

SOLUTION AND IONIZATION OF SOME CARBOXYLIC ACIDS IN WATER AND DIMETHYL SULFOXIDE

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ABSTRACT

Enthalpy data were obtained for the solution and ionization in water of acetic acid, trifluoro-, dichloro-, and monochloro-acetic acids, benzoic acid and 4-aminobenzoic acid. Single-ion enthalpies of transfer from water to dimethyl sulfoxide were calculated for the carboxylate anions using recent ionization data in Me_2SO and a transfer value for H^+ , $-27.4 \text{ kJ mol}^{-1}$. The transfer processes are increasingly endothermic from CF_3CO_2^- ($+30.9 \text{ kJ mol}^{-1}$) to $\text{CHCl}_2\text{CO}_2^-$ ($+36.5 \text{ kJ mol}^{-1}$), $\text{CH}_2\text{ClCO}_2^-$ ($+49.1 \text{ kJ mol}^{-1}$), and CH_3CO_2^- ($+65.4 \text{ kJ mol}^{-1}$). These values reflect in part the increasingly strong H-bonding interactions of carboxylates with water when passing from CF_3CO_2^- to CH_3CO_2^- . The very poor solvation of CH_3CO_2^- in Me_2SO accounts for the insolubility of glycine, $\text{NH}_3^+ \text{CH}_2\text{CO}_2^-$, in Me_2SO . 4-Aminobenzoic acid is essentially present as the same molecular species in both water and Me_2SO . The ionization data combined with literature data for vaporization or sublimation of the acids and their gas phase ionization yield enthalpy changes for the solvation of the gaseous carboxylate anions. These solvation enthalpies, which vary from -307 kJ mol^{-1} (CF_3CO_2^-) to -356 kJ mol^{-1} (CH_3CO_2^-) in Me_2SO , suggest small effective ionic radii for the carboxylate ions. The radius indicated for CH_3CO_2^- is close to its thermochemical value of 1.59 \AA .

INTRODUCTION

We have recently compared the ionization of sulfonic acids in water and Me_2SO and discussed our results in terms of enthalpies of transfer, from water to Me_2SO , for the proton and sulfonate ions [1]. We have now turned our attention to carboxylic acids, a particularly interesting class of acids because of their importance in the biochemical field. In addition, data are available for the gas phase ionization of these acids [2], so that our solution data will lead to the enthalpies of solvation of gaseous carboxylate ions in both solvents. We have supplemented existing calorimetric data with new

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data for the solution and ionization of carboxylic acids in water. These results are combined with our recently reported solution and ionization enthalpies in Me_2SO [3]. Transfer and solvation enthalpies of single carboxylate ions can then be calculated using extrathermodynamic assumptions.

EXPERIMENTAL

Materials

The sources and purity of the substituted acetic acids and benzoic acid have been reported previously [3]. The purity of 4-aminobenzoic acid (Aldrich), as determined by acidimetric titration in glacial acetic acid, was $99.2 \pm 0.2\%$.

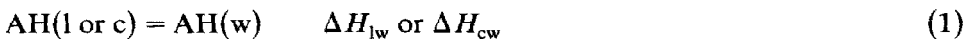
Calorimetry

The calorimetric work involved the determination at $25.00 \pm 0.01^\circ\text{C}$ of the heats of solution in water, and the heats of reaction of the acids in 0.01–0.05 M NaOH or 0.05–0.10 M HCl, using an LKB model 8725-2 isoperibol calorimeter fitted with the 100 ml cell [3]. The amounts of acids $[(4-11) \times 10^{-4} \text{ mol}]$ dissolved or reacted were deduced from the weights of the glass ampoules. For each acid at least three measurements were made at different concentrations.

RESULTS

Enthalpies of solution and ionization

Dissolving the liquid (l) or solid (c) acids, AH, in the various aqueous media may involve several of the following reactions with their corresponding enthalpy changes



The global reaction (3) is of particular interest for obtaining the enthalpies of transfer from water to Me_2SO from previous data [3]



The extent of reaction (2) depends on the ionization of the acid AH, so that we observe



TABLE 1

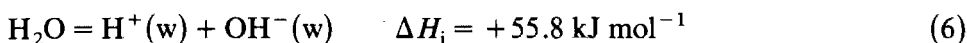
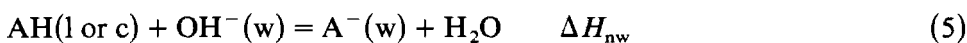
Enthalpies of solution and of ionization of AH in water at 25°C (kJ mol⁻¹)

AH(l or c)	$\Delta H_{lwi}^{\circ a}$	$\Delta H_{cwi}^{\circ a}$	$\Delta H_{lw}^{\circ b}$	$\Delta H_{cw}^{\circ b}$	$\Delta H_{wi}^{\circ c}$
CF ₃ CO ₂ H(l)	-27.3		-29.0		+1.7 ^d
CHCl ₂ CO ₂ H(l)	-17.0		-6.0		-11.0
CH ₂ ClCO ₂ H(c)		+9.3	(-3.9) ⁱ	+14.6	-5.3
CH ₃ CO ₂ H(l)	-1.6		-1.2		-0.4 ^e
C ₆ H ₅ CO ₂ H(c)		+23.7		+23.3 ^f	+0.4 ^g
<i>p</i> -NH ₂ C ₆ H ₄ CO ₂ H(c)		+27.7		+24.8	+2.9 ^h

^a Reaction (3): AH(l or c) = A⁻(w) + H⁺(w); ^b reaction (1): AH(l or c) = AH(w); ^c reaction (2): AH(w) = A⁻(w) + H⁺(w); ^d Ref. 4; ^e Ref. 5; ^f Ref. 7; ^g Ref. 6; ^h Ref 8; ⁱ see text.

where α , which is the degree of ionization of AH, can be calculated from the pK_a value.

We have also combined eqns. (5) and (6) to obtain ΔH_{lwi}



We will examine in turn the data for each acid. The values of ΔH_{lwi} , ΔH_{cwi} , ΔH_{lw} , ΔH_{cw} and ΔH_{wi} , which are given in Table 1, are corrected for ionic strength effects when necessary, and are essentially infinite dilution values.

CF₃CO₂H

The values of the heat of solution of CF₃CO₂H(l) in water were plotted against the number of moles of dissolved acid, and the slope of the least-squares line gave $\Delta H_{\text{obs}} = -27.3 \pm 0.4 \text{ kJ mol}^{-1}$. Kurz and Farrar [4] determined the pK_a of CF₃CO₂H as 0.50 at 25°C, and from pK_a values between 15 and 50°C they also calculated $\Delta H_{wi} = +1.7 \text{ kJ mol}^{-1}$. Our value, $\Delta H_{\text{obs}} = -27.3 \text{ kJ mol}^{-1}$, does not permit us to calculate ΔH_{wi} from eqn. (4) because $\alpha \geq 0.97$ at the concentrations we used and also because $\Delta H_{wi} \ll \Delta H_{lw}$. We can only suggest $\Delta H_{\text{obs}} \approx \Delta H_{lwi} = -27.3 \text{ kJ mol}^{-1}$. The result was confirmed by the value we obtained for the dissolution of CF₃CO₂H(l) in 0.01 M NaOH, $\Delta H_{nw} = -82.5 \text{ kJ mol}^{-1}$, which gave $\Delta H_{lwi} = -26.7 \text{ kJ mol}^{-1}$. We also calculated from the values of $\Delta H_{lwi} = -27.3 \text{ kJ mol}^{-1}$ and $\Delta H_{wi} = +1.7 \text{ kJ mol}^{-1}$ [4] a value of $\Delta H_{lw} = -29.0 \text{ kJ mol}^{-1}$.

CHCl₂CO₂H

The values of the heat of solution of CHCl₂CO₂H(l) in 0.055 M NaOH plotted against the number of moles dissolved gave a straight line with slope $\Delta h_{nw} = -72.0 \pm 0.2 \text{ kJ mol}^{-1}$, which when corrected for the ionic strength effect [1] gave $\Delta H_{nw} = -72.8 \text{ kJ mol}^{-1}$ and thence $\Delta H_{lwi} = -17.0 \pm 0.2 \text{ kJ}$

mol⁻¹. Two other determinations were made, dissolving the acid first in water then in 0.10 M HCl. Both ΔH_{obs} values were corrected for ionic strength effect and, calculating α in both cases (0.87 and 0.50 respectively) from $\text{p}K_a = 1.36$ [4], we finally obtained $\Delta H_{\text{wi}} = -11.0 \text{ kJ mol}^{-1}$ and $\Delta H_{\text{lw}} = -6.0 \text{ kJ mol}^{-1}$ [eqn. (4)].

CH₂ClCO₂H

The plot of the values of the heat of solution of CH₂ClCO₂H(c) in 0.055 M NaOH against the number of moles dissolved gave ΔH_{nw} , which was corrected for the ionic strength effect to yield $\Delta H_{\text{cwi}} = +9.3 \pm 0.6 \text{ kJ mol}^{-1}$. The heat of solution of CH₂ClCO₂H(c) in 0.05 M HCl was also determined as $\Delta H_{\text{obs}} = +15.3 \text{ kJ mol}^{-1}$ and corrected to $\Delta H_{\text{obs}} = +14.5 \text{ kJ mol}^{-1}$. With $\text{p}K_a = 2.86$ [5] we calculated $\alpha = 0.021$ after correction for ionic strength. Solving eqns. (3) and (4) gave $\Delta H_{\text{wi}} = -5.3 \text{ kJ mol}^{-1}$ and $\Delta H_{\text{cw}} = +14.6 \text{ kJ mol}^{-1}$.

CH₃CO₂H

The plot of the heat of solution of CH₃CO₂H(l) in water gave directly $\Delta H_{\text{obs}} \approx \Delta_{\text{lw}} = -1.2 \text{ kJ mol}^{-1}$ [eqn. (4)], since $\alpha \Delta H_{\text{wi}} \ll \Delta H_{\text{lw}}$. This ΔH_{lw} value, when combined with $\Delta H_{\text{wi}} = -0.4 \text{ kJ mol}^{-1}$ [5], gave $\Delta H_{\text{lwi}} = -1.6 \text{ kJ mol}^{-1}$.

C₆H₅CO₂H

Accurate literature data are available for both $\Delta H_{\text{wi}} (+0.4 \text{ kJ mol}^{-1})$ [6] and $\Delta H_{\text{cw}} (+23.3 \text{ kJ mol}^{-1})$ [7]. We calculate $\Delta H_{\text{cwi}} = +23.7 \text{ kJ mol}^{-1}$.

p-NH₂C₆H₄CO₂H

The enthalpy of solution of this acid in water was obtained indirectly because of the slow dissolution rate. We determined $\Delta H_{\text{nw}} = -27.1 \pm 0.4 \text{ kJ mol}^{-1}$ for the solution in 0.10 M NaOH. After correction for the ionic strength effect and using $\Delta H_{\text{wi}} = +2.9 \text{ kJ mol}^{-1}$ [8] we calculated $\Delta H_{\text{cwi}} = +27.7 \text{ kJ mol}^{-1}$ and $\Delta H_{\text{cw}} = +24.8 \text{ kJ mol}^{-1}$.

Enthalpies of transfer of carboxylate anions

Our previously reported values for the enthalpies of solution and ionization of the carboxylic acids in Me₂SO(s) [3] were used to calculate the ΔH_{lsi} values (Table 2) corresponding to eqn. (7)

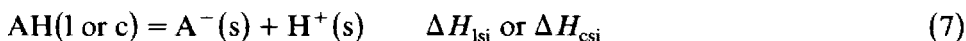


TABLE 2

Enthalpies of solution and ionization of carboxylic acids AH in water(w) and Me₂SO(s) and enthalpies of transfer of A⁻ and AH at 25° C (kJ mol⁻¹)

AH(l or c)	ΔH_{lwi}° ^a	ΔH_{cwi}° ^a	ΔH_{lsi}° ^{b,c}	ΔH_{csi}° ^{b,c}	ΔH_{ws}° (A ⁻) ^{d,e}	ΔH_{ws}° (AH) ^f
CF ₃ CO ₂ H(l)	-27.3	-	-23.8	-	+30.9	+3.4
CHCl ₂ CO ₂ H(l)	-17.0	-	-8.0	-	+36.4	-19.6
CH ₂ ClCO ₂ H(c)	-	+9.3	-	+31.0	+49.1	-14.9
CH ₃ CO ₂ H(l)	-1.6	-	+36.4	-	+65.4	-7.2
C ₆ H ₅ CO ₂ H(c)	-	+23.7	-	+43.4	+47.1	-18.0
<i>p</i> -NH ₂ C ₆ H ₄ CO ₂ H(c)	-	+27.7	-	-	-	-34.5

^a Reaction (3): AH(l or c) = A⁻(w) + H⁺(w); ^b reaction in Me₂SO: AH(l or c) = A⁻(s) + H⁺(s); ^c Ref. 1; ^d reaction A⁻(w) = A⁻(s); ^e based on $\Delta H_{ws}^{\circ}(H^+) = -27.4$ kJ mol⁻¹ (see text); ^f reaction AH(w) = AH(s).

By combining these values with the corresponding ones ΔH_{lwi} or ΔH_{cwi} for water [eqn. (3)] (Table 1), we calculate the enthalpies of transfer for the pair A⁻, H⁺ from water to Me₂SO according to

$$\Delta H_{ws}(A^-, H^+) = \Delta H_{ws}(A^-) + \Delta H_{ws}(H^+) = \Delta H_{lsi} - \Delta H_{lwi} \quad (8)$$

In order to obtain $\Delta H_{ws}(A^-)$, the enthalpy of transfer of the carboxylate single ion, we need to know $\Delta H_{ws}(H^+)$ on the basis of an extrathermodynamic assumption. We take $\Delta H_{ws}(H^+) = -27.4$ kJ mol⁻¹, the value we derived from our ionization data for sulfonic acids in water and Me₂SO, and the tetraphenylarsonium–tetraphenylborate assumption [1]. The values of $\Delta H_{ws}(A^-)$ are listed in Table 2.

Enthalpies of vaporization or sublimation of the acids

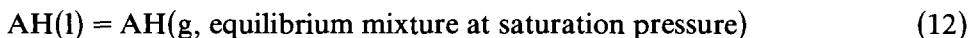
In order to calculate the enthalpies of solvation of the carboxylate anions from our solution data and gas phase ionization data we need to consider reactions (9) and (10)



Since the molecules of carboxylic acids in the vapor phase are involved in a dimer–monomer equilibrium, ΔH_{lg} is obtained from the following equation

$$\Delta H_{lg} = \Delta H_v + (1 - \alpha) \Delta H_{dm} \quad (11)$$

where ΔH_v (per gram formula weight) corresponds to the process



α is the degree of dissociation in the gas phase, and ΔH_{dm} is the gas phase enthalpy of dissociation of the dimer.

For $\text{CF}_3\text{CO}_2\text{H}$, at 25°C we calculated from the vapor pressure data of Taylor and Templeman [9] a heat of vaporization of 8.1 kcal per mole of mixture. Taking $\alpha = 0.11$ from the data of the same authors and $\Delta H_{\text{dm}} = 7.0$ kcal, we obtained $\Delta H_{\text{lg}} = 45 \text{ kJ mol}^{-1}$.

For $\text{CHCl}_2\text{CO}_2\text{H}$ and $\text{CH}_2\text{ClCO}_2\text{H}$, whose boiling points are close (194.4 and 189.5°C respectively), we found from vapor pressure data essentially the same value, 13.4 kcal per mole of mixture, for both acids. In accordance with the views of Konicek and Wadsö [10] we took $\Delta H_{\text{diss}} = 62 \text{ kJ mol}^{-1}$ (per mole of dimer) since the ΔH_{dm} values are approximately the same for a number of carboxylic acids. We noted that, because the heats of vaporization and dissociation are close, ΔH_{lg} varies but little with α ; for example, when α increases from 0 to 1, ΔH_{lg} decreases only from 59 to 56 kJ mol^{-1} , which is fortunate because the α values are poorly known. We selected $\Delta H_{\text{lg}} = 58 \text{ kJ mol}^{-1}$.

For $\text{CHCl}_2\text{CO}_2\text{H}$ we also had to estimate its heat of fusion ΔH_{fus} . We proceeded as follows: we determined the heat of solution of $\text{CH}_2\text{ClCO}_2\text{H(c)}$ and $\text{CHCl}_2\text{CO}_2\text{H(l)}$ in cyclohexane as $+22.6$ and $+4.2 \text{ kJ mol}^{-1}$ respectively, and we took $\Delta H_{\text{fus}} \approx 22.6 - 4.2 = 18.4 \text{ kJ mol}^{-1}$. Using CCl_4 as the solvent, the heats of solution were respectively 19.2 and 0.8 kJ mol^{-1} , giving the same ΔH_{fus} . There is also a literature value for $\Delta H_{\text{fus}} = +19.2 \text{ kJ mol}^{-1}$ at 61°C for the α -form of the acid. Finally we obtained for $\text{CH}_2\text{ClCO}_2\text{H(c)}$, $\Delta H_{\text{cg}} = \Delta H_{\text{fus}} + \Delta H_{\text{lg}} = 77 \text{ kJ mol}^{-1}$.

For $\text{CH}_3\text{CO}_2\text{H}$ we took $\Delta H_{\text{lg}} = +51.6 \pm 1.5 \text{ kJ mol}^{-1}$, as reported by Konicek and Wadsö [10].

For $\text{C}_6\text{H}_5\text{CO}_2\text{H(c)}$ we selected a recent value of 91 kJ mol^{-1} [11] for the heat of sublimation, and there is no appreciable dimerization of this acid in the gas phase.

Enthalpies of solvation of carboxylate anions

The enthalpies of ionization of the carboxylic acids in the gas phase, which are listed in Table 3, correspond to eqn. (13)



The thermodynamic cycle linking the ionization process in the gas phase and the condensed phase (water or Me_2SO) leads us to the enthalpies of solvation (gas to water or Me_2SO) for the pair A^- , H^+ according to

$$\Delta H_{\text{gw}}(\text{A}^-) + \Delta H_{\text{gw}}(\text{H}^+) = -\Delta H_{\text{gi}} - \Delta H_{\text{lg}} + \Delta H_{\text{lwi}} = -\Delta H_{\text{gi}} + \Delta H_{\text{gwi}} \quad (14)$$

The values of ΔH_{gi} , ΔH_{lg} and ΔH_{gwi} are in Table 3, those of ΔH_{lwi} in Table 1.

In order to calculate the single ion enthalpies of hydration of A^- we have selected $\Delta H_{\text{gw}}(\text{H}^+) = -1091 \text{ kJ mol}^{-1}$ ($-260.7 \text{ kcal mol}^{-1}$) [12]. Then the values of $\Delta H_{\text{gs}}(\text{A}^-)$, the enthalpies of solvation of gaseous A^- in Me_2SO ,

TABLE 3

Enthalpies of deprotonation of acids AH in gas phase and enthalpies of solvation in water (w) and Me₂SO (s) of gaseous A⁻ and AH at 25 °C (kJ mol⁻¹)

AH	$\Delta H_{\text{gi}}^{\circ}$ ^{a,b}	$\Delta H_{\text{lg}}^{\circ}$ ^c	$\Delta H_{\text{gwi}}^{\circ}$ ^c	$\Delta H_{\text{gw}}^{\circ}$ (A ⁻) ^{f,g}	$\Delta H_{\text{gs}}^{\circ}$ (A ⁻) ^{f,g}	$\Delta H_{\text{gw}}^{\circ}$ (AH) ^h
CF ₃ CO ₂ H	+1357	+45	-72	-338	-307	-74
CHCl ₂ CO ₂ H	+1316	+58	-75	-360	-324	-64
CH ₂ ClCO ₂ H	+1406	+76 ^d	-67	-382	-333	-61
CH ₃ CO ₂ H	+1458	+52	-54	-421	-356	-53
C ₆ H ₅ CO ₂ H	+1423	+91 ^d	-67	-399	-352	-68
ClH	+1396	-	-75	-380	-360	-

^a Reaction (13): AH(g) = A⁻(g) + H⁺(g); ^b Ref. 2; ^c reaction (9): AH(l or c) = AH(monomer g); ^d $\Delta H_{\text{cg}}^{\circ}$; ^e reaction AH(g) = A⁻(w) + H⁺(w); ^f reaction A⁻(g) = A⁻(w or s); ^g based on $\Delta H_{\text{gw}}^{\circ}(\text{H}^+) = -1091$ kJ mol⁻¹ (see text); ^h reaction AH(g) = AH(w).

are deduced from $\Delta H_{\text{gw}}^{\circ}(\text{A}^-)$ and the enthalpies of transfer of A⁻, $\Delta H_{\text{ws}}^{\circ}(\text{A}^-)$, in Table 2. Both $\Delta H_{\text{gw}}^{\circ}(\text{A}^-)$ and $\Delta H_{\text{gs}}^{\circ}(\text{A}^-)$ values are given in Table 3.

DISCUSSION

We will first review the data for the enthalpies of solution and of ionization of the carboxylic acids AH in water. Then we will examine the enthalpies of transfer of AH and A⁻ from water to Me₂SO. Finally we will consider the enthalpies of solvation of the gaseous carboxylates A⁻ in water and Me₂SO.

Enthalpies of solution and of ionization of the acids in water

The determination of the enthalpies of solution (ΔH_{lw} or ΔH_{cw}) of the weaker acids CH₃CO₂H, C₆H₅CO₂H and *p*-NH₂C₆H₄CO₂H is straightforward, and the values quoted in Table 1 are reliable. However, the values for the stronger acids are less reliable because they are obtained from eqn. (4) and are therefore dependent on the accuracy of ΔH_{wi} . The value found for CF₃CO₂H, $\Delta H_{\text{lw}} = -29.0$ kJ mol⁻¹, is particularly difficult to assess. When we compare it to the other ΔH_{lw} values, CHCl₂CO₂H (-6.0), CH₂ClCO₂H (-3.9) and CH₃CO₂H (-1.2 kJ mol⁻¹) the CF₃CO₂H value (-29.0) appears very exothermic, assuming H-bonding contributions should show a smoother trend towards lower exothermicity in the series. If ΔH_{lw} for CF₃CO₂H is too negative it may be because ΔH_{wi} is too positive and, interestingly, a less positive ΔH_{wi} for CF₃CO₂H would also be easier to reconcile with the ΔH_{wi} trend for the other acids (Table 1). However, when we consider the heats of solution of the monomeric gaseous acids ΔH_{gw}

(Table 3), instead of the ΔH_{1w} values, the value for $\text{CF}_3\text{CO}_2\text{H}$ does not appear out of line, so that it is difficult to draw conclusions as to the reliability of the ΔH_{1w} value of $-29.0 \text{ kJ mol}^{-1}$ for $\text{CF}_3\text{CO}_2\text{H}$.

The determination of the enthalpies of ionization ΔH_{wi} (Table 1) of the stronger acids presents some difficulties, since they are dependent on somewhat uncertain $\text{p}K_a$ values. For $\text{CH}_2\text{ClCO}_2\text{H}$ ($\text{p}K_a = 2.86$) our $\Delta H_{wi} = -5.3 \text{ kJ mol}^{-1}$ is in fair agreement with a -4.9 kJ mol^{-1} value determined from $\text{p}K_a$ variations between 0 and 40°C [5]. For $\text{CHCl}_2\text{CO}_2\text{H}$ ($\text{p}K_a = 1.36$) our value $\Delta H_{wi} = -11 \text{ kJ mol}^{-1}$ is halfway between two others, -7.9 kJ mol^{-1} [4] and $-13.8 \text{ kJ mol}^{-1}$ [4], but an older value, 0.7 kJ mol^{-1} [4], appears to be out of line. Finally, for the strongest acid of the series $\text{CF}_3\text{CO}_2\text{H}$, we could not determine ΔH_{wi} and had to use the value of Kurz and Farrar [4], $+1.7 \text{ kJ mol}^{-1}$, which was calculated from $\text{p}K_a$ variations between 15 and 50°C . However, since there is already some uncertainty on the $\text{p}K_a$ itself at 25°C , 0.50 (see, for example, Ref. 5), $\Delta H_{wi} = +1.7 \text{ kJ mol}^{-1}$ is somewhat uncertain.

The ionization enthalpies in water, ΔH_{wi} , of the substituted acetic acids (Table 1) become slightly more exothermic from $\text{CH}_3\text{CO}_2\text{H}$ to $\text{CH}_2\text{ClCO}_2\text{H}$ and $\text{CHCl}_2\text{CO}_2\text{H}$, but the trend is broken with $\text{CF}_3\text{CO}_2\text{H}$; however, as we have seen, the $\text{CF}_3\text{CO}_2\text{H}$ value may be in error. At any rate, the trend towards higher exothermicity is much more pronounced in the solvent Me_2SO , where ΔH_{si} varies from $+44.8 \text{ kJ mol}^{-1}$ ($\text{CH}_3\text{CO}_2\text{H}$) to $+1.8 \text{ kJ mol}^{-1}$ ($\text{CF}_3\text{CO}_2\text{H}$). Since the $\text{p}K_a$ trends of the acids in water and Me_2SO [3] are similar, the different behavior of the enthalpy of ionization for the acids in both solvents implies different patterns for the variations of the entropy of ionization.

Enthalpies of transfer

Acids

The enthalpies of transfer from water to Me_2SO of the undissociated substituted acetic acid, ΔH_{ws} (Table 2), show a trend towards higher exothermicity from $\text{CH}_3\text{CO}_2\text{H}$ to $\text{CH}_2\text{ClCO}_2\text{H}$ and $\text{CHCl}_2\text{CO}_2\text{H}$, but the trend is broken with $\text{CF}_3\text{CO}_2\text{H}$. This may be due to a too exothermic enthalpy of solution ΔH_{1w} of this acid in water, or to a peculiarity in the solvation of $\text{CF}_3\text{CO}_2\text{H}$ in water, rather than in Me_2SO .

Looking now at the enthalpy of transfer ΔH_{ws} of $p\text{-NH}_2\text{C}_6\text{H}_4\text{CO}_2\text{H}$ ($-34.5 \text{ kJ mol}^{-1}$), it is close to what is calculated ($-29.2 \text{ kJ mol}^{-1}$), assuming additive group contributions, from transfer values ΔH_{ws} for $\text{C}_6\text{H}_5\text{CO}_2\text{H}$ ($-18.0 \text{ kJ mol}^{-1}$) (Table 2) and for $\text{NH}_2\text{C}_6\text{H}_5$ ($-11.2 \text{ kJ mol}^{-1}$) [13]. This indicates that aminobenzoic acid is essentially present as the same molecular species in both water and Me_2SO ([13] and references therein). The calculated transfer value for the zwitterionic species $p\text{-NH}_3^+\text{C}_6\text{H}_4\text{CO}_2^-$, with $\Delta H_{ws}(\text{C}_6\text{H}_5\text{CO}_2^-) = +47.1 \text{ kJ mol}^{-1}$ and $\Delta H_{ws}(\text{NH}_3^+ -$

C_6H_5) = $-37.4 \text{ kJ mol}^{-1}$ [13], would have given $\Delta H_{ws}(NH_3^+C_6H_4CO_2^-) = +9.7 \text{ kJ mol}^{-1}$, a value completely at odds with the experimental value of $-34.5 \text{ kJ mol}^{-1}$ (Table 2).

Carboxylate anions

First it is worth pointing out that the enthalpies of transfer of the carboxylate anions are not affected by possible errors in ΔH_{lw} or ΔH_{wi} , since they are determined directly [eqn. (8)].

The enthalpies of transfer, from water to Me_2SO , for the carboxylate anions in Table 2 are all highly positive. This indicated poorer carboxylate solvation in Me_2SO comes from the absence of H-bonding contribution to anion solvation in this dipolar aprotic solvent. The more positive ΔH_{ws} value for aliphatic $CH_3CO_2^-$ ($+65.4 \text{ kJ mol}^{-1}$) than for aromatic $C_6H_4CO_2^-$ ($+47.1 \text{ kJ mol}^{-1}$) is in line with our previous results for $CH_3SO_3^-$ and $C_6H_5SO_3^-$ [1] and can be linked to positive transfer values for alkanes and a value near zero for benzene. The increasingly endothermic ΔH_{ws} values when passing from $CF_3CO_2^-$ ($+30.9 \text{ kJ mol}^{-1}$) to $CH_3CO_2^-$ ($+65.4 \text{ kJ mol}^{-1}$) reflect a stronger H-bonding component to solvation in water, as will be clearer when we later compare the solvation enthalpies of both anions in water and Me_2SO . It is interesting to note that the difference of ΔH_{ws} between $CF_3CO_2^-$ and $CH_3CO_2^-$ (34.5 kJ mol^{-1}) parallels the ΔH_{ws} difference previously noted for the pair $CF_3SO_3^-$ – $CH_3SO_3^-$ (27.7 kJ mol^{-1}) [1]. This difference appears to be due to different H-bonding interactions of both anions with water through the polar groups $-CO_2^-$ and $-SO_3^-$ rather than to contrasting interactions of the $-CH_3$ and $-CF_3$ groups [1]. Our transfer value from water to Me_2SO for $CF_3CO_2^-$ (30.9 kJ mol^{-1}) is in nice agreement with two reported values for the transfer of $CF_3CO_2^-$ between related solvents: water–dimethylformamide (25.9 kJ mol^{-1}) [14] and water–propylene carbonate (32.7 kJ mol^{-1}) [14].

The much weaker solvation found for $CH_3CO_2^-$ in Me_2SO than in water ($\Delta H_{ws} = +65.4 \text{ kJ mol}^{-1}$) has an interesting consequence. We had previously noted that, while the solubility of the aminosulfonic acid $NH_3^+CH_2SO_3^-$ is about equal (0.2 M) in water and Me_2SO , glycine, $NH_3^+CH_2CO_2^-$, which is very soluble in water ($\approx 3.3 \text{ molal}$), is totally insoluble in Me_2SO . The contrasting transfer enthalpies of $CH_3SO_3^-$ ($+29.6 \text{ kJ mol}^{-1}$) [1] and of $CH_3CO_2^-$ ($+65.4 \text{ kJ mol}^{-1}$) can be shown to explain this solubility difference between the aminosulfonic and aminocarboxylic acids: we will assume additive group contributions for the transfer of $-NH_3^+$, $-SO_3^-$ and $-CO_2^-$ and neglect entropy effects. Then, using the 36 kJ mol^{-1} difference in the above ΔH_{ws} values for $CH_3SO_3^-$ and $CH_3CO_2^-$ and the 0.2 M solubility of $NH_3^+CH_2SO_3^-$ in both solvents we can estimate that the solubility of glycine should be $10^{6.3}$ lower in Me_2SO than in water, which is in qualitative agreement with experimental observations. However crude this calculation may be, it clearly shows that the very large solubility difference of glycine in

water and Me₂SO is caused by the strong solvation through H-bonding of the -CO₂⁻ group in water, and the very poor solvation of -CO₂⁻ in Me₂SO. Apparently the molecular form of glycine, NH₂CH₂CO₂H, is not stabilized enough in Me₂SO to counteract the aforementioned effect.

Recent attempts have been made to rationalize the free energies and enthalpies of transfer of ions from water into nonaqueous solvents in terms of the properties of the ions and solvents [15]. However, the available data base used by the authors, particularly for the enthalpies, is restricted to mostly spherical anions, and there are no data for carboxylate anions to test our results.

Solvation enthalpies of carboxylate anions

While a full discussion of the solvation enthalpies of the polyatomic carboxylate anions, in water and Me₂SO, in terms of ions and solvents properties, is beyond the scope of this paper, some interesting observations can be drawn from the ΔH_{gs} values in Table 3. First, as we would expect on the basis of increasing ionic radii, the solvation enthalpies in Me₂SO decrease from CH₃CO₂⁻ (-356 kJ mol⁻¹) to CH₂ClCO₂⁻ (-333 kJ mol⁻¹) and CHCl₂CO₂⁻ (-324 kJ mol⁻¹), and the value is -307 kJ mol⁻¹ for CF₃CO₂⁻. Thus the difference between the solvation enthalpies of CH₃CO₂⁻ and CF₃CO₂⁻ is 49 kJ mol⁻¹ in Me₂SO, while the comparable figure in H₂O is 83 kJ mol⁻¹. Since there is no H-bonding contribution to solvation in Me₂SO, we could suggest that there is an additional H-bonding contribution of some 34 kJ mol⁻¹ to ionic hydration when passing from CF₃CO₂⁻ to CH₃CO₂⁻. Similarly, the solvation enthalpies of CH₃CO₂⁻ and Cl⁻ are very close in Me₂SO, while in water, CH₃CO₂⁻ solvation is some 40 kJ mol⁻¹ more exothermic than that of Cl⁻. This difference would be attributed to an additional H-bonding contribution to CH₃CO₂⁻ solvation. Both previous comparisons, while suggesting a particularly strong solvation of the acetate anion in water because of H-bonding, are hampered by the lack of knowledge of the influence of ionic size on the solvation enthalpy. The earliest and simplest model for calculating solvation enthalpies in relation to ionic size is that of Born [16]. While it is well known that this model fails for water as the solvent, we first examined whether the related equation $\Delta H_{gs} = -680/r$ kJ mol⁻¹ for solvation in Me₂SO of an ion of radius r [16] would account for the data available for the simple spherical anions Cl⁻ (Table 3), Br⁻, I⁻ and a cation K⁺. The required ΔH_{gs} values for Cl⁻ (-360 kJ mol⁻¹), Br⁻ (-342 kJ mol⁻¹), I⁻ (-316 kJ mol⁻¹) and K⁺ (-357 kJ mol⁻¹) were obtained from the known enthalpies of hydration ΔH_{gw} and the recommended values of the enthalpies of transfer ΔH_{ws} [14]. If we use Pauling's crystal radii, we obtain Cl⁻ (-374), Br⁻ (-344), I⁻ (-306) and K⁺ (-490). With the more recent Shannon's radii, we calculate Cl⁻ (-407), Br⁻ (-374), I⁻ (-330) and K⁺ (-453). It is clear that Pauling's radii do

not give the proper dependence on $1/r$ for the anions, and the value for K^+ is much too high. With Shannon's radii, all values are too high and should be decreased by some 10% to give better agreement, but the dependence on $1/r$ is still not well accounted for, although the K^+ value is in better agreement. This brief examination shows that the simple Born model does not work well in Me_2SO , a solvent simpler than water, even with simple spherical ions. A better approach to relate the solvation enthalpies to ions and solvents properties might be to follow the lines used by Marcus et al. [15]. These authors subjected data on the ionic enthalpies of transfer from water to solvents to multiparameter correlations, in order to determine in particular the significant properties of the ions other than ion size, such as polarizability and softness. An added difficulty when considering our results with the non-spherical carboxylate anions is the selection of ion size. In this respect it is worth pointing out the small effective ionic sizes of the carboxylate ions, which are indicated from a comparison of their solvation enthalpies (Table 3) in Me_2SO with those of spherical halide ions as quoted above. For example, the ionic radii of CH_3CO_2^- and Cl^- in Me_2SO would appear to be close, and interestingly the thermochemical radius quoted for CH_3CO_2^- , 1.59 Å [17], is also near that of Shannon's radius for Cl^- , 1.67 Å.

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