TABLE VII

PART OF THE SYSTEM n-C_6F_{14}–C_2F_5COOH

Mole fraction n-C_6F_{14}	Dew point pressure, mm.	Bubble point pressure, mm.
0.000	30.0	
0.496[a]	142.6	183.0
0.755	174.7	201.5
1.000	219.2	

[a] Solutions of mole fraction less than 0.496 could not be used in the apparatus because no suitable stopcock grease was found for the gas buret.

Discussion

The close resemblance of the system argon-perfluoro-n-pentane to ideal behavior was to be expected because of the low polarizability of molecules of both substances and because of the general physical resemblance of the rare gases to the fluorocarbons.

The system perfluoro-n-hexane–pentafluoropropionic acid deviates greatly from ideality, the pressures being greater than ideal. This might be expected in the case of substances differing as these do. The deviation, however, is probably not as great as it appears to be, because polymerization of the acid causes its true mole fraction to be less than indicated in Table VII.

It is of interest to compare the observed behavior of systems described by Tables I to VI with that predicted by the theory of Hildebrand[4] and Scatchard.[5] This theory results in the equation

$$RT \ln \gamma_1 = V_1\phi_2{}^2(\delta_1 - \delta_2)^2$$

in which the symbols have the following meanings: R is the gas constant, T the absolute temperature, γ_1 the activity coefficient of component 1, V_1 the molar volume of component, 1, ϕ_2 the volume fraction of component two in the liquid solution and δ_1 and δ_2 are the "solubility parameters" of the two components. A similar equation may be used to calculate the activity coefficient of the second component. From the two activity coefficients one may calculate the pressures of the components over a solution. To do this, δ for each component has first been calculated by the usual method: $\delta = (\Delta E_v/V)^{\frac{1}{2}}$. The quantity ΔE_v is the energy of vaporization per mole of the component at 25° and V is its molar volume when a liquid. Table VIII gives the calculated values of δ.

TABLE VIII

SOLUBILITY PARAMETERS AT 25°

Substance	C_5F_{10}	n-C_5F_{12}	n-C_6F_{14}	SF_6	$(C_4F_9)_3N$	$C_6F_{12}O$
δ	6.09	5.77	5.96	3.57	5.52	6.03

Since all of these values except that for sulfur hexafluoride are close to each other, the term $(\delta_1 - \delta_2)$ is small for mixtures of these substances, unless sulfur hexafluoride is one component. The systems as predicted by the theory are very close to ideal, as shown in Table IX.

TABLE IX

CALCULATED TOTAL PRESSURE (IN MM.) AT 25° FOR SYSTEMS AT LIQUID MOLE FRACTION 0.500

System	C_5F_{10}–C_5F_{12}	C_5F_{10}–C_6F_{14}	SF_6–C_5F_{12}	C_6F_{14}–$(C_4F_9)_3N$	C_6F_{14}–$C_6F_{12}O$
Ideal	740.0	526.3	9289	110.1	230.0
From eq. 1	745.3	527.1	12700	114.2	230.1

The system SF_6–n-C_5F_{12} is without question more nearly ideal than is predicted from the δ-values. In a case such as this, it is common practice to use the system to calculate an arbitrary δ-value for the component which seems to misbehave. To make the system in question ideal, δ for SF_6 would be 5.77. A value as low as 5.3 would still give reasonably good agreement with experiment. For other fluorocarbon systems involving sulfur hexafluoride a δ-value in this neighborhood should lead to better predictions than the value 3.57, given in Table VII.

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SEATTLE 5, WASHINGTON

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

Some Metal Complexes of Glycine and Valine[1]

BY NORMAN C. LI, JAMES M. WHITE AND ROBERT L. YOEST

RECEIVED APRIL 19, 1956

The formation constants of the nickel(II) and copper(II) complexes of glycine and valine at different temperatures have been measured. From these data, the enthalpy and entropy changes for the reaction $M^{2+} + 2A^- = MA_2$ have been calculated for M^{2+} = nickel(II) and copper(II) ions, and A^- = glycinate and valinate ions. Only data for the nickel chelates are in agreement with the "iceberg-forming tendency" of Frank and Evans and of Robinson. In 45% by weight dioxane, the entropy of formation of Ni(glycinate)$_2$ complex is much more positive than in aqueous medium, presumably in part because of "sorting-desorting" effect. A linear relationship exists between log k^N of nickel–glycine complexes and mole fraction of dioxane in the range $N_2 = 0$ to $N_2 = 0.323$, whereas the variation of $pK_2{}^N$ of glycine with mole fraction of dioxane is not linear. The highest order cadmium complex of glycine is CdA_3^-; log $k_3 = 1.8$, compared to log $k_1k_2 = 8.1$. These values suggest that in the highest order complex, two glycinates are chelated, but the third is not chelated.

Introduction

For the purpose of obtaining a better understanding of the factors which cause complex formation to take place, it is desirable to consider the free energy change to be a consequence of the enthalpy and entropy changes accompanying complex formation and to measure the relative contribution of these factors.[2] Such a study is described herein for the nickel(II) and copper(II)

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[1] This investigation was supported by Grant No. NSF-G1926 from the National Science Foundation.

[2] C. G. Spike and R. W. Parry, THIS JOURNAL, **75**, 2726 (1953).

complexes of glycine and valine. These two amino acids were chosen because the results are also of interest in connection with the "iceberg-forming tendency" proposal of Frank and Evans,[3] inasmuch as Robinson[4] and Mason, Kampmeyer and Robinson[5] have used the iceberg picture to interpret the thermodynamic and flow properties of aqueous solutions of amino acids.

The effect of the solvent itself upon the "measured" formation constants of the chelate compounds formed between the divalent metal ions and glycinate can be demonstrated by varying the mole fraction of water in solution. As in previous studies,[6] the ionic strength of the aqueous solutions was 0.15. In a medium of low dielectric constant, there will be greater electrostatic interactions and consequent ionic association. In order that the activity coefficients of electrolytes remain comparable in mixed organic–water media as in water,[7] the ionic strengths of the solutions in 45 and 70% by weight dioxane were kept at 0.004 and 0.001, respectively.

Experimental

Materials.—All chemicals were C.P. reagent grade products. Stock solutions of copper(II) nitrate were analyzed by addition of excess KI and titration of the liberated iodine; stock solutions of nickel(II) nitrate by precipitation with dimethylglyoxime. Standard solutions of the amino acids were prepared directly from the vacuum-dried compounds, and only freshly prepared solutions were used. Dioxane was refluxed with sodium and fractionally distilled, b.p. 101–101.5°.

Apparatus.—The *p*H measurements were made with a Beckman *p*H meter, Model G, equipped with external electrodes. Aqueous buffer solutions, *p*H values of 4 and 7, were used to standardize the instrument. Polarographic current–voltage curves were made with a Sargent Recording Polarograph, Model XXI, and manually with a Fisher Elecdropode. All potentials were measured against saturated calomel electrode (S.C.E.) and the half-wave potentials were corrected for the *IR* drop, as previously described.[6] The characteristics of the capillary were: $m = 2.33$ mg. sec.$^{-1}$, $t = 3.74$ sec. (open circuit) in water, at a height of the mercury column of 50 cm.

Calculation of Constants

The stepwise formation constants for equilibria of the type $MA_{p-1} + A = MA_p$ are designated by the expression $k_p = (MA_p)/(MA_{p-1})(A)$, and were determined by means of the Bjerrum method.[8] Since one does not get a true reading of *p*H in the 45 and 70% by weight dioxane solutions, the observed readings were corrected. Correction factors, obtained by comparing the calculated values of *p*H[9] for the alkali titration of glycine with experimentally determined values, were added to the observed *p*H readings.

The over-all formation constants, k_f, of complexes were determined by means of the polarographic method. Where only one divalent metal cation was present in solution, the data obtained were used to calculate the number of groups, p, coördinated to each metal ion and the over-all formation constant by means of the equation[6d]

$$(E_{1/2})_c - (E_{1/2})_s = -(RT/nF) \ln k_f - p(RT/nF) \ln C_A \quad (1)$$

where C_A is the concentration of free ligand in solution. In order for this equation to be valid, the dropping mercury electrode reaction must be reversible.

Since the reduction of the nickel ion and some of the nickel complexes[6c,10] are irreversible, we have devised the following polarographic method for the determination of the formation constants of nickel complexes. In essence, the half-wave potentials of solutions (i) and (ii) are determined: solution (i) consisting of 5.00×10^{-4} *M* $Cu(NO_3)_2$, 0.15 *M* KNO_3, 0.200*M* glycine, 0.100 *M* KOH; solution (ii) has the same composition as solution (i), except that 0.0495 *M* $Ni(NO_3)_2$ solution replaces 0.15 *M* KNO_3. Since the first polarographic waves in both solutions are due to the reduction of cupric ion, the dropping mercury electrode reactions in both are reversible. These half-wave potentials for solutions (i) and (ii) may therefore be given by the expressions

$$(E_{1/2})_{c,(i)} - (E_{1/2})_s = -(RT/nF) \ln k_f - p(RT/nF) \ln C_{A,(i)} \quad (2)$$

$$(E_{1/2})_{c,(ii)} - (E_{1/2})_s = -(RT/nF) \ln k_f - p(RT/nF) \ln C_{A,(ii)} \quad (3)$$

Subtracting equation 3 from equation 2, one obtains

$$(E_{1/2})_{c,(i)} - (E_{1/2})_{c,(ii)} = -p(RT/nF) \ln (C_{A,(i)}/C_{A,(ii)}) \quad (4)$$

Since Li and Doody[6b] had previously shown that the values of log k_f and p for the cupric complex of glycinate are 15.1 and 2, respectively, the value of $C_{A,(i)}$ may be taken to be equal to 0.099 *M*. The value of $C_{A,(ii)}$ is then easily calculated from equation 4, and is equal to $0.099M - qx$, where x is the molar concentration of the NiA_q complex. The equilibrium constant of the reaction

$$Ni^{++} + qA^- = NiA_q^{(2-q)+}$$

can therefore be calculated and this is the over-all formation constant of the NiA_q complex. The value of q is determined from an independent measurement such as potentiometric or conductometric titration.[6b]

Results and Discussion

The values of pK_2' for the amino acids and the formation constants of the metal chelates are listed in Tables I and II, respectively. The enthalpy and entropy changes for the reaction $M^{++} + 2A^- = MA_2$ are calculated from the values of log k_1k_2 at different temperatures in the usual manner, and are listed in Table III. A consideration of the

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(3) H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 531 (1945).

(4) A. L. Robinson, *ibid.*, **14**, 588 (1946).

(5) L. S. Mason, P. M. Kampmeyer and A. L. Robinson, THIS JOURNAL, **74**, 1287 (1952).

(6) (a) N. C. Li and E. Doody, *ibid.*, **74**, 4184 (1952); (b) **76**, 221 (1954); (c) N. C. Li, T. L. Chu, C. T. Fujii and J. M. White, *ibid.*, **77**, 859 (1955); (d) N. C. Li and R. A. Manning, *ibid.*, **77**, 5225 (1955).

(7) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd ed., Reinhold Publ. Corp., New York, N. Y., 1950. The activity coefficient of hydrochloric acid in water, $\mu = 0.15$, is about the same as in 45% dioxane, $\mu = 0.004$, and in 70% dioxane, $\mu = 0.001$.

(8) J. Bjerrum, "Metal Ammine Formation in Aqueous Solutions," P. Haase & Sons, Copenhagen, 1941.

(9) The calculated values of *p*H were based on the pK_2 of glycine in the corresponding dioxane solution and ionic strength. The latter values were in turn calculated from the values of K_B of glycine (H. S. Harned and C. M. Birdsall, THIS JOURNAL, **65**, 1117 (1943)) and K_W (H. S. Harned and L. D. Fallon, *ibid.*, **61**, 2374 (1939)), which were determined from cells without liquid junction.

(10) I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd ed., Interscience Publishers, New York, N. Y., 1952, p. 486.

possible errors in log k_1k_2 makes it appear that ΔH may be uncertain by about 2 kcal., and ΔS by about 4 entropy units. The values of ΔH and ΔS in Table III have been rounded to the nearest half unit.

TABLE I

ACID DISSOCIATION CONSTANTS

	pK_2' (aq.)	pK_2' (45% dioxane)	pK_2' (70% by wt. dioxane)
μ =	0.15	0.004	0.001
Glycine, 25°	9.68	10.13	11.18
30	9.52	10.02	11.08
40	9.21	9.79	
Valine, 25°	9.61		
30	9.46		
40	9.15		

TABLE II

CONCENTRATION FORMATION CONSTANTS IN

	log k_1	log k_2	log k_1k_2
(A) Aqueous medium, μ = 0.15			
Ni^{++}–Glycinate			
25°	5.97	4.95	10.92
30	5.88	4.86	10.74
40	5.72	4.70	10.42
Ni^{++}–Valinate			
25°	5.37	4.16	9.53
30	5.27	4.07	9.34
35	5.17	3.99	9.16
40	5.11	3.91	9.02
Cu^{++}–Glycinate[a]			
25°			15.10
30			14.83
35			14.60
Cu^{++}–Valinate[a]			
25°			14.76
30			14.51
35			14.28
(B) 45% by wt. dioxane, μ = 0.004			
Ni^{++}–Glycinate			
25°	7.16	6.06	13.22
30	7.09	5.97	13.06
40	6.96	5.77	12.73
(C) 70% by wt. dioxane, μ = 0,001			
Ni^{++}–Glycinate			
25°	8.51	7.24	15.75
30	8.45	7.22	15.67

[a] Polarographic data.

TABLE III

ENTHALPY AND ENTROPY CHANGES FOR THE REACTION $M^{++} + 2A^- = MA_2$ AT 25°

Aqueous medium, μ = 0.15, unless otherwise noted.

	ΔH, kcal.	ΔS, e.u.
Ni^{++}-Glycinate	−14.0	2.5
Ni^{++}–Glycinate (45% dioxane, μ = 0.004)	−14.0	14.0
Ni^{++}–Valinate	−14.5	−5.5
Cu^{++}–Glycinate	−21.0	−1.0
Cu^{++}–Valinate	−20.5	0

As seen from Tables II and III, the enthalpy values for the formation of the Ni(glycinate)$_2$ and Ni(valinate)$_2$ complexes are essentially the same, whereas their stabilities differ by approximately 1.5 log units. This must mean, then, that the difference in stabilities is due predominantly to an entropy effect.

According to the "iceberg-forming tendency" proposal of Frank and Evans,[3] we might expect the entropy of formation of the M(valinate)$_2$ complex to be more negative than the corresponding quantity for the M(glycinate)$_2$ complex, both in aqueous medium. This could be because the isopropyl group in the valine structure imposes a greater iceberg-forming tendency on the uncharged M(valinate)$_2$ complex than on the valinate anion. This would lower the partial molal entropy of the product more than that of the reactant in the equation $M^{2+} + 2A^- = MA_2$ and produce a negative contribution to ΔS. Since no alkyl group is present in the glycine structure no such influence on ΔS would be expected. Our data on the entropy of formation of the aqueous nickel(II) complexes of glycinate and valinate therefore are in agreement with this hypothesis.

The values of ΔS for the copper(II) complexes of glycinate and valinate, however, are about equal, as are also the ΔS values found by Basolo and Murmann[11] for the copper(II) complexes of ethylenediamine, en, and N-methylethylenediamine, meen, so that the iceberg hypothesis finds no support from the data on copper complexes.

We have found that in general the magnitudes of the formation constants of copper(II) chelates are relatively insensitive to the nature of the side chains, at least when compared to the corresponding chelates of other metal ions. Thus, the values of log k_T for the copper complexes of oxidized glutathione and glycine differ by only 0.46 unit whereas the difference in the corresponding values for the zinc complexes[12] amounts to 2.74 units. Numerous other examples of this kind can be cited. As seen from Table III, the values of ΔH for copper complexes are relatively constant and, since formation constants of the copper complexes are also relatively constant, the values of ΔS must be also.

In 45% by weight dioxane, the entropy of formation of Ni(glycinate)$_2$ complex, 14.0 e.u., is much more positive than in aqueous medium. This could be in part because in the mixed dioxane–water solvent, the solvent molecules are sorted with the more polar water molecules congregating around the nickel(II) and glycinate ions, while some desorting takes place around the uncharged Ni(glycinate)$_2$ complex. The question of how homogenous a mixed solvent is in the presence of an ionic solute is important, and the sorting by ions has been discussed by Scatchard[13] and Frank[14] from a theoretical point of view. In the mixed ethanol–water solvents, for instance, the calcula-

(11) F. Basolo and R. K. Murmann, THIS JOURNAL, **76**, 211 (1951); **74**, 5243 (1952). The authors found that when ΔH is determined calorimetrically, ΔS (Cu en$_2$) = 7, ΔS (Cu meen$_2$) = 8 and that when ΔH is determined from the temperature effect on formation constants, ΔS(Cu en$_2$) = 35, ΔS(Cu meen$_2$) = 36.

(12) N. C. Li, O. Gawron and G. Bascuas, *ibid.*, **76**, 224 (1954).

(13) G. Scatchard, *J. Chem. Phys.*, **9**, 34 (1941).

(14) H. S. Frank, *ibid.*, **23**, 2023 (1955).

tion[15] predicts that the molecules in contact with an ion are the more polar water molecules even though the mixed solvent is 99% alcohol. It is interesting to note that in 45% by weight dioxane, the entropies of formation[16] of formic acid, acetic acid and propionic acid from proton and the corresponding anion of the acid are about 10, 9, 8 e.u., respectively, more positive than in aqueous medium, whereas the corresponding difference in ΔS values for the Ni(glycinate)$_2$ complex is about 11 e.u.

Figure 1 gives plots of log k^N of nickel glycinate complexes and pK^N of glycine *vs.* mole fraction of dioxane. Included as reference are data on pK^N of acetic acid, calculated from ref. 16. These constants are in mole fraction concentration units, and are calculated from the concentration formation constants (molar concentration scale) listed in Tables I and II, by means of the equation

$$\log k^N = \log k + \log (1000d_0/M_0) \qquad (5)$$

In this equation d_0 and M_0 are the density and mean molecular weight of the solvent, respectively. King[15] and Adamson[17] have shown that it is a more sound procedure from a theoretical point of view to use mole fraction concentration units and that correlation with theory is much better when the constants are calculated on the basis of this scale.

A linear relationship exists between log k^N and the mole fraction of dioxane. Table IV gives mathematical expressions for the curves which fit experimental data within ± 0.05 log unit.

TABLE IV

LOG k^N EQUATIONS FOR THE RANGE N_2 = 0 TO N_2 = 0.323[a] (70% BY WEIGHT DIOXANE) FOR NICKEL–GLYCINATE CHELATES

25°	$\log k_1^N = 7.71 + 6.90N_2$
	$\log k_2^N = 6.69 + 6.10N_2$
30°	$\log k_1^N = 7.62 + 7.00N_2$
	$\log k_2^N = 6.60 + 6.30N_2$

[a] These equations fit the experimental points to ±0.05 log unit.

As can be seen from Fig. 1 and Table IV, the slope of the log k_1^N *vs.* N_2 line is greater than that of the log k_2^N *vs.* N_2 line. This is probably because the effect of the dielectric constant of the medium is greater when divalent nickel ion is a reactant in forming the Ni(glycinate)$^+$ complex, than when univalent Ni(glycinate)$^+$ is a reactant in forming the uncharged Ni(glycinate)$_2$ complex. Of course, changes in the effective solvation of the various species involved in going from water to 70% medium would affect the formation constants also.

Figure 1 shows that the variation of pK_2^N of glycine with mole fraction of dioxane is not linear, whereas the corresponding variation for acetic acid is linear. The direction of the deviation for glycine is in agreement with the accepted concept that in predominantly aqueous media, glycine is dipolar, $^+H_3NCH_2COO^-$, and that in predominantly non-aqueous media glycine is less polar, H_2NCH_2COOH. The pK_2 in predominantly aqueous media is then $pK_{NH_3^+}$, while that in predominantly non-aqueous media might come to be pK_{COOH}. Acetic acid, on the other hand, may well have the same structure in water–dioxane mixtures within the range studied; hence the linear relationship between pK^N of acetic acid and mole fraction of dioxane is as expected.

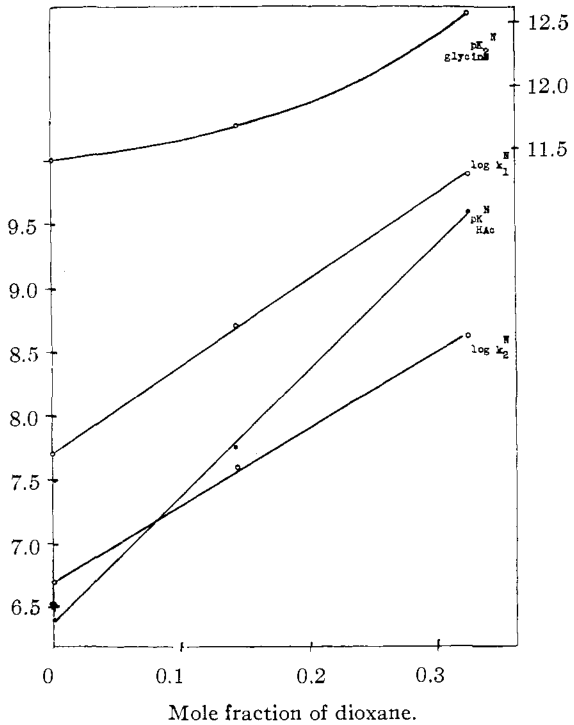

Fig. 1.—Log k^N of Ni^{++}-glycine complexes and pK^N *vs.* mole fraction of dioxane.

A survey of the literature reveals that the formation constants of nickel complexes of amino acids have not heretofore been determined by the polarographic method. This is probably because the polarographic wave for the reduction of nickel(II) is irreversible. As mentioned in the section "Calculation of Constants," we have determined the half-wave potentials for the reduction of copper(II) complexes in two solutions (i) and (ii), both solutions have an ionic strength of 0.25. The values of $(E_{1/2})_{c,(i)}$ and $(E_{1/2})_{c,(ii)}$ in aqueous medium at 25° are −0.369 and −0.186 v., respectively. With the use of equation 4 and putting q = 2, we have obtained for Ni(glycinate)$_2$: log k_f = 11.2, in fair agreement with the more accurate value, log k_1k_2 = 10.92, obtained by the Bjerrum pH method and listed in Table II. Other values recorded for log k_1k_2 are: 11.14,[18] 11.0,[18] 10.64.[19]

Table V lists the polarographic results for cadmium–glycine complex. A plot of $-E_{1/2}$ *vs.*

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[15] E. L. King, in P. H. Emmett, "Catalysis," Vol. 2, Reinhold Publ. Corp., New York, N. Y., 1955, p. 377.

[16] The entropies were calculated from the pK's of the organic acids in water and in 45% by weight dioxane listed in R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Academic Press, Inc., New York, N. Y., 1955, p. 504. The pK values were determined from cells without liquid junction.

[17] A. W. Adamson, THIS JOURNAL, **76**, 1578 (1954).

[18] A. E. Martell and M. Calvin, "Chemistry of Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, p. 528.

[19] F. Basolo and T. Y. Chen, THIS JOURNAL, **76**, 953 (1954).

$-\log C_A$, according to equation 1, yields a straight line. The value of p is calculated from the slope of the line to be 3.04, so that the highest order complex is Cd(glycinate)$_3$. The electrode reaction is reversible, and the average value of $\log k_f$ is calculated by means of equation 1 to be 9.94.

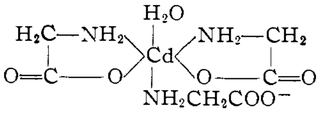
TABLE V

POLAROGRAPHIC RESULTS FOR CADMIUM–GLYCINE COMPLEX

Each solution contains 5×10^{-4} M Cd(NO$_3$)$_2$, glycine half neutralized with KOH, KNO$_3$ to keep $\mu = 0.15$, 25°.

$C_{\text{glycinate}}$	$-E_{1/2}$	$-\log C_A$	$\log k_f$ ($k_f = k_1k_2k_3$)
0.000	0.583		
.020	.726	1.699	9.93
.030	.743	1.523	9.96
.040	.753	1.398	9.93
.050	.762	1.301	9.97
.060	.769	1.222	9.93
		Av.	9.94

The value of $\log k_1k_2$ for the cadmium–glycine complex is reported as 8.1,[18] obtained by the pH method, so that $\log k_3$ becomes 1.8. It is obvious from these values that the tendency to form the highest order complex is extremely weak, and a possible structure for the complex is therefore



in which two glycinate ions are chelated but the third is not chelated. Douglas, Laitinen and Bailar[20] note that monodentate groups usually give a coördination number of four for the cadmium ion, but the coördination number of six seems to be more common for polydentate groups. In the structure postulated above, the coördination number is six, with one of the positions occupied by the solvent.

We have also investigated polarographically the cadmium complexes of leucine, isoleucine and norleucine and found that the highest order complex in each case is CdA$_3^-$, where A is the amino acid ion. These complexes are less stable than the glycinate complex, presumably because of steric hindrance. However, since the polarographic waves for these complexes are not strictly reversible, no quantitative values for the formation constants were calculated.

Acknowledgment.—The authors are indebted to Professor Henry S. Frank, University of Pittsburgh, for suggesting the entropy studies and for helpful discussions, to Mr. R. A. Manning for carrying out some of the experiments. This research was sponsored by the National Science Foundation.

(20) B. E. Douglas, H. A. Laitinen and J. C. Bailar, Jr., THIS JOURNAL, **72**, 2484 (1950).

PITTSBURGH, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Theory of Elastic Mechanisms in Fibrous Proteins

BY PAUL J. FLORY

RECEIVED APRIL 30, 1956

This paper is concerned with problems relating to dimensional changes in systems comprising long chain molecules so constituted as to occur, under suitable conditions, in the state of high order characteristic of native fibrous proteins. Particular attention is given to the process of disordering of the molecular chains, which is treated as a reversible phase change between crystalline and amorphous states. Thermodynamic relations between the force f, the temperature T and the length L are developed for fibers of uniform constitution, for fibers whose properties vary axially, and for systems containing a second component (diluent). The hitherto unexplained thermoelastic characteristics of typical fibrous proteins are readily accounted for by the hypothesis that decrease in length signifies melting of crystalline regions. Network structures formed by cross-linking polymeric chains in the oriented (crystalline) state are considered from the point of view of the statistical mechanical theory of elasticity of polymeric systems. Significant differences as compared to networks formed by cross-linking disordered chains in the usual manner are noted: the length to which the cross-linked fiber will shrink on melting in the absence of a force is predicted to increase approximately as the square root of the degree of cross-linking; at extensions substantially greater than this relaxed length, the force of retraction should be independent of the degree of cross-linking. By combining these results of the statistical theory of elasticity with the thermodynamic relationship $\partial(f/T)/\partial(1/T) = \Delta H/\Delta L$, where ΔH and ΔL are the latent changes in heat and length accompanying melting, the force, length and temperature may be related over ranges which include the phase change. The elevation of the melting point which should result from cross-linking in the ordered state is treated theoretically.

Introduction

The physical structures of fibrous proteins have been extensively investigated by the techniques of X-ray diffraction, electron microscopy, optical birefringence and polarized infrared absorption. The principal features of the arrangement of the polypeptide chains consequently are reasonably well established, although certain details remain obscure. A state of molecular organization appropriately designated as crystalline is the dominant structural characteristic brought to light by these studies.

In contrast to the comparatively advanced state of knowledge concerning the structures of fibrous proteins, little progress has been achieved toward an understanding of the physical properties of proteins. In particular, the mechanism by which protein fibers undergo major changes in length has not been satisfactorily explained. Analogies to the deformation of rubber have been suggested,[1,2] but with no more than limited success. This is not

(1) K. H. Meyer, *Proc. Roy. Soc. (London)*, **B139**, 498 (1952); K. H. Meyer, A. J. A. van der Wyk, W. Gonon and C. Haselbach, *Trans. Faraday Soc.*, **48**, 669 (1952).

(2) E. Guth, *Ann. N. Y. Acad. Sci.*, **47**, 715 (1947).