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The Densities and Specific Heats of Aqueous Solutions of *dl*- α -Alanine, β -Alanine and Lactamide^{1,2}

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A systematic study of the heat capacities, heats of dilution, and densities of aqueous solutions of the amino acids and their uncharged isomers was begun in this Laboratory four years ago in an effort to measure the effect of the dipole moment on the thermodynamic behavior of the solutions. The work developed from calculations of the heat capacities of *zwitterions* made by Edsall³ and from a discussion with Professor E. J. Cohn of the Department of Physical Chemistry of the Harvard Medical School. Earlier papers⁴ describe measurements of the specific heats and densities of aqueous solutions of glycine and glycolamide over a range of concentration from 0.1 or 0.2 molal to the nearly saturated solution. The apparent molal heat capacities seemed to be linear functions of the molality at low concentrations, and the apparent molal volumes were strictly linear functions of the molarity throughout the concentration range. The present paper shows that the same relationships hold for *dl*- α - and β -alanine and lactamide. These results allow us to test more fully the effect of the charged groups on the thermodynamic properties of the solutes.

(1) Part of this paper was presented before the Symposium on "The Thermodynamics of Electrolytic Dissociation" held by the Division of Physical and Inorganic Chemistry at the St. Louis Meeting of The American Chemical Society, April, 1941.

(2) This work was supported by a Grant-in-Aid from the Permanent Science Fund of the American Association of Arts and Sciences.

(3) Edsall, *THIS JOURNAL*, **57**, 1506 (1935).

(4) (a) Gucker, Ford and Moser, *J. Phys. Chem.*, **43**, 153 (1939); (b) Gucker and Ford, *ibid.*, **45**, 309 (1941).

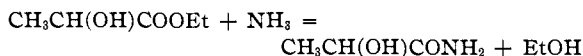
Materials and Solutions

Samples of each of the materials were kindly supplied to us by Professor John T. Edsall, of the Department of Physical Chemistry of the Harvard Medical School. These were supplemented by additional material from various sources.

C. P. *dl*- α -alanine was obtained from the Amino Acid Manufacturers of the University of California at Los Angeles. The material gave no test for ammonia with Nessler reagent, or for chloride with silver nitrate. Conductance measurements on a 1 molar solution indicated a salt content of less than 0.05%, calculated as ammonium chloride. One or two further recrystallizations, by the addition of 2 volumes of ethanol to 1 volume of a saturated aqueous solution, reduced the ionic impurity to about 0.02%.

About 250 g. of β -alanine was prepared by Professor Marvel at the University of Illinois. This was purified by successive charcoal treatments and filtrations, and the total material recrystallized several times by the addition of 4 volumes of ethanol to 1 volume of a saturated aqueous solution. Conductance measurements on the final product showed a salt content of about 0.02% (as ammonium chloride). Later we obtained 300 g. of very fine material from the Gelatin Products Co. of Detroit, Michigan.

Additional lactamide was synthesized in this Laboratory by the reaction between ethyl lactate and ammonia



The usual method of preparing such amides is to dissolve the ester in a large volume of alcohol into which dry ammonia is led. We found that the yield could be improved and the reaction hastened by passing the ammonia *directly* into the *liquid* ester. A typical synthesis follows: 500 g. of Eastman Kodak Co. "White Label" ethyl lactate was distilled under reduced pressure (20 mm.). Dry ammonia gas was passed directly into the freshly-distilled liquid, and

the vessel was stoppered and allowed to stand. The reaction was extremely rapid, and overnight produced plate-like crystals of lactamide two inches high. These crystals were then sucked dry on a sintered glass filter and thrice recrystallized from a 15% solution of water in ethyl acetate. This solution effectively removed ionic impurities and permitted a maximum recovery of the lactamide. The purified yield was over 70% of the theoretical, and had less than 0.01% salt content. It gave no test for ammonia with Nessler reagent and melted at 76-77°, corrected, which agreed with the melting points given in the literature and was the same as that of Dr. Edsall's sample.

All materials were carefully dried in a vacuum desiccator using "Dehydrite" (magnesium perchlorate) as the desiccant. All solutions were made up determinate from distilled water and the solid to a volume of about 300 ml. This gave enough solution to fill the working calorimeter and to make duplicate density determinations in 10-ml. pycnometers. The weights were calibrated and all weighings reduced to the vacuum standard, using the values 1.424,⁵ 1.404,⁶ and 1.249⁷ for the densities of solid *dl*- α -alanine, β -alanine, and lactamide, respectively. The density of each solution was used as a check upon its concentration.

Because of the limited supply at our disposal, the solutes were reclaimed from each solution after use. The solutions were evaporated to dryness under reduced pressure at about 50° and the solutes recrystallized from the appropriate solvent. Since it was necessary to protect the solutions from contamination by microorganisms, they were used immediately after making up and, after use, they were filtered through a sterilized Mandler filter of diatomaceous earth before reclamation of the solutes.

Specific Heats and Apparent Molal Heat Capacities.

The specific heats were measured with an accuracy of about 0.01%, using the differential apparatus, employing variable heaters, which has been developed in this Laboratory.⁷ Two closed calorimeters, of 270-ml. capacity, were enclosed in a submarine jacket surrounded by an adiabatic water-bath. A fixed weight of water in the "tare" calorimeter was balanced first against an identical weight of water in the "working" calorimeter, and then against a known weight of solution, occupying the same volume. In each case, the resistances were adjusted until the temperatures of the two calorimeters rose almost identically, over a 1°-interval. The difference, a few ten thousandths of a degree, was measured by a 20-junction thermal connected to a sensitive galvanometer. The ratio X of the resistance of the heaters (plus their leads) was measured during the experiment by means of a Wheatstone bridge. At least two experiments were carried out, with the heaters changed so that the ratio was slightly high in one case and low in the other. The exact balancing ratio was then determined by interpolation. A full discussion of the theory and practice of the experiments is contained in the original article.⁷ The same experimental procedure was followed in this work, but the method of calculation, which was somewhat changed and simplified, will be indicated here.

If r_1 and r_2 are the resistances of the working and tare calorimetric heaters, respectively, then we will define the resistance ratio as

$$x = r_1/r_2$$

(This is the reciprocal of the ratio used in the previous article.) The ratio x may be determined from the observed ratio X and the value of the lead resistance, l , by the equation

$$x = r_1/r_2 = X - \frac{l}{r_2}(1 - X) \quad (1)$$

If x_0 and x are the ratios which balance W_0 grams of water and W grams of solution, respectively, against the tare, the specific heat, s , of the solution in caloric units at the temperature of the experiment is

$$s = \frac{W_0}{W} \left[x - \frac{c_1}{W_0} \left(1 - \frac{x}{x_0} \right) \right] \quad (2)$$

where c_1 is the heat capacity of the working calorimeter. Since x_0 is within 0.01% of unity, $x_0 \simeq X$. The whole correction term is less than 1%, so that the last term may be written $(1 - X)$. Substituting (1) into (2) with these simplifications gives

$$s = \frac{W_0}{W} \left[\frac{X}{X_0} - \left(\frac{c_1}{W_0} + \frac{l}{r_2} \right) (1 - X) \right] \quad (3)$$

This single equation involves the correction for the lead resistance and also for the heat capacity of the calorimeter, both of which can be lumped into a single numerical factor at any temperature. Measurement showed that $l = 0.103$ ohm. Since r_2 is between 98.95 and 100.00 ohm, $l/r_2 \simeq 1.03 \times 10^{-3}$ and the lead correction is only 0.01% when $X = 0.90$ and negligible when X is 0.99. For c_1 we took the values determined by Ayres,⁸ namely, 10.62 cal₅ at 5°, 10.80 cal₂₅ at 25°, and 10.91 cal₄₀ at 40°. We carried out nine more water standardizations at temperatures from 5 to 40° and combined these results with those of Ayres to determine the values of l/X_0 at different temperatures. The best straight line, determined by the method of least squares, gave values of 1.00005, 1.00006, and 1.00007 at 5, 25 and 40°, respectively. These are within 0.003% of the values found by Ayres. At 25°, the value of c_1/W_0 therefore is 0.0403 and the numerical value of equation (3) is

$$s = \frac{W_0}{W} [1.00006X - 0.0413(1 - X)] \quad (4)$$

The specific heats and apparent molal heat capacities for the *dl*- α -alanine, β -alanine and lacta-

(5) Cohn, *et al.*, *This Journal*, **56**, 2270 (1934).

(6) Private communication from Dr. Edsall.

(7) Gucker, Ayres and Rubin, *This Journal*, **58**, 2118 (1936).

(8) Gucker and Ayres, *ibid.*, **59**, 2152 (1937).

mid solutions are contained in Tables I, II and III, respectively. The experiments are numbered chronologically, and none have been discarded.

In these tables the molality, m , was calculated directly from the weights of the constituents, using for the molecular weight of the solutes the

TABLE I^a
SPECIFIC HEATS AND APPARENT MOLAL HEAT CAPACITIES OF *dl*- α -ALANINE AT 5, 25 AND 40°

Expt.	c at 25°	m	5°C.			25°C.			40°C.		
			s	$\frac{10^5}{\Delta s}$	ΦC_{p_2}	s	$\frac{10^5}{\Delta s}$	ΦC_{p_2}	s	$\frac{10^5}{\Delta s}$	ΦC_{p_2}
9	0.10001	0.10092	0.99684	2	24.40	0.99411	8	34.72	0.99456	4	37.25
1	.10056	.10147				.99444	-1	33.80			
2	.19843	.20143				.98912	2	34.10			
3	.29197	.29812				.98401	-3	34.03			
10	.30437	.31102	.98054	-2	24.80	.98320	1	34.19	.98426	-5	37.09
4	.40282	.41414				.97798	-14	33.96			
11	.50612	.42381	.96819	-9	25.54	.97263	-5	34.49	.97425	-2	37.63
5	.59487	.61903				.96813	7	34.78			
12	.70743	.74160	.95643	4	26.45	.96224	-3	34.80	.96447	0	38.02
6	1.00042	1.06870				.94760	1	35.40			
15	1.00915	1.07860	.93940	1	27.51	.94720	3	35.44	.95031	5	38.60
13	1.20943	1.31030	.92858	-1	28.23	.93753	6	35.85	.94106	-2	38.87
8	1.28961	1.40434				.93369	1	35.97			
7	1.59122	1.76897				.91964	-15	36.51			
14	1.59382	1.77220				.91979	10	36.69	.92410	0	39.50
Average				± 3			± 5			± 3	

^a In Tables I, II, and III, experiments are numbered in chronological order; c (at 25°) is the molarity and m is the molality; Δs is the difference between the observed specific heat, s , and that calculated from the equation for the apparent molal heat capacity, ΦC_{p_2} , listed in Table IV.

TABLE II
SPECIFIC HEATS AND APPARENT MOLAL HEAT CAPACITIES OF β -ALANINE AT 5, 25 AND 40°

Expt.	c at 25°	m	5°C.			25°C.			40°C.		
			s	$\frac{10^5}{\Delta s}$	ΦC_{p_2}	s	$\frac{10^5}{\Delta s}$	ΦC_{p_2}	s	$\frac{10^5}{\Delta s}$	ΦC_{p_2}
1	0.10489	0.10585	0.99115	0	4.70	0.99260	0	18.50	0.99305	-8	22.80
2	.20150	.20451	.98308	-11	4.80	.98584	-4	18.60	.98678	-9	23.30
4	.39724	.40795	.96743	-10	6.36	.97236	-16	18.89	.97444	-1	24.16
3	.68110	.71182	.94612	14	8.59	.95380	-1	20.07	.95704	8	24.91
5	1.00722	1.07466	.92298	26	10.56	.93315	-2	20.93	.93755	8	25.42
8	1.50251	1.65580	.89012	-3	12.94	.90370	11	22.36	.90990	12	26.65
7	2.48820	2.94138	.83281	-30	17.36	.85082	20	25.09	.85943	27	28.78
6	3.53658	4.52903	.78120	19	21.29	.80138	0	27.54	.81182	6	30.78
9	4.55853	6.37495	.73714	-4	24.44	.75805	-24	29.60	.76951	-24	32.41
10	5.35080	8.06559				.72781	33	31.10	.73947	+27	33.58
Average				± 13			± 11			± 13	

TABLE III
SPECIFIC HEATS AND APPARENT MOLAL HEAT CAPACITIES OF LACTAMIDE AT 5, 25 AND 40°

Expt.	c at 25°	m	5°C.			25°C.			40°C.		
			s	$\frac{10^5}{\Delta s}$	ΦC_{p_2}	s	$\frac{10^5}{\Delta s}$	ΦC_{p_2}	s	$\frac{10^5}{\Delta s}$	ΦC_{p_2}
3	0.19782	0.20133	0.99275	2	52.46	0.99385	-5	58.00	0.99447	6	61.14
7	.30619	.31420	.98863	-12	51.89	.99056	-1	58.21	.99127	-6	60.52
1	.38548	.39787	.98586	0	52.29	.98814	1	58.23	.98914	5	60.84
8	.71928	.76174	.97376	11	52.30	.97793	9	58.15	.97968	7	60.61
4	.97923	1.05833	.96422	6	52.10	.96991	9	57.99	.97232	13	60.48
9	1.54079	1.74275	.94378	0	51.83	.95232	-15	57.49	.95587	-21	59.84
5	1.95456	2.28933	.92877	-11	51.63	.93958	-7	57.32	.94387	-26	59.58
11	2.50551	3.08042	.90923	0	51.54	.92244	-9	57.01	.92814	4	59.37
6	2.93797	3.75834	.89416	11	51.50	.90902	-6	56.78	.91548	5	59.08
10	3.53892	4.79822	.87323	-13	51.38	.89020	-6	56.43	.89772	6	58.67
2	3.96812	5.61113	.85923	0	51.47	.87723	25	56.28	.88511	11	58.38
12	5.05345	8.07365				.84268	-4	55.59	.85215	4	57.61
Average				± 6			± 8			± 9	

TABLE IV

EQUATIONS FOR THE APPARENT MOLAL HEAT CAPACITIES OF *dl*- α -ALANINE, β -ALANINE, AND LACTAMIDE AND THE PARTIAL MOLAL HEAT CAPACITIES OF SOLUTE AND SOLVENT AT 5, 25 AND 40°

	<i>dl</i> - α -Alanine	β -Alanine	Lactamide
5°	$\Phi C_{p_2} = 23.75 + 3.70m - 0.20m^2$	$4.04 + 6.67m - 0.86m^2 + 0.05m^3$	$52.44 - 0.43m + 0.05m^2$
	$\bar{C}_{p_2} = 23.75 + 7.40m - 0.60m^2$	$4.04 + 13.34m - 2.58m^2 + 0.20m^3$	$52.44 - 0.86m + 0.15m^2$
	$\bar{C}_{p_1} - \bar{C}_{p_2} = 0.666m^2 - 0.0072m^3$	$0.1200m^2 - 0.0310m^3 + 0.0027m^4$	$-0.0078m^2 + 0.0016m^3$
25°	$\Phi C_{p_2} = 33.69 + 1.48m + 0.09m^2$	$18.27 + 2.64m - 0.13m^2$	$53.38 - 0.48m + 0.02m^2$
	$\bar{C}_{p_2} = 33.69 + 2.96m + 0.27m^2$	$18.27 + 5.28m - 0.39m^2$	$53.83 - 0.96m + 0.06m^2$
	$\bar{C}_{p_1} - \bar{C}_{p_2} = 0.0267m^2 + 0.0032m^3$	$0.0475m^2 - 0.0047m^3$	$-0.0087m^2 + 0.0006m^3$
40°	$\Phi C_{p_2} = 36.66 + 1.99m - 0.22m^2$	$23.34 + 2.12m - 0.10m^2$	$60.92 - 0.57m + 0.02m^2$
	$\bar{C}_{p_2} = 36.66 + 3.98m - 0.66m^2$	$23.34 + 4.24m - 0.30m^2$	$60.92 - 1.14m + 0.06m^2$
	$\bar{C}_{p_1} - \bar{C}_{p_2} = 0.0359m^2 + 0.0079m^3$	$0.0381m^2 - 0.0036m^3$	$-0.0103m^2 + 0.0007m^3$

value, $M_2 = 89.094$ (1941 atomic weights). The molarity, c , was calculated from the weights and densities in every experiment. The specific heat is relative to water at the same temperature. The apparent molal heat capacities were calculated from the usual equation

$$\Phi C_{p_2} = s \left[\frac{1000}{m} + M_2 \right] - \frac{1000}{m} \quad (5)$$

where s is the specific heat and m the molality. They are therefore expressed in calorie units at the temperature of the experiment. The corresponding values in terms of the calorie defined as

4.1833 int. j./gm./deg. may be calculated, using the heat capacities of water determined recently by Osborne, Stimson and Ginnings⁹ by multiplying by the factors 1.0043, 0.9989 and 0.9987 at 5, 25 and 40°.

The values of the apparent molal heat capacities were found to lie on smooth curves, linear in the dilute region, when they were plotted against the molarity or the molality. The molality was used as abscissa for convenience in calculation and a power series of the type

$$\Phi C_{p_2} = \Phi C_{p_2}^0 + am + bm^2 + \dots \quad (6)$$

(where $\Phi C_{p_2}^0$ is the apparent molal heat capacity at infinite dilution, and a and b are constants) proved adequate to reproduce nearly all the data over the whole range of concentration. Least square analyses at each temperature gave $\Phi C_{p_2}^0$ and the coefficients a and b . In these analyses each value of the apparent molal heat capacity was weighted according to its probable accuracy, measured by the reciprocal of $(1000/m + M_2)$. In the case of β -alanine at 5° an additional term, cm^3 , was necessary in equation (6) to express the data satisfactorily. The average value of Δs in Tables I, II and III and the curves of Fig. 1 indicate how well the equations of Table IV fit the data. The agreement is least satisfactory in the case of β -alanine, where the deviations are about twice as large as in the case of the other solutes. Cubic equations were tried at 25 and 40°, but gave even larger deviations.

The partial molal heat capacities of solute and solvent are readily calculated from the equations

$$\bar{C}_{p_2} = \Phi C_{p_2}^0 + 2am + 3bm^2 \quad (7)$$

and

$$\bar{C}_{p_1}^0 - \bar{C}_{p_1} = 10^{-3}M_1(am^2 + 2bm^3) \quad (8)$$

where M_1 is the molecular weight and $C_{p_1}^0$ the

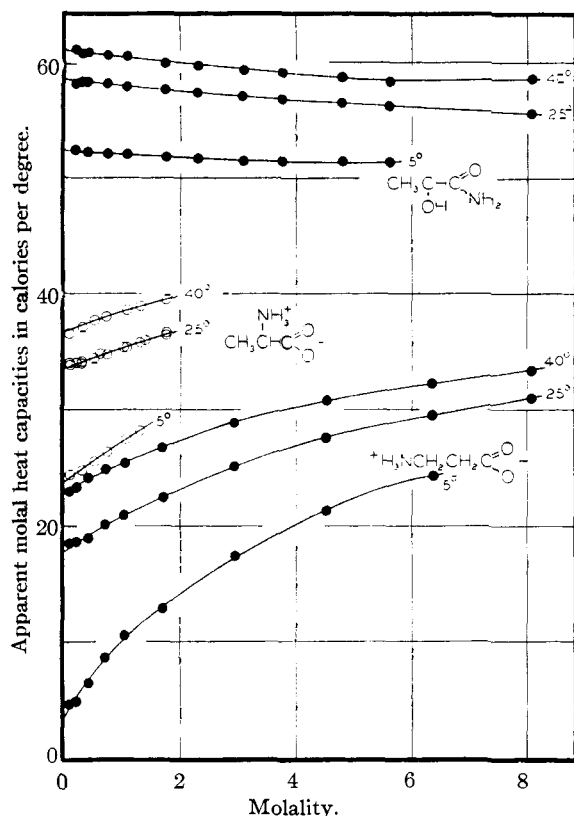


Fig. 1.—The apparent molal heat capacities of *dl*- α -alanine, β -alanine and lactamide at 0, 25 and 40°.

(9) Osborne, Stimson and Ginnings, *Bur. Standards J. Research*, **28**, 197 (1939).

molecular heat capacity of pure water, both of which have the value 18.016, since the thermal unit is the calorie per degree at the temperature of the experiment.

Comparison with Other Investigators.—Specific heats of solutions of β -alanine and lactamide could not be found in the literature, but Zittle and Schmidt¹⁰ have studied *dl*- α -alanine solutions at 25°. We recalculated the apparent molal heat capacities from their specific heat data, corrected to the 25° calorie, and found that their values agreed with our curve within the limits of their experimental accuracy, which was about 1%.

Densities and Apparent Molal Volumes

The densities of all solutions were determined in duplicate, with a pair of 10-ml. pycnometers. The densities were calculated from the weight of solution and the volumes obtained by calibration at 25° with distilled water. All weighings were reduced to the vacuum standard and the agreement between the two pycnometers was 0.005% or better in almost every case.

The apparent molal volumes were calculated from the usual equation

$$\Phi V_2 = \frac{1000}{c} \left[\frac{d_1 - d}{d_1} \right] + \frac{M_2}{d_1} \quad (9)$$

where d_1 and d are the densities of water and solution, and the other symbols have their previous significance.

Densities of lactamide solutions could not be found in the literature. Densities of aqueous solutions of *dl*- α -alanine at 25° have been studied by Cohn and Daniel¹¹ and by Dalton and Schmidt¹² from 0.13 *M* to the saturated solution (1.7 *M*). Cohn and Daniel also have measured the densities of solutions of β -alanine at 25° from 0.25 *M* to 4.0 *M*. They found that the apparent molal volumes of *dl*- α - and β -alanine are linear functions of the molarity throughout the range studied. This is confirmed by our determinations, the results of which are listed in Tables V, VI and VII. All of our results are included in these tables.

A plot of the apparent molal volumes at 25° against the molarity for all three substances is shown in Fig. 2. The solid lines correspond to the equations of Table VIII. In the cases of *dl*- α -alanine and β -alanine, the coefficients of Table VIII were obtained from a least-square analysis of our data and those of Cohn. Each result was

(10) Zittle and Schmidt, *J. Biol. Chem.*, **108**, 161 (1935).

(11) Cohn and Daniel, *THIS JOURNAL*, **58**, 415 (1936).

(12) Dalton and Schmidt, *J. Biol. Chem.*, **108**, 549 (1933).

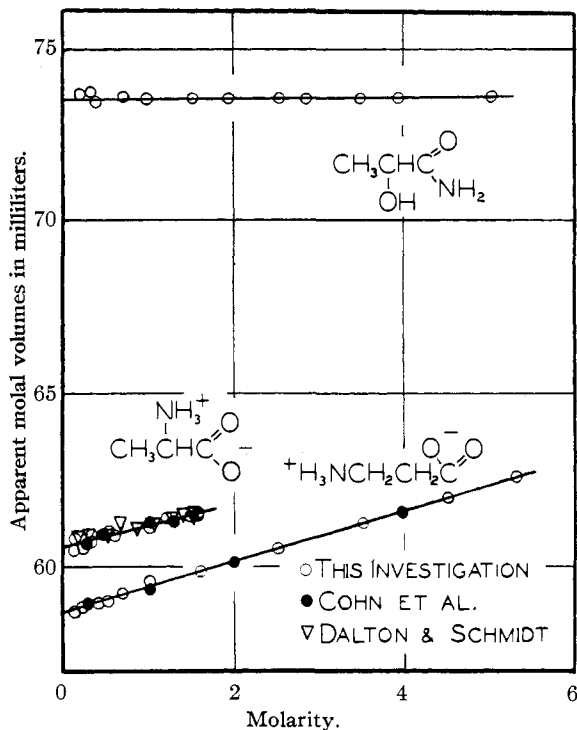


Fig. 2.—The apparent molal volumes of *dl*- α -alanine, β -alanine and lactamide at 25°.

weighted by the factor $p(d_1 - d)$, where p was estimated from the self-consistency of the series. It was assigned the value of 1 for our experiments and 2 for those of Cohn. The density may be satisfactorily expressed by a quadratic equation in c

$$d = d_1 + Ac + Bc^2 \quad (10)$$

where A and B are constant coefficients which may be evaluated from the equation

$$\Phi V_2 = \Phi V_2^0 + ac \quad (11)$$

which expresses the apparent molal volume as a linear function of the molarity. The excellent agreement (better than 0.01%) between calculated and observed densities is shown by the average values of Δd listed in Tables V, VI and VII. The partial molal volumes of solute and solvent, calculated from equations derived in previous papers,^{13,4a} are given in the tables. Table VIII lists all of these equations.

Discussion of the Results

The similarity between the curves of apparent molal volume and apparent molal heat capacity is apparent from Figs. 1 and 2. In each case the slopes increase in the order, lactamide, *dl*- α -alanine, β -alanine, which is the order of increasing dipole

(13) Gucker, Gage and Moser, *THIS JOURNAL*, **60**, 2582 (1938).

TABLE V^a
DENSITIES OF AQUEOUS SOLUTIONS OF *D*- α -ALANINE AT 25° AND CORRESPONDING APPARENT AND PARTIAL MOLAL VOLUMES

Expt.	c	m	d	$\frac{\Delta d}{10^6}$ (in p. p. m.)	ΦV_2 (obsd.)	\bar{V}_2 (calcd.)	\bar{V}_1 (calcd.)
	0.00000	0.00000	0.997074			60.61	18.0691
9	.10001	.10092	.99992	-10	60.82	60.72	18.0691
1	.10056	.10147	.99998	40	60.33	60.72	18.0691
2	.19843	.20143	1.00279	60	60.44	60.83	18.0687
3	.29197	.29812	1.00541	30	60.71	60.94	18.0682
10	.39437	.31102	1.00572	-20	60.87	60.95	18.0681
4	.49282	.4444	1.00862	100	60.60	61.06	18.0675
11	.59612	.52381	1.01129	-140	61.18	61.18	18.0665
5	.59487	.61903	1.01397	50	60.80	61.27	18.0655
12	.70743	.74160	1.01695	-110	61.18	61.40	18.0640
6	1.00042	1.06876	1.02524	70	61.12	61.72	18.0588
15	1.00915	1.07860	1.02522	-190	61.09	61.73	18.0586
13	1.20943	1.31030	1.03078	-110	61.40	61.94	18.0541
8	1.28961	1.40434	1.03320	120	61.20	62.02	18.0519
7	1.59122	1.76897	1.04129	60	61.49	62.34	18.0429
14	1.59382	1.77220	1.04135	50	61.50	62.34	18.0427
Average				≈ 73			

^a In Tables V, VI and VII the experiments are numbered in chronological order; c and m represent the molarity and the molality, respectively, as in Tables I, II and III; d the density of the solution in grams per milliliter; and Δd the difference, in parts per million, of the observed density minus that calculated from the equation in Table VIII. The density of pure water is taken from the "International Critical Tables," Vol. III, p. 25.

TABLE VI
DENSITIES OF AQUEOUS SOLUTIONS OF β -ALANINE AT 25° AND CORRESPONDING APPARENT AND PARTIAL MOLAL VOLUMES

Expt.	c	m	d	$\frac{\Delta d}{10^6}$ (in p. p. m.)	ΦV_2 (obsd.)	\bar{V}_2 (calcd.)	\bar{V}_1 (calcd.)
	0.00000	0.00000	0.997074			58.72	18.0691
1	.10489	.10585	1.00028	10	58.71	58.87	18.0690
2	.20150	.20451	1.00322	20	58.77	59.01	18.0686
4	.39724	.40795	1.00914	50	58.89	59.29	18.0670
3	.68110	.71182	1.01753	-10	59.24	59.68	18.0629
5	1.00722	1.07436	1.02309	-120	59.57	60.12	18.0555
8	1.50251	1.65580	1.04129	-60	59.84	60.78	18.0389
7	2.48820	2.94138	1.06865	0	60.47	62.03	17.9862
6	3.53658	4.52903	1.09598	-170	61.31	63.27	17.9015
9	4.55853	6.37495	1.12121	-240	62.05	64.38	17.7907
10	5.35980	8.04559	1.14914	300	62.54	65.10	17.6855
Average				≈ 78			

TABLE VII
DENSITIES OF AQUEOUS SOLUTIONS OF LACTAMIDE AT 25° AND CORRESPONDING APPARENT AND PARTIAL MOLAL VOLUMES

Expt.	c	m	d	$\frac{\Delta d}{10^6}$ (in p. p. m.)	ΦV_2 (obsd.)	\bar{V}_2 (calcd.)	\bar{V}_1 (calcd.)
	0.00000	0.00000	0.997074			73.51	18.0691
3	.19782	.20133	1.00016	-40	73.69	73.51	18.0691
7	.30619	.31420	1.00179	-120	73.90	73.51	18.0691
1	.38548	.39787	1.00322	60	73.36	73.52	18.0691
8	.71928	.76174	1.00835	-80	73.62	73.53	18.0689
4	.97923	1.05833	1.01250	-30	73.55	73.54	18.0689
9	1.54079	1.74275	1.02140	20	73.52	73.55	18.0684
5	1.95456	2.28933	1.02791	10	73.53	73.57	18.0680
11	2.50551	3.08042	1.03669	40	73.53	73.58	18.0673
6	2.93797	3.75834	1.04348	130	73.51	73.59	18.0666
10	3.53892	4.79822	1.05285	60	73.55	73.61	18.0653
2	3.96812	5.61113	1.05970	190	73.53	73.62	18.0644
12	5.05345	8.07365	1.07616	-340	73.65	73.64	18.0613
Average				≈ 93			

TABLE VIII

EQUATIONS FOR THE DENSITIES AND APPARENT MOLAL VOLUMES OF *DL*- α -ALANINE, β -ALANINE, AND LACTAMIDE AND THE PARTIAL MOLAL VOLUMES OF SOLUTE AND SOLVENT AT 25°

DL- α -Alanine

$$\begin{aligned}d &= 0.997074 + 0.028663c - 5.73 \times 10^{-4}c^2 \\ \Phi V_2 &= 60.609 + 0.5731c \\ \bar{V}_2 &= 60.609 + 1.1462c - 0.03473c^2 \\ \bar{V}_1 &= 18.0691 - 0.01035c^2\end{aligned}$$

 β -Alanine

$$\begin{aligned}d &= 0.997074 + 0.030543c - 7.147 \times 10^{-4}c^2 \\ \Phi V_2 &= 58.723 + 0.7168c \\ \bar{V}_2 &= 58.723 + 1.4336c - 0.04209c^2 \\ \bar{V}_1 &= 18.0691 - 0.01340c^2\end{aligned}$$

Lactamide

$$\begin{aligned}d &= 0.997074 + 0.015802c - 1.684 \times 10^{-4}c^2 \\ \Phi V_2 &= 73.508 + 0.0169c \\ \bar{V}_2 &= 73.508 + 0.0338c - 0.00124c^2 \\ \bar{V}_1 &= 18.0691 - 0.000305c^2\end{aligned}$$

moment. The small change of the apparent molal volume with concentration, in the case of lactamide, shows the close approach of lactamide to an ideal solute (for which ΦV_2 would be constant).

When lactamide, with a molal volume of 71.3 ml., is dissolved to form an infinitely dilute solution, there is an *increase* in volume of 2.2 ml., which corresponds roughly to the usual expansion on melting a solid. However, when *DL*- α -alanine, with a molal volume of 62.5 ml., is dissolved in an infinitely dilute solution, there is a *decrease* in volume of 1.9 ml., and with β -alanine, the molal volume of which is 63.4 ml., there is an even greater decrease in volume of 4.7 ml. This shows that electrostriction in the liquid is even greater than the close packing in the solid.

The apparent molal volume of *DL*- α -alanine at infinite dilution is 12.90 ml. less than that of lactamide. This is very close to the difference of 12.96 ml. between the limiting values of the apparent molal volumes of glycolamide and glycine. The apparent molal volume of β -alanine at infinite dilution is 14.78 ml. less than that of lactamide, showing the increased electrostriction with increased charge separation. These figures give a reliable measure of the electrostriction due to the *zwitterion* in solution.

These differences are paralleled in the apparent molal heat capacities at infinite dilution. At 25°, that of α -alanine is 24.7 cal. per deg. per mole less than that of lactamide, and that of β -alanine is 40.1 cal. per deg. per mole less than that of lactamide. As in the case of glycine and glycolamide,

the electrostriction is accompanied by a corresponding decrease in heat capacity in solution.

It was pointed out,^{4a} in a discussion of the apparent molal volumes and heat capacities for glycine and glycolamide, that although we have as yet no theory which will quantitatively predict the behavior of aqueous solutions of dipolar solutes like the amino acids, Fuoss¹⁴ has attempted to describe the thermodynamic behavior of such solutions in terms of the mutual interaction of pairs of spherical solute molecules containing central point dipoles. The original theory makes use of a parameter

$$x = \frac{\mu^2}{a^3 D k T}$$

where μ is the dipole moment, a the molecular diameter, D the dielectric constant of the solvent, T the absolute temperature, and k the Boltzmann constant. This parameter has been modified, in accordance with the suggestion of Kirkwood,¹⁵ to take into account the discontinuity of the dielectric constant at the surface of the solute molecule. The new parameter y is

$$y = \left[\frac{3D}{2D + D_i} \right]^2 \frac{\mu^2}{a^3 D k T}$$

where D_i is the dielectric constant within the spherical cavity containing the dipole.

The senior author, in collaboration with Dr. W. L. Ford,¹⁶ has employed these ideas to calculate the contribution of the dipole-dipole interaction to the apparent molal volumes and heat capacities of dipolar solutes. For more details and the theoretical equations, the reader is referred to a forthcoming article by the present authors and Dr. Irving M. Klotz, to be published in *Chemical Reviews*. In addition to the use of a different parameter, our equation for the apparent molal heat capacity differs from that of Fuoss in considering the temperature coefficient of the dielectric constant of the medium. His treatment apparently considered the dielectric constant of the medium independent of temperature, and hence is not applicable to aqueous solutions. Fuoss did not treat the apparent molal volume. It will suffice to indicate here the theoretical results that apply to α - and β -alanine, assuming their molecules are spheres of radius 6.16 and 5.94 Å. (calculated from the molal volumes of the solid substances), containing point dipoles of moments

(14) Fuoss, *THIS JOURNAL*, **58**, 982 (1936).

(15) Kirkwood, *Chem. Rev.*, **19**, 275 (1936).

(16) Ford, Ph.D. Dissertation, Northwestern University, 1940.

15 and 18.9 Debye units. The theoretical limiting values at infinite dilution at 25° are

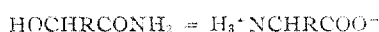
$$\begin{aligned}\frac{\partial \bar{C}_{p2}}{\partial m} &= 0.31 \quad (\alpha\text{-alanine}) \\ \frac{\partial \bar{C}_{p2}}{\partial m} &= 0.78 \quad (\beta\text{-alanine}) \\ \frac{\partial \bar{V}_2}{\partial c} &= 0.16 \quad (\alpha\text{-alanine}) \\ \frac{\partial \bar{V}_2}{\partial c} &= 0.54 \quad (\beta\text{-alanine})\end{aligned}\quad (12)$$

The closest approximation to the experimental values of the limiting slope for "pure" dipole-dipole interaction are obtained by subtracting the limiting slope of lactamide from those of the two amino acids. The results are

$$\begin{aligned}\frac{\partial \bar{C}_{p2}}{\partial m} (\text{exp.}) &= \left[\frac{\partial \bar{C}_{p2}}{\partial m} (\alpha\text{-alanine}) - \frac{\partial \bar{C}_{p2}}{\partial m} (\text{lactamide}) \right] = 4.83 \\ \frac{\partial \bar{C}_{p2}}{\partial m} (\text{exp.}) &= \left[\frac{\partial \bar{C}_{p2}}{\partial m} (\beta\text{-alanine}) - \frac{\partial \bar{C}_{p2}}{\partial m} (\text{lactamide}) \right] = 6.98 \\ \frac{\partial \bar{V}_2}{\partial c} (\text{exp.}) &= \left[\frac{\partial \bar{V}_2}{\partial c} (\alpha\text{-alanine}) - \frac{\partial \bar{V}_2}{\partial c} (\text{lactamide}) \right] = 1.11 \\ \frac{\partial \bar{V}_2}{\partial c} (\text{exp.}) &= \left[\frac{\partial \bar{V}_2}{\partial c} (\beta\text{-alanine}) - \frac{\partial \bar{V}_2}{\partial c} (\text{lactamide}) \right] = 1.39\end{aligned}\quad (13)$$

The agreement between theoretical and experimental values is somewhat better for the volumes than for the heat capacities. In both cases the agreement between theory and experiment is approximately of the same order for α -alanine and β -alanine as it was for glycine.¹⁵ The discrepancy between theory and experiment may not be significant, however, when one considers the very simple Fuoss model of a point dipole at the center of a sphere, and the sensitivity of the parameter μ^2/a^3 to the choice of values for μ and a .

To account for the magnitude of some of the thermodynamic properties of dipolar ions in an infinitely dilute aqueous solution, we have adopted an electrostatic approach employing the Kirkwood¹⁷ formula for the charging energy of a spherical ion of arbitrary charge distribution. With the aid of this general formula for the free energy, and the usual thermodynamic relationships,¹⁸ we have derived expressions for the changes in apparent molal heat capacity and volume in the reaction



Using the equation of Åkerlöf and Short¹⁹ to express the change of dielectric constant with temperature, the calculated changes in heat capacity are about 30% of those observed experimentally. The agreement is best for glycine, which approximates a sphere most closely, but even in this case

only 40% of the heat capacity can be accounted for by the theoretical model. It is important to note, however, that the calculated values are extremely sensitive to the form of the equation used for expressing the variation of the dielectric constant with temperature.

In the evaluation of the volume changes we have used the work of Kyropoulos,²⁰ which was carried out at 20°, and have assumed that the pressure coefficient of the dielectric constant of water would be the same at 25°. We also considered the value of $(\partial D/\partial P)_T$ determined by Redlich²¹ from the limiting slopes of the partial molal volumes of electrolytes in aqueous solutions, but this did not improve our calculated results. The agreement between the calculated and observed values for \bar{V}_2^0 is about the same as that for \bar{C}_{p2}^0 .

Acknowledgment.—It is a pleasure to acknowledge our indebtedness to the American Academy of Arts and Sciences for a Grant-in-Aid from their Permanent Science Fund which helped to make the experimental part of this work possible, and to Dr. Irving M. Klotz for his assistance in connection with the theoretical treatment.

Summary

The specific heats of aqueous solutions of lactamide, *dl*- α -alanine, and β -alanine have been measured at 5, 25 and 40°, over a range of concentration from 0.1 or 0.2 *M* to the nearly saturated solution. The apparent molal heat capacities of the solutes evidently are linear functions of the molality at low concentrations, although they may show curvature at higher concentrations. The slopes, at corresponding temperatures, increase markedly in the order: lactamide, *dl*- α -alanine, β -alanine. The value at infinite dilution is about 25 calories per degree per mole less for α -alanine than for lactamide, and about 40 units less for β -alanine than for lactamide.

The densities of aqueous solutions of the same solutes have been measured at 25° over the same concentration ranges. The apparent molal volume in each case is a linear function of the molality. The differences between the limiting values for α -alanine and lactamide, and β -alanine and lactamide, are 12.90 and 14.78 ml., respec-

¹⁹⁾ Kyropoulos, *Z. Physik*, **40**, 507 (1926).

²¹⁾ Redlich, paper before the Symposium on "The Thermodynamics of Electrolytic Dissociation," St. Louis Meeting of the American Chemical Society, April, 1941.

¹⁷⁾ Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934).

¹⁸⁾ Gucker, *Chem. Rev.*, **13**, 111 (1933).

¹⁹⁾ Åkerlöf and Short, *This Journal*, **58**, 1241 (1936).

tively, which may be taken as the values of the electrostriction of the solvent.

The limiting slopes of the partial molal heat capacities and volumes for α -alanine and β -alanine have been calculated from a modification of the Fuoss theory of dipolar solute interaction. Observed and calculated slopes agree within a factor of about 10 for the heat capacities and slightly better for the volumes.

The differences in the heat capacities and volumes at infinite dilution have been estimated from an electrostatic standpoint. The calculated values are approximately one-third of the experimental.

An article that will appear shortly in the *Chemical Reviews* will discuss the theoretical considerations in detail.

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Color and Constitution. V.¹ The Absorption of Unsymmetrical Cyanines. Resonance as a Basis for a Classification of Dyes

BY L. G. S. BROOKER, G. H. KEYES AND W. W. WILLIAMS

For a number of years it has been accepted as axiomatic that the absorption band of an unsymmetrical cyanine should be intermediate in position between those of the parent symmetrical dyes. Thus Mills and Odams² considered the structure of 2,4'-carbocyanine to be confirmed by the fact that it absorbed almost exactly midway between 2,2'- and 4,4'-carbocyanine.

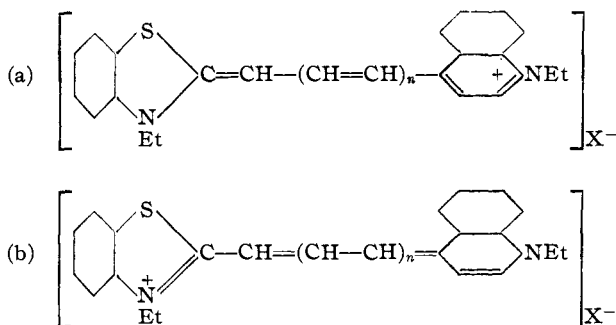
From the resonance standpoint, however, this relationship would not necessarily be expected. An unsymmetrical dye differs from a symmetrical dye in the important respect that the two extreme resonance configurations of the former are not identical. Thus, for example, 1',3-diethylthia-4'-cyanine iodide (I, $n = 0$), which has two different nuclei, is represented by the two distinct configurations: (a) in which the 4-quinoline

rings differ, (a) and (b) would not be expected to have the same energy, since that configuration should be the more stable in which the nitrogen of the more basic nucleus is quaternary. The degeneracy of the configurations should therefore be incomplete, a condition which is obviously impossible with a symmetrical dye.

It has been suggested that if it happens that the two nuclei of an unsymmetrical cyanine have the same basicity, so that the two extreme resonance configurations are of equal energy, then absorption should occur at a point midway between the absorptions of the parent symmetrical dyes. If, however, the nuclei are not equally basic, so that the configurations do not have the same energy, then absorption should occur at a shorter wave length than this intermediate position.¹

Since a rather wide variety of nuclei have been combined in unsymmetrical cyanines, it might have been expected that this latter situation would be commonly encountered, but, in actual fact, although many dozens of these dyes have been examined in recent years,³ agreement between the found and calculated values of λ_{\max} is reasonably good, and no consistent tendency for absorption to occur at significantly shorter wave length than the calculated, has been reported.

It would seem that in these unsymmetrical dyes the nuclei that were combined together were not sufficiently different in basicity for deviations to appear, the highly degenerate cyanines not being as sensitive to small changes in structure as



nitrogen is quaternary and (b) in which the benzothiazole nitrogen is quaternary. If now the basicities of these two rings are not identical, or, more precisely, if the relative stabilities of the N^{11} and N^{1V} forms of the benzothiazole and 4-quinoline

(1) Part IV, THIS JOURNAL, 63, 3214 (1941).

(2) Mills and Odams, *J. Chem. Soc.*, 125, 1913 (1924).

(3) (a) Beilenson, Fisher and Hamer, *Proc. Roy. Soc. (London)*, A168, 138 (1937); (b) Yoshimura and Sakurai, *Bull. Inst. Phys. and Chem. Res., Tokyo*, 16, 1270 (1937).