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Thermodynamics of the 4-chlorobenzene sulphonic acid–water system[☆]

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Abstract

A vapour–liquid equilibrium study of the 4-chlorobenzene sulphonic acid–water system has been carried out at atmospheric and reduced pressure, and the 100°C isothermal VLE diagram derived. The vapour pressure of $ClC_6H_4SO_3H \cdot 0.5H_2O$ was measured at 100–130°C and provides improved definition of the liquid curve at very high acid concentration. There is evidence of strong acid–water association in this range.

The enthalpies of solution of crystalline anhydrous and hydrated 4-chlorobenzene sulphonic acid in water at 30°C have been measured by isoperibol calorimetry and the enthalpy of fusion of the anhydrous acid by differential scanning calorimetry. The enthalpy of solution is strongly dependent on the degree of hydration but for the crystalline and liquid anhydrous acid, $\Delta_{sol}H = -22.2 \pm 1.0$ and -33 ± 2 kJ mol^{-1} respectively. Hydrate association energies are derived. The results are assessed in relation to other types of acids.

Keywords: Chlorobenzene sulphonic acid; Enthalpy; Solution; VLE

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1. Introduction

Until recently [1, 2], relatively little attention has been paid to the thermodynamics of sulphonic acids or the acid + water systems, although sulphonic acids are compounds of considerable commercial importance, being widely used in, for example, dyestuffs, surfactants, pharmaceuticals and ion exchange resins. An understanding of

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the thermodynamics of the acids and their aqueous solutions is therefore important to both product and process development. Many sulphonic acids are highly corrosive, hygroscopic, and difficult to obtain pure, however, and these features may have contributed to their neglect.

Industrial thermodynamic requirements are based on the need to understand the physical chemistry of a process, principally for process and plant design, improvement of efficiency, ensuring safe operation, and understanding novel product applications. These factors may provide the driving force for research into systems not widely studied elsewhere but it is likely to be focused on a specific system and properties rather than form part of a wider study for scientific interest alone. This paper reports such a study of the vapour–liquid equilibria of the 4-chlorobenzene sulphonic acid–water system and the solution thermochemistry in relation to the degree of hydration. Normal predictive methods were inapplicable because of the almost complete absence of relevant data.

Scientific interest in the thermodynamics of sulphonic acids centres on comparison with other acids in relation to their pK_a values. Intermediate between strong mineral acids and carboxylic acids, as exemplified in Table 1, they are generally considered to resemble more closely the acid properties of the former. Whereas the VLE of some carboxylic acid–water systems are strongly influenced by dimer formation, there is no indication of this phenomenon in the liquid phase of sulphonic acids but the greater acid strength suggests a much stronger affinity for water. A previous phase equilibrium study [6] reported the existence of solid hydrates, suggesting strong acid–water association. Recent work showed, however, that solution is thermoneutral or even endothermic [1].

2. Experimental and results

2.1. Materials

Previously dried anhydrous 4-chlorobenzene sulphonic acid (CBSA) was used; analysis showed it to contain < 0.05% w/w H_2O. Two commercial samples of nominal

Table 1
Comparison of acid pK_a values

Mineral acids	pK_a	Ref.	Sulphonic acids	pK_a	Ref.
H_2SO_4	−3, 1.96	[3]	$NH_2CH_2SO_3H$	6.01	[1]
HNO_3	−1.44	[3]	$NH_2(CH_2)_2SO_3H$	9.1	[4]
H_3PO_4	2.1, 7.2	[3]	$HN_2C_6H_4SO_3H$	2.5–3.7	[4]
Carboxylic acids			$C_{10}H_7SO_3H$	0.57	[5]
$HCOOH$	3.75	[3]			
CH_3COOH	4.76	[3]			
C_6H_5COOH	4.20	[3]			
$NH_2C_6H_4COOH$	4.8	[3]			
ClC_6H_4COOH	2.9–4.0	[3]			
$C_{10}H_7COOH$	3.7–4.1	[3]			

CBSA monohydrate were obtained but analysis showed that the actual degrees of hydration were close to CBSA$\cdot$0.2H_2O and CBSA$\cdot$0.5H_2O. All three materials were shown to contain small amounts (2.0–2.9% w/w) of sulphuric acid. In view of the purpose of the study, no attempt was made to remove the sulphuric acid but a correction was made for its calorimetric effect.

2.2. *Vapour–liquid equilibria*

The VLE was studied using a modified Fowler recyling still for homogeneous mixtures to obtain samples of liquid and vapour condensate in their equilibrium compositions at measured temperatures. Reduced pressures were measured by means of a mercury manometer and temperature by a thermocouple in an oil-filled pocket in the vapour–liquid disengagement chamber. The condensate return line was heated to prevent recrystallisation at the higher concentrations. Measurements were made with a range of compositions up to approx. 80% w/w at (a) atmospheric pressure and (b) reduced pressure and approx. 100°C.

Liquid compositions at atmospheric pressure showed a smooth relationship with temperature up to approx. 80% w/w, above which condensate recrystallisation prevented circulation despite the heated line. The vapour compositions formed a smooth curve only up to approx. 40% w/w, above which they were erratic and wholly unreliable. These isobaric curves are shown in Fig. 1. It is assumed that as the liquid concentration was progressively increased, a stage was reached where partial crystallisation of the vapour condensate caused the composition of the condensate samples to vary substantially. Because the volume of the condensate is small relative to that of the boiler, the effect on the constancy of liquid composition during a given period of equilibration is small.

Samples were taken after equilibration alternately at atmospheric pressure and reduced pressure corresponding to approx. 100°C. Assuming a simple linear relation between log P and reciprocal absolute temperature, the reduced pressure measurements were adjusted to the isothermal pressures at exactly 100°C. Table 2 presents the isothermal pressures and liquid compositions. The interpolated vapour compositions were considered too variable to present as formal results but an indication of their range is shown in the isothermal VLE diagram in Fig. 2.

2.3. *Vapour pressure*

The vapour pressure of CBSA$\cdot$0.5H_2O was determined using a glass isoteniscope with a mercury U-tube as internal manometer. The sample was initially degassed at −78°C to ensure that no water was removed simultaneously, by alternate evacuation and warming in the closed isoteniscope until molten, then thermostatted in an oven until a stable pressure was attained. The observed pressures, measured in mm Hg, were corrected to standard conditions (0°C and standard gravity) and expressed in kPa, using the relation 1 mm Hg = 0.1333 kPa. Results of measurements at four temperatures are shown in Table 3.

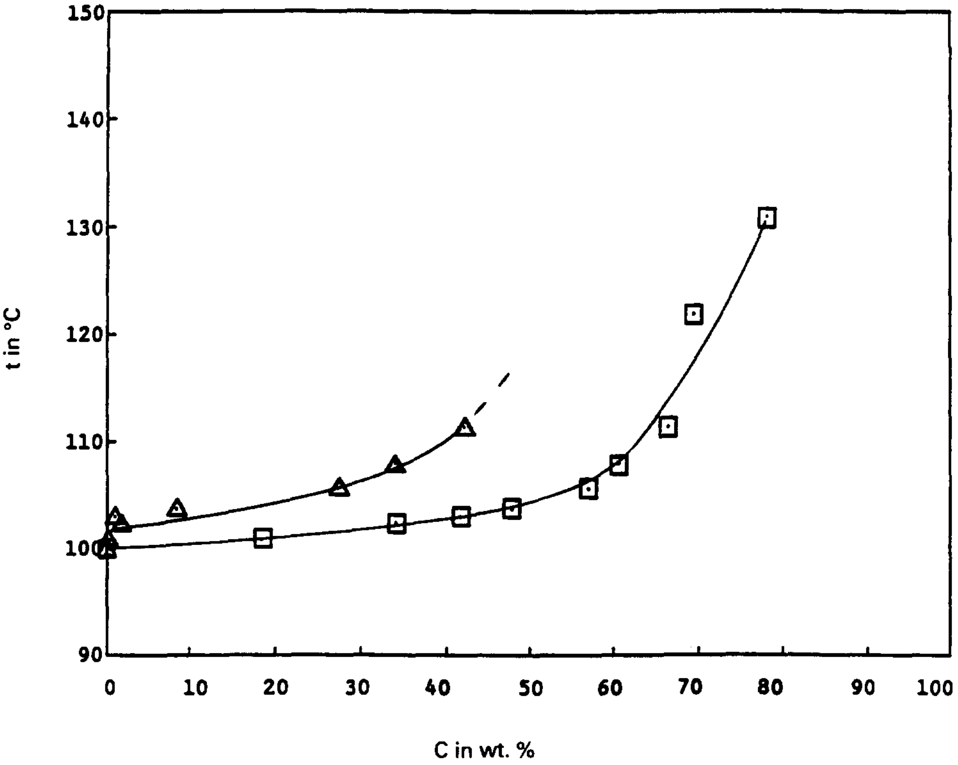

Fig. 1. Vapour–liquid equilibrium of 4-chlorobenzene sulphonic acid + water at 101.325 kPa. Plots of CBSA concentrations C in liquid and vapour against temperature: △, vapour; □, liquid.

Correlation of these results with the Antoine equation gives the following relationship

$$\mathrm{Log}\,(P/\mathrm{kPa}) = 16.691 - \frac{5361.1}{t + 210} \tag{1}$$

The Antoine C coefficient was set at 210 to limit the curvature caused by the pressure at 120°C, which appears slightly high, but Eq. (1) is not regarded as accurate significantly outside the measurement limits. Extrapolation to 100°C by Eq. (1) gives a pressure of 0.25 kPa. This value can be regarded as a further point on the liquid curve in Fig. 2, corresponding to CBSA·$0.5H_2O$, i.e. 95.5% w/w CBSA. No correction was made for depletion of water from the liquid phase by vapourisation.

2.4. *Solution calorimetry*

The enthalpies of solution/dilution were measured using an LKB 8700 Solution Calorimeter at 30°C. This operates on the isoperibol principle: approx. 1 g samples

Table 2
Vapour liquid equilibria: CBSA concentrations in liquid (X_1) and total pressures at 100°C

X_1/% w/w	p/kPa
18.5	98.6
34.1	93.0
41.7	90.9
47.8	88.0
56.9	82.4
60.6	76.0
66.4	66.0
66.0	58.0
69.4	50.4
79.2	41.6
81.9	27.1
85.8	15.5

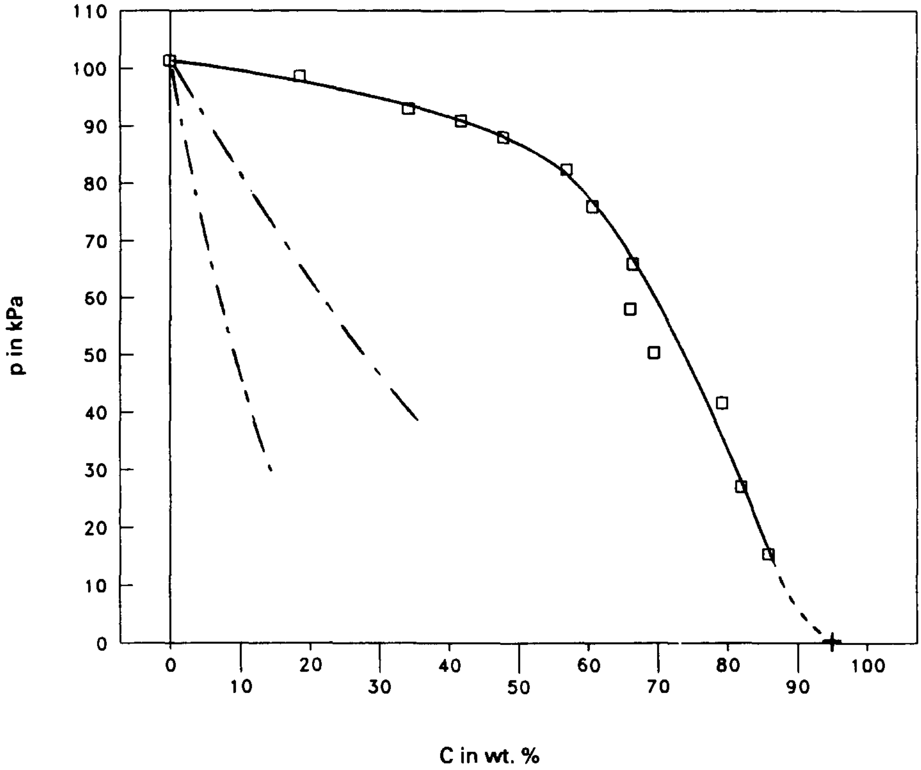

Fig. 2. Isothermal vapour–liquid equilibrium of 4-chlorobenzene sulphonic acid + water at 100°C. Plots of CBSA concentrations C in liquid and vapour against pressure: —, VLE liquid; +, static vapour pressure; – – –, vapour.

Table 3
Vapour pressure of CBSA·$0.5H_2O$

t/°C	p/kPa
103.9	0.41
114.6	1.52
120.0	3.06
129.2	7.50
100.0[a]	0.25

[a] By extrapolation using Eq. (1).

contained in sealed glass ampoules were equilibrated thermally with approx. 100 ml of distilled water in a glass cell prior to breaking the ampoule. The solution temperature was measured by means of a thermistor and Solartron 7065 digital voltmeter, giving a detection sensitivity of 0.0005 K. Calibration was by means of an electric heater within the cell, controlled by an electric timer. The thermostat bath temperature was constant to ± 0.005 K. The corrected temperature rise was calculated from temperature measurements before and after breaking the ampoule, and thence the corresponding enthalpy change. It had been shown previously that the energy of ampoule fracture was negligible.

The enthalpy change initially obtained is the absolute change for the quantities reacting. This figure was corrected for the enthalpy of solution of sulphuric acid impurity in the samples using literature data [7] and the corrected enthalpy change then expressed per mole of CBSA. This is the differential enthalpy of solution and results are shown in Table 4. It is noted that as the degree of initial hydration increases, the enthalpy of solution decreases. Table 5 lists the results when combined and re-expressed as integral enthalpies of solution per mole of CBSA when 1 mole acid is dissolved in n moles water. The measurements relate mainly to substantial dilution but

Table 4
Differential molar enthalpies of solution per mol CBSA at 30°C in water and aqueous solutions of concentration C

Sample	Sample H_2O content (% w/w)	C/(% w/w)	$-\Delta_{sol}H$/(kJ mol^{-1})
1	0.0	0.0	22.2
1	0.0	0.7	22.5
1	0.0	47.1	17.9
2	1.9	0.0	20.0
2	1.9	46.9	11.6
3	4.3	0.0	14.4
3	4.3	52.6	7.9
Sol	52.5	0.0	3.4

Table 5
Integral enthalpies of solution per mol CBSA in *n* moles water at 30°C

Sample	*n*/mol	$-\Delta_{sol}H/(\mathrm{kJ\,mol^{-1}})$
Anhydrous	12	17.9
	749	22.5
	1607	22.2
	1800	21.3
CBSA·0.2H_2O	12	11.6
	1958	20.0
CBSA·0.5H_2O	10	7.9
	1994	14.4

they allow outline integral enthalpy curves to be drawn as shown in Fig. 3. There are insufficient observations to confirm that the apparent dip in $\Delta_{sol}H$ for anhydrous acid as *n* increases is a real trend: it is more probably a measure of the reproducibility of the system, and the mean $\Delta_{sol}H$ value is taken as -22.2 ± 1.0 kJ mol^{-1}.

2.5. *Differential scanning calorimetry*

The enthalpy of fusion of anhydrous CBSA was measured in a Mettler TA3000 using both sealed aluminium crucibles and those with pin-holes in the lid. Samples were scanned at 5 K min^{-1} in a nitrogen purge at 100 cm^3 min^{-1}. Long and slightly irregular melting peaks at around 50–65°C were observed and integration gave a mean enthalpy of fusion of 55 ± 10 J g^{-1} (10.6 ± 2.0 kJ mol^{-1}). The measurements were repeated in gold crucibles to verify that no reaction with aluminium was interfering with the melting profile. Combining this figure with the mean enthalpy of solution of crystalline anhydrous CBSA gives an enthalpy of solution of liquid anhydrous CBSA of -33 ± 2 kJ mol^{-1}.

3. Discussion

The liquid composition points in Fig. 2 derived from the VLE measurements clearly do not extrapolate in a continuous curve to 100% CBSA and a point of inflection must occur at > 85% w/w CBSA. This is confirmed by the additional data point provided by the vapour pressure measurement, which improves the definition of the curve at high CBSA concentrations. This behaviour indicates strong CBSA–H_2O attraction in this composition range and it is probably significant that it corresponds approximately to the acid monohydrate (91.4% w/w CBSA).

The absence of both reliable vapour compositions (except at low concentrations at atmospheric pressure) and the vapour pressure curve of anhydrous CBSA precludes the

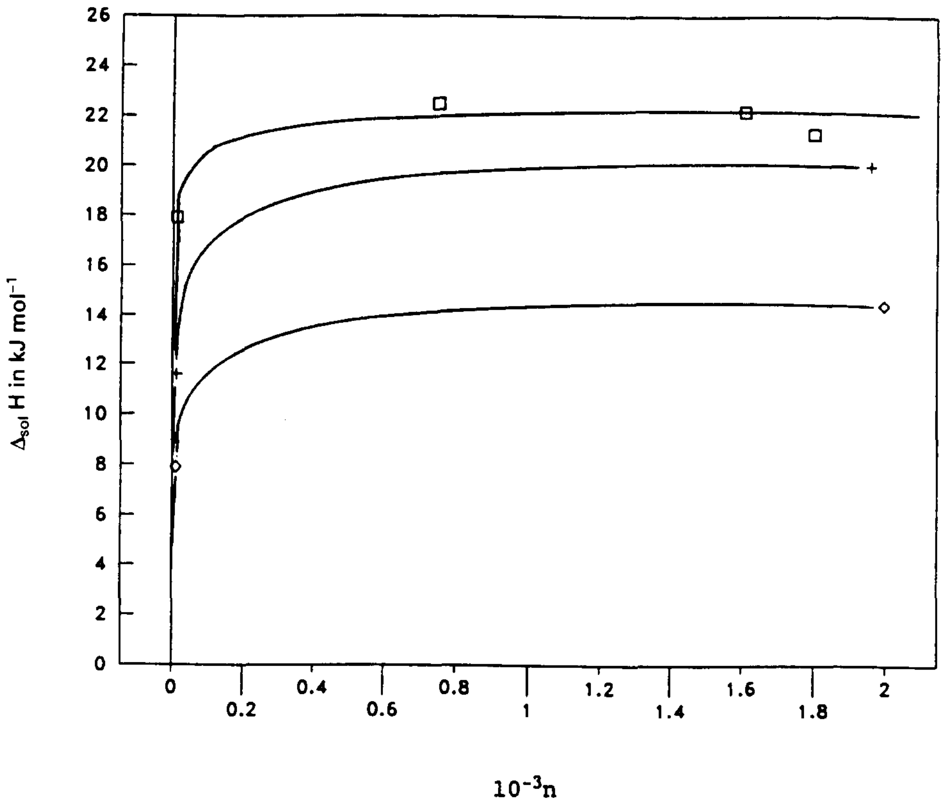

Fig. 3. Integral molar enthalpies of solution of anhydrous and hydrated 4-chlorobenzene sulphonic acid in *n* moles water: +, CBSA·0.2H_2O; ◇, CBSA,·0.5H_2O; □, anhydrous.

more rigorous quantification of the VLE by means of activity coefficients or interaction parameters. The available vapour composition results do, however, indicate that substantial separation occurs over much of the liquid composition range. Separation must become much more difficult at > 90% acid because of the liquid curve behaviour but further work would be required to quantify it accurately. It appears that some modification to the apparatus and method would be required to obtain reliable vapour composition data.

The markedly exothermic $\Delta_{sol}H$ values are in contrast to the thermoneutral or endothermic values reported by Bickerton *et al.* [1] for several sulphonic acids. These were, however, mainly aminosulphonic acids, which are a special case because of their existence as zwitterions, or monohydrates. Specifically, their value of $\Delta_{sol}H = -0.14$ kJ mol^{-1} for CBSA relates to the monohydrate (confirmed by analysis as CBSA·H_2O). Combining that value and those from the present work, Fig. 4 shows the relation between crystalline enthalpies of solution and the degree of hydration. The apparent contrast betwen the two sets of results is thus explained.

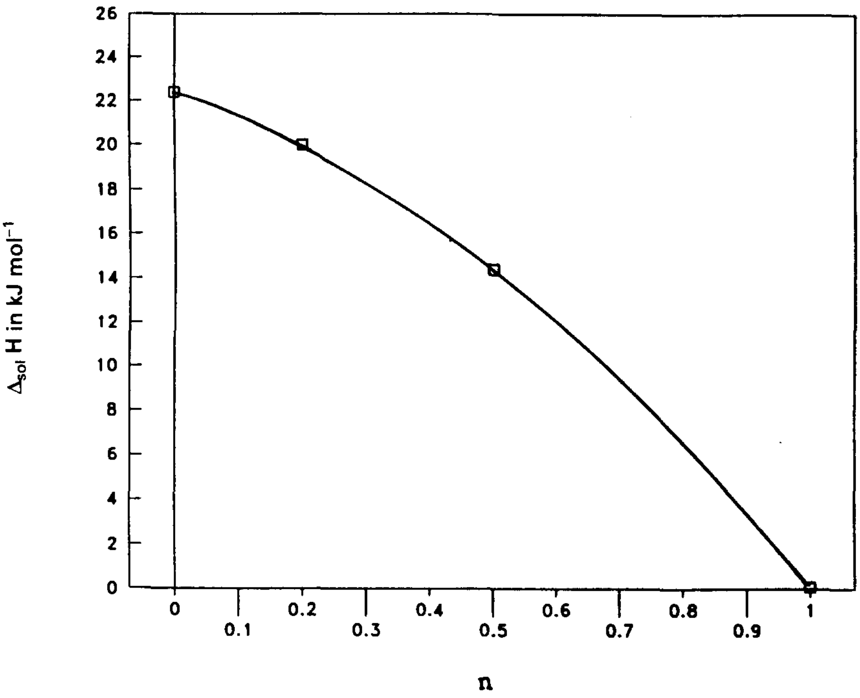

Fig. 4. Variation of enthalpy of solution with degree of hydration n of crystalline CBSA where n = mol H_2O/mol CBSA.

Strong mineral acids have $\Delta_{sol}H$ values ranging from -95.4 kJ mol^{-1} for sulphuric acid to -33.2 and -26.8 kJ mol^{-1} for nitric and phosphoric acids respectively [7]. In contrast, carboxylic acids have values of approx. -1 kJ mol^{-1}. The value of $\Delta_{sol}H$ (CBSA, l) = -33 kJ mol^{-1} therefore places it clearly alongside the strong acids.

The strength of the acid–H_2O association can also be measured by the hydration enthalpy of hydrates. The hydration enthalpy of the crystalline hydrate $\Delta_{hyd}H$ is the difference between the enthalpies of solution, to a given degree of dilution, of the hydrates and the anhydrous acid. Taking $\Delta_{sol}H$(CBSA, cr) = -22.2 ± 1.0 kJ mol^{-1}, $\Delta_{sol}H$(CBSA·0.5 H_2O, cr) = -14.4 kJ mol^{-1} (present work) and $\Delta_{sol}H$(CBSA·H_2O, cr) = -0.14 kJ mol^{-1} [1], the corresponding hydration enthalpies are obtained. These are listed in Table 6 and compared with values for strong acids calculated from literature data [7] as $\Delta_{hyd}H = \Delta_f H(n \text{ hydrate}) - [\Delta_f H(\text{acid}) + n\Delta_f H(H_2O)]$.

4. Conclusion

Both the VLE and thermochemical studies show there is strong interaction between CBSA and water and its behaviour is closer to that of strong acids. The apparently unexpected report of thermoneutral solution has been explained satisfactorily.

Table 6
Hydration enthalpies $\Delta_{hyd}H$ of acids

Hydrate	Phase	$\Delta_{hyd}H/(\mathrm{kJ\,mol^{-1}})$	Ref.
$H_2SO_4 \cdot H_2O$	1	27.8	[7]
$H_2SO_4 \cdot 2H_2O$	1	41.5	[7]
$HNO_3 \cdot H_2O$	1	13.5	[7]
$HNO_3 \cdot 3H_2O$	1	24.4	[7]
$HClO_4 \cdot 2H_2O$	1	65.7	[7]
$H_3PO_4 \cdot 0.5H_2O$	cr	9.4	[7]
$ClC_6H_4SO_3H \cdot 0.5H_2O$	cr	7.8	This work
$ClC_6H_4SO_3H \cdot H_2O$	cr	22.1	This work
$C_6H_5SO_3H \cdot H_2O$	cr	94.1 [a]	[6]
$BrC_6H_4SO_3H \cdot H_2O$	cr	59.0 [a]	[6]

[a] From dissociation to $H_2O(g)$ by vapour pressure measurements.

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