# Heats of Mixing of 1 to 1 Electrolytes in Methanol–Water Solutions

## HCl–NaCl, LiCl–NaCl, KCl–NaCl, and HCl–KCl Systems at 25°

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**Heats of mixing of equimolal 1 molal solutions of HCl–NaCl, LiCl–NaCl, KCl–NaCl, and HCl–KCl in methanol-water as a function of solute mole fraction were determined calorimetrically at 25°. The heats are compared with similar studies on the same electrolyte systems in pure water. Significant differences have been observed. HCl–NaCl is comparable in magnitude but the curve exhibits considerable asymmetry, while the symmetric thermal interactions of LiCl–NaCl and KCl–NaCl are about twice those observed in pure water. An inversion of heats was observed for the HCl–KCl system.**

THE PHYSICOCHEMICAL properties of strong electrolytes in organic-water solutions have been the subject of recent experimental papers. Among these are conductance (*2*) and activity coefficient (*7*) studies of uni-univalent strong halides in aqueous solutions with organic hydroxy solvents, such as methanol and ethanol. Experiments in such solvent systems are of interest when compared with similar studies in pure water. They allow an examination of the part taken by the solvent in such ionic solutions and provide an insight on ion-ion and ion-solvent interactions.

Very few experiments with mixed 1 to 1 strong electrolytes in such solutions have been reported. Notable is the electromotive force measurement of the activity coefficient of HCl in NaCl solutions at 1 molal total concentration, in mixtures of methanol and water (0 to 60 wt. % of methanol), from 0° to 40°, in 5° intervals. Akerlof, Teare, and Turck (*1*) found that the activity coefficient of HCl obeyed Harned's Rule (*4*) :

$$\log \gamma_2 = \log \gamma_{2(0)} - \alpha_{23}[m(1 - X_2)] \qquad (1)$$

where $\gamma_2$ is the activity coefficient of HCl in the presence of NaCl at solute mole fraction $(1 - X_2)$ and total molality $m$. $\gamma_{2(0)}$ is the activity coefficient of pure HCl at molality $m$. $\alpha_{23}$ is an empirical coefficient independent of solute mole fraction, but in general is a function of the total molality $m$, temperature, and pressure.

These authors observed that at a given temperature the Harned coefficient $\alpha_{23}$ was independent of the weight % of methanol over the entire range of measurement. That is, it was possible to calculate the activity coefficient of HCl in the mixed electrolyte by using values of $\alpha_{23}$ determined similarly in pure water as the solvent (*3*). Based on these results, Harned (*5*) has suggested that the activity coefficient of the salt is also independent of solvent composition and may be obtained from its behavior in pure water:

$$\log \gamma_3 = \log \gamma_{3(0)} - \alpha_{32}[m(X_2)] - \beta_{32}[m(X_2)]^2 \qquad (2)$$

Thus, it is assumed that at a given temperature and molality the coefficients $\alpha$ and $\beta$ remain invariant regardless of solvent composition. The data of Akerlof, Teare, and Turck indicate that the temperature dependence of these coefficients should also be independent of solvent composition.

For systems obeying Harned's Rule, the heat of mixing of equimolal solutions of two 1 to 1 electrolytes at $X = 0.50$ is (*6*):

$$\Delta H_m = \frac{2.303RT^2m}{4} \frac{\partial}{\partial T} [\alpha_{23} + \alpha_{32} + m(\beta_{23} + \beta_{32})] \qquad (3)$$

Thus, $\Delta H_m$ at a given temperature and molality is a function of the sum of the temperature derivatives of the Harned coefficients, and its measurement in pure water and mixed solvent should provide an accurate test of the validity of the above assumptions. If the temperature variation of the Harned coefficients is indeed independent of solvent composition, then $\Delta H_m$ should behave similarly. Differing heats however may be a result of stronger interionic forces in solvent systems of reduced dielectric constant. The present study describes heats of mixing of HCl-NaCl, LiCl-NaCl (1$m$, 50-50 weight % methanol and water), and KCl-NaCl, HCl-KCl (1$m$, 40 weight % methanol, 60% water), all at 25°. Earlier contributions (*8-11*) reported the investigation of these mixed electrolytes in pure water at the same molality and temperature.

## EXPERIMENTAL

**Calorimeter.** The calorimeter (*8*) and mixing procedure (*11*) have been described elsewhere. The over-all experimental error was ±1%.

**Materials.** All chemicals, A.R. grade, were dissolved in triple-distilled water and A.R. methanol. All solutions were freshly prepared prior to each run.

## RESULTS AND DISCUSSION

Observed values of $\Delta H_m$ for all systems as a function of solute mole fraction are shown in Table I and are represented by symbols in Figure 1. The data reported (*8-11*) in pure water are shown by dashed lines. Curves for HCl-NaCl, LiCl-NaCl, and KCl-NaCl represent the fit of all data, by the method of least squares, arranged in analytical equations of the type (*8*):

$$\Delta H_m = 2.303RT^2m(X)(1 - X)(A + BX) \qquad (4)$$

Table I. Heats of Mixing, $\Delta H_m$ (Cal. per Mole), as a Function of Solute Mole Fraction $X$

| HCl-NaCl |  | LiCl-NaCl |  |
|---|---|---|---|
| $\Delta H_m$ | $X_{HCl}$ | $\Delta H_m$ | $X_{LiCl}$ |
| 6.82 | 0.110 | 16.2 | 0.111 |
| 12.8 | 0.208 | 28.2 | 0.210 |
| 18.0 | 0.295 | 35.4 | 0.298 |
| 22.4 | 0.373 | 40.7 | 0.377 |
| 26.8 | 0.618 | 42.8 | 0.627 |
| 26.4 | 0.697 | 39.1 | 0.705 |
| 23.1 | 0.787 | 32.9 | 0.792 |
| 15.1 | 0.887 | 20.4 | 0.890 |
| **KCl-NaCl** |  | **HCl-KCl** |  |
| $\Delta H_m$ | $X_{KCl}$ | $\Delta H_m$ | $X_{HCl}$ |
| -7.05 | 0.110 | -2.48 | 0.111 |
| -12.0 | 0.208 | -3.55 | 0.212 |
| -15.0 | 0.296 | -3.35 | 0.300 |
| -17.4 | 0.374 | -2.66 | 0.379 |
| -18.3 | 0.622 | -0.97 | 0.625 |
| -15.9 | 0.701 | 0.25 | 0.703 |
| -12.0 | 0.789 | 1.18 | 0.790 |
| -7.10 | 0.888 | 1.33 | 0.891 |

Table II. Summary of Parameters $A$, $B$ and $B'$

| System | $A \times 10^4$ | $B \times 10^4$ | $B' \times 10^4$ |
|---|---|---|---|
| HCl-NaCl | 1.42 | 2.39 | ... |
| LiCl-NaCl | 3.80 | 1.25 | ... |
| KCl-NaCl | -1.78 | -0.10 | ... |
| HCl-KCl | -0.63 | 0.58 | 0.54 |

Table III. Summary of $\Delta H_m$ at $X = 0.50$, Cal. per Mole

|  | Solvent System |  |
|---|---|---|
| Electrolyte | $H_2O$ | $CH_3OH$-$H_2O$ |
| HCl-NaCl | 30.6 | 26.6 |
| LiCl-NaCl | 20.9 | 45.0 |
| KCl-NaCl | -9.6 | -18.6 |
| HCl-KCl | -3.5 | -2.1 |

For the system HCl-KCl, a third constant $B'$ was necessary:

$$\Delta H_m = 2.303RT^2 m(X)(1 - X)(A + BX + B'X^2) \qquad (5)$$

Table II shows a summary of these parameters for all systems.

An examination of $\Delta H_m$ in Figure 1 shows considerable differences in the behavior of each system in pure water and methanol-water, respectively. Table III shows values of $\Delta H_m$ at $X = 0.50$ for both solvent systems. The HCl-NaCl curve in Figure 1*A* shows a maximum sharply displaced from $X = 0.50$ toward the HCl-rich side. $\Delta H_m$ is always more endothermic in mixtures rich in HCl than in NaCl-rich solutions of corresponding composition. The magnitude of the thermal effect is comparable to that in aqueous solution. The pronounced asymmetry may in part be attributed to ion pairing in HCl.

Although the thermodynamic properties of aqueous HCl and LiCl are similar in the presence of NaCl, their behaviors differ sharply in the organic-water solution. The endothermic LiCl-NaCl system in Figure 1*B* is approximately symmetrical about $X = 0.50$ in both water and water-methanol. However, the heats compare in magnitude to those expected for 3.4 molal solutions in pure water (*8*). The exothermic KCl-NaCl system in Figure 1*C* is also symmetrical about $X = 0.50$, and the heat has twice the magnitude of that observed in pure water at the same concentration. Therefore, specific interactions in LiCl-NaCl and KCl-NaCl are much stronger in methanol-water solutions than in water. Consequently, the Harned coefficients and their temperature derivatives may be considerably larger in methanol-water than in pure water. The HCl-KCl system exhibits very unusual behavior, since no inversions in heat have been observed for any other systems studied at this laboratory. The absolute magnitude of the thermal effect is very small, as in the exothermic aqueous system, however, in HCl-rich solutions the heats become endothermic.

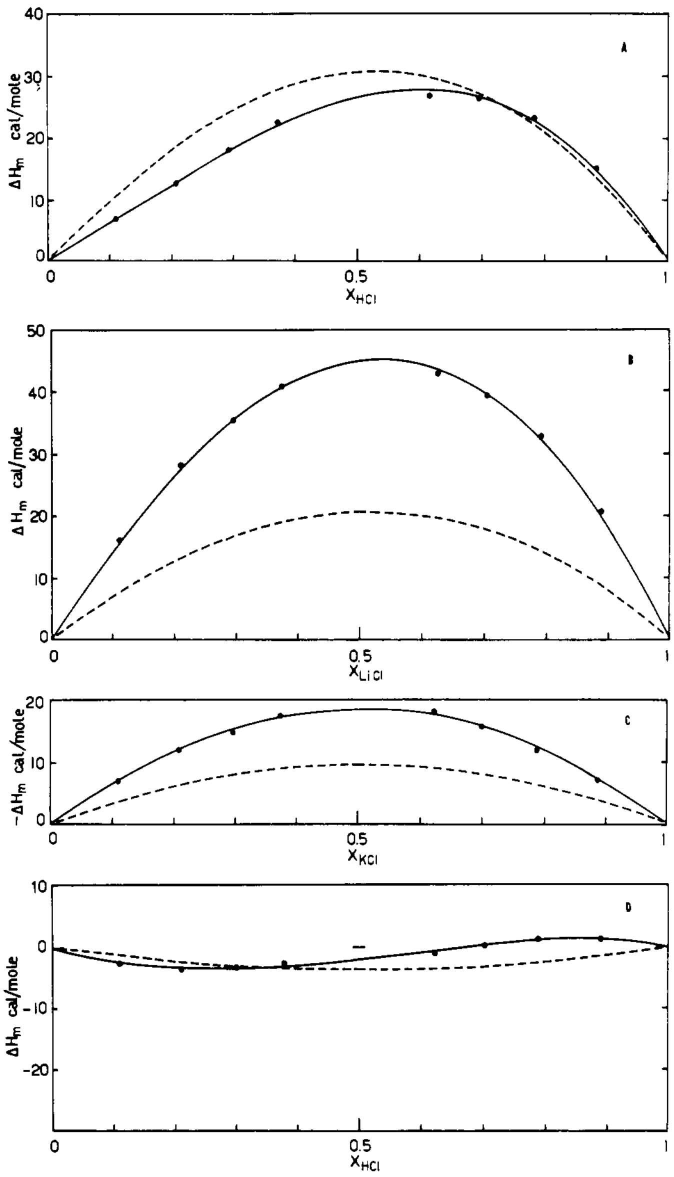

Figure 1. Heats of mixing ($\Delta H_m$) as a function of the solute mole fraction

*A*. System, HCl-NaCl; solute mole fraction of HCl ($X_{HCl}$), in 50-50 wt. % methanol and water, 25°.
——— $CH_3OH$-$H_2O$, - - - $H_2O$, Ref. (*9*)

*B*. System, LiCl-NaCl; solute mole fraction of LiCl ($X_{LiCl}$), in 50-50 wt. % methanol and water, 25°.
——— $CH_3OH$-$H_2O$, - - - $H_2O$, Ref. (*8*)

*C*. System, KCl-NaCl; solute mole fraction of KCl ($X_{KCl}$), in 40 wt. % methanol and 60% water, 25°.
——— $CH_3OH$-$H_2O$, - - - $H_2O$, Ref. (*10*)

*D*. System, HCl-KCl; solute mole fraction of HCl, ($X_{HCl}$), in 40 wt. % methanol and 60% water, 25°.
——— $CH_3OH$-$H_2O$, - - - $H_2O$, Ref. (*11*)

Many further thermodynamic studies must be made over wide ranges of temperature, molality, and solvent type before any adequate theory can be developed to account for the observed behavior.

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# Low Temperature Heat Capacity and Entropy of Oxamide, 10° to 310° K.

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**The heat capacity of triclinic oxamide, $(CONH_2)_2$, was measured over the temperature range 10° to 310° K. The calculated entropy at 298.15° K. is 28.23 e.u. and the enthalpy 4407 cal. per mole. A small anomalous peak was observed between 262° and 277° K. with a maximum at 273° K. A table of thermodynamic functions for the ideal gas state is included.**

OXAMIDE, $(CONH_2)_2$, mol. wt. 88.0664, is of interest as a fertilizer material—it has a relatively high nitrogen content (31.81%N), it is slightly soluble in water, and its rate of release of nitrogen varies inversely with its particle size (*3*). In a continuing program of collection of thermodynamic data on fertilizer materials, the low temperature heat capacity of triclinic oxamide was measured over the temperature range 10° to 310° K., and the entropy and enthalpy were calculated from the results.

Oxamide exists in at least two crystalline forms, triclinic and orthorhombic, but the orthorhombic form reverts spontaneously to the triclinic form on standing at room temperature (*6*). These measurements were made on the apparently stable triclinic form.

## MATERIALS AND APPARATUS

Triclinic oxamide was recrystallized, at least twice, from a distilled water solution that was saturated at 95° C. and cooled slowly to room temperature in an insulated beaker. It contained 31.7%N (stoichiometric, 31.81%) and was in the form of a single phase of severely intergrown crystals with only a small fraction of single crystals.

A second sample of oxamide was prepared by subliming the recrystallized material at 180° C. in a stream of dry nitrogen at atmospheric pressure and retaining the portion of crystals that condensed from the vapor phase near 165° C. The sublimed crystals were expected to be anhydrous, but they apparently contained traces of water; analysis showed 31.80, 31.70, and 31.74%N. On petrographic examination, the sublimed crystals appeared the same as those crystallized from solution. Infrared and x-ray examination did not distinguish between the preparations, but differential thermal analysis showed a distinct difference in behavior between 200° and 300° C.

The low temperature calorimeter has been described (*4, 5*). Temperatures were measured to 0.0001° for use in calculation of temperature differences; they were rounded to two decimal places in the preparation of tables. The defined calorie is taken as 4.1840 absolute joules—the ice point as 273.15° K. The density of oxamide to be used in vacuum corrections is 1.667 grams per cc. (*1*). The heat capacities were corrected for curvature where it was significant. The calculations were made on a digital computer (*4*).

## OBSERVATIONS

The observed heat capacities of oxamide that had been crystallized from solution (not reported) showed a complex peak that extended from 235° to 305° K. with a sharp maximum at 273° K. The peak was reproducible if the sample was held at 195° K. overnight or longer; otherwise, the observed values depended on the thermal history of the sample. Variation in the conditions of crystallization from solution had little effect on the shape or magnitude of the peak.

The observed heat capacities of sublimed oxamide showed a peak of about the same shape that started at 262° K. and extended to 277° K. with a maximum at 273° K., but the peak was about a tenth the size of that of the oxamide crystallized from water.

The excess heat capacity in the region of the peak for both water-crystallized and sublimed oxamide is shown in Figure 1. The "normal" heat capacities under the peak were calculated from a least-squares fourth-degree polynomial that fitted six observed points between 226° and 261° K. and 11 observed points between 277° and 305° K. with an average deviation of 0.01%.