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Acceptor Power of Cations in Donor–Acceptor Interactions

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Abstract—Published data concerning quantitative evaluation of the reactivity of cations in donor–acceptor interactions were analyzed. The "relative acceptor numbers" of $C\text{o}^{2+}$, Mn^{2+}, Ni^{2+}, Al^{3+}, and Ga^{3+} were determined polarographically: 2.16 ± 0.32, 2.25 ± 0.23, ~1.70, 2.35 ± 0.27, and 2.42 ± 0.21, respectively. The known "relative acceptor numbers" for 21 cations were systematized, and a linear correlation between the ionization potentials and "relative acceptor numbers" of "hard" cations was revealed.

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Procedures based on leaching with nonaqueous (organic) solvents find increasing use in processing of primary and secondary raw materials for nuclear power engineering. Application of these procedures to production and purification of a wide range of noble, rare, and radioactive metals led to the development of solvometallurgy as a new direction in processing of metal raw materials [1].

The features of dissolution of inorganic compounds in nonaqueous media are largely determined by the energy of solvation of ions and molecules. Estimation and prediction of the energy characteristics of the solvation of cations requires refinement of our views on the reactivity (acceptor power) of cations in donor–acceptor interactions.

Numerous attempts were made to solve this problem. In particular, Kumok [2] used as the measure of the reactivity of cations the quantity a_{M_i} defined as the slope of relationship (1):

$$\log \beta_{M_i} = a_{M_i} \log \beta_R + \text{const.} \tag{1}$$

where β_{M_i} and β_R are the stability constants of a cation M_i and a reference cation R with a certain set of ligands L_i.

Correlation (1) is valid only because both $\log \beta_{M_i}$ and $\log \beta_R$ depend on the properties of ligand L similarly, in accordance with the linear free energy relationship:

$$\log \beta_{M_i} = a_{M_i} f(\text{L}) + b_{M_i}, \tag{2}$$

$$\log \beta_{M_R} = a_{M_R} \boldsymbol{f(L)} + b_{M_R}, \tag{3}$$

where a_{M_i} and a_{M_R} are constants characterizing the properties of the cations; b_{M_i} and b_{M_R} are constants; and $f(\text{L})$ is a parameter characterizing the properties of a ligand (e.g., pK_a) and equal for both cations.

Equations (1)–(3) are valid for mono- and polydentate ligands of type H_nL_m at complete realization of the denticity of the ligand and coordination capacity of the cation [2].

Table 1 lists data characterizing the properties of cations subdivided by Kumok [2] into three subgroups: (1) eight-electron and *f*-element ("hard") cations (reference element La); (2) *d*-element ("soft") cations (reference element Ca); and (3) intermediate cations (reference element Zn).

As shown in [2], the parameter a_{M_i} is close to the ratio $\varphi_{M_i}/\varphi_{R_i}$, where $\varphi_{M_i} = Z/r_{M_i}$ and $\varphi_{R_i} = Z/r_{R_i}$ (*Z* is cation charge; r_{M_i} and r_{R_i} are the radii of the M_i and R_i cations, respectively). In essence, a_{M_i} is mainly determined by the effect of electrostatic forces.

As for characterization of the reactivity of cations in donor–acceptor interactions, this problem was discussed in most detail in [4]. It is based on the following assumptions.

The modern concepts of cation solvation allow ΔG of solvation to be a priori characterized as a sum of two terms: electrostatic and donor–acceptor [5]. The first term can be adequately calculated today using the improved Born theory [6].

Since early studies [7], in calculations of the energy of hydration and solvation of cations, the effective dielectric permittivity related to the nearest surround-

Table 1. Characteristic of the complexing power of cations according to Kumok [2, 3]

Types of cations								
8-electron and *f* elements ("hard" cations)			*d* elements ("soft" cations)			intermediate elements		
M_i	R_i	a_{M_i} (exp.)	M_i	R_i	a_{M_i} (exp.)	M_i	R_i	a_{M_i} (exp.)
Y^{3+}	La^{3+}	1.14	Zn^{2+}	Ca^{2+}	1.25	In^{3+}	Zn^{2+}	2.28
Ln^{3+}	La^{3+}	1.20	Mg^{2+}	Ca^{2+}	1.35	Fe^{3+}	Zn^{2+}	1.32
Sc^{3+}	La^{3+}	1.48	Ni^{2+}	Ca^{2+}	1.45	Al^{3+}	Be^{2+}	1.00
Mg^{2+}	La^{3+}	0.98	Mn^{2+}	Ca^{2+}	1.12	Cu^{2+}	Zn^{2+}	1.365
Th^{4+}	La^{3+}	1.46	Co^{2+}	Ca^{2+}	1.33			
Ce^{3+}	La^{3+}	1.55	Be^{2+}	Mg^{2+}	2.16			
Ba^{2+}	La^{3+}	0.58						
Zr^{4+}	La^{3+}	1.87						
Sr^{2+}	Ba^{2+}	1.12						
Ca^{2+}	Ba^{2+}	1.35						

ing of an ion is used instead of the macroscopic dielectric permittivity characterizing the solvent [8]. The effective dielectric permittivity is approximately equal for different solvents, which leads to equal values of the electrostatic term in the energy of solvation of cations. Similar conclusions were made in [9], where the conclusion that the energies of solvation of Rb^+ and Cs^+ in different solvents (in these systems the effect of donor–acceptor interactions is negligible) are constant actually means that specifically the electrostatic contribution is constant. For other cations, an increase or a decrease in the energy of solvation is primarily due to changes in the energy of donor–acceptor interactions. Kanevskii [10] confirmed this assumption experimentally: The electrostatic term in the energy of solvation of proton remains constant in a wide range of solvents, whereas the donor–acceptor term grows with an increase in the donor power of solvents.

The Gibbs energy ΔG of donor–acceptor reactions is determined by the efficiency of the pair interaction of a donor B and an acceptor A (cation in our case). The higher the donor and acceptor powers of B and A, the higher the efficiency of the interaction.

In this paper, quantitative prediction of the efficiency of donor–acceptor interactions is based on the presentation, as it is often done in theoretical inorganic chemistry, of a thermodynamic characteristic of a process [in our case, $\Delta G^0_{\mathrm{sol}}(\mathrm{M}_i^{n+})$ or $\Delta H^0_{\mathrm{sol}}(\mathrm{M}_i^{n+})$] in the form of a dependence on the multiplicative function defined as the product of a donor factor and an acceptor factor [11–13].

The donor power of bases (solvents) is characterized by the donor number *DN* [14], and the acceptor power of cations (parameter *a*), by the slope of the dependence of the Gibbs energy of solvation $\Delta G^0_{\mathrm{sol}}(\mathrm{M}_i^{n+})$ on the solvent donor number [4].

The experimental procedure used by Kanevskii is based on measuring the standard electrode potentials ($E^0_{\mathrm{M/M}^{n+}}$]).

It can be readily shown by the method of cycles that the standard Gibbs energy of an electrode process (4), ΔG^0_{ep}, is given by relationship (5):

$$\mathrm{M_T} \rightleftarrows \mathrm{M_S^{n+}} + n\bar{e}, \tag{4}$$

$$\Delta G^0_{\mathrm{ep}} = \Delta G^0_{\mathrm{at}} + \Delta G^0_{\mathrm{ion}} + \Delta G^0_{\mathrm{sl}}, \tag{5}$$

where ΔG^0_{at}, $\Delta G^0_{\mathrm{ion}}$, and ΔG^0_{sl} are the standard Gibbs energies of the atomization (sublimation) of a metal, ionization of its atoms in the gas phase, and solvation of the ion formed, respectively.

In the general case, as shown above, relationship (6) is valid:

$$\Delta G^0_{\mathrm{sl}} = \Delta G^0_{\mathrm{nc}} + \Delta G^0_{\mathrm{d-a}}, \tag{6}$$

where $\Delta G^0_{\mathrm{d-a}}$ is the donor–acceptor term, and ΔG^0_{nc}, electrostatic (non-coordination) term of the energy of solvation of a cation; then we obtain

$$E^0_{\mathrm{M/M_S^{z+}}} = -\frac{\Delta G^0_{\mathrm{at}} + \Delta G^0_{\mathrm{ion}} + \Delta G^0_{\mathrm{nc}}}{nF} - \frac{\Delta G^0_{\mathrm{d-a}}}{nF}$$
$$= \mathrm{const}' - \frac{\Delta G^0_{\mathrm{d-a}}}{nF}. \tag{7}$$

Here const' has the meaning of the electrode potential in an inert solvent S_i exhibiting no complexing properties.

Since the relative standard electrode potential E^0 differs from the corresponding thermodynamic potential by the thermodynamic electrode potential of the reference electrode, it can be considered as a measure of changes in the donor–acceptor term of the standard energy of solvation. Comparison of the potentials in different solvents shows how the solvent donor power affects the solvation of a cation. The researcher’s task is to measure $E^0_{\mathrm{M/M}^{n+}}$ in various solvents and correlate the potentials with the solvent donor numbers *DN*.

This approach was realized for the first time by Kanevskii [10]. A comparison of the relative standard electrode potentials of a hydrogen electrode $(E^0_{\mathrm{H^+/H_2}})_\mathrm{S}$ in various solvents revealed a correlation between $(E^0_{\mathrm{H^+/H_2}})_\mathrm{S}$ and *DN*:

$$(E^0_{\mathrm{H^+/H_2}})_\mathrm{S} = a + bDN. \tag{8}$$

Similar equation correlates $(E^0_{\mathrm{M^{n+}/M}})_\mathrm{S}$ and *DN* for M = $\mathrm{Li^+}$, $\mathrm{Na^+}$, $\mathrm{K^+}$, $\mathrm{Rb^+}$, $\mathrm{Cs^+}$, $\mathrm{Tl^+}$, and $\mathrm{Ag^+}$ [4, 10].

The slopes of these dependences were used for evaluating the acceptor power of cations:

$$\alpha_\mathrm{ac}(\mathrm{M}_i) = b_i nF, \tag{9}$$

where *F* is the Faraday number and $\alpha_\mathrm{ac}(\mathrm{M_i})$ is the relative acceptor number of the cation. The results are given below (for $\mathrm{Mg^{2+}}$, the calculation was based on data from [5]).

Cation	$\mathrm{Cs^+}$	$\mathrm{Rb^+}$	$\mathrm{K^+}$	$\mathrm{Na^+}$	$\mathrm{Tl^+}$	$\mathrm{H^+}$	$\mathrm{Ag^+}$	$\mathrm{Mg^{2+}}$
$\alpha_\mathrm{ac}(\mathrm{M}_i)$	0.02	0.03	0.05	0.2	0.3	1.14	0.6	1.15

Strictly speaking, to calculate $\alpha_\mathrm{ac}(\mathrm{M}_i)$ of cations, Kanevskii [10] used Eq. (10) following from (8) and (9):

$$\alpha_\mathrm{ac}(\mathrm{M}_i) = \frac{[E^0_{\mathrm{S}_1} - E^0_{\mathrm{S}_2} + \Delta\chi]}{DN_2 - DN_1}, \tag{10}$$

where $E^0_{\mathrm{S}_1}$ and $E^0_{\mathrm{S}_2}$ are the electrode potentials in solvents S_1 and S_2; DN_1 and DN_2, donor numbers of solvents S_1 and S_2; and $\Delta\chi$, difference between the surface potentials of solvents S_1 and S_2.

Jakuszewski and Taniewska-Osinska [16] determined the standard electrode potentials $E^0(\mathrm{Ca^{2+}|Ca})$, $E^0(\mathrm{Sr^{2+}|Sr})$, and $E^0(\mathrm{Ba^{2+}|Ba})$ in aqueous and methanolic solutions using the cell $\mathrm{Pb|PbCO_3}$, $\mathrm{MCO_3}$, $\mathrm{MX_2}$ (solution) $\mathrm{HgX_2|Hg}$, where Œ = Cl or Br, M = $\mathrm{Ca^{2+}}$, $\mathrm{Sr^{2+}}$, $\mathrm{Ba^{2+}}$, and obtained the following values (V): $E^0(\mathrm{Ca^{2+}, CH_3OH|Ca}) = -2.929$, $E^0(\mathrm{Sr^{2+}, CH_3OH|Sr}) = -2.938$, and $E^0(\mathrm{Ba^{2+}, CH_3OH|Ba}) = -2.943$. The electrode potentials in aqueous solutions are as follows (V): $E^0(\mathrm{Ca^{2+}, H_2O|Ca}) = -2.868$, $E^0(\mathrm{Sr^{2+}, H_2O|Sr}) = -2.886$, and $E^0(\mathrm{Ba^{2+}, H_2O|Ba}) = -2.912$. These values are close to the best modern data given in [17], namely, $E^0(\mathrm{Ca^{2+}, H_2O|Ca}) = -2.866$, $E^0(\mathrm{Sr^{2+}, H_2O|Sr}) = -2.888$, and $E^0(\mathrm{Ba^{2+}, H_2O|Ba}) = -2.906$ V.

The use of the above voltaic cell ensures high accuracy of the measurements, because the cell contains only one liquid phase, and, hence, the errors associated with the elimination or calculation of the liquid–liquid interphase potential are excluded.

The donor number of methyl alcohol was determined calorimetrically by Olofsson [18]: 79.8 ± 0.1 kJ $\mathrm{mol^{-1}}$. The donor number of water was taken equal to 103.0 kJ $\mathrm{mol^{-1}}$ as the average of close values obtained by direct calorimetric measurement [19] (101.7 ± 1.2 kJ $\mathrm{mol^{-1}}$) and by the calculation from the energies of transfer of cations and salts from organic solvents into water [20] (104.2 ± 1.2 kJ $\mathrm{mol^{-1}}$).

Substitution of these values in Eq. (10) gives the following values of the relative complexing power of the cations: $\alpha_\mathrm{ac}(\mathrm{Ca^{2+}})$ 0.52, $\alpha_\mathrm{ac}(\mathrm{Sr^{2+}})$ 0.42, and $\alpha_\mathrm{ac}(\mathrm{Ba^{2+}})$ 0.31. The relative acceptor powers of these cations, determined polarographically [21], are as follows: $\alpha_\mathrm{ac}(\mathrm{Ca^{2+}})$ 0.53 ± 0.03, $\alpha_\mathrm{ac}(\mathrm{Sr^{2+}})$ 0.50 ± 0.03, and $\alpha_\mathrm{ac}(\mathrm{Ba^{2+}})$ 0.28 ± 0.09.

The polarographic method is an alternative to the potentiometric method [22–24].

Indeed, the reduction half-wave potential of the cations on a mercury dropping electrode and the corresponding standard electrode potential are related by the well-known dependence (11)

$$E_{1/2} = E^0 - (RT/nF)\ln\sqrt{D_\mathrm{ox}/D_\mathrm{rd}}, \tag{11}$$

where D_ox and D_rd are the diffusion coefficients of the oxidized and reduced forms, respectively. The quantity D_ox is determined by the nature of the solvent. However, for solvents with close dielectric permittivities and viscosities, the second term in the right part of (11) is, to a certain approximation, constant, i.e., in (7) the standard potential can be replaced by the half-wave potential.

It was demonstrated by the example of $\mathrm{Tl^+}$, $\mathrm{Cd^{2+}}$, $\mathrm{Zn^{2+}}$, $\mathrm{Co^{2+}}$, $\mathrm{Ni^{2+}}$, $\mathrm{Mn^{2+}}$, and $\mathrm{In^{3+}}$ [22–24] that the reduction half-wave potentials of these cations linearly correlate with the donor numbers of solvents:

$$-E_{1/2} = a + bDN. \tag{12}$$

Table 2. Reduction half-wave potentials of Co^{2+}, Mn^{2+}, Ni^{2+}, Al^{3+}, and Ga^{3+} in various solvents vs. saturated calomel electrode [$E_{1/2}$(SCE)]

Solvent (ε)	*DN*	Co^{2+}		Mn^{2+}		Ni^{2+}		Al^{3+}		Ga^{3+}	
		$-E_{1/2}$, V	ΔV, V	$-E_{1/2}$, V	ΔV, V	$-E_{1/2}$, V	ΔV, V	$-E_{1/2}$, V	ΔV, V	$-E_{1/2}$, V	ΔV, V
I (41)	14.1	0.61	0.031	1.08	0.028	0.29	0.061	1.53	0.021	0.86	0.019
II (36)	26.6	1.30	0.031	1.58	0.030	1.02	0.053	1.84	0.026	1.26	0.022
III (45)	29.8	1.54	0.033	1.92	0.031	1.07	0.042	1.98	0.022	1.32	0.024
IV (31)	38.8	1.88	0.035	2.27	0.035	1.19	0.060			1.72	0.026
V (37)	2.7							1.03	0.020		

Analysis of (12) shows that the constant a in this equation corresponds to $-E_{1/2}$ for the given ion at $DN = 0$, i.e., is the half-wave potential in an inert solvent and is independent of a particular acceptor with which the donor numbers were determined, because in any relative scale of the donor power $DN = 0$ corresponds to the lack of complexing power. Since the half-wave potentials do not depend on the choice of this scale either, it is clear from (7) and (12) that the product $b \times DN$ is also independent of particular donor scale and expresses the energy of the donor–acceptor interaction:

$$b \times DN = -G^0_{da}/nF. \tag{13}$$

By analogy with [11–13], presenting $-\Delta G_{da}$ in the form of a dependence on the multiplicative function, a product of an acceptor factor and a donor factor, Kanevskii [25] describes ΔG_{da} by Eq. (14):

$$\Delta G_{da} = -L\alpha_{(A)}\alpha_{(D)}, \tag{14}$$

where $\alpha_{(D)}$ is a donor factor, $\alpha_{(A)}$ is an acceptor factor, and L is a constant.

In accordance with this approach, since DN in Eq. (13) characterizes the donor power of a solvent, the second factor in the left side of this equation, i.e., b, should characterize the acceptor power of an ion. Therefore, Eq. (11) can rewritten in the form

$$b_i nF DN = \alpha_{ac}(M_i)DN = -\Delta G^0_{da}. \tag{15}$$

Hence follows Kanevskii's definition $\alpha_{ac}(M_i) = b_i nF$.

Since the quantities *DN* and $-\Delta G_{da}$ have the same dimension (kJ mol^{-1} or kcal mol^{-1}), $bnF = \alpha_{ac}(M_i)$ is a dimensionless quantity. This quantity was termed in [4] the dimensionless characteristic of the acceptor power of the cation.

The acceptor powers of cations, calculated from the reduction half-wave potentials of these cations in organic solvents [26, 27], are as follows.

Cation	Tl^+	Cd^{2+}	Zn^{2+}	Co^{2+}	Ni^{2+}	In^{3+}	Mn^{2+}
$\alpha_{ac}(M_i)$	0.27	1.3	1.5	2.1	1.57	2.3	2.4

It is emphasized that Eq. (12) is valid only if the effect of donor–acceptor interaction on the reduction half-wave potential is not distorted by other factors, in particular, by irreversibility of the process.

At the same time, the experimental data given in [24] clearly indicate that the reduction of Co^{2+}, Mn^{2+}, and Ni^{2+} in the majority of the examined solvents is irreversible.

To refine the data given in [4], we reproduced the experiments on determination of the reduction half-wave potentials of rare-earth elements, Co^{2+}, Mn^{2+}, and Ni^{2+} in acetonitrile (**I**), dimethylformamide (**II**), and dimethyl sulfoxide (**III**). Particular attention was given to the problem of dehydration of the reagents and solvents as one of the major factors determining the irreversibility of the reduction of these cations [18, 19]. Furthermore, we examined the behavior of Co^{2+}, Mn^{2+}, and Ni^{2+} in hexamethylphosphoramide (**IV**) and of Al^{3+} and Ga^{3+} in all the above-mentioned solvents and in nitromethane (**V**). The results are given in Table 2.

The results of the study showed that rare-earth cations were reduced irreversibly.[1] As for transition elements, data of logarithmic analysis [28] given in Table 2 indicate that in anhydrous solvents the reduction of Co^{2+} and Mn^{2+} is reversible, whereas nickel is reduced irreversibly. For Ga^{3+}, the effect of the irreversibility on the reduction is manifested insignifi-

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[1] The acceptor numbers of rare-earth cations, given in [4], were obtained without taking this fact into account and cannot be considered as a criterion of the reactivity.

Table 3. Results of statistical analysis of the linear correlation of the reduction half-wave potentials of Co^{2+}, Mn^{2+}, Ni^{2+}, Al^{3+}, and Ga^{3+} with the solvent donor numbers and the calculated values of the relative acceptor power

Parameter	Co^{2+}	Mn^{2+}	Ni^{2+}	Al^{3+}	Ga^{3+}
a'	0.01	0.37	–0.13	0.909	0.35
b'	0.047 ± 0.007	0.049 ± 0.005	0.037 ± 0.01	0.034 ± 0.004	0.035 ± 0.003
R	0.957	0.978	0.879	0.972	0.987
F	44.9	88.2	14	71.8	149
Relative acceptor power $\alpha_{ac}(M_i)$	2.16 ± 0.32	2.25 ± 0.23	~1.70 ± 0.46	2.35 ± 0.27	2.42 ± 0.21

cantly in solvents **III** and **IV**, and for Al^{3+}, in DMF, and it does not affect the reproducibility of the results. In solvent **IV**, Al^{3+} is reduced irreversibly. Therefore, in the subsequent analysis of the dependence of the reduction half-wave potential of Al^{3+} on the donor numbers of solvents, we used the data obtained for the reduction of Al^{3+} in nitromethane.

The reduction half-wave potentials of Co^{2+} and Mn^{2+} in solvents **I** and **II** coincide with the data obtained in [29, 30]. For Ni^{2+}, coincidence with the published data [24] is observed only for the case of the reduction in acetonitrile. In all the other cases, the potentials are shifted toward the negative values. This is particularly clearly manifested for solvent **III**: The shift for Ni^{2+} is 0.12 V (for Co^{2+}, 0.05 V; for Mn^{2+}, 0.18 V). These deviations are most probably associated with different degrees of drying of the solvents and reagents used.

The results of treatment of the experimental data are listed in Table 3.

These results show that, for all the examined cations except Ni^{2+}, the dependence of $E_{1/2}$ on *DN* of solvents is indeed described by Eq. (12). The quantities $\alpha_{ac}(M_i)$ calculated by Eq. (9) for Co^{2+}, Mn^{2+}, Ni^{2+}, Al^{3+}, and Ga^{3+} are listed in Table 3.

The relative acceptor powers evaluated for Co^{2+} and Mn^{2+} coincide with those given in [4, 22–24]. The value of α_{ac} for Ni^{2+} should be considered only as an estimate.

For cations whose direct polarographic reduction is complicated by the occurrence of side processes, an "indirect" polarographic method was suggested. This method is based on measuring the reduction potentials of β-naphthoquinones bound in a complex with the examined metal cation in various organic solvents [4]. The results thus obtained [4, 22–24] are given below.

Cation	K^+	Na^+	Li^+	Mg^{2+}	Zn^{2+}
$\alpha_{ac}(M_i)$	0.04	0.19	0.40	0.80	1.57

It should be emphasized here that the "indirect" method has serious limitations. The authors do not take into account the possibility of stepwise complexation of naphthoquinones with Zn^{2+} and Mg^{2+}, and also ignore the fact that the complexes with Mg^{2+} are reduced irreversibly. This leads to significant discrepancies with the data obtained using standard electrode potentials.

The most reliable values of the acceptor numbers of cations, obtained by Kanevskii's method, are given in Table 4. In addition to the already considered data, the acceptor numbers are given in Table 4 for Fe^{3+} (4.1) [4] and Cu^{2+} (2.44) [31]. The latter value was obtained using *DN* of ammonia, equal to 31.85 (instead of 30.8 used in [31]; 31.85 is the arithmetic mean of all the published values, and not of selected values presented in [31]).

The data obtained account for the well-known order of an increase in the stability of coordination compounds: $Cs^+ < Rb^+ < K^+ < Na^+ < Li^+ \le Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Zn^{2+} < Cu^{2+}$, found in [14] from data collected in [32]: With an increase in the acceptor power of cations, characterized by $\alpha_{ac}(M_i)$, the stability of complexes increases.

Table 4 shows that the sequence of the variation of the acceptor numbers of cations, on the whole, adequately reflects the well-known trends in the variation of their complexing power in relation to the position in the periodic table [2, 3, 33]: the acceptor power of cations decreases in going from higher to lower elements of Groups I and II (main subgroups).

In Group III (Al^{3+}, Ga^{3+}. In^{3+}), the reactivity of the cations, as expected, decreases in the order $Ga^{3+} \ge Al^{3+} \ge In^{3+}$.

Attempts to correlate the reactivity of all the examined cations with the electronegativity or ionization potential of cations failed. It can be noted, however, that in the series of "hard" cations the correlation between $\alpha_{ac}(M_i)$ and ionization potential (*J/z*, where

Table 4. Relative complexing power of cations

Cation	J/z, eV	$\alpha_{ac}(M_i)$	Cation	J/z, eV	$\alpha_{ac}(M_i)$
Cs^+	3.51	0.01 – 0.02	Cd^{2+}		1.30 ± 0.20
Rb^+	3.86	0.02 – 0.03	Zn^{2+}		1.50 ± 0.20
K^+	4.14	0.05 ± 0.02	Fe^{2+}	10.82	1.60 ± 0.20
Na^+	4.95	0.19 ± 0.02	Ni^{2+}		~1.70 ± 0.46
Ba^{2+}	7.67	0.28 ± 0.09	Co^{2+}		2.16 ± 0.32
Li^+	6.01	0.40 ± 0.02	Mn^{2+}		2.25 ± 0.23
Ca^{2+}	9.06	0.50 ± 0.03	Al^{3+}	17.27	2.35 ± 0.27
Sr^{2+}	8.38	0.53 ± 0.03	In^{3+}	15.3	2.32 ± 0.20
H^+	12.36	1.1 ± 0.1	Ga^{3+}	17.32	2.42 ± 0.21
Mg^{2+}	10.87	1.15	Cu^{2+}		2.44
			Fe^{3+}		4.1 ± 0.20

J is the total ionization potential $\sum_1^n J_n$) is fairly well described by linear equation (16):

$$\alpha_{ac}(M_i) = -0.833 + 0.190J/z,\quad R = 0.942. \qquad (16)$$

For double-charged transition metal cations (“soft”: Cd^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+}), with increasing J/z, $\alpha_{ac}(M_i)$ increases and reaches a maximum for Cu^{2+} and Mn^{2+}.

EXPERIMENTAL

The polarograms were recorded on a PU-1 polarograph with a three-electrode system in a cell with a porous partition; capillary characteristics: t 2.6 s, m 1.02 mg s^{-1}. The reference electrode was aqueous saturated calomel electrode (SCE). The solvents were purified by standard procedures [34] and dehydrated in a high vacuum over P_2O_5 in a field of IR thermal radiation; the water content of the solvents, determined by Fischer titration, did not exceed 0.005%.

Metal cations in a concentration of 0.002 M were introduced into organic solvents in the form of perchlorates. The perchlorates were prepared from hydroxides by dissolution in perchloric acid [28]. Water was removed by drying in a vacuum at 100°C [35]. Tetraethylammonium perchlorate (0.05 M) served as supporting electrolyte. The solutions were deoxygenated by bubbling argon presaturated with the solvent vapor.

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