form of flat needles which melted at 156°. This compound is less soluble than the methyl ester of the hydroxy acid. Hydrolysis with potassium hydroxide in methyl alcohol gave the hydroxy acid, m. p. 236°; 26.8 mg. in 2 cc. of chloroform solution gave $\alpha^{20}\text{D}$ −0.25°, 1-dm. semi-micro tube, $[\alpha]^{20}\text{D}$ −18.7°.

Anal. Calcd. for $C_{27}H_{42}O_4$: C, 75.30; H, 9.84. Found: C, 75.44; H, 9.85.

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Summary

Dehydroandrosterone and Δ^5-3-hydroxycholenic acid have been prepared from cholesterol by oxidation. This oxidation is possible provided both the double bond and the hydroxyl group in cholesterol are protected against oxidation. This has been accomplished by oxidation of cholesteryl acetate dibromide with chromic acid. A detailed description of the oxidation process has been given. This method of preparation locates definitely the double bond and determines the spatial arrangement of the hydroxyl group in dehydroandrosterone.

PRINCETON, N. J. RECEIVED JUNE 21, 1935

NOTES

Apparent Molal Heat Capacities of Amino Acids and Other Organic Compounds

BY JOHN T. EDSALL

The heat capacities of organic substances in aqueous solution have never been extensively studied. Zwicky[1] pointed out that the apparent molal heat capacities of several organic molecules in water were nearly identical with their molal heat capacities in the pure crystalline state, in other words, that the law of the ideal solution is approximately obeyed. For other substances, however, this is far from true.[2] A survey of the available data in "International Critical Tables," and of the recent data of Zittle and Schmidt[3] on amino acids in water, reveals certain relations between chemical structure and apparent molal heat capacity in water which appear worthy of consideration. In Table I are recorded the apparent molal heat capacities (ϕ) in dilute aqueous solution, and the molal heat capacities (Cp) in the pure state, for a number of substances.[4]

In the three homologous series recorded (alcohols, fatty acids, amino acids) it will be observed that the introduction of a CH_2 group increases ϕ by 20 to 30 calories per mole (see column headed Δ in Table I), while Cp increases by only 5 to 8 calories per mole for each CH_2 group introduced. Thus the presence of a hydrocarbon chain tends to produce a *positive* deviation from the ideal solution law with respect to heat capacity. This trend is approximately indicated by the series of values of $\phi - Cp$ given in the last column of Table I. On the other hand, substances such as glycerol, urea, dextrose and sucrose, which contain many polar groups and no hydrocarbon chain, behave much more nearly like ideal solutes in water. The substances cited by Zwicky all belong to this latter class.

It remains to be seen how far these suggested approximate rules will hold good when a wider range of substances has been investigated.

The apparent molal volumes of amino acids in water are known to be lower than those of most organic compounds, due to electrostriction of the solvent.[5] The calculations of Zwicky[1] on the heat capacities of electrolyte solutions suggest that the values of apparent molal heat capacity for the amino acids should be lowered by the charged NH_3^+ and COO^- groups which they con-

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[1] Zwicky, *Physik. Z.*, **27**, 271 (1926).

[2] See for instance Bose, *Z. physik. Chem.*, **58**, 585 (1907).

[3] Zittle and Schmidt, *J. Biol. Chem.*, **108**, 161 (1935).

[4] To make all the data comparable, the value of Cp should preferably be given for the pure *liquid* state. This is impossible for many substances, such as the amino acids which decompose on melting. In general, the value of Cp for any substance is distinctly higher in the liquid state than for the solid at or near the same temperature. This fact should be remembered in considering the data in Table I, but it does not essentially affect the arguments here advanced.

[5] Cohn, McMeekin, Edsall and Blanchard, THIS JOURNAL, **56**, 784 (1934).

TABLE I

APPARENT MOLAL HEAT CAPACITIES IN WATER

Substance	Temp., °C.	N_2	ϕ	Δ	Cp	$\phi - Cp$
Formic acid	16–50	0.02	17		24.6	− 8
Acetic acid	25	.02	38	21	32.2	6
Propionic acid	22–50	.02	63	25	38.8	24
n-Butyric acid	23–50	.02	85	22	44.5	40
Methyl alcohol	20	.03	36		20.4	16
Ethyl alcohol	20	.03	57	21	26.6	30
Propyl alcohol	20	.015	88	31	34.2	54
i-Butyl alcohol	25–29	.02	[160]		42.4	?
Glycine	25	.01	8.0		24^a	−16
dl-Alanine	25	.01	38	30	29^a	9
dl-Valine	25	.01	85	24		
Glycerol	15	.02	59		51.1	8
Urea	16–20	.01	23		19.3^a	4
Dextrose	20	.005	60		54^a	6
Sucrose	20	.003	115		102.2^a	13

[a] Indicates that substance in pure state is a crystalline solid.

N_2 represents approximately the molecular fraction of solute at which the measurement was made; ϕ represents the apparent molal heat capacity of the solute in calories per degree; Δ represents the increment in ϕ per CH_2 group in the homologous series studied; Cp is the molal heat capacity of the substances in the pure state at approximately the same temperature at which the solution was measured; $\phi - Cp$ represents the deviation between apparent molal heat capacity and heat capacity in the pure state. The value of ϕ for isobutyl alcohol is abnormally high and is to be regarded as very dubious.

It should be noted that valine differs from alanine by *two* CH_2 groups, and the given value of Δ is estimated accordingly.

Data on amino acid solutions from Zittle and Schmidt, *J. Biol. Chem.*, **108**, 161 (1935). Cp for glycine from Parks, Huffman and Barmore, THIS JOURNAL, **55**, 2733 (1933); for alanine from Huffman and Borsook, *ibid.*, **54**, 4297 (1932). Other data from "International Critical Tables," Vol. V, and from Landolt–Börnstein.

tain. The effects due to these groups may be approximately estimated from available data on the ionization of fatty acids, ammonia and water. Reported values of ΔCp for the ionization of these substances are as follows

$$CH_3COOH \longrightarrow CH_3COO^- + H^+ \qquad \Delta Cp_{298°} = -33.9 \text{ cal./deg.} \quad (1a)^6$$

$$C_2H_5COOH \longrightarrow C_2H_5COO^- + H^+ \qquad \Delta Cp_{298°} = -37.7 \text{ cal./deg.} \quad (1b)^6$$

$$NH_3 + H_2O \longrightarrow NH_4^+ + OH^- \qquad \Delta Cp_{298°} = -52 \quad \text{cal./deg.} \quad (2)^7$$

$$H^+ + OH^- \longrightarrow H_2O \qquad \Delta Cp_{298°} = +42.5 \text{ cal./deg.} \quad (3)^8$$

On adding (1a) or (1b) to (2) and (3) we obtain

$$RCOOH + NH_3 \longrightarrow RCOO^- + NH_4^+ \qquad \Delta Cp_{298°} = -43 \text{ to } -47 \text{ cal./deg.} \quad (4)$$

This should give the order of magnitude of the molal change in heat capacity accompanying the formation of a carboxyl and an ammonium ion, separated by a large distance, in dilute aqueous solution, whether the charges reside on the same or on different molecules. In α-amino acids, owing to the close proximity of the charges, the effect should be less.

Existing data are insufficient to test the validity of this reasoning, but it may be noted that the value of ϕ for glycine (Table I) is only 8 calories per mole at 0.5 molal. This is the lowest of all the ϕ values recorded in Table I, even though glycine is a larger and more complicated molecule than several others given in the table. This would suggest that the hypothesis just stated is at least qualitatively correct. Considerable light might be thrown on the problem by heat capacity measurements on solutions of isomeric amino acids with varying separation of the charged groups (for instance α- and β-alanine, or α- and ϵ-aminocaproic acid). Measurements on the solution of a betaine and of the uncharged isomeric ester (for instance N-trimethylglycine and N-dimethylglycine methyl ester) should also prove valuable in the study of the influence of electric charge on apparent molal heat capacity.

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(6) Harned and Ehlers, THIS JOURNAL, **55**, 652, 2379 (1933).

(7) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 314. It would be preferable to use data for a primary amine rather than for ammonia in this calculation, but no such data have been reported, so far as I am aware.

(8) Harned and Hamer, THIS JOURNAL, **55**, 2194 (1933). See also Rossini, *Bur. Standards J. Research*, **4**, 313 (1930).

The Density of Aqueous Solutions of Lanthanum, Cerous, Praseodymium and Neodymium Chlorides at 25°

BY CHARLES M. MASON AND HOLLIS L. LELAND

A survey of the literature did not reveal any reports on the density of aqueous solutions of the rare earth chlorides. In this Laboratory these data were required for work now in progress. The densities were therefore determined by the pycnometric method with an estimated accuracy of ±0.0002 g. per cc. Inspection of the data showed the density to be a linear function of the percentage composition by weight and on this basis the following empirical formulas were obtained by the method of least squares: