ments. In every case the order of appearance of the minima was the same in every compound of the same element. The results are shown in Table I.

The most abundant isotope of sodium must have an atomic mass of 23 as this is the only one detected by Aston[2] and Bainbridge.[2] Since the lightest isotope corresponds to the greatest scale reading,[5] the lightest isotope is the second in abundance and the heaviest the least abundant. Therefore, the atomic weight of sodium would be less than 23. This agrees with the chemically determined value of 22.997. The differences between the circle readings of the sodium minima are abnormally large, which probably indicates that the two least abundant sodium isotopes are present in very minute quantities.

The most abundant cesium isotope must have an atomic mass of 133 as this is the only one previously detected.[2] The isotopes which are second, third, and sixth in order of abundance are lighter than Cs^{133}, whereas the isotopes that are fourth and fifth in order of abundance are heavier than Cs^{133}. Therefore, cesium should have an atomic weight less than 133, which is consistent with the older chemically determined value of 132.81 or with the recent value of 132.91 obtained by Baxter and Thomas[6] or with Aston's value of 132.917.[7]

Summary

The magneto-optic method shows that sodium has three isotopes, one heavier and one lighter than 23, and that cesium has six isotopes, three lighter and two heavier than 133.

(5) Bishop, Lawrenz and Dollins, *Phys. Rev.*, [2] **43**, 43 (1933).

(6) Baxter and Thomas, THIS JOURNAL, **55**, 858–859 (1933).

(7) Aston, *Proc. Roy. Soc.* (London), **134**, 517 (1932).

AUBURN, ALABAMA

RECEIVED MAY 29, 1933
PUBLISHED NOVEMBER 7, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, COLLEGE OF PHYSICIANS AND SURGEONS, COLUMBIA UNIVERSITY]

Solubility of Thallous Iodate and Thallous Chloride in the Presence of Amino Acids[1]

BY CRAWFORD F. FAILEY

The view that aliphatic amino acids exist in aqueous solution as molecules each of which bears both a positive and a negative charge has met with increasing acceptance. One question which arises in connection with this theory of ampholytes concerns their effect on the activity coefficients of electrolytes; does $\log \gamma_{\pm}$ of a salt vary with the square root of concentration, as if amino acids contributed to the ionic strength, or is their known influence on the dielectric constant of the medium sufficient to account for any changes observed?

---

[1] This work was aided by a grant from The Chemical Foundation.

La Mer and Goldman[2] have measured the solubility of thallous iodate in ethyl alcohol–water mixtures, and found that the reasonable value, r = 0.78 Å., for the mean ionic radius satisfies the equation

$$\log_{10} S_1/S_2 = (0.4343/2r)\ \epsilon^2/kT\ \ (1/D_2 - 1/D_1) \qquad (1)$$

where S_1 and S_2 are the solubilities in media of dielectric constant D_1 and D_2, respectively. No measurements of the dielectric constant in dilute alcohol were available to them, but data recently published by Wyman[3] indicate an apparent variation in r of only 30% over the entire solubility range.

Experimental

The preparation and method of analysis of thallous iodate were those of La Mer and Goldman.[4] The thallous chloride used was a C. P. preparation twice recrystallized, and its solubility was determined by gravimetric chloride analyses. Dimethylglycine was prepared by hydrolyzing its ethyl ester (b. p. 148–149°) with sulfuric acid and removing the acid with baryta. β-Alanine was prepared from succinimide by the process of Holm.[5] The remaining substances, recrystallized from commercial material, were all salt free and had the following nitrogen content: glycylglycine 20.90%, glycine 18.70%, α-alanine 15.59%, sarcosine 15.57%, α-

TABLE I

SOLUBILITY OF $TlIO_3$ IN WATER = S_0 = 1843 × 10^{-6} AT 25°

Solvent, N =		Soly. × 10^6	Solvent, N =		Soly. × 10^6
Glycylglycine	0.20	2282	α-Amino-*n*-butyric acid	0.10	1906
				.20	1971
Glycine	0.025	1875	Dimethylglycine	0.025	1859
	.05	1907		.05	1873
	.10	1971		.10	1901
	.15	2033		.20	1957
	.20	2098			
α-Alanine	.025	1872	α-Amino-isobutyric acid	.05	1874
	.05	1907		.10	1901
	.10	1963		.15	1934
	.20	2084		.20	1956
β-Alanine	.025	1863	α-Amino-*n*-valeric acid	.10	1895
	.05	1884		.20	1939
	.10	1919			
	.15	1964	Urea	.025	1845
	.20	2001		.05	1851
Sarcosine	.05	1880		.10	1861
	.10	1917		.15	1876
	.15	1954		.20	1891
	.20	1993	Diketopiperazine	.10	1844

---

(2) V. K. La Mer and F. H. Goldman, THIS JOURNAL, **53**, 473 (1931).

(3) Wyman, *ibid.*, **53**, 3292 (1931).

(4) V. K. La Mer and F. H. Goldman, *ibid.*, **51**, 2632 (1929).

(5) F. H. Holm, *Arch. Pharm.*, **242**, 590 (1904).

amino-*n*-butyric acid 13.72%, α-aminoisobutyric acid 13.56%, α-amino-*n*-valeric acid 11.84%, urea 46.64%, diketopiperazine 24.57%. Samples were rotated overnight in a water thermostat at 25.00 ± 0.01°, it having been shown that the same solubility was observed on approaching equilibrium from a higher temperature. Thallous iodate solubilities are the mean of duplicate analyses, the average difference between duplicates being 0.16%. In a series of twelve independent determinations of the water solubility the greatest difference between any two measurements was 0.3%. All concentrations are expressed as moles per liter.

Discussion

The results with thallous iodate are given in Table I. They are plotted in Fig. 1 with log S/S_0 as ordinate and amino acid concentration as abscissa, S_0 being the solubility in water.

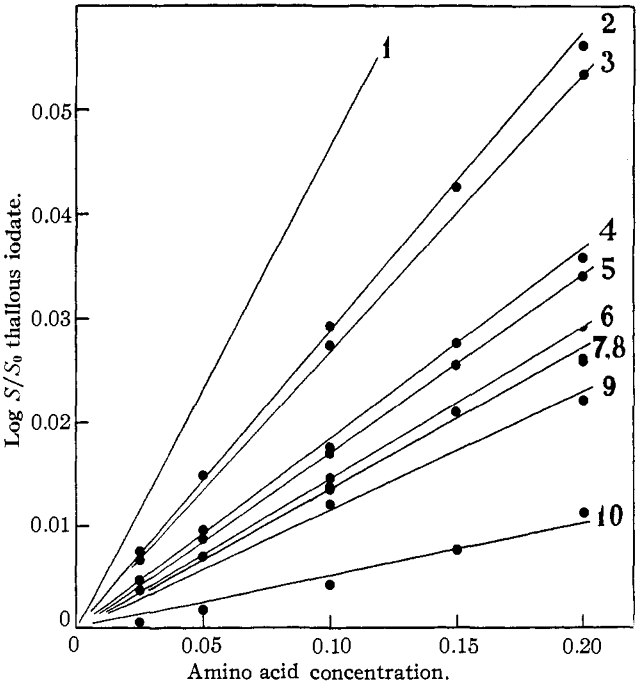

Fig. 1.—1, Glycylglycine; 2, glycine; 3, β-alanine; 4, α-alanine; 5, sarcosine; 6, α-amino-*n*-butyric acid; 7, dimethylglycine; 8, α-aminoisobutyric acid; 9, α-amino-*n*-valeric acid; 10. urea.

It may be seen that log S/S_0 for thallous iodate is approximately a linear function of amino acid concentration. From the dielectric constant measurements of Wyman and McMeekin[6] one may calculate the following values for r in equation 1: in the presence of glycine 1.49 Å., β-alanine

---

(6) J. Wyman, Jr., and T. L. McMeekin, This Journal, 55, 908 (1933).

2.36 Å., α-alanine 2.43 Å., glycylglycine 2.56 Å., α-amino-*n*-butyric acid 2.98 Å., and α-amino-*n*-valeric acid 3.83 Å. Although these radii are of the right order of magnitude, their differences indicate that the simple theory is inadequate. For example, all four normal α-amino acids have nearly the same effect on the dielectric constant of water and should, mole for mole, change the solubility of a salt equally. Diketopiperazine, which according to Devoto[7] decreases slightly the dielectric constant of water, is found to be without solvent action. Since log solubility is a linear function of amino acid concentration and not of its square root, the interaction is of a different character from that between strong electrolytes.

Glycine and its three N-methyl derivatives form an interesting series, the solvent action decreasing with increasing molecular weight. Again it may be observed that the isomers alanine and sarcosine have almost the same effect, likewise dimethylglycine, α-amino-isobutyric acid and α-amino-*n*-butyric acid. The separation of the positive and negative groups in going from α- to β-alanine which enhances the effect on the dielectric constant of water is accompanied by an increased dissolving power.

A test of equation 1 independent of dielectric constant measurements may be applied by considering the solubilities of two different salts in the same aqueous solvent. In this case we should find that a constant K satisfies the following equation and is independent of the solvent.

$$(\log S_{1A}/S_{0A})/(\log S_{1B}/S_{0B}) = r_B/r_A = K \qquad (2)$$

where S_{1A} is the solubility of salt A in solvent 1, S_{0A} its solubility in water, and r_A its mean radius.

In Table II are given some solubilities of thallous chloride in amino acid solutions. The last column, which shows the value of K in equation 2, indicates that, while it is not strictly constant, the variations are not wide.

TABLE II

SOLUBILITY TlCl IN WATER = S_0 = 1611 × 10^{-5} AT 25°

Solvent	Soly. TlCl × 10^5	K
Glycylglycine, $N = 0.2$	1835	1.64
Glycine, $N = 0.2$	1725	1.91
α-Alanine, $N = 0.2$	1703	1.49
α-Amino-*n*-butyric acid, $N = 0.1$	1648	1.46
$N = 0.2$	1688	1.45
α-Amino-isobutyric acid, $N = 0.2$	1679	1.45
α-Amino-*n*-valeric acid, $N = 0.1$	1627	2.82
$N = 0.2$	1633	3.75
Urea, $N = 0.2$	1642	1.81
Diketopiperazine, $N = 0.1$	1604	

Summary

The solubilities of thallous iodate and thallous chloride in the presence of amino acids have been determined. The logarithm of thallous iodate

---

(7) G. Devoto, *Gazz. chim. ital.*, **61**, 897 (1932).

solubility is approximately a linear function of the concentration of added substance. The dielectric constants of the solutions do not account for differences observed between the α-amino acids but permit the calculation of ionic radii for the salts which are of the right order of magnitude.

NEW YORK CITY RECEIVED MAY 31, 1933
PUBLISHED NOVEMBER 7, 1933

[CONTRIBUTION FROM THE FERTILIZER AND FIXED NITROGEN DIVISION OF THE BUREAU OF CHEMISTRY AND SOILS, AND THE BUREAU OF STANDARDS]

Low Temperature Specific Heats. I. An Improved Calorimeter for Use from 14 to 300°K. The Heat Capacity and Entropy of Naphthalene[1]

BY J. C. SOUTHARD AND F. G. BRICKWEDDE

The calorimeter described in this paper has been constructed for the determination of the specific heats of liquids and solids of interest in fertilizer and nitrogen fixation investigations. Slow thermal changes anticipated in some of the substances to be investigated made it desirable to prevent as far as possible any transfer of heat between the substances and the surroundings.

Systematic and reliable low temperature specific heat determinations date from the design of the "vacuum" calorimeter first used by Eucken[2] in Nernst's laboratory, 1909. In principle the specific heat of a substance is determined by observing the rise in temperature produced when a measured amount of heat is added electrically to the substance suspended, for purposes of thermal insulation, in an evacuated space. The "vacuum" calorimeter was modified and improved by later investigators. The apparatus described here is a refinement of a "vacuum" calorimeter used by F. Lange[3] which was the first intended to operate "adiabatically," that is, so there should be no transfer of heat between the substance and its surroundings. This is accomplished by surrounding the substance, in a thin-walled container, with a "thermal" shield whose temperature can be

---

(1) This paper is the first of a series communicating the results of two years of coöperative work by the Fixed Nitrogen Research Laboratory and the Bureau of Standards on the specific heats of compounds important in connection with fertilizer and fixed nitrogen investigations of the former laboratory. The experimental work was carried out in the Cryogenic Laboratory of the Bureau of Standards.

The series will include five papers, which with the exception of III will appear in THIS JOURNAL. Number III has already been published in the *Journal of Chemical Physics*, **1**, 95 (1933). The sub-titles of this series for which the principal title is "Low Temperature Specific Heats" are as follows: I. An Improved Calorimeter for use from 14 to 300°K. The Heat Capacity and Entropy of Naphthalene. II. The Calibration of the Thermometer and the Resistance of Pt, Pt–10% Rh and Constantan between −259 and −190°. III. Molecular Rotation in Crystalline Primary Normal Amylammonium Chloride. IV. The Heat Capacities of Potassium Chloride, Potassium Nitrate and Sodium Nitrate. V. The Heat Capacities of β- and α-Tricalcium Phosphate. Publication approved by Director of Bureau of Standards, Department of Commerce, and Chief, Bureau of Chemistry and Soils, Department of Agriculture.

(2) Eucken, *Physik. Z.*, **10**, 586 (1909).

(3) Lange, *Z. physik. Chem.*, **110A**, 343 (1924).