Spectrophotometric Determination of Stability Constants of Formato, Acetato, Propionato, Butyrato, Glycolato and Chloroacetato Complexes of Cobalt, Nickel and Copper

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Spectrophotometric investigations were performed in the visible spectral region of Co(II), Ni(II) and Cu(II) solutions in the presence of sodium salt of formic, acetic, propionic, butyric, glycolic and chloroacetic acid. On the ground of spectrophotometric data, applying the method of corresponding solutions after J. Bjerrum, the stability constants of present complexes were determined by Fronaeus' graphic method. On the basis of these values the values of stability constants were then calculated together with the corresponding error limits by means of a digital computer by applying the Gauss Z programme after R. S. Tobias.

In the systematic investigation of complexes of metal ions with the ions of unsubstituted and substituted monocarboxylic acids the polarographic method had been used[1-3]. In order to be able to appreciate critically the values of stability constants obtained by the polarographic method, we applied essentially different methods from the polarographic one, and these are the spectrophotometric method, primarily, and then the potentiometric method of measuring the changes of pH of the buffer solution. This paper reports the results of investigations of monocarboxylato complexes of cobalt, nickel and copper by the spectrophotometric method.

Among numerous spectrophotometric methods[4,5] the method of corresponding solution after J. Bjerrum[6] was applied. This method proved to be a very suitable one for the investigated systems in the visible spectral region. The possibility of the application of K. B. Yatsimirskii's method[7] was also investigated.

EXPERIMENTAL

The measurement of the extinction of investigated solutions was performed by means of a Universal VSU 1 spectrophotometer (Carl Zeiss, Jena), equipped for work in the visible spectral region. All investigated systems had a constant ionic strength of 2 and a constant $pH = 4.1 \pm 0.1$, with the exception of chloroacetate, where $pH = 3.8 \pm 0.1$. The light absorption curves were recorded at room temperature (20—25° C), except for chloroacetato complexes which were recorded at 10° C (because of the hydrolysis of chloroacetate at higher temperatures). The reproducibility of the extinction measurement (at the extinction value of 0.4) was ± 0.001 for the same solution, and within ± 0.005 for repeatedly prepared solutions of the same kind.

From the recorded light absorption curves in the visible spectral region (Figs. 1—3) wavelengths were chosen so as to achieve the greatest possible separation of absorption curves with respect to the change of concentration and the kind of ligand. Measurements of extinction were performed at following wavelengths: for copper 760 nm, for nickel 670 nm and for cobalt 520 nm.

Solutions for measurements were prepared from analytical pure chemicals. Cobalt and nickel pechlorate were prepared from the corresponding carbonates and copper perchlorate from oxide. Salts obtained by crystallization were twice recrystallized and then the stock solutions were prepared. Solutions of mono-carboxylic acids and their salts were prepared as described earlier[1,3]. Buffer solutions of a constant acid to salt ratio were prepared, this ratio being 1 : 2 for formate and glycolate, 1 : 8 for chloroacetate, 5 : 1 for acetate, and 6 : 1 for propionate and acetate solutions. The ionic strength of buffer solutions of the metal ion was kept at a constant value of 2 by adding sodium perchlorate.

RESULTS

The applied method of corresponding solutions according to J. Bjerrum[6] requires the extinction of the ligand (L) to be negligibly small in comparison with the extinction of the formed complex (ML_n), that the ionic strength of solutions is constant, that no association and dissociation of system components occur and that Lambert-Beer's law is valid for single complex species. Then, the total extinction is equal to:

$$E = d \sum_{n=1}^{n=N} \varepsilon_n \, [ML_n]$$

where d is the length of the optical path, ε_n is the molar extinction coefficient of the single complex species and $[ML_n]$ is its concentration. When two solutions with different total concentrations of metal ligand have the same extinction, they also have the same percentage share of single complex species. In other words, such solutions have the same average ligand number $\bar{n}$ and the same concentration of the free ligand [L]. Then:

$$\bar{n} = \frac{C'_L - [L]}{C'_M} = \frac{C''_L - [L]}{C''_M}$$

where C_L is the total concentraion of the ligand and C_M the total concentration of the metal ion. Therefrom:

$$\bar{n} = \frac{C'_L - C''_L}{C'_M - C''_M}$$

and

$$[L] = \frac{C'_M \, C''_L - C''_M \, C'_L}{C'_M - C''_M}$$

Accordingly, for one series of solutions, maintaining a constant concentration of the metal ion C'_M and a constant optical path d', extinctions $(E)_\lambda$ were recorded at the determined wavelength, for different ligand concentrations $(C_L)_n$ (n = 1, 2 .... j). Thus the $(E)_\lambda = f'(C_L)_n$ curve was obtained. Then, at another metal ion concentration C''_M and another thickness of the cuvette d", satisfying the condition that $C''_M \times d'' = C'_M \times d'$, extinctions for

different concentrations of the ligand $(C_L)_n$ were recorded. Thus the second $(E)_\lambda = f''(C_L)_n$ curve was obtained. The third $(E)_\lambda = f'''(C_L)_n$ curve was obtained analogously. From these three curves pairs of corresponding solutions were obtained, i. e. solutions of the same extinction with different C_L', C_M'; C_L'', C_M'', and C_L''', C_M'''. If a linear dependence C_L on C_M is obtained for every group of corresponding solutions, of course within the experimental error, it can be concluded that there are no polynuclear complexes in the system, and in this case $\bar{n}$ and [L] can be obtained, namely [L] as the intercept on the ordinate and $\bar{n}$ as the slope of the straight line. $\bar{n}$ and [L] are evaluated numerically using the method of least squares. On the ground of these magnitudes stability constants were graphically determined[9] by applying the method of S. Fronaeus[8]. This method enabled the assumption that there are several complexes in the system and then, by a more detailed analysis, it was established how many complex species were actually present.

Stability constants, estimated by the above mentioned graphical method, together with C_M, log [L] and $\bar{n}$ values, were treated using the Gauss Z programme devised by R. S. Tobias[10] for non-linear least-squares refinement of equilibrium constants. The calculations were performed by a CAE 90-40 (SDS 930) digital computer in the Institute »Ruđer Bošković«. The computer performed (according to the programme) 10 refinement cycles. Output data contained the stability constants and their standard errors as well as correlation matrix and calculated formation function. In some cases the above mentioned programme yielded results converging in a wrong direction. This happened most frequently when the correlation between the constants was strongly expressed or when graphically obtained stability constants differed greatly from the values that would best satisfy the experimental data. In the latter case the system was again treated by the graphical method, and — if necessary — a smaller number of existing complex species assumed, and then again treated on the digital computer. In these cases satisfactory refined values for the stability constants were obtained.

Extinction curves, as the functions of the total ligand concentration, were recorded for three different metal ion concentrations. When doing this, a constant product of the total metal concentration and the thickness of the cuvette was maintained in every series. During the change of the metal ion concentration (without the addition of the ligand) and the thickness of the cuvette Lambert-Beer's law was satisfied. Results of measurements are given in Tables I, III and V. From the curves obtained the corresponding solutions were determined, having the same extinction for the different total metal ion and total ligand concentrations. Data for such solutions are given in Tables II, IV and VI.

With copper ion solutions in the presence of acetate, propionate, butyrate and glycolate the measurement could not be performed at higher monocarboxylate concentrations because of the precipitation of a weakly soluble complex. Therefore, measurements in these systems could comprise only lower complex species present in the solution.

The values of stability constants of the investigated complexes, obtained by the graphical and computational methods are given in Table VII.

TABLE I

Cobalt Solutions

C_L mM	Formate			Acetate			Propionate		
	Extinction				$\lambda = 520$ nm				
	1	2	3	1	2	3	1	2	3
20	0.352	0.347	0.343	0.355	0.349	0.343	0.355	0.352	0.345
40	0.361	0.353	0.347	0.363	0.356	0.351	0.366	0.358	0.351
60	0.371	0.361	0.352	0.373	0.363	0.353	0.375	0.365	0.355
80	0.380	0.368	0.359	0.383	0.371	0.360	0.385	0.373	0.362
100	0.387	0.375	0.364	0.392	0.379	0.365	0.397	0.381	0.366
130	0.400	0.386	0.370	0.403	0.389	0.371	0.409	0.392	0.375
170	0.413	0.396	0.381	0.416	0.401	0.381	0.425	0.407	0.385
200	0.422	0.407	0.387	0.427	0.412	0.388	0.437	0.418	0.393
250	0.436	0.419	0.398	0.445	0.425	0.399	0.455	0.433	0.405
300	0.448	0.432	0.410	0.459	0.435	0.412	0.474	0.452	0.419
350	0.461	0.445	0.419	0.475	0.454	0.422	0.493	0.469	0.432
400	0.475	0.455	0.428	0.489	0.468	0.433	0.508	0.482	0.445
450	0.485	0.466	0.435	0.502	0.480	0.444	0.524	0.498	0.460
500	0.494	0.475	0.443	0.513	0.493	0.454	0.540	0.515	0.472
550	0.506	0.484	0.449	0.524	0.504	0.465	0.555	0.531	0.483
600	—	0.494	0.455	0.535	0.512	0.475	—	—	0.498

C_L mM	Butyrate			Glycolate			Chloroacetate		
	Extinction				$\lambda = 520$ nm				
	1	2	3	1	2	3	1	2	3
20	0.348	0.349	—	0.405	0.361	0.352	0.342	0.342	0.342
40	0.355	0.354	—	0.458	0.393	0.370	0.345	0.345	0.344
60	0.367	0.366	0.361	0.510	0.421	0.383	0.348	0.347	0.346
80	0.375	0.373	0.364	0.555	0.447	0.400	0.351	0.350	0.348
100	0.385	0.381	0.369	0.592	0.477	0.412	0.354	0.353	0.351
130	0.402	0.393	0.376	0.642	0.515	0.439	0.358	0.356	0.354
170	0.417	0.406	0.385	0.690	0.565	0.460	0.364	0.362	0.359
200	0.422	0.418	0.395	0.720	0.594	0.478	0.468	0.366	0.362
250	0.452	0.438	0.405	0.752	0.638	0.518	0.374	0.371	0.367
300	0.472	0.458	0.418	0.785	0.680	0.545	0.381	0.378	0.374
350	0.495	0.478	0.437	0.809	0.710	0.575	0.387	0.384	0.379
400	0.519	0.495	0.449	0.830	0.750	0.610	0.393	0.390	0.385
450	0.544	0.525	0.473	0.852	0.775	0.640	0.398	0.395	0.390
500	0.564	0.542	0.489	0.865	0.800	0.662	0.403	0.400	0.394
550	0.497	0.568	0.504	0.875	0.816	0.695	0.408	0.405	0.399
600	0.622	0.595	0.520	—	0.830	0.720	0.412	0.409	0.403

1 : 36 mM Co^{2+}; d = 2 cm   2 : 144 mM Co^{2+}; d = 0.5 cm   3 : 360 mM Co^{2+}; d = 0.2 cm

TABLE II
Cobalt Solutions

E $\lambda = 520$ nm	Formate C_L mM			Acetate C_L mM			Propionate C_L mM		
	1	2	3	1	2	3	1	2	3
0.375	—	—	—	67	92	139	55	85	134
0.381	—	—	—	—	—	—	68	101	158
0.387	104	137	194	97	125	191	81	117	182
0.394	—	—	—	112	145	216	95	134	204
0.400	131	180	255	127	165	245	108	150	230
0.406	150	201	285	144	186	273	122	168	253
0.412	168	223	318	160	205	301	135	185	279
0.419	188	244	353	178	226	329	150	203	303
0.425	209	269	389	196	248	357	165	220	327
0.431	232	294	427	213	268	387	182	237	352
0.437	255	320	468	231	290	414	198	256	375
0.444	277	348	518	251	313	447	216	275	401
0.450	303	378	558	269	336	476	233	294	424
0.456	328	408	603	290	359	504	250	314	448
0.462	—	—	—	310	383	536	266	334	472
0.469	—	—	—	332	408	569	284	352	495
0.475	—	—	—	353	433	600	302	372	521
0.481	—	—	—	375	460	634	319	392	545
0.487	—	—	—	398	485	667	337	412	568
0.494	—	—	—	421	512	702	374	453	616
0.500	—	—	—	445	539	736	356	433	592

E $\lambda = 520$ nm	Butyrate C_L mM			E $\lambda = 520$ nm	Glycolate C_L mM			E $\lambda = 520$ nm	Chloroacetate C_L mM		
	1	2	3		1	2	3		1	2	3
0.360	50	60	94	0.460	37	88	172	0.355	107	115	135
0.370	70	85	130	0.480	46	103	201	0.360	144	155	181
0.380	92	114	170	0.500	52	117	232	0.365	180	195	225
0.390	112	140	205	0.520	63	133	260	0.370	219	230	268
0.400	130	168	242	0.540	71	149	293	0.375	256	277	314
0.410	152	197	274	0.560	82	168	327	0.380	295	318	361
0.420	174	223	306	0.580	91	186	361	0.385	336	362	410
0.430	198	250	335	0.600	103	206	393	0.390	378	406	460
0.440	218	275	365	0.620	115	228	426	0.395	422	453	512
0.450	242	300	396	0.640	127	252	460	0.400	467	502	565
0.460	262	324	424	0.660	143	275	498	0.405	515	552	623
0.470	284	347	453	0.680	160	300	532	0.410	570	609	690
0.480	307	372	481	0.700	178	328	568				
0.490	328	359	507	0.720	200	356	609				
0.500	350	418	534	0.740	227	387	655				
0.510	371	441	562	0.760	258	420	705				
0.520	392	464	587	0.780	292	459	762				
0.530	415	486	614	0.800	330	503	825				
0.540	435	509	638	0.820	374	564	900				
0.550	458	530	663								
0.560	479	552	687								
0.570	500	573	712								

1 : 36 mM Co^{2+}; d = 2 cm   2 : 144 mM Co^{2+}; d = 0.5 cm   3 : 360 mM Co^{2+}; d = 0.2 cm

TABLE III

Nickel Solutions

C_L mM	Formate			Acetate			Propionate		
	Extinction			$\lambda = 670$ nm					
	1	2	3	1	2	3	1	2	3
40	—	—	—	—	—	—	0.302	0.298	0.297
60	—	—	—	0.302	0.299	0.297	0.309	0.304	0.300
80	—	—	—	0.305	0.301	0.298	0.311	0.306	0.302
100	0.305	0.303	0.301	0.308	0.303	0.299	0.315	0.310	0.303
150	0.312	0.308	0.303	0.315	0.310	0.303	0.324	0.318	0.309
200	0.317	0.314	0.308	0.323	0.316	0.308	0.333	0.326	0.315
250	0.322	0.318	0.312	0.328	0.322	0.314	0.341	0.333	0.320
300	0.328	0.323	0.317	0.336	0.327	0.317	0.349	0.340	0.326
350	0.332	0.328	0.319	0.341	0.332	0.321	0.357	0.347	0.332
400	0.338	0.332	0.323	0.346	0.338	0.326	0.368	0.353	0.337
450	0.342	0.336	0.328	0.352	0.343	0.330	0.371	0.359	0.342
500	0.347	0.340	0.331	0.357	0.348	0.335	0.377	0.364	0.347
550	0.352	0.344	0.334	0.360	0.353	0.339	—	—	—
600	0.356	0.348	0.337	0.365	0.357	0.344	—	—	0.356
700	0.361	0.354	0.344	—	—	—	—	—	—
800	0.366	0.360	0.349	—	—	—			

C_L mM	Butyrate			Glycolate			Chloroacetate		
	Extinction			$\lambda = 670$ nm					
	1	2	3	1	2	3	1	2	3
40	0.299	0.297	0.295	0.377	0.342	0.321	—	—	—
60	0.303	0.300	0.297	0.413	0.367	0.331	0.294	0.293	0.293
80	0.305	0.303	0.299	0.444	0.392	0.347	0.294	0.293	0.293
100	0.310	0.306	0.301	0.476	0.415	0.358	0.294	0.293	0.293
150	0.318	0.312	0.307	0.543	0.467	0.390	0.294	0.293	0.293
200	0.328	0.319	0.312	0.594	0.514	0.423	0.294	0.293	0.293
250	0.338	0.328	0.317	0.633	0.555	0.449	0.294	0.293	0.293
300	0.347	0.335	0.323	0.662	0.595	0.484	0.294	0.294	0.293
350	0.356	0.342	0.330	0.685	0.625	0.509	0.294	0.294	0.293
400	0.366	0.351	0.336	0.705	0.648	0.537	0.294	0.294	0.293
450	0.375	0.359	0.343	0.722	0.675	0.567	0.294	0.294	0.293
500	0.385	0.368	0.350	0.740	0.692	0.586	0.295	0.294	0.293
550	0.397	0.377	0.358	0.753	0.708	0.609	0.295	0.294	0.293
600	—	—	0.368	0.762	0.722	0.635	0.295	0.295	0.293
700	—	—	0.383	0.778	0.747	0.666	0.297	0.294	0.293
800	—	—	—	0.788	0.772	0.690	0.297	0.295	0.293

1 : 80 mM Ni^{2+}; d = 2 cm   2 : 160 mM Ni^{2+}; d = 1 cm   3 : 320 mM Ni^{2+}; d = 0.5 cm

TABLE IV

Nickel Solutions

E $\lambda = 670$ nm	Formate C_L mM			Acetate C_L mM			Propionate C_L mM		
	1	2	3	1	2	3	1	2	3
0.300	54	67	93	—	—	—	—	—	—
0.305	94	116	158	—	—	—	—	—	—
0.308	116	140	193	—	—	—	—	—	—
0.310	137	163	225	113	150	218	—	—	—
0.313	160	190	256	—	—	—	—	—	—
0.315	180	215	288	146	190	272	95	129	202
0.318	252	293	387	163	212	299	112	145	225
0.320	227	266	355	180	234	327	123	161	245
0.323	251	293	389	198	256	355	140	178	268
0.325	274	320	422	218	278	380	150	195	290
0.328	298	350	456	238	300	408	167	212	314
0.330	322	380	493	255	323	438	178	229	336
0.333	346	409	528	275	347	468	195	246	358
0.335	371	440	566	294	372	500	207	264	383
0.338	395	470	603	318	395	530	225	282	408
0.340	423	499	643	337	420	560	239	300	432
0.343	450	530	680	360	445	588	256	320	457
0.345	476	562	720	380	470	625	270	338	482
0.348	503	595	768	—	—	—	288	358	508
0.350	—	—	—	—	—	—	303	377	534
0.353	—	—	—	—	—	—	320	397	560
0.355	—	—	—	—	—	—	337	417	590

E $\lambda = 670$ nm	Butyrate C_L mM			E $\lambda = 670$ nm	Glycolate C_L mM		
	1	2	3		1	2	3
0.300	44	60	85	0.375	40	67	130
0.305	75	97	135	0.425	68	110	210
0.310	104	132	183	0.450	82	133	252
0.315	133	168	227	0.475	100	156	291
0.320	162	202	273	0.500	114	185	338
0.325	190	235	315	0.525	135	213	377
0.330	218	268	356	0.550	155	244	424
0.335	244	300	395	0.575	180	275	470
0.340	272	333	433	0.600	207	310	525
0.345	298	364	467	0.625	240	350	590
0.350	324	395	500	0.650	280	400	660
0.355	350	425	534	0.675	325	450	795
0.360	375	455	565	0.700	390	520	825
0.365	399	483	595	0.725	460	605	920
0.370	423	512	626				
0.375	448	540	655				
0.380	470	568	685				

1 : 80 mM Ni^{2+}; d = 2 cm   2 : 160 mM Ni^{2+}; d = 1 cm   3 : 320 mM Ni^{2+}; d = 0.5 cm

TABLE V

Copper Solutions

C_L mM	Formate Extinction, $\lambda = 760$ nm			C_L mM	Acetate Extinction, $\lambda = 760$ nm			C_L mM	Propionate Extinction, $\lambda = 760$ nm		
	1	2	3		1	2	3		1	2	3
10	0.214	0.182	0.167	5	0.204	0.171	—	10	—	0.190	0.174
20	0.237	0.204	0.177	10	0.236	0.187	—	20	0.294	0.237	0.184
40	0.282	0.248	0.206	15	0.269	0.207	0.170	30	0.333	0.274	0.208
60	0.320	0.286	0.234	20	0.293	0.229	0.178	40	0.365	0.307	0.230
80	0.347	0.313	0.257	25	0.313	0.251	0.190	50	0.385	0.335	0.255
100	0.367	0.338	0.282	30	0.327	0.268	0.204	60	0.409	0.365	0.278
130	0.393	0.366	0.313	40	0.356	0.298	0.225	80	0.440	0.413	0.321
170	0.418	0.393	0.345	50	0.379	0.327	0.246	100	0.463	0.458	0.367
200	0.430	0.410	0.364	60	0.398	0.350	0.264				
250	0.450	0.435	0.388	80	0.426	0.385	0.304				
300	0.465	0.450	0.413	100	0.445	0.416	0.340				
350	0.473	0.462	0.432	130	0.469	0.454	0.385				
400	0.485	0.472	0.446	170	0.489	0.490	0.440				
450	0.495	0.486	0.455								
500	0.503	0.496	0.465								

C_L mM	Butyrate Extinction, $\lambda = 760$ nm			C_L mM	Glycolate Extinction, $\lambda = 760$ nm			C_L mM	Chloroacetate Extinction, $\lambda = 760$ nm		
	1	2	3		1	2	3		1	2	3
5	0.205	0.173	0.171	5	0.217	0.177	0.170	10	0.190	—	—
10	0.235	0.189	0.175	10	0.250	0.189	0.176	20	0.201	0.192	0.178
15	0.268	0.217	0.182	15	0.283	0.205	0.181	40	0.230	0.214	0.195
20	0.295	0.236	0.190	20	0.298	0.220	0.186	60	0.259	0.237	0.215
25	0.313	0.255	0.201	30	0.324	0.250	0.198	80	0.277	0.260	0.230
30	0.343	0.277	0.211	40	0.337	0.273	0.212	100	0.301	0.276	0.247
40	0.372	0.316	0.233	50	0.352	0.293	0.228	130	0.325	0.299	0.270
50	0.407	0.359	0.263	60	0.362	0.315	0.240	170	0.352	0.328	0.294
				80	0.375	0.340	0.266	200	0.371	0.343	0.312
				100	0.387	0.360	0.289	250	0.392	0.367	0.333
				120	0.398	0.374	0.310	300	0.409	0.389	0.360
				140	0.408	0.385	0.329	350	0.425	0.405	0.375
				160	0.412	0.393	0.344	400	0.437	0.420	0.390
				180	0.418	0.400	0.358	450	0.448	0.429	0.405
				200	0.423	0.406	0.372	500	0.457	0.440	0.414

1 : 5 mM Cu^{2+}; d = 3 cm   2 : 30 mM Cu^{2+}; d = 0.5 cm   3 : 75 mM Cu^{2+}; d = 0.2 cm

TABLE VI
Copper Solutions

E λ = 760 nm	Formate C_L mM			E λ = 760 nm	Acetate C_L mM			E λ = 760 nm	Propionate C_L mM		
	1	2	3		1	2	3		1	2	3
0.280	39	59	99	0.210	6.5	16.0	32.5	0.230	9.5	19.0	40.0
0.290	43	65	108	0.220	7.5	18.5	37.0	0.240	10.0	21.5	44.5
0.300	49	71	117	0.230	9.0	21.5	42.5	0.250	11.5	24.0	48.0
0.310	54	78	128	0.240	11.0	23.5	47.5	0.260	13.0	27.0	53.0
0.320	60	86	138	0.250	12.5	26.0	52.5	0.270	15.0	29.5	57.5
0.330	67	94	150	0.260	14.5	29.0	57.5	0.280	16.5	32.5	62.0
0.340	74	102	162	0.270	16.5	32.0	63.0	0.290	18.5	35.0	67.0
0.350	82	113	177	0.280	18.0	35.0	68.5	0.300	21.0	38.0	71.5
0.360	93	124	193	0.290	20.5	38.5	73.5	0.310	23.0	41.0	75.5
0.370	104	137	210	0.300	22.5	41.5	78.5	0.320	26.0	44.5	80.0
0.380	115	150	230	0.310	25.0	45.0	84.0	0.330	29.0	48.5	84.5
0.390	129	165	251	0.320	28.0	48.5	90.0	0.340	31.5	52.5	89.0
0.400	142	182	273	0.330	30.5	52.5	95.0	0.350	35.0	55.5	93.0
0.410	158	201	297	0.340	34.5	57.5	101.0	0.360	38.5	59.0	98.0
0.420	176	220	320	0.350	38.5	62.0	107.5	0.370	42.0	63.0	102.0
0.430	199	243	348	0.360	42.5	66.5	113.5	0.380	46.5	66.5	106.0
0.440	225	272	380	0.370	47.0	73.0	120.5				
				0.380	52.0	79.0	127.0				
				0.390	57.5	85.0	134.0				
				0.400	62.5	91.5	141.5				

E λ = 760 nm	Butyrate C_L mM			E λ = 760 nm	Glycolate C_L mM			E λ = 760 nm	Chloroacetate C_L mM		
	1	2	3		1	2	3		1	2	3
0.190	3.0	9.0	20.5	0.200	4.0	13.5	29.5	0.250	57	73	104
0.200	4.5	12.0	26.0	0.210	4.5	16.5	36.0	0.260	63	84	118
0.210	6.0	14.0	31.0	0.220	6.0	20.0	43.0	0.270	72	93	130
0.220	7.5	16.5	35.0	0.230	7.5	23.0	51.0	0.280	81	105	145
0.230	8.5	18.5	39.5	0.240	9.0	27.0	58.5	0.300	100	129	178
0.240	10.5	21.0	43.0	0.250	10.5	30.0	66.0	0.310	111	144	197
0.250	12.0	23.5	47.0	0.260	11.0	34.5	76.0	0.320	122	158	215
0.260	14.0	26.0	50.5	0.270	13.0	39.0	83.5	0.330	135	173	237
0.270	15.5	28.5	53.5	0.280	15.0	43.0	91.5	0.340	149	190	260
0.280	17.5	31.0	57.0	0.290	17.5	47.5	100.0	0.350	164	208	285
				0.300	20.5	52.5	110.0	0.360	181	229	312
				0.310	24.0	57.5	120.0	0.370	199	252	340
				0.320	28.5	63.5	132.0	0.380	219	276	370
				0.330	34.0	70.5	144.0	0.390	242	304	403
				0.340	40.5	80.0	157.0	0.400	270	335	437
				0.350	50.0	89.0	170.0				
				0.360	60.0	100.0	184.0				
				0.370	72.0	114.0	198.0				
				0.380	88.0	130.0	214.0				

1 : 5 mM Cu^{2+}; d = 3 cm   2 : 30 mM Cu^{2+}; d = 0.5 cm   3 : 75 mM Cu^{2+}; d = 0.2 cm

TABLE VII

Stability Constants (± standard errors)

Ligand	Metal Ion	β_1		β_2		β_3	
		graph.	comp.	graph.	comp.	graph.	comp.
Formate	Co²⁺	2.9	2.5 ± 0.3	6.2	8.3 ± 1.0	—	—
	Ni²⁺	3.8	2.5 ± 0.4	6.9	7.2 ± 1.5	—	—
	Cu²⁺	45	45 ± 6	515	355 ± 62	1270	2100 ± 300
Acetate	Co²⁺	4.5	4.1 ± 0.1	2.2	4.1 ± 0.5	—	—
	Ni²⁺	6.5	6.6 ± 0.3	9.9	9.8 ± 0.7	—	—
	Cu²⁺	155	129 ± 3	880	730 ± 30	—	—
Propionate	Co²⁺	6.3	6.0 ± 0.2	1.2	1.3 ± 0.1	—	—
	Ni²⁺	7.5	7.2 ± 0.6	16	18 ± 2	—	—
	Cu²⁺	139	145 ± 3	—	—	—	—
Butyrate	Co²⁺	4.2	4.1 ± 0.1	—	—	—	—
	Ni²⁺	6.5	6.5 ± 0.7	6.5	6.3 ± 2.6	—	—
	Cu²⁺	120	121 ± 5	—	—	—	—
Glycolate	Co²⁺	20	20 ± 1	120	115 ± 3	—	—
	Ni²⁺	51	42 ± 6	508	503 ± 43	—	—
	Cu²⁺	200	171 ± 10	17 000	17 400 ± 400	—	—
Chloroacetate	Co²⁺	0.9	1.0 ± 0.1	—	—	—	—
	Cu²⁺	18	18 ± 8	40	38 ± 24	603	831 ± 169

DISCUSSION

Literature data about the spectrophotometric determination of stability constants of monocarboxylato complexes which were the subject of our investigations are very scarce[11]. Besides, the published values of stability constants for the same complex differ greatly. Thus, the values 42 (S. Fronaeus) and 155 (W. D. Bale *et al.*) are given for β_1 of the copper acetato complexes, and the values 13 (S. K. Siddhanta and S. N. Banerjee) and 45 (G. Watelle-Morion) of the nickel acetato complexes. The value 105 was quoted for β_1 of the copper formato complex (W. D. Bale *et al.*) and 270 (S. Fronaeus) of the glycolato complexes. These literature data do not agree with the values given in Table VII. One of the reasons for this is the difference in the composition of the medium, and most probably, the difference in the treatment of results. A comparison of the obtained values of stability constants with the values obtained by the polarographic[1,3] and potentiometric method, as well as a discussion of the compared results will be given in another paper.

From the values of the first stability constant (β_1) it can be seen (Table VII) that the stability of the monoligand complex increases for all investigated systems in the series:

Co $<$ Ni $<$ Cu

ClAc $<$ Form $<$ Ac, But $<$ Prop $<$ Glycol
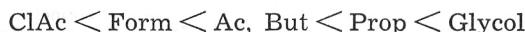
The first series is in agreement with the natural order established by Irving and Williams[12]. Considerably higher stability of copper complexes is attributed to the additional Jahn-Teller stabilization effect and, partially to the relatively stronger acceptor properties of the basic state of the copper(II) ion[13-15].

The second series, with the exception of glycolate, is in agreement with the increase of the basicity of the electron donor ligand[11]. The position of glycolate in the order is due to the presence of the OH group in the ligand so that the ligand is also bonded with the metal ion over the OH group[16]. Chloroacetato complexes of cobalt and nickel are so weak that their presence
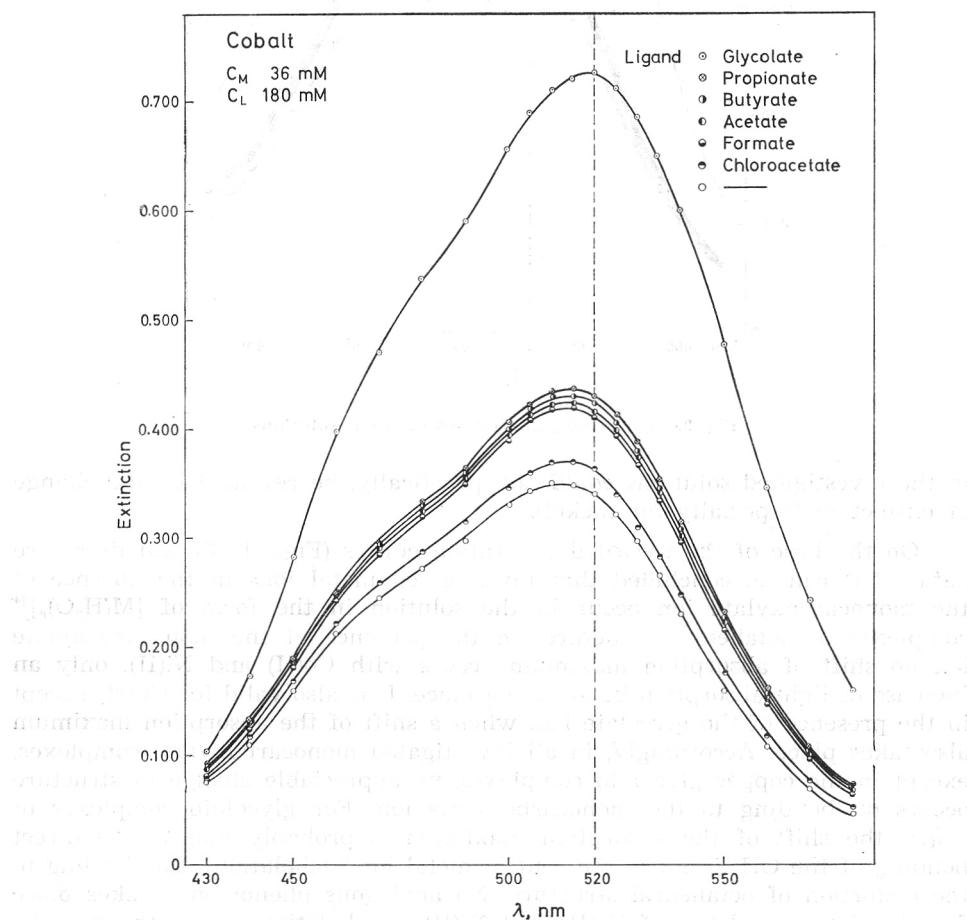
Fig. 1. Light absorption curves of Co(II) solutions.
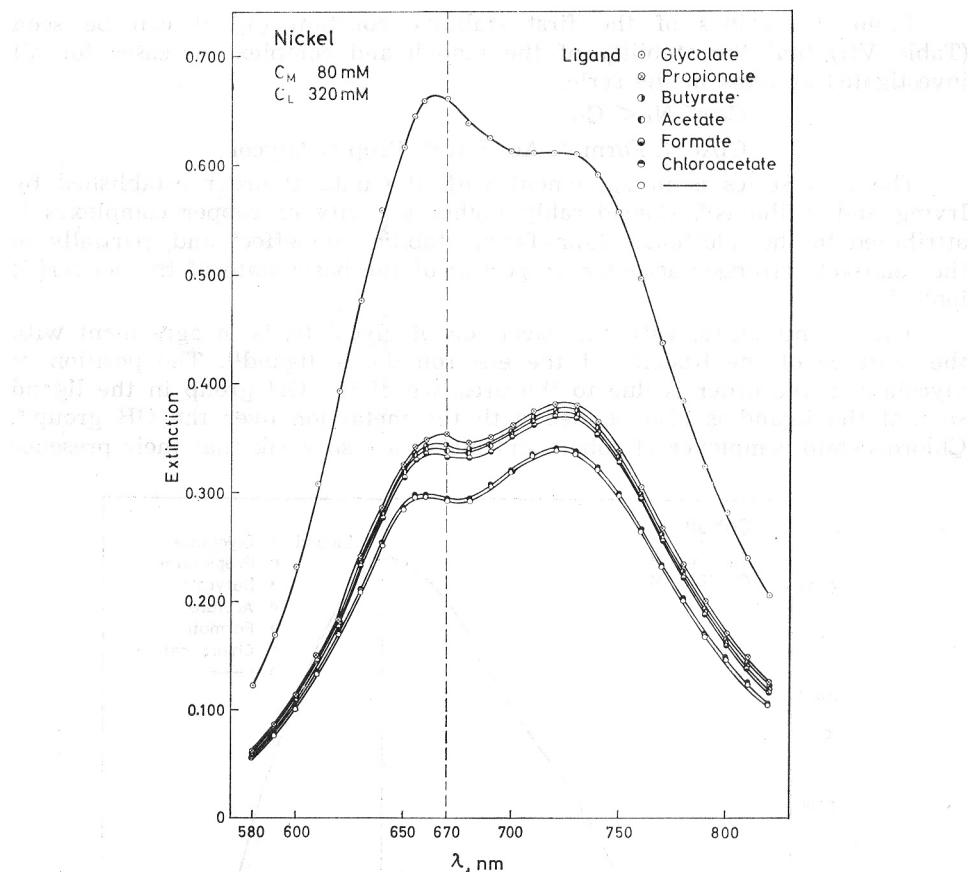
Fig. 2. Light absorption curves of Ni(II) solutions.

in the investigated solutions could not, practically, be revealed by the change of extinction (especially for nickel).

On the base of the recorded absorption curves (Figs. 1—3) and literature data[17-19] it can be concluded that investigated metal ions in the absence of the monocarboxylate ion occur in the solution in the form of $[M(H_2O)_6]^{2+}$ complexes of octahedral structure. In the presence of the monocarboxylate ion no shift of absorption maximum occurs with Co(II) and Ni(II), only an increase of light absorption band taking place. It is also valid for Cu(II) except in the presence of the glycolate ion, when a shift of the absorption maximum also takes place. Accordingly, in all investigated monocarboxylato complexes, except in the copper glycolato complexes, no appreciable change in structure occurs on bonding to the monocarboxylate ion. For glycolato complexes of Cu(II) the shift of the absorption maximum is probably due to the direct bonding of the OH group to the central metal ion[16] (chelation), this leading to the distortion of octahedral structure. No analogous phenomenon takes place for glycolato complexes of Co(II) and Ni(II), as chelation occurs through the water molecules[16].
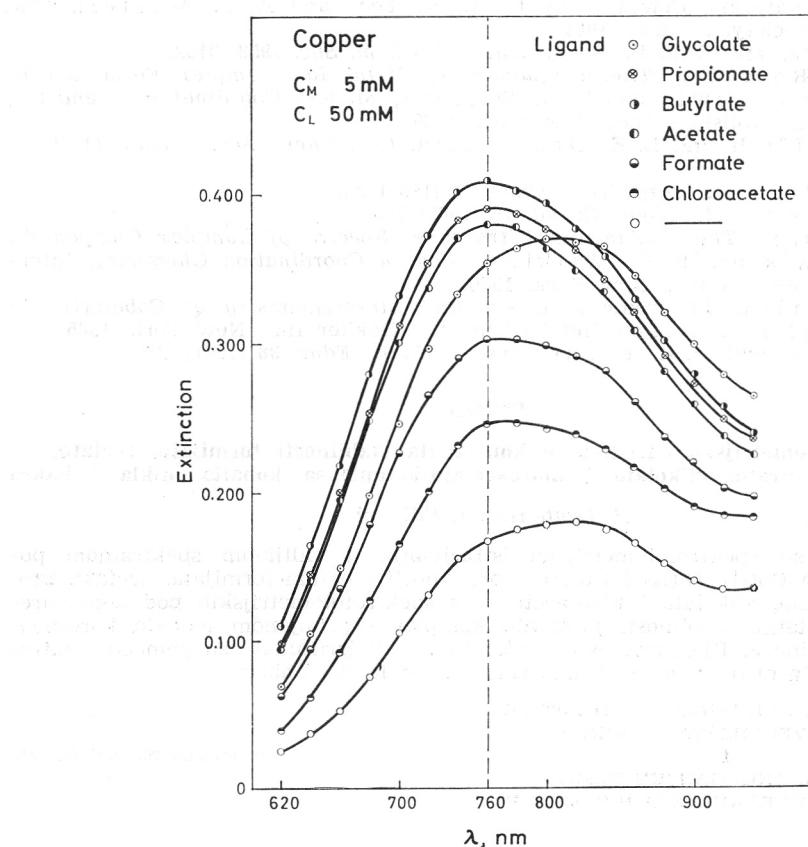
Fig. 3. Light absorption curves of Cu(II) solutions.

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IZVOD

Spektrofotometrijsko određivanje konstanata stabilnosti formijato, acetato, propionato, butirato, glikolato i kloroacetato-kompleksa kobalta, nikla i bakra

B. Grabarić i I. Filipović

Izvršena su spektrofotometrijska istraživanja u vidljivom spektralnom području otopina Co(II), Ni(II) i Cu(II) u prisutnosti natrium-formijata, acetata, propionata, butirata, glikolata i kloroacetata. Iz spektrofotometrijskih podataka određene su konstante stabilnosti prisutnih kompleksa primjenom metode korespondirajućih otopina J. Bjerruma. Konstante stabilnosti izračunate su pomoću elektroničkog računala primjenom programa Gauss Z od R. S. Tobiasa.