Nomenclature

K-point = singular point where L2 is in critical identity with V in the presence of L1 phase
L1 = CO_2-lean liquid phase
L2 = CO_2-rich liquid phase
N_i = number of moles of component i
P = pressure, atm
$Q1$ = quadruple point 1 (coexistence of the four-phase V-L1-L2-S1)
S1 = solid 2-methylnaphthalene
T = temperature, °C
$UCST$ = upper critical solution temperature of L1 and L2
V = vapor phase
$\bar{V}$ = partial molar volume, cc/g-mol
x_i = mole fraction of species i in the liquid phase

Greek Letter

β = extractive solvent (CO_2) free selectivity

Subscripts

2mn = 2-methylnaphthalene
10 = n-decane

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Calorimetric Investigation of Salt–Amide Interactions in Aqueous Solution

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Enthalpies of solution of the liquid amides, formamide, *N*-methylformamide, *N,N*-dimethylformamide, *N,N*-dimethylacetamide, and *N*-methylpropionamide and of acetamide (c) and *N*-methylacetamide (c) were determined in water and in solutions of electrolytes, mainly alkali and alkaline earth halides, over a range of salt molalities at amide molalities below 0.05*m* at 25°C. Enthalpies of transfer of the amides from water to salt solution were calculated from these data. With formamide, these quantities were negative for all salts investigated. For a series of salts having an ion in common, the transfer enthalpies of formamide became increasingly negative with increasing crystal radius of the other ion. Enthalpies of transfer of the other amides were more positive than for formamide, reflecting the contribution of added nonpolar groups. Enthalpies of transfer of *N,N*-dimethylacetamide differed markedly for the same salt from those of *N*-methylpropionamide, suggesting steric or charge distribution differences between structural isomers.

The thermodynamic quantities relating to the transfer of amides and peptides from water to salt solutions are useful in understanding processes involving the interaction of proteins and salts as, for example, the denaturation of proteins by electrolytes (*17*). Of particular interest is the relative importance of structural features of the amide and peptide molecules, such as number, kind, and arrangement of nonpolar groups, dipole moment, and hydrogen bonding ability, in affecting the sign and magnitude of these quantities. Although free energies of transfer for various compounds have been obtained (*7, 10, 11*), there has been little in the way of direct measurement of the enthalpy changes attending the transfer of amides and peptides from water to salt solution (*2*).

The present study had the aim of developing enthalpy of transfer data for a number of amides and peptides with a variety of salts. A qualitative comparison of the different structural influences could then be made as well as a correlation of various trends with salt type. Since Stern and his collaborators (*14, 15*) had measured enthalpies of transfer for several nonelectrolytes other than amides, a general comparison of trends for different nonelectrolytes was also possible.

Experimental

Materials. Formamide was obtained from either Nuclear Enterprises or Eastman Kodak Co. It was fractionally recrystallized twice under dry nitrogen (*18*). The recrystallized material had a melting point of 2.55°C. *N*-methylformamide (Eastman) was dried over phosphorus pentoxide, vacuum distilled, and stored over molecular

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sieves. Acetamide (Eastman) was recrystallized from ethyl ether (*18*). *N*-methylacetamide (Eastman) was purified by fractional freezing. The crystalline product was stored over P_2O_5. *N,N*-dimethylformamide and *N,N*-dimethylacetamide were obtained from Burdick and Jackson Laboratories. These were reported to be chromatographically homogeneous when received and were not purified further before use. *N*-methylpropionamide (obtained from Eastman) was purified by vacuum distillation. The constant-boiling middle fraction was collected under nitrogen and stored over molecular sieves.

The salts used in this investigation were reagent grade or other good quality materials. They were assayed for purity by conventional techniques, e.g., titration of halide with the absorption indicator, dichlorofluorescein. Some were recrystallized where necessary, but generally they were merely dried and used without further purification.

Air-equilibrated double-distilled water was used in the preparation of the solutions. All solutions were made up on a molality basis, i.e., moles of solute/1000 grams of *water* as the solvent.

Calorimetric measurements. The enthalpies of solution used to evaluate enthalpies of transfer for the systems of interest were measured with the LKB Model 8700-1 precision calorimeter. This is an isoperibol calorimeter which consists of three major components, a thermostated bath; the calorimeter assembly including a brass jacket, a thin-walled glass reaction cell containing a motor driven stirrer, and an automatic ampul breaker; and the electronic console with an external recorder.

The assembled reaction vessel contained a thermistor, an electrical heater for calibration, a combination gold stirrer–ampul sample holder, and an embedded sapphire tip at the bottom for heat-free punctures of the ampuls. The reaction vessel was contained in a reflective, chrome-washed brass jacket which was sealed, evacuated, and submerged into the thermostated bath.

The reaction was initiated by the mechanical crushing of the ampul on the sapphire tip, and the heat liberated or absorbed was observed as a resistance change of the thermistor in the reaction vessel. The procedure for making a calorimetric run was a modification of that suggested by the manufacturer (*16*). The temperature of the thermostating bath was maintained at 25.00° ± 0.01°C during the runs. Reactions were initiated and completed within ±0.05°C of this reference temperature.

Some sources of systematic error in the measurements can be enumerated. These include errors in the measurement of electrical quantities during calibration and in the measurement of the time interval during which electrical power is supplied. These errors appear to be negligible. Potentially more significant errors may result as a combination of the heat of ampul breaking together with a corresponding change in the vapor space in the reaction vessel. Empirical tests showed that this combined effect would amount in the worst case to less than 0.1% of the measured enthalpy of solution.

Table I. Enthalpies of Solution of Amides in Water at 25°C

Compound	Molecular wt	Enthalpy of solution, ΔH_{soln}^{w}, kcal/mol		Ref.
		This work	Literature	
Formamide	45.04	0.4848 ± 0.0016	0.48 ± 0.01	(*1*)
N-methylformamide	59.07	−1.706 ± 0.002	. . .	
N,N-dimethylformamide	73.09	−3.635 ± 0.005	−3.640 ± 0.029	(*13*)
Acetamide	59.07	2.305 ± 0.001	2.28 ± 0.03	(*1*)
N-methylacetamide	73.09	−0.9402 ± 0.0013	−1.10 ± 0.03	(*1*)
			−1.195	(*5*)
N,N-dimethylacetamide	87.11	−5.116 ± 0.002	−5.20 ± 0.03	(*1*)
			−5.010	(*5*)
N-methylpropionamide	87.11	−3.569 ± 0.005	−3.552 ± 0.005	(*4*)

Results

Calorimeter tests. The enthalpies of solution of tris(methylhydroxy)aminomethane (Sigma Chemical Co.) in 0.1*M* hydrochloric acid and potassium chloride (J. T. Baker) in water were measured as −7.114 ± 0.005 and 4.100 ± 0.005 kcal/mol (corrected to infinite dilution), respectively. Accepted literature values for the ΔH_{soln} of tris and KCl are −7.115 ± 0.001 kcal/mol (*9*) and 4.115 ± 0.010 kcal/mol (*8*), respectively. The agreement is satisfactory in both cases.

Enthalpies of solution of amides in water. Table I gives values of the enthalpies of solution, ΔH_{soln}^{w}, in water at 25°C for the amides in water. The superscript, *w*, designates enthalpies derived from measurements made in water alone as opposed to results obtained in water–salt solutions given below for which the enthalpies of solution will be identified with the superscript, *ws*. The number of determinations for each amide varied with four being the norm, although 14 determinations were carried out with *N,N*-dimethylacetamide. The uncertainty limits given in the table are generally standard deviations of the mean value of these measurements. In the course of these experiments, it was shown that, at amide molalities below 0.05*m*, the enthalpy of solution is independent of the amide molality. All ΔH_{soln}^{w} values in Table I were obtained under experimental conditions which would give final amide molalities below this value.

The results for four of the seven amides are in agreement with previous literature values. The present value for *N,N*-dimethylacetamide is in between the previous results. The enthalpy of solution of *N*-methylacetamide differs appreciably from previous results. The difficulty of maintaining this compound in a dry state may be significant. When *N*-methylacetamide crystals were damp, more exothermic enthalpies of solution were observed than that reported here. This suggests a possible reason for the discrepancy.

Enthalpies of solution of amides in salt solution. Measurements were made of the enthalpies of solution, ΔH_{soln}^{ws}, of all the amides mentioned above, with the exception of *N,N*-dimethylformamide, in various salt solutions. The dependence of the enthalpy of solution on salt molality for a number of salt–amide pairs was studied. As before, keeping the amide molality below 0.05 in the final solution produced values of ΔH_{soln}^{ws} which were independent of amide molality. The data are presented in Table II. Nearly all the points given are the result of replicate determinations. Uncertainty limits for replicate measurements are either standard deviations of the mean or average deviations as appropriate for the number of measurements involved.

Discussion

For the purposes of examining the trends in these data, it is useful to define the enthalpy of transfer as

$$\Delta H_{tr} = \Delta H_{soln}^{ws} - \Delta H_{soln}^{w} \qquad (1)$$

This quantity is the enthalpy gained or lost when a mole of amide is transferred from water to salt solution of a particular salt molality. If the experimental conditions are such that the individual terms on the right hand side of Equation 1 are independent of amide molality, no specifi-

Table II. Enthalpies of Solution of Amides in Aqueous Salt Solutions at 25°C

Salt	Salt molality, m_s	ΔH_{soln}^{ws}, kcal/mol
	Formamide	
NaCl	0.2787	0.4194 ± 0.0001
	0.5235	0.3740 ± 0.0003
	0.7556	0.3348 ± 0.0021
	1.0690	0.2862 ± 0.0013
	1.7821	0.1954 ± 0.0007
	3.4513	0.0793 ± 0.0003
NaBr	0.1059	0.4550 ± 0.0015
	0.3594	0.3930
	0.7013	0.3198
	1.5644	0.1746 ± 0.0039
	2.2015	0.0790 ± 0.0017
	3.3087	0.0390
NaI	0.5013	0.3342
	0.7880	0.2304
	1.0567	0.1415
	3.8967	−0.1396
LiCl	0.5845	0.3947 ± 0.0010
	1.1489	0.3252 ± 0.0011
KCl	0.4988	0.3709
	1.0341	0.2871 ± 0.0010
	3.4305	0.0340 ± 0.0042
KBr	0.5074	0.3600 ± 0.0006
KI	0.5123	0.3456 ± 0.0002
CsCl	0.5167	0.3611 ± 0.0050
GuHCl[a]	0.5163	0.3337 ± 0.0005
NaSCN	0.6343	0.3072 ± 0.0008
	0.9661	0.2407 ± 0.0017
$MgCl_2$	0.5043	0.2905 ± 0.0017
$CaCl_2$	0.4012	0.2918 ± 0.0031
$SrCl_2$	0.5112	0.2084 ± 0.0016
$BaCl_2$	0.4895	0.1795 ± 0.0033
SrI_2	0.5000	0.2180 ± 0.0004
$LaCl_3$	0.3822	0.2018 ± 0.0023
	N-Methylformamide	
NaCl	1.0498	−1.691
	2.8840	−1.645 ± 0.012
KCl	4.7505	−1.622 ± 0.001
KBr	0.3254	−1.721
	0.5200	−1.753 ± 0.008
	1.0223	−1.768 ± 0.006
	2.1637	−1.764 ± 0.005
	2.6934	−1.763 ± 0.008
	3.1937	−1.735 ± 0.002
	4.7719	−1.672 ± 0.007
$LiClO_4$	2.0218	−1.784 ± 0.001
	Acetamide	
NaCl	0.2631	2.295 ± 0.003
	0.5160	2.291 ± 0.001
	1.0498	2.289
	1.5985	2.294 ± 0.000
	2.0854	2.303
	2.8840	2.324
	N-Methylacetamide	
NaBr	1.0209	−0.817 ± 0.008
	3.3003	−0.477 ± 0.022
	4.5304	−0.242 ± 0.005
	N,*N*-Dimethylacetamide	
NaCl	0.2787	−5.110
	0.5235	−5.096 ± 0.002
	0.7556	−5.079 ± 0.003
	1.0690	−5.055 ± 0.003
	1.7821	−4.969 ± 0.002
	3.2684	−4.838 ± 0.005
	5.9681	−4.387 ± 0.004
NaBr	0.1059	−5.145 ± 0.006
	0.3594	−5.140 ± 0.003
	N,*N*-Dimethylacetamide	
NaBr	0.5020	−5.156 ± 0.012
	0.7013	−5.148 ± 0.009
	1.0477	−5.137 ± 0.011
	1.5644	−5.105 ± 0.001
	2.2015	−5.054 ± 0.003
	3.3087	−4.959 ± 0.002
	4.4564	−4.769 ± 0.004
	6.9718	−4.418
NaI	0.1144	−5.132
	0.2083	−5.168
	1.0349	−5.193 ± 0.005
	2.1720	−5.144 ± 0.001
	4.9085	−4.853 ± 0.013
	5.7841	−4.710
KCl	0.1014	−5.124 ± 0.002
	0.3041	−5.107 ± 0.005
	0.5076	−5.103 ± 0.005
	0.7766	−5.095 ± 0.001
	1.0369	−5.080 ± 0.005
	1.5728	−5.041 ± 0.003
	2.1282	−4.976 ± 0.015
	3.3123	−4.852 ± 0.008
KBr	0.1011	−5.136 ± 0.001
	0.2533	−5.145 ± 0.015
	0.5134	−5.166
	1.0404	−5.157 ± 0.003
	1.5955	−5.127 ± 0.001
	2.1649	−5.095 ± 0.004
	3.3709	−4.956 ± 0.001
	4.4634	−4.805 ± 0.010
KI	0.7799	−5.207 ± 0.006
	1.0519	−5.214 ± 0.005
	2.2088	−5.136 ± 0.003
	3.5384	−4.954 ± 0.004
	4.5708	−4.823 ± 0.002
	6.9355	−4.431 ± 0.005
$LiClO_4$	0.1837	−5.103 ± 0.005
	0.3875	−5.096 ± 0.012
	0.4968	−5.074 ± 0.006
	0.9693	−5.008 ± 0.002
	2.0218	−4.898 ± 0.005
	3.2839	−4.495
	N-Methylpropionamide	
NaCl	0.1022	−3.571
	0.2631	−3.521 ± 0.008
	0.5160	−3.468 ± 0.010
	0.9899	−3.353 ± 0.001
	1.5985	−3.210 ± 0.005
	2.0854	−3.097 ± 0.004
	2.3822	−3.033 ± 0.008
	4.4087	−2.531 ± 0.011
NaBr	0.1018	−3.559 ± 0.002
	0.2777	−3.521 ± 0.006
	0.5081	−3.476 ± 0.010
	1.0209	−3.356 ± 0.005
	1.5898	−3.224 ± 0.004
	2.0697	−3.119
	2.6900	−2.964 ± 0.006
	3.3003	−2.810 ± 0.004
	4.5304	−2.492 ± 0.003
NaI	0.5073	−3.428 ± 0.002
	0.7880	−3.370
	1.0775	−3.303 ± 0.005
	2.7323	−2.871
	3.8967	−2.572 ± 0.005

Table II. Continued

Salt	Salt molality, m_s	ΔH_{soln}^{ws}, kcal/mol
	N-Methylpropionamide	
KCl	0.4988	−3.482 ± 0.002
	1.0476	−3.375
	1.6576	−3.235 ± 0.013
	3.3834	−2.851 ± 0.021
KBr	0.1000	−3.548 ± 0.002
	0.2494	−3.531 ± 0.004
	0.5113	−3.493 ± 0.002
	0.7536	−3.434 ± 0.002
	1.0482	−3.378 ± 0.003
	1.5805	−3.261
	2.1782	−3.142 ± 0.002
	2.7745	−3.013
	3.3874	−2.869
	4.0710	−2.701 ± 0.007
	4.8251	−2.530 ± 0.005
KI	0.2523	−3.513 ± 0.005
	0.5442	−3.455 ± 0.000
	0.7844	−3.411 ± 0.001
	1.0684	−3.342 ± 0.003
	1.6430	−3.189 ± 0.003
	2.8497	−2.878 ± 0.000
	3.5131	−2.701
	4.9476	−2.359 ± 0.003

[a] Guanidinium hydrochloride.

Table III. Heats of Transfer of Formamide from Water to 0.50m Salt Solutions at 25°C

Salt	ΔH_{tr}, cal/mol of amide	Salt	ΔH_{tr}, cal/mol of amide
LiCl	−78	CsCl	−119
NaCl	−107	GuHCl[a]	−119
NaBr	−130	$MgCl_2$	−194
NaI	−150	$CaCl_2$	−240
NaSCN	−130	$SrCl_2$	−270
KCl	−114	SrI_2	−267
KBr	−124	$BaCl_2$	−311
KI	−136	$LaCl_3$	−316

[a] Guanidinium hydrochloride.

cation of the amide molality is required. The uncertainties in the enthalpies of transfer are the sum of the individual uncertainties of the terms comprising them.

Figure 1 shows the enthalpies of transfer of formamide from water to NaCl, NaBr, and NaI solutions as a function of salt molality. The values are negative and become increasingly more negative as the salt molality increases. In addition, the values become more negative at a given salt molality as the radius of the anion increases. Table III gives a compilation of the enthalpies of transfer of formamide from water to a variety of salt solutions at a common salt molality of 0.50*m*. In some cases, a small linear interpolation of ΔH_{soln}^{ws} was required to obtain these values. The trends in these data are very marked. The values within a given series of salts with the same anion increase with cationic radius. A similar increase is noted with increasing anionic radius. There is also a roughly 1:2:3 ratio of the numerical values of ΔH_{tr} from the alkali halides to the alkaline earth halides to lanthanum chloride.

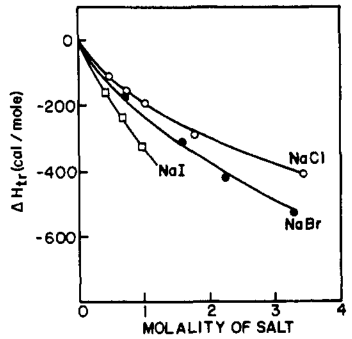

Figure 1. Enthalpies of transfer, ΔH_{tr}, of formamide from water to NaCl, ○, NaBr, ●, and NaI, ☐, solutions as function of salt molality at 25°

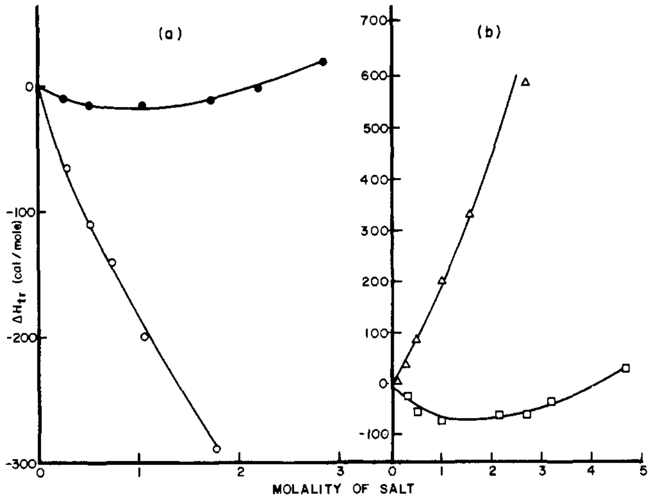

Figure 2. (a) Enthalpies of transfer, ΔH_{tr}, of formamide, ○, and acetamide, ●, from water to sodium chloride solutions as function of salt molality at 25°. (b) Enthalpies of transfer, ΔH_{tr}, of *N*-methylformamide, ☐, and *N*-methylpropionamide, △, from water to potassium bromide solutions as function of salt molality at 25°

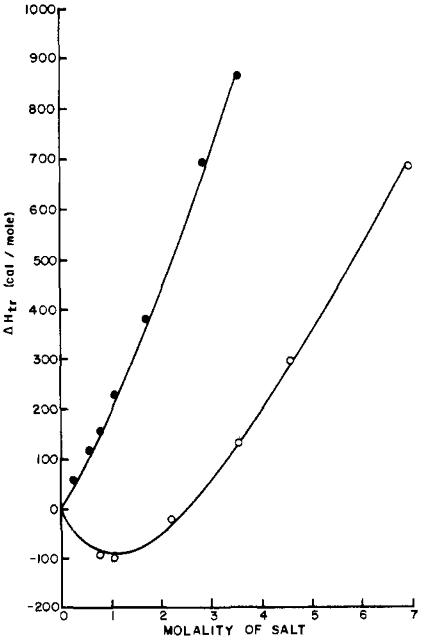

Figure 3. Enthalpies of transfer, ΔH_{tr}, of *N,N*-dimethylacetamide, ○, and *N*-methylpropionamide, ●, from water to potassium iodide solutions as function of salt molality at 25°

The addition of nonpolar groups produces a significant increase in the heats of transfer, as would be expected from corresponding data for the free energies (*7, 10, 11*). This is shown graphically in Figure 2. In Figure 2 (a), the heats of formamide and acetamide for the transfer from water to sodium chloride solutions are given as a function of salt molality. A similar comparison is made in Figure 2 (b), where the heats for the transfer of *N*-methylformamide and *N*-methylpropionamide from water to various potassium bromide solutions are shown. The influence of the ethyl group on *N*-methylpropionamide compared to the hydrogen on *N*-methylformamide is clearly seen.

Figure 3 shows the heats of transfer of *N,N*-dimethylacetamide and *N*-methylpropionamide from water to potassium iodide solutions. Small variations in the geometry and the functionality of these two structural isomers lead to important differences in the behavior of their transfer enthalpies with changing salt concentration. The minimum at low concentrations in the *N,N*-dimethylacetamide system is absent for *N*-methylpropionamide. In addition, while the heats of transfer for *N,N*-dimethylacetamide undergo a subsequent rise, a substantial difference exists between the enthalpies of transfer for the two substances at a given salt concentration.

The trends in the enthalpies of transfer of formamide given in Table III, i.e., exothermicity increasing with increasing ion size, can be examined more closely. Stern and his collaborators (*14, 15*) have obtained enthalpies of transfer of nitromethane, ethyl acetate, and acetic acid from water to salt solutions. Even though many of their transfer enthalpies are endothermic, the general trend of their data is the same as found here—the larger ions (with the exception of perchlorate) tend to interact more favorably (or less unfavorably) with the nonelectrolyte than do the smaller ions. If we consider free energies, we observe that the classical salting behavior of nonpolar nonelectrolytes manifests this trend (*6*). The situation is much the same for small polar nonelectrolytes analogous to formamide (*6*).

How is this trend explained? One possibility is to note that the polarizability of the ions increases with increasing ion size. The application of scaled particle theory to salt effects by Shoor and Gubbins (*12*) makes use of polarizabilities of the ions in the calculation of the limiting parameter for interaction of salts with nonpolar nonelectrolytes. Direct application of this theory in the present case is not possible because of the presumed importance of the dipole moment of formamide in terms of its interaction with an ion and because of its orienting effect on the water molecules directly surrounding it. It is likely that terms involving the *ionic* polarizability do make a contribution to the observed trend, however (*16*).

Perturbations of the structure of normal water may also play a part. Recently, Friedman et al. (*3*) have proposed that a displacement of some part of the cospheres of water molecules surround each of two isolated solute particles in aqueous solution may occur when they interact with each other. Model calculations have been made for the case of nonpolar nonelectrolytes interacting with ions. The trend of increasingly favorable free energies of cosphere displacement with increasing ionic radius was evident in the results. Similar calculations involving the enthalpies will aid in further elaboration of this hypothesis.

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