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

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

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

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

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

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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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:

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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).

TABLE I

Salt	Density at 25°
$LaCl_3$	$0.99707 + 0.00912\,P$
$CeCl_3$	$.99707 + .00915\,P$
$PrCl_3$	$.99707 + .00917\,P$
$NdCl_3$	$.99707 + .00920\,P$

where P is the weight percentage of the salt. These formulas reproduce the experimental data within the above stated accuracy except for the most concentrated solution of lanthanum chloride (4.67%) whose observed density was 1.0403 instead of the 1.0396 calculated.

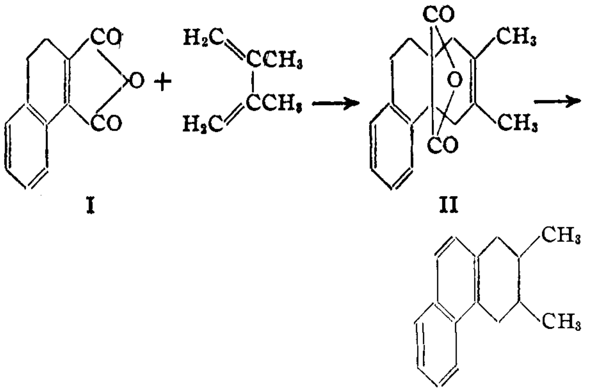
UNIVERSITY OF NEW HAMPSHIRE
DURHAM, N. H.
RECEIVED JUNE 11, 1935

COMMUNICATIONS TO THE EDITOR

A NEW PHENANTHRENE SYNTHESIS

Sir:

A new route to polynuclear aromatic and hydroaromatic types containing the phenanthrene ring system has been found in the addition of dienes to cyclic maleic anhydride derivatives such as 3,4-dihydronaphthalene-1,2-dicarboxylic acid anhydride (I) [von Auwers and Möller, *J. prakt. Chem.*, **217**, 124 (1925)]. The adduct II, m. p. 75.5–76.5° (calcd.: C, 76.57; H, 6.45. Found: C, 76.56; H, 6.44) was obtained from I and 2,3-dimethylbutadiene in 97% yield.



(All melting points reported are corrected.) Hydrogenation, using Adams' catalyst, gave the dihydro adduct, m. p. 117–118°. On fusing II with potassium hydroxide at 320–400° and distilling the product, there was obtained in 70% yield a hydrocarbon (b. p. 194–197° (19 mm.)) having the analysis and properties (resistant to catalytic hydrogenation) corresponding to the formula III. Hydrogen was evolved during the fusion. Dehydrogenation of III with selenium gave in excellent over-all yield a hydrocarbon which we believe to be pure 2,3-dimethylphenanthrene, m. p. 78–78.5° (calcd.: C, 93.16; H, 6.85. Found: C, 92.86; H, 7.08); picrate, m. p. 146–147°; quinone, m. p. 237.5–238.5° (calcd.: C, 81.32; H, 5.13. Found: C, 81.23; H, 5.37); quinoxaline, m. p. 208–209°. The constants found for the last two derivatives agree well with the values reported by Haworth, Mavin and Sheldrick [*J. Chem. Soc.*, 454 (1934)], but our hydrocarbon melts considerably higher than that synthesized by these investigators. The structure of our material was established by oxidation with nitric acid to pyromellitic anhydride.

In a similar reaction series, using butadiene, we obtained phenanthrene, m. p. 96.5–97.5°, showing no depression when mixed with a purified sample from coal tar (m. p. 97–98°).

Starting with ethyl γ-[1-naphthyl]-butyrate and oxalic ester, we have synthesized 3,4-dihydrophenanthrene-1,2-dicarboxylic acid anhydride, m. p. 263.5–264.5° (calcd.: C, 76.77; H, 4.04. Found: C, 76.83; H, 4.37), and from it the 2,3-dimethylbutadiene adduct, m. p. 196–196.5°. Dehydrogenation of the dihydrophenanthrene derivative with sulfur gave in good yield phenanthrene-1,2-dicarboxylic acid anhydride, m. p. 311–312° (calcd.: C, 77.39; H, 3.25. Found: C, 77.55; H, 3.62). By the same method naphthalene dicarboxylic acid anhydride was obtained from I in 76% yield.

In view of the active interest in the types of compounds made available by these new synthetical methods, and considering the recently reported attempts to apply to the problem other modifications of the Diels–Alder reaction [Cohen,