TITRIMETRIC DETERMINATION OF SOME ANALYTICALLY SIGNIFICANT ORGANIC REAGENTS USING A Cd^{2+}-SELECTIVE ELECTRODE CRYTUR

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Dedicated to Professor A. Okáč, corresponding member of the Czechoslovak Academy of Sciences, on the occasion of his 75th birthday.

A Cd^{2+} selective electrode Crytur 48—17 proved to serve well for the titrimetric determination of some types of organic reagents, particularly of 8-hydroxyquinoline and its derivatives, sodium N,N-diethyldithiocarbaminate, pyridylazo dyes (PAN, PAR), and aminocarboxylic acids (NTA, EDTA, DCTA) with 0·01M cadmium nitrate solution in the medium of ammoniacal or borate buffers. The titrimetric determinations examined can be classified as precise analytical methods.

Analytical applications of Cd^{2+}-selective electrodes have been recently reported in the reviews[1-5]. In addition to direct potentiometric measurements, the electrodes can also be employed for potentiometric indication of chelometric titrations. This is frequently a more convenient method for the determination of the ion concentration in the sample, as the electrode sensitivity is not constant over the whole concentration region, the working curve slope varies with the temperature and ageing of the membrane, and, moreover, some ions exhibit interfering effects. Indication of chelometric titrations of cadmium ions is usually recommended even in the electrode instruction manuals.[6] In addition to ethylenediaminotetraacetic acid (EDTA), also nitrilotriacetic acid (NTA) and 8-hydroxyquinoline have been used as titrants for the determination of cadmium[7]. Since in many analytical procedures and particularly in physicochemical studies the concentration of the organic reagent is relevant, we studied in this work the possibility of the reverse approach, *i.e.* the determination of organic substances containing chelating functional groups with a cadmium nitrate solution.

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EXPERIMENTAL

Solutions, Apparatus and Measurement Procedures

Cadmium nitrate solutions (0·1M and 0·01M) were prepared from a reagent grade purity chemical (Lachema) and standardized chelometrically in ammoniacal buffer using Eriochrome Black T (ref.[8]). The 0·01M-EDTA solution used was standardized using recrystallized lead dichloride in the medium of hexamine buffer[9].

The stock solutions of the substances titrated were prepared from the available chemicals in approximately 0·01M and 0·001M concentrations. The low-soluble organic acids were converted to their sodium salts by adding sodium hydroxide. The following preparations were used: 8-hydroxyquinoline, EDTA, NTA, and sodium N,N-diethyldithiocarbaminate reagent grade purity, 8-hydroxyquinoline-5-sulfonic acid pure, PAN, PAR, and Indoferrone "indicator" grade (all Lachema), 8-hydroxyquinoline-7-iodo-5-sulfonic acid pure (Sanitas), Bismuton pro grav. (IBA), and diaminocyclohexane-N,N,N',N'-tetraacetic acid (DCTA) pure (IEL). Acetate[10], hexamine, borate, and ammoniacal[11], and maleic[12] buffers were prepared.

The measurement cell for the potentiometric titrations was set up from a Cd^{2+}-selective electrode Crytur type 48—17 (Monokrystaly, Turnov, Czechoslovakia) and saturated calomel electrode. The changes of the equilibrium voltage were read by means of a Universal pH-meter OP-204/1 (Radelkis, Budapest). The pH values of the solutions titrated were measured by using a cell set up from a glass electrode OP-7171 (Radelkis) and a saturated calomel electrode, calibrated by employing standard solutions of the conventional activity scale.

RESULTS AND DISCUSSION

The shape of a potentiometric titration curve is governed first of all by the solubility of the precipitate created in the case of precipitation titrations, or by the stability of the complex formed. These principal equilibria are additionally affected by other side equilibria involved. The most substantial is the affecting of the shape of the titration curve by the pH value, determining not only the degree of protonation of the organic substance to be determined, but also the hydrolytic reactions of the cadmium salt. Significantly can in the side equilibria participate also the buffer components.

The above effects can well be demonstrated on a case of titration of 8-hydroxyquinoline in various media (Fig. 1). The steepest shape of the titration curve was achieved in a medium buffered with borate to pH 9·1; 8-hydroxyquinoline is not completely deprotonized yet ($pK_a(H_2L) = 5{\cdot}0$, $pK_a(HL) = 9{\cdot}9$ – see[13]), the titration curve after the attaining of the equivalence point is, however, not affected by the formation of cadmium hydroxo complexes. The titration curve in the ammoniacal buffer medium is very steep, too, the bends before and after the inflexion point are, however, influenced by the formation of cadmium ammo complexes. Similarly, the precipitation titrations of 1-(2-pyridylazo)-2-naphthol (PAN), sodium N,N-diethyldithiocarbaminate (Kupral), and 3-phenyl-5-mercapto-2-thio-1,3,4-thiadiazolone-2 potassium salt (Bismuton) can be interpreted. Save the last reagent, the titration curves possess very favourable shapes, so that precise results with relative error below $\pm 1\%$ can be obtained even for titrations with 0·01M-$Cd(NO_3)_2$.

The titration curves of aminocarboxylic acids (NTA, EDTA, DCTA) possess favourable shape, too, as anticipated (Fig. 2). Since reliable data concerning the side equilibria are available for this case[13], we attempted to compare the experimental shape of the titration curve with the theoretical shape. We expressed the magnitude of the titration jump by the difference of the pCd values for the half and double consumption to the end point (for $a = n_{Cd}/n_L = 0{\cdot}5$ and 2). We have

$$pCd_{a=0.5} = \log \beta(CdL) + \log \alpha_{CdL} - \log \alpha_L = \log \beta'(CdL) + \log \alpha_{Cd} \qquad (1)$$

$$pCd_{a=1} = 1/2 \log \beta'(CdL) + \log \alpha_{Cd} - 1/2 \log c_L \qquad (2)$$

$$pCd_{a=2} = \log \alpha_{Cd} - \log c_L \qquad (3)$$

where $\beta(CdL)$ is the stability constant of the CdL complex, β' is the conditional stability constant, and the symbols α_{Cd}, α_L, and α_{CdL} denote the coefficients of the side reactions of the ions Cd^{2+}, L^{n-}, and $CdL^{(n-2)-}$, respectively (for more detail see,

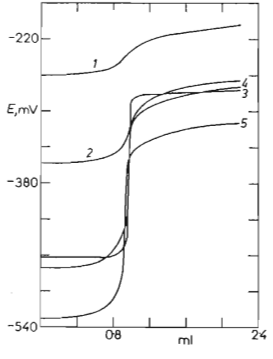

FIG. 1

Potentiometric Titration Curves for the Determination of ~0·005M 8-Hydroxyquinoline with 0·1M-$Cd(NO_3)_2$ Solution

Titrated in medium buffered with *1* hexamine, pH 5·3, *2* maleinate, pH 6·45, *3* borate, pH 9·1, *4* ammonia, pH 8·7, *5* ammonia, pH 9·7.

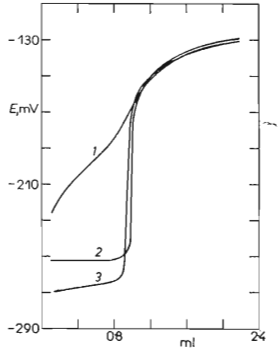

FIG. 2

Potentiometric Titration Curves for the Determination of ~0·005M Solutions of Aminocarboxylic Acids with 0·1M-$Cd(NO_3)_2$ Solution

Acetate buffer, pH 4·7; *1* NTA, *2* EDTA, *3* DCTA.

e.g., ref.[14]). For the height of the titration jump we have thus

$$\Delta\mathrm{pCd} = \mathrm{pCd}_{a=0.5} - \mathrm{pCd}_{a=2} = \log \beta'(\mathrm{CdL}) + \log c_{\mathrm{L}}\,, \qquad (4)$$

hence the height of the titration jump depends upon the stability of the complex forming and the concentration of the substance titrated. These relations can serve also for the estimation of the titration jump height in the measured electromotoric force units. One has, however, to take into account the confined detection limit of the Cd^{2+}-selective electrode (the calibration graph[12] can be employed up to approximately pCd $\approx$ 6). Working in the low concentration range, the extended Nikolsky equation for the equilibrium voltage has to be used in the form

$$E = \mathrm{const} + S \log \{a_{\mathrm{Cd}} + \sum_{i=1}^{n} K^{\mathrm{pot}}_{\mathrm{Cd}/N_i} \cdot a_{N_i}^{2/z(N_i)} + D_{\mathrm{Cd}}\}\,, \qquad (5)$$

where $K^{\mathrm{pot}}_{\mathrm{Cd}/N_i}$ is the selectivity constant with respect to the interfering ion N_i, $z(N_i)$ is the charge of the ion N_i, S the slope for the cell in question. Here the limit of determination D_{Cd} is governed predominantly by the solubility of the membrane material, it has not, however, a constant value and depends on the conditions in the solution measured. Inasmuch as in the end these calculation are of informative value only, we did not concern ourselves with the precise determination of the D_{Cd} value, estimating it rather from the limiting voltage values read from the calibration curves[12]. The comparison of the calculated and observed data for acetate-buffered

TABLE I

Comparison of the Calculated ΔpCd and ΔE Values with the Experimental ΔE Values for the Titrations of Aminocarboxylic Acids in Acetate Buffer

pH 4·7, $c_{\mathrm{HOAc}} = 0{\cdot}1$ mol l^{-1}.

Values	NTA		EDTA		DCTA	
	pCd	E, mV	pCd	E, mV	pCd	E, mV
$a = 0{\cdot}5$	4·8	−208	9·4	−300	9·9	−300
$a = 1$	3·9	−186	6·2	−230	6·5	−231
$a = 2$	2·8	−158	2·8	−158	2·8	−158
ΔpCd	2·0		6·6		7·1	
ΔE_{cal}		50		142		142
ΔE_{exp}		70		120		136

medium is given in Table I; the results are in a fairly good agreement. It is noteworthy that the differences in the titration curve shapes for the aforesaid acids in ammoniacal buffers are suppressed and the titration jump height, particularly for titrations with 0·01M-$Cd(NO_3)_2$, remains roughly the same.

TABLE II
Characterization of the Titration Curves and Statistical Evaluation of the Results

Substance titrated	Weighed mg	Titration curve	
		ΔE_{tot} mV	$(\Delta E/\Delta V)_{infl}$ mV/ml
8-Hydroxyquinoline	29·03	170—180	25/0·01[b]
	29·03	100—120	11/0·1[d]
	2·90	140—150	20/0·01[c]
8-Hydroxyquinoline-5-sulfonic acid	104·50		
	78·37	200—250	18/0·1[b]
	52·25		
8-Hydroxyquinoline-7-iodo-5-sulfonic acid	70·22	100—120	26/0·1[b]
	7·02	50—70	7/0·1[c]
1-(2-Pyridylazo)-2-naphthol	4·98	90—130	10/0·01[c]
4-(2-Pyridylazo)resorcinol	51·04	140—160	50/0·1[b]
	5·10	130—140	50/0·1[c]
Sodium N,N-diethyldithiocarbaminate	11·27	140—160	70/0·1[c]
3-Phenyl-5-mercapto-2-thio-1,3,4-thiadiazolone-2, K salt	13·88	60	4/0·1[c]
NTA	19·11	160—170	8/0·01[b]
	19·11	—	—[e,b]
	9·46	160—170	30/0·1[c]
	1·89		
EDTA	36·90	220—230	45/0·01[b]
	36·90	—	—[e,b]
	18·61	160—170	60/0·1[c]
	3·72		
DCTA	34·63	200—230	35/0·01[b]
	34·63	—	—[e,b]
	17·32	160—170	75/0·1[c]
	3·46		
Indoferrone	24·82	60	3/0·1[c]

[a] n Total number of measurements, $\bar{x}$ arithmetic mean, s_R standard deviation calculated from the range R, s_{rel} relative standard deviation; the level of significance $\alpha = 0{\cdot}05$ was considered for the u and u_0 tests; [b] 0·1M-$Cd(NO_3)_2$, [c] 0·01M-$Cd(NO_3)_2$, [d] 2·5% sodium tetraphenylborate

The statistical evaluation[15] for all the substances titrated is given in Table II. The evaluation of the accuracy by means of the Lord's test u_0 was performed with respect to the weighed amounts of the chemicals. Except for the aminocarboxylic acids NTA and EDTA, however, the differences are statistically significant, and

TABLE II
(*Continued*)

pH	n	Found[a]			Lord's test		Moor's test	
		$\bar{x}$ mg	s_R mg	s_{rel} %	u_0	u_0^{crit}	u	u^{crit}
9·1[f]	5	27·92	0·22	0·79	2·18	0·51	0·12	0·31
2·5[g]	5	28·17	0·64	2·27	0·58	0·51		
9·1[f]	5	2·71	0·01	0·37	9·50	0·51		
9·7[h]	5	96·34	1·12	1·16	3·14	0·51		
9·7[h]	6	72·59	1·03	1·41	2·22	0·40		
9·7[h]	5	47·91	0·89	1·85	2·09	0·51		
9·1[f]	4	53·60	0·68	1·27	11·87	0·72		
9·1[f]	5	6·06	0·15	2·47	2·74	0·51		
9·5[f]	4	2·93	0·01	0·34	89·13	0·72		
10·0[f]	5	32·00	0·22	0·69	37·30	0·51		
10·0[f]	3	3·21	0·04	1·25	31·50	1·30		
9·3[h]	4	10·50	0·09	0·86	4·03	0·72		
9·3[h]	3	10·60	1·19	2·06	1·59	1·3		
9·7[h]	5	19·00	0·20	1·05	0·24	0·51	1·37	0·31
9·7[h]	5	17·81	0·15	0·84	3·59	0·51		
9·3[h]	3	9·33	0·06	0·67	1·23	1·3		
9·3[h]	3	1·78	0·11	6·18	0·58	1·3		
9·7[h]	5	36·86	0·25	0·68	0·07	0·51	0·01	0·31
9·7[h]	5	36·85	0·07	0·19	0·31	0·51		
9·3[h]	3	18·60	0·03	0·18	0·18	1·3		
9·3[h]	3	3·64	0·09	2·40	0·53	1·3		
9·7[h]	5	32·76	0·24	0·73	3·40	0·51	0·01	0·31
9·7[h]	5	32·75	0·06	0·18	12·53	0·51		
9·3[h]	3	15·89	0·07	0·45	11·63	1·3		
9·3[h]	3	3·13	0·21	6·71	0·92	1·3		
7[i]	2	20·89	0·46	2·20	7·56	6·4		

served as the titrating agent; [e] visual indication using Eriochrome Black T; titrated in the medium of [f] borate buffer ($Na_2B_4O_7$ in mixture with NaOH or HCl), [h] ammoniacal buffer (NH_4Cl/NH_3); buffered with [g] hydrochloric acid, [i] ammonium acetate.

although corrections were made for the content of the substance declared by the manufacturer (*e.g.*, for 8-hydroxyquinoline min 99·0%) the results are somewhat lower with respect to the amounts used. In some cases we attempted to choose some other reference method (determination of the 8-hydroxyquinolinium cation by titration with sodium tetraphenylborate[16] or visual indication during the titrations of NTA, EDTA, and DCTA, for instance) and to compare the results by means of the *u* test. The differences between the methods proved to be statistically insignificant, with the exception of NTA, where the colour change of the indicator during the visual monitoring was not sharp enough. It should be pointed out that generally, a sufficiently reliable check determination, particularly in organic dye solutions, depends largely upon the choice of the standard substance, and that in the case of titration methods based on the formation of sufficiently strong chelates or sufficiently insoluble precipitates, systematic errors are negligible[17,18].

Finally it should be emphasized that not all organic reagents recommended for gravimetric, spectrophotometric, or other determinations of cadmium are amenable to direct titration with a cadmium salt. Indoferrone (2,6-dibromophenol-indo--5′-di(carboxymethyl)aminomethyl-*o*-cresol sodium salt) in the medium of ammoniacal buffer (pH 9 – 10) gave a curve involving two inflexion points, corresponding to the formation of the complexes with the 1 : 2 and 1 : 1 Cd/L ratios; in neutral medium buffered with ammonium acetate to pH ~ 7, a titration curve was obtained involving a single inflexion point, corresponding to the stoichiometry 1 : 2. 8-Hydroxyquinoline-5-sulfonic acid and its 7-iodo derivative (Ferrone) afford the titration curves which are less steep near the inflexion point, the determination is thus less precise. Azo dyes derived from this acid (the reagents SNAZOXS and Naphthylazoxine 6S) afforded irreproducible results. Similarly we failed to find the optimum conditions for the determination of quinaldinic and anthranilic acids, which with cadmium ions form crystalline salts of well-defined compositions and which are currently recommended[19] for gravimetric determination of cadmium, the precipitation of which, however, proceeds slowly and the course cannot be monitored potentiometrically. Attempts at the titration of *o,o′*-dihydroxyazodyes failed, too.

On the other hand, the titrations of 8-hydroxyquinoline, sodium N,N-diethyldithiocarbaminate, NTA, EDTA, and DCTA employing the Cd^{2+}-selective electrode Crytur 48 – 17 can be classified as very precise analytical methods and can be recommended not only for the direct determination of the above substances, but also for the determination of other inorganic ions by back-titration of the excess reagent with a cadmium salt.

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