

so that the anisotropy is

$$\Delta\chi^{G'} = \Delta\chi^G(1 - \frac{3}{2} \sin^2 \vartheta), \quad (7)$$

which gives the formula for the shielding effect

$$\sigma_A^G = \frac{\Delta\sigma^G}{3R^3N_0} (1 - 3 \cos^2 \gamma) (1 - \frac{3}{2} \sin^2 \vartheta). \quad (8)$$

The assumptions and approximations involved are apparent from the description of the model used. It should be emphasized that they are essentially those of the point-dipole approximation, so within the applicability of this approximation the formula (8) is as exact as the formula (2). Numerical calculations for CH₃ group showed that Eq. (8) gives results of the same sign and order of magnitude Eq. (3) for a wide range of values of R (3–10 Å) and γ (0–90°). The difference between the two expressions varied according to the values of R and γ but in the average it amounted to some 25% of the calculated values.

Clarifying discussions with Drs V. Špirko and I. Boháček, Institute of Physical Chemistry, Czechoslovak Academy of Sciences, Prague, are gratefully acknowledged.

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STABILITY CONSTANTS OF CHLORIDE AND BROMIDE COMPLEXES OF BIVALENT COBALT AND NICKEL IN EUTECTIC MELT OF LITHIUM, SODIUM AND POTASSIUM NITRATES

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Received July 6th, 1970

Study of composition and stability of complexes in molten salts is of importance for estimating the properties of molten salts, which represent the widest scope of inorganic solvents. Moreover, it is important also from the practical point of view, *e.g.* for the applica-

tion of ionic melts as catalysts. The existence of complex ions in molten salts has been proved by several authors. Some of them also measured the stability constants of the investigated complex ions¹⁻⁷, mostly using alkali nitrates as solvents. Alkali nitrates are best accessible both to theoretical and experimental treatment, thanks to their low melting points and because they do not form stable complexes with bivalent metal ions.

The present paper deals with the study of stability constants of halides complexes of cobalt and nickel in molten alkali nitrates by means of potentiometry, at the temperatures of 161° and 180°C.

EXPERIMENTAL

Chemicals

Eutectic mixture $\text{LiNO}_3\text{-KNO}_3\text{-NaNO}_3$ (30 : 53 : 17 mol %, m.p. 120°C) was used as solvent. It was prepared in the following way: The respective nitrates were first dried under vacuum at 120°C and then were melted in the appropriate molar ratio at 180°C. 1 ml of hydrogen peroxide was then added per 100 g of the molten eutectic mixture and nitrogen was bubbled through it for about 20 h. This resulted in the separation of the main part of heavy metals directly in the melt and in the oxidation of all organic impurities. The melt was afterwards filtered through a quartz frit with crushed asbestos. After adding a small amount (c. 0.3 ml per 100 g of melt) of hydrogen peroxide and after six hours' bubbling with nitrogen the melt was set aside to solidify in a platinum dish and was then stored in a polyethylene flask placed in an exsiccator over phosphorus pentoxide. When preparing the eutectic it is important not to exceed the temperature of 200°C to avoid the formation of nitrites in the melt.

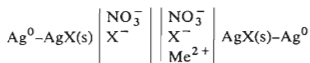
Metal ions were added as nitrates and were dried under vacuum at 60°C. The content of cobalt and nickel in the samples to be added was determined by chelatometric titration against murexide.

Potassium chloride and bromide were dried *in vacuo* at 120°C and their content in the samples was determined argentometrically to be 100%.

Nitrogen used was deoxidized by bubbling through the solution of chromium(II) chloride and was further dried with sulphuric acid and potassium hydroxide.

Apparatus and Method

Equilibrium electric tensions were measured in the concentration cell



where Ag(X(s)) is solid silver chloride or bromide, NO_3^- is the eutectic $\text{LiNO}_3\text{-KNO}_3\text{-NaNO}_3$ mixture, X^- stands for Cl^- or Br^- in the form of potassium salts and Me^{2+} is $\text{Co(NO}_3)_2$ or $\text{Ni(NO}_3)_2$.

Electrodes were prepared by electrolytical silver-coating of a Pt wire of 0.5 mm diameter and 20 mm length, sealed into a glass tube, and by subsequent anodic polarization of the silver coating in 0.1M-HCl or KBr solution⁸.

Reference electrode (left-hand side of the cell) was formed by a glass tube of 8 mm diameter with a sealed-in frit S_4 into one of its ends. This half-cell contained the eutectic mixture of nitrates with constant concentration of halide ions ($N_x = 10^{-3}$) and had its own separate silver halide electrode. The right-hand side of the cell was formed by a glass test-tube of 3 cm diameter and

11 cm length, containing 20 g of the nitrate eutecticum with a defined amount of KX to which cobalt or nickel nitrates were stepwise added. Both half-cells were joined by inserting the reference electrode into the test tube. The whole cell was placed into a thermostat with silicone oil in which the temperature was maintained within $\pm 0.5^\circ\text{C}$. The temperature was checked by a mercury Anschütz thermometer.

Potential difference was measured using a QTK bridge with the accuracy of ± 0.1 mV which was calibrated by means of a normal Wheatstone cell. Measurements were carried out in the concentration range $N_{\text{KX}} = 0.15$ to $1.5 \cdot 10^{-3}$ and $N_{\text{Me}(\text{NO}_3)_2} = 0.2$ to $2.5 \cdot 10^{-3}$, at 161° and 180°C .

RESULTS AND DISCUSSION

As the content of alkali halides (KX), and cobalt and nickel nitrates in the solutions employed was always lower than 10^{-2} (in molar fraction), the diffusion electric tension on the boundary of both electrode parts due to X^- and Co^{2+} or Ni^{2+} ion transfer was small and therefore was neglected. Provided that the activity of the solid silver halide is constant and the halide-silver electrodes are reversible with respect to halide ions in alkali nitrate melts¹⁰, the difference of equilibrium potentials is given by the equation

$$\Delta E = (2 \cdot 303RT/F) \log (a_{\text{KX}}/a'_{\text{KX}}), \quad (1)$$

where a_{KX} is the activity of KX in the measured half-cell, a'_{KX} is the activity of KX in the reference half-cell. For dilute solutions in which the Henry law holds (c. to 0.5 mol % of the soluble component⁹) activities can be substituted by concentrations. From the verification of the Nernst equation which was performed using our electrodes, it follows that the above mentioned assumption is fulfilled over the concentration range used in our experiments, in which the molar fraction varies between $0.2 \cdot 10^{-3}$ – $5 \cdot 10^{-3}$.

By addition of cobalt(II) or nickel(II) ions into the right-hand part of the cell its electromotive force changes and the stoichiometric activity coefficient is given by the relation

$$\log \gamma_{\text{KX}} = - (F/2 \cdot 303RT) \Delta E, \quad (2)$$

where ΔE denotes the change of the cell voltage.

The stability constants were calculated using the method of Blander⁷ which in several aspects is more advantageous than other methods. Extrapolation functions, calculated from experimental data, are chosen so that their probable error is constant over the whole concentration range studied. This allows to use simple statistical or graphical method for calculation. The other methods¹¹⁻¹³ make use of a function in which the probable error decreases with decreasing ligand concentration, thus making a simple extrapolation incorrect.

When it is possible, the functions calculated from experimental data are expressed in terms of stoichiometric concentrations of the solutes. In this manner different approximations are eliminated and the calculation is more simple and more accurate. Stability constants are calculated for infinite dilution of all solutes so that they can be considered as true thermodynamic constants.

If the stability constants of complex ions CoX^+ , CoX_2 , Co_2X^{3+} are defined as

$$K_{11} = \frac{N_{\text{CoX}^+}}{N_{\text{Co}^{2+}} \cdot N_{\text{X}^-}}, \quad (3)$$

$$K_{12} = \frac{N_{\text{CoX}_2}}{N_{\text{CoX}^+} \cdot N_{\text{X}^-}}, \quad (4)$$

$$K_{21} = \frac{N_{\text{Co}_2\text{X}^{3+}}}{N_{\text{CoX}^+} \cdot N_{\text{Co}^{2+}}}, \quad (5)$$

where N are molar fractions, then the stoichiometric activity coefficients of KX can be expressed in terms of Mac Laurin power series:

$$-\ln \gamma_{\text{KX}} = K_{11}N_{\text{Co}(\text{NO}_3)_2} + (K_{11}K_{21} - \frac{1}{2}K_{11}^2)N_{\text{Co}(\text{NO}_3)_2}^2 + (2K_{11}K_{12} - K_{11}^2)N_{\text{Co}(\text{NO}_3)_2} \cdot N_{\text{KX}}. \quad (6)$$

Activity coefficients are accounted for to deviations from ideality caused only by association. Comparison with the general form of Mac Laurin series yields the following expressions for graphical calculation of K_{11} and K_{12}

$$-K_{11} = \lim_{\substack{N_{\text{Co}(\text{NO}_3)_2} \rightarrow 0 \\ N_{\text{KX}} \rightarrow 0}} \frac{\partial \ln \gamma_{\text{KX}}}{\partial N_{\text{Co}(\text{NO}_3)_2}}, \quad (7)$$

$$K_{11}(2K_{12} - K_{11}) = \lim_{\substack{N_{\text{Co}(\text{NO}_3)_2} \rightarrow 0 \\ N_{\text{KX}} \rightarrow 0}} \frac{\partial^2 \ln \gamma_{\text{KX}}}{\partial N_{\text{Co}(\text{NO}_3)_2} \partial N_{\text{KX}}}. \quad (8)$$

A complete derivation of the above expressions may be found in the original paper by Braunstein and coworkers¹⁷. For each concentration of KX the slope of the dependence of $\ln \gamma_{\text{KX}}$ on the molar fraction of $\text{Co}(\text{NO}_3)_2$, extrapolated to zero $\text{Co}(\text{NO}_3)_2$ concentration, is determined.

TABLE I

Values of Stability Constants and Specific Association Energies of the Formation of Co and Ni Bromide and Chloride Complexes

Central ion	Ligand	°C	K_{11}^a	A_{11} kcal mol ⁻¹	K_{12}^b	ΔA_{12} kcal mol ⁻¹
Co^{2+}	Cl^-	161	220	3.46	34	2.75
		180	204	3.55	35	2.9
	Br^-	161	136	3.06	5	1.42
		180	107	3.0	5	1.47
Ni^{2+}	Cl^-	161	127	3.0	5	1.42
		180	116	3.06	4	1.35
	Br^-	161	88	2.7	4	1.3
		180	71	2.65	3	1.22

Relative error: $a \pm 5\%$, $b \pm 100\%$.

The first stability constants K_{11} are calculated by extrapolating the dependence of the limiting slopes on the concentration of KX to zero KX concentration. The intercept on the slope axis gives K_{11} and from the slope in the point $KX = 0$ K_{12} can be calculated. With respect to small values of K_{11} and K_{12} the latter ones are charged by a considerable error ($\pm 100\%$). With K_{11} , the error is less than $\pm 5\%$. The values of K_{11} and K_{12} , together with the association energy of complex ion formation, are presented in Table I. The constant K_{21} was not calculated owing to insufficient accuracy.

Higher stability constants could be calculated by expanding Eq. (6) to higher terms, however, their meaning is dubious when taking into account the increasing errors of calculation and the inaccuracies of experimental data at higher concentrations of the solutes.

Thermodynamic stability constants of nickel(II) ion with chloride ions as determined in the present work are about four times higher than the values found by Christie and Osteryoung⁶ ($K_{11} = 26$, $K_{12} = 2$) who used polarography for their measurement in $\text{LiNO}_3\text{-KNO}_3$ eutectics at 280°C . Norman² determined the stability constant of complex CoCl^+ ion from spectroscopic measurements only by order of magnitude ($K_{11} = 40$ to 300). However, none of these authors performed this calculation for infinite dilution of all solved components.

As can be seen from Table I, the stability constants of bromide complexes of both cobalt and nickel are lower than those of chloride complexes. This indicates, that in this case the contribution of structural factor, controlling the electrostatic component of the binding energy, is probably higher than the contribution of π -bonds (*i.e.* bonds of covalent character). This contribution is higher with Co complexes than with Ni complexes. According to Sundheim and Harrington¹⁵, the complexes are of the tetrahedral type with the configuration d^7 and d^8 for Co and Ni, respectively. From the theory of crystal field it follows that each t_2 electron of the tetrahedral complex with free spin represents a lowering of the stabilization energy of the crystal field. This fact is in accordance with our finding that stability constants of the bromide and chloride complex of Co are higher than those of nickel complexes.

Specific association energy, A_{ij} , of the formation of Co and Ni halide complexes were calculated on the basis of quasi-lattice model (asymmetric approximation)¹⁴, assuming the coordination number to be $Z = 4$.

$$K_{11} = Z(\beta_{11} - 1), \quad (9)$$

$$K_{11}K_{12} = Z \left(\frac{Z-1}{2} \right) (\beta_{11}\beta_{12} - 2\beta_{11} + 1), \quad (10)$$

where

$$\beta_{ij} = \exp(-\Delta A_{ij}/RT). \quad (11)$$

Since the equations of this model were derived for ions of the same charge, they need not apply to a system of ions of different charges. However, the relatively small change of A_{ij} with temperature indicates that the quasi-lattice model may, at least in semiquantitative scale, be applied to the determination of the temperature dependence of stability constants of univalent ions with the multivalent ones.

We have also tried to establish the stability constants of iodide complexes of Co and Ni, however, the reproducibility of the measured values was very poor. In our opinion, this is caused by the oxidation of iodide ions in the medium of nitrate melt in the presence of cobalt(II) and nickel(II) cations.

Our thanks are due to Mrs H. Oesterreicherová for technical assistance.

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Translated by V. Čermáková.

DISSOZIATIONSKONSTANTEN EINIGER SÄUREN IN WASSER-METHANOL-GEMISCHEN

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Eingegangen am 7. August 1970

Im Zusammenhang mit dem systematischen Studium der Aziditätseigenschaften eines Gemisches von Wasser mit Methanol war es erforderlich, die Dissoziationskonstanten einiger Säuren zu messen, die evtl. zur Herstellung von Pufferlösungen dienen könnten. Von den möglichen Methoden, wie die direkte Potentiometrie mit Verwendung einer Wasserstoff- und Silberchloridelektrode, evtl. die Konduktometrie oder die Spektrophotometrie usw., wurde die von Kilpi¹ vorgeschlagene und später von Grunwald^{2,3} benützte differentielle potentiometrische Titration gewählt. Diese Methode fußt nicht auf den Werten der Standardpotentiale, deren Kenntnis in nichtwäßrigen Lösungen zweifelhaft ist, und ermöglicht, die Messung zumindest teilweise zu automatisieren, gegebenenfalls die Wasserstoffelektrode gegen eine Glaselektrode zu vertauschen.

EXPERIMENTELLER TEIL

Die Dissoziationskonstanten der Ameisen-, Essig- und Benzoesäure wurden in wäßrigen Lösungen mit 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 95 und 99 Gew.-% Methanol gemessen.