Enthalpies and Heat Capacities of Dissolution of Some Sodium Carboxylates in Water and Hydrophobic Hydration

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Integral heats of solution ΔH_s of sodium carboxylates, $C_nH_{2n+1}COONa$ (n = 0, 1, 2, 3, 4, 5, and 7) and $C_6H_5(CH_2)_nCOONa$ (n = 0, 1, 2, and 3), in water at 25 and 35°C have been determined at very low concentrations. The heat capacities of dissolution at infinite dilution, ΔC_p°, of sodium carboxylates have been derived by the integral heat method. The $-CH_2-$ increment of ΔC_p° in aliphatic carboxylates has been found to be 14 cal-deg^{-1}-mole^{-1}, which is close to the value derived from other series of compounds, indicating that the interaction of nonpolar moieties with water is independent of the hydrophilic group attached to it. On the other hand, the $-CH_2-$ increment for the aromatic sodium carboxylates is much less (about 6 cal-deg^{-1}-mole^{-1}) than for the aliphatic sodium carboxylates, indicating that the hydrophobic interaction is affected by the aromatic end group.

1. INTRODUCTION

Studies on aqueous solutions of R_4N^+ salts have provided useful information about the interaction of nonpolar moieties with water.[1] These salts have been used because of their appreciable solubility in water and also because they provide a systematic variation in the chain length of the alkyl group. It would be interesting to see how the interactions of nonpolar moieties are affected if they form part of an anion and are aliphatic as well as aromatic in nature. Though studies on aqueous solutions of salts of large aryl anions such as

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Ph_4B^- and of aryl cations such as Ph_4P^+ and Ph_4As^+ have been reported,[1-6] these have been inadequate in giving the effect of a systematic increase in the size of the alkyl or aryl group. In this respect, sodium salts of carboxylic acids form a convenient set of solutes (somewhat analogous to R_4N^+ salts). Lindenbaum[7] has recently reported heats-of-dilution studies on sodium carboxylates and has concluded that the hydrophobic alkyl chain increases the solvent hydrogen bonding effect. Since the heat capacity of dissolution at infinite dilution, ΔC_p°, of solutes in water reflects the structural changes occurring in their aqueous solutions, we thought it would be interesting to determine the enthalpies and heat capacities of dissolution of sodium carboxylates and thereby derive in a quantitative manner the effect of increasing the alkyl and aryl nonpolar group chain length of the anions on their interactions with water. In this paper we report the ΔH_s° (at 25 and 35°C) and ΔC_p° (at 30°C) values of seven aliphatic sodium carboxylates $RCOO^-Na^+$, where R varies from H to $CH_3(CH_2)_6$, and of four aromatic sodium carboxylates $RCOO^-Na^+$, where R varies from C_6H_5 to $C_6H_5(CH_2)_3$.

2. EXPERIMENTAL

The calorimeter and the procedure for measurements of enthalpies of solution have been described in earlier reports from this laboratory.[2,8] The temperature of the thermostat was maintained to $\pm 0.002°C$ by a Sargent Thermonitor. The minimum temperature change that could be detected was of the order of 2×10^{-5} deg. The operation of the calorimeter was checked by measuring the enthalpies of solution of KCl in water and of THAM [tris(hydroxymethyl)amino methane] in 0.1 M HCl at 25°C. The values obtained were within 0.3% of those reported by Gunn.[9] Sodium salts of carboxylic acids were prepared by neutralizing pure-grade solutions of the acids (which were in slight excess) with sodium hydroxide. The excess acid was removed from the solution mixture with pure ether. The salts were obtained by evaporation, recrystallized from methanol–water and ether, and finally dried in an oven at 90°C. The purity of the salts was found to be 98–99% as determined by microanalysis. The sample bulbs filled with salts were kept in an oven at 90°C, dried to constant mass, and sealed under vacuum. The water used was conductivity water obtained by passing distilled water through a Barnstead mixed-bed ion-exchange resin column.

3. RESULTS

The enthalpies of solution ΔH_s of sodium salts of carboxylic acids in water were determined at molalities ranging from 1×10^{-3} to about 13×10^{-3} at 25 and 35°C. The corrections to the heats of solution of sodium

Table I. Enthalpies and Heat Capacities of Dissolution at Infinite Dilution of Sodium Salts of Carboxylic Acids in Water

Salt	ΔH_{s}°, cal-mole^{-1}		ΔC_{p}°, cal-deg^{-1}-mole^{-1} at 30°C	$\Delta C_{p}^{\circ}(-CH_2-)$, cal-deg^{-1}-mole^{-1} at 30°C
	25°C	35°C		
HCOONa	176 ± 7^{a} (4)^{b}	-23 ± 5^{a} (6)^{b}	-20 ± 1^{c}	
CH$_3$COONa	-3966 ± 25 (5)	-3983 ± 30 (5)	-2 ± 4	18
C$_2$H$_5$COONa	-3050 ± 29 (8)	-2922 ± 21 (5)	13 ± 4	15
C$_3$H$_7$COONa	-3366 ± 24 (7)	-3046 ± 17 (7)	32 ± 3	19
C$_4$H$_9$COONa	-2604 ± 27 (7)	-2157 ± 9 (5)	45 ± 3	13
C$_5$H$_{11}$COONa	-2120 ± 30 (7)	-1539 ± 27 (8)	58 ± 4	13
C$_7$H$_{15}$COONa	282 ± 15 (5)	1052 ± 27 (7)	77 ± 3	10
C$_6$H$_5$COONa	-518 ± 17 (5)	-210 ± 8 (7)	31 ± 2	
C$_6$H$_5$CH$_2$COONa	-3376 ± 17 (5)	-3015 ± 25 (6)	36 ± 3	5
C$_6$H$_5$(CH$_2$)$_2$COONa	-545 ± 21 (7)	-124 ± 5 (5)	42 ± 2	6
C$_6$H$_5$(CH$_2$)$_3$COONa	-2288 ± 31 (7)	-1798 ± 22 (7)	49 ± 4	7

^{a} Standard deviation from the mean value.

^{b} Numbers in parentheses represent the number of measurements made for a particular salt.

^{c} The uncertainty in the ΔC_{p}° value at temperature T ($e\Delta C_{pT}^{\circ}$) is calculated as follows:

$$e\Delta C_{pT}^{\circ} = [1/(T_2 - T_1)][(e\Delta H_{sT1}^{\circ})^2 + (e\Delta H_{sT2}^{\circ})^2]^{1/2}$$

where $T = (T_1 + T_2)/2$.

carboxylates for the hydrolysis of the sodium carboxylates (heats of hydrolysis), as calculated from the degrees of hydrolysis and heats of ionization reported in the literature,[10] were found to be negligible and within the experimental error. The values of the enthalpy of solution at infinite dilution ΔH_{s}°, given in Table I, were obtained by averaging the ΔH_{s} values since the determined values were made in very dilute solutions wherein any effect of molality is masked by the experimental error. The uncertainties reported in the values of ΔH_{s}° are the standard deviations from the mean values. We estimate that the total uncertainty in our ΔH_{s}° values is ± 35 cal-deg^{-1}-mole^{-1}. Earlier ΔH_{s}° values for sodium carboxylates, except those of sodium formate, sodium acetate, sodium propionate, sodium butyrate, and sodium benzoate (at 25°C only), are not available for comparison. The ΔH_{s}° values (at 25°C) -3973 ± 38, -3015 ± 16, and -3385 ± 22 cal-mole^{-1} for sodium acetate, sodium propionate, and sodium butyrate, respectively, as reported by Snell and Greyson[11] and -565 ± 35 cal-mole^{-1} (extrapolated from higher concentration values) for sodium benzoate as reported by Fernandez and Hepler[12] agree well (within the combined uncertainty) with our ΔH_{s}° values. However, the ΔH_{s}° value of 269 ± 3 cal-mole^{-1} for sodium formate as
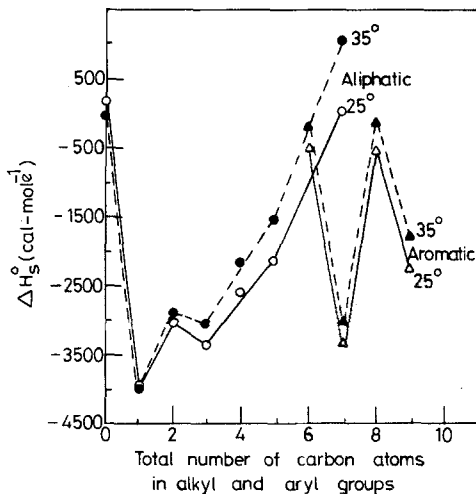
Fig. 1. Enthalpies of solution at infinite dilution ΔH_s° for some sodium carboxylates versus total number of carbon atoms in the alkyl and aryl groups at 25 and 35°C.

reported by Snell and Greyson[11] is not in agreement with our value of 176 ± 7 cal-mole^{-1}. Since the value obtained by Snell and Greyson is for higher concentrations of sodium formate, we believe our value to be more reliable. In Fig. 1 the ΔH_s° values of sodium carboxylates at 25 and 35°C are plotted as a function of total number of carbon atoms in the alkyl or aryl groups.
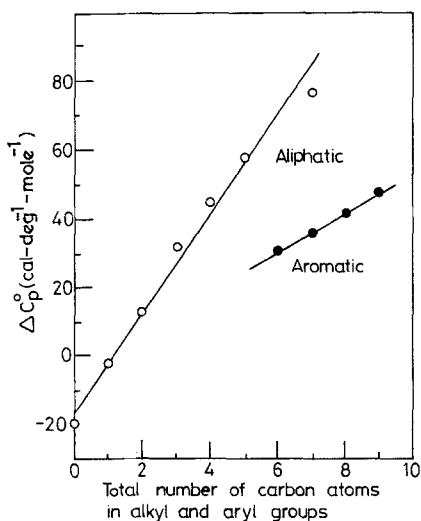

Fig. 2. Excess partial molal heat capacities at infinite dilution ΔC_p° for some sodium carboxylates versus total number of carbon atoms in alkyl and aryl groups at 30°C.

The values of the heat capacities of dissolution at infinite dilution ΔC_p° [where $\Delta C_{p30}^\circ = (\Delta H_{s35}^\circ - \Delta H_{s25}^\circ)/10]^{(13)}$ at 30°C are given in Table I. The values of ΔC_p° per –CH_2– group increment in the alkyl and aryl groups are also given in Table I. In Fig. 2 are plotted the ΔC_p° values as a function of total number of carbon atoms in the alkyl and aryl groups.

4. DISCUSSION

The enthalpies of solution at infinite dilution ΔH_s° have been observed to vary with the length of the alkyl chain in a characteristic manner. For instance, Konicek and Wadsö[14] observed minima in ΔH_s° of carboxylic acids, alcohols, and amides at a chain length of 2–4 carbon atoms. Corkill et al.[15] found minima for ΔH_s° of several liquid, nonionic, alkyl compounds at a chain length of 3–5 carbon atoms. For the amines above C_2 a constant increment in ΔH_s° per CH_2 group was observed.[14] The plots of ΔH_s° of aliphatic and aromatic sodium carboxylates versus number of carbon atoms in alkyl and aryl groups (see Fig. 1) indicate two minima, one at C_1 and the other at C_3 for aliphatic salts at 25°C. The trend at 35°C is similar to that at 25°C. For the aromatic sodium carboxylates, minima are found at C_7 and C_9. Since the enthalpies of solution represent a combined contribution of various effects, it is difficult to give an unambiguous explanation for the observed minima.

Since the difference in the limiting partial molal heat capacity $(\bar{C}_{p_2}^\circ)$ and intrinsic heat capacity $(C_{p_{int}})$ of a solute is recognized to reflect the structural changes in aqueous solutions, and since the intrinsic heat capacity of a solute can be reasonably approximated to the heat capacity of the pure solute (C_{p_2}), the heat capacity of dissolution at infinite dilution $(\Delta C_p^\circ = \bar{C}_{p_2}^\circ - C_{p_2})$ can be assumed to reflect the structural changes in aqueous solutions.

The ΔC_p° values indicate that sodium formate is a structure breaker, and sodium acetate is a borderline case, while all other sodium carboxylates are structure makers and their structure-making propensity (or their effect in the enhancement of hydrogen bonding) increases with the increasing chain length of the alkyl and aryl group, as was also observed in the case of R_4N^+ salts.[3] Similar conclusions have also been arrived at from the heats-of-dilution studies by Lindenbaum,[7] from near-infrared spectral studies by Worley and Klotz,[16] and from the studies of enthalpies of transfer of sodium carboxylates from normal to heavy water by Snell and Greyson.[11] The ΔC_p° studies on aliphatic sodium carboxylates having larger than 8 carbon atoms could not be carried out even in the submicelle concentration range because of slow dissolution of these carboxylates in water. The straight lines obtained in Fig. 2 both for aliphatic and aromatic carboxylates indicate a constant contribution to ΔC_p° per –CH_2– group increment in both types of compounds, although it is considerably smaller in the case of chains containing an

aromatic group. The average contribution to ΔC_p° per $-CH_2-$ increment in the alkyl group of aliphatic sodium carboxylates amounts to about 14 cal-deg^{-1}-mole^{-1}, which is very close to the value of about 16 cal-deg^{-1}-mole^{-1} observed in the case of R_4N^+ salts[3] when the alkyl group is lengthened from $R = CH_3$ to $R = C_4H_9$. Recently, Konicek and Wadsö[14] have observed from their accurate measurements of ΔC_p° and C_p for compounds of the series RCOOH, RNH$_2$, MeNHCOR, and RNHCOMe that the increment in $\bar{C}_{p_2}$ per $-CH_2-$ group of about 20 cal-deg^{-1}-mole^{-1} at 25°C remains constant. We have estimated the increment in ΔC_p° per $-CH_2-$ group from their results to be about 14 cal-deg^{-1}-mole^{-1}. The increment in ΔC_p° per $-CH_2-$ group for compounds of the series ROH,[17,18] RCOOH,[19] and ROSO$_3$Na,[20] while not as accurate as that of Konicek and Wadsö,[14] also amounts to 13–16 cal-deg^{-1}-mole^{-1}.

These observations indicate that the contribution to ΔC_p° from the interaction of the aliphatic nonpolar moiety with water is roughly independent of the nature of the hydrophilic group attached to the nonpolar moiety. A similar conclusion has also been arrived at by Konicek and Wadsö[14] and by Rüterjans et al.[21]

However, the $-CH_2-$ group increment of ΔC_p° in the aromatic sodium carboxylates on the average is found to be about 6 cal-deg^{-1}-mole^{-1}, which is much less than the 14 cal-deg^{-1}-mole^{-1} value observed in aliphatic compounds. This must be attributed to the presence of the phenyl ring. The methyl and phenyl groups have opposite inductive effects on the charge of the

functional group (
$$
-C\overset{\displaystyle O}{\underset{\displaystyle O^-}{\big<}}
$$
). The inductive effect of the phenyl ring acts so

as to increase the polarity of the CH$_2$ group (located between the
$$
-C\overset{\displaystyle O}{\underset{\displaystyle O^-}{\big<}}
$$

and phenyl groups), thus reducing its positive contribution to ΔC_p°.

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