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Enthalpy Characteristics of Solution and Solvation of $CuCl_2$ in Water–Acetonitrile Mixtures at 298.15 K

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Abstract—Thermochemical characteristics of solution of copper(II) chloride were found from calorimetric data, and values describing solvation processes in a water–acetonitrile mixed solvent were calculated for the entire range of compositions. Enthalpy characteristics of solvation of individual Cu^{2+} ions in water–acetonitrile mixtures were found and analyzed.

Thermodynamic characteristics of solvation of electrolytes in solutions are a valuable source of information about solvation power of solvents, their structural features, and selective solvation of ions. Analysis of published thermochemical characteristics of electrolytes [1–3] points to their direct dependence on ion nature. In this connection, the importance of research into solutions of transition metal compounds should be noted, since these metals play an essential role in various processes. This work is a continuation of our studies of solvation processes in mixed solvents involving both "simple" and complex-forming ions. The thermochemical characteristics of solution and the methods of their analysis make it possible to obtain and analyze various contributions to the solvation enthalpy of ions as a function of the composition and physicochemical properties of the mixed solvent [3–5].

The results of a thermochemical study of copper(II) chloride solvation in mixtures of water with dimethyl sulfoxide (DMSO) [6] and dimethylformamide (DMF) [7] point to strengthened solvation with increasing content of the nonaqueous component in the mixture as compared to straight water. Proton magnetic relaxation and spectrometric data [8] indicate that copper solvates in these non-aqueous mixtures are more stable than Co^{2+} and Ni^{2+} solvates. The referees explained this fact by additional stabilization of Cu^{2+} ions by the Jahn–Teller effect. The Gibbs energies of Cu^{2+} transfer from water into its mixtures with dipolar aprotic solvents, obtained in [8], suggest that the solvation power of mixed solvents in relation to *d*-metal ions depends on both electrostatic and donor–acceptor properties of the non-aqueous component. In our opinion, the thermodynamics of solvation processes in solutions cannot be thoroughly understood without thermochemical data. It seems of importance to study enthalpy characteristics of Cu^{2+} solvation in water–acetonitrile (MeCN) mixtures with various electrondonor, electron-acceptor, and dielectric properties. In this study we used the approach developed in [3], which takes into account electrostatic and donor-acceptor ion–solvent interactions.

We obtained the standard enthalpies of $CuCl_2$ solution in water–acetonitrile mixtures for the entire range of compositions of the mixed solvent (Table 1) from calorimetric data on heat effects of solution. On the basis of these data, we calculated the enthalpies of transfer of a stoichiometric mixture ΣCu^{2+}, $2Cl^-$ from water into its mixture with acetonitrile (Fig. 1). Figure 1 also reperents data for mixtures of water with the other aprotic solvents, such as DMSO and hexamethylphosphoric triamide (HMPT) [9].

Examination of the transfer isotherms (Fig. 1) points to distinctions in the mechanism of copper chloride solvation, that is evidently connected to the nature of the nonaqueous components of mixtures. Thus, the complicated nature of the dependences for water–acetonitrile mixtures can be explained by the diversity of associative processes in this mixed solvent [8], as well as by the behavioral features of the Cu^{2+} ion. Additions of acetonitrile to water reduce the

Table 1. Standard enthalpies of $CuCl_2$ solution in water–acetonitrile mixtures and their rms deviations S_f (kJ/mol)

$X_{MeCN}{}^{a}$	$-\Delta H^0_{soln} \pm S_f$	$X_{MeCN\%i}{}^{a}$	$-\Delta H^0_{soln} \pm S_f$
0.000	51.78 ± 0.17	0.698	67.32 ± 0.23
0.105	37.97 ± 0.19	0.905	44.12 ± 0.24
0.297	22.62 ± 0.15	1.000	32.02 ± 0.13
0.501	86.62 ± 0.17		

[a] X_{MeCN} is the molar fraction of acetonitrile.

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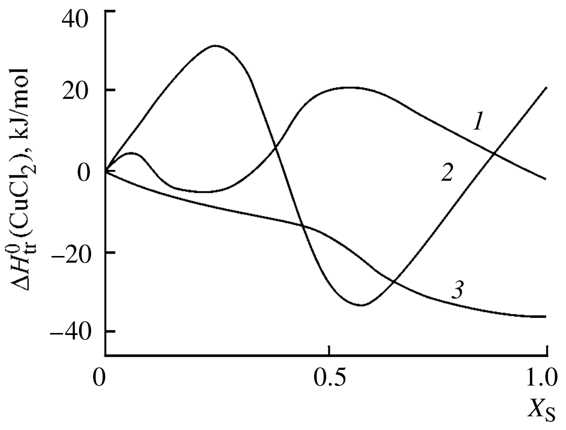

Fig. 1. Dependences of the enthalpies of $CuCl_2$ transfer from water into its mixtures with (*1*) HMPA, (*2*) acetonitrile, and (*3*) DMSO on the molar fraction of the nonaqueous component in the mixture (X_S).

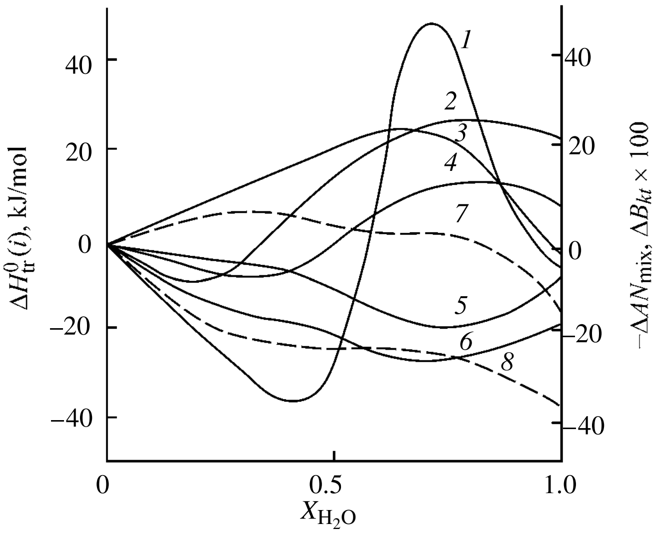

Fig. 2. Dependences of the enthalpies of transfer of ions from acetonitrile into its mixtures with water on the molar fraction of water: (*1*) Cu^{2+}, (*2*) Na^+, (*3*) Bu_4N^+, (*4*) Li^+, (*5*) Cl^-, (*6*) Br^-, and on the relative (*7*) electron-acceptor ($-\Delta AN_{mix} = AN_{mix} - AN_{MeCN}$) and (*8*) electron-donor power $B_{kt} \times 10^2$ (kcal/mol) of the mixed solvent.

solvation power of the mixed solvent in relation to the electrolyte, as evidenced by the increasing endothermicity of transfer (Fig. 1). On the contrary, water additions to acetonitrile (up to a molar fraction of 0.50) increase the exothermicity of salt solution (Table 1). Note that first additions of acetonitrile, as well as additions of HMPA, weaken solvation of the stoichiometric mixture ΣCu^{2+}, $2Cl^-$, whereas additions of DMSO enhance solvation, which, according to [6], is exolained by increasing basicity of the mixed solvent. Let us pay attention to the fact that the hydrophobic radical in CN_3CN, DMSO, and HMPA contains one, two, and six CH_3 groups, respectively. Therefore, there is no need to consider stabilization of the water structure by hydrophobic hydration of copper chloride in the acetonitrile-poor region, but the participation of nitrile groups in the solvation process is here evident. In [10], too, the higher stronger donor–acceptor power of water–acetonitrile mixtures compared with water–DMF and water –HMPA was explained by the presence of the CN group in the acetonitrile molarcule. Probably, the increase in the endothermicity of transfer with increasing fraction of acetonitrile (molar fraction of acetonitrile > 0.5) suggests that in the system under study, unlike the other two systems, acetonitrile contributes little into solvation of the stoichiometric mixture ΣCu^{2+}, $2Cl^-$. As we indicated in [9], the presence of an endothermicity maximum of electrolyte transfer in the region of small additions of the nonaqueous component is caused by the nature not only of the latter, but also of the solvated ion (charge, size, electronic structure, etc.). Therefore, to elucidate the reasons for the features of behavior of *d*-metal ions in water–acetonitrile mixtures, as compared to other mixtures, requires knowledge of ionic characteristics. Let us address to the earlier proposed technique [11] for separating the transfer enthalpy of a stoichiometric mixture of ions into ionic components, i.e. to the so-called "rule of differences." Having the transfer enthalpies of Na^+ [12], NaCl [13], and $CuCl_2$ (Table 1), we can easily calculate transfer enthalpies for Cu^{2+} and Cl^- ions. The calculated data are shown in Fig. 2, from which it is seen that the trends in the solvation enthalpies of single-charged and copper(II) cations in water–acetonitile mixtures are similar. This is proved by the increasing exothermicity of transfer of both Cu^{2+} and Li^+ and Na^+ from acetonitrile into its mixtures with water with the molar fractions of the latter less than 0.40, and, according to the available published data for Na^+ [1], can be related to formation of aqua complexes. There is no question that the above can be related the complexforming copper cation. The changes in the transfer isotherms on further increase in the water fraction points to weakening solvation of the cations. In terms of the concepts proposed in [14], the latter can be connected to increasing contribution of the enthalpy of cavity formation and to the weakening electron-donor power of the acetonitrile–water mixed solvent up to the molar fraction of water 0.70. The parameter B_{kt} was used as a characteristic of this weakening [15]. As the water content increases further (molar fraction > 0.70), an endothermicity maximum is observed in the transfer isotherms of all the cations, well-defined for Cu^{2+}

having a stronger charge but smaller size than Na^+. To reveal and examine distinctive features of solvation of copper ions, it is necessary to separate the ionic characteristics into contributions. For this purpose, using the method [16], we calculated the contributions of universal, electrostatic, and chemical ion–solvent interactions to the enthalpy of Cu^{2+} transfer. This method [4, 12] allows quantitative estimation of the ability of ions to chemical interactions. Therewith, the universal component of the solvation enthalpy of an ion is taken equal to the solvation enthalpy of a hypothetical uncharged particle (*n*-alkane) equal in size to the ion. Earlier [17, 18] we derived approximating equations which allow estimation of the universal component of solvation enthalpy for ions of any size in the entire range of compositions of mixtures of water with DMF and HMPA. The calculations of solvation enthalpies by these equations take into account the size of the nonpolar particle (van der Waals molar volume V_W) and a property of the mixed solvent (cohesive energy density P_{mix}) relating to the energy required to produce a cavity in the solvent for accommodating the solvated particle. In [12], we obtained coefficients of linear equations that relate solvation of *n*-alkanes in water–acetonitrile mixtures of various composition to the size of the *n*-alkane. Equation (1) for the enthalpy of solvation (transfer) of *n*-alkane of any size in the entire range of compositions of the mixed solvent was obtained from the P_{mix} value by fitting these coefficients by a third-degree polynomial.

$$\Delta H^0_{solv}(A) = (0.664 - 0.127P_{mix} + 0.296P^2_{mix} - 0.158P^3_{mix}) + (-0.007 + 0.505P_{mix} - 0.554.3P^2_{mix} + 0.162P^3_{mix})V_W;$$

$$S_f\ 0.992,\ R\ 0.980. \qquad (1)$$

The P_{mix} values for the mixed solvent were determined by the formula: $P_{mix} = (\Delta H^{mix}_{vap} - RT)/V_W$, kJ/cm^3. The vaporization enthalpies of the mixted solvent were calculated by known equations with data on density [19], vaporization enthalpies [20], and enthalpies of mixing [21].

By Eq. (1) we estimated solvation enthalpies for a hypothetical "model" alkane simulating Cu^{2+} and Cl^- ions, i.e. the universal components of the solvation (transfer) enthalpies of these ions, for the entire range of compositions of the mixed solvent (Table 2). The charge component of the transfer enthalpy includes electrostatic, chemical, and structural contributions [22]. It was determined as a difference between the transfer enthalpy of an ion and its universal component. We calculated the electrostatic component for acetonitrile and its mixtures with water by the Born–Bjerrum equation [23]. We pointed out in [12] that the structural contribution to the charge component of ion transfer must be estimated. This contribution to the solvation enthalpy of an ion characterizes the energy of structural rearrangement (reorganization) in the solution, caused by chemical interaction of the ion with its immediate solvation environment [24]. As noted in [12, 22], this characteristic and its quantitative assessment are especially important for H-bonded solvents. Batov [25] offered to estimate the structural contribution to the solvation enthalpy of a polar particle as a value proportional to the product of the structuring parameter of the solvent by the van der Waals molar volume of the substance. The structuring parameter of a mixed solvent is the cohesive energy density (P_{mix}).

$$\Delta H^{str}_{solv} = kP_{mix}V_W. \qquad (2)$$

The coefficient *k* defines, on the one hand, the fraction of broken intermolarcular bonds in the solvent, and, on the other, the proportionality between the volume of a solute particle and the volume of the solvent in its solvation shell [25]. For the subsequent calculations we let *k* to be 1 for all solvent compositions to meet the condition that the structural contribution reflects the energy of the structural rearrangement of the solution in immediate solvation environment of a particle of given size. In our case, the structural contribution to the enthalpy of ion transfer from acetonitrile into its mixtures with water was calculated by Eq. (3).

$$\Delta H^{str}_{tr}(i) = (P_{mix} - P_1)V_W. \qquad (3)$$

The molar volume of the ion was calculated by the formula: $V_W = 4/3N_A r^3_W$, mol/cm^3; P_1 is a property of acetonitrile; N_A is Avogadro's number; r_W is the van der Waals radius of the ion.

As seen from Table 2, the structural contribution increases in absolute value in the entire range of compositions with increasing water content. It indirectly suggests a high reactivity of Cu^{2+} ions and confirmed by increasing exothermicity of the charge component for Cu^{2+} at $X_{H_2O} < 0.50$. This phenomenon is accounted for by enhancing chemical interaction between the cation and the solvent whose electron-donor power increases in this region of compositions as compared to acetonitrile. Further increase in the water fraction produces increase in the endothermicity of the charge component of the enthalpy of Cu^{2+} transfer, which implies weakening chemical interaction of the positively charged cation with the solvent and is assignable to fact that in this region of compositions of the mixed solvent its electron-donor power slightly decreases and the electron-acceptor

Table 2. Contributions to the enthalpy of Cu^{2+} and Cl^- transfer from acetonitrile into its mixtures with water (kJ/mol)[a]

X_{H_2O}	ΔH^1_{tr}		ΔH^2_{tr}		ΔH^3_{tr}		ΔH^4_{tr}		ΔH^5_{tr}	
	Cu^{2+}	Cl^-	Cu^{2+}	Cl^-	Cu^{2+}	Cl^-	Cu^{2+}	Cl^-	Cu^{2+}	Cl^-
0.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.10	2.8	0.4	–10.7	–2.5	1.6	0.12	–12.3	–2.6	0.02	0.15
0.30	5.5	1.0	–32.5	–5.2	3.8	2.8	–36.3	–8.0	0.03	0.50
0.50	9.4	1.7	–24.4	–12.3	9.2	6.8	–32.6	–19.1	0.04	0.75
0.70	10.2	2.2	42.5	–23.8	16.1	12.2	26.4	–36.0	0.05	1.05
0.90	5.4	0.4	13.6	–13.1	29.8	22.5	–16.8	–35.6	0.06	1.35
1.00	–9.1	–13.8	6.4	5.3	38.6	29.1	–32.2	–23.8	0.07	1.50

[a] X_{H_2O} is the molar fraction of H_2O. Numerical indices relate to the (1) universal, (2) charge, (3) structural, (4) chemical, and (5) electrostatic components of the enthalpies of transfer.

power [26] continues to increase. Decreased number of electron-donor centers in acetonitrile–water associates seems to be responsible for weakened solvation of Cu^{2+} and the stoichiometric mixture of ions as a whole. This changes the solvation environment Cu^{2+} ions, i.e. to resolvation, and is still accompanied by increase in the structural contribution to the enthalpy of ion transfer. Thus, the increase in the endothermicity of the charge component of the enthalpy of Cu^{2+} transfer at X_{H_2O} 0.50–0.70 is due to resolvation of copper in the solution and is accompanied by weakening chemical ion–solvent interaction and structural changes in the system. Further increase in the water fraction ($X_{H_2O} > 0.70$) strengthens the network of water–water H bonds and thus further increase in the structural contribution to the charge component of the enthalpy of ion. However, the structural contribution may also be increased by a sharply enhanced chemical interaction of copper with water (hydration). Evidence for the latter assumption comes from increasing exothermicity of the chemical component of transfer for this region of compositions (Table 2). The enhancement of the chemical interaction can be explained in terms of the Marcus solvent donocity scale [27]. In this case, the donor number of water in bulk solvent (*DN* 40) is much higher than that of acetonitrile (*DN* 14).

The solvation of Cl^- anions in the entire range of compositions appears explicable on the basis of the classic notion [3, 4, 14] of the donor-acceptor nature of interaction of the anion with a solvent whose electron-acceptor power increases with increasing water fraction (Fig. 2). This is confirmed by the calculations results (Table 2).

Thus, the thermochemical characteristic of $CuCl_2$ solvation in water–acetonitrile is conditioned by a higher reactivity of copper(II) cations toward the mixed solvent, compared with single-charged cations; it revealed copper resolvation in the region of medium compositions of the mixed solvent.

EXPERIMENTAL

The enthalpies of $CuCl_2$ solution in mixtures of water with acetonitrile in the entire range of compositions were measured with an error of ≤ 1% on an isothermal microcalorimeter [28] at 298 K (volume of the calorimetric vessel 50 cm^3). The range of electrolyte concentration in the experiments, 0.004–0.05 mol/kg solvent [29], was selected according to the recommendations in [30] so as to exclude association of the stoichiometric mixture of ions at infinite dilution. Anhydrous copper chloride was obtained according to the procedure in [31] by single recrystallization of pure grade $CuCl_2 \cdot 2H_2O$ from twice distilled water with subsequent drying in a vacuum at 150°C for 6–7 h. Nonaqueous solvents were purified by known procedurs [32]. The integral enthalpies of $CuCl_2$ solution in the mixtures under study we gave earlier in [9, 29]. According to [33], copper(II) ions in aqueous solutions can form complexes with both Cl^- ions and water. Taking this fact into account, we fulfilled calculations with the equilibrium constants to show that the fraction of chloride complexes in the working range of electrolyte concentrations does not exceed 0.6%. In addition we also measured the heat effects of $CuCl_2$ solution in neutral and acidified (pH 3) solutions for mixtures with molar fractions of the non-aqueous component of no more than 0.5. The resulting values coincided with each other within the error limits, thus pointing to an insignificant contribution of solvolysis in the heat effect of $CuCl_2$ solution. In view of the aforesaid, we did not account for side effects in determining the integral heat of solution. The standard enthalpies of the electrolyte solution

(Table 1) were calculated by the extended second-order Debye–Huckel equation [34]. Additional physicochemical characteristics of water–acetonitrile mixtures for calculating the enthalpies of dilution by the above equation were taken from the references given in [12]. It is accepted that the parameter of the closest approach of ions in mixtures changes additively from 6 nm in water to 10 nm in acetonitrile [13].

REFERENCES

1. Krestov, G.A., Novoselov, N.P., and Perelygin, I.S., *Ionnaya sol'vatatsiya* (Ionic Solvation), Moscow: Nauka, 1987.
2. Beck, M.T., *Chemistry of Complex Equilibria,* Budapest: Akad. Kiado, 1970.
3. Vandychev, V.N., Korolyov, V.P., and Krestov, G.A., *Thermochim. Acta,* 1990, vol. 169, no. 1, p. 57.
4. Korolyov, V.P., Vandychev, V.N., and Krestov, G.A., *Thermochim. Acta,* 1993, vol. 214, no. 1, p. 203.
5. Vandychev, V.N. and Serebryakova, A.L., *Zh. Obshch. Khim.,* 1998, vol. 68, no. 6, p. 915.
6. Mikheev, S.I., Sharnin, V.A., and Shormanov, V.A., *Zh. Fiz. Khim.,* 1993, vol. 67, no. 7, p. 1776.
7. Gusev, V.D., Shormanov, V.A., and Krestov, G.A., *Zh. Fiz. Khim.,* 1982, vol. 56, no. 10, p. 2499.
8. Devyatov, F.V., Safina, V.F., and Lazareva, L.G., *Zh. Neorg. Khim.,* 1993, vol. 38, no. 6, p. 1085.
9. Vandychev, V.N. and Serebryakova, A.L., Abstracts of Papers, *Int. Conf. "The Problems of Solvation and Complex Formation in Solution,"* Ivanovo, 1998, p. 322.
10. Vandychev, V.N. and Serebryakova, A.L., *Zh. Obshch. Khim.,* 1997, vol. 67, no. 4, p. 579.
11. Vorob'ev, A.F. and Padunova, I.D., *Zh. Obshch. Khim.,* 1978, vol. 48, no. 1, p. 11.
12. Vandychev, V.N., *Zh. Obshch. Khim.,* 1995, vol. 65, no. 8, p. 1279.
13. *Termodinamicheskie kharakteristiki nevodnykh rastvorov elektrolitov: Spravochnik* (Thermodynamic Characteristics of Non-aqueous solutions of Electrolytes: Handbook), Poltoratskii, G.M., Moscow: Khimiya, 1984.
14. Vandychev, V.N., *Cand. Sci. (Chem.) Dissertation,* Ivanovo, 1988.
15. Wrona, P.K., Krugowski, T.M., and Zielkowska, U., *Z. Naturforsch. B,* 1989, vol. 44, no. 6, p. 673.
16. Krestov, G.A., Korolev, V.P., and Vandychev, V.N., *Dokl. Akad. Nauk SSSR,* 1990, vol. 313, no. 3, p. 641.
17. Vandychev, V.N., *Zh. Obshch. Khim.,* 1996, vol. 66, no. 1, p. 35.
18. Vandychev, V.N., *Zh. Obshch. Khim.,* 2002, vol. 72, no. 1, p. 32.
19. Krestov, G.A., Afanas'ev, V.N., and Efremova, L.S., *Fiziko-khimicheskie svoistva binarnykh rastvoritelei* (Physicochemical Properties of Binary Solvents), Leningrad: Khimiya, 1988.
20. Lebedev, Yu.A. and Miroshnichenko, A.G., *Termokhimiya paroobrazovaniya organicheskikh veshchestv* (Thermochemistry of Vaporization of Organic Substances), Moscow: Khimiya, 1981.
21. Belousov, V.P. and Morachevskii, A.G., *Teploty smesheniya zhidkostei* (Heats of Mixing of Liquids), Leningrag: Khimiya, 1970.
22. Manin, N.G., Korolev, V.P., and Krestov, G.A., *Zh. Obshch. Khim.,* 1991, vol. 61, no. 6, p. 1301.
23. Bjerrum, N., Larsson, E., and Lawwrece, K.G., *J. Chem. Soc., Faraday Trans. 1,* 1988, vol. 84, no. 1, p. 175.
24. Borisover, M.D., Solomonov, B.N., and Konovalov, A.O., *Zh. Obshch. Khim.,* 1991, vol. 61, no. 2, p. 329.
25. Batov, D.V., *Zh. Obshch. Khim.,* 1998, vol. 68, no. 2, p. 210.
26. Mayer, U., Gerger, W., and Gutman, V., *Monatsh. Chem.,* 1977, vol. 109, no. 2, p. 489.
27. Marcus, Y., *J. Solution Chem.,* 1984, vol. 13, no. 9, p. 599.
28. Korolev, V.P., Batov, D.V., Vandychev, V.N., and Krestov, G.A., *Zh. Fiz. Khim.,* 1983, vol. 57, no. 1, p. 253.
29. Vandychev, V.N. and Serebryakova, A.L., Abstracts of Papers, *2 Mezhdunarodnaya nauchno-tekhnicheskaya konferentsiya "Aktual'nye problemy khimii i khimicheskoi tekhnologii"* (2-nd Int. Scientific and Technical Conf. "Actual Problems of Chemistry and Chemical Technology,") Ivanovo, 1997, p. 39.
30. Krestov, G.A., *Termodinamika ionnykh protsessov v rastvorakh* (Thermodynamics of Ionic Processes in Solutions), Leningrag: Khimiya, 1984.
31. Karyakin, Yu.V. and Angelov, I.I., *Chistye khimicheskie veshchestva* (Pure Chemical Substances), Moscow: Khimiya, 1974.
32. Gordon, A.J. and Ford, R.A., *The Chemist's Companion,* New York: Wiley, 1972.
33. Lur'e, Yu.Yu., *Spravochnik po analiticheskoi khimii* (Handbook on Analytical Chemistry), Moscow: Khimiya, 1967.
34. Solov'ev, S.N., Privalov, N.M., and Vorob'ev, A.F., *Zh. Fiz. Khim.,* 1976, vol. 50, no. 10, p. 2719.