

Enthalpies of solution of some aromatic sulphonic acids and of some aminosulphonic acids

J. Bickerton ^a, J.I. MacNab ^b, H.A. Skinner ^a and G. Pilcher ^{a,*}

^a *Department of Chemistry, University of Manchester, Manchester M13 9PL (UK)*

^b *ZENECA Ltd., P.O. Box 42, Hexagon House, Blackley, Manchester M9 3DA (UK)*

(Received 13 November 1992; accepted 11 December 1992)

Abstract

The molar enthalpies of solution at 298.15 K of several aromatic sulphonic acids and of some aminosulphonic acids were measured in water, in aqueous acid, and in aqueous alkali. Molar enthalpies of ionization in aqueous solution were derived for orthanilic acid ($11.86 \pm 0.53 \text{ kJ mol}^{-1}$), metalinic acid ($20.79 \pm 2.1 \text{ kJ mol}^{-1}$), sulphanilic acid ($17.91 \pm 0.63 \text{ kJ mol}^{-1}$), aminomethanesulphonic acid ($29.14 \pm 0.32 \text{ kJ mol}^{-1}$) and taurine ($43.39 \pm 0.65 \text{ kJ mol}^{-1}$).

INTRODUCTION

The ability of the sulphonic acid group to confer solubility in water to otherwise insoluble materials has led to a wide range of applications, in particular in the dye-stuffs industry, in detergents, and in oil additives for engine protection. There have been very few reported measurements concerning the thermodynamics of the solution of sulphonic acids, including the aminosulphonic acids, for which the main species in aqueous solution is expected to be the zwitterion form.

In this paper we report the enthalpies of solution of some aromatic sulphonic acids, together with those of some of their sodium salts and of some aminosulphonic acids, in water, in aqueous alkali, and in aqueous acid. From the enthalpies of solution of the aminosulphonic acids, the enthalpies of ionization of the $-\text{NH}_3^+$ group have been derived.

EXPERIMENTAL

Materials

Sulphamic acid (B.D.H., analytical standard) was used, which from microanalysis and acidimetric titration was assessed to be >99% pure.

* Corresponding author.

Aminomethanesulphonic acid (Aldrich) and taurine (1-aminoethane-2-sulphonic acid) (Aldrich) were purified by crystallization from water and dried in vacuo over P_4O_{10} . 4-Methylbenzenesulphonic acid monohydrate (B.D.H., microanalytical grade) was stored over P_4O_{10} because it is hygroscopic. 4-Nitrobenzenesulphonic acid (Eastman Kodak) was dried in vacuo; acidimetric titration indicated only 96% purity but attempts to purify by sublimation in vacuo resulted in decomposition. The three aminobenzenesulphonic acids (Aldrich) were dried before use; microanalyses and acidimetric titrations indicated purities >99%. 4-Chlorobenzenesulphonic acid monohydrate, 2-nitrobenzenesulphonic acid monohydrate, and 3-nitrobenzenesulphonic acid monohydrate were prepared from the corresponding sodium salts by ion exchange using an Amberlite® IR 120 (hydrogen form) resin column. Checks on the sodium content of the eluate were made to ensure this to be <1 ppm and to demonstrate the absence of sulphate ions. The acids were prepared by evaporating the eluates to dryness in a rotatory evaporator and storing the samples over P_4O_{10} . 3-Nitrobenzenesulphonic acid monohydrate decomposes at room temperature in the presence of light so this sample was immediately transferred to a nitrogen-filled dry box to be sealed into glass ampoules for measurement and analysis. Microanalyses of the final products showed that these three acids were monohydrates.

Sodium 4-methylbenzenesulphonate was prepared from the corresponding acid by adding a slight excess of sodium hydroxide and concentrating the solution in a rotary evaporator. A solution of the dried salt had a pH of 7.0, indicating the absence of sodium hydroxide. Sodium 4-chlorobenzenesulphonate and sodium 2-nitrobenzenesulphonate were stored over P_4O_{10} . The purities of these salt samples were confirmed by microanalyses.

Solution-reaction calorimeter

The calorimeter has been previously reported [1] and only a brief description is given here. An unsilvered glass Dewar containing 130 cm³ of solvent was equipped with a twin-bladed glass stirrer rotating at 7.5 Hz. Temperatures were measured by a thermistor; the thermistor resistance was averaged over 30 s intervals by a Solartron 7065 DVM and the values transferred to a microcomputer for calculation of ΔT_{ad} , the temperature rise that would have occurred if the calorimeter were adiabatic and there was no work of stirring. An electric heater (100 Ω) in an oil-filled tube was used for electrical calibration; the potential difference across the heater was measured with a Solartron A210 DVM and the current determined from the potential drop across a standard 1 Ω resistance. The time for electrical heating was controlled by generating 0.1 s square-wave pulses from the 200 kHz Droitwich signal, then switching the current to the calorimeter

heater for a pre-set pulse count. Samples were sealed in thin glass ampoules which were broken under the solvent at the appropriate time by compression between two glass rings. The calorimeter top plate was sealed to the Dewar using an O-ring and the calorimeter was submerged in a water thermostat maintained at 298.150 ± 0.001 K.

The calorimeter and procedure were tested by measuring the enthalpy of solution of THAM (NBS SRM 724) in HCl (aq) (0.1 mol dm^{-3}) at 298.15 K; the mean of five experiments gave $\Delta_r H_m = -29.75 \pm 0.08 \text{ kJ mol}^{-1}$, in agreement with the value of Kilday and Prosen [2], -29.77 ± 0.03 .

RESULTS

Table 1 lists the results for the enthalpies of solution in water, where n is the ratio of the number of moles of water to one mole of the compound. Uncertainties are twice the standard deviation of the mean, except when the number of experiments was less than three, due to limited amounts of pure material: the uncertainties were then assessed by comparison with the other measurements. Solution of the hydrated sulphonic acids is markedly less endothermic than for the anhydrous acids.

Table 2 lists the results for the enthalpies of solution in 0.1 mol dm^{-3} NaOH(aq), where m is the ratio of the number of moles of $[\text{NaOH} \cdot 550\text{H}_2\text{O}, \text{l}]$ to one mole of the compound.

Table 3 lists the enthalpies of solution in 0.05 mol dm^{-3} $\text{H}_2\text{SO}_4(\text{aq})$, where m is the ratio of the number of moles of $[\text{H}_2\text{SO}_4 \cdot 1100\text{H}_2\text{O}, \text{l}]$ to one mole of the compound.

TABLE 1

Molar enthalpies of solution in n moles of water at 298.15 K

	No. of expts.	n	$\Delta H(1)/\text{kJ mol}^{-1}$
$\text{NH}_2\text{SO}_3\text{H}$	2	1245	18.78 ± 0.54
$\text{NH}_2\text{CH}_2\text{SO}_3\text{H}$	4	1972	25.14 ± 0.23
$\text{NH}_2(\text{CH}_2)_2\text{SO}_3\text{H}$	4	3070	24.15 ± 0.35
$4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$	2	3005	0.16 ± 0.50
$4\text{-ClC}_6\text{H}_4\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$	1	2279	-0.14 ± 0.70
$2\text{-NO}_2\text{C}_6\text{H}_4\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$	2	2405	0.80 ± 0.67
$3\text{-NO}_2\text{C}_6\text{H}_4\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$	2	2459	-7.10 ± 3.40
$4\text{-NO}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$	2	1821	17.25 ± 0.17
$2\text{-NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$	4	1753	22.72 ± 0.11
$3\text{-NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$	4	2302	19.43 ± 1.70
$4\text{-NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$	5	2088	17.35 ± 0.21
$4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{Na}$	2	1750	10.85 ± 0.40
$4\text{-ClC}_6\text{H}_4\text{SO}_3\text{Na}$	3	2050	19.41 ± 0.25
$2\text{-NO}_2\text{C}_6\text{H}_4\text{SO}_3\text{Na}$	4	1735	56.91 ± 0.65

TABLE 2

Molar enthalpies of solution in m moles of $[\text{NaOH} \cdot 550\text{H}_2\text{O}]$ at 298.15 K

	No. of expts.	m	$\Delta H(2)/\text{kJ mol}^{-1}$
$\text{NH}_2\text{SO}_3\text{H}$	2	3.88	-37.69 ± 0.37
$\text{NH}_2\text{CH}_2\text{SO}_3\text{H}$	4	3.56	-4.32 ± 0.22
$\text{NH}_2(\text{CH}_2)_2\text{SO}_3\text{H}$	4	3.98	11.32 ± 0.06
$4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$	4	3.48	-56.14 ± 0.19
$4\text{-ClC}_6\text{H}_4\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$	1	11.48	-57.72 ± 1.20
$2\text{-NO}_2\text{C}_6\text{H}_4\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$	2	13.82	-57.34 ± 0.60
$3\text{-NO}_2\text{C}_6\text{H}_4\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$	1	10.60	-65.46 ± 1.30
$4\text{-NO}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$	2	4.32	-39.50 ± 0.60
$2\text{-NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$	3	2.51	-25.37 ± 0.24
$3\text{-NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$	6	5.16	-17.55 ± 0.20
$4\text{-NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$	3	5.17	-23.23 ± 0.33
$4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{Na}$	2	3.61	11.38 ± 0.30
$4\text{-ClC}_6\text{H}_4\text{SO}_3\text{Na}$	2	3.62	19.64 ± 0.40
$2\text{-NO}_2\text{C}_6\text{H}_4\text{SO}_3\text{Na}$	2	3.11	56.68 ± 1.04

TABLE 3

Molar enthalpies of solution in m moles of $[\text{H}_2\text{SO}_4 \cdot 1100\text{H}_2\text{O}]$ at 298.15 K

	No. of expts.	m	$\Delta H/\text{kJ mol}^{-1}$
$\text{NH}_2\text{SO}_3\text{H}$	2	1.77	19.97 ± 0.52
$\text{NH}_2\text{CH}_2\text{SO}_3\text{H}$	3	1.61	24.49 ± 0.36
$\text{NH}_2(\text{CH}_2)_2\text{SO}_3\text{H}$	2	2.66	23.62 ± 0.54
$4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$	4	1.51	2.42 ± 0.22
$4\text{-ClC}_6\text{H}_4\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$	1	1.77	2.59 ± 0.70
$2\text{-NO}_2\text{C}_6\text{H}_4\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$	1	1.88	1.68 ± 0.65
$3\text{-NO}_2\text{C}_6\text{H}_4\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$	1	2.38	-3.97 ± 0.90
$4\text{-NO}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$	2	1.78	20.15 ± 0.50
$2\text{-NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$	3	1.94	21.00 ± 0.20
$3\text{-NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$	3	2.12	17.70 ± 0.60
$4\text{-NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$	3	1.94	14.50 ± 0.10
$4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{Na}$	2	1.52	10.39 ± 0.36
$4\text{-ClC}_6\text{H}_4\text{SO}_3\text{Na}$	2	1.46	18.21 ± 0.11
$2\text{-NO}_2\text{C}_6\text{H}_4\text{SO}_3\text{Na}$	2	2.23	28.46 ± 0.40

DISCUSSION

Table 4 lists comparisons of the results with previously reported calorimetric measurements of the enthalpies of solution of sulphamic acid, taurine, and sulphanilic acid in water and in $\text{NaOH}(\text{aq})$. Although the concentrations of the final solutions do not precisely correspond, the results are close, suggesting that for these solutions, enthalpies of dilution will be small.

TABLE 4

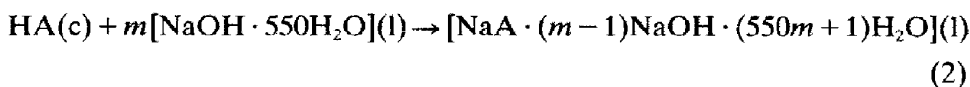
Comparisons with previous measurements at 298.15 K

	Solvent	n/m	$\Delta H/\text{kJ mol}^{-1}$	Reference
NH ₂ SO ₃ H	H ₂ O	$n = 2645$	19.03 ± 0.12	3
NH ₂ SO ₃ H	H ₂ O	$n = 1245$	18.78 ± 0.54	This work
NH ₂ (CH ₂) ₂ SO ₃ H	H ₂ O	$n = 2033$	24.18 ± 0.21	4
NH ₂ (CH ₂) ₂ SO ₃ H	H ₂ O	$n = 3070$	24.15 ± 0.35	This work
4-NH ₂ C ₆ H ₄ SO ₃ H	H ₂ O	$n = 10120$	18.80 ± 0.63	4
4-NH ₂ C ₆ H ₄ SO ₃ H	H ₂ O	$n = 2088$	17.35 ± 0.21	This work
NH ₂ SO ₃ H	NaOH	$m = 2.42$	-37.20 ± 0.23	4
NH ₂ SO ₃ H	NaOH	$m = 3.88$	-37.69 ± 0.37	This work
4-NH ₂ C ₆ H ₄ SO ₃ H	NaOH	$m = 5.17$	-23.56 ± 0.06	4
4-NH ₂ C ₆ H ₄ SO ₃ H	NaOH	$m = 3.81$	-23.23 ± 0.33	This work

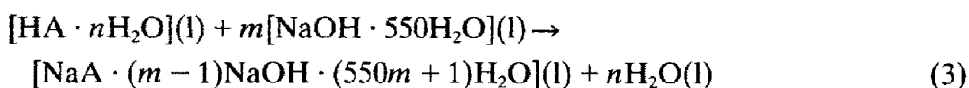
Although the concentrations of the final solutions in water and in NaOH(aq) are small, nevertheless they are somewhat removed from infinite dilution and rigorous corrections to infinite dilution are not possible due to lack of information concerning dilution enthalpies. An approximate correction can be made as follows. The processes measured are



and

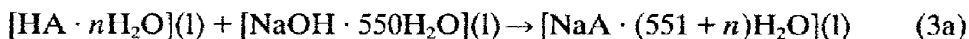


By subtraction

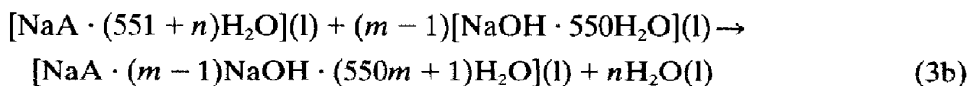


where $\Delta H(3) = \Delta H(2) - \Delta H(1)$.

Process (3) may be considered as occurring in two stages



and



where process (3b) involves the mixing of 0.1 mol dm^{-3} NaA(aq) with 0.1 mol dm^{-3} NaOH(aq) in the ratio $1:(m-1)$. Although no data are available on these mixing enthalpies, at the concentrations used they are almost certainly very small so that the approximation $\Delta H(3) = \Delta H(3a)$ can be made. The dilution enthalpies for $[\text{HA} \cdot n\text{H}_2\text{O}](l)$ and for

TABLE 5

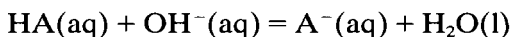
Molar enthalpies, Gibbs energies and entropies of ionization at 298.15 K

	$\Delta H^\ominus(3)/\text{kJ mol}^{-1}$	$\Delta H_{\text{ion}}^\ominus/\text{kJ mol}^{-1}$	$\text{p}K_a$	$\Delta G_{\text{ion}}^\ominus/\text{kJ mol}^{-1}$	$\Delta S_{\text{ion}}^\ominus/\text{J K}^{-1} \text{mol}^{-1}$
$\text{NH}_2\text{SO}_3\text{H}$	-55.97 ± 0.65	1.97 ± 0.57 [7]	0.988 [7]	5.64	-12.3
$\text{NH}_2\text{CH}_2\text{SO}_3\text{H}$	-28.96 ± 0.32	29.14 ± 0.32	6.01	34.30	-17.3
$\text{NH}_2(\text{CH}_2)_2\text{SO}_3\text{H}$	-12.33 ± 0.36	43.39 ± 0.65	9.06 [7]	51.71	-27.9
$4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$	-55.80 ± 0.53				
$4\text{-ClC}_6\text{H}_4\text{SO}_3\text{H}$	-57.08 ± 1.40				
$2\text{-NO}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$	-57.64 ± 0.90				
$3\text{-NO}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$	-57.86 ± 3.60				
$4\text{-NO}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$	-56.25 ± 0.62				
$2\text{-NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$	-47.59 ± 0.26	11.86 ± 0.53	2.46 [7]	14.04	-7.3
$3\text{-NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$	-36.48 ± 1.71	20.79 ± 2.10	3.74 [7]	21.35	-1.9
$4\text{-NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$	-40.08 ± 0.39	17.91 ± 0.63	3.23 [7]	18.44	-1.8

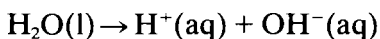
$[\text{NaA} \cdot 550\text{H}_2\text{O}](\text{l})$ to infinite dilution are expected to be small and are mutually cancelling, so that the essential dilution term to correct $\Delta H(3a)$ to infinite dilution is for $[\text{NaOH} \cdot 550\text{H}_2\text{O}](\text{l})$, for which $\Delta H(\text{dilution}) = -0.48 \text{ kJ mol}^{-1}$ [5], so that $\Delta H^\ominus(3) = [\Delta H(3a) + 0.5] \text{ kJ mol}^{-1}$.

The derived $\Delta H^\ominus(3)$ values are listed in the first column of Table 5. For the monofunctional sulphonic acids, $\Delta H^\ominus(3)$ is essentially indistinguishable from the standard enthalpy of formation of water from $\text{H}^+(\text{aq})$ and $\text{OH}^-(\text{aq})$, $-55.84 \pm 0.04 \text{ kJ mol}^{-1}$ [6], consistent with the view that these are strong acids and at the concentrations employed in this study they will be effectively completely dissociated.

Because of the ease of dissociation of the sulphonic acid group, the undissociated aminosulphonic acids are expected to be in a zwitterion form, $\text{NH}_3^+\text{-R-SO}_3^-$. The standard enthalpy of ionization can be derived from the standard enthalpy of reaction (3), now written as



and the standard enthalpy of ionization of water, $\Delta H^\ominus(\text{w})$



Hence for



$\Delta H^\ominus(4) = \Delta H^\ominus(3) - \Delta H^\ominus(\text{w})$. It is necessary, however, to correct the observed $\Delta H^\ominus(3)$ for the degree of dissociation of the aminosulphonic acid in water.

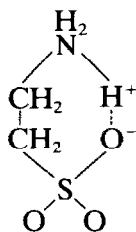
For sulphamic acid, $\text{p}K_a = 0.988$ [7], and at the concentrations used in this work, the aqueous acid will be approximately 90% dissociated. Previous determinations of the enthalpy of ionization of sulphamic acid show this to be small, $1.97 \pm 0.67 \text{ kJ mol}^{-1}$ [7] and $1.05 \pm 0.63 \text{ kJ mol}^{-1}$ [4], so that $-\Delta H^\ominus(3)$ without correction for dissociation is equal to the

enthalpy of ionization of water to within the limits of experimental uncertainty. For the aminomethanesulphonic acid, $pK_a = 6.01$ was determined by measuring the pH during the titration with alkali of three solutions at concentrations less than $10^{-3} \text{ mol dm}^{-3}$ and extrapolating to zero concentration. The value is reasonably close to, but is preferred to, that reported by Rumpf [8], $pK_a = 5.75$, because the latter value was measured at an unstated concentration and temperature. The degree of dissociation in an aqueous solution of an aminosulphonic acid was derived from pK_a and activity coefficients calculated using the formula proposed by Davies [9], i.e. at 298.15 K

$$\log_{10} \gamma_{\pm} = \frac{-0.5115I^{1/2}}{1 + I^{1/2}} + 0.01I$$

Fortunately, uncertainty in the values of the activity coefficients does not have a marked effect on the calculated degree of dissociation and consequently on ΔH^{\ominus} (ionization). The enthalpies of ionization are listed in Table 5 and compared with values reported in the literature in Table 6, showing that good agreement has been obtained.

Table 5 lists the standard Gibbs energies and entropies of ionization. The entropies of ionization are small, consistent with the undissociated acids being in the zwitterion form in aqueous solution. For taurine, the enthalpy of ionization is large and the entropy of ionization has the largest negative value suggesting that this molecule forms a six-membered ring structure with an intramolecular hydrogen bond.



The effect may be present to a smaller degree in aminomethanesulphonic acid and in orthanilic acid where five-membered rings may be present.

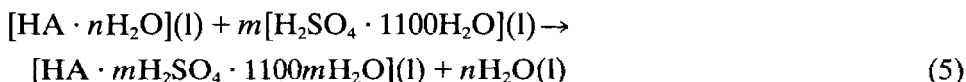
TABLE 6

Comparison of $\Delta H_{\text{ion}}^{\ominus}$ values at 298.15 K in kJ mol^{-1}

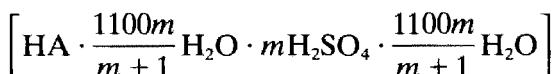
	This work	Ref. 7	Ref. 4
$\text{NH}_2(\text{CH}_2)_2\text{SO}_3\text{H}$	43.39 ± 0.65		41.80 ± 0.25
$2\text{-NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$	11.86 ± 0.53	10.16 ± 0.21	
$3\text{-NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$	20.79 ± 2.10	21.00 ± 0.21	
$4\text{-NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$	17.91 ± 0.63	18.58 ± 0.21	17.57 ± 0.84

Enthalpies of solution in sulphuric acid

By subtraction of the enthalpy in water from that in sulphuric acid (0.05 mol dm⁻³), the enthalpy of process (5) is derived



The final acid solution can be written in the form



in which the water is associated equally between the acids HA and $m\text{H}_2\text{SO}_4$. Examination of process (5) shows that $m(\text{H}_2\text{SO}_4 \cdot 1100\text{H}_2\text{O})$ dilutes to $m(\text{H}_2\text{SO}_4 \cdot 1100m/(m+1)\text{H}_2\text{O})$ and $(\text{HA} \cdot n\text{H}_2\text{O})$ dilutes to $(\text{HA} \cdot 1100m/(m+1)\text{H}_2\text{O})$. The enthalpy of dilution of the sulphuric acid is readily calculated from data tables, and that for the acid HA is expected to be small. Hence, by applying the dilution correction, $\Delta H(\text{corr})$, the enthalpy of mixing very dilute aqueous solutions of the sulphonic acids and sulphuric acid, $\Delta H(6) = \Delta H(5) + \Delta H(\text{corr})$, can be derived; the values are listed in Table 7.

For the monofunctional sulphonic acids, $\Delta H(6)$ is effectively zero, as anticipated because protonation of the sulphonic acid group is not expected in sulphuric acid at these concentrations. For the aminosulphonic acids, however, protonation of the $-\text{NH}_2$ group in $\text{NH}_2\text{-R-SO}_3^-$ is expected, leading to an exothermic process. It is not feasible to calculate the extent of protonation in these cases because of lack of information on the activity coefficients of the species concerned in 0.05 mol dm⁻³ sulphuric acid.

TABLE 7

Enthalpies of mixing of $\text{HA} \cdot n\text{H}_2\text{O}(\text{l})$ with $\text{H}_2\text{SO}_4(\text{aq})$ 0.05 mol dm⁻³ at 298.15 K

	$\Delta H(\text{corr})/\text{kJ mol}^{-1}$	$\Delta H(6)/\text{kJ mol}^{-1}$
$\text{NH}_2\text{SO}_3\text{H}$	2.20	-1.01 ± 0.75
$\text{NH}_2\text{CH}_2\text{SO}_3\text{H}$	2.19	-1.54 ± 0.44
$\text{NH}_2(\text{CH}_2)_2\text{SO}_3\text{H}$	2.38	-2.91 ± 0.64
4- $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$	2.17	0.09 ± 0.54
4- $\text{ClC}_6\text{H}_4\text{SO}_3\text{H}$	2.20	0.53 ± 0.99
2- $\text{NO}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$	2.23	-1.35 ± 0.93
3- $\text{NO}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$	2.23	0.90 ± 3.5
4- $\text{NO}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$	2.20	0.70 ± 0.53
2- $\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$	2.25	-3.97 ± 0.23
3- $\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$	2.30	-4.03 ± 1.80
4- $\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$	2.25	-5.10 ± 0.23

Enthalpies of solution of the sodium salts of sulphonic acids

Except for the sodium salt of 2-nitrobenzene sulphonic acid, the enthalpies of solution of the sodium salts show little change for solution in solvents of low, neutral, and high pH values. For the salt of 2-nitrobenzenesulphonic acid, dissolution in acid is less endothermic than expected, possibly due to an acid-catalysed denitration which is expected to be an exothermic process.

REFERENCES

- 1 M.J. Akello, M.I. Paz-Andrade and G. Pilcher, *J. Chem. Thermodyn.*, 15 (1983) 949.
- 2 M.V. Kilday and E.J. Prosen, *J. Res. Natl. Bur. Stand., Sect. A*, 77 (1973) 581, 599.
- 3 C. Wu and L.G. Helper, *J. Chem. Eng. Data*, 7 (1962) 536.
- 4 H.P. Hopkins, C. Wu and L.G. Hepler, *J. Phys. Chem.*, 69 (1965) 2244.
- 5 The NBS Tables of Chemical Thermodynamic Properties, *J. Phys. Chem. Ref. Data*, 11 (1982) Suppl. 2.
- 6 CODATA, *J. Chem. Thermodyn.*, 10 (1978) 903.
- 7 J.J. Christensen, R.M. Izatt, D.P. Wrathall and L.D. Hansen, *J. Chem. Soc. A*, (1969) 1212.
- 8 D. Rumpf., *Bull. Soc. Chim. Fr.*, 5 (1938) 871.
- 9 C.W. Davies, *J. Chem. Soc.*, (1938) 2093.