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THERMODYNAMIC CHARACTERISTICS OF A VISCOUS FLOW IN AQUEOUS SOLUTIONS OF BARIUM NITRATE

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An experimental investigation of the dynamic viscosity of aqueous solutions of $Ba(NO_3)_2$ at temperatures of 298–598 K and pressures of 5–40 MPa is carried out on a setup based on the extension-capillary method. The uncertainty of the data does not exceed 1.5%. An equation that describes the experimental data is constructed. The free energy and enthalpy of viscous flow activation have been calculated.

A considerable amount of research is being performed to investigate the viscosity of binary and multicomponent aqueous solutions of electrolytes [1–9], but it should be admitted that experiments are usually performed at atmospheric pressure and in a narrow temperature range, sometimes only at 25^{o}C. The present work is a part of the cycle of extensive investigations of the physicochemical properties [10–18] of various electrolytes in a wide range of state parameters, in particular, study of the processes of a viscous flow in water-salt systems.

The aim of the present work is to obtain precise experimental data on the coefficient of dynamic viscosity in aqueous solutions of barium nitrate and, using them, to perform calculation of the thermodynamic parameters that characterize the viscous flow.

To experimentally determine the viscosity of solutions, we used a setup, the principles of the operation of which are based on the capillary method of measuring viscosity (Fig. 1). The viscosimeter consists of a capillary 1 of inner diameter 0.3 mm and length 220 mm made from stainless steel. The capillary is soldered to an extension 2, through which a test fluid flow is directed to a cold zone. The extension is soldered into flange 3. Thereafter, the fluid flow is directed to a system that records the volume and time of discharge: a mobile cylinder 4 and an immobile one 5 connected by a flexible capillary 6. Both cylinders are equipped with expanding bottles of equal volume needed to preliminarily stabilize the regime of fluid discharge from the capillary. The viscosimeter is placed in an autoclave 7. The discharge of the fluid from the measuring capillary occurs when the mobile cylinder begins to move upwards (an excess pressure is created). The mercury contained in the flexible capillary 6 plays the role of a liquid-metal piston. Both cylinders, which have the same volume, are furnished with viewing windows 8 made from acrylic plastic. On the autoclave, a massive red copper tank 9 is press-fitted with two electrical heaters 10 double-wound over the entire length of the tank surface. The heaters are covered by a heat-insulating layer of asbestos, basalt wool, and glass cloth, as well as a metal casing. The setup is filled with a test fluid through a valve 11. The pressure in the system is created and measured by an MP-600 manometer of class 0.05. The temperature is measured by a PTS-10 platinum resistance thermometer 12 by a compensation method using an R363-3 potentiometer. To strictly ensure a laminar flow in the capillary, its surface was carefully treated as recommended in [19].

The computational equation for determining the coefficient of dynamic viscosity has the form

$$\eta = A\tau \frac{\rho_{\text{cap}}}{\rho_{\text{cyl}}} \left(1 - \frac{\rho_{\text{cyl}}}{\rho_{\text{mer}}}\right) (1 + \alpha\Delta t)^3 - B \frac{\rho_{\text{cyl}}}{\tau} , \qquad (1)$$

where

$$A = \frac{g\pi r^4 \Delta H_0 \rho_{0\text{mer}}}{8LV_{\text{cyl}}} ; \quad B = \frac{mV_{\text{cyl}}}{8\pi L} .$$

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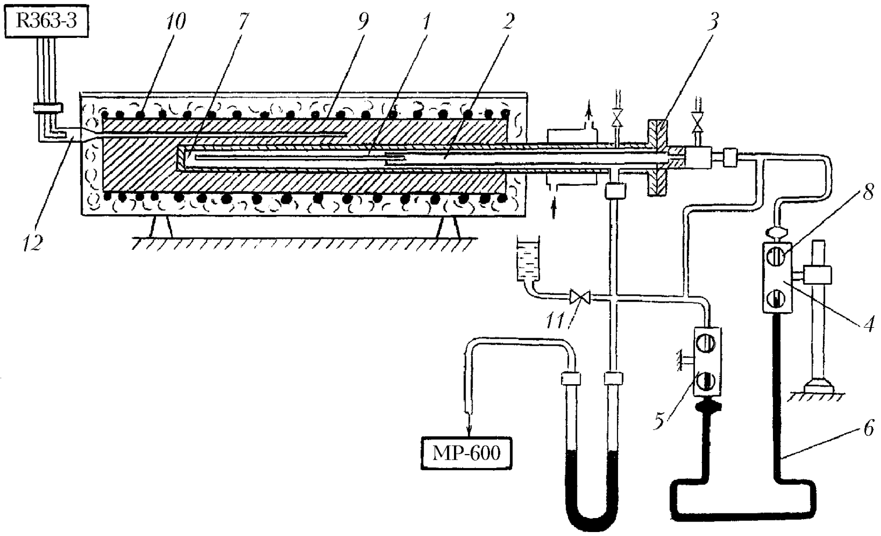


Fig. 1. Schematic of the experimental setup for determining the viscosity of substances in a wide range of temperatures and pressures.

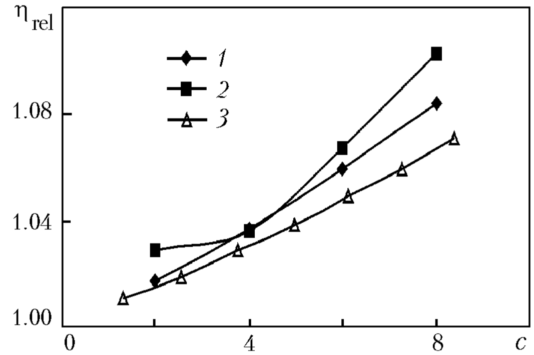


Fig. 2. Comparison of experimental data with literature data at 25°C: 1) present work; 2) [21]; 3) [9]. *c*, %.

The data on the density of aqueous solutions of barium nitrate were taken from [20]. The error in finding the basic experimental data was: temperature 0.01 K, pressure 0.05%, and time of discharge 0.1 sec. With allowance for the errors in characterization of the measured quantities, as well as the accuracy of determining the concentration of the solution, the error of the data obtained on the setup described is ±1.5%. Preliminarily, control measurements of the viscosity of distilled water were performed. Comparison of the data obtained with the data of International Skeletal Tables has shown that discrepancies do not exceed 1.2% at temperatures of up to 600 K and pressures up to 40 MPa.

To prepare solutions, we used analytical-grade barium nitrate and twice-distilled water.

The experimental values of the dynamic viscosity of barium nitrate solutions are listed in Table 1.

The data obtained were compared with those available in literature [9] and reference data [21] (Fig. 2). The disagreement with [9] is increased with concentration and attains 1.45% at a concentration of 8%, with the values of the coefficient of dynamic viscosity from [9] having lower values. The discrepancies with [21] do not exceed 1.75%, with the latter data being overstated as against those obtained by us.

To process experimental data on viscosity, calculate the derivatives of the functional dependence $\eta = f(P, t, m)$, and to conveniently use the data in practice, one must have an analytical expression of the dependence indicated. In contrast to [1], in the present work the temperature interval of investigations was extended. Checking of the equation suggested in [1] has shown that it can be used also for the range 298–598 K:

$$\eta[\text{Pa·sec}]\cdot 10^4 = A_1 + B_1 t + C_1/t + D_1/t^{2.5}, \qquad (2)$$

TABLE 1. Experimental Data on the Viscosity of the $Ba(NO_3)_2–H_2O$ System at Various Concentrations

t	P				t	P			
	10	20	30	40		10	20	30	40
	$c = 2\%$					$c = 4\%$			
24.92	9108	9108	9109	9112	24.79	9323	9325	9323	9325
37.95	7073	7098	7121	7140	38.34	7172	7198	7228	7258
51.74	5490	5517	5545	5572	51.83	5609	5634	5668	5702
62.23	4651	4676	4705	4730	64.92	4583	4610	4638	4666
73.85	3959	3886	4012	4037	73.91	4058	4073	4111	4149
86.14	3409	3435	3460	3483	88.12	3425	3451	3475	3499
96.73	3038	3063	3088	3112	96.51	3131	3155	3180	3205
105.24	2791	2816	2840	2863	109.62	2757	2785	2804	2824
118.46	2473	2497	2521	2545	118.34	2551	2574	2598	2622
130.42	2239	2261	2286	2310	132.57	2271	2295	2317	2339
154.25	1878	1902	1925	1942	151.04	1984	2007	2030	2053
175.89	1634	1657	1680	1702	174.84	1701	1725	1749	1773
198.34	1436	1460	1483	1509	198.21	1488	1514	1539	1563
205.16	1385	1409	1432	1451	209.35	1403	1430	1456	1482
224.82	1255	1278	1302	1321	224.80	1300	1327	1354	1381
253.16	1104	1129	1152	1171	251.24	1153	1180	1210	1245
274.32	1012	1037	1062	1085	274.28	1047	1077	1109	1141
300.29	918.5	944.3	969.2	990.5	300.46	947.8	980.7	1014	1040
324.87	–	871.3	896.5	920.3	322.75	–	906.0	940.9	972.3
	$c = 6\%$					$c = 8\%$			
25.23	9454	9456	9457	9457	24.83	9709	9710	9712	9713
37.45	7463	7489	7517	7545	39.46	7331	7365	7389	7412
49.62	5960	5988	6020	6048	52.35	5821	5851	5883	5911
66.81	4571	4603	4629	4652	63.71	4889	4919	4949	4973
75.90	4056	4086	4111	4136	74.21	4245	4275	4303	4328
87.42	3541	3566	3594	3620	89.15	3564	3590	3619	3632
98.45	3151	3176	3203	3228	95.24	3343	3368	3397	3425
107.31	2893	2920	2944	2968	106.82	2986	3013	3040	3065
119.45	2597	2623	2648	2672	119.31	2675	2700	2728	2753
134.81	2297	2322	2347	2372	131.52	2425	2452	2479	2500
153.04	2016	2040	2066	2090	152.34	2089	2116	2143	2161
175.82	1745	1770	1797	1822	176.21	1799	1827	1855	1881
194.45	1570	1597	1624	1649	199.35	1584	1613	1642	1669
211.24	1439	1469	1495	1520	206.27	1529	1558	1588	1612
226.42	1337	1367	1394	1421	223.84	1404	1435	1465	1492
253.71	1185	1215	1246	1272	252.13	1241	1272	1305	1329
276.25	1082	1113	1144	1171	276.15	1128	1162	1196	1219
301.75	985.2	1020	1053	1082	300.24	1034	1069	1106	1128
324.11	–	950.2	984.7	1017	325.12	–	987.0	1019	1039

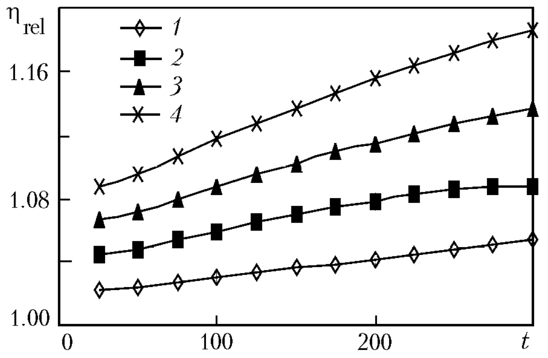
where $\eta \cdot 10^4$ Pa·sec, A_1, B_1, C_1, and D_1 are the functions of pressure and concentration:

$$A_1 = \sum_{i=1}^{1} \sum_{j=0}^{1} a_{ij} P^i c^j , \quad B_1 = \sum_{i=1}^{1} \sum_{j=0}^{1} b_{ij} P^i c^j , \quad C_1 = \sum_{i=1}^{1} \sum_{j=0}^{1} c_{ij} P^i c^j , \quad D_1 = \sum_{i=1}^{1} \sum_{j=0}^{1} d_{ij} P^i c^j . \qquad (3)$$

The values of the empirical coefficients a_{ij}, b_{ij}, c_{ij}, and d_{ij} are listed in Table 2. The standard error of description of experimental data by the proposed equation is ±0.9%.

TABLE 2. Coefficients of the Viscosity Equation

j	a_{ij} at i		b_{ij} at i	
	0	1	0	1
0	–279.4115	–1.327588	0.2378233	$4.997686 \cdot 10^{-3}$
1	15.25246	0.1619971	$-2.285477 \cdot 10^{-2}$	$7.548459 \cdot 10^{-4}$
	c_{ij} at i		d_{ij} at i	
	0	1	0	1
0	320264.8	163.5401	$-1.135721 \cdot 10^{7}$	–31801.44
1	2883.8	7.331302	–101801.2	1326.87



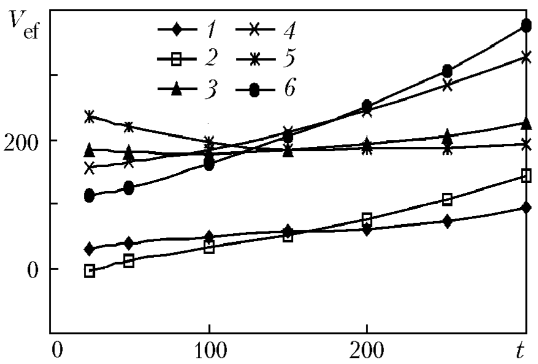


Fig. 3. Relative viscosity vs. temperature for various concentrations of electrolyte: 1) 2; 2) 4; 3) 6; 4) 8%. t, °C.

Fig. 4. Temperature dependences of molar volumes of the hydrate complexes of some electrolytes: 1) $LiNO_3$; 2) KNO_3; 3) $MgCl_2$; 4) $BaCl_2$; 5) Li_2SO_4; 6) $Ba(NO_3)_2$.

Figure 3 shows the temperature dependence of the relative viscosity of barium nitrate solutions. For all concentrations an increase in the relative viscosity is observed, with this dependence manifesting itself more strongly on increase in the concentration.

Investigation of the process of a viscous flow was also carried out on the basis of the hydrodynamic model of [22]. An aqueous solution of electrolyte was considered as a system consisting of ions with a certain number of water molecules adsorbed on them, which, in the process of viscous flow, move in an homogeneous medium. The hydrated ions can be regarded as solid balls suspended in a liquid.

We will use an equation of the form [23]

$$\eta_{rel} = 1 + 2.5 V_{ef} l + B V_{ef}^2 l^2 . \tag{4}$$

The volume of the hydrated ions can be determined in the following way. We will represent Eq. (4) as

$$(\eta_{rel} - 1)/l = 2.5 V_{ef} + B V_{ef}^2 l . \tag{5}$$

We will construct the dependence of $(\eta_{rel} - 1)/l$ on l, perform its linear extrapolation, and find the quantity V_{ef} as a segment cut off from the ordinate axis and divided by 2.5. The values of l at different temperatures and concentrations were determined using the experimental data on the density of solutions obtained in the present work. The obtained results of calculations of the volumes of hydrated ions at different temperatures and at a pressure of 10 MPa are listed in Table 3.

TABLE 3. Molar Volumes of Hydrate Complexes in the $Ba(NO_3)_2$–H_2O System at a Pressure of 10 MPa

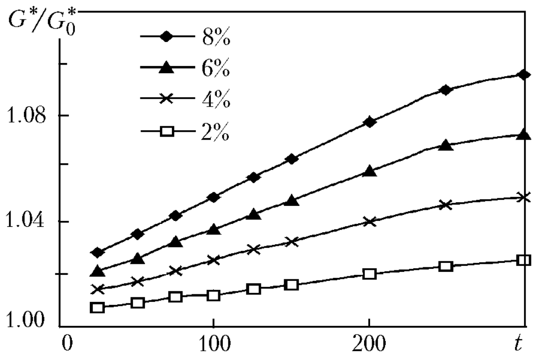
t	V_{ef}	t	V_{ef}
25	114.7	175	226
50	127.0	200	250
75	144.4	225	276
100	163	250	305
125	183	275	338
150	204	300	377

TABLE 4. Gibbs Viscous-Flow Activation Energy in Barium Nitrate Solutions

t	$G^{*}\cdot 10^{-3}$	G^{*}/G_0^{*}	t	$G^{*}\cdot 10^{-3}$	G^{*}/G_0^{*}
	$c = 2\%,\ P = 10$ MPa			$c = 4\%,\ P = 10$ MPa	
25	9.210	1.007	25	9.274	1.014
50	8.733	1.009	50	8.809	1.017
75	8.372	1.011	75	8.460	1.021
100	8.145	1.012	100	8.245	1.025
125	8.000	1.014	125	8.113	1.029
150	7.911	1.016	150	8.037	1.032
200	7.857	1.02	200	8.009	1.040
250	7.972	1.023	250	8.150	1.046
300	8.341	1.025	300	8.539	1.049
	$c = 6\%,\ P = 10$ MPa			$c = 6\%,\ P = 30$ MPa	
25	9.338	1.021	25	9.316	1.019
50	8.885	1.026	50	8.887	1.027
75	8.547	1.032	75	8.561	1.034
100	8.344	1.037	100	8.371	1.040
125	8.224	1.043	125	8.267	1.048
150	8.161	1.048	150	8.223	1.056
200	8.159	1.059	200	8.269	1.073
250	8.324	1.069	250	8.480	1.088
300	8.732	1.073	300	8.896	1.093
	$c = 8\%,\ P = 10$ MPa			$c = 8\%,\ P = 30$ MPa	
25	9.402	1.028	25	9.380	1.026
50	8.960	1.035	50	8.962	1.035
75	8.634	1.042	75	8.648	1.044
100	8.442	1.049	100	8.470	1.052
125	8.334	1.057	125	8.346	1.058
150	8.283	1.064	150	8.346	1.072
200	8.306	1.078	200	8.417	1.093
250	8.494	1.090	250	8.652	1.110
300	8.920	1.096	300	9.089	1.117

These results evidence a monotonic increase in the volume of the hydrate complex in barium nitrate solutions. For comparison, Fig. 4 presents the temperature dependences of the molar volumes V_{ef} and of certain binary water-salt systems investigated by us earlier ($LiNO_3$–H_2O, KNO_3–H_2O, Li_2SO_4–H_2O, $MgCl_2$–H_2O, and $BaCl_2$–H_2O) [12, 13].

To characterize a viscous flow in barium nitrate solutions from the thermodynamic point of view, we used the Eyring method. Calculations of the Gibbs energy G^{*} and the enthalpy of activation of a viscous flow ΔH^{*} were performed by the formulas



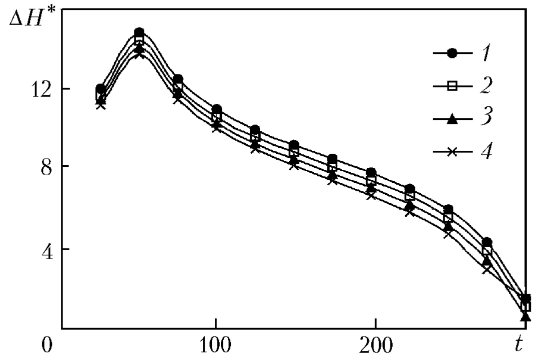


Fig. 5. Relative Gibbs activation energy of a viscous flow vs. temperature.

Fig. 6. Temperature dependence of the viscous flow activation enthalpy at various concentrations of barium nitrate: 1) 2; 2) 4; 3) 6; 4) 8%.

$$G^* = RT \ln \frac{\eta V}{hN}, \tag{6}$$

$$\Delta H^* = -T^2 \frac{\partial}{\partial T}\left(R \ln \frac{\eta V}{hN}\right). \tag{7}$$

The molar volume of the solution was calculated on the basis of the data of [20] on the density of barium nitrate solutions.

The results of calculations of the Gibbs activation energy are listed in Table 4. The error of the quantity G^* is composed of the error of the dynamic viscosity coefficient (1.5%) and the error of the data on the density (0.07%) and does not exceed 1.6%. The error of the differential quantity ΔH^* is 6–8%.

The dependence of the Gibbs activation energy of a viscous flow on temperature is of an extreme character. As the temperature increases, G^* decreases, attaining the minimum in a temperature region of 150–200^{o}C, and then, on further increase in the temperature, it increases. Analysis of the values of G^* that were calculated by us from the data of [12, 13] made it possible to reveal the shift of the minimum of G^* towards lower temperatures on increase in the salt content. Thus, while in the studied system $Ba(NO_3)_2$–H_2O in a 2% solution the minimum lies at a temperature of about 200^{o}C, for an 8% solution the minimum corresponds to about 170^{o}C, with the exception of, probably, lithium sulfate, for which in the studied range of concentrations the minimum of G^* lies at 470 K. It has been established that pressure insignificantly influences the value of G^* at moderate temperatures, but in the region of elevated temperatures its increase entails an increase in the free energy. Characteristic of this situation is the fact that, on addition of a salt into the solution, the influence of pressure on G^* becomes stronger. New portions of electrolyte shift the minimum on the temperature dependence of the Gibbs activation energy of a viscous flow toward lower values of T. This dependence is shown in Fig. 5 and in Table 4.

Figure 6 presents the dependences of the enthalpy of the aqueous solutions of barium nitrate on temperature. The activation enthalpy ΔH^* decreases with an increase in the temperature and pressure. Addition of new portions of a salt also does not influence the change in the enthalpy, and this effect is especially evident at high temperatures.

NOTATION

A, B, coefficients; c, weight concentration, %; G^*, Gibbs activation energy of a viscous flow, J/mole; ΔH^*, enthalpy of viscous flow activation, J/mole; ΔH_0, mean integral difference between the levels of mercury in cylinders at room temperature and atmospheric pressure; g, free fall acceleration; h, Planck constant; L, length of the capillary, m; l, molarity, mole/liter; m, coefficient, equal to 1.12, which takes into account pressure losses over the initial portion of the capillary and kinetic energy losses; N, Avogadro number, mole^{-1}; P, pressure, MPa; R, universal gas constant, J/(mole·K); r, inner radius of the capillary, m; T, temperature, K; t, temperature, ^{o}C; Δt, difference between the experimental temperature and room temperature, $^{\mathrm{o}}$C; V, molar volume of solution, m^3/mole; V_{cyl}, volume of the measuring cylinder, equal to $1.2182 \cdot 10^{-6}$ m^3; V_{ef}, molar volume of hydrated ions, cm^3/mole; α, coefficient of linear extension of the capillary material [19], K^{-1}; η, coefficient of dynamic viscosity, Pa·sec; η_{rel}, relative viscosity of a solution, equal to the ratio of the coefficient of dynamic viscosity of a solution to the coefficient of dynamic viscosity of water; ρ_{cap}, density of the test substance at the parameters of the experiment, kg/m^3; ρ_{cyl}, density of the test solution at room temperature and the pressure of the experiment, kg/m^3; ρ_{mer}, density of mercury at room temperature and the pressure of the experiment, kg/m^3; $\rho_{0\mathrm{mer}}$, density of mercury at room temperature and atmospheric pressure, kg/m^3; τ, time of liquid outflow, sec. Subscripts: cap, capillary; cyl, cylinder; mer, mercury; rel, relative; ef, effective.

REFERENCES

1. Robert J. Correia and Joseph Kestin, Viscosity and density of aqueous sodium and potassium sulfate solutions in the temperature range 20–90$^{\mathrm{o}}$C and the pressure range 0–30 MPa, *J. Chem. Eng. Data*, **26**, No. 1, 43–47 (1981).
2. Sekh Mahiuddin and Kochi Ismail, Temperature and concentration dependence of the viscosity of aqueous sodium nitrate and sodium thiosulphate electrolytic systems, *Fluid Phase Equilibria*, **124**, Nos. 1–2, 231–243 (1996).
3. Jin-Soo Kim and Huen Lee, Solubilities, vapor pressures, densities, and viscosities of the LiBr + LiI + $HO(CH_2)_3OH + H_2O$ system, *J. Chem. Eng. Data*, **46**, No. 1, 79–83 (2001).
4. Kee-Kahb Koo, Hyung-Rae Lee, Young-sam Oh, Dal-Ryung Park, and Young-Soon Baek, Densities, viscosities, and surface tensions of the (water + lithium bromide + lithium nitrate + lithium iodide + lithium chloride) system, *J. Chem. Eng. Data*, **44**, No. 6, 1175–1177 (1999).
5. Francisco Chenlo, Ramon Moreira, Gerardo Pereira, and Maria J. Vazquez, Viscosities of aqueous solutions of $Fe_2(SO_4)_3$ containing $NaNO_3$, KNO_3, NaBr, or KBr from 293.1 to 323.1 K, *J. Chem. Eng. Data*, **43**, No. 3, 325–328 (1998).
6. Hai-Lang Zhang, Geng-Hua Chen, and Shi-Jun Han, Viscosity and density of H_2O + NaCl + $CaCl_2$ and H_2O + KCl + $CaCl_2$ at 298.15 K, *J. Chem. Eng. Data*, **42**, No. 3, 526–530 (1997).
7. Shigeki Iyoki, Shozo Iwasaki, Yutaka Kuriyama, and Tadashi Uemura, Densities, viscosities, and surface tensions for the two ternary systems water + lithium bromide + lithium iodide + lithium chloride + lithium nitrate, *J. Chem. Eng. Data*, **38**, No. 2, 302–305 (1993).
8. J. Martin Wimby and Trore S. Berntsson, Viscosity and density of aqueous solutions of lithium bromide, lithium chloride, zinc bromide, calcium chloride and lithium nitrate, *J. Chem. Eng. Data*, **40**, No. 1, 73–78 (1995).
9. Thi Hoa Doan and James Sangster, Viscosities of concentrated aqueous solutions of some 1:1, 2:1, and 3:1 nitrates at 25$^{\mathrm{o}}$C, *J. Chem. Eng. Data*, **26**, No. 2, 141–144 (1981).
10. N. D. Azizov, Bulk properties of the aqueous solutions of barium chloride, *Inzh.-Fiz. Zh.*, **76**, No. 2, 182–186 (2003).
11. N. D. Azizov and T. S. Akhundov, Thermodynamic characteristics of activation of a viscous flow in $LiNO_3$, KNO_3, and Li_2SO_4 solutions, *Teplofiz. Vys. Temp.*, **38**, No. 4, 683–686 (2000).
12. N. D. Azizov, Basic results of investigation of the viscosity of aqueous solutions of electrolytes, *Teplofiz. Vys. Temp.*, **37**, No. 3, 404–410 (1999).
13. N. D. Azizov and T. S. Akhundov, Parameters of activation of viscous flow in $MgCl_2$ and $BaCl_2$ solutions, *Zh. Fiz. Khim.*, **73**, No. 8, 1489–1501 (1999).
14. N. D. Azizov and T. S. Akhundov, Viscosity of aqueous solutions of magnium and barium chlorides at 293–573 K, *Zh. Fiz. Khim.*, **71**, No. 11, 1959–1962 (1997).
15. A. B. Zeinalova, A. I. Iskenderov, A. B. Tairov, and T. S. Akhundov, Dynamic viscosity of aqueous solutions of calcium nitrate, *Izv. Vyssh. Uchebn. Zaved., Neft' Gaz*, No. 1, 53–55 (1991).
16. N. D. Azizov, Main results of high-temperature tensometric studies of aqueous solutions of electrolytes, *Teplofiz. Vys. Temp.*, **35**, No. 3, 379–385 (1997).
17. N. D. Azizov and T. S. Akhundov, Density and limiting partial molar volumes of electrolyte in aqueous solutions of $MgCl_2$ and $BaCl_2$, *Teplofiz. Vys. Temp.*, **36**, No. 1, 385–390 (1998).

18. N. D. Azizov and T. S. Akhundov, Experimental study of the elasticity of solvent vapor and calculation of thermodynamic properties of $NaNO_3$–H_2O and KNO_3–H_2O systems, *Zh. Neorg. Khim.*, No. 10, 1723–1728 (1998).
19. S. L. Rivkin, A. Ya. Levin, and L. B. Izrailevskii, *Viscosity of Water and Steam* [in Russian], Izd. Standartov, Moscow (1979).
20. T. S. Akhundov, I. N. Akhmedova, A. D. Tairov, A. I. Iskenderov, and M. B. Imanova, Thermal properties of aqueous solutions of $Ba(NO_3)_2$ at high pressures and temperatures, in: *Results of Studying the Processes of Water Preparation, Water Regime on Thermal Electric Plants, and Thermophysical Properties of Coolant Solutions* [in Russian], AzINEFTEKhIM (1988), pp. 10–17.
21. I. D. Zaitsev, *Physicochemical Properties of Binary and Multicomponent Solutions* [in Russian], Khimiya, Leningrad (1987).
22. R. W. Gurney, *Ionic Processes in Solution*, London (1953).
23. T. Erdey-Gruz, *Transport Phenomena in Aqueous Solutions* [Russian translation], Mir, Moscow (1976).