Russian Chemical Bulletin, International Edition, Vol. 54, No. 10, pp. 2325—2329, October, 2005

Intermolecular interactions in orthophosphoric acid—*N*,*N*-dimethylformamide system according to viscometric data

Yu. A. Fadeeva,[a]* L. E. Shmukler,[a] and L. P. Safonova[a,b]

[a]Institute of Solution Chemistry, Russian Academy of Sciences,
1 ul. Akademicheskaya, 153045 Ivanovo, Russian Federation.
Fax: +7 (093 2) 33 6237. E-mail: jaf@isc-ras.ru
[b]Ivanovo State University of Chemistry and Technology,
7 prosp. F. Engel´sa, 153460 Ivanovo, Russian Federation

The viscosity of an orthophosphoric acid—*N*,*N*-dimethylformamide system was measured in the whole region of compositions at 298—338 K. An excess viscosity of the system was analyzed by the data obtained using different model concepts. Calculations suggested that strong intermolecular interactions and the formation of complexes $(H_3PO_4)_2 \cdot DMF$ occur in the system.

Key words: orthophosphoric acid, *N*,*N*-dimethylformamide, viscosity, intermolecular interactions, complexation.

Interest in solutions of orthophosphoric acid is caused by its wide use in food, textile, and pharmaceutical industries[1—4] and manufacturing of proton-conducting polymeric electrolytes for fuel cells.[5,6] Aqueous solutions of orthophosphoric acid were studied in detail,[7—15] while data on its mixtures with organic solvents are almost lacking.[16,17] Depending on the solvent nature and the concentration of the acid, the latter can participate in reactions of dissociation, autoprotolysis, complexation, and polymerization.[7—9] Aprotic solvents (for instance, *N*,*N*-dimethylformamide) having basic properties are of greatest interest in studies of the mechanism of acid—base interaction of orthophosphoric acid with different organic solvents. Various experimental methods and approaches are needed to study these processes, because some of them are the most sensitive to ion-ionic interactions (for example, conductometry) and others are sensitive to intermolecular interactions (spectral methods, viscometry).

A dependence of the viscosity on the composition is widely used for purposes of physicochemical analysis, because the viscosity is rather sensitive to the associative state of the substance, intermolecular interactions, and structural changes that occur during the formation of solutions. A relationship between the deviation of the parameter from additivity and the character of interaction of the components can be determined from an analysis of composition—property diagrams.[18] If these interactions produce stable complexes, associates, *etc.*, then their stoichiometry can be determined.[19] For instance, in binary systems with a strong interaction of components during the formation of a compound that does not dissociate in solution, a maximum corresponding to this compound should exist in the composition—viscosity diagram. If the compound dissociates, the viscosity maximum is less pronounced depending on the degree of dissociation.

The purpose of the present work is to study the character of intermolecular interactions in an orthophosphoric acid—*N*,*N*-dimethylformamide system by viscometry.

Experimental

Orthophosphoric acid (100%) was prepared from the 85% acid (reagent grade) and P_2O_5 (reagent grade) by the concentrating method: excess P_2O_5 was dissolved in the 85 wt.% H_3PO_4 at 418 K, and the hot solution was filtered through a glass filter. The concentration of the resulting solution was determined by potentiometric titration with a solution of NaOH and from density.[9] The acid obtained was brought to 100% by the addition of the calculated amount of water and kept for 1 day at 373 K for equilibration.

N,*N*-Dimethylformamide (reagent grade) was doubly distilled *in vacuo* (P = 133 Pa) at 310 K, collecting the medium fraction. The distilled solvent was dehydrated with molecular sieves 4A for 72 h and repeatedly distilled, collecting the medium fraction (60% of the total amount). The water content in DMF was at most 0.03 wt.% according to the data of amperometric titration with Fischer´s reagent.

An Ubbelohde viscometer with hanging meniscus and automated measurement of the liquid efflux time and a BROOKFIELD DV-II rotational viscometer were used to determine viscosity. The error of viscosity determination on both instruments was at most 1%.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 2252—2256, October, 2005.

Table 1. Dynamic viscosity (η) of the H_3PO_4—DMF system at different temperatures

$x(H_3PO_4)$	η/mPa s				
	298 K	308 K	318 K	328 K	338 K
0.0	0.800	0.707	0.629	0.526	0.408
0.103	2.10	1.82	1.58	1.41	1.27
0.118	2.58	2.19	1.92	1.66	1.46
0.142	3.68	2.84	2.42	2.14	1.80
0.186	6.49	5.19	3.85	3.56	2.82
0.265	29.8	21.1	15.7	12.0	9.35
0.359	232	139	88.4	59.3	41.3
0.390	347	200	122	79.2	54.2
0.500	1470	711	379	220	129
0.550	2170	1070	560	301	174
0.600	3150	1495	807	401	231
0.650	3800	1740	853	445	258
0.700	3600	1740	846	445	258
0.750	2660	1350	688	374	218
0.800	1600	874	467	271	169
0.850	906	498	288	175	112
0.900	535	300	183	118	80.0
0.960	246	144	87.4	66.9	53.2
1.000	185	127	81.7	58.0	43.9

Note: $x(H_3PO_4)$ is the mole fraction of H_3PO_4.

Results and Discussion

As can be seen from the data in Table 1, with an increase in the H_3PO_4 content in the mixture, the dynamic viscosity increases and passes through a maximum, whose magnitude increases with a temperature decrease.

As mentioned above, the composition—property diagrams are often plotted and used as a method of physicochemical analysis. The absolute value of the property itself and its deviation from additivity, or an excess value can be considered in this diagram. We chose the second approach to study intermolecular interactions in the H_3PO_4—DMF system.

There is no strict equation that describes the viscosity of ideal mixtures in terms of the properties of individual components. All equations proposed are mainly semiempirical, and their common disadvantage is that they describe well the viscosity isotherms of specified systems, being quite unsatisfactory for other systems.

The correlation based on the Eyring equation assuming the mole-fractional additivity of the free Gibbs activation energy of viscous flow is widely popular for solutions of non-electrolytes[20]

$$\ln\eta_{mix} = x_1\ln(\eta_1V_1) + x_2\ln(\eta_2V_2) - \ln V_{mix}, \qquad (1)$$

where V_1, V_2, V_{mix} and η_1, η_2, η_{mix} are the mole volumes and viscosities of pure components and their mixtures, respectively; x_1 and x_2 are the analytical mole fractions of the components.

Sometimes the equation for the mole-fractional additivity of the logarithm of viscosity is used instead of Eq. (1)

$$\ln\eta_{mix} = x_1\ln\eta_1 + x_2\ln\eta_2.$$

However, this equation can be used only if $V_{mix} \approx V_1 \approx V_2$.

Other equations for calculation of the viscosity of mixtures are also known. They have the general formula

$$\eta_{mix}^m = x_1\eta_1^m + x_2\eta_2^m \qquad (m = 1/3, 1/2, 1).$$

It is shown that the equation of mole-fractional additivity of the molar viscosity can be used for a series of systems[20] ($\eta_M = \eta V$)

$$\eta_{M_{mix}} = x_1\eta_{M_1} + x_2\eta_{M_2}. \qquad (2)$$

We calculated the excess molar viscosity ($\eta^E_{M_{mix}}$) and excess dynamic viscosity (η^E_{mix}) for the H_3PO_4—DMF system (Fig. 1)

$$\eta^E_{M_{mix}} = \eta^{exp}_{M_{mix}} - \eta^{calc}_{M_{mix}} = \eta^{exp}_{mix}V^{exp}_{mix} - (x_1\eta_1V_1 + x_2\eta_2V_2), \qquad (3)$$

$$\eta^E_{mix} = \eta^{exp}_{mix} - \eta^{calc}_{mix}, \qquad (4)$$

where η_{mix}^{calc} was calculated by Eq. (1).

As can be seen from the data in Fig. 1, the position of the maximum in the excess viscosity isotherm of the system under study is independent of the chosen additivity scheme and lies at $x(H_3PO_4) \approx 0.7$. Therefore, hereinafter we consider the deviation of the molar viscosity from additivity.

If the interaction between the components of a mixture is stronger than in the pure substances, then the deviation of the viscosity of the system from additivity is positive, which is observed, indeed, in the system under study. If these intermolecular interactions result in the formation of a complex, the composition can be deter-

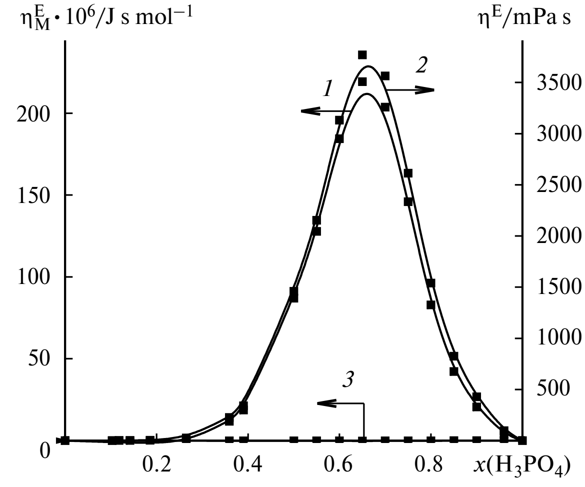

Fig. 1. Excess molar (η^E_M) (*1*, *3*) and dynamic (η^E) (*2*) viscosities of the H_3PO_4—DMF system at 298 K calculated by Eqs (3) (*1*), (4) (*2*), (8) and (9) (*3*).

mined from the position of an extreme. For instance, if only the equimolar **A**·**B** complex is formed in a binary system consisting of components **A** and **B**, then the extreme in the plot of the deviation of the properties of an equilibrium mixture from additivity always corresponds to the stoichiometry of this process ($x = 0.5$). If the system contains the **A**·**B**$_2$ complex, then the position of an extreme corresponds to $x_A = 0.33$ regardless of the value of the constant. When an equilibrium mixture contains simultaneously two or more complexes with different compositions, the extreme of deviation of the property from additivity corresponds to the composition $0.33 < x_A < 0.5$.

The extreme observed in the excess viscosity isotherms indicates, possibly, the predominant formation of the $(H_3PO_4)_2 \cdot$DMF complex in the system.

The concentration plots of the excess viscosity for mixtures of orthophosphorus acid with other organic solvents and water are shown in Fig. 2 for comparison. It is seen that this plot is similar for all nonaqueous systems under study. The maximum of the deviation from additivity lies in the same concentration region. It can be assumed that the complexes of predominantly the same stoichiometric composition (2 : 1) are formed in all the systems under study. This behavior is probably determined by a specific interaction of orthophosphoric acid with a solvent and also by specific features of the acid itself. Orthophosphoric acid is known[21] to exist as dimers in concentrated aqueous solutions. We have previously[22] shown that such dimers can exist in almost the whole region of compositions in an orthophosphoric acid—DMF mixture. It is most likely that the acid dimers interact with the solvent molecules to form complexes $(H_3PO_4)_2 \cdot S$ (S is solvent). In addition, all the solvents under question are oxygen-containing, which determines the interaction of the same type.

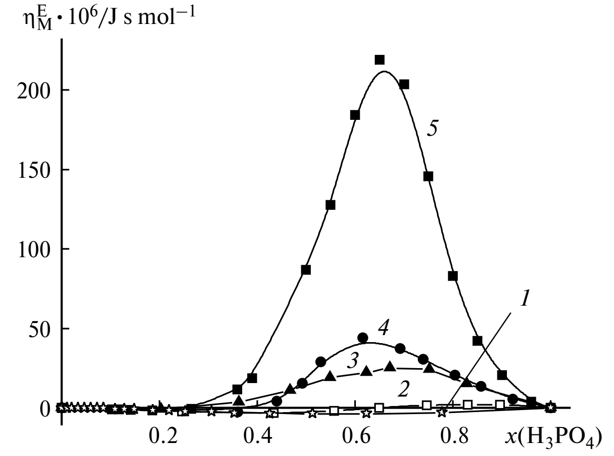

Fig. 2. Excess molar viscosity (η_M^E) of solutions of H_3PO_4 in water[9] (*1*) and different organic solvents: butyl formate[16] (*2*), formamide[16] (*3*), diisopropyl ether[16] (*4*), and DMF (*5*) (at 298 K).

Aqueous solutions of orthophosphoric acid exhibit a small negative deviation of the molar viscosity from additivity, and the maximum deviation also falls on the acid concentration x = 0.6—0.7 mole fraction. The absolute deviation for aqueous solutions is much smaller ($3.8 \cdot 10^{-6}$ J s mol^{-1}) than that for the most part of organic solvents ($(8.6—44.3) \cdot 10^{-6}$ J s mol^{-1}, and for DMF it is $\approx 220 \cdot 10^{-6}$ J s mol^{-1}), which is probably related to the compensation of different contributions from ion-ionic, ion-molecular, and intermolecular interactions in an aqueous solution (dissociation constant of orthophosphoric acid in water[7,23,24] is by three—five orders of magnitude higher than that in organic solvents[17]).

The MacAllister approach[20] is very popular for the description of viscosity of liquid systems with interacting components. The approach is based on the modified Eyring model and assumes that intermolecular interactions between three types of particles (1—1—1, 2—2—2, 1—2—1, 2—1—2, 1—1—2, 1—2—2) occur in a binary mixture

$$\begin{aligned}\ln\nu_{mix} &= x_1^3\ln\nu_1 + x_2^3\ln\nu_2 + x_1^3\ln M_1 + \\ &+ x_2^3\ln M_2 - \ln(x_1M_1 + x_2M_2) + \\ &+ 3x_1^2x_2\ln(2M_1 + M_2/3) + 3x_1x_2^2\ln(M_1 + 2M_2/3) + \\ &+ 3x_1^2x_2\ln\nu_{12} + 3x_1x_2^2\ln\nu_{21}, \qquad (5)\end{aligned}$$

where ν_{mix} is the kinematic viscosity of the mixture (η/ρ); ν_1 = 0.0085 cm^2 s^{-1} and ν_2 = 0.9879 cm^2 s^{-1} are the kinematic viscosities of DMF and H_3PO_4, respectively; M is the molecular weight; ν_{12} and ν_{21} are the parameters of interaction.

When equation (5) was derived, it was assumed that the parameters of interaction depend on the stoichiometry of this interaction only, *i.e.*,

$$\nu_{1-2-1} = \nu_{1-1-2} = \nu_{12} \cdot \nu_{2-1-2} = \nu_{1-2-2} = \nu_{21}$$

(indices 1 and 2 concern DMF and orthophosphoric acid, respectively). The ν_{12} and ν_{21} values can formally be considered as the kinematic viscosity of the system consisting of complexes $(H_3PO_4)_2 \cdot$DMF (ν_{21}) or $H_3PO_4 \cdot$(DMF)$_2$ (ν_{12}) only. The calculations by Eq. (5) gave the following values of the parameters of interaction: $\nu_{21} = 794 \pm 2$ and $\nu_{12} = 0.2 \pm 1.8$.

Since $\nu_{12} \ll \nu_{21}$, the parameter of interaction ν_{12} and, hence, interactions of the $H_3PO_4 \cdot$(DMF)$_2$ type can be neglected. The ν_{21} value is much higher than the kinematic viscosity of the pure components (ν_1 and ν_2), which confirms additionally that strong interactions resulting in the formation of stable $(H_3PO_4)_2 \cdot$DMF complexes occur in the system.

When assuming that the complex of a given composition is formed in the system with the 100% conversion in the whole composition region and the kinematic viscosity of this complex is ν_{21}, then the true value of molar viscosity is

$$\eta_{M_{\rm mix}}^{\rm exp} = \eta_{\rm mix}^{\rm exp} V_{\rm mix} = \nu_{\rm mix}^{\rm exp}(x_1' M_1 + x_2' M_2 + x_3' M_3), \quad (6)$$

where indices 1, 2, and 3 refer to DMF, H_3PO_4, and $(H_3PO_4)_2 \cdot DMF$, respectively; $\nu_{\rm mix}^{\rm exp}$ are the experimental values of the kinematic viscosity of the system under study; x' are the true mole fractions of the components.

Then the calculated value based on additivity of the molar viscosity is

$$\eta_{M_{\rm mix}}^{\rm calc} = x_1\nu_1 M_1 + x_2\nu_2 M_2 + x_3\nu_3 M_3. \quad (7)$$

The stoichiometry of the complex shows that its molecular weight is $M_3 = M_1 + 2M_2$.

After the corresponding transformations, the equations for the experimental, calculated, and molar viscosities take the forms

(1) in excess acid ($x_2 \geq 0.667$ and $x_1 \leq 0.333$)

$$\eta_{M_{\rm mix}}^{\rm exp} = \nu_{\rm mix}^{\rm exp}\left(\frac{x_1 M_1 + x_2 M_2}{1 - 2x_1}\right),$$

$$\eta_{M_{\rm mix}}^{\rm calc} = \frac{x_1\nu_1 M_1 + x_2\nu_2 M_2 + x_1 M_1(\nu_3 - \nu_1) + 2x_1 M_2(\nu_3 - \nu_2)}{1 - 2x_1},$$

$$\eta_{M_{\rm mix}}^{\rm E} = \frac{C - D}{1 - 2x_1}, \quad (8)$$

$$C = x_1 M_1(\nu_{\rm mix}^{\rm exp} - \nu_1) + x_2 M_2(\nu_{\rm mix}^{\rm exp} - \nu_2),$$

$$D = x_1[M_1(\nu_3 - \nu_1) + 2M_2(\nu_3 - \nu_2)];$$

(2) in excess DMF ($x_2 \leq 0.667$ and $x_1 \geq 0.333$)

$$\eta_{M_{\rm mix}}^{\rm exp} = \nu_{\rm mix}^{\rm exp}\left(\frac{x_1 M_1 + x_2 M_2}{1 - x_2}\right),$$

$$\eta_{M_{\rm mix}}^{\rm calc} = \frac{x_1\nu_1 M_1 + x_2\nu_2 M_2 + \frac{1}{2}x_2[M_1(\nu_3 - \nu_1) + 2M_2(\nu_3 - \nu_2)]}{1 - x_2},$$

$$\eta_{M_{\rm mix}}^{\rm E} = \frac{C - G}{1 - x_2}, \quad (9)$$

$$C = x_1 M_1(\nu_{\rm mix}^{\rm exp} - \nu_1) + x_2 M_2(\nu_{\rm mix}^{\rm exp} - \nu_2),$$

$$G = \frac{x_2}{2}[M_1(\nu_3 - \nu_1) + 2M_2(\nu_3 - \nu_2)].$$

The results of calculation of the excess molar viscosity with allowance for complexation are presented in Fig. 1 (curve *3*). It is seen that the maximum in the concentration plot of η_M^E disappears if the complexation is taken into account. Therefore, it can be assumed that the earlier observed deviation of the viscosity of the system from additivity (see Fig. 1, curve *1*) is related, to a considerable extent, to the formation of the $(H_3PO_4)_2 \cdot DMF$ complexes.

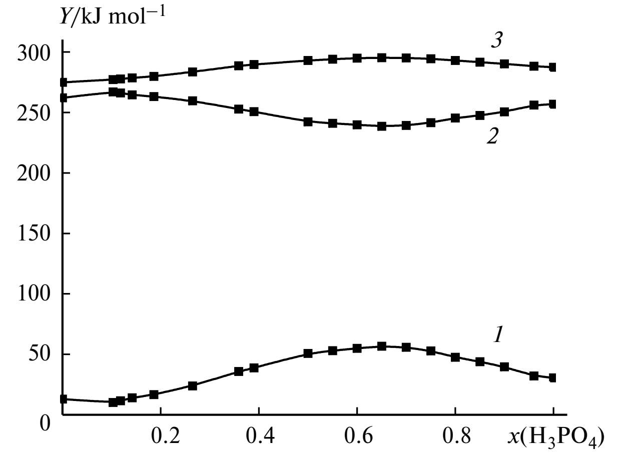

Fig. 3. Thermodynamic activation characteristics of viscous flow (Y) of the H_3PO_4—DMF system at 298 K: $\Delta H_\eta^{\neq}$ (*1*), $T\Delta S_\eta^{\neq}$ (*2*), and $\Delta G_\eta^{\neq}$ (*3*).

Based on the temperature plot of the dynamic viscosity, we calculated the thermodynamic characteristics of viscous flow (Fig. 3). The following equation is valid for the dynamic viscosity of liquids:

$$\eta = \frac{hN_A}{\chi V}\exp[\Delta G_\eta^{\neq}/(RT)], \quad (10)$$

where h is the Planck constant, χ is the transmission coefficient that is most often accepted to be unity, and V is the mole volume of the liquid. An uncertainty in estimation of the pre-exponential factor in Eq. (10) permits a comparative estimation of these magnitudes for systems similar in chemical nature and intermolecular interactions only.

The Gibbs activation energies of viscous flow ($\Delta G_\eta^{\neq}$) at all temperatures studied were determined using Eq. (10) for $\chi = 1$. The activation entropy of viscous flow ($\Delta S_\eta^{\neq}$) was calculated as follows:

$$\Delta S_\eta^{\neq} = -{\rm d}\Delta G_\eta^{\neq}/{\rm d}T.$$

For the system under study, the $\Delta G_\eta^{\neq} = f(T)$ plot is linear and, hence, the $\Delta S_\eta^{\neq}$ value is temperature-independent. The activation energy of viscous flow ($\Delta H_\eta^{\neq}$) was obtained from the equation

$$\Delta G_\eta^{\neq} = \Delta H_\eta^{\neq} - T\Delta S_\eta^{\neq}.$$

As can be seen from Fig. 3, the entropy component makes the main contribution to the Gibbs activation energy of viscous flow of the H_3PO_4—DMF system, which is characteristic of highly viscous systems prone to polymerization.

Thus, the present viscometric study and analysis of the concentration dependence of the excess molar viscosity suggest that strong intermolecular interactions resulting in the formation of the $(H_3PO_4)_2 \cdot DMF$ complexes occur in the orthophosphoric acid—DMF system.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 05-03-32092), the Grant of President of the Russian Federation (Program of State Support for Young Russian Scientists, Grant MK-1593.2005.3), and the Ministry of Education and Science of the Russian Federation (Grant for Young Scientists of the Leading Scientific Pedagogical Collectives of the Higher Educational and Scientific Institutions, PD02-1.3-305).

References

1. M. Jagtoyen and F. Derbyshire, *Carbon*, 1998, 36, 1085.
2. L. B. Khalil, B. S. Girgis, and T. A. M. Tawfik, *Adsorpt. Sci. Technol.*, 2000, **18**, 373.
3. J. B. Castro, P. P. Bonelli, E. G. Cerrella, and A. L. Cukierman, *Ind. Eng. Chem. Res.*, 2000, 39, 4166.
4. S. Wei, V. Kumar, and G. S. Banker, *Int. J. Pharm.*, 1996, **142**, 175.
5. G. Zukowska, M. Rogowska, A. Wojda, E. Zygadlo-Monikowska, Z. Florjanczyk, and W. Wieczorek, *Solid State Ionics*, 2000, **136—137**, 1205.
6. D. Raducha, W. Wieczorek, Z. Florjanczyk, and J. R. Stevens, *J. Phys. Chem.*, 1996, **100**, 20126.
7. J. R. Van Wazer, *Phosphorus and Its Compounds*, St. Louis, Missouri, 1958.
8. D. E. C. Corbridge, *Phosphorus: an Outline of its Chemistry, Biochemistry and Technology*, Elsevier, Amsterdam—Oxford—New York, 1980.
9. N. N. Postnikov, *Termicheskaya fosfornaya kislota* [*Thermal Orthophosphoric Acid*], Khimiya, Moscow, 1970, 304 pp. (in Russian).
10. Ch. Jiang, *Chem. Eng. Sci.*, 1996, **51**, 689.
11. A. A. Ivanov, *Izv. Vuz. Khim. Khim. Tekhnol.*, 1989, **32**, 3 [*Izv. Vuz. Khim. Khim. Tekhnol.*, 1989, **32** (Engl. Tranl.)].
12. D.-T. Chim and H. H. Chang, *J. Appl. Electrochem.*, 1989, **19**, 95.
13. M. Cherif, A. Mqaidi, N. Ammar, M. Abderrabba, and W. Furst, *Fluid Phase Equilib.*, 2000, **175**, 197.
14. M. Cherif, A. Mqaidi, N. Ammar, G. Vallee, and W. Furst, *J. Sol. Chem.*, 2000, **29**, 255.
15. M. Cherif, A. Mqaidi, N. Ammar, M. Abderrabba, and W. Furst, *Fluid Phase Equilib.*, 2002, **194—197**, 729.
16. G. A. Krestov, V. N. Afanas´ev, and L. S. Efremova, *Fiziko-khimicheskie svoistva binarnykh rastvoritelei* [*Physicochemical Properties of Binary Solvents*], Khimiya, Leningrad, 1988, 688 pp. (in Russian).
17. G. Bandyopadhyay and S. C. Lahiri, *Int. J. Res. Phys. Chem. Chem. Phys.*, 2002, **216**, 729.
18. V. Ya. Anosov, M. I. Ozerova, and Yu. Ya. Fialkov, *Osnovy fiziko-khimicheskogo analiza* [*Foundations of Physicochemical Analysis*], Nauka, Moscow, 1976, 504 pp. (in Russian).
19. V. I. Dulova, N. R. Molchanova, L. I. Gureeva, N. S. Gordienko, N. A. Skidan, L. T. Kalinichenko, A. L. Brezhe, and V. N. Grebenkina, *Vestn. Khar´kovskogo Universiteta* [*Bulletin of Kharkov University*], 1979, **192**, 21 (in Russian).
20. V. N. Afanas´ev and O. I. Davydova, *Eksperimental´nye metody khimii rastvorov: densimetriya, viskozimetriya, konduktometriya i drugie metody* [*Experimental Methods of Chemistry of Solutions: Densimetry, Viscometry, Conductometry, and Other Methods*], Nauka, Moscow, 1997, 351 pp. (in Russian).
21. D. L. Wertz and G. A. Cook, *J. Sol. Chem.*, 1985, **14**, 41.
22. Yu. A. Fadeeva, Ph. D. (Chem.) Thesis, Institute of Solution Chemistry, Russian Academy of Sciences, Ivanovo, 2003, 134 pp. (in Russian).
23. A. E. Martell and R. M. Smith, *Critical Stability Constants: Inorganic Complexes*, Plenum Press, New York,—London, 1982, **5**, 604.
24. *Handbook of Chemistry and Physics*, Ed. D. R. Lide, 81st ed., CRC Press, Boca Raton, 2000.

Received October 29, 2004;
in revised form September 5, 2005