

## Thermochemical Properties of Some Carboxylic Acids, Amines and *N*-Substituted Amides in Aqueous Solution

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Aqueous enthalpies of solution have been determined calorimetrically at 20, 25, and 30°C at different concentrations for a number of amines,  $\text{RNH}_2$ , carboxylic acids,  $\text{RCOOH}$ , and *N*-substituted amides,  $\text{RCONHR}'$ , where R and R' are alkyl groups. For the amines and for some of the other compounds, enthalpies of solvation have been calculated. Heat capacities have been determined for most of the compounds (25°C).  $\Delta C_{p,2}^\circ$  for the solution processes as well as partial molar heat capacities for the compounds at infinite solution have been calculated. The thermodynamic results obtained are correlated with structural parameters, and their significance is discussed briefly.

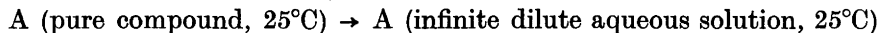
Thermodynamic investigations in biochemistry are important because they form part of the quantitative description of the biochemical systems. Modern calorimetry, in particular "microcalorimetry",<sup>1,2</sup> offers powerful experimental tools in this connection. However, thermochemical results from measurements on compounds like proteins are very complex, and it is usually not possible to discuss them in such detail as often is done with results referring to low molecular compounds. An obvious approach toward a better understanding of thermochemical data for biochemical compounds is to study also biochemical model compounds. Within a series of model compounds, the structure can be varied systematically, and it will thus be possible to correlate the values obtained with structural details. It is clear that such model studies form part of the general field of thermochemistry, and it is therefore desirable that they are broad in their scope even if, for a certain biochemical problem, a more narrow investigation would suffice.

The main aim of the present work is to provide some basic thermodynamic data for the interaction between simple protein constituents and water. Various thermodynamic studies on amino acids and peptides have provided valuable information on protein-water interactions (see *e.g.* Ref. 3). However, it may be argued that the structures of amino acids are quite complex without closely reflecting the properties of the groups forming the protein molecules. It was

felt, therefore, that systematic studies on still simpler models are more rewarding in connection with discussions of protein reactions, including the interactions between reactants and the medium.

In the present work, results are reported from calorimetric measurements on amines,  $\text{RNH}_2$ , carboxylic acids,  $\text{RCOOH}$ , and  $N$ -alkylamides,  $\text{RNHCOR}'$ , where R, R' are alkyl groups. Enthalpies of solution,  $\Delta H_{\text{soln}}$ , in water have been determined at 20, 25, and 30°C at different concentrations. Heat capacities at 25°C ( $C_p$ ) have been determined for the pure compounds by a novel microcalorimetric technique.

From results of the solution experiments at different temperatures, the change in heat capacity ( $\Delta \bar{C}_{p,2}^\circ$ ) for the process



has been calculated. Combination of  $C_p$  and  $\Delta \bar{C}_{p,2}^\circ$  will lead to the partial molar heat capacities for the compounds at infinite dilution,  $\bar{C}_{p,2}^\circ$ . For the amines and for some of the other compounds, reliable enthalpies of vaporization data are available, and for these compounds it has thus been possible to evaluate enthalpies of solvation.

## EXPERIMENTAL

*Materials.* Pivalic acid (Fluka *puriss.*) was purified by fractional freezing out. The other carboxylic acids as well as the amines were of the same samples as described in connection with the vaporization work.<sup>4,5</sup>

Except for *i*-PrNHCOMe and MeNHCOBu, all amide samples are described in Ref. 6. The amides were prepared from the appropriate amine and acid anhydride or acyl chloride.<sup>7</sup> After a crude distillation of the reaction mixture, the product was purified by repeated fractional distillation under reduced pressure.

For all samples used in this work, the purities as judged by gas chromatography were 99.8 %, or better. Water content was < 0.03 weight %, as determined by gas chromatography using a Porapac column. Water used for preparation of the calorimetric liquids was glass distilled, and was in equilibrium with air.

*Calorimetric apparatus and procedure.* For the heat of solution measurements, an LKB 8721-1 Precision Calorimeter was used. The volume of the reaction vessel was 100 ml. In order to suppress ionization reactions, 0.1 M hydrochloric acid and 0.1 M sodium hydroxide were used as calorimetric liquids for the acids and the amines, respectively. Measurements were performed at 20, 25, and 30°C. The absolute temperatures were determined by use of a calibrated ( $\pm 0.01^\circ\text{C}$ ) Hewlett Packard quartz thermometer. Electrical calibrations were performed on the initial calorimetric systems. Small temperature corrections were applied, so that the derived  $\Delta H$  values referred to the stated temperatures.

In the  $C_p$ -determinations, a newly developed drop calorimetric method was used.<sup>8</sup> A twin microcalorimetric unit, similar to that described earlier,<sup>9</sup> was employed as receiver for the sample. In the present measurements, the calorimetric unit was kept at 28°C, and the sample was thermostatted to 22°C before it was dropped. Test experiments on benzoic acid, octane and water gave within uncertainty limits (0.5 %) results identical with the literature values.

## RESULTS

*Determination of enthalpies of solution.* Measurements of solution enthalpies were made at 20, 25, and 30°C. At 25°C, at least four measurements were made at different concentrations in the range 0.01 – 0.1 M. Values for the enthalpies

of solution at zero concentration,  $\Delta H_{\text{soln}}^{\circ}$ , were obtained by linear extrapolation. At 20 and 30°C, two or three measurements were made for each compound. The concentration dependency was in these cases assumed to be the same as those found for 25°C. As a representative example of the measurements, the results for butylamine are shown in Fig. 1,  $\Delta H_{\text{soln}}^{\circ}$  values are summarized in Table 1. Uncertainties given are estimates.

For acetic acid, butylamine, and butylacetamide, enthalpies of solution in water were determined in earlier studies<sup>10</sup> at 25°C and at the concentration 0.05

Table 1. Enthalpies of solution in water at infinite dilution ( $\Delta H_{\text{soln}}^{\circ}$ ) and aqueous enthalpies of solvation ( $\Delta H_{\text{solv}}^{\circ}$ ) for some carboxylic acids, amines and *N*-substituted amides.

Compound	$-\Delta H_{\text{soln}}^{\circ}$ , kJ mol <sup>-1</sup>				$-\Delta H_{\text{solv}}^{\circ}$ , kJ mol <sup>-1</sup>
	This work			Earlier work	
	20°C	25°C	30°C	25°C	
HCOOH (l)	0.662 ± 0.003	0.678 ± 0.001	0.697 ± 0.002		47.0 ± 0.5
MeCOOH (l)	1.385 ± 0.008	1.176 ± 0.004	0.958 ± 0.008	{ 1.38 ± 0.04 <sup>a</sup> 1.19 ± 0.08 <sup>b</sup>	52.8 ± 1.5
EtCOOH (l)	2.062 ± 0.008	1.544 ± 0.004	1.050 ± 0.008		
PrCOOH (l)	2.251 ± 0.004	1.460 ± 0.004	0.669 ± 0.004	1.54 ± 0.08 <sup>b</sup>	56.5 ± 2
<i>i</i> -PrCOOH (l)	2.251 ± 0.004	1.418 ± 0.004	0.648 ± 0.004	1.51 ± 0.12 <sup>c</sup>	59.5 ± 4
BuCOOH (l)				0.37 ± 0.08 <sup>b</sup>	54.4 ± 4
<i>t</i> -BuCOOH (s)	-1.27 ± 0.04	-2.51 ± 0.04	-3.66 ± 0.04		
PrNH <sub>2</sub> (l)	25.66 ± 0.02	24.62 ± 0.02	23.77 ± 0.02		55.75 ± 0.10
<i>i</i> -PrNH <sub>2</sub> (l)	28.33 ± 0.08	27.45 ± 0.08	26.53 ± 0.08		55.05 ± 0.15
BuNH <sub>2</sub> (l)	24.49 ± 0.02	23.33 ± 0.01	22.15 ± 0.02	23.26 ± 0.08 <sup>a</sup>	59.04 ± 0.07
<i>i</i> -BuNH <sub>2</sub> (l)	24.50 ± 0.04	23.37 ± 0.02	22.27 ± 0.04		57.13 ± 0.07
<i>t</i> -BuNH <sub>2</sub> (l)	30.38 ± 0.03	29.34 ± 0.03	28.24 ± 0.03		58.98 ± 0.07
PeNH <sub>2</sub> (l)	23.51 ± 0.02	22.04 ± 0.02	20.54 ± 0.02		62.12 ± 0.07
HexNH <sub>2</sub> (l)	22.43 ± 0.02	20.66 ± 0.02	18.92 ± 0.02		65.76 ± 0.07
MeNHCOEt (l)	15.66 ± 0.02	14.87 ± 0.02	14.11 ± 0.02		
MeNHCOPr (l)	17.15 ± 0.02	16.02 ± 0.02	14.81 ± 0.02		
MeNHCO- <i>i</i> -Pr (l)	16.89 ± 0.03	15.79 ± 0.02	14.67 ± 0.03		
MeNHCOBu (l)	16.43 ± 0.02	15.03 ± 0.02	13.58 ± 0.02		
MeNHCO- <i>t</i> -Bu (s)	7.64 ± 0.03	6.26 ± 0.03	4.72 ± 0.03		
EtNHCOMe (l)	16.31 ± 0.02	15.48 ± 0.02	14.67 ± 0.02	15.50 ± 0.08 <sup>d</sup>	
PrNHCOMe (l)	16.91 ± 0.02	15.76 ± 0.02	14.62 ± 0.02		
<i>i</i> -PrNHCOMe (l)	18.39 ± 0.02	17.24 ± 0.02	16.09 ± 0.02		
BuNHCOMe (l)	16.00 ± 0.03	14.72 ± 0.03	13.26 ± 0.03	{ 14.8 ± 0.1 <sup>a</sup> 15.2 ± 0.2 <sup>d</sup>	88.3 ± 0.8
<i>t</i> -BuNHCOMe (s)	4.08 ± 0.02	2.54 ± 0.02	1.00 ± 0.02		

<sup>a</sup> Ref. 10.

<sup>b</sup> Ref. 11. These values, which were kindly communicated to us by Prof. E. M. Arnett, have not been published elsewhere. We like to acknowledge that the study by Arnett and Carter<sup>11</sup> was supported by the U. S. Office of Saline Water.

<sup>c</sup> Ref. 12.

<sup>d</sup> Ref. 15.

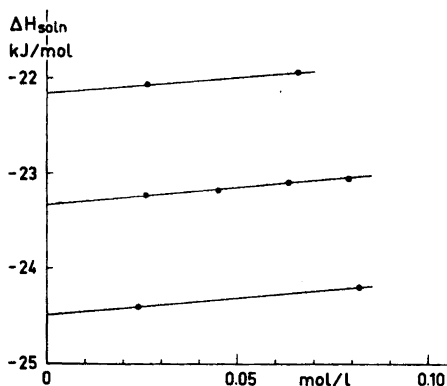


Fig. 1. Enthalpies of solution of BuNH<sub>2</sub> in aqueous 0.1 M NaOH solution versus final concentration of amine.

M. For butylamine and butylacetamide, the present result agrees well with the earlier values. However, for acetic acid, the earlier value appears to be significantly in error.

The values for acetic acid, propionic acid, and butyric acid, which recently were determined by Arnett and Carter,<sup>11</sup> are in good agreement with the present results. Also the value for *i*-PrCOOH, determined by Krescheck and Benjamin,<sup>12</sup> agrees with the present result within limits of error.

Arnett and McKelvey<sup>15</sup> recently reported results from measurements on a number of substituted amides. Values for EtNHCOMe and *t*-BuNHCOMe agree well with the present results, whereas our value for BuNHCOMe is slightly less exothermic.

*Solvation enthalpies, ΔH<sub>solv</sub><sup>o</sup>.* The aqueous solvation enthalpy value expresses the enthalpy change for the transfer of one mole of a compound from the ideal gaseous state to aqueous solution at infinite dilution. ΔH<sub>solv</sub><sup>o</sup> values were calculated by eqn (1).

$$\Delta H_{\text{solv}}^{\circ} = \Delta H_{\text{soln}}^{\circ} - \Delta H_{\text{v}}^{\circ} \quad (1)$$

where ΔH<sub>v</sub><sup>o</sup> is the enthalpy of vaporization to form the ideal monomer gas. For most of the carboxylic acids, ΔH<sub>v</sub><sup>o</sup> values at 25°C have recently been calculated<sup>4</sup> by combining results of direct calorimetric determinations with gas phase equilibrium data. Enthalpies of vaporization to form the real gases at 25°C are believed to be accurately known. Except for formic acid, however, the gas phase equilibrium data are rather uncertain at 25°C, and therefore, for most carboxylic acids no accurate ΔH<sub>solv</sub><sup>o</sup> values are as yet available.

For the amines, the differences between the real and the ideal gas can in the present case be neglected, and the calorimetrically determined vaporization enthalpies<sup>9</sup> were directly used. ΔH<sub>v</sub> values were not determined calorimetrically for PrNH<sub>2</sub> and *i*-PrNH<sub>2</sub>. For these compounds, the ΔH<sub>v</sub> values used are estimates based on results from the calorimetric study.<sup>9</sup>

For the amides, the only available ΔH<sub>v</sub> value is that for BuNHCOH<sub>3</sub>.<sup>16</sup> ΔH<sub>solv</sub><sup>o</sup> values are summarized in the last column of Table 1.

*Heat capacity values.* It is surprising that for most of the simple and generally important compounds of the present study, no reliable C<sub>p</sub> values have been

reported previously. Heat capacities at 25°C were therefore determined for all compounds included in this study, except for formic acid and acetic acid, for which compounds literature values were judged to be satisfactory. For each compound, at least four determinations were made. Results are summarized in Table 2. Uncertainties given are average deviation of the mean.

Results from the  $\Delta H_{\text{soln}}^\circ$  determinations were used to calculate the change in apparent heat capacity in going from the pure compound to aqueous solution at infinite dilution,  $\Delta C_{p2}^\circ$ .

$$\Delta C_{p2}^\circ = \frac{d(\Delta H_{\text{soln}}^\circ)}{dT} \cong \frac{\Delta(\Delta H_{\text{soln}}^\circ)}{\Delta T} \quad (2)$$

Values for the temperature ranges 20–25°C and 25–30°C, respectively, were calculated, and the mean values,  $\Delta C_{p2}^\circ$  at 25°C, are summarized in Table

Table 2. Heat capacities ( $C_p$ ) for some carboxylic acids, amines and *N*-substituted amides,  $\Delta C_{p2}^\circ$  values for the aqueous solution processes and partial molar heat capacities,  $\overline{\Delta C_{p2}^\circ}$ , for the compounds at infinite dilution. All values refer to 25°C.

Compound	$C_p$ , J/deg mol	$\Delta C_{p2}^\circ$ , J/deg mol	$\overline{\Delta C_{p2}^\circ}$ , J/deg mol	
			This work	Earlier work
HCOOH (l)	99.0 ± 0.2 <sup>a</sup>	− 3.5 ± 0.5	95.5 ± 1	71 <sup>c</sup> , 88 <sup>d</sup> , 84.5 <sup>e</sup>
MeCOOH (l)	123 ± 1 <sup>b</sup>	42 ± 2	165 ± 3	159 <sup>c</sup> , 167 <sup>d</sup> , 154 <sup>e</sup>
EtCOOH (l)	151 ± 1	102 ± 2	253 ± 3	264 <sup>c</sup> , 259 <sup>d</sup> , 248 <sup>e</sup>
PrCOOH (l)	178 ± 2	159 ± 1	337 ± 3	355 <sup>c</sup> , 330 <sup>d</sup>
<i>i</i> -PrCOOH (l)	173 ± 1	161 ± 1	334 ± 2	418 <sup>f</sup>
BuCOOH (l)	197 ± 1	235 ± 6 <sup>g</sup>	432 ± 7	
<i>t</i> -BuCOOH (s)	178 ± 1	239 ± 8	417 ± 9	
PrNH <sub>2</sub> (l)	160 ± 1	167 ± 4	327 ± 5	
<i>i</i> -PrNH <sub>2</sub> (l)	164 ± 2	178 ± 16	342 ± 18	
BuNH <sub>2</sub> (l)	188 ± 1	234 ± 3	422 ± 4	
<i>i</i> -BuNH <sub>2</sub> (l)	194 ± 1	222 ± 8	416 ± 9	
<i>t</i> -BuNH <sub>2</sub> (l)	190 ± 1	213 ± 6	403 ± 7	
PeNH <sub>2</sub> (l)	218 ± 1	297 ± 4	515 ± 5	
HexNH <sub>2</sub> (l)	252 ± 2	351 ± 4	603 ± 6	
MeNHCOEt (l)	179 ± 1	155 ± 3	334 ± 4	
MeNHCOPr (l)	207 ± 1	227 ± 4	434 ± 5	
MeNHCO- <i>i</i> -Pr (l)	209 ± 1	222 ± 5	431 ± 6	
MeNHCOBu (l)	229 ± 1	286 ± 4	515 ± 5	
MeNHCO- <i>t</i> -Bu (s)	183 ± 1	293 ± 6	476 ± 7	
EtNHCOMe (l)	180 ± 1	163 ± 4	343 ± 5	
PrNHCOMe (l)	207 ± 1	230 ± 4	437 ± 5	
<i>i</i> -PrNHCOMe (l)	211 ± 1	230 ± 4	441 ± 5	
BuNHCOMe (l)	236 ± 1	270 ± 6	506 ± 5	
<i>t</i> -BuNHCOMe (s)	190 ± 1	308 ± 4	498 ± 5	

<sup>a</sup> Ref. 13.

<sup>b</sup> Ref. 14. Uncertainty limit is estimated.

<sup>c</sup> Ref. 17. Temperature range 10–50°C.

<sup>d</sup> Ref. 18. 15°C.

<sup>e</sup> Ref. 19.

<sup>f</sup> Ref. 12.

<sup>g</sup> Ref. 11. Cf. note b, Table 1.

2. The uncertainty limits given are the maximum errors as derived from the estimated uncertainties in the  $\Delta H_{\text{soln}}^{\circ}$  values.

Arnett and Carter<sup>11</sup> calculated  $\Delta C_p^{\circ}$  values for MeCOOH, EtCOOH, and PrCOOH to be  $63 \pm 10$ ,  $118 \pm 15$ , and  $172 \pm 8$  J/deg mol, respectively, which thus all are somewhat higher than the present results. For BuCOOH, which compound was not included in the present study, Arnett and Carter obtained  $\Delta C_{p2}^{\circ} = 235 \pm 6$  J/deg mol.

Heat capacity data for the pure compounds were combined with corresponding  $\Delta C_{p2}^{\circ}$  values in order to arrive at partial molar heat capacities at infinite dilution,  $\bar{C}_{p2}^{\circ}$ .

$$\bar{C}_{p2}^{\circ} = C_p + \Delta C_{p2}^{\circ}$$

$\bar{C}_{p2}^{\circ}$  values are summarized in the last column of Table 2.

$\bar{C}_{p2}^{\circ}$  values have been determined earlier for several of the carboxylic acids. Most of these values, however, are not strictly comparable with the present results, as they were derived from measurements on rather concentrated solutions and at temperatures other than 25°C.

The  $\bar{C}_{p2}^{\circ}$  value for *i*-PrCOOH earlier reported by Kresheck and Benjamin,<sup>12</sup>  $420 \pm 40$  J/deg mol, is significantly higher than the present result,  $334 \pm 2$  J/deg mol.

#### DISCUSSION

When enthalpy of heat capacity values for compounds in aqueous solution are discussed, it should be remembered that water structure and effects by solutes on the water structure are not well understood. Discussions of thermodynamic results in this field must therefore be cautious at the present time, and merely have the character of empirical correlations. It may sometimes be suitable to carry out such discussions using pictures like "iceberg formation", "structure forming" or "structure breaking", *etc.* However, it must be recog-

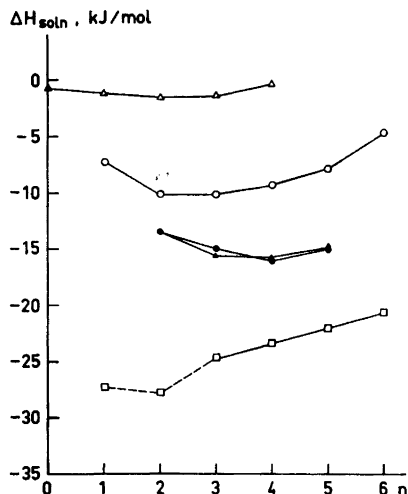


Fig. 2. Aqueous enthalpies of solution at infinite dilution,  $\Delta H_{\text{soln}}^{\circ}$ , for some straight chain carboxylic acids, amines, *N*-substituted amides, and alcohols versus total number of carbon atoms in the alkyl groups, *n*. The value for MeNHCOR (m.p. 30.56°C) in the hypothetical  $\Delta H_{\text{soln}}^{\circ}$  value at 25° for the liquid compound, as calculated from data in Ref. 22. ○, ROH. △, RCOOH. □, RNH<sub>2</sub>. ●, MeNHCOR. ▲, RNHCOMe.

nized that observations which currently are discussed in these terms well may turn out to be associated with phenomena having a nature different from the usual meaning of these expressions.

*Solution enthalpies.* Corkhill *et al.*<sup>20</sup> recently noted that aqueous  $\Delta H_{\text{soln}}^{\circ}$  values vary with the length of the alkyl chain in a characteristic manner. For several liquid, nonionic, alkyl compounds they found a minimum for  $\Delta H_{\text{soln}}^{\circ}$  at a chain length of 3–5 carbon atoms.

In Fig. 2,  $\Delta H_{\text{soln}}^{\circ}$  (25°) for the *n*-alkyl compounds is plotted *versus* the total number of carbon atoms in the alkyl groups. As a comparison, corresponding values for alcohols (Table 3) are also given. It is seen that for carboxylic acids, alcohols, and for the amide series, there are minima at a chain length of 2–4 carbon atoms. For the amines, there is a linear increase in the  $\Delta H_{\text{soln}}^{\circ}$  value above C<sub>2</sub>. Values for MeNH<sub>2</sub> and EtNH<sub>2</sub><sup>21</sup> are indicated, but are judged to be uncertain.

Table 3. Calorimetric values for some alcohols at 25°C for the aqueous enthalpies of solution ( $\Delta H_{\text{soln}}^{\circ}$ ), enthalpies of vaporization ( $\Delta H_{\text{v}}^{\circ}$ ), and enthalpies of solvation ( $\Delta H_{\text{solv}}^{\circ}$ ).

Compound	$-\Delta H_{\text{soln}}^{\circ}$ kJ/mol	$\Delta H_{\text{v}}^{\circ}$ kJ/mol	$-\Delta H_{\text{solv}}^{\circ}$ kJ/mol
MeOH	7.24 ± 0.06 <sup>a</sup>	37.28 ± 0.08 <sup>d</sup>	44.52 ± 0.14
EtOH	10.10 ± 0.08 <sup>a</sup>	42.30 ± 0.08 <sup>d</sup>	52.40 ± 0.16
PrOH	10.13 ± 0.08 <sup>a</sup>	47.32 ± 0.08 <sup>d</sup>	57.45 ± 0.16
<i>i</i> -PrOH	12.98 ± 0.11 <sup>a</sup>	45.23 ± 0.12 <sup>d</sup>	58.21 ± 0.23
BuOH	9.28 ± 0.08 <sup>a</sup>	52.30 ± 0.08 <sup>d</sup>	61.58 ± 0.16
<i>i</i> -BuOH	9.31 ± 0.04 <sup>b</sup>	50.84 ± 0.08 <sup>d</sup>	60.15 ± 0.12
<i>s</i> -BuOH	13.18 ± 0.05 <sup>b</sup>	49.66 ± 0.08 <sup>d</sup>	62.80 ± 0.13
<i>t</i> -BuOH	17.31 ± 0.14 <sup>a</sup>	46.61 ± 0.08 <sup>d</sup>	63.92 ± 0.22
PeOH	7.81 ± 0.05 <sup>b</sup>	56.94 ± 0.17 <sup>d</sup>	64.75 ± 0.22
HexOH	4.6 ± 0.3 <sup>c</sup>	61.63 ± 0.17 <sup>d</sup>	66.2 ± 0.5

<sup>a</sup> Ref. 23.

<sup>b</sup> Ref. 24.

<sup>c</sup> Ref. 25.

<sup>d</sup> Ref. 26.

Solution enthalpies,  $\Delta H_{\text{soln}}$ , represent the transfer of molecules from a state where they are solvated by molecules of the same species, or are part of a crystal lattice, to a state where they are solvated by the solvent, and where the solvent structure may change under the influence of the solute. Solution enthalpies are thus very complex numbers, and regularities of the kind referred to above can hardly be expected to be generally valid.

*Solvation enthalpies.* Solvation enthalpies are somewhat less complex than solution enthalpies, as here the reference state is the ideal gas. In Fig. 3,  $\Delta H_{\text{solv}}$  values are plotted *versus* chain length for the straight chain amines and for the three lowest carboxylic acids. The value for BuNHCOH<sub>2</sub> is also indicated. The  $\Delta H_{\text{solv}}^{\circ}$  values for alcohols included in the figure (Table 3) were calculated from the solution enthalpies reported by Alexander and Hill,<sup>23</sup>

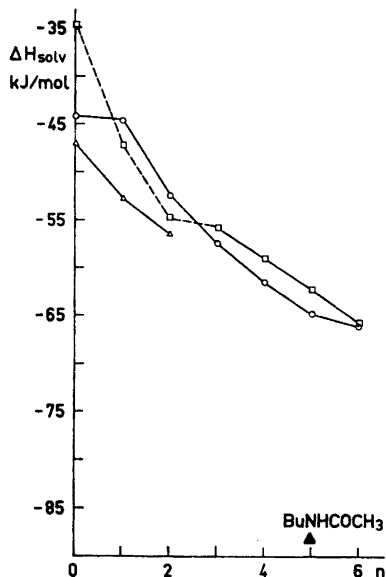


Fig. 3. Aqueous enthalpies of solvation,  $\Delta H_{\text{solv}}^\circ$ , for some straight chain carboxylic acids, amines, *N*-substituted amides, and alcohols versus total numbers of carbon atoms in the alkyl groups, *n*. O, ROH.  $\Delta$ , RCOOH.  $\square$ , RNH<sub>2</sub>.  $\blacktriangle$ , RNHCOMe.

Arnett *et al.* (PeOH),<sup>24</sup> and Aveyard and Lawrence (HexOH),<sup>25</sup> and from calorimetric enthalpies of vaporization values.<sup>26</sup> The  $\Delta H_{\text{solv}}$  values for H<sub>2</sub>O and NH<sub>3</sub> are from Ref. 21.

It is seen that the values for RCOOH, RNH<sub>2</sub>, and ROH are quite close, whereas the single amide value is highly exothermic and is far outside the region of the other compounds.

As noted earlier, the literature values for EtNH<sub>2</sub> and MeNH<sub>2</sub> ( $\Delta H_{\text{soln}}$ ,  $\Delta H_{\text{solv}}$ ) are judged to be uncertain, and the shape of the  $\Delta H_{\text{solv}}$  curve indeed suggests that they are wrong.

For the amines, the CH<sub>2</sub>-increment for  $\Delta H_{\text{solv}}$  has an essentially constant value of 3.4 kJ after 3 carbon atoms. Nearly the same value is found for the alcohols between C<sub>3</sub> and C<sub>5</sub>. Comparison between solution enthalpy values from Ref. 25 with those from Refs. 23 and 24 suggests that the value for HexOH might be too exothermic. If so, the results would indicate that the influence from the polar groups on the solvation of the alkyl chain is close to zero after a distance of  $\geq 3$  CH<sub>2</sub> groups (*cf.* Ref. 20).

The effect of branching on the  $\Delta H_{\text{solv}}^\circ$  values does not follow any simple rule. The values for *i*-PrOH and *t*-BuOH are more exothermic than corresponding straight chain compounds, whereas the value for *i*-BuOH is less exothermic than that for BuOH. Corresponding comparison for the amines shows a different picture. *i*-PrNH<sub>2</sub> and *i*-BuNH<sub>2</sub> are less exothermic than the parent straight chain compound, whereas the values for BuNH<sub>2</sub> and *t*-BuNH<sub>2</sub> are nearly identical.

*Heat capacity values.*  $\Delta C_p$  values for a solution process reflect the properties of pure compounds as well as those for the solvated compound, including the effects on the solvent. However, if values for a series of related liquid com-



pounds are compared, we may as a rough approximation consider the pure compounds as being in a common standard state.<sup>24</sup> Under such circumstances, differences between  $\Delta C_{p2}^\circ$  values will directly reflect the differences in solute-solvent interactions.

$\bar{C}_{p2}^\circ$  values, partial molar heat capacities, may be considered as less complex numbers than  $\Delta C_{p2}^\circ$  values, as they are not affected by contributions due to interactions between the molecules in the pure compound. We therefore consider  $\bar{C}_{p2}^\circ$  values as a better base for comparison than the  $\Delta C_{p2}^\circ$  values, in particular as the former are not affected by differences in aggregation states for the compounds.

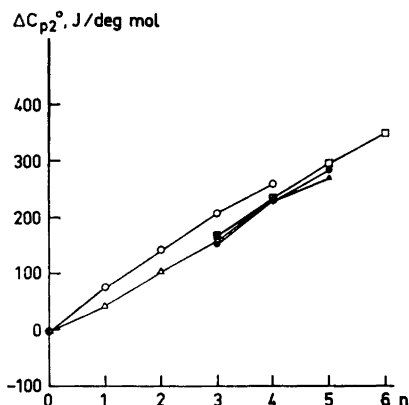


Fig. 4.  $\Delta C_{p2}^\circ$  for the aqueous solution process for some straight chain carboxylic acids, amines, *N*-substituted amides, and alcohols *versus* total number of carbon atoms in the alkyl groups,  $n$ . ○, ROH. △, RCOOH. □,  $\text{RNH}_2$ . ●, MeNHCOR. ▲,  $\text{RNHCOMe}$ .

In Fig. 4,  $\Delta C_{p2}^\circ$  values are plotted *versus* number of carbon atoms in the alkyl groups. Values for the branched compounds are not included. As a comparison, the  $\Delta C_{p2}^\circ$  values for alcohols reported by Alexander and Hill<sup>23</sup>

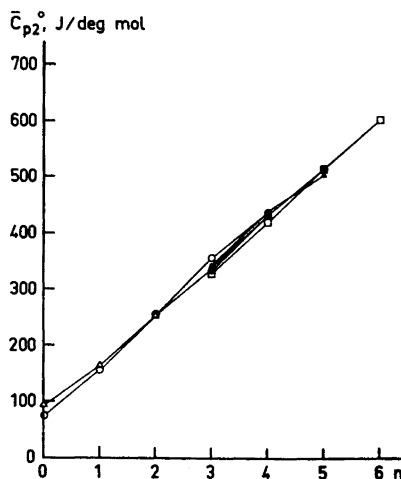


Fig. 5. Partial molar heat capacities at infinite dilution,  $\bar{C}_{p2}^\circ$ , for some straight chain carboxylic acids, amines, *N*-substituted amides, and alcohols *versus* total number of carbon atoms,  $n$ , in the alkyl groups. ○, ROH. △, RCOOH. □,  $\text{RNH}_2$ . ●, MeNHCOR. ▲,  $\text{RNHCOMe}$ .

are also given. The  $\Delta Cp_2^\circ$  values for alcohols determined by Arnett *et al.*<sup>24</sup> form a line positioned slightly higher.

We see that for carboxylic acids, amines, and the lower amides, the values fall nearly along the same straight line, whereas the alcohol values are slightly higher. No simple picture emerges from the effect of branching.

In Fig. 5, the corresponding plot is made for the  $\bar{C}_{p2}^\circ$  values. Here the values for the different series of compounds are still closer than those in Fig. 4, and in most cases they are within uncertainty limits the same. As seen from the results in Table 2, the effect of branching is insignificant, except for the pair of compounds MeNHCOBu – MeNHCO-*t*-Bu.

It has long been known that  $\Delta Cp_2$  values for aqueous solution processes involving compounds with alkyl groups are large and positive. This is also reflected in the large  $\bar{C}_{p2}^\circ$  values for such compounds in aqueous solution. These heat capacity values are generally believed to be connected with the formation of an ordered water structure ("iceberg") around the alkyl group. A large part of these (apparent) heat capacity values can thus be thought of as being contributions from the enthalpy of "melting" of the water structure. With this in mind, it is interesting that the CH<sub>2</sub>-increment of  $\bar{C}_{p2}^\circ$  for the compounds considered here is constant, about 85 J/deg mol, and it is not affected by the nature of the hydrophilic group. We also note that the distance to the hydrophilic group does not significantly effect the CH<sub>2</sub>-increment value. The present results, therefore, seem to indicate that the water structure around the hydrophobic groups are only slightly affected by polar groups like –OH –COOH, NH<sub>2</sub>, and –NHCO–. A similar conclusion has recently been made by Rüterjans *et al.*<sup>27</sup> from a comparison of  $\bar{C}_{p2}^\circ$  values for the pair MeNH<sub>3</sub>Cl – EtNH<sub>3</sub>Cl, and those for the three lowest carboxylic acids.<sup>19</sup>

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