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Beverly Bendiksen

Stig Friberg

Missouri University of Science and Technology, stic30kan@gmail.com

Patricia L.M. Plummer

Missouri University of Science and Technology

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CNDO Calculations on the Structure of a Liquid Sodium Carboxylate-Carboxylic Acid Compound

BEVERLY BENDIKSEN AND STIG E. FRIBERG¹

Chemistry Department, University of Missouri at Rolla, Rolla, Missouri 65401

AND

PATRICIA L. M. PLUMMER

Department of Physics and Graduate Center for Cloud Physics, University of Missouri at Rolla, Rolla, Missouri 65401

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The molecular interactions in a carboxylic acid/sodium carboxylate compound which is a liquid at room temperature were calculated using a CNDO/2 approach. The calculations gave results distinguishing the energy for different conformations in the molecular compound. The maximum binding energy was found for a structure in which the four acids were bridging with a hydrogen bond from the acid OH group to the carboxylate group and the acid carbonyl groups forming a ligand bond to the carboxylate sodium ion.

The problem of the structure of microemulsions has stimulated research in several areas following the modified perception of their nature. When it was realized that the interfacial free energy is not the only free energy component of importance (1), the initial opinion on stability (2-7) emphasizing only interfacial properties changed to a more general approach (8) including several interdroplet enthalpic and entropic free energy components.

Since the microemulsion droplets obviously are of colloidal size, a description of them as colloidal solutions containing inverse micelles was introduced by Adamson (9). This approach is useful for practical applications (10-13) and has also given a simple distinction between W/O and O/W systems (14). The O/W microemulsions have later been found to be thermodynamically unstable.

Not all "microemulsion" combinations deserve the epithet emulsions as pointed out by Shah and Hamlin (15). In these systems the surfactant molecules are not aggregated, but consist of monomeric molecules associated with a cluster of water molecules and one or two alcohol molecules (16, 17). The areas of microemulsion compositions with no intersurfactant association are important because electrolytes cannot be dissolved in these areas. The micellization to larger aggregates (18) takes place stepwise giving aggregates with different dielectric properties (19).

The traditional research on surfactant association in nonpolar solvents (20) has been restricted to inverse micellar aggregates formed by a single component, an oil-soluble hydrophobic surfactant. The thermodynamic basis for such concentration-dependent association conditions has been clarified in the recent contributions by Eicke and Christen (21, 22), who laid the

¹ To whom correspondence should be directed.

foundation for the energy involved in the stepwise association mechanisms experienced for such compounds. The analysis included enthalpy contributions from van der Waals and dipolar interactions demonstrating a free energy minimum for a certain size of the association aggregate. In a recent publication Müller (23) has presented electrostatic calculations for small aggregates of this kind in which internal entropy contributions were also taken into account. The results displayed the importance of the dielectric constant of the medium. High medium dielectric constant in combination with large headgroups of the associating molecules favored stepwise association to relatively large aggregates and vice versa. The stepwise association with variations in the association structure and conformation has received support from investigations using position annihilation techniques by Jean and Ache (24). These results are essential in order to understand phenomena in which compositions with only one surfactant is involved. One such area of pronounced importance is the mechanism for catalysis by inverse micelles (25, 26).

However, microemulsions stabilized by an ionic surfactant (1–19) usually employ a *combination* of a predominantly hydrophilic surfactant and a hydrophobic amphiphile, which is called the cosurfactant, usually consisting of a medium chain length alcohol. The hydrophilic surfactant is in itself only poorly soluble in hydrocarbon; high solubility is reached first when water, cosurfactant, and surfactant are combined (17). One interesting feature of the solubility conditions is the *minimum* water content for solubility. At this solubility limit no micelles exist in the system; they are formed first at increased water content with a stepwise association (16).

Although this stepwise association process of combined surfactants in all certainty will show similarities to the one described for a single hydrophobic surfactant (21–23), for example, the dependence on the polarity of

the solvent (16, 23), it appears that a better understanding of the special combination conditions is essential for the continuing development of the comprehension of microemulsions. With this in mind, a program has been initiated to contribute to the information about the relation between structure and energy in small combination aggregates.

It was considered essential to use an experimentally well-verified compound with characteristic features for the first evaluation of the structure–energy relationships. Such a compound was found in the liquid carboxylic acid/sodium carboxylate complex which exists for carboxylic acids of medium chain length in nonpolar solvents or in the liquid native acid (27). Molecular weight determinations have shown these aggregates to consist of two soap and four acid molecules (28). Their structure is not known in detail, but NMR and IR spectra have demonstrated the acid dimers to be disrupted (29) and also the formation of a hydrogen bond of enhanced strength in comparison to the one in the acid dimer. These results have been rationalized into a structure (28) with a strong hydrogen bond between the ionized carboxylic group and the OH group of a carboxylic acid molecule. The carbonyl group of the carboxylic acids was assumed forming a ligand with the sodium ion in a distorted octahedral arrangement with the four oxygens from the ionized carboxylic groups. Quadrupolar splitting from ^{23}Na has indicated a strongly bonded sodium in good agreement with this picture (30).

It is important to emphasize the distinction between these medium chain length *liquid* molecular compounds and the long chain “acid soaps.” These “acid soaps” are crystalline compounds (31–33) that depend on the lattice energy of the hydrocarbon chain for their stability; this lattice energy will modify the bonds and geometrical conformation of the polar groups. Very short chain “acid soaps” (34) form a

three-dimensional infinite structure in which the energy and bonds are cooperative elements in a multipoint lattice.

This distinction is the basis for our approach using a semiempirical quantum mechanical approach and the medium chain length soaps and acids are in fact the only possible components for such an application. The long chain acid soaps are molecules too large for convenient calculations and furthermore the optimum energy is difficult to find because of the influence both from the lattice energy of the hydrocarbon chains and the polar interactions. The short chain acid soaps present corresponding problems in evaluating the cooperative effects in a three-dimensional polar lattice with reasonable computer expenses.

The present structure with the polar groups centrally being surrounded by 6 liquid hydrocarbon chains appears optimal for calculations of this kind, since the geometrical arrangement (a) limits the number of the central polar groups and also (b) leaves the conformation of the hydrocarbon chains without structural influence. This latter postulate is verified by the fact that dilution with nonpolar solvents (28) left the structure unchanged. With this basis direct quantum mechanical calculations of the energy of different polar group conformations were considered justified. One of the semiempirical approaches that have been developed in recent years, the CNDO/2 approach originally developed by Pople and co-workers (35), was used. It has been extensively used for describing hydrogen bonded systems (36–38) and has given good results for the interactions in water clusters around metal ions in aqueous solutions (39, 40). The technique gives good agreement with *ab initio* calculations in predicting relative stabilities of closely related structures contrary to the case of MINDO/3 that recently has been shown not to be reliable for such configurations (41). One notable exception to the good performance of

CNDO/2 has recently been reported; an $(\text{H}_2\text{O})_2$ structure with the two oxygens facing each other gave a substantial minimum (42) in the interaction/distance relationship.

It is expected that the results reported here are subject to the usual difficulties inherit in CNDO calculations, namely, bond lengths which are somewhat shorter and larger energies than those experimentally observed. However, the relative stabilities of the geometries investigated should realistically mimic those experimentally observed or obtained from subsequent more detailed calculations with less approximations. In addition, the CNDO was chosen instead of modeling the system via empirical pairwise potentials as cooperative effects would be expected to be important in the relatively large aggregates formed. CNDO has been demonstrated to reproduce these effects in hydrogen bonded systems (43).

The original experimental results (27) on the system under calculation were obtained for sodium octanoate with its corresponding acid, chosen because it is a liquid at room temperature. The CNDO/2 program cannot accommodate molecules as large as octanoic acid and in view of the predominance of the polar group interaction for the stability sodium acetate and formic acid were chosen to represent the carboxylate ion and carboxylic acid. It is essential to understand the insignificance of this change. The experimental results (28, 29) have given evidence of an isolated polar case of four carboxylic acid groups and two carboxylate groups. The only modification brought forward by the shorter chains in the calculations is a reduction of the overall electron density of the polar group bonds.

COMPUTER PROGRAM

In brief, the CNDO (the acronym stands for complete neglect of differential overlap) approach is an all valence electron, self-consistent field calculation in which multi-center integrals have been neglected and

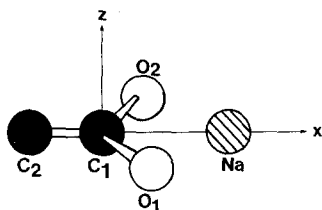


FIG. 1. The common notion of the structure of a sodium carboxylate with the sodium ion symmetrically in the extension of the carboxylate group.

some of the two electron integrals parameterized using atomic data. Slater-type atomic orbitals are used as the basis set. Thus the basis consisted of 1s orbitals for H, 3s for Na, and 2s, 2p_x, 2p_y, 2p_z for carbon and oxygen. In these calculations two-electron integrals are approximated as

$$(\mu\nu/\lambda\sigma) = \delta_{\mu\nu}\delta_{\lambda\sigma}(\mu\mu/\lambda\lambda) = \gamma_{\mu\lambda}$$

where μ etc. stands for Slater Orbitals ϕ_{μ} , . . . centered on the nuclei. The electron interaction integrals are assumed to depend only on the atoms to which ϕ_{μ} , ϕ_{ν} belong, and not on the specific orbitals, e.g.,

$$\gamma_{\mu\nu} = \gamma_{AB} = \iint s_A^2(1)(r_{12})^{-1}s_B^2(2)d\tau_1d\tau_2.$$

Further

$$(\mu/V_B/\nu) = \delta_{\mu\nu}V_{AB}$$

where $-V_B$ is the potential due to the nucleus of charge Z_B and the inner shell of atom B and

$$V_{AB} = Z_B \int s_A^2(1)(r_{1B})^{-1}d\tau_1.$$

In addition, the off-diagonal core matrix elements, $H_{\mu\nu}$, are set proportional to the overlap integral, $S_{\mu\nu}$.

$$H_{\mu\nu} = \beta_{AB}^0 S_{\mu\nu}$$

where β_{AB}^0 is a parameter determined from atomic spectral data for atoms A and B. The specific parameterization used is called CNDO/2.

The computer codes used for these calculations are modifications of Dobosh's

program supplied by QCPE (44). The modifications principally consisted of increased dimensions to handle the larger systems, and a matrix extrapolation routine incorporated into the SCF portion of the program to enhance convergence.

The output from the CNDO calculations was used to calculate electron densities (45) for several of the configurations examined. These densities were calculated in the usual fashion with contour maps and density plots generated to enhance interpretation of the results.

RESULTS AND COMMENTS

With the experimental results (27–29) as a basis, the investigation could be focused on four major problems.

- (1) The most stable configuration of the ion pair carboxylate/alkali metal ion,
- (2) The most stable configuration of two such ion pairs,
- (3) The relative energy of the interactions from the carboxylic acid with (a) the carboxylate and (b) the sodium ion, and
- (4) The energy differences between different connecting paths by the carboxylic acid molecules between the sodium carboxylate ion and the sodium ion.

These problems will be treated in the following sections.

The Carboxylate/Sodium Combination

The common notion (27) about the alkyl carboxylate/sodium system is illustrated in Fig. 1 where the sodium ion is symmetrically placed between the two oxygens. The geometry of the group is of pronounced importance for the energy of the system (23) and an evaluation of the stability of alternative geometries was judged appropriate.

The calculations were performed on sodium acetate giving the essential electron excess of a carboxylic chain with a minimum of computer time. The coordinates for the acetate anion are found in Table I and were not varied in the calculations. The change in

binding energy in relation to the separated atoms was calculated as a function of the Na-acetate distance along the extension of the C-C bond (Fig. 2, ■). The interaction energy showed a distinct minimum at an X coordinate equal to 0.325 nm that is a distance of 0.25 nm from the connection line between the oxygen-oxygen centers; the total binding energy for the aggregate at this separation being -7.51 MJ/mole (1795 kcal mole $^{-1}$).

Two other configurations were also examined, both having the sodium ion out of the plane of the carboxylate groups. In the first, the sodium was placed vertically above the middle point between the carboxylic C atom and the connection line between the two oxygens (0.0289,0, Z). The interaction curve (Fig. 2, ▲) showed a minimum at (0.0289, 0,0.270) with a binding energy significantly higher (-7.72 MJ/mole, 1845 kcal mole $^{-1}$) than for the minimum along the X axis. Moving the sodium ion to a position vertical to the connection between the carboxylic oxygens, (0.0577,0, Z) gave only an insignificant difference in binding energy. Calculations along the line ($X,0,0.270$) above the C-C bond showed no significant minimum (see Table II).

Since the electron density is greater along the carbon/oxygen bond than in the XZ plane (45) the possibility of a position with greater stability for Y values other than zero was evaluated. The results (Table III) dis-

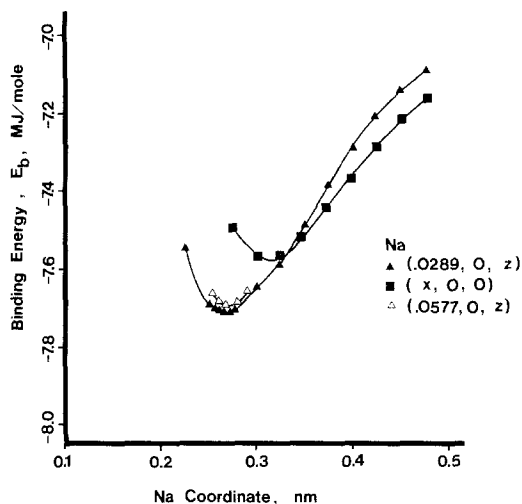


FIG. 2. The binding energy of sodium acetate versus the location of the sodium ion. The coordinates are given in Table I and Fig. 1.

played a greater binding energy for the symmetrical positions in the XY plane.

In summary the values strongly indicate the position of the sodium ion to be above the COO plane of the carboxylate group for a single sodium carboxylate molecule. The exact magnitude of the enhanced stability may probably not be as great as these results indicate due to the inherent deficiencies of the CNDO technique.

Combination of Two Carboxylates

Since experimental investigations (28) have earlier shown the complex to contain two carboxylates the energy involved in different structures with two carboxylate ions and two sodium ions were calculated. The arrangements investigated are shown by Figs. 3 and 4, top.

Three positions of the two carboxylates were used and the binding energy was calculated as function of the separation distance. The binding energy for two isolated carboxylates with identical sodium carboxylate geometry was subtracted from the value obtained for the dimer, the difference being called the stabilization energy, E_{stab} .

TABLE I

Acetate Anion Coordinates^a

	X	Y	Z
C ₁	0.0	0.0	0.0
C ₂	-0.1497	0.0	0.0
O ₁	+0.0577	0.1109	0.0
O ₂	+0.0577	-0.1109	0.0
H ₁	-0.1902	0.1001	0.0
H ₂	-0.1902	-0.0501	-0.0867
H ₃	-0.1902	-0.0501	0.0867

^a Notations according to Fig. 1.

TABLE II
 Binding Energy

$Z = 0.270 \text{ nm}$	$X, \text{ nm}$	0	-0.01	-0.02	-0.03	-0.04	-0.05	-0.06	-0.07
	E_B								
	MJ mole ⁻¹	-7.735	-7.738	-7.743	-7.743	-7.743	-7.743	-7.738	-7.732
	kcal mole ⁻¹	1849	1849	1851	1851	1851	1851	1849	1848

The energy for the position with the two molecules on top of each other (Fig. 3, top left and ■) was calculated fixing the distance between the sodium atom and the COO plane of "its" carboxylate group at its optimum value. Intuitively, an enhanced stabilization energy should be expected for the sodium ion symmetrically placed between the two COO planes. Such a structure is by no means a necessity; the different kinds of structures experienced with hydrogen bonds (46) is a good illustration of this point. Calculations showed the optimal sodium distance to the second carboxylate plane to be slightly in excess of the one to the plane of the primary bonding carboxylate group. Table IV gives the two distances as 0.280 and 0.270 nm.

Identical sodium ion positions were used for the arrangement with the carboxylate groups in parallel, side by side with the same direction (Fig. 3, top right □). The stabilization energy for this case was sig-

nificantly higher than for the first arrangement (~70 kT/molecule), but an optimization in combined X - Y coordinates was deleted in view of the results from arrangements in the X direction.

In the calculations for the configuration in which the carboxylate molecules were placed with opposite directions (Fig. 4, top) the distance between the carboxylates including sodium ions was first optimized. The results showed a maximum for an X distance of 0.320 nm (Fig. 4, Δ). Using this carboxylate/carboxylate distance the difference of X coordinate for two sodium atoms

TABLE III

Binding Energies versus Sodium Position

Na position			E_B	
X	Y	$Z(\text{Å})$	MJ mole ⁻¹	kcal mole ⁻¹
+0.300	0.0	0.00	-7.569	1809
	0.027725		-7.564	1808
	0.055450		-7.545	1803
	0.083175		-7.522	1798
	0.110900		-7.501	1793
+0.0289	0.0	0.270	-7.716	1844
	0.018480		-7.713	1843
	0.036960		-7.711	1843
	0.055440		-7.703	1841
	0.083175		-7.686	1837

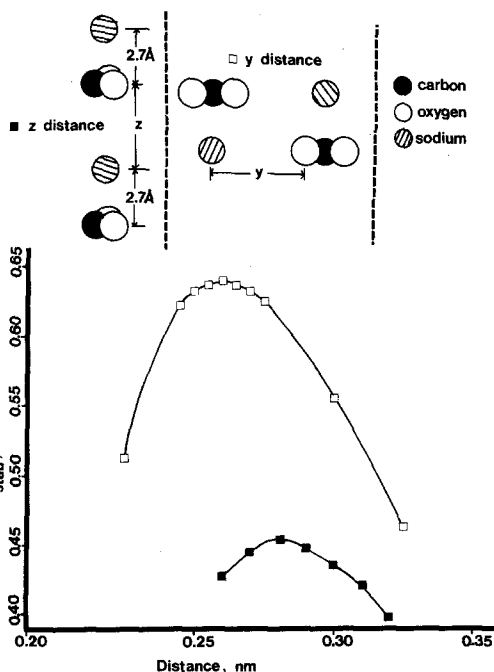


FIG. 3. The stabilization energy when two carboxylate molecules are paired with different geometries (top). ■ Molecules on top of each other (top left). □ Molecules at the side of each other (top right).

was subsequently varied. The maximum was sharp at an Na-Na distance of 0.30 nm in the *X* direction. It is obvious that the Na/Na and the Na/COO interactions are critically dependent on the distance in the *X* direction. The difference between this result and the one for a single sodium carboxylate constellation (Table II) is pronounced and instructive.

The results convincingly showed the preferred orientation to be according to Fig. 4; the difference corresponds to 76.1 kT molecule⁻¹. This is a decisive energy change between configurations showing one to be stable and the reliability of the result must be examined, especially concerning the deficiencies inherent in the CNDO approach. However, it is difficult to envision the CNDO shortcomings being responsible for the divergence in energy in this case. The

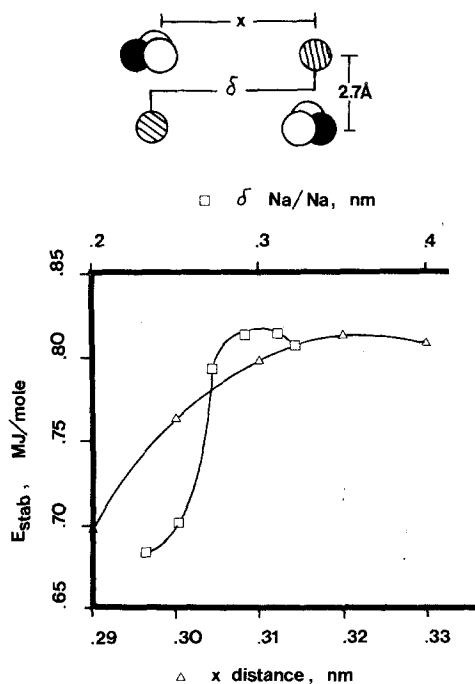


FIG. 4. The stabilization energy when two carboxylates are paired facing each other. Δ The distance between carboxylates varied with the sodium ions fixed with regard to the vertical carboxylate group. \square The carboxylate ions fixed, the sodium ions moved in *X* direction.

TABLE IV
Z Layer Separation^a

z, nm	E_B		
	MJ mole ⁻¹	kcal mole ⁻¹	
0.260	-15.862	3791	
0.270	-15.878	3795	
0.280	-15.887	3797	
0.290	-15.882	3796	
Z = 0.270nm	0.300	-15.870	3793

^a Binding energy *not* the stabilization energy!

enhanced description of isolated fragments that occur when they are brought into contact should rather favor the two alternate positions; both of them (Fig. 3) offer more contact area than the more stable configuration (Fig. 4).

Carboxylate/Carboxylic Acid Interactions

The results described in the preceding section offered a sufficient basis to assume a final configuration of the aggregate of four carboxylic groups/two carboxylates with the two carboxylates arranged as shown in Fig. 4. The spectroscopic data (28, 29) have earlier given evidence of a hydrogen bond from each of the OH groups of the acid to one of the carboxylate oxygens; the limitation of stability (27) to the maximum ratio two carboxylic acid groups/one carboxylate group is an indirect but further support for this opinion.

Against this background the carboxylic groups of the acid were arranged with the OH group in a hydrogen bond to one of the oxygens of the carboxylate group, the carbonyl group of the acid being part of the coordination sphere around the sodium ion. With these bonding characteristics two configurations were studied. In the first one all acids were "vertically" arranged (Fig. 5A), and in the second alternative (Fig. 5B) all four molecules were horizontally arranged.

The results (Fig. 5) gave significantly higher stabilization energy for the arrangement with all four acid molecules in the horizontal, the bridging position. The dif-

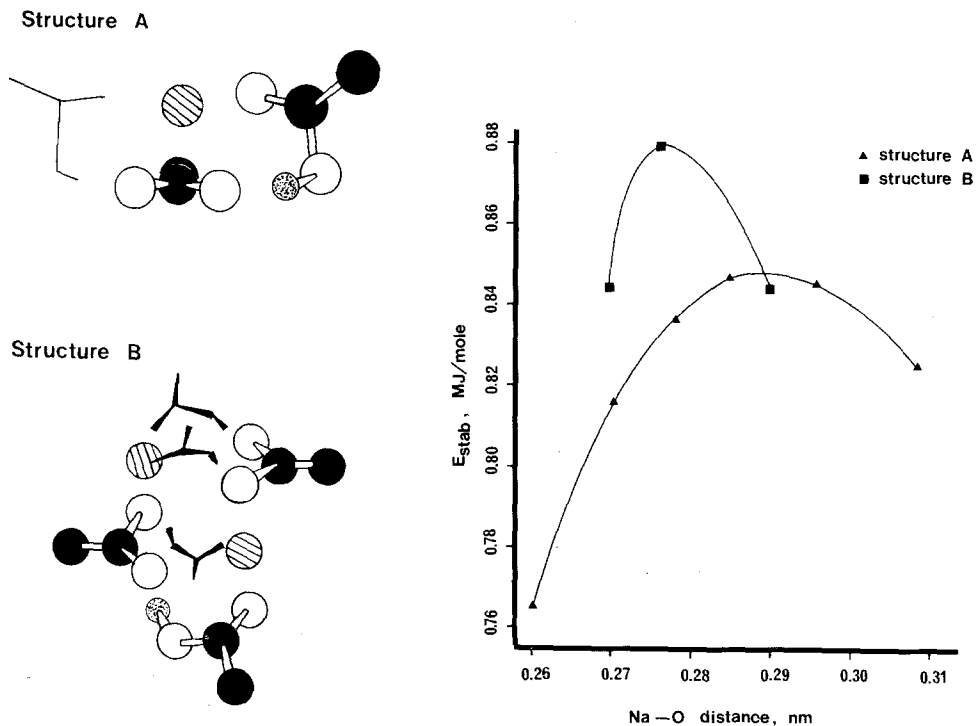


FIG. 5. The two structures and their corresponding interaction energies for varied Na-O distance. The hydrogen bond distance was optimized to 0.253 nm.

ference between the stabilization energy of the second, the entirely horizontal position and the highest value of the others corresponds to 38 kT per molecule, a significant energy difference for the total population to be in the arrangement with the acids horizontally.

The stabilization energy of the carboxylic acid addition was $0.22 \text{ MJ mole}^{-1}$ ($52.6 \text{ kcal mole}^{-1}$) counted per acid monomer. The value was obtained by subtracting the energy of aggregate from the energy of the two soap molecules with the configuration according to Fig. 4 and four carboxylic acid monomers. This energy is a combination of the energies of the hydrogen bond and of the carbonyl oxygen/sodium ligand bond. A separation of these two was obtained by corresponding calculations with a carboxylic acid attached with identical bond distance unchanged but the O-Na distance vastly increased to one molecule of sodium acetate. The correspond-

ing value for the $\text{CO} \dots \text{Na}$ interaction was obtained in a similar manner. The results showed an energy of $0.082 \text{ MJ mole}^{-1}$ ($19.5 \text{ kcal mole}^{-1}$) for the hydrogen bond and $0.151 \text{ MJ mole}^{-1}$ ($36.1 \text{ kcal mole}^{-1}$) for the sodium ion ligand bond. The sum of these values differs $0.013 \text{ MJ mole}^{-1}$ from the combined interaction demonstrating the fact that the minor change of electron density distribution due to one of the two attaching bonds has some importance for the strength of the second one.

The calculation was made with excess energy compared to four acid monomers instead of to two acid dimers. A comparison with the hydrogen bond strength of the acid dimer is useful and informative also to the question of reliability of the program for hydrogen bonded systems of this kind. The hydrogen bond strength for an acid dimer was found to be $0.068 \text{ MJ mole}^{-1}$ ($14.96 \text{ kcal mole}^{-1}$) (dimer) in excellent

agreement with experimental values for the acid dimer with an O(. . . H-)O distance of 0.273 nm.

The values display an energy difference per acid monomer molecule of 0.050 MJ mole⁻¹ (12.0 kcal mole⁻¹) for the hydrogen bond; with the Na ligand bond included the energy difference was 0.19 MJ mole⁻¹ (45.1 kcal mole⁻¹). The difference is striking and it appears obvious that this strong bond is one important factor for the stability of the complex.

DISCUSSION

The results illustrate the usefulness of the CNDO/2 program for obtaining information about the structure of small association aggregates in a nonpolar environment. The limitations have been discussed in an earlier session, the main problem being the exaggerated interaction when fragments are brought in contact. These are deficiencies that until a wider basis of comparison is available necessitate comparison with reliable experimental material in the individual case before final conclusions are drawn about structural details.

In the present case the separation of the acid dimer and the formation of a strong hydrogen bond between the acid carboxylic OH group and the ionized carboxylate group of the soap at the formation of the complex from soap and acid both have a reliable experimental basis in the results from NMR and IR spectroscopy (29). The calculations showed a pronounced increase of hydrogen bond strength in the carboxylate/carboxylic OH group hydrogen bond compared to the state in an acid dimer.

The energy of that bond was high, 0.082 MJ mole⁻¹ (20 kcal mole⁻¹) per monomer, and a comparison with experimental material is in order to determine the reliability of the CNDO/2 approach. The energy of a series of strong hydrogen bonds has recently (46) been determined using infrared spectroscopy. Five bases: diphenyl sulfoxide, dibenzyl sulfoxide, dimethyl sulfoxide,

triphenylphosphine oxide, and diphenyl selenoxide and three acids: mono-, di-, and trichloroacetic acid were used. The ΔH for the hydrogen bond formation varied from -0.027 MJ mole⁻¹ (6.5 kcal mole⁻¹) (monochloroacetic acid/diphenyl sulfoxide) to -0.067 MJ mole⁻¹ (16 kcal mole⁻¹) (trichloroacetic acid/diphenyl selenoxide). The value obtained in the present investigation, 0.082 MJ mole⁻¹ (20 kcal mole⁻¹), is slightly higher than the highest of these values. This is, however, expected against the fact that it is a bond between a charged group and a carboxylic acid and the present calculated value may be considered of the correct magnitude.

The acid carbonyl group/sodium ion ligand bond was not detected spectroscopically; its existence must be judged on the present results. Given the hydrogen bond described and the fact that the acid carbonyl group is not involved in a hydrogen bond it appears reasonable and sound to envision a structure in which the electron-rich carbonyl group would be bonded to the positive sodium. Its energy is high, 0.15 MJ mole⁻¹ (36 kcal mole⁻¹), and has to be justified by comparison with experimental values. These (39) show considerably higher values; 0.405 MJ mole⁻¹ (97 kcal mole⁻¹) (per water molecule) has been determined. Comparison between water of hydration and the present aggregate is difficult; suffice to point out that the present value appears to be of the right magnitude.

CONCLUSIONS

The calculations gave results to distinguish (a) between different positions of the sodium ion in single carboxylate molecules, (b) between different arrangements of a carboxylate dimer, and (c) between different conformations of the carboxylic acid molecules.

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