This estimate was made by using the temperature coefficient obtained by us at low concentrations.

The effect of temperature is very marked. However, the relative change with concentration in dilute solution is almost independent of temperature. For a concentration of 0.01 N the ratio D/D_0 is 0.9593, 0.9591, and 0.9589 at 20, 25 and 30°, respectively.

Summary

1. Determinations of the diffusion coefficient of potassium chloride in water at 20°, 25° and 30° have been obtained by a conductance method previously described by us.[19]

2. In the region of concentration from 0.001 to 0.01 N, excellent agreement with the theory of Onsager and Fuoss is obtained, and the Nernst limiting law for electrolytic diffusion is confirmed.

3. Comparison of our results with those obtained by the diaphragm cell method, by layer analysis and by the optical scale method indicates good agreement considering the wide variety of mechanisms and theories of these methods.

(19) Ref. 1.

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The Heats of Dilution of Aqueous Solutions of Four Amino Acids at 25°[1]

BY L. S. MASON, W. F. OFFUTT[2,3] AND A. L. ROBINSON

Previous communications from this Laboratory have reported on the heats of dilution of aqueous solutions of glycine,[4] α- and β-alanine,[5] and four aminobutyric acids.[6] Examination of the results for these seven amino acids indicated that the structure of the organic radical was more important than the location of the amino group in determining the thermochemical properties studied.[6] The same conclusion was reached when the differential entropies of dilution of these same aqueous solutions were calculated.[7] Study of the heats of dilution of aqueous solutions of amino acids was continued to obtain further evidence affecting this conclusion. This paper reports results for α-amino-*n*-valeric acid, valine, norleucine and ε-aminocaproic acid.

Experimental

Apparatus and Method.—Except for minor changes, the calorimeter is the same as that used in previous investigations.[6] The thermopile had been sealed into the Dewar vessel, which comprises the calorimeter vessel, with wax, thus dividing the vessel into two watertight compartments. The junctions of the thermopile had been separated from the solutions in the calorimeter by a plastic coating, so that dilutions in organic solvents might be made if desired, two copper vessels were constructed, one for each half of the calorimeter, which conformed to the inner surface of the Dewar vessel and whose flat surfaces fitted snugly against the junctions of the thermopile. The interiors of these vessels could not be satisfactorily gold plated; instead, a plastic coating was baked on. This coating provided an electrical resistance greater than 10 megohms. Electrical resistance of 1000 megohms between the thermopile junctions and the copper vessels was furnished by sheets of mica of 0.04 mm. thickness.

The two electrical heaters were made by winding no. 40 Advance wire spirally around a glass tube. The wire was soldered to platinum nibs which lead through the wall of the tube to heavy copper leads. Several coats of a silicone resin were baked on over the wire for insulation from the solutions in the calorimeter.

The volumes of the monel metal dilution pipets were 10.36 (left) and 10.32 (right) ml. To maintain a constant dilution ratio of one to 100 in the two halves of the calorimeter, the twin calorimeters held 1036 and 1032 ml. of water, respectively.

The amino acid solutions were prepared immediately before each day's series of measurements to minimize bacterial action. Following each day's measurements, the calorimeter was rinsed with distilled water. The calorimeter was disinfected periodically with 10% formaldehyde solution.

Solutions were made up by volume. Concentrations were converted to molalities using the density data of Dalton and Schmidt[8] for valine and the data of Daniel and Cohn[9] for ε-aminocaproic acid. The densities of α-amino-*n*-valeric acid and norleucine solutions were determined by standard methods using specific gravity bottles. The results may be expressed by the following equations for 25°

α-Amino-*n*-valeric acid (m <0.6)	$d = 0.9971 + 0.0240\,m$
Norleucine (m <0.05)	$d = 0.9971 + 0.0188\,m$

It has been suggested[10] that atmospheric carbon dioxide dissolved in the dilution water may affect the heats of dilution of amino acids at low concentrations by disturbing their dissociation equilibria. This effect was not observed in the previous studies[4,5,6] of this series. A further test was made by performing dilutions with norleucine solutions using water in equilibrium with atmospheric carbon dioxide and with free access of the atmosphere to the interior of the calorimeter. Results were compared with runs made with carbon dioxide-free water (specific conductance 0.4×10^{-6} ohm^{-1} cm.$^{-1}$) and with the calorimeter sealed from the atmosphere. The results agreed within the limits of the experimental error.

Dilutions were made to the limits of solubility of the

(1) This investigation was supported by the Buhl Foundation.

(2) The material of this paper is taken from the thesis submitted to the Graduate School, University of Pittsburgh, by W. F. Offutt, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1948.

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(4) W. E. Wallace, W. F. Offutt, and A. L. Robinson, THIS JOURNAL, **65**, 347 (1943).

(5) H. A. Benesi, L. S. Mason, and A. L. Robinson, *ibid.*, **68**, 1755 (1946).

(6) L. S. Mason and A. L. Robinson, *ibid.*, **69**, 889 (1947).

(7) A. L. Robinson, *J. Chem. Phys.*, **14**, 588 (1946).

(8) J. B. Dalton and C. L. A. Schmidt, *J. Biol. Chem.*, **103**, 549 (1933).

(9) J. Daniel and E. J. Cohn, THIS JOURNAL, **58**, 415 (1936).

(10) J. M. Sturtevant, *ibid.*, **62**, 3519 (1940).

TABLE I

INTERMEDIATE HEATS OF DILUTION, CALORIES

Moles/1000 g. of water 10^4m_1	10^4m_2	10^4m_3	Expts.	Expt. -10^3 $q_{1\to2}$	$10^3\delta$	Eq. -10^3 $q_{1\to2}$	10^3 $\Delta q_{1\to2}$	Expt. -10^3 $q_{3\to2}$	$10^3\delta$	Eq. -10^3 $q_{3\to2}$	10^3 $\Delta q_{3\to2}$	Cal./mole of acid $-\Delta H_{1\to2}$	$-\Delta H_{3\to2}$
α-Amino-*n*-valeric Acid													
						Eq. 3				Eq. 2			
6932	65.23	129.9	3	1021	4	1011	−10	14	12	12	− 2	150.52 ± 0.38	1.05 ± 0.82
3361	32.61	64.91	4	242.0	1.4	245.1	+ 3.1	+ 0.9	3.2	3.1	+ 2.2	71.68 ± .29	0.13 ± .39
1655	16.30	32.45	6	56.7	3.5	60.3	+ 3.6	− 1.1	3.1	0.8	+ 1.9	33.56 ± 1.74	− .33 ± .76
821.9	8.150	16.22	4	16.7	1.4	15.0	− 1.7	+ 0.1	2.1	0.2	+ 0.1	19.72 ± 1.26	+ .03 ± 1.01
409.0	4.074	8.109	4	4.6	0.7	3.7	− 0.9	− 0.2	0.6	0.1	− 0.3	10.73 ± 1.42	− .26 ± 0.55
Valine													
						Eq. 8				Eq. 7			
6388	60.41	120.3	2	772.2	3.0	748.6	−24.6	− 4.1	10.3	−17.8	−13.7	123.46 ± 0.40	−0.33 ± 0.45
3104	30.20	60.11	2	190.4	1.9	181.8	− 9.2	+ 2.7	0.1	− 4.4	− 7.1	60.90 ± .43	0.43 ± .01
1530	15.10	30.05	2	47.6	1.4	44.6	− 3.0	− 0.7	0.2	− 1.1	− 0.4	30.42 ± .59	−2.26 ± 1.52
759.9	7.548	15.02	2	11.2	0.3	11.1	+ 0.1	− 1.1	0.6	− 0.3	+ 0.7	14.35 ± 1.78	−0.71 ± 0.19
Norleucine													
						Eq. 13				Eq. 12			
860.7	8.526	16.97	8	24.8	1.4	23.0	− 1.8	− 1.7	1.8	− 3.0	− 1.2	28.08 ± 0.04	−1.23 ± 0.42
644.0	6.394	12.74	10	14.2	1.6	12.9	− 1.3	− 1.1	0.9	− 1.8	− 0.3	22.76 ± 1.21	−0.80 ± .60
428.3	4.263	8.486	7	4.8	0.4	5.7	+ 0.9	− 1.1	0.4	− 0.8	− 0.3	10.98 ± 0.75	−0.94 ± .91
ε-Aminocaproic Acid													
						Eq. 18				Eq. 17			
4143	39.74	79.11	4	604.2	8.5	599.3	− 4.9	− 7.3	7.2	− 9.0	− 1.7	147.27 ± 1.84	−1.11 ± 0.38
3079	29.85	59.42	2	344.6	5.2	339.3	− 5.3	− 7.9	3.6	−12.8	− 4.9	111.82 ± 1.15	−1.28 ± .39
2038	19.96	39.74	4	136.4	14.7	143.0	+ 6.6	− 6.0	3.6	− 7.2	− 1.2	73.26 ± 0.34	−2.11 ± .10
1523	15.00	29.85	4	74.3	5.1	78.3	+ 4.0	−19.3	2.6	− 4.0	+15.3	47.95 ± 2.73	−6.24 ± .63
1013	10.04	19.96	4	30.1	0.6	23.3	− 6.8	− 7.6	3.2	− 1.8	+ 5.8	29.04 ± 0.48	−0.36 ± .12
506.6	5.040	10.04	2	6.7	0.2	6.9	+ 0.2	− 6.3	..	− 0.4	+ 5.9	12.96 ± 0.28	−0.61 ± .09

TABLE II

DERIVED VALUES FOR S, ϕL_2, $\bar{L}_1$, AND $\bar{L}_2$

	α-Amino-*n*-valeric acid[a]	Valine	Norleucine	ε-Aminocaproic acid
S	(1) 280	(6) −476	(11) −2030	(16) $-514 - 293 \times 10^3m + 54.2 \times 10^6m^2$
ϕL_2 (m <0.015)	(2) 280 m	(7) −476 m	(12) −2030 m	(17) $-514m - 147 \times 10^3m^2 + 18.1 \times 10^6m^3$
ϕL_2	(3) 218 m	(8) 189 m	(13) 306 m	(18) $-3.23 + 3.23\ e^{-474m} + 294m + 437m^2 - 689m^3$
$\bar{L}_1$	(4) $-3.93\ m^2$	(9) $-3.40\ m^2$	(14) $-5.51\ m^2$	(19) $(27.58e^{-474m} - 5.30)m^2 - 15.75m^3 + 37.24m^4$
$\bar{L}_2$	(5) 436 m	(10) 378 m	(15) 612 m	(20) $-3.23 + 3.23\ (1 - 474m)e^{-474m} + 588m + 1311m^2 - 2756m^3$

[a] Numbers in parentheses identify the equations.

amino acids except for ε-aminocaproic acid. In this case the highest concentration diluted was about 0.4 m since the heat effects produced were near the upper limit of the useful capacity of the calorimeter.

Materials.—Distilled water from the stock supply was distilled again from a Yoe still and stored in Pyrex flasks. The specific conductance of this water in equilibrium with the carbon dioxide of the atmosphere was about 10^{-6} ohm^{-1} cm.$^{-1}$.

α-Amino-*n*-valeric acid and valine were purchased from the Eastman Kodak Company. They were recrystallized once from water and three times from alcohol-water mixtures. The most soluble and least soluble fractions from water were discarded, as were the most soluble fractions from the alcohol-water solutions.

ε-Aminocaproic acid was obtained from Dr. H. R. Snyder of the University of Illinois. It was dissolved in water and sufficient alcohol was added to form a 90% alcoholic solution from which most of the amino acid precipitated. Three such precipitations were carried out.

Norleucine of Analytical Purity was supplied by Amino Acid Manufacturers of the University of California. Specified impurities were so low that this acid was not purified further.

Ash content determinations and elementary analysis for nitrogen gave the results:

	Ash, %	Nitrogen, % Found	Theoretical
α-Amino-*n*-valeric acid	0.01	12.13	11.96
Valine	.02	12.27	11.96
Norleucine	.04	10.88	10.68
ε-Aminocaproic acid	.21	10.73	10.68

The analyses for nitrogen agree with the theoretical values within the limits of error of the determination.

The purified acids were dried to constant weight at 80° in a vacuum oven and stored in a desiccator until used.

Experimental Results and Treatment of Data

Relative Apparent Molal Heat Contents.—The experimentally determined intermediate heats of dilution are given in Table I. The average values of the measured heat effects for the long chord dilutions (m_1 to m_2) are listed in column 5, the number of experiments in column 4, the av-

erage deviation from the mean value in column 6, and the molal heats of dilution with their probable errors in column 13. The corresponding quantities for the short chord dilutions (m_3 to m_2) are listed in columns 9, 4, 10, and 14. Calculated heat effects are given in columns 7 and 11; the equations referred to are listed in Table II. The differences between measured and calculated heat effects are shown in columns 8 and 12.

Established methods[11,12,13] were used for the treatment of the heats of dilution data.

Figures 1, 2, 3 and 4 are plots of the short chords, $\overline{P} = \Delta H_{3\to 2}/\Delta m_{3\to 2}$, derived from the heats of dilution in the very dilute region. Each chord represents the average value of the derivative of the apparent molal heat content with respect to the molality in the range covered by the length of the chord. The intercept of a curve drawn through the chords gives the limiting slope of the apparent molal heat content and the area under a curve to a concentration m gives the relative apparent molal heat content (ϕL_2), or the negative of the integral heat of dilution at that concentration.

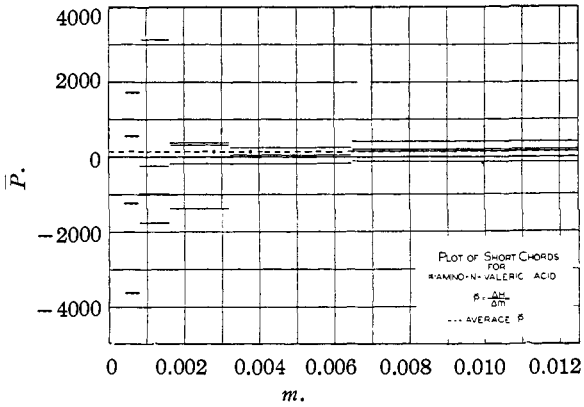

Fig. 1.—Plot of short chords for α-amino-*n*-valeric acid: $\overline{P} = \Delta H/\Delta m$; – – –, average $\overline{P}$.

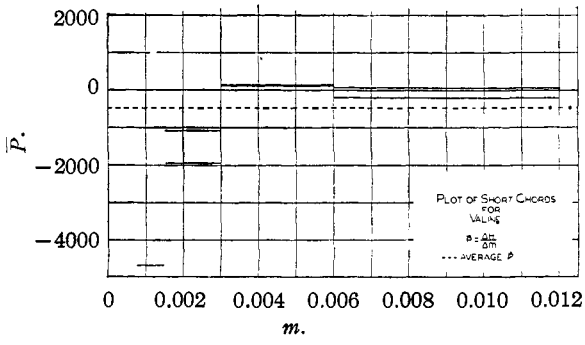

Fig. 2.—Plot of short chords for valine: $\overline{P} = \Delta H/\Delta m$; – – –, average $\overline{P}$.

(11) T. F. Young, *et al.*, THIS JOURNAL, **54**, 3030 (1932); **58**, 187 (1936); **60**, 2379 (1938).

(12) A. L. Robinson and W. E. Wallace, *ibid.*, **63**, 1582 (1941).

(13) A. L. Robinson and W. E. Wallace, *Chem. Revs.*, **30**, 195 (1942).

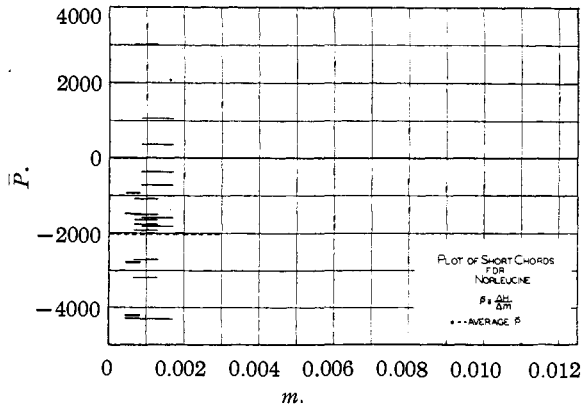

Fig. 3.—Plot of short chords for norleucine: $\overline{P} = \Delta H/\Delta m$; – – –, average $\overline{P}$.

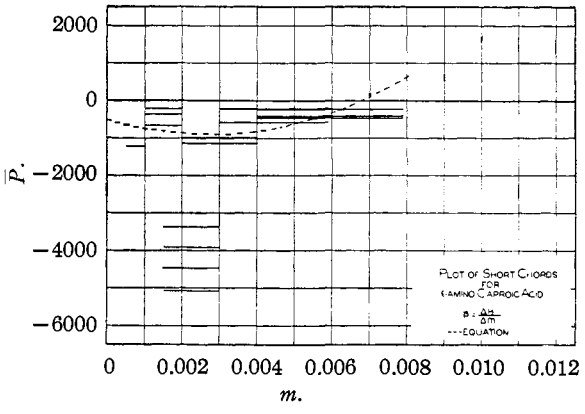

Fig. 4.—Plot of short chords for ε-aminocaproic acid: $\overline{P} = \Delta H/\Delta m$; – – –, equation.

For α-amino-*n*-valeric acid, valine, and norleucine, an inspection of the plots of $\overline{P}$ vs. m, shown in Figs. 1, 2, and 3, respectively, indicated that an analytical derivation for the slope, $S = \partial(\phi L_2)/\partial m$, was unwarranted. Instead, average $\overline{P}$ values for the entire concentration range of the short chords were obtained by averaging the mean values of the chords for each concentration interval, weighting each mean value according to its probable error. The dotted lines represent these average $\overline{P}$ values.

For ε-aminocaproic acid, Fig. 4, there seemed to be a trend in the $\overline{P}$ values sufficiently pronounced to justify an analytical treatment. A three-constant least-squares equation was derived which is shown in the figure by a dotted line.

Equations for the slopes for the four acids are given in Table II (eq. 1, 6, 11, and 16). Integration of these equations gives expressions for $\phi L_2 (m < 0.015)$, equations 2, 7, 12, and 17 of Table II.

ϕL_2 values calculated from equations 2, 7, 12, and 17, for m_2 were combined with the experimental $\Delta H_{1\to 2}$'s for the long chord dilutions to give ϕL_2 values for the concentrations m_1. Least

TABLE III

RELATIVE PARTIAL MOLAL HEAT CONTENTS

	α-Amino-n-valeric acid			Valine			Norleucine			ε-Aminocaproic acid		
m	ϕL_2, cal./mole acid	$-\bar{L}_1$, cal./mole water	$\bar{L}_2$, cal./mole acid	ϕL_2, cal./mole acid	$-\bar{L}_1$, cal./mole water	$\bar{L}_2$, cal./mole acid	ϕL_2, cal./mole acid	$-\bar{L}_1$, cal./mole water	$\bar{L}_2$, cal./mole acid	ϕL_2, cal./mole acid	$-\bar{L}_1$, cal./mole water	$\bar{L}_2$, cal./mole acid
0.001	0.218	3.93×10^{-6}	0.436	0.189	3.40×10^{-6}	0.378	0.306	5.51×10^{-6}	0.612	−0.93	-12×10^{-6}	−1.58
.005	1.09	98.3×10^{-6}	2.18	0.945	85.0×10^{-6}	1.89	1.53	138×10^{-6}	3.06	−1.45	-68×10^{-6}	−0.668
.01	2.18	3.93×10^{-4}	4.36	1.89	3.40×10^{-4}	3.78	3.06	5.51×10^{-4}	6.12	−0.22	$+5.22 \times 10^{-4}$	2.67
.05	10.9	98.3×10^{-4}	21.8	9.45	85.0×10^{-4}	18.9	15.3	138×10^{-4}	30.6	12.5	150×10^{-4}	32.3
.1	21.8	3.93×10^{-2}	43.6	18.9	3.40×10^{-2}	37.8				29.9	6.50×10^{-2}	69.2
.2	43.6	0.157	87.2	37.8	0.136	75.6				67.5	0.278	148
.3	65.4	.354	131	56.7	.306	113				106	.600	220
.4	87.4	.629	174	75.6	.544	151				140	.903	269
.5	109	.983	218	94.5	.850	189						
.6	138	1.415	262	113	1.22	227						

squares equations for ϕL_2 for the entire concentration range studied were then derived, the data being weighted according to the reciprocal of the squares of the probable errors. These are equations 3, 8, 13 and 18 of Table II. For α-amino-*n*-valeric acid, valine and norleucine, linear equations adequately represent the data, but for ε-aminocaproic acid a cubic equation seemed necessary with an added exponential term to show the reversal of slope of ϕL_2 at the lowest concentrations. Although the $\bar{P}$ *vs.* *m* plots indicate a reversal of slope for valine and norleucine at their lowest concentrations, the data in the most dilute region were not considered sufficiently precise to justify showing this reversal in the ϕL_2 equations which cover the entire concentration range of this study.

Plots of equations 3, 8, 13 and 18 and the experimental points from which they were derived are shown in Fig. 5. ϕL_2 values from these equations at rounded concentrations are listed in Table III. *q*-Values for the long chord dilutions, calculated from equations 3, 8, 13 and 18, are listed in column 7 of Table I. The differences between measured and calculated values are given in column 8 of Table I. *q*-Values for the short chord dilutions, calculated from equations 2, 7, 12 and 17, and the differences between measured and calculated values are given in columns 11 and 12 of Table I.

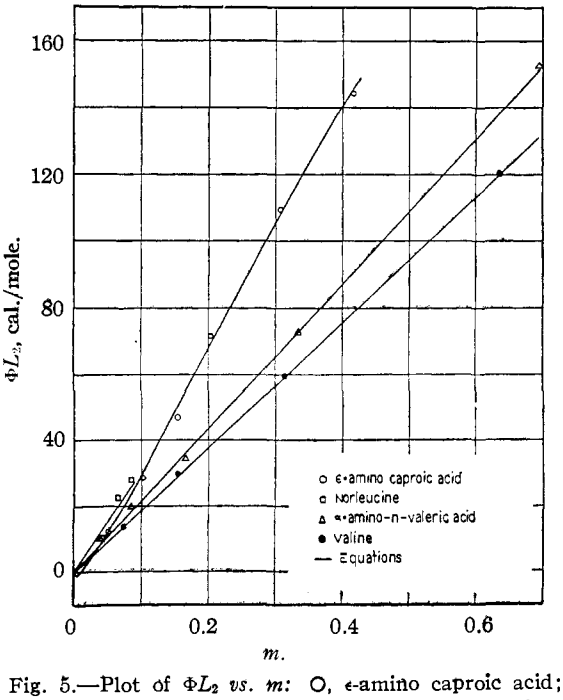

Fig. 5.—Plot of ΦL_2 *vs.* *m*: O, ε-amino caproic acid; □, norleucine; △, α-amino-*n*-valeric acid; ●, valine; —, equations.

Valine is the only acid studied in this investigation for which heats of dilution have been measured previously. Values calculated from equation 8 are compared with the data of Zittle and Schmidt:[14]

m	ϕL_2 cal. mole^{-1} Zittle and Schmidt	This work
0.1	15	19
.2	60	38
.5	125	96
.63	150 ± 25	119

The probable errors of the ϕL_2 values of this study are less than 2 calories per mole. The apparatus used by Zittle and Schmidt gave values with probable errors of 25 calories per mole.

Relative Partial Molal Heat Contents.—Equations for the relative partial molal heat contents of solvent ($\bar{L}_1$) and solute ($\bar{L}_2$) for each of the four amino acids are listed in Table II. These equations were derived from the equations for ϕL_2 by the procedure due to Rossini.[15]

Relative Partial Molal Entropy of Water.—($\bar{S}_1 - \bar{S}_1^0$) values (differential entropies of dilution) for three of these systems were calculated by the procedure used[7] for glycine, the alanines, and four aminobutyric acids. The activity values for water used in the calculations were taken from the vapor pressure studies of Smith and Smith.[16] No activity measurements for norleucine solutions are available. The ($\bar{S}_1 - \bar{S}_1^0$) values calculated for α-amino-*n*-valeric acid, valine, and ε-aminocap-

(14) C. A. Zittle and C. L. A. Schmidt, *J. Biol. Chem.*, **108**, 161 (1935).

(15) F. D. Rossini, *J. Res. Bur. Stand.*, **4**, 313 (1930).

(16) E. R. B. Smith and P. K. Smith, *J. Biol. Chem.*, **117**, 209 (1937); **132**, 47 (1940).

roic acid are listed in Table IV. $(\bar{S}_1 - \bar{S}_1^0)$ values for ten amino acids are plotted in Fig. 7. These values in all cases are the non-ideal parts of the differential entropies of dilution.

TABLE IV

DIFFERENTIAL ENTROPY OF DILUTION AT 25°

	$-(\bar{S}_1 - \bar{S}_1^0)$, cal. deg.$^{-1}$ mole^{-1}		
m	α-Amino-n-valeric acid	Valine	ε-Amino-caproic acid
0.1	0.00011	0.00009	0.00019
.2	.00044	.00034	.00080
.3	.00099	.00077	.00173
.4	.00174	.00135	.00249
.5	.00274	.00212	
.6	.00393	.00304	

Discussion of Results

Plots of ϕL_2 *vs.* m for the eleven amino acids studied in this laboratory are shown in Fig. 6. To a first approximation the variation of ϕL_2 is linear in m in all cases, neglecting minor uncertain features of several of the plots at very low concentrations. To a grosser first approximation the ϕL_2 values increase regularly with the number of carbon atoms in the aliphatic radical. This observation has been made before.[6,7] Excluding glycine, the ϕL_2 values for the ten amino acids with n = 2, 3, 4, and 5 carbon atoms in the aliphatic radical are coarsely represented by $\phi L_2 \cong (45 + (n - 2)85)m$. The data for all acids studied are much better than this coarse approximation, but it serves to emphasize the relative unimportance of the location of the NH_3^+ group in the molecule for determining the thermochemical properties studied in these investigations. In contrast, the dielectric increments for these same solutions[17] show a strong dependence on the location of the NH_3^+ groups.

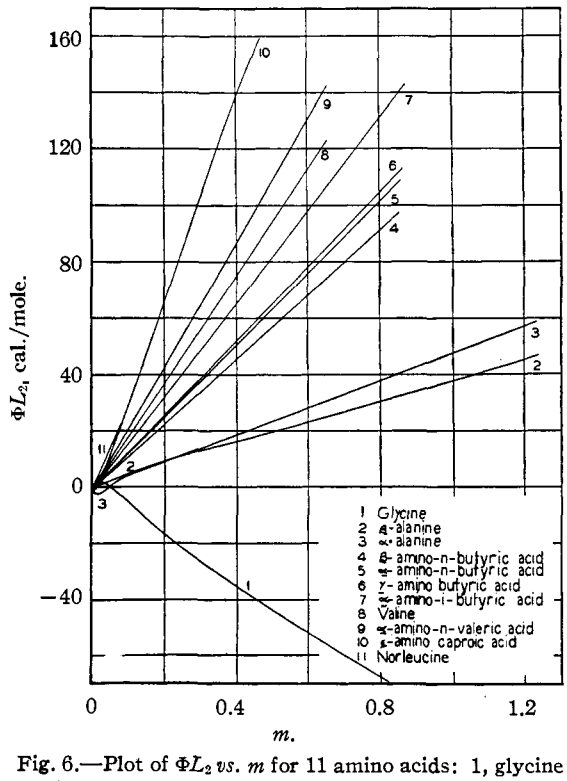

Fig. 6.—Plot of ΦL_2 *vs.* m for 11 amino acids: 1, glycine; 2, β-alanine; 3, α-alanine; 4, β-amino-n-butyric acid; 5, α-amino-n-butyric acid; 6, γ-aminobutyric acid; 7, α-amino-i-butyric acid; 8, valine; 9, α-amino-n-valeric acid; 10, ε-amino caproic acid; 11, norleucine.

A possible explanation for the rough regularity of ϕL_2 with n for these solutions lies in the configurations of the amino acid molecules in solution. If this is a coiled configuration, with close approach of the NH_3^+ and COO^- groups, the dipole moments of all these amino acids would be approximately equal. Changing dipole–dipole interactions with dilution would make a fairly constant contribution to ϕL_2 (the ϕL_2 of glycine), and the varying interactions of the hydrophobic aliphatic radicals with water would be responsible for the dependence of ϕL_2 on n. A coiled configuration for an amino acid molecule in solution seems plausible because of electrostatic interaction between NH_3^+ and COO^-. Differences among isomers could be attributed to slight differences of dipole moments and to differences in water-radical interactions due to radical configurations imposed by the electrostatic interaction.

The differential entropies of dilution plotted in Figure 7 likewise show a strong dependence on n, regardless of the location of the NH_3^+ group, because of the minor importance of the free energy term in the expression[7]

$$\bar{S}_1 - \bar{S}_1^0 = (\bar{L}_1 - RT \ln (a_1/N_1))/T$$

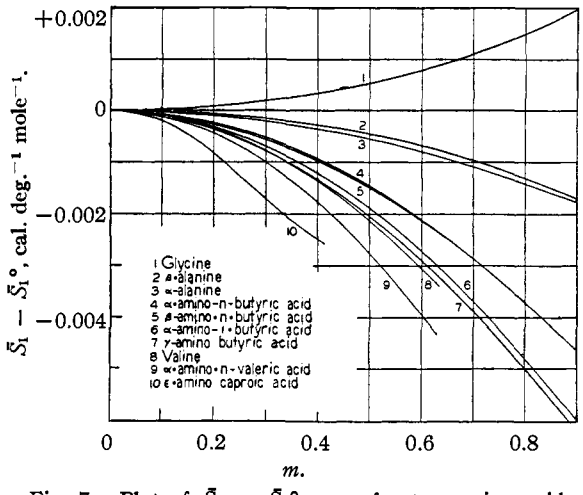

Fig. 7.—Plot of $\bar{S}_1 - \bar{S}_1^0$ *vs.* m for ten amino acids: 1, glycine; 2, β-alanine; 3, α-alanine; 4, α-amino-n-butyric acid; 5, β-amino-n-butyric acid; 6, α-amino-i-butyric acid; 7, γ-aminobutyric acid; 8, valine; 9, α-amino-n-valeric acid; 10, ε-aminocaproic acid.

(17) E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids, and Peptides," Reinhold Publishing Corporation, New York, N. Y., 1943, p. 146.

from which they were calculated. For the ten amino acids the relation $(\bar{S}_1 - \bar{S}_1^0) = km^2$ holds fairly well; the dependence on m^2 is a further reflection of the relative importance of the heat content term in the equation for $(\bar{S}_1 - \bar{S}_1^0)$. The k values are listed.

	k
Glycine	0.0023
α-Alanine	−.0023
β-Alanine	−.0020
α-Amino-*n*-butyric	−.0058
α-Amino-*i*-butyric	−.0076
β-Amino-*n*-butyric	−.0056
γ-Aminobutyric	−.0076
α-Amino-*n*-valeric	−.0109
Valine	−.0084
ε-Aminocaproic	−.0185

These negative $(\bar{S}_1 - \bar{S}_1^0)$ values (for all cases except glycine) have been interpreted[7] as structure strengthening effects on the water, the effect increasing with the size of the hydrocarbon residue.

Regardless of the value of these suggestions, it seems clear that purely electrostatic interactions, calculated[18,19,20] for various simplified models, do not suffice to explain the thermochemical behavior of these solutions. The aliphatic radicals seem responsible for the large differences of properties measured.

Summary

Heats of dilution of aqueous solutions of α-amino-*n*-butyric acid, valine, norleucine and ε-aminocaproic acid at 25° have been measured to below 0.001 *m*. From these measurements relative apparent molal heat contents, relative partial molal heat contents, and differential entropies of dilution have been calculated.

Results for eleven amino acids are compared and discussed.

(18) G. Scatchard and J. G. Kirkwood, *Physik. Z.*, **33**, 297 (1932).

(19) J. G. Kirkwood, *Chem. Revs.*, **19**, 275 (1936).

(20) R. M. Fuoss, THIS JOURNAL, **56**, 1027 (1934); **58**, 982 (1936).

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The Liquidus Curve for Aluminum in Mercury

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The liquidus curve for the aluminum–mercury system is well established above 400° by the concordant results of two investigations.[1,2] Data which complete this curve were obtained in 1934 as part of an investigation into the chemical problems of the mercury boiler and are given below.

Experimental

The "solubility" of commercial (99+%) aluminum in pure mercury was measured by rotating an aluminum-glass stirrer (see Fig. 1) in the solubility vessel, which was inside a cylindrical furnace whose temperature was taken as the temperature of the experiment. Because aluminum amalgam is very easily oxidized, the experiments were carried out in a hydrogen atmosphere. (The hydrogen, passed over copper at 400° and then through a liquid air trap, was pure enough not to cause appreciable oxidation of the amalgam. Since the analytical method measured dissolved metal only, a slight oxidation would not have vitiated the results.) The stirrer fitted into a metal chuck and was driven at approximately 300 r. p. m. with an electric motor. From time to time, samples of amalgam were withdrawn by means of previously evacuated sampling tubes, whose lower tips could easily be broken by forcing them against the bottom of the solubility vessel. The mercury withdrawn was usually replaced.

These samples were immediately analyzed by breaking the bulbs beneath approximately 2 *N* hydrochloric acid in the reaction vessel (Fig. 1) and measuring the evolved hydrogen in a gas buret containing mercury. The vessel was flushed out with hydrogen, stoppered tightly, and connected to the gas buret before each bulb was broken. Gentle warming ensured complete liberation of hydrogen. When the analytical system had returned to room temperature, the volume of hydrogen (assumed to be saturated with water vapor) was read on the buret. The volume of mercury was measured in the graduated side tube attached to the reaction vessel. With room temperature and pressure known, the aluminum content of the sample of amalgam could then be calculated.

As in all investigations of the interaction of mercury with metals, wetting—which does not occur until the natural oxide (or oxygen) film on the metal has been penetrated or removed—had first to be established. In this investigation, wetting was accomplished by simply heating the stationary stirrer in the assembled apparatus in the presence of hydrogen, the rod having been previously sandpapered and rubbed with a clean towel. Usually the wetting was uniform; for example, when such a rod was immersed in mercury and rapidly heated to 360°, wetting began within ten minutes and was complete on the immersed portion of the rod in approximately ten minutes more. Wetting above the liquid line did not occur, which shows that mercury vapor is not so effective in penetrating the natural oxide film. Occasionally, wetting occurred preferentially on the immersed area; aluminum would then disappear most rapidly from the wetted areas, where the rod would be eaten away. The experiments were scheduled so that the amount of aluminum passing into the mercury from the stationary rod did not exceed the solubility at the temperature of the first experiment after a new rod was wetted. Since the hydrogen atmosphere was usually maintained even between experiments, it was possible to use a wetted rod more than once.

The time required to saturate the relatively small volume (*ca.* 35 cc.) of mercury used in the experiments could not be readily determined. With an unwetted rod, this time would depend largely upon the rate at which the mercury penetrated the natural oxide (or oxygen) film, and this unreproducible rate increases markedly with the temperature. For a wetted rod, the usual case, detailed experimental data indicated that the time in question was probably less than an hour. When only one value of the

(1) (a) Smits and de Gruijter, *Proc. Kon. Akad. Wetensch Amsterdam*, **23**, 966 (1921); (b) Smits, *Z. Elektrochem.*, **30**, 423 (1924).

(2) Klemm and Weiss, *Z. anorg. allgem. Chem.*, **245**, 285 (1940).