.045	-0.132	-0.070	0.049	0.481	1.259
	-0.148	-0.063	0.041	0.479	1.218

Table 3. The dilution heats, Q_{dil} , for the additions of 2.009 ml acetic acid solution into 100.0 ml 3.000 M NaClO_4 . The given values of Q_X are averages of two series. $C_{\text{NaClO}_4} = 3.000$ (M) in the T solutions.

v (ml)	Q_{dil} (cal)			
	$C_{\text{HA}} = 0.5$	$C_{\text{HA}} = 1$	$C_{\text{HA}} = 2$	$C_{\text{HA}} = 3$
2.009	0.001	0.070	0.379	0.854
4.018	-0.002	0.066	0.370	0.828
6.027	0.002	0.071	0.396	0.793
8.036	0.000	0.057	0.379	0.776
10.045	0.004	0.058	0.377	0.742
	0.001	0.052	0.357	0.714

Table 4. The reaction heats, Q_X , for the additions of 2.009 ml acetate buffer into 100.0 ml 3.000 M NaClO_4 . The given values of Q_X are averages of two series. $C_A = 1.000$ (M) and $C_{\text{NaClO}_4} = 2.000$ (M) in the T solutions.

v (ml)	Q_X (cal)	
	$C_{\text{HA}} = 0$	$C_{\text{HA}} = 1$
2.009	-0.030	0.288
4.018	-0.032	0.289
6.027	-0.039	0.267
8.036	-0.029	0.255
10.045	-0.022	0.256
	-0.025	0.242

and correcting for the dilution heats of Ac^- and HAc it is possible to derive reaction heats which mainly can be assigned to the dissociation of that species. In T, C_A was first fixed to 1.500 (M) and C_{HA} varied from 0 to 3 (M). Then C_A was 0 (M) and the dilution heats obtained for different C_{HA} are related to

Table 5. Corresponding values of $Q_{\text{react.}}$, amounts of HAc_2^- dissociated, b , and $-\Delta H_{12}^\circ$. The values of C_A and C_{HA} for each buffer used are also given.

C_A (M)	C_{HA} (M)	$Q_{\text{react.}}$ (cal)	$b \times 10^3$ (mole)	$-\Delta H_{12}^\circ \times 10^{-3}$ (cal mole $^{-1}$)
1.500	0.500	0.192	0.271	0.708
1.500	1.000	0.338	0.496	0.681
1.500	2.000	0.568	0.844	0.673
1.500	3.000	0.741	1.095	0.677
1.000	1.000	0.248	0.355	0.697

the dilution of HAc and the dissociation of H_2Ac_2 . The experimental data are collected in Tables 2 and 3. The values in Figs. 1 and 2 were obtained by extrapolations of the measured series to infinite dilution of the final buffer concentrations. From Fig. 1 it may be seen that the dilution heat of Ac^- found at $C_{\text{HA}} = 0(\text{M})$ (-0.156 cal) does not exactly coincide with the value, which can be extrapolated from a curve drawn through points, where $C_{\text{HA}} \neq 0$. This extrapolated value (-0.125 cal) was used as the dilution heat of acetate ions in the buffers above. In Table 5 the values of $Q_{\text{react.}}$ obtained after corrections for dilution of HAc and Ac^- are collected (see also Fig. 3) and $-\Delta H_{12}^\circ$ was calculated by use of the assumed stability constants. To check the value obtained, series with $C_A = C_{\text{HA}} = 1.000$ (M) were measured, and dilution heats of HAc and Ac^- determined at this concentration (see Tables 3 and 4). The experimental value found here agreed with the previous one (see Table 5) and $-\Delta H_{12}^\circ$ is determined to $-(0.69 \pm 0.07) \times 10^3$ (cal mole $^{-1}$).

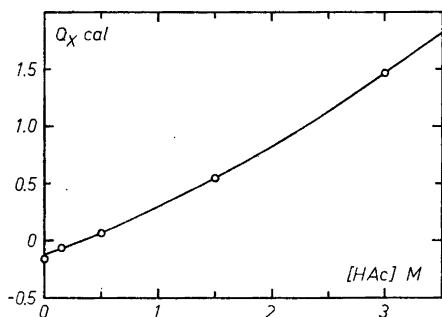


Fig. 1. The extrapolated reaction heats for the additions of 2.009 ml acetate buffer into 3.000 M NaClO_4 at different concentrations of C_{HA} . $C_A = 1.500$ (M) and $C_{\text{NaClO}_4} = 1.500$ (M) in the T solutions.

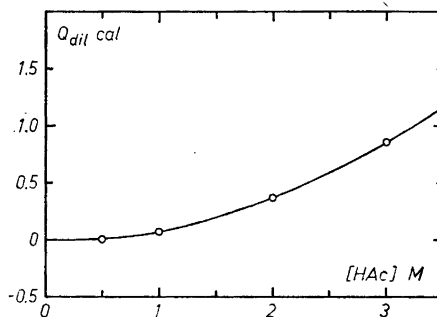


Fig. 2. The extrapolated dilution heats for the additions of 2.009 ml acetic acid solution into 3.000 M NaClO_4 at different concentrations of C_{HA} . $C_{\text{NaClO}_4} = 3.000$ (M) in the T solutions.

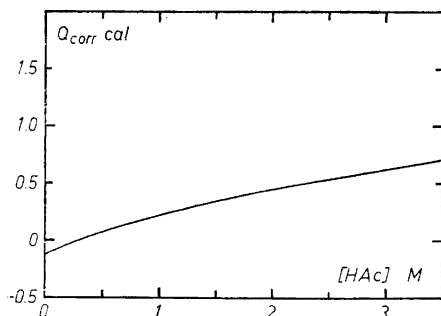


Fig. 3. The differences between the extrapolated values of reaction heats and dilution heats for the additions of 2.009 ml acetate buffer and acetic acid solution, respectively, into 3.000 M NaClO₄ at different concentrations of C_{HA}.

$HAc + HAc \rightarrow H_2Ac_2$. The method used to determine ΔH_{12}° was designed to avoid the effect of the heat of dissociation of H_2Ac_2 . It is difficult to separate this heat of dissociation from the heat of dilution of HAc. The value given by Schlyter and Martin¹⁰ must be considered as a maximum value, which is confirmed by the results reported here. Wadsö¹¹ reported that he did not find any effect from the dissociation of this species, and he concluded that the dimerization heat of acetic acid in water solution is very small — or that the dimerization is not as extensive as has been reported. Measurements at various temperatures also indicate a value of $\Delta H_{22}^\circ \approx 0.3$.

Change of ionic strength. To check the effect of variations in ionic strength, dilutions of acetate buffers of ionic strength 3.000 M into 3.000 M NaClO₄ and 2.500 M NaClO₄, respectively, were performed (see Table 6). The differences are much larger than if 3.000 M NaClO₄ is diluted into 2.500 M NaClO₄ and not even the sign is the same. However, this may be explained by the change in ΔH_{11}° with ionic strength found by Hansson¹⁵ (see Table 7).

Table 6. The dilution heats, Q_{dil} , for the additions of 2.009 ml 3.000 M NaClO₄ and some acetate buffers of ionic strength 3.000 M into 3.000 M NaClO₄ and into 2.500 M NaClO₄.

T solution	v (ml)	Q_{dil} (cal)		ΔQ_{dil} (cal)
		$C_{NaClO_4} = 3.0$	$C_{NaClO_4} = 2.5$	
$C_{NaClO_4} = 3.0$	2.009	0.003	-0.087	-0.090
	4.018	-0.009	-0.102	-0.093
$C_A = 1.5, C_{HA} = 0.15$	2.009	-0.053	0.431	0.484
	4.018	-0.045	0.422	0.467
$C_A = 1.5, C_{HA} = 1.5$	2.009	0.543	1.015	0.472
	4.018	0.530	0.970	0.440
$C_A = 3.0, C_{HA} = 1.0$	2.009	0.331	1.437	1.106
	4.018	0.281	1.414	1.133

Table 7. The $-\Delta H_{11}^{\circ}$ -values in different ionic strengths and ionic media.

Ionic strength	$-\Delta H_{11}^{\circ} \times 10^{-3}$ (cal mole ⁻¹)			
	Ref. 15 NaClO ₄	Ref. 15 NaCl	Ref. 11 NaCl	Ref. 17 NaCl
3.000	0.77	1.49		
1.000	0.36	0.63		
0.500	0.22	0.45		
0.300	0.14	0.23		
0.200			0.18	
0.100				0.09

Table 8. The formation constants used and the calculated values of free energy, enthalpy, and entropy changes for the proton acetate system.

Reaction	K (M ⁻¹)	$-\Delta G^{\circ} \times 10^{-3}$ (cal mole ⁻¹)	$-\Delta H^{\circ} \times 10^{-3}$ (cal mole ⁻¹)	ΔS° (cal mole ⁻¹ degree ⁻¹)
H ⁺ + Ac ⁻ → HAc	$(1.035 \pm 0.015) \times 10^5$	6.84 ± 0.01	0.745 ± 0.009	20.3 ± 0.1
HAc + Ac ⁻ → HAc ₂ ⁻	0.28 ± 0.04	-0.75 ± 0.09	-0.69 ± 0.07	-0.2 ± 0.4
HAc + HAc → H ₂ Ac ₂	0.05 ± 0.02	-1.77 ± 0.30	-0.0 ± 0.4	-5.7 ± 1.7

DISCUSSION

For the formation of HAc the enthalpy change has been determined in the medium used with a high degree of accuracy. The value obtained agrees on the whole with earlier results^{10,15} and the small differences existing can be explained.

The enthalpy changes of the two other reactions assumed to take place are more difficult to determine. If the most probable values of formation constants given in the literature^{6,7,9} are chosen, a good fit with the experimental data is found and the formation heat of HAc₂⁻ can be calculated — ΔH_{12}° stays within the limits given above for all $|\Delta H_{22}^{\circ}| < 0.4$ (cal mole⁻¹) — and that of H₂Ac₂ may be estimated to zero (see also Davies *et al.*³ and Wadsö¹¹). The experimental data could not be explained if quite different sets of formation constants than those stated were used.

Variations in the ionic strength of acetate buffers cause surprisingly high reaction heats. This may be accounted for by the variation with ionic strength of the formation heat of HAc found by Wadsö,¹¹ Hansson,¹⁵ and Nelander¹⁷ (see Table 7). The enthalpy value depends both on the ionic strength and the medium used.

Only the first of the reactions investigated is found to be entropy stabilized, while the other two have low or negative entropy values (see Table 8). This would indicate, as the stability constants already do, that: *a*, the last two reactions are uniform and quite different to the first one *b*, this system in

contrast to the metal acetate systems investigated previously (see the lanthanoid acetates studied by Grenthe¹⁸ and the copper(II), zinc(II), cadmium(II), and lead(II) acetates studied by the present author¹²) cannot be formed by similar, consecutive, stepwise reactions. Even if the proton may be considered as a small metal ion surrounded by a sphere of water only the first acetate ion can be firmly bound during a release of several water molecules causing a high entropy change.

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