

## Heats of ionization of acetic acid and halogen-acetic acids in water–ethanol and water–dimethyl formamide mixtures <sup>α</sup>

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(Received 13 August 1990)

### Abstract

The heats of ionization of acetic, chloroacetic, bromoacetic and iodoacetic acids at 6 temperatures from 20 to 45 °C, those of acetic acid in eleven water–ethanol mixtures and those of acetic acid in nine water–dimethyl formamide mixtures, all at 20 °C, were determined in an LKB bioactivity monitor.

### INTRODUCTION

The dissolution of solutes in solvents depends very strongly upon the nature of both the solutes and solvents. In polar solvents, particularly in water, weak electrolytes, such as organic acids, are dispersed as molecules and ions, coexisting by ionization and combination. But with mixed solvents containing water, the ratio between molecules and ions changes significantly with decreasing water content in the mixed solvent. The heats of ionization of these organic acids were determined calorimetrically in order to gain some understanding of the interactions between solute species and solvent molecules.

In a previous study, the heats of ionization of benzoic acid and nine mono-substituted benzoic acids in water–ethanol mixtures were measured [1]. Their ionization constants at ambient temperatures are comparable to that of acetic acid, a typical weak organic acid. The work is continued in the present study with the calorimetric measurements of the heats of ionization of acetic acid and halogen-acetic acids in water at several temperatures, and of acetic acid in water–ethanol and water–dimethyl formamide mixtures.

### EXPERIMENTAL AND RESULTS

The heats of ionization of acetic acid and three mono-substituted halogen-acetic acids (chloro-, bromo- and iodo-) were calculated indirectly from

<sup>α</sup> Paper presented at the Second Japan–China Joint Symposium on Calorimetry and Thermal Analysis, 30 May–1 June 1990, Osaka, Japan.

the heats of liberation of these acids from the corresponding sodium salt solutions measured in an LKB Bioactivity Monitor (calorimeter). The temperature dependence (at 5 °C increments from 20 to 45 °C) of the heats of ionization of these four acids in pure water were studied. The influence of mixed solvents, eleven water–ethanol mixtures (at 10% increments from 0% to 80%, and also with 5% and 17% ethanol by volume) and nine water–dimethyl formamide mixtures (at 10% increments from 0% to 80% of dimethyl formamide by volume), on the heat of ionization of acetic acid at 20 °C was also studied.

Appropriate amounts of the acid samples were neutralized with almost sufficient amounts of sodium hydroxide in order to prepare the required sodium salt solution ( $C_s$ ) in the respective solvents. A perchloric acid solution ( $C_a$ ) was prepared in a similar manner. The two solutions were fed continuously at known rates ( $f_s$  for the salt solution and  $f_a$  for the acid solution) through the mixing cell in the calorimeter to measure the total heat effect ( $W$ ), consisting principally of the heat effect due to the liberation of the acetic acids ( $f_s C_s \Delta H$ ,  $\Delta H$  being the molar heat effect). During mixing, dilution of the salt solution and of the acid solution were invariably involved, their effects ( $Q_s$  for the salt solution and  $Q_a$  for the acid solution) being included in the total effect ( $W$ ). The dilution heat effects were determined independently by mixing the respective solutions with the corresponding solvents. In order to account for any stray heating effects during operation, solvents were mixed to ascertain the necessary corrections. By summing all the measured heat effects, the heats of ionization of the acetic acids ( $\Delta H_i$ ) were calculated as the reversed equivalent of  $\Delta H$

$$W = f_s C_s \Delta H + Q_s + Q_a \quad (1)$$

$$-\Delta H_i = \Delta H = (W - Q_s - Q_a) / f_s C_s \quad (2)$$

Theoretically, the heat of ionization of the acetic acids thus calculated cannot be the total amount but only that part accounted for by the acetate ions which are neutralised, forming acetic acids at equilibrium with the remaining hydrogen and acetate ions. The ionization constants of the acetic acids at the temperatures investigated are quite small, in the order of  $10^{-3}$ – $10^{-5}$  mol l<sup>-1</sup> [2]. Actual calculations showed that the corrections were quite small, warranting little or no adjustment.

These calculated heats of ionization are values at actual concentrations, with ionic interactions incurred. Duplicate runs at five different salt concentrations for each acetic acid at different temperatures, and for pure acetic acid in water–ethanol and water–dimethyl formamide mixtures at 20 °C, were carried out and extrapolated graphically to obtain heats of ionization at infinite dilution ( $\Delta H_i^0$ ) for the acetic acids concerned.

The heats of ionization of acetic acid and the three halogen-acetic acids at infinite dilution at six temperatures are tabulated in Table 1. The heats of

TABLE 1

Heats of ionization of acetic acid and halogen-acetic acids at infinite dilution ( $\text{kJ mol}^{-1}$ )

$t$ ( $^{\circ}\text{C}$ )	$\text{CH}_3\text{COOH}$	$\text{ClCH}_2\text{COOH}$	$\text{BrCH}_2\text{COOH}$	$\text{ICH}_2\text{COOH}$
20	$0.316 \pm 0.015$	$-3.802 \pm 0.049$	$-4.370 \pm 0.070$	$-5.075 \pm 0.090$
25	$-0.436 \pm 0.014$	$-4.630 \pm 0.075$	$-4.905 \pm 0.047$	$-5.570 \pm 0.040$
30	$-1.104 \pm 0.008$	$-5.208 \pm 0.055$	$-5.512 \pm 0.100$	$-6.215 \pm 0.085$
35	$-1.779 \pm 0.007$	$-6.155 \pm 0.013$	$-6.165 \pm 0.025$	$-6.790 \pm 0.039$
40	$-2.468 \pm 0.028$	$-6.850 \pm 0.085$	$-6.850 \pm 0.050$	$-7.455 \pm 0.058$
45	$-4.156 \pm 0.064$	$-7.480 \pm 0.070$	$-7.670 \pm 0.080$	$-8.050 \pm 0.070$

TABLE 2

Heats of ionization of acetic acid in water-ethanol mixtures at infinite dilution at  $20^{\circ}\text{C}$  ( $\text{kJ mol}^{-1}$ )

Wt. %	$x_{\text{EtOH}}$	This work	Ref. 3
0	0	$-0.436 \pm 0.014$	-0.377
5	0.0202	$-0.384 \pm 0.002$	
10	0.0417	$-0.366 \pm 0.012$	-0.711
17	0.0750	$-0.188 \pm 0.008$	-0.418
20	0.0891	$-0.158 \pm 0.004$	-0.460
30	0.144	$-0.156 \pm 0.002$	-0.418
40	0.207	$-0.588 \pm 0.008$	-0.628
50	0.281	$-1.388 \pm 0.014$	-1.674
60	0.370	$-2.537 \pm 0.023$	-2.092
70	0.477	$-3.555 \pm 0.018$	-3.012
80	0.610	$-6.810 \pm 0.110$	-5.188

TABLE 3

Heats of ionization of acetic acid in water-dimethyl formamide mixtures at infinite dilution at  $20^{\circ}\text{C}$  ( $\text{kJ mol}^{-1}$ )

Wt. %	$x_{\text{DMF}}$	This work
0	0	$-0.436 \pm 0.014$
10	0.0256	$0.232 \pm 0.010$
20	0.0559	$0.677 \pm 0.023$
30	0.0921	$1.056 \pm 0.046$
40	0.1364	$1.528 \pm 0.034$
50	0.1915	$2.188 \pm 0.067$
60	0.2621	$3.332 \pm 0.074$
70	0.3559	$5.741 \pm 0.055$
80	0.4865	$9.700 \pm 0.180$

ionization of acetic acid in eleven water–ethanol mixtures at infinite dilution are in fair agreement with those measured by Avedikian and Dollet at 20 °C [3], see Table 2. In a previous study [1], the heats of ionization of benzoic acid in nine water–ethanol mixtures at infinite dilution were also in good agreement with those measured by Avedikian and Dollet at 20 °C [3]. These agreements assure the credibility of all the data obtained. Table 3 shows the heats of ionization of acetic acid in nine water–dimethyl formamide mixtures at infinite dilution at 20 °C.

All reagents were further purified before use. The acetic acid was distilled twice. The halogen-acetic acids were recrystallised twice from anhydrous benzene [4]; no contamination with other acetic acids was detected by NMR analyses. Then dimethyl formamide was treated with 0.5 nm molecular sieves. The purity of the remaining reagents was ascertained by conventional treatments.

## DISCUSSION

The heats of ionization of the four acetic acids at infinite dilution plotted against temperature are shown in Fig. 1. All the heats of ionization, except one for pure acetic acid at 20 °C, are negative values, indicating that the

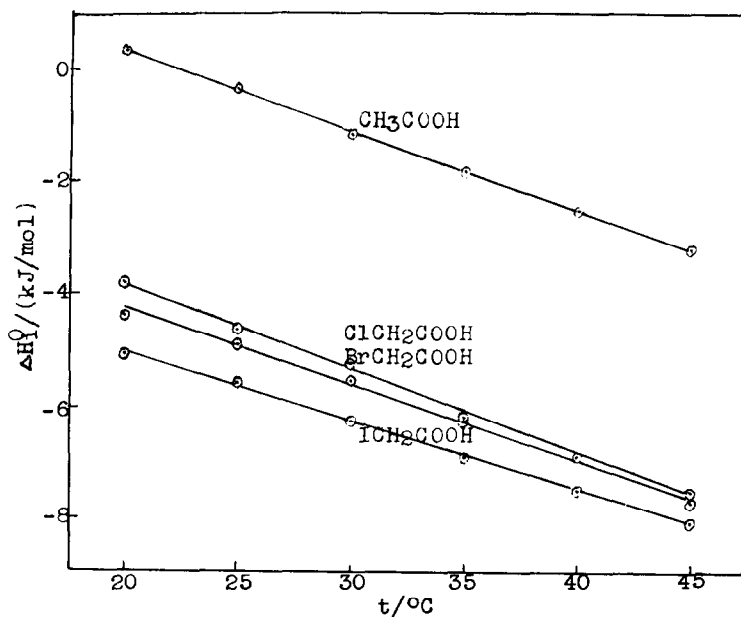


Fig. 1.  $\Delta H_i^0$  of four acetic acids vs. temperature.

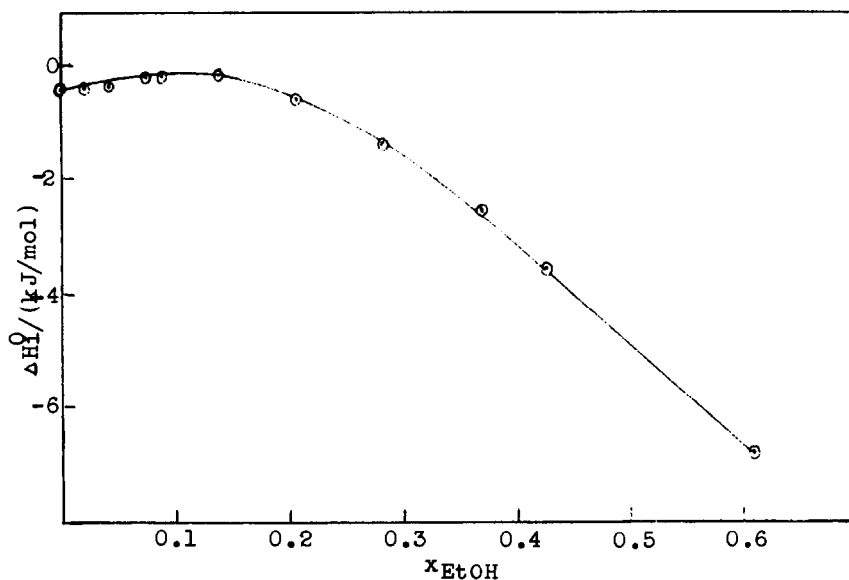


Fig. 2.  $\Delta H_i^0$  of acetic acid vs.  $x_{\text{EtOH}}$ .

ionization reactions are mostly exothermic. The heats of ionization of all four acetic acids at infinite dilution decrease linearly with increase in temperature.

The heats of ionization of acetic acid in water-ethanol mixtures at infinite dilution plotted against mole fractions of ethanol at 20°C and the heats of ionization of acetic acid in water-dimethyl formamide mixtures at infinite

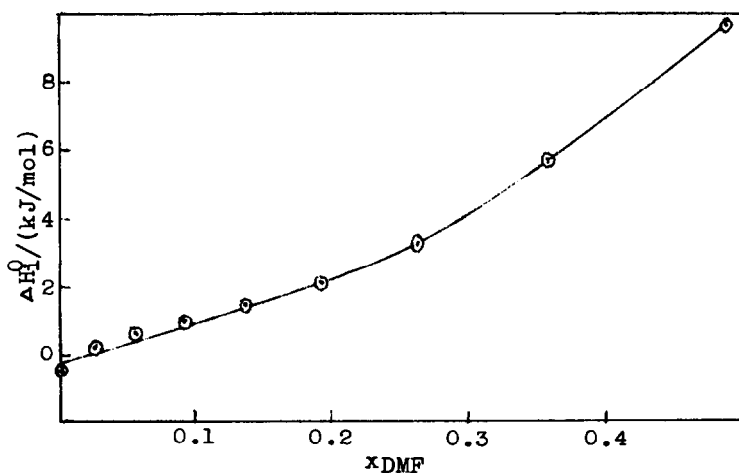


Fig. 3.  $\Delta H_i^0$  of acetic acid vs.  $x_{\text{DMF}}$ .

dilution plotted against mole fractions of dimethyl formamide are shown in Figs. 2 and 3. The heats of ionization in water-ethanol mixtures are all negative, while the heats of ionization in water-dimethyl formamide mixtures are all positive. Those in water-ethanol mixtures increase slightly at first to a maximum in the water-rich region, and then decrease almost linearly with increase in mole fraction of ethanol in the region which is richer in ethanol. Those in water-dimethyl formamide mixtures increase monotonically with increase in mole fraction of dimethyl formamide.

Theoretically, ionization in a vacuum is an endothermic reaction, in which molecules dissociate into co-existing ions. But with ionization in solvents, all solute species interact with solvent molecules, which is generally named solvation. In the case of acetic acids dissolved in water, the heats of ionization at infinite dilution are the sum totals of energy changes due to molecular dissociation and solvation of acetic acid molecules, and of acetate and hydrogen ions. Presuming equivalent solvation energies of acetic acid molecules and acetate ions, negative heats of ionization at infinite dilution may be assumed to be combinations of positive dissociation values and very large negative solvation values of hydrogen ions. Halogen-acetic acid molecules dissociate more than ten times as readily as acetic acid molecules, with ascending order from chlorine to iodine, as generally expected, thus ionizing with much larger negative heat effects because of their smaller positive energies for dissociation.

For the gaseous dissociation of the acetic acid molecule, the energy of dissociation does not change significantly, especially when the range of temperatures involved is quite limited (20–45 °C). The larger negative heats of ionization can be attributed only to the larger negative solvation energies of all solute species at higher temperatures.

In mixed solvents, solute solvation is highly influenced by the solvent media, but molecular dissociation energies remain unchanged if kept at a constant temperature.

In water-ethanol mixtures containing acetic acid, it is appropriate to consider an esterification reaction. Thus, with constant positive dissociation values, the opposing effects of increasing positive values of esterification and increasing negative values of hydrogen ion solvation, therefore, result in a combined increase to a maximum followed by a linear decrease in the region richer in ethanol, possibly indicating stronger solvation by ethanol molecules than by water molecules.

In water-dimethyl formamide mixtures containing acetic acid, with constant positive dissociation values, the ever-increasing values of solvation from very large negative to smaller negative values, make the heats of ionization more and more positive in the region richer in dimethyl formamide. Dimethyl formamide is an interesting solvent; further investigation of its solvent behaviour is desirable.

## REFERENCES

- 1 X. Zhang, Heats of ionization of mono-substituted benzoic acids in water-ethanol mixtures, Ph.D. Dissertation, Zhejiang University, Hangzhou, People's Republic of China, 1988.
- 2 D.H. Evertt and W.F.K. Wynne-Jones, *Trans. Faraday Soc.*, 35 (1939) 1380.
- 3 P.L. Avedikian and N. Dollet, *Bull. Soc. Chim.*, (1967) 4551.
- 4 D.J.G. Ives and J.H. Pryor, *J. Chem. Soc.*, (1955) 2104.