Thermodynamics of Ion Association

Transition-Metal β-Alanine and Glycine Complexes

S. BOYD[1], J. R. BRANNAN[2], H. S. DUNSMORE[3], and G. H. NANCOLLAS
Department of Chemistry, State University of New York at Buffalo, Buffalo, N. Y. 14214

Thermodynamic equilibrium constants have been derived from low ionic strength potentiometric measurements at temperatures from 0° to 45° C. for the association in aqueous solution of nickel and cobalt (II) ions with the β-alanine anion. Values of ΔG, ΔH, ΔS, and ΔC_p have been calculated for the reaction $M^{2+} + A^- \rightleftarrows MA^+$. The enthalpies of formation of cobalt and nickel mono-β-alaninate, nickel and zinc monoglycinate, and cobalt and copper mono- and diglycinate complexes have been measured at an ionic strength of 0.1M using a sensitive differential calorimeter. The thermodynamic functions are discussed and compared with similar data for other amino acid and carboxylic acid complexes.

MOST studies of transition metal amino acid complexes have been directed towards the determination of stability constants at one or more temperatures. Although there is a measure of agreement in some systems between thermodynamic data obtained by different workers (*3, 18*) widely different values have been reported in other cases where only a relatively narrow temperature range was studied (*6, 7*). The use of calorimetric methods for the direct determination of the enthalpy changes accompanying the association reactions is clearly desirable.

There have been very few calorimetric studies of complex formation involving amino acids and the divalent transition metal ions; most of these have been concerned with Cu (II) complexes (*1, 6*). To obtain reliable data for the glycinates and β-alaninates is of interest in order to compare in more detail, the properties of five- and six-membered rings involving nitrogen and oxygen coordination. Corresponding data for the dicarboxylate complexes have already been obtained (*12*) and so the effect of replacing a nitrogen by oxygen in the chelate ring can be discussed. In the present work, the precise potentiometric measurements made with the glycinates (*3*) have been extended to cobalt and nickel β-alaninates, and the heats of formation of the complexes have been measured. Calorimetric determinations have also been made of the enthalpies of association for the formation of nickel and zinc monoglycinate and of cobalt and copper mono- and diglycinate complexes.

EXPERIMENTAL

Analytical reagent grade reagents and grade A glassware were used throughout. Cupric and zinc perchlorate solutions were made by dissolving the oxides in perchloric acid; analysis for copper ions was made by thiosulfate titration and for zinc ions by complexometric titration (*19*).

Potentiometric Experiments. E.m.f. values of the cells

$$H_2Pt/HA\ (m_1),\ NaOH(m_2),\ M\ Cl_2(m_3)/AgCl/Ag \qquad (1)$$

where HA = β-alanine, and M^{2-} = Ni^{2-} or Co^{2-} have been measured to within ±15 μv. at 0°, 15°, 25°, 35°, and 45° C. Details of cell design and experimental technique have been given (*14*).

Calorimetric Experiments. The calorimeter has been described (*2, 16*). Temperature changes were measured to $\pm 5 \times 10^{-5}$ ° C. on the addition of identical 10.0-ml. volumes of a relatively concentrated solution of the amino acid in potassium hydroxide to: 300 ml. of divalent metal ion solution of ionic strength 0.1M maintained with potassium chloride (sodium perchlorate in the cases of copper and zinc); and 300 ml. of 0.1M potassium chloride (or sodium perchlorate) solution. Where necessary, hydrochloric (or perchloric) acid was added to the solution of metal ion in order to arrive at a suitable final pH after mixing; the same volume of acid was also used in the corresponding blank experiments. Measurement of the pH of the final solutions with a glass electrode enabled corrections to be made for the heat effects associated with changes in the concentrations of protonated and unprotonated anions (*16*). Concentrations were chosen such that not more than two complexes, MA^+ and MA_2, were formed in the calorimeters. In experiments directed at the determination of ΔH_1 values, the concentration of the second complex, MA_2, was negligible.

RESULTS AND DISCUSSION

It was first necessary to determine the protonation dissociation constants of β-alanine, $k_1 = [H^+][HA]/[H_2A^+]$ and $k_2 = [H^+][A^-]f_1^2/[HA]$ k_1 was obtained from the e.m.f., E, of cells

$$H_2,\ Pt/HA(m_4),\ HCl(m_5)/AgCl/Ag \qquad (2)$$

in which the molality of the hydrogen ion is given by

$$-\log[[H^+] = (E - E^0)/k + \log m_5 + 2 \log f_1$$

Table I. Determination of k_1 at 25° C.

10^3m_4	10^3m_5	$(E - E^0)$	$10^4[H^+]$	$10^3[H_2A^+]$	$10^3[HA]$	10^4k_1
11.1456	5.0344	0.35697	2.139	4.820	6.325	2.81
13.5367	3.9242	0.38016	1.094	3.815	9.722	2.79
10.5218	3.2742	0.38222	1.197	3.154	7.367	2.80
7.7396	2.0512	0.39957	0.949	1.956	5.783	2.81
7.8944	5.1638	0.33869	4.256	4.738	3.156	2.84
7.5282	5.0572	0.33804	4.450	4.612	2.916	2.81
9.4399	4.5933	0.35616	2.406	4.374	5.065	2.79
9.0871	4.1341	0.36183	2.127	3.921	5.166	2.80

	0°	15°	25°	35°	45°
Mean 10^4k_1	2.24	2.61	2.81	2.95	3.04
10^4k_1 (*8*)	2.21	2.61	2.81	2.99	

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[1] Present address: Dunlop Research Center, Sheridan Park, Ontario, Canada

[2] Present address: Research Department, Central Electricity Generating Board, Leatherhead, Surrey, England

[3] Present address: Chemistry Department, The University, Glasgow, W2, Scotland

Table II. Determination of k_2 at 25° C.

$10^3 m_6$	$10^3 m_7$	$10^3 m_8$	$(E - E^0)$	$10^{11}[H^+]f_1^2$	$10^3[A^-]$	$10^3[HA]$	$10^{11}k_2$
5.1640	1.5290	2.7297	0.73614	0.319	1.453	3.711	5.16
5.4704	1.3377	2.8025	0.72929	1.677	1.278	4.193	5.19
4.3634	0.9654	2.7789	0.72612	1.913	0.913	3.451	5.06
7.3054	0.9955	3.0129	0.70973	3.340	0.965	6.340	5.09
14.0563	2.4697	6.4307	0.69859	2.415	2.428	11.628	5.04
13.3120	1.0338	6.6041	0.67429	6.055	1.017	12.295	5.01
12.2758	1.8575	5.7960	0.69692	2.859	1.822	10.454	4.98
13.4139	2.8135	6.3115	0.70459	1.948	2.762	10.652	5.05
Mean	0°	15°	25°	35°	45°		
$10^{11}k_2$	0.891	2.62	5.07	9.35	16.6		
$10^{11}k_2$ (*8*)	0.999^a	2.98	5.83	10.88			

where m represents molality, and $k = 2.3026\ RT/F$. The concentrations of ionic species were calculated from equations for total β-alanine

$$m_4 = [H_2A^+] + [HA]$$

and for electroneutrality

$$[H^+] + [H_2A^+] = m_5$$

Activity coefficients were obtained from the Davies equation (*5*) with the ionic strength, $I = m_2$ (Table I).

k_2 was obtained from the e.m.f. of the cell

$$H_2,\ Pt/HA(m_6),\ NaOH(m_7),\ KCl(m_8)/AgCl/Ag \qquad (3)$$

in which $[H_2A^+]$ could be neglected. Concentrations of species were calculated from the equations for total β-alanine

$$m_6 = [HA] + [A^-]$$

for electroneutrality

$$[H^+] + m_7 + [K^+] = m_8 + [OH^-] + [A^-]$$

and for the ionic product of water (*17*)

$$K_w = [H^+][OH^-]f_1^2$$

Computations were made by successive approximations for I using an electronic computer, (Table II).

May and Felsing (*8*) have made similar measurements of the ionization constants of β-alanine and their results are included in Tables I and II. Agreement between the k_1 values is good but the k_2 values calculated from their results are consistently higher than those of the present study. May and Felsing reported their high pH measurements as k_2^1, the equilibrium constant for the reaction

$$HAOH^- \rightleftarrows HA + OH^-$$

and there was a distinct curvature of the log k_2^1 *vs.* I plots. In contrast, log k_2^1 values calculated from the data of Table II show the expected slight linear dependence on ionic strength and are therefore considered to be more reliable than the values obtained by the above authors.

Concentrations of ionic species in the presence of metal ions were calculated from the e.m.f. of cells of Type 1 by using equations for total β-alanine

$$m_1 = [H_2A^+] + [HA] + [A^-] + [MA^+]$$

for total metal ion

$$m_3 = [M^{2+}] + [MA^+]$$

for electroneutrality

$$[H^+] + 2[M^{2+}] + [MA^+] + m_2 + [H_2A^+] = [A^-] + 2m_3$$

and for the dissociation constants of β-alanine. Association constants, $K_1 = [MA^+]/[M^{2+}][A^-]\ f_2$, were calculated by successive approximations for the ionic strength

$$I = \tfrac{1}{2}\{[H^+] + [MA^+] + [H_2A^+] + [A^-] + m_2 + 2m_3 + 4[M^{2+}]\}$$

using an electronic computer and the activity coefficient expression:

$$\log f_z = -Az^2\left[\frac{I^{1/2}}{1 + I^{1/2}} - CI\right] \qquad (4)$$

The small increase in dielectric constant of the amino acid solution (≈0.2*D*) over that of pure water was taken into account in calculating the Debye-Huckel constant A. The effect was negligible in the nickel β-alanine systems but amounted to increases of from 0.5 to 2.0% in f_2 for the cobalt β-alanine experiments with their higher free metal ion concentrations. Calculations were made at each temperature with values of C = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, and 1.0 in order to determine the best value of this parameter. There was little to choose between values in the range 0.1 to 0.5, and the data given in Table III have been calculated with the $C = 0.3$ recommended by Davies (*5*). The consistency of the K_1 values adds support to the assumption made that only one complex, MA^+, is present in the solutions. Introduction of $K_2[= [MA_2]/[MA^+][A^-]f_1^2]$ values up to 10^3 liter mole^{-1} has only a very small effect (<0.6%) on the calculated K_1 values.

The nonlinear variation of log K_1 with the reciprocal temperature could be expressed, with an accuracy of about 1%, by the equation $\log K_1 = a + bT + cT^2$. Values of the parameters, evaluated as previously described (*9*) are given in Table IV. ΔG and ΔH_T calculated from $\Delta G = -RT\ln K_1$ and $\Delta H_t = 2.303\ RT^2(b + 2cT)$ at 298° K. are included in Table IV. As was found with the corresponding dicarboxylates (*9, 10, 15*) and the glycinates (*3*), accurate measurements over a range of temperature indicate non zero ΔC_p values $[\Delta C_p = 4.606RT(b + 3cT)]$, for CoA^+ of 35 ± 13 cal. mole^{-1} degree^{-1} and for NiA^+ of 31 ± 6 cal. mole^{-1} degree^{-1}.

The results of the calorimetric experiments are summarized in Table V in which ΔH_1^1 and ΔH_2^1 are the stepwise enthalpies of formation at an ionic strength of 0.1*M*. The concentrations of ionic species in the solutions were calculated using values for the dissociation constants for glycine (*4*) (H_2G^+), $k_1 = 4.46 \times 10^{-3}$ and $k_2 = 1.67 \times 10^{-10}$ and the association constants (*3, 13*) $K_1\ (CoG^+) = 1.18 \times 10^5$, $K_1(NiG^+) = 1.51 \times 10^6$, $K_1(ZnG^+) = 3.39 \times 10^5$, $K_1(CuG^+) = 4.17 \times 10^8$, $K_2(CoG_2) = 9.40 \times 10^4$, $K_2(CuG_2) = 9.35 \times 10^6$ liters mole^{-1}. The mean enthalpy values in Table V have been corrected to the ΔH_c values at $I = 0$ (*11*) given in Table VI. The agreement with the values obtained from the potentiometric measurements over a wide range of temperature is very satisfactory. The recently reported calorimetrically determined enthalpy values (*1*) for the formation of copper mono- and diglycinate complexes, $\Delta H_1 = -6.22$ kcal. mole^{-1} and $\Delta H_2 = -6.96$ kcal. mole^{-1}, are in good agreement with the values given in Table VI.

Table III. E.m.f. Measurements

Nickel β Alaninate

Expt.	1	2	3	4	5	6	7
10^2m_1	1.6932	2.0039	1.7436	2.0836	2.0804	2.4171	2.8592
10^4m_2	4.3522	4.0373	3.5896	2.3231	2.5888	3.1735	3.1933
10^3m_3	1.8946	1.7210	1.6613	0.9657	1.2571	1.4238	1.7505

Expt.	$(E - E^0)$	10^3I	$10^8[H^+]$	$10^2[HA]$	$10^6[A^-]$	$10^4[MA^+]$	$10^{-5}K_1$
			Temp. = 0° C.				
1	0.52310	5.249	6.832	1.649	2.496	4.378	1.62
2	0.52211	4.757	7.791	1.962	2.588	4.081	1.60
3	0.52163	4.623	8.222	1.706	2.128	3.632	1.74
4	0.53236	2.661	9.199	2.059	2.354	2.380	1.73
5	0.52278	3.507	8.686	2.053	2.034	2.663	1.69
6	0.51936	3.948	10.177	2.383	2.313	3.263	1.67
7	0.50610	4.917	10.463	2.823	1.918	3.367	1.66
				Mean $K_1 = 1.67\ (\pm0.04) \times 10^5$			
			Temp = 15° C.				
1	0.53352	5.246	14.329	1.648	3.512	4.409	1.17
2	0.53280	4.754	16.127	1.961	3.688	4.124	1.15
3	0.53362	4.621	16.133	1.706	3.200	3.665	1.18
4	0.54383	2.657	17.807	2.058	3.385	2.432	1.24
5	0.53374	3.502	20.852	2.051	2.926	2.726	1.22
6	0.53026	3.941	21.337	2.381	3.344	3.337	1.20
7	0.51688	4.905	30.174	2.821	2.841	3.495	1.18
				Mean $K_1 = 1.19\ (\pm0.02) \times 10^5$			
			Temp. = 25° C.				
1	0.54121	5.245	21.90	1.647	4.450	4.439	0.939
2	0.53943	4.750	25.67	1.960	4.487	4.175	0.961
3	0.54033	4.617	25.62	1.705	3.901	3.709	0.988
6	0.53740	3.934	33.15	2.380	4.165	3.416	0.996
7	0.52396	4.893	46.15	2.818	3.595	3.626	0.983
				Mean $K_1 = 9.73\ (\pm0.19) \times 10^4$			
			Temp. = 35° C.				
1	0.54788	5.240	33.83	1.646	5.328	4.491	0.800
2	0.54621	4.743	39.37	1.958	5.408	4.249	0.820
3	0.54720	4.611	39.21	1.703	4.713	3.773	0.841
6	0.54456	3.924	50.00	2.377	5.105	3.531	0.852
7	0.53115	4.875	68.39	2.814	4.483	3.808	0.843
				Mean $K_1 = 8.31\ (\pm0.17) \times 10^4$			
			Temp. = 45° C.				
1	0.55431	5.233	51.33	1.644	6.244	4.573	7.03
2	0.55296	4.734	58.94	1.956	6.422	4.359	7.19
3	0.55336	4.602	60.04	1.701	5.471	3.877	7.54
6	0.55201	3.909	72.78	2.374	6.230	3.687	7.44
7	0.53878	4.852	97.35	2.809	5.594	4.048	7.34
				Mean $K_1 = 7.31\ (\pm0.16) \times 10^4$			

Cobalt β-Alaninate

Expt.	1	2	3	4	5	6
10^2m_1	8.5765	9.1761	8.9598	9.4520	8.1413	7.8930
10^4m_2	3.9641	3.5492	5.1183	4.0928	3.3713	3.2554
10^2m_3	0.8291	0.6990	1.4153	1.1316	0.8364	1.0386

Expt.	$(E - E^0)$	10^2I	$10^7[H^+]$	$10^2[HA]$	$10^6[A^-]$	$10^4[MA^+]$	$10^{-4}K_1$
			Temp. = 0° C.				
1	0.46023	2.438	2.605	8.517	3.903	4.919	2.90
2	0.46263	2.051	2.734	9.118	3.901	4.627	3.13
4	0.44778	3.340	3.369	9.383	3.459	5.474	2.86
5	0.45665	2.465	3.009	8.086	3.211	4.429	3.14
6	0.45031	3.072	3.261	7.838	2.952	4.371	2.83
				Mean $K_1 = 2.97\ (\pm0.13) \times 10^4$			
			Temp. = 15° C.				
1	0.47074	2.433	4.752	8.506	6.328	5.458	2.03
2	0.47440	2.046	4.764	9.107	6.619	5.154	2.10
4	0.45877	3.334	5.870	9.369	5.876	6.152	1.93
5	0.46820	2.460	5.224	8.075	5.472	4.942	2.09
6	0.46056	3.067	5.886	7.825	4.840	4.982	2.01
				Mean $K_1 = 2.03\ (\pm0.05) \times 10^4$			
			Temp. = 25° C.				
1	0.47798	2.429	6.805	8.496	8.569	5.946	1.66
2	0.48245	2.042	6.641	9.097	9.207	5.618	1.67
3	0.46130	4.170	8.210	8.857	7.968	7.639	1.52
4	0.46624	3.328	8.206	9.356	8.157	6.756	1.55
5	0.47608	2.456	7.273	8.066	7.623	5.394	1.67
6	0.46821	3.062	8.186	7.815	6.753	5.477	1.61
				Mean $K_1 = 1.61\ (\pm0.05) \times 10^4$			
			Temp. = 35° C.				
1	0.48575	2.423	9.332	8.483	11.577	6.544	1.37
2	0.49061	2.036	9.019	9.085	12.555	6.213	1.38
3	0.46816	4.163	11.423	8.840	10.619	8.450	1.29
4	0.47393	3.321	11.127	9.340	11.150	7.519	1.29
5	0.48398	2.450	9.900	8.053	10.375	5.983	1.38
6	0.47594	3.056	11.114	7.801	9.218	6.116	1.34
				Mean $K_1 = 1.34\ (\pm0.04) \times 10^4$			
			Temp. = 45° C.				
1	0.49365	2.416	12.503	8.467	15.391	7.309	1.18
2	0.49905	2.029	11.914	9.069	16.925	6.950	1.17
3	0.47488	4.152	15.668	8.817	13.799	9.545	1.14
4	0.48191	3.312	14.667	9.321	15.075	8.458	1.10
5	0.49221	2.444	13.079	8.038	13.989	6.706	1.17
6	0.48402	3.048	14.628	7.785	12.479	6.895	1.14
				Mean $K_1 = 1.15\ (\pm0.02) \times 10^4$			

Table IV. Parameters for Temperature Dependence of log *K*

Reaction	*a*	-10^2b	10^5c
$Ni^{2+} + A^-$	12.988	4.612	6.475
$Co^{2+} + A^-$	13.242	5.183	7.218

The special stability of the five-membered glycinate compared with the six-membered β-alaninate chelate rings is seen by comparing the ΔG values in Table VI. β-Alanine, containing the $—NH_2$ group in the β position undergoes complex formation with a considerably smaller positive entropy change than the corresponding α-substituted

Table V. Calorimetric Results at 25° C. (*I* = 0.1*M*)

10^3m_3, *M*	10^3m_1, *M*	pH	$10^3[MA^+]$, *M*	$-\Delta H'_1$, K cal. Mole^{-1}
		Cobalt Mono-β-alaninate		
19.99	2.000	7.39	0.3150	3.31
19.99	2.000	7.35	0.2924	3.38
19.99	10.01	7.75	2.743	3.67
19.99	10.01	7.79	2.905	4.16
13.21	9.997	7.96	2.702	3.67
16.51	9.997	7.87	2.799	3.83
		Mean $-\Delta H'_1$ = 3.67 ± 0.22 kcal. mole^{-1}		
		Nickel Mono-β-alaninate		
13.10	10.00	6.95	1.927	4.08
13.10	10.00	6.95	1.927	4.10
6.548	10.00	7.34	1.926	4.06
6.548	10.00	7.34	1.926	4.38
		Mean $-\Delta H'_1$ = 4.16 ± 0.14 kcal. mole^{-1}		
		Cobalt Monoglycinate		
6.548	1.676	8.13	1.436	2.84
9.822	1.676	7.76	1.360	2.91
8.185	1.676	7.76	1.277	2.75
9.822	1.676	7.78	1.371	2.95
8.185	1.676	7.72	1.277	2.72
		Mean $-\Delta H'_1$ = 2.83 ± 0.05 kcal. mole^{-1}		
		Copper Monoglycinate		
5.257	1.676	5.30	1.607	7.10
6.308	1.676	5.00	1.572	6.99
6.308	1.676	5.03	1.579	7.11
5.257	1.676	5.33	1.611	7.18
4.205	1.676	5.48	1.612	7.20
4.205	1.676	5.45	1.608	7.07
		Mean $-\Delta H'_1$ = 7.11 ± 0.04 kcal. mole^{-1}		
		Zinc Monoglycinate		
6.823	12.17	5.15	0.2741	3.97
6.303	12.33	5.02	0.2829	4.05
9.100	2.500	5.18	0.08567	3.20
9.100	2.500	5.57	0.1982	3.78
9.100	2.500	5.20	0.08954	3.71
		Mean $-\Delta H'_1$ = 3.74 ± 0.17 kcal. mole^{-1}		

10^3m_1, *M*	10^3m_2, *M*	pH	$10^3[MA^+]$, *M*	$10^3[MA_2]$, *M*	$-\Delta H'_2$, Kcal. Mole^{-1}
		Cobalt Diglycinate			
1.637	6.704	9.300	0.2238	1.386	2.75
1.964	6.704	9.110	0.3932	1.531	2.76
1.801	6.704	9.180	0.3083	1.460	2.71
1.637	6.704	9.310	0.2209	1.389	2.69
1.964	6.704	9.310	0.3932	1.531	2.65
1.801	6.704	9.210	0.2962	1.472	2.78
			Mean $-\Delta H'_2$ = 2.72 ± 0.02 kcal. mole^{-1}		
		Copper Diglycinate			
3.280	6.704	7.69	0.1697	3.110	7.06
2.628	6.704	10.03	0.466	2.628	7.38
2.944	6.704	9.55	1.490	2.942	6.82
3.280	6.704	7.71	0.1650	3.115	6.94
2.628	6.704	9.99	0.480	2.628	7.19
2.944	6.704	9.53	0.153	2.942	6.99
			Mean $-\Delta H'_2$ = 7.06 ± 0.09 kcal. mole^{-1}		

Table VI. Thermodynamic Properties at 25° C.

Reaction	$-\Delta H_c$, Kcal. Mole^{-1}	$-\Delta H_T$, Kcal. Mole^{-1}	$-\Delta G$, Kcal. Mole^{-1}	ΔS^a, Cal. Deg.$^{-1}$ Mole^{-1}
		Metal β-Alaninates		
$Co^{2+} + A^-$	3.32 ± 0.22	3.60	5.74 ± 0.02	8.1 ± 0.8
$Ni^{2+} + A^-$	3.81 ± 0.14	3.46	6.84 ± 0.01	10.2 ± 0.5
		Metal Glycinates		
$Co^{2+} + G^-$	2.48 ± 0.05	2.82(*3*)	6.29 ± 0.01	12.8 ± 0.3
$Ni^{2+} + G^-$	4.14 ± 0.10	4.09(*3*)	8.43 ± 0.01	14.4 ± 0.4
$Cu^{2+} + G^-$	6.76 ± 0.04		11.71 ± 0.01	16.6 ± 0.3
$Zn^{2+} + G^-$	3.39 ± 0.17		7.50 ± 0.02	13.8 ± 0.7
$CoG^+ + G^-$	2.55 ± 0.02	3.55	5.42 ± 0.02	9.6 ± 0.2
$CuG^+ + G^-$	6.89 ± 0.09		9.47 ± 0.02	8.7 ± 0.3

[a] Calculated ΔS values are based upon the calorimetric ΔH_c.

glycine. This probably reflects the greater loss of librational entropy of the substituted ligand when it chelates with the metal ion.

For the corresponding five- and six-membered ring oxalate and malonate complexes, the heats of formation are endothermic (*12*) which is consistent with the essentially electrostatic forces involved. Their stabilities are wholly dependent on the large favorable entropy changes accompanying the reactions which offset the unfavorable enthalpy effects. In contrast, the inclusion of a nitrogen atom in the chelate ring gives rise to a greater covalency, owing to the increased electron-donor capability of the nitrogen atom, and this is reflected by the exothermic heats of complex formation. In Table V the calorimetric heats of formation follow the order predicted from a consideration of ligand field stabilization, increasing in exothermicity from Co^{2+} to Cu^{2+}.

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Ethanol–Acetic Acid Esterification Equilibrium with Acid Ion-Exchange Resin as Catalyst

ALAN DARLINGTON and WILLIAM B. GUENTHER
University of the South, Sewanee, Tenn.

Equilibrium coefficients, $Q = (X_{EtA})(X_{H_2O})/(X_{HA})(X_{EtOH})$, in terms of mole fractions, X, were determined in various mixtures of the four substances in contact with sulfonic acid resin at 15°, 25°, 35°, and 50° C. At 25° C., Q varied from 1.91 to 4.58 over the composition range studied. The effect of temperature on Q was small. The times required for equilibration were about the same as those with strong acid homogeneous catalysts which, however, give higher Q values.

SINCE the work of Berthelot and St. Gilles in 1862, the ethyl acetate equilibrium has been studied extensively with strong acid homogeneous catalysts or at high temperatures to accelerate the slow reactions. Published equilibrium coefficient values, Q, at room temperatures range from about 3 to 15. (Q is dimensionless and numerically the same whether concentrations are expressed in molality, molarity, or mole fraction.) Q is used in place of a true equilibrium constant because activity coefficients are not available and they may vary as much as 100-fold in these concentrated, nonideal solutions. Studies employing HCl (*1*) and $HClO_4$ (*5*) as homogeneous catalysts yield results different from each other. An ebullioscopic study (*4*) and experiments in which dioxane was used as an inert solvent (*3*), among many others, also give divergent results. Data obtained before 1950 are reviewed in (*2*).