Thermodynamic Properties of Some Carbamates and Thiolcarbamates in Aqueous Solution

The solubility of several carbamates and thiolcarbamates in aqueous solution has been reported. From the temperature coefficient of solubility, the heat of solution and other thermodynamic parameters have been evaluated. The solubility of thiolcarbamates decreases with an increase in temperature; this unusual behavior may be due to hydrogen bonding between thiolcarbamate and water.

Alkyl carbamates and thiolcarbamates are soluble sparingly in water. However, their aqueous solutions show appreciable biological activity and are important to agriculture (Brian, 1964). In spite of their great use, little is known about their physical properties in aqueous solution. The present study was undertaken to furnish the thermodynamic properties of such compounds. In the present communication, the solubility, heat of solution, free energy change, and entropy change data of some of these compounds in aqueous solution are presented.

EXPERIMENTAL

The thiolcarbamates and carbamates used were of the highest purity obtainable. Several methods, of which the best known is reported here, were tried to solubilize these compounds in water. In general, the compound under investigation was shaken gently with water at a constant temperature in glass-stoppered bottles. The concentration of the compound in aqueous solution was measured at different intervals of time until a constant value of the solubility was obtained. Normally, two to three days were required to reach equilibrium. The concentration of the compound was determined by first extracting it into carbon disulfide from the aqueous phase, then subsequently injecting it into a gas chromatograph having a hydrogen flame detector.

RESULTS AND DISCUSSION

The solubility of the compounds under investigation is reported in Table I. In general, the solubility of most of the compounds decreases with an increase in the molecular weight. This has been demonstrated by plotting the logarithm of solubility against the molecular weight (Figure 1). This could be compared with the work of Schatzberg (1963), who noticed a decrease in the solubility of water in different alkanes as a function of molecular weight of the alkane.

The most interesting feature of the study is the effect of temperature on the solubility of these compounds. The solubility of carbamates increases with an increase in the temperature, while the reverse is noticed for thiolcarba-mates. The decrease in solubility with increasing temperature is commonly observed with gases, but infrequently seen for solids in solution. Some instances where the solubility decreases with an increase in temperature are the solubility of some amines (secondary and tertiary), ketones, ethers, or alcohol ethers in water (Cox and Cretcher, 1926; Copp and Everett, 1953; Rothmund, 1898). However, no clear explanation has been put forward. At the present time, with the limited data available on the properties of thiolcarbamates, it is difficult to explain this behavior. However, since the solubility of these compounds in aqueous solution is very low, there is a large excess of water present in comparison to the solute. Hence, water molecules will have a great influence on the surroundings of the solute particle. Each solute molecule will be hydrated with one or more hydration shells. The chances of direct contact between the solutes will be negligible. The hydration of the molecules may involve the formation of hydrogen bonds between water and the solute molecule (Pimental and McClellan, 1959). The number and the strength of the hydrogen bond will depend on the relative electronegativities of the solute molecule and water. Possibly, during the hydration of these molecules in solution, considerable hydrogen bonding is taking place, and the strength of the hydrogen bond may govern the solubility at different temperatures.

Considering that water is present in large excess, one can write the expression for free energy change, ΔG, for such a process as follows:

$$\Delta G = -RT \ln (a)$$

where a is the activity of the solute, R is the gas constant, and T is the absolute temperature. Since the solution is very dilute, the concentration can be assumed to be the same as activity. The ΔG values calculated in such a way are given in Table I.

When one dissolves a solid substance in aqueous solution, the dissolution takes place through two processes:

(1) Solid solute → aqueous solute

and

(2) Aqueous solute → solute in aqueous solution

Table I. Solubility, Free Energy Change, Heat of Solution, and Entropy of Solution of Some Carbamates and Thiolcarbamates in Aqueous Solution

| Compound	Mol. Wt.	Temp., °K.	Solubility P.p.m.	Solubility Mmoles/Liter	Free Energy Change + ΔG, KCal./Mole	Heat of Solution, ΔH, KCal./Mole	Entropy of Soln., ΔS, Cal./Degree
Carbamates							
Isopropyl N-(3-chlorophenyl)-CIPC	213.7	275	52.3	0.245	4.55	4.89	1.24
		297	102.5	0.480	4.50		1.31
Isopropyl N-(phenyl)-IPC	179.2	276	150.0	0.837	3.78	3.90	0.44
		298	254.0	1.420	3.89		0.34
4-(Chloro-2-butyl) N-(3-chlorophenyl)-Barban	258.1	276	4.02	0.0155	6.09	8.50	8.7
		296	12.10	0.0464	5.86		
sec-Butynyl N-(3-chlorophenyl)-BCPC	223.7	276	61.6	0.276	4.50	5.56	3.8
		303	153.0	0.680	4.40		3.8
Thiolcarbamates							
Ethyl N,N-dipropyl-EPTC	189.3	276	636	3.36	3.12	−3.93	−25.5
		297	375	1.98	3.69		−25.7
tert-Butyl N,N-dipropyl-1856	217.4	277	65.0	0.300	4.49	−5.60	−36.2
		297	35.0	0.160	5.16		−36.2
Propyl N,N-dipropyl-Vernolate	203.4	277	162.0	0.80	3.92	−3.2	−25.7
		297	109.0	0.536	4.45		−25.7
N-Propyl-ethyl butyl-Tillam	203.1	276	130.0	0.640	4.03		−25.2
		298	90.0	0.442	4.58	−2.74	−24.6
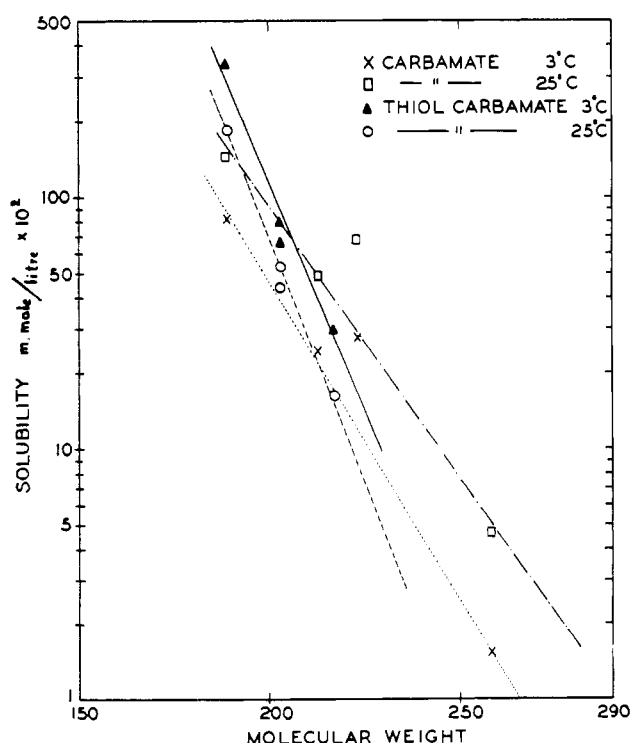
Figure 1. Relation between solubility of carbamates and thiolcarbamates and their molecular weight

and consequently, two enthalpy terms corresponding to each process are involved. For an ideal solution, the enthalpy change due to the second process is zero, and the heat of solution could be calculated simply by substituting the solubility values at two temperatures in the Clausius-Clapeyron equation. Since the solubility of carbamates increases with an increase in temperature, one can calculate the heat of solution for these compounds as described above. The heats of solution, ΔH, for carbamates are given in Table I.

Since the solubility of thiolcarbamates decreases with an increase in temperature, it may not be forming an ideal solution. To calculate the true heat of solution for these compounds, a knowledge of heat capacity, ΔC_p, at different temperatures is required (Hildebrand and Scott, 1950). Apparently these values for thiolcarbamates are not available. However, one can obtain an enthalpy value for these compounds by using the same procedure as for carbamates described above, and can call it apparent heat of solution. To call this apparent heat of solution the true heat of solution will depend upon the magnitude of the enthalpy change due to the second process as described above. These values are also included in Table I. The values of the entropy change, ΔS, can be obtained by the following expression:

$$\Delta G = \Delta H - T\Delta S$$

and are given in Table I.

The enthalpy and the entropy changes for thiolcarbamates are negative. This could be compared with the work of Copp and Everett (1953) on the thermodynamic properties of amines in aqueous solution. Copp and Everett noticed a large negative excess entropy and a small negative heat of mixing when amines were dissolved in various solvents, and they attributed this to association between the components through hydrogen bonding. Hence, this work gives further support to the authors' hydrogen bonding hypothesis.

Several instances have been encountered where thiolcarbamates show some unique behavior as far as their biological activity is concerned. Danielson *et al.* (1961) studied the persistence and activity of several thiolcarbamates in soils. These authors report an unusual persistence pattern of these herbicides in soils under varied temperature, moisture, and soil application conditions. This and other unusual behavior of thiolcarbamates may be attributed to the unique solubility behavior and the hydrogen-bonding tendency of these compounds.

LITERATURE CITED

Brian, R. C., "The Physiology and Biochemistry of Herbicides," L. J. Audus, Ed., Academic Press, London, New York, 1964.
Copp, J. L., Everett, D. H., *Discussion Faraday Soc.* **15**, 174 (1953).
Cox, H. L., Cretcher, L. H., *J. Am. Chem. Soc.* **48**, 451 (1926).
Danielson, L. L., Gentner, W. A., Jansen, L. L., *Weeds* **9**, 463 (1961).
Hildebrand, J. H., Scott, R. L., "The Solubility of Non-Electrolytes," Reinhold, New York, 1950.
Pimental, G. C., McClellan, A. L., "The Hydrogen Bond," Reinhold, New York, 1959.
Rothmund, V., *Z. Physik. Chem.* **26**, 433 (1898).
Schatzberg, P., *J. Phys. Chem.* **67**, 776 (1963).

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