CALORIMETRIC INVESTIGATIONS OF THERMODYNAMIC PROPERTIES OF AQUEOUS SULPHAMIC ACID SOLUTIONS

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ABSTRACT

Enthalpies of dilution of aqueous sulphamic acid solutions were measured at 25°C and the results of these measurements were used to calculate the standard enthalpy of ionization of sulphamic acid. The average ΔH_{ion}° obtained in this work was 0.74 ± 0.20 kJ·mol^{-1}. Enthalpies of solution of crystalline sulphamic acid in water at 25°C were also measured. The results from both measurements were combined with some earlier results from Wu and Hepler to obtain the "best" standard enthalpy of solution, which is $\Delta H_s^\circ = 19.2 \pm 0.2$ kJ·mol^{-1}.

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INTRODUCTION

Sulphamic acid (HSO_3NH_2) has been widely used in analytical chemistry and in many industrial processes. In analytical chemistry, sulphamic acid is used for determination of nitrite ions. It is recommended as a standard in acid-base titrimetry and in non aqueous titrimetry (1-3). Another important application of sulphamic acid in analytical chemistry is to reduce inorganic or organic nitrates to N_2O in the microgasometric technique (4). Sulphamic acid has been widely used in many industrial processes (5). For example, sulphamic acid is used as a catalyst for many organic reactions such as polymerization and is very extensively used in the electroplating and electrodeposition of metals; it is also used as an anticorrosive agent, as a cleaning agent for air, as a scale removal agent, and an agent for cleaning metal. This study arises from the fact that the sulphamic acid has been used as an effective agent for water treatment and sludge treatment. Murray reported that sulphamic acid was used in state of California for taste and odour control in drinking water (6). Ichikawa Woolen Textile Co. (Japan) has used sulphamic acid and polyelectrolyte solutions for sludge treatment (7).

In addition to its wide-ranging applications, theoretically, sulphamic acid is known as an "almost-strong" electrolyte that exists mostly as a zwitterion in its un-ionized form. It is neither like a strong acid, where all species exist in ionized state, nor a very weak acid such as acetic acid that can be readily studied using many thermodynamic approaches with good accuracy. Sulphamic acid has a relatively large ionization constant and the thermodynamic properties of ionization are difficult to determine.

King and King reported the ionization constant of sulphamic acid from electromotive force measurements (8). They recommended 0.103 as the most probable value of the ionization constant at 25°C. From the temperature dependence of the ionization equilibrium constant and by using the conventional thermodynamic method (dlnK/dT), they obtained free energy, enthalpy, and entropy of ionization. However, the enthalpy of ionization calculated by this method had a large uncertainty, with values ranging from 1.13 $kJ \cdot mol^{-1}$ to 1.92 $kJ \cdot mol^{-1}$. Kurz and Farrar also determined the equilibrium constant by glass electrode measurements (9). Hopkins et al. reported enthalpies of ionization of sulphamic acid which were calculated from the enthalpies of solution of sulphamic acid in water and in 0.05M NaOH solution (10). The $\Delta H_{ion}°$ values from these measurements were 0.795 $kJ \cdot mol^{-1}$ and 0.586 $kJ \cdot mol^{-1}$, respectively. Recently, Benoit reported the thermodynamic properties of ionization of sulphamic acid in dimethylsulfoxide (11).

Another acid which belongs to the same group of "almost-strong" electrolytes is iodic acid (HIO_3), which has an ionization constant 0.157 at 25°C. Wooley et al. determined the thermodynamic properties of ionization of iodic acid from the measurement of enthalpies of dilution of iodic acid in water and in other electrolytes (12). Hepler and Hopkins have suggested that this method is better than dlnK/dT for determination of ionization of "almost-strong" electrolytes (13). Another similar "almost-strong" electrolyte has been studied by Larson et al., who investigated the thermodynamics of ion pairing of M^{2+} and $SO4^{2-}$ (14).

Because of the potential use of sulphamic acid as a waster water and sludge treatment agent, and as part of the water and sludge treatment project at the Fuel Processing Laboratory, calorimetric measurements have been made on the enthalpies of solution (ΔH_s) and enthalpies of dilution (ΔH_{dil}). The measurement results have been used to calculate enthalpies of ionization of sulphamic acid and standard enthalpies of solution.

EXPERIMENTAL

Crystalline sulphamic acid supplied by Baker Chemical Co was dried in a vacuum oven at 40°C for two hours, then placed in a vacuum desiccator. BDH reagent-grade KCl was also vacuum dried and kept in a desiccator. For ΔH_s measurement, dried sulphamic acid crystals were carefully placed in a small glass ampoule which was then flame-sealed. For ΔH_{dilu} measurement, a 1.000-mol·kg^{-1} (molal, m) sulphamic acid solution was prepared with deionized water.

The measurements were made with a Tronac titration calorimeter, model 1250. While this calorimeter can be operated in either isothermal or isoperibol mode, our measurements were conducted in the isoperibol mode. For ΔH_s measurements, the ampoule in which the crystal was sealed was suspended at the end of a stirrer. The stirrer and ampoule were immersed into water in a 50-mL dewar. The dewar was then immersed into a large water bath at 25.000±0.001°C. After waiting at least one hour to ensure complete temperature equilibrium, the ampoule was broken and the solid was dissolved in water. The temperature change due to the dissolution of the solid was detected by a thermistor and the micro-voltage signal was recorded by computer. At the end of the run, a Joule-effect calibration was conducted. The calibration power is chosen to produce an amount of heat as close to the reaction heat as possible.

For ΔH_{dil} measurements, 0.1M sulphamic acid solution was titrated into the dewar, which contained 50.0 g of deionized water, using a motor-driven burette. The liquid reservoir of titrate, all titration lines, and the dewar were kept in the water bath for at least one hour to reach temperature equilibrium before the titration started. The heat associated with the dilution of sulphamic acid was determined in the same way as in the ΔH_s experiments, followed by a Joule-effect calibration.

RESULTS AND DISCUSSION

The precision and accuracy of the calorimeter were tested by measuring the ΔH_s of KCl (for ampoule mode) and the heat of reaction of standard 0.1-mol·L^{-1} THAM [tris(hydroxymethyl)aminomethane] with 0.1-mol·L^{-1} HCl (for titration mode). Tables 1 and 2 show the results. The data shown in Table 1 for the enthalpies of solution at infinite dilution of KCl in water were calculated from our measured ΔH_s and for ΔH_{dil} of KCl reported in the literature (15). The average enthalpy of solution obtained was 17.23 kJ·mol^{-1}, compared with the standard value recommended by NBS, 17.217 kJ·mol^{-1}. The standard deviation for five runs was ±0.14 kJ·mol^{-1} or 0.8%. The enthalpy of reaction of THAM with HCl as determined in this work was 47.42 kJ·mol^{-1} as compared to a literature value of 47.40 kJ·mol^{-1} (16). The standard deviation for five measurements was ±0.35 kJ·mol^{-1} or 0.7%.

STANDARD ENTHALPY OF SOLUTION

The experimental results for the ΔH_s of HSO_3NH_2(c) are given in Table 3. Figure 1 shows the enthalpies of solution vs concentration. These measurements covered a concentration range of 0.0024 to 0.082 mol·kg^{-1}. As can be seen from Fig. 1, at very dilute concentrations (<0.01 mol·kg^{-1}) ΔH_s increases as the solution becomes more dilute. However, at higher concentrations (>0.01 mol·kg^{-1}) there is no obvious dependence of ΔH_s on concentration. The standard deviation for the last seven runs in this higher concentration range is 0.6% which is within the precision of the calorimeter. Some years ago Wu and Hepler also measured enthalpies of solution of crystalline sulphamic acid into water, and their results are listed in Table 3 (11).

In their concentration range, between 0.01 and 0.03 mol·kg^{-1}, they found that ΔH_s was almost independent of concentration. Their results (average 19.0 ± 0.12 kJ·mol^{-1}) were slightly higher than values obtained in this study for a similar concentration range (18.7 ± 0.4 kJ·mol^{-1}, from last seven runs).

The experimental enthalpies of solution were combined with the experimental enthalpies of dilution (see Table 4, to be discussed later in this report) to obtain the corresponding standard enthalpies of solution, $\Delta H_s°$ that are also presented in Table 3, with an average value, 19.0±0.3 kJ·mol^{-1}. Wu and Hepler used estimated enthalpies of dilution in combination with their experimental enthalpies of solution to obtain the desired standard-state enthalpy of solution (11). Now the estimation part of this earlier calculation can be eliminated by combining their experimental enthalpies with enthalpies of dilution measured in this study to obtain the standard-state enthalpies of solution, also listed in Table 3. This combination of results leads to an average $\Delta H_s° = 19.32$ kJ·mol^{-1}, with a standard deviation of 0.11 kJ·mol^{-1}.

This study also obtained an average overall $\Delta H_s° = 19.17$ kJ·mol^{-1} with standard deviation = 0.27 kJ·mol^{-1}. Since there is less scatter in the earlier (11) enthalpies of solution than in the values obtained in the present study (because these experiments covered a much wider concentration range than earlier work), it is possible that the earlier values are slightly more accurate, which leads to a weighted average $\Delta H_s° = 19.2 \pm 0.2$ kJ·mol^{-1} , which is recommended as the "best" available value for the standard enthalpy of solution and associated *total* uncertainty.

ENTHALPIES OF DILUTION

The enthalpies of dilution of sulphamic acid were obtained by a series of titrations. The stock solution containing 1.000 mol·kg sulphamic acid in water was titrated into 50 g deionized water. At each step, the enthalpy of dilution detected by calorimetry reflected the process

$$HS(m_s) \longrightarrow HS(m_f) \qquad \text{Eq 1}$$

where HS represents the sulphamic acid, m_s is the molality of the stock solution, and m_f is the molality of the final diluted solution in the dewar. The molalities for final solutions and the corresponding enthalpies of dilution are shown in Table 4.

ENTHALPY OF IONIZATION

To carry out further thermodynamic calculations to obtain the enthalpy of ionization, consider the dilution of one mole of sulphamic acid from some m_f to m=0, which can be described as

$$(1-\alpha)HS\,[m=(1-\alpha)m_f] + \alpha H^+ (m=\alpha m_f) + \alpha S^- (m=\alpha m_f)$$

$$\rightarrow H^+(m=0) + S^-(m=0) \qquad \text{Eq 2}$$

in which α represents the degree of ionization and S^- represents the sulphamate ion. The total enthalpy of dilution represented by Eq 2, $\Delta H_{dil}°$, can be obtained from the experimental data of ΔH_{dil} (from 1.000m to m_f). The graph of ΔH_{dil} vs $(\alpha m_f)^{1/2}$ (determination of α will be discussed later) gave a good straight line as shown in Fig 2. The intercept of this line gives the ΔH_{dil} for the dilution of 1.000m stock solution to infinite dilution, which, combined with the directly measured ΔH_{dil} (from 1.000m to some m_f), gives the $\Delta H_{dil}°$ (from some m_f to infinite dilution). The $\Delta H_{dil}°$ consists of three components: 1) enthalpy of dilution of un-ionized HS from $(1-\alpha)m_f$ to m=0; 2) enthalpy of dilution of H^+ and S^- from αm_f to m=0, ΔH_{dil}^{ion}; and 3) enthalpy of ionization of un-ionized HS, $\Delta H_{ion}°$. It is assumed that the enthalpy of dilution for un-ionized HS is negligible (10,12) so that we obtain

$$\Delta H_{dil}^{\circ} = \alpha \Delta H_{dil}^{ion} + (1-\alpha)\Delta H_{ion}^{\circ} \qquad \text{Eq 3}$$

and

$$\Delta H_{ion}^{\circ} = (\Delta H_{dil}^{\circ} - \alpha \Delta H_{dil}^{ion}) / (1-\alpha) \qquad \text{Eq 4}$$

In Eq 3 and 4 ΔH_{dil}^{ion} is the enthalpy of dilution of hydrogen ions and sulfamate ions, which has been assumed to be equal to the enthalpy of dilution of an equal amount of HCl solution at the same ionic concentration (18). The degree of ionization, α, is calculated as follows.

The ionization equilibrium for a solution with molality m_f, can be described by

$$HS\ [m=(1-\alpha)m_f] = H^+ (m=\alpha m_f) + S^- (m=\alpha m_f) \qquad \text{Eq 5}$$

The thermodynamic equilibrium constant for this ionization process can be written as

$$K = \alpha m_f \gamma_+ \cdot \alpha m_f \gamma_- / \gamma_o (1-\alpha) m_f = \alpha^2 m_f \gamma_\pm^2 / \gamma_o (1-\alpha) \qquad \text{Eq 6}$$

where γ_+ and γ_- are activity coefficients for H^+ ions and S^- ions, respectively, γ_o is the activity coefficient of un-ionized HS, and $\gamma_\pm$ is the mean activity coefficient of ions, which can be calculated by the extended Debye-Huckel equation

$$-\log \gamma_\pm = A\, \mu^{0.5} / (1 + B\, a\, \mu^{0.5}) \qquad \text{Eq 7}$$

where a is the ion size parameter and is taken to be 3.85 Å as recommended by King and King (8), and μ is the ionic strength which equals αm_f. Equations 6 and 7 are solved simultaneously to obtain α and $\gamma_\pm$ by successive approximations. In these calculations the equilibrium constant K was taken to be 0.103 as reported by King and King (8), and γ_o was taken to be 1.0.

The enthalpies of ionization of sulphamic acid calculated from Eq 6 are presented in Table 4. The average ΔH_{ion}° from ten runs is 0.74 kJ·mol^{-1} with standard deviation of 0.05 kJ·mol^{-1}. Although the statistical deviation is only about 0.05 kJ·mol^{-1}, our estimates of uncertainties due to calorimetric measurements, auxiliary data such as K and $\gamma_{\pm}$, and assumptions about γ_o and $\Delta H_{dil}{}^{ion}$ lead us to estimate that the *total* uncertainty in $\Delta H°$ is about ±0.20 kJ·mol^{-1}.

We now compare our $\Delta H_{ion}° = 0.74 \pm 0.2$ kJ·mol^{-1} with results of earlier investigations. As previously mentioned, King and King (8) derived $\Delta H_{ion}° = 1.13$ and 1.92 kJ·mol^{-1} by way of dlnK/dT. Kurz and Farrar obtained $\Delta H_{ion}° = 1.72$ kJ·mol^{-1}, also from dlnK/dT (9). Because of the difficulties in determining accurate K values for "almost-strong" electrolytes and the magnification of uncertainties associated with differentiation as in dlnK/dT, uncertainties in these $\Delta H_{ion}°$ values are quite large.

Calorimetric measurements by Hopkins et al. led to $\Delta H_{ion}° = 0.59$ and 0.79 kJ·mol^{-1} (10). These authors chose a "best" $\Delta H_{ion}° = 1.0 \pm 0.6$ kJ·mol^{-1}, based on their own calorimetric results and the earlier (8) values from dlnK/dT. We calculate that their calorimetric results lead to a weighted "best" $\Delta H_{ion}° = 0.75 \pm 0.3$ kJ·mol^{-1}, in which 0.3 kJ·mol^{-1} is our estimate of the *total* uncertainty. In our opinion, their calorimetric $\Delta H_{ion}°$ was sufficiently better than values from dlnK/dT that dlnK/dT values were not considered in obtaining the value 0.75 ± 0.3 kJ·mol^{-1}.

It is evident that our $\Delta H_{ion}° = 0.74 \pm 0.2$ kJ·mol^{-1} is in good agreement with the earlier $\Delta H_{ion}° = 0.75 \pm 0.3$ kJ·mol^{-1} (2) . Differences between the calorimetric values of $\Delta H_{ion}°$ and those from dlnK/dT range from 0.38 to 1.2 kJ·mol^{-1}; most of these differences can be attributed to large uncertainties in the dlnK/dT values. Large differences have also been observed for iodic acid for which the method of dlnK/dT led to $\Delta H_{ion}°$=-10 kJ mol^{-1} with large uncertainties, while calorimetric measurements led to $\Delta H_{ion}°$ (from calorimetric measurement) =-2.8 ±0.5 kJ mol^{-1} (13).

It is our opinion that $\Delta H_{ion}°$ values (10) from enthalpies of solution and neutralization have larger uncertainties than $\Delta H_{ion}°$ determined from enthalpies of dilution in this study because analyses of the latter results avoid taking the differences between relatively large enthalpies, which was required in obtaining the earlier results.

The equilibrium constant K = 0.103 at 25°C reported by King and King (8) was used to calculate the free energy of ionization $\Delta G° = 5.6\ kJ{\cdot}mol^{-1}$. Combination of $\Delta H°$ and $\Delta G°$ gives the entropy of ionization $\Delta S° = -16.3\ J{\cdot}mol^{-1}{\cdot}K^{-1}$.

CONCLUSIONS

1. Ionization of an "almost-strong" electrolyte can be studied by measurements of enthalpies of dilution using a calorimeter.
2. The "best" thermodynamic properties for ionization of sulphamic acid are recommended as $\Delta H_{ion}° = 0.74 \pm 0.2\ kJ{\cdot}mol^{-1}$, $\Delta G° = 5.6\ kJ{\cdot}mol^{-1}$, and $\Delta S° = -16.3\ J{\cdot}mol^{-1}$
3. The standard enthalpies of solution of sulphamic acid is $19.2 \pm 0.2\ kJ{\cdot}mol^{-1}$.

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Table 1- Heat of solution of KCl in deionized water

Run #	Mass KCl g	Mass H_2O g	KCl/H_2O mol/mol	Q J	ΔH_s kJ·mol^{-1}	ΔH_s° kJ·mol^{-1}
1	0.0867	58.99	3.55x10-4	20.030	17.223	17.008
2	0.0223	56.69	9.51x10-5	5.180	17.317	17.189
3	0.0416	51.41	1.96x10-4	9.757	17.485	17.314
4	0.0518	51.41	2.44x10-4	12.21	17.573	17.384
5	0.0507	51.42	2.38x10-4	11.870	17.454	17.267
					Average	17.23±0.14

Table 2- Heat of reaction of THAM (0.10M) with HCl (0.1M)

Run#	Volume THAM cm^3	Mass H_2O g	Q J	ΔH_r kJ·mol^{-1}
1	0.400	50.00	1.917	47.925
2	0.050	50.40	0.236	47.240
3	0.400	50.45	1.900	47.510
4	0.600	50.85	2.901	47.557
5	0.300	51.45	1.406	46.853
			Average	47.42±0.35

Table 3- Measured enthalpies of solution (ΔH_S) and calculated standard enthalpies of solution (ΔH_S°) at 25°C

This work			Wu and Hepler		
m $mol\cdot kg^{-1}$	ΔH_S $kJ\cdot mol^{-1}$	ΔH_S° $kJ\cdot mol^{-1}$	m $mol\cdot kg^{-1}$	ΔH_S $kJ\cdot mol^{-1}$	ΔH_S° $kJ\cdot mol^{-1}$
0.002102	19.51	19.62	0.01046	19.12	19.34
0.006816	19.23	19.42	0.01420	19.08	19.32
0.01240	18.60	18.84	0.01694	19.08	19.35
0.02101	18.44	18.75	0.01911	18.83	19.11
0.03266	18.34	18.71	0.02052	19.04	19.33
0.04362	18.49	18.91	0.02304	19.08	19.38
0.04653	18.56	19.00	0.02474	19.16	19.48
0.06344	18.34	18.84	0.02895	18.83	19.17
0.08214	18.59	19.15	0.03231	19.04	19.41

Table 4- Enthalpies of dilution and corresponding calculated Eenthalpies of ionization for sulphamic acid

m, mole·kg^{-1}	ΔH_{dil}* J·mol^{-1}	ΔH_{ion}° J·mol^{-1}
0.007937	1048	831
0.01186	1018	651
0.01575	975	701
0.01961	953	690
0.02344	926	726
0.02724	896	777
0.03101	881	744
0.03475	866	717
0.03846	842	761
0.04215	830	749

* The values are for dilution from stock solution (m=1.000 mol·kg^{-1}) to m, The values for ΔH_{dil} from m to m=0 are the differences between ΔH_{dil} for stock solution from m=1.000 mol·kg^{-1} to m=0, (1249 J·mol^{-1}, obtained in Fig. 1) and the values in this table.

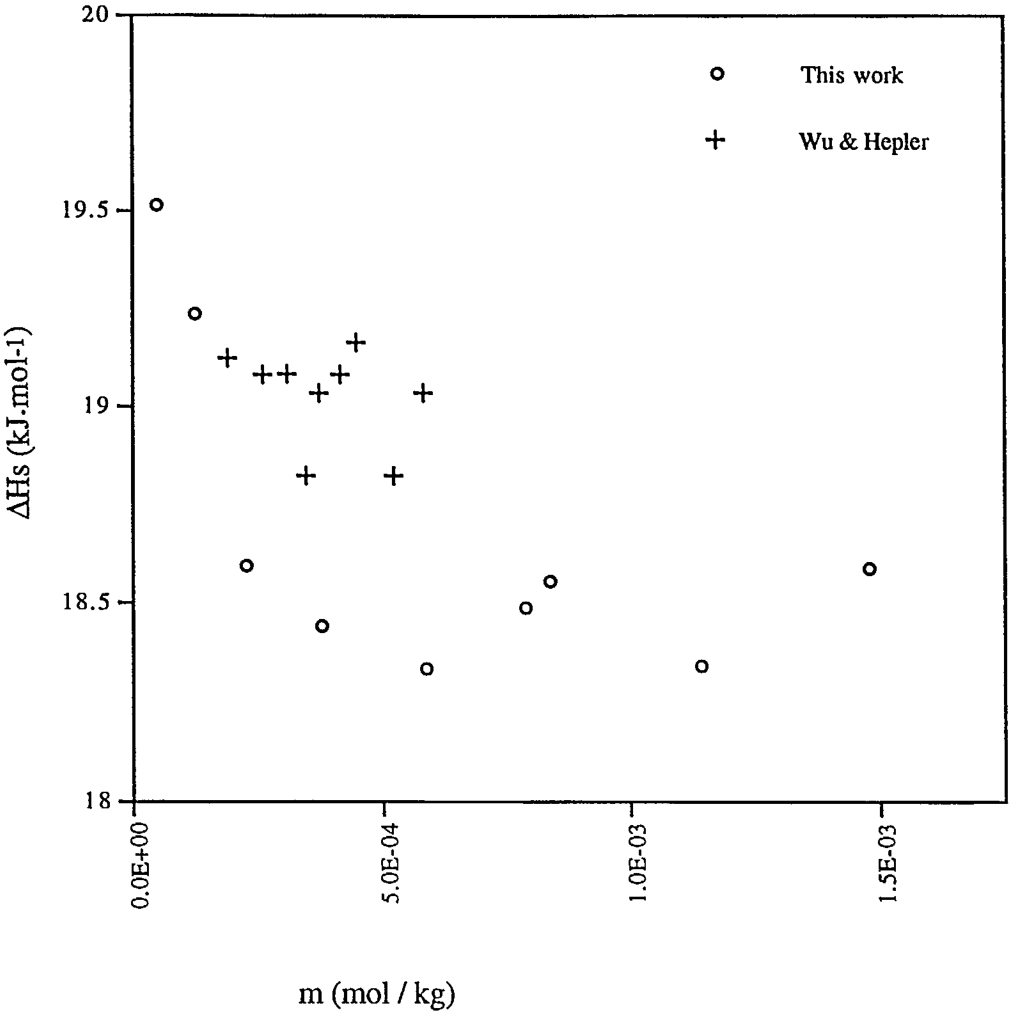

Fig. 1- Enthalpy of solution vs concentration for sulphamic acid

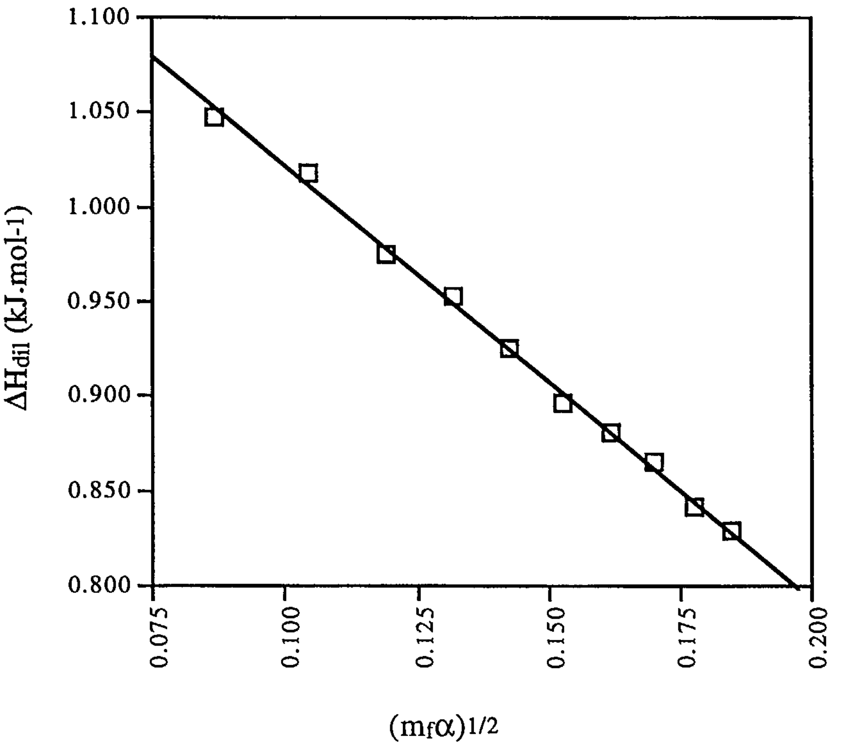

Fig. 2- ΔH_{dil} vs $(m\alpha)^{1/2}$. The intercept of the straight line gives $\Delta H_{dil}°$ for stock solution from m=1.000 to m=0