
**CONTRIBUTIONS TO THE CHEMISTRY OF HIGHLY
CONCENTRATED AQUEOUS ELECTROLYTE SOLUTIONS. XXII.*****A STUDY OF THE TRANSFORMATION OF Me^{2+} AMMINES
TO CYANO COMPLEXES BY THE DENSIMETRIC TITRATION**

J. ČELEDA and Z. PLZÁK

*Department of Nuclear Fuels Technology and Radiochemistry,
Institute of Chemical Technology, Prague 6**Dedicated to Professor S. Škramovský on the occasion of his 70th birthday.*

Received January 18th, 1971

Based on our previous studies on the apparent ionic volumes a method for studying complexes in aqueous solutions is proposed, using the changes of density of the solution as a function of the volume of the added titrant. The position of breaks on the density curves indicates the stoichiometric ratio in which the two components react and, moreover, from the slope of the individual sections of the curve the nature of the reaction can be determined (*i.e.*, the number and character of ligands exchanged in the inner coordination sphere, inclusive of H_2O ligands). This method has been applied to the reaction $[Me(NH_3)_x]^{2+} \rightarrow [Me(CN)_4]^{2-}$. The octahedral complexes $[Me(NH_3)_x(H_2O)_{6-x}]^{2+}$ of Ni^{2+} and Cd^{2+} ions in an ammonia medium are transformed in a single step into $[Me(CN)_4]^{2-}$ whereas in the case of Zn^{2+} this change is going in two steps *via* an intermediate octahedral electroneutral dicyano-ammine complex.

The idea that the formation of compounds in solution can be traced by discontinuities in the density was already formulated by Mendělejev who proved thus the formation of molecular adducts of water and alcohol. This method can be viewed as a special case of the so-called Kurnakov's physico chemical analysis based on studies of the "property-composition" curves or of the Job's method of continual variations which, however, have been so far applied in electrolyte solutions to other physical properties but density. The breaks on density curves were used by Titov^{1,2} for the determination of stoichiometric ratios of components, namely for the formation of complexes in solutions. More recently it was Krishnamurti and Venkataraman³ who used it for the control of stoichiometry in simple precipitation reactions (CdS , $BaSO_4$, $BaCrO_4$) and Tsujioka⁴ who studied the neutralization of acids by strong bases. However, the interpretation of the experimental data had to be restricted to the determination of the overall stoichiometric ratios in which the two compounds react. Any direct identification of the chemical composition and structure of the products formed, based on the observed volume changes, was impossible because no general relations between the chemical structure of the component and its volume in the solution were available.

The recent formulation of the relationship between the apparent molar volume of the complex in the solution φ and its chemical composition⁵⁻⁸ disclosed a path leading to the exploitation

* Part XXI: This Journal 36, 3071 (1971).

of the density changes in ionic reactions in solutions not only for the quantitative determination of the stoichiometric ratio of formation but also for the qualitative identification of the formed and disappeared species.

THEORETICAL

It has been derived^{5,6} and experimentally proved⁷⁻¹¹ that the coordination of a ligand in the inner coordination sphere of the central ion is in the aqueous solution accompanied by a considerable change of the volume which can be calculated with a sufficient accuracy (from the point of view of complex identification) from the ionic and van der Waals radii, respectively, of the corresponding atoms using a relatively simple model. The apparent molar volume φ^0 of the complex in the solution, not taking into account the contraction due to the action of its electrostatic field on the neighbouring water molecules, is within 1–2 ml/mol equal to the sum of the molar hard-sphere volumes of the participating particles, if they are regarded as rigid spheres in the spherical packing, and corrected for the structural discontinuity due to their contact with the neighbouring structure of liquid water. This correction corresponds to a continuous vacancy situated on the surface of the ion and surrounding it as a continuous layer of constant thickness, common for all ions, for which the value of $0.37 \pm 0.02 \text{ \AA}$ has been derived from experimental data. As the dilution increases we have to take into account also the empirical correction for the contraction of the neighbouring water⁶ which, however, in the case of more voluminous complexes is of low importance and is compensated from the major part in the total volume balance of the reaction as far as the charge of the complex remains unchanged.

Thus, for instance, the H_2O ligand, spherically packed in the coordinated state, has the molar volume of 9.5 ml/mol ⁶, *i.e.* about half as much as the volume of free liquid water. The difference between the apparent molar volume of the complex with the coordination number 4, with a shape that is close enough to the sphere (*e.g.* with the tetrahedral configuration of ligands), and that of the complex, the coordination number of which is increased up to 6 by two other H_2O ligands, is – according to these considerations – equal to

$$[(v_1 + 19)^{1/3} + d(4\pi N/3)^{1/3}]^3 - [v_1^{1/3} + d(4\pi N/3)^{1/3}]^3,$$

where v_1 is the molar volume of the first of the two ions, N is the Avogadro number and d is the correction for contact vacancies, $d(4\pi N/3)^{1/3} = 0.50 \text{ ml}^{-1/3} \text{ mol}^{1/3}$. For $v_1 = 50 \text{ ml/mol}$ this difference amounts to $97.4 - 73.2 = 24.2 \text{ ml/mol}$, what means a decrease of -11.8 ml/mol per two additional molecules of water bound in the complex if compared with the volume of 2 mol of free water. On the other hand, the release of water from the inner coordination sphere of the complex by the ligands

Cl^- , CN^- , NO_3^- , etc., the apparent volume of which is in the free state similar or even less than that in the bound state (due to the electrocontraction), is accompanied by the increase of the total volume of the same order as the preceding decrease. These volume changes cause overall density changes which take place when the titrant (b) is added to the solution of the studied component (a), which reacts with it. From the graph of the dependence of density change on the amount of the added agent conclusions can be made on the stoichiometry and nature of the chemical processes that take place in the solution. The described procedure can be therefore called "a densimetric titration".

In the most general case a multicomponent titrant solution must be considered containing — along with c_b (mol l^{-1}) of the component b acting as the titrant — other $i - 1$ components which do not enter into the reactions or which are present in the stoichiometric excess and the concentration of which is v_i^0 mol per one mol of the titrant. (For the titrant $v_i^0 = v_b^0 = 1$.) The apparent molar volumes of these components in the final titrated solution (if they are not transformed by reactions) will be denoted by φ_i (ml mol^{-1}).

Moreover, in reactions proceeding in m consecutive steps it is necessary to consider in every step the whole set of products formed in the amounts of $n_{j,m}$ mol per x ml of the added titrant solution. The apparent volume of the j -th product in the resulting solution will be $\varphi_{j,m}$ (ml mol^{-1}). To everyone of these steps corresponds a consumption of $n_{i,m}$ mol of every of the i components of the titrant solution and, of course, also a consumption of $n_{k,m}$ mol of the k participating components of the titrated solution in which — along with the titrated component (a) — there are $k - 1$ components that do not enter into the reaction or that are present in an excess. (For the non-reacting components all the corresponding $n_{k,m}$'s are zero.) The total volume V (ml) of the solution which initially contained m_s grams of the solvent of density d_s and n_k^0 mol of each k -th component will be — after the addition of x ml of the titrant solution and under the given conditions — equal to

$$V = (m_s/d_s) + \sum_k n_k^0 \varphi_k + x(1 - 10^{-3} \cdot c_b \sum_i v_i^0 \varphi_i^0) + \\ + \sum_j \sum_m n_{j,m} \varphi_{j,m} + \sum_i (10^{-3} \cdot x c_b v_i^0 - \sum_m n_{i,m}) \varphi_i - \sum_k (\varphi_k \sum_m n_{k,m}), \quad (1)$$

where the third term represents the volume of water introduced into the solution together with the titrant and φ_i^0 are the apparent molar volumes of the components in the titrant solution alone.

If the reactions do not proceed quantitatively, all the products of all steps are present in the solution (along with each other) in detectable amounts, in equilibrium with the remaining agent and with the titrated component. In the general case their contents n depend non-linearly on the amount of the added agent so that in this case all n 's and all $\partial n/\partial x$ depend on x .

If the reactions proceed quantitatively, at any particular value of x the transformation is practically complete up to the step for which there was enough of the added agent and the whole excess of the agent is quantitatively used up for the single subsequent (m^* -th) step of the reaction. This means that in this region all n_m 's up to $m = m^* - 1$ are practically constant, independent of x , and all n_m 's for $m \geq m^* + 1$ are still equal to zero. For the m^* -th step, which is just under reaction, the values of $\partial n/\partial x$ give the numbers of mol of components and products that are formed or consumed in the given m^* -th reaction per 1 ml of the added solution, *i.e.* per $c_b/1000$ mol of the titrant in agreement with the stoichiometric coefficients of the corresponding chemical equation. Denoting by v_{m^*} the number of mol of components formed or consumed in the m^* -th reaction per 1 mol of the agent, we get in agreement with the preceding discussion these equations for all the present species:

$$\left. \begin{aligned} (\partial n_m/\partial x)_{m=m^*} &= 10^{-3} \cdot c_b v_{m^*} \\ (\partial n_m/\partial x)_{m \neq m^*} &= 0 \end{aligned} \right\} \quad (2)$$

$$\left. \begin{aligned} (\partial n_m/\partial x)_{m=m^*} &= 10^{-3} \cdot c_b v_{m^*} \\ (\partial n_m/\partial x)_{m \neq m^*} &= 0 \end{aligned} \right\} \quad (3)$$

(For species that do not enter into the m^* -th reaction, there is $v_{m^*} = 0$.)

Addition of the titrant solution changes, however, not only the numbers of mol of the participating components but also the apparent volumes φ of all components present in the solution; generally, they increase with concentration due to the diminishing electrocontraction of the solvent present in the solution per one solute particle. The expression for the change of the total volume, $\partial V/\partial x$, caused by the addition of the titrant solution, as obtained by differentiation of Eq. (1), will therefore contain also terms $n \cdot (\partial \varphi/\partial x)$. Changes in φ are, however, small so that their effect can be neglected if the titrant solution is as concentrated as possible and the amount of the titrated component n_a is so small that the total concentration of the solution changes only very little in the whole range of the titration curve. In this case, all the terms $n \cdot (\partial \varphi/\partial x)$ for the agent and for all other formed or consumed components are negligibly small and must be taken into account only for those components of the initial solution that are present from the beginning in much higher amounts n_k^0 .

Therefore, if the reactions proceed quantitatively, the total change of the volume V , caused by the addition of the titrant solution, is given by Eq. (4), if Eq. (2) and (3) are taken into account:

$$\partial V/\partial x = [1 + 10^{-3} c_b \sum_i v_i^0 (\varphi_i - \varphi_i^0)] + \sum_k n_k^0 (\partial \varphi_k/\partial x) + 10^{-3} c_b \Delta \Phi, \quad (4)$$

where the first term represents the contribution of the volume of the added titrant solution, corrected for the change of the apparent molar volumes of its components when transferred into the titrated solution, the second term is due to the dilution changes of apparent volumes of components that are initially present in the titrated

solution in high concentrations. The third term is the volume effect of the given chemical change itself, where $\Delta\Phi$ stands for

$$\Delta\Phi = \sum_j v_{j,m^*} \varphi_{j,m^*} - \sum_i v_{i,m^*} \varphi_i - \sum_k v_{k,m^*} \varphi_k. \quad (5)$$

It represents the volume balance of the current m^* -th reaction taken per one mol of the titrant.

Subtracting the volume x of the added solution — *i.e.* subtracting 1 from $\partial V/\partial x$ in Eq. (4) — we get the difference corresponding only to the deviation from additivity, *i.e.* the difference of the volume changes arising from the chemical reaction and from changes of molar volumes due to the mixing of the solutions:

$$\partial \Delta V_{\text{mix}}/\partial n_b = \Delta\Phi + \sum_i v_i^0 (\varphi_i - \varphi_i^0) + \sum_k n_k^0 (\partial \varphi_k/\partial n_b), \quad (6)$$

where $n_b = x c_b/1000$ is the number of mol of the added titrant. The values of ΔV_{mix} can be obtained from the solution density during the course of titration for which we have:

$$d = (V_a d_a + x d_b)/(V_a + x + \Delta V_{\text{mix}}) \quad (7)$$

and hence

$$\partial d/\partial x = -(d/V) (\partial \Delta V_{\text{mix}}/\partial x) + (d_b - d)/V, \quad (8)$$

where V is the total volume of the two mixed solutions. As far as the volume increase during the titration remains within few per cent of its initial value, the changes of d and V in Eq. (8) as well as the changes of φ_i and $\partial \varphi_k/\partial n_b$ in Eq. (6) are negligible over the whole titration curve so that these quantities can be taken as constants with values roughly equal to their initial values, d_a and V_a , respectively. Hence, taking into account Eq. (6), Eq. (8) can be reduced by approximation to

$$\partial d/\partial n_b = -(d_a/V_a) \cdot \Delta\Phi + A, \quad (9)$$

where A is a constant independent of the amount x of the titrant added. In this case the densimetric titration curve — in the region where the m^* -th reaction prevails — has an approximately constant slope corresponding to the molar-volume balance $\Delta\Phi$ of this reaction and it maintains this slope up to the corresponding equivalence point where one of the present species disappears and the reaction is replaced by another one so that the balance of apparent volumes resumes a different value and a break on the curve appears in the equivalence point.

Beyond the last equivalence point all chemical transformations cease and the coefficient $\Delta\Phi$ is equal to zero. The titration curve turns into the straight line with the slope

$$(\partial d/\partial n_b)_{\text{exc}} = A. \quad (10)$$

This can be used to reduce the slopes in all other rectilinear sections to volume balances $\Delta\Phi$ of reactions corresponding to the respective section. Substituting (10) into (9) we get

$$\Delta\Phi = -(V_a/d_a) \cdot [\partial d/\partial n_b - (\partial d/\partial n_b)_{\text{exc}}]. \quad (11)$$

If the density of the solution is measured by the suspended plunger of the volume V_p and mass m_p , the value m read on the balances (the correction for vacuum is neglected as it is roughly constant during the titration) is given by

$$m = m_p - V_p d, \quad (12)$$

so that we get a curve with a slope

$$\partial m/\partial n_b = -V_p(\partial d/\partial n_b) = d_a(V_p/V_a) \Delta\Phi + (\partial m/\partial n_b)_{\text{exc}} \quad (13)$$

and for the evaluation of the volume balance of the reactions from the slopes of the densimetric titration curves $m - n_b$ we get

$$\Delta\Phi = (V_a/V_p d_a) \cdot [\partial m/\partial n_b - (\partial m/\partial n_b)_{\text{exc}}]. \quad (14)$$

If it was impossible to perform the measurement in such a way that the total volume increase were within 10% of V_a , we cannot use this approximation and it is necessary to convert to ΔV_{mix} each individual value of m . According to Eqs (7) and (12) this conversion may be done by using the following relations (written in a form suitable for numerical calculations):

$$\Delta V_{\text{mix}} = -[(V_a/d_a) + (d_b/d_a^2) x] \Delta d' + [(d_b/d_a) - 1] x \quad (15)$$

$$\Delta V_{\text{mix}} = [(V_a/V_p d_a) + (d_b/V_p d_a^2) x] \Delta m' + [(d_b/d_a) - 1] x, \quad (16)$$

where $\Delta d' = \Delta d/(1 + \Delta d/d_a)$ and $\Delta m' = \Delta m/[1 - \Delta m/(V_p d_a)]$ are the corrected increments of the density d and of the plunger weight m , respectively, usually identical with the measured values $\Delta d = d - d_a$ and $\Delta m = m - m_a$. By plotting the experimental values of ΔV_{mix} , evaluated by this method, as a function of the number of mol of the titrant n_b , we obtain a curve from which the slopes $\partial \Delta V_{\text{mix}}/\partial n_b$ and

$(\partial \Delta V_{\text{mix}}/\partial n_b)_{\text{exc}}$, respectively, can be directly read. After having subtracted the correction for the non-chemical volume effects, $x(\partial \Delta V_{\text{mix}}/\partial x)_{\text{exc}}$, it is possible to compare the remaining chemical effect ΔV_{chem} with the volume balances calculated theoretically from Eq (5).

The evaluation of curves according to Eqs (15)–(16) is more tedious than the direct determination of balances from the slopes of curves $d - x$ or $m - x$ according to Eqs (11) and (14). To avoid these tedious calculations it is advisable to use the titrant solution as concentrated as possible and, on the other hand, to keep the concentration of the titrated component in the initial solution as low as possible. Its weight, however, must be sufficient for distinguishing the measured values of $\Delta\Phi$. According to Eq. (13) the differences in values of m are equal to $n_b d_a (V_p/V_a) \Delta\Phi$. As demonstrated in the case of aquo complexes, the molar-volume balances in complex formation are of the order of units or tens of ml mol^{-1} . This means that – if the ratio of the plunger-to-solution volumes is 0.3 (a higher ratio would hinder an efficient mixing) – the differences in values of m are in units of grams per one mol of the consumed agent and hence of the same order of magnitude also per 1 mol of the studied component. It is therefore necessary to choose sample weights at least within 10^{-3} to 10^{-2} mol ensuring thus well measurable differences in the plunger weight (of the order of tens of milligrams). For the titrated-solution volumes of 100 ml this corresponds to the lowest concentrations of the order of 0.1 mol l^{-1} . To fulfil the condition that the consumption of the titrant solution should not exceed 10% of V_a it is necessary to use concentrations at least one order higher, *i.e.* in units of mol/l , which means that the consumptions are of the order of units of ml for the whole curve.

This method – in the above-mentioned adaptation – has been applied to the studies of formation of complex ions of polyvalent metals in aqueous solutions. The transformation of amines of Ni^{2+} , Zn^{2+} and Cd^{2+} , respectively, into the corresponding cyano complexes has been chosen as an example of reactions proceeding quantitatively.

EXPERIMENTAL

The measurements were done using the device developed by Jedináková^{9,10} for the determination of apparent volumes of electrolytes in solutions. The volume of the studied solutions was $V_a = 110\text{--}120 \text{ ml}$, the plunger volume $V_p = 37.66 \text{ ml}$, the concentration of NaCN in the titrant solution $c_b = 5.76 \text{ mol l}^{-1}$ (as determined by titration with mercury nitrate), $d_b = 1.121 \text{ g ml}^{-1}$. The titrant solution was added from a microburette with a capillary extension and with the mouth submerged under the surface of the titrated solution in a cylinder containing the plunger. The temperature of the cylinder was kept at $25.00 \pm 0.05^\circ\text{C}$ by a thermostat. The Me^{2+} ions were sampled by pipetting the stock solutions of their salts, the titre of which was controlled by chelatometry. The sample weights were chosen so that the total volume of the solution after the last point of equivalence did not exceed 105% of the initial volume V_a , *i.e.* about 0.005 mol. All the

chemicals used were of the analytical grade. The solutions were prepared using water boiled-out to expell all the dissolved gases, the bubbles of which interfere in the measurements. The equivalence points and the slopes on the titration curves have been determined graphically. Instead of the directly measured values of m (mg) the differences

$$\Delta m_k = \Delta m - kx,$$

where the coefficient k (mg ml^{-1}) is the average slope of the titration curve from the beginning up to the reference point on the final section (chosen so that k is an integer), have been plotted to make the differences between the slopes of individual sections more distinct.

RESULTS AND DISCUSSION

Ni^{2+} Ion

The stock solution contained $n_k^0 = 3.95$ millimol of NiCl_2 , i.e. $1.58 \cdot 10^{-2}$ val, as calculated for the formation of $[\text{Ni}(\text{CN})_4]^{2-}$. The concentration of ammonia was 2 mol l^{-1} and the solution contained 1 mol l^{-1} of NaCl as an inert electrolyte used to stabilize the ionic medium and to diminish the concentration changes of molar volumes φ . The initial volume V_a was 110 ml, $d_a = 1.0235 \text{ g ml}^{-1}$. The densimetric titration curve in units of $m_k - x$, for $k = 41 \text{ mg ml}^{-1}$, is given in Fig. 1.

The Ni^{2+} ion in the ammonia medium forms a well-defined aquo- and ammine complexes with the coordination number 6, with the octahedral configuration of ligands which has been proved by several methods¹²⁻¹⁴. The ligands H_2O and NH_3 substitute mutually each other without any change of the coordination number forming the mixed complexes $[\text{Ni}(\text{NH}_3)_x(\text{H}_2\text{O})_{6-x}]^{2+}$, some of which are known even in the

TABLE I

The Volume Balances $\Delta V = c_b \Delta \Phi$ ($\mu\text{l ml}^{-1}$) Calculated from Eq. (5) per 1 ml of the Added Titrant Solution ($c_b = 5.76 \text{ mol l}^{-1}$ of NaCN) for the Transformation of the Octahedral Complexes of Me^{2+} into the Cyano Complexes, at 25°C

Initial species	Product of transformation	L = L' = = H_2O		L = NH_3 , L' = H_2O		L = L' = = NH_3	
		ΔV^∞	ΔV^0	ΔV^∞	ΔV^0	ΔV^∞	ΔV^0
$[\text{MeL}_4\text{L}'_2]^{2+}$	$[\text{MeL}_4(\text{CN})_2]^0$	72	20	75	23	66	14
$[\text{MeL}_4\text{L}'_2]^{2+}$	$[\text{MeL}_2(\text{CN})_2]^0$	106	55	101	49	92	40
$[\text{MeL}_4\text{L}'_2]^{2+}$	$[\text{Me}(\text{CN})_2]^0$	141	89	130	78	121	69
$[\text{MeL}_4\text{L}'_2]^{2+}$	$[\text{MeL}_2(\text{CN})_4]^{2-}$	39	20	36	17	32	13
$[\text{MeL}_4\text{L}'_2]^{2+}$	$[\text{Me}(\text{CN})_4]^{2-}$	51	39	45	33	40	29

crystalline form¹⁴. They are characterized by a distinct $d-d$ absorption spectrum, corresponding to the d^8 ion with two unpaired electrons $e_g(3d_{z^2}, 3d_{x^2-y^2})$ in the octahedral ligand field (e.g., ref.^{15,16}). The ion-ligand distances in these paramagnetic complexes, as measured by X-rays¹⁷, correspond generally to the hard-sphere ionic and van-der-Waals radii. In the aqueous solution it was possible to follow by the spectral method¹⁸ and by the isotope-exchange method ($^{15}\text{NH}_3$) (ref.¹⁹) the substitution of water by ammonia up to the highest degree of substitution, i.e. to $[\text{Ni}(\text{NH}_3)_6]^{2+}$.

The CN^- ions displace ligands NH_3 and H_2O in the inner coordination sphere of these complexes. The final product is a well-defined diamagnetic square-planar complex $[\text{Ni}(\text{CN})_4]^{2-}$ (ref.¹⁴) with the $3d_{z^2}$ configuration and with the hybrid dsp^2 bonds with the participation of the vacant orbital $3d_{x^2-y^2}$. In the case of aquo complexes in the aqueous solution this change proceeds in two steps with the formation of the intermediate dicyano complex that condenses into polynuclear polymer chains of partly or totally dehydrated $\text{Ni}(\text{CN})_2$ which coagulates in the isoelectric point and then dissolves in the excess of the cyanide by a simple addition of CN^- ions. The polynuclear complexes are thus transformed into the mononuclear tetracyanonickolate. In this case in the intermediate dicyano complex the coordination number decreases from 6 to 4. No precipitate is formed in the ammonia solution; there are no published data on the mixed cyano-ammine complexes.

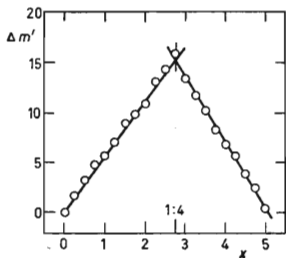


FIG. 1

Differential Densimetric Titration Curve of the Solution of 3.95 mmol of NiCl_2 in $2\text{M-NH}_3 + 1\text{M-NaCl}$

x (ml) is the added volume of the titrant solution of 5.76M-NaCN , $\Delta m' = \Delta m - kx$ (mg); $k = 41 \text{ mg ml}^{-1}$.

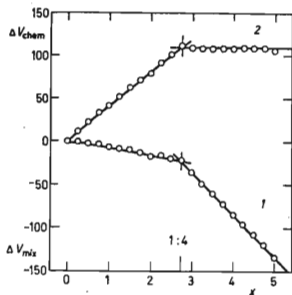


FIG. 2

The Densimetric Titration Curve of $\text{Ni}^{2+}(\text{NH}_3)\text{-CN}^-$ from Fig. 1, Recalculated to the Volume Differences

1 ΔV_{mix} (μl), 2 $\Delta V_{\text{chem}} = \Delta V_{\text{mix}} - x(\partial \Delta V_{\text{mix}} / \partial x)_{\text{exc}}$ (μl).

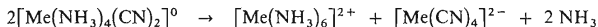
Having this in mind, the results were compared with the volume balances calculated for intermediates with both coordination numbers 6 and 4 (Table I). Because of the tendency of planar complexes to bind two other ligands in the apexes of the octahedron the balances were calculated also for the octahedral diammine and diaquotetracyanonickolate, in spite of the diamagnetism and yellow colour of the product that witnesses against its existence.

The following values of the apparent volumes have been used for the calculations [φ^0 is the apparent molar volume without the electroconstriction, *i.e.* extrapolated to the zero concentration of the solvent when the reacting components would fill up the total volume of the solution, φ^∞ is the volume of the infinitely diluted solution, $\varphi^{(k)}$ is the coordination volume in the complex (ml mol^{-1}): H_2O : $\varphi^0 = 18.0$, $\varphi^\infty = 18.0$, $\varphi^{(k)} = 9.5$; NH_3 : $\varphi^0 = 17.5$, $\varphi^\infty = 17.5$, $\varphi^{(k)} = 10.0$; CN^- : $\varphi^0 = 30.0$, $\varphi^\infty = 25.0$, $\varphi^{(k)} = 22.0$.

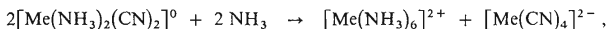
For the volume of the central ion Me^{2+} the mean value of 2 ml mol^{-1} has been used but it is not very important because in the first approximation it is eliminated from the overall balance. The correction d for the structural ion-water discontinuities has been taken in all cases equal to 0.37 \AA , *i.e.* $(\frac{4}{3}\pi N)^{1/3} d = 0.50 \text{ ml}^{1/3} \text{ mol}^{-1/3}$. As shown in Table I, the two-step reaction going *via* the electroneutral species has in the first step always much higher volume balance than the reaction going directly to the complex anion because the electroneutral complex causes practically no electroconstriction of the solvent. The balance values ΔV^0 for the "anhydrous" solution are in this case substantially lower so that ΔV decreases with the increasing concentration, but — considering that the concentration corresponding to the "anhydrous" state is very far from the usual concentrations (by about $15\text{--}20 \text{ mol. l}^{-1}$) — the balance to the first step remains at usual concentrations always higher than the balance of the full transformation and the difference must be compensated in the second step so that in the two-step reaction there will be a break on the curve at the ratio of $\text{Me}^{2+} : \text{CN}^- = 1 : 2$.

But this is not the case. The curve has a constant slope (Fig. 1) up to the complete formation of the tetracyanonickolate that — after conversion into ΔV_{mix} by Eq. (16) and to $\Delta\Phi$ (by subtracting the slope of the final section (Fig. 2)) — give approximately $42 \mu\text{l}$ per 1 ml of the titration solution of 5.76M-NaCN , well within the limits calculated for the direct reaction $[\text{MeL}_6]^{2+} \rightarrow [\text{Me}(\text{CN})_4]^{2-}$.

All the calculated values for the other imaginable combinations of coordination numbers of both the initial cation and the resulting anion lie about $10\text{--}15 \mu\text{l}$ lower; on the other hand, slopes corresponding to the reaction with a neutral intermediate are substantially higher. This means that in the solution there is no significant formation of mixed complexes, not even at the substoichiometric amounts of the cyanide. Evidently, these mixed complexes are not stable and undergo a coordinative disproportionation:



and



respectively. This indicates that the covalent character of the bonds $\text{Me}-\text{NH}_3$ is not strong enough to form, in combination with two CN ligands, the low-spin planar complex, energetically advantageous only in the case of ligands forming strong covalent bonds, so that the whole system reaches a higher stability in the state when all the added CN^- ions are used up for the formation of the diamagnetic tetracyano complexes and the remaining Ni^{2+} ions are present in the form of paramagnetic ammine-aquo complexes with the coordination number 6, instead of the random distribution of CN^- ions in paramagnetic mixed complexes.

Zn^{2+} Ion

In contrast to Ni^{2+} , with Zn^{2+} two breaks on the densimetric curves were obtained when titrated by the cyanide. The titration was also performed at other concentrations of the inert electrolyte (NaCl), the high concentrations of which generally increase the activity coefficients of ions and therefore also the stability constants of complexes. The breaks remained unchanged even under these conditions and they are well observable even on the un-recalculated densimetric curves $\Delta m - x$ (Fig. 3, $n_{\text{Zn}} = 4.80$ millimol, $c_{\text{NH}_3} = 0.8 \text{ mol l}^{-1}$).

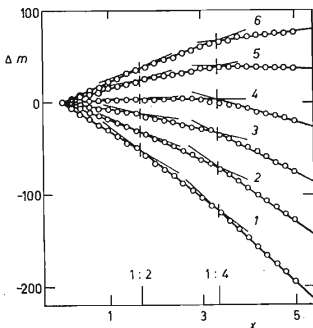


FIG. 3

The Densimetric Titration Curves of the Solutions of 4.80 mmol of ZnSO_4 in 0.8M- $\text{NH}_3 + \text{NaCl}$

x (ml) is the volume of the added titrant solution of 5.76M- NaCN , Δm (mg) is the overall change of the plunger weight; the NaCl concentrations used: 1 0, 2 1, 3 2, 4 3, 5 4, 6 5 mol l^{-1} .

Zinc has already a distinct A-character according to the Phillips-Williams classification²⁰. The electrostatic component predominates in bonds of its complexes which is evident also from the fact that the stability of its halogen complexes in the aqueous solutions increases from I^- to F^- (ref.²⁰). In the formation of complexes there is therefore a tendency to form such configurations that are energetically the most favorable from the electrostatic point of view: it is the octahedron for the electro-neutral polar ligands and the tetrahedron for anions. The participation of covalent sp^3 bonds plays here an unimportant role as evident from the relatively small difference in stabilities of complexes with strong and weak donors. This fact is witnessed by the low stability of the cyano complexes of zinc because in the aqueous solutions the ligands OH^- ²¹ (and even H_2O ligands) successfully compete with CN^- ligands so that along with $[Zn(CN)_4]^{2-}$ it is possible to detect observable amounts of tri-cyanozincate²².

Raman spectra²³ reveal that the Zn^{2+} ion in the aqueous solution does exist as the octahedral hexaquo ion, well-known even from crystals, where the distance $Zn-H_2O$ measured by X-rays¹⁷ corresponds to the hard-sphere radii. The apparent volumes⁷⁻¹⁰ also indicate the presence of the octahedral hexaquo ion in the aqueous solutions of $Zn(II)$ salts. It can be therefore expected that the complexes in which

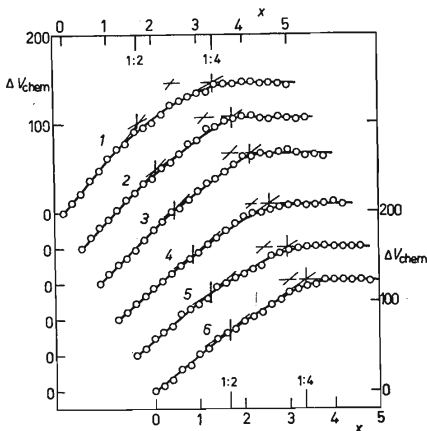


FIG. 4

The Densimetric Titration Curves of $Zn^{2+} (NH_3)-CN^-$ from Fig. 3, Recalculated to $\Delta V_{chem} = \Delta V_{mix} - x(\partial \Delta V_{mix} / \partial x)_{T, P, c}$ (μl)

TABLE II

The Volume Balances $\Delta V = c_b \Delta \Phi$ ($\mu\text{l ml}^{-1}$) Calculated from Eq. (5) for $c_b = 5.76 \text{ mol l}^{-1}$ of NaCN for the Transformation of the Tetrahedral Complexes of Me^{2+} into the Cyano Complexes, at 25°C

Initial species	Product of transformation	L = H ₂ O		L = NH ₃	
		ΔV^∞	ΔV^0	ΔV^∞	ΔV^0
$[\text{MeL}_4]^{2+}$	$[\text{MeL}_2(\text{CN})_2]^0$	78	23	69	14
$[\text{MeL}_4]^{2+}$	$[\text{Me}(\text{CN})_2]^0$	112	58	98	43
$[\text{MeL}_4]^{2+}$	$[\text{Me}(\text{CN})_4]^{2-}$	36	23	29	16

water is substituted by ammonia have the same structure. The octahedral configuration for the highest complex, $[\text{Zn}(\text{NH}_3)_6]^{2+}$, has been proved in crystals, in solutions, however, its existence is denied (ref.¹⁴).

The ion $[\text{Zn}(\text{CN})_4]^{2-}$ is tetrahedral with the hybrid sp^3 bonds (ref.¹⁴) and, as shown by Raman spectra²⁴, it preserves this coordination number and this structure even in the aqueous solution. In strongly concentrated solutions with a highly decreased activity of water the Raman spectra²⁵ identified the tetramminezinc ion as the anhydrous tetrahedral complex $[\text{Zn}(\text{NH}_3)_4]^{2+}$. Because of this tendency of zinc to form tetrahedral ions even with rather weak donors, the volume balances ΔV_{mix} and $\Delta \Phi$, respectively, obtained from the transformed experimental curves (Fig. 4), were compared also with values computed for the initial complexes with the coordination number 4 (Table II).

From these recalculated curves it is evident that there are really two breaks and not only one curved smooth transition in the vicinity of the equivalence point resulting from a shifted equilibrium. This is proved by the fact that the point of intersection of the initial and final tangent shifts with the increasing concentration of the inert electrolyte to higher values of the consumption and corresponds to non-integer molar ratios whereas the points of intersection with the straight line of the intermediate step remain invariably on the ratios Zn : CN equal to 1 : 2 and 1 : 4. The total volume difference between the final and initial point of the complex formation amounts up to 44 μl per 1 ml of the titrant solution which again corresponds to the change of the octahedral aquo-ammine complex to the cyanozincate with the coordination number 4 (Tables I and II). Hence, if there are some lower ammine complexes of zinc in the solution, these are the octahedral mixed complexes $[\text{Zn}(\text{NH}_3)_x(\text{H}_2\text{O})_{6-x}]^{2+}$ and not complexes with the coordination number 4.

As demonstrated by the slope in Fig. 4, in the first step these complexes change into the octahedral complexes $[\text{ZnL}_4(\text{CN})_2]^0$ again; the transformation into a tetra-

hedral complex would lead to a slope much higher (over 90 $\mu\text{l/ml}$) than actually found (about 60 $\mu\text{l/ml}$). Addition of NaCl decreases the slope still further (as corresponds to the high difference between $\Delta\Phi^\infty$ and $\Delta\Phi^0$ for electroneutral complexes, Table I) and in the 5M-NaCl both sections practically melt together, what would never be the case if $[\text{ZnL}_2(\text{CN})_2]^0$ were formed. Therefore, we can conclude that in the first step the CN^- ligands replace ligands H_2O and NH_3 , respectively, without any change of the coordination number. Only in the second step another two CN^- ligands substitute the remaining 4 original ligands and the coordination number decreases to 4.

The formation of mixed cyano-ammine complexes of zinc can be explained by the predominant electrostatic character of the bond which erases the specific differences between the donor abilities of ligands. The coordination of CN^- ligands in the complex affects but slightly the interaction of the central ion with other ligands and the CN^- ions can be equally distributed between Zn^{2+} cations. In this case energy changes very little with the distribution of ligands and from the point of view of entropy the configuration with equally distributed CN ligands is favoured.

The transformation of the octahedrons $[\text{MeL}_4(\text{CN})_2]$ into the tetrahedrons $[\text{Me}(\text{CN})_4]^{2-}$ when additional CN^- ligands are coordinated is not due to the competition of covalent and electrostatic bonds (as in the case of nickel) but it is rather due to the mutual repulsion of CN^- ligands which is higher in strongly polarized bonds than the repulsion of the electroneutral ligands. The smoothing of breaks in the equivalence points indicates the presence of a small amount of other intermediate species, i.e. of the octahedral $[\text{ZnL}_5(\text{CN})]^+$ and tetrahedral $[\text{ZnL}(\text{CN})_3]^-$ but the shape of the curve shows that the dicyano complex predominates, probably due to the energetically favourable trans configuration of the anionic ligands which is similar to the well-known²³ configuration of the halogen-aquo complexes of Me^{2+} (cf.¹⁴).

Cd^{2+} Ion

In the case of the Cd^{2+} ion the reaction leading to the cyano complex proceeds again in a single step. The break is sharp and this is particularly well demonstrated on curves plotted in the transformed coordinates $\Delta m_k - x$ (Fig. 5, 4.76 millimol of CdSO_4 , 1.5 mol l^{-1} of NH_3 , plotted with $k = 44 \text{ mg ml}^{-1}$). This proves that the reaction proceeds quantitatively and that no observable intermediates are present. (Only at $c_{\text{NaCl}} = 0$ there seems to be an indication of a two-step transformation.)

Also in this case the slopes of curves recalculated to ΔV_{mix} and $\Delta\Phi$, respectively (Fig. 6), are rather high (46, 41 and 45 $\mu\text{l/ml}$, respectively) in the whole titration region. They correspond to the transformation of the octahedral ammine complex into the anhydrous tetrahedral cyano complex in spite that for the pure aquo complex of cadmium in aqueous solutions and in absence of ammonia it follows from the

apparent molar volumes^{7,26} that the coordination number is 4. In crystalline sulfates the existence of the octahedral hexaquo ion¹⁷ has been proved both by X-rays and infrared spectra²⁷, as well as the mixed complex²⁸ $[\text{Cd}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ and even the hexamminecadmium(II) ion in spite that by the method of isotope exchange in aqueous-ammonia solutions it is possible to follow the substitution of water by ammonia only to the tetrammine complex step.¹⁹

The single-step character of the transformation to the tetracyanocadmiate indicates a distinct coordinative disproportionation of mixed cyano-ammine complexes in to the terminal members of the series. In this case the reason, however, is different from that of nickel where this disproportionation is due to the competition between the paramagnetic configuration in the octahedral field of weak donors and the diamagnetic configuration in the tetragonal planar field of strong donors. In contrast to zinc, cadmium is already an element with a distinct B-character²⁰, the ions of which have a high acceptor ability and with good donors they form bonds with a high degree

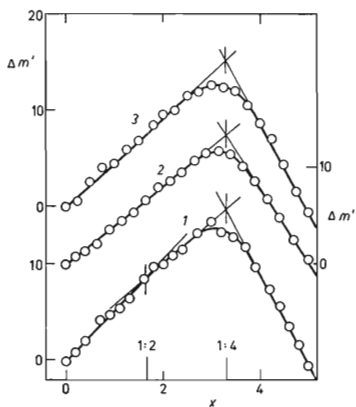


FIG. 5

The Densimetric Titration Curves of the Solutions of 4.76 mmol of CdSO_4 in 1.5M- $\text{NH}_3 + \text{NaCl}$

x (ml) is the volume of the added titrant solution of 5.76M- NaCN , $\Delta m' = \Delta m - kx$ (mg); 1 0M- NaCl , $k = 44 \text{ mg ml}^{-1}$, 2 1M- NaCl , $k = 32.6 \text{ mg ml}^{-1}$, 3 2M- NaCl , $k = 20.8 \text{ mg ml}^{-1}$.

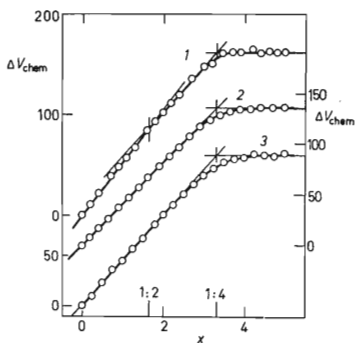


FIG. 6

The Densimetric Titration Curves of $\text{Cd}^{2+}(\text{NH}_3)\text{-CN}^-$ from Fig. 5, Recalculated to $\Delta V_{\text{chem}} = \Delta V_{\text{mix}} - x(\partial \Delta V_{\text{mix}} / \partial x)_{\text{exc}}(\mu)$

of covalence as witnessed by the increase of the stability of halogen complexes from F^- to I^- (ref.²⁰). This causes a strong differentiation of ligands according to their donor ability.

Strong donors CN are concentrated in complexes in which they can form strong covalent bonds and these are — in this case — the tetrahedral complexes with hybrid sp^3 bonds on $5s$ - and $5p$ -orbitals. With cadmium ion the octahedral configuration presents no possibility to form such stable covalent bonds because with completely occupied $4d$ -orbitals the octahedral hybridization can be formed only by admixing the energetically unfavourable $5d$ -orbitals. This is why — at the substoichiometric amount of the cyanide — the CN^- ions are distributed among Cd atoms unequally: they concentrate on certain atoms where they form the tetrahedral configuration with strong hybrid sp^3 bonds whereas other Cd^{2+} ions remain in the octahedral ammine complexes in which the H_2O and NH_3 ligands are concentrated. These ligands, as weaker donors, can to full extent display in the electrostatic binding interaction in these complexes while in covalent cyano complexes they would act as energetically unfavourable perturbations.

The authors are indebted to Dr V. Jedináková for useful discussions and for the technical help with measurements.

REFERENCES

1. Titov A. V.: *Ž. Obšč. Chim.* 4, 567 (1934).
2. Titov A. V.: *Ž. Obšč. Chim.* 19, 458 (1949).
3. Krishnamurti K., Venkataraman P.: *Research Corresp., Suppl. Research 7* (London), No 2, 15 (1954).
4. Tsujioka A.: *Bull. Chem. Soc. Japan* 32, 685 (1959).
5. Čeleda J.: *Sci. Papers of the Inst. Chem. Technology, Prague, Fac. Inorg. and Org. Technology* 3, 15 (1959).
6. Čeleda J.: *Sci. Papers of the Inst. Chem. Technology, Prague, Fac. Inorg. Technology* 5, 17 (1964).
7. Jedináková V., Čeleda J.: *This Journal* 32, 1679 (1967).
8. Jedináková V., Čeleda J.: *J. Inorg. Nucl. Chem.* 30, 555 (1968).
9. Jedináková V.: *Thesis*. Institute of Chemical Technology, Prague 1966.
10. Jedináková V., Čeleda J.: *Sci. Papers of the Inst. Chem. Technology, Prague, B* 7, 79 (1966); *B* 11, 41 (1967).
11. Čeleda J., Jedináková V., Šmirouš F.: *Chem. zvesti* 22, 93 (1968).
12. Holmes O. G., McClure D. S.: *J. Chem. Phys.* 26, 1686 (1957).
13. Siebert H.: *Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie*, p. 143. Springer, Berlin 1966.
14. Cotton F. A., Wilkinson G.: *Advanced Inorganic Chemistry* (German Ed.: *Anorganische Chemie*). Verlag Chemie, Weinheim 1967.
15. Jörgensen C. K.: *Acta Chim. Scand.* 8, 1502 (1954).
16. Kiss A.: *Z. Anorg. Chem.* 282, 141 (1955).
17. Lingafelter E. C., Montgomery H.: *Proc. 8th Internat. Conf. on Coordination Chemistry, Vienna 1964*, p. 129. Springer, Wien 1964.

18. Poulsen I., Bjerrum J.: *Acta Chem. Scand.* 9, 1407 (1955).
19. Ishimori T.: *Bull. Chem. Soc. Japan* 33, 520 (1960).
20. Phillips C. S. G., Williams R. J. P.: *Inorganic Chemistry*, Vol. 2. *Metals*. Clarendon Press, Oxford 1966.
21. Titov P. S., Boldanova N. N.: Yubil. Sbornik Nauč. Trudov Inst. Cvet. Metallov i Zolota (Sci. Papers of the Inst. of Rare Metals and Gold), p. 580, 1940; Ref. Ž. Chim. 4, No 5, 84 (1941).
22. Masaki K.: *Bull. Chem. Soc. Japan* 6, 89 (1931).
23. Irish D. E., McCarroll D., Young T. F.: *J. Chem. Phys.* 39, 3436 (1963).
24. Damaschun I.: *Z. Physik. Chem. B* 16, 81 (1932).
25. Plane R. A.: *Proc. 8th Internat. Conf. on Coordination Chemistry*, Vienna 1964, p. 17. Springer, Vienna 1964.
26. Jedináková V., Čeleda J.: *J. Inorg. Nucl. Chem.* 31, 2793 (1969).
27. Kermarrec Y.: *Compt. Rend.* 258, 5836 (1964).
28. Remy H.: *Lehrbuch der Anorganischen Chemie*, Vol. 2, p. 466. Geest und Portig, Leipzig 1954.

Translated by Z. Prášil.