Viscosity of the Aqueous $Ca(NO_3)_2$ Solutions at Temperatures from 298 to 573 K and at Pressures up to 40 MPa

Ilmutdin M. Abdulagatov,*,† Adelia A. Zeinalova,‡ and Nazim D. Azizov‡,§

Institute for Geothermal Problems of the Dagestan Scientific Center of the Russian Academy of Sciences,
367003 Makhachkala, Shamilya Str. 39-A, Dagestan, Russia, and Azerbaijan State Oil Academy,
Baku, 370601, Azerbaijan

Dynamic viscosities of seven (0.3207, 0.6771, 1.5235, 2.0310, 2.6118, 3.2810, and 4.0628) $mol \cdot kg^{-1}$ and kinematic viscosities of two (4.9861 and 6.0941) $mol \cdot kg^{-1}$ aqueous $Ca(NO_3)_2$ solutions have been measured in the liquid phase with a capillary flow technique. Measurements were made at six isobars (0.1, 5, 10, 20, 30, and 40) MPa. The range of temperatures was from (298 to 573) K. The total uncertainty of viscosity, pressure, temperature, and concentration measurements were estimated to be less than 1.5%, 0.05%, 15 mK, and 0.014%, respectively. The reliability and accuracy of the experimental method was confirmed with measurements on pure water for five selected isobars (1, 10, 20, 40, and 50) MPa and at temperatures between (294.5 and 597.6) K. The experimental and calculated values from International Association for the Properties of Water and Steam formulation for the viscosity of pure water show excellent agreement within their experimental uncertainty (average absolute deviation, AAD = 0.27%). A correlation equation for viscosity of solutions was obtained as a function of temperature and pressure for each measured composition by a least-squares method from the experimental data. The AAD between measured and calculated values from this correlation equation for the viscosity was 0.6 %. The measured values of viscosity at atmospheric pressure were directly compared with the data reported in the literature by other authors.

Introduction

Knowledge of the pressure, temperature, and composition dependence of viscosity of aqueous salt solutions is essential to understand a variety of problems in a number of technological and engineering applications such as geothermal power, hydrothermal formation of minerals, for understanding various geologic processes, to understand the mass and heat transfer phenomena in the hydrothermal environments, and design calculation. However, the lack of the reliable thermodynamic and transport property data over temperature, pressure, and concentration ranges makes it necessary to estimate the missing properties by extrapolating low-temperature, low-pressure, and low-concentration results. Since the transport properties of aqueous salt solutions undergo dramatic changes as T and m are increased (Abdulagatov and Azizov)[1,2] it is impossible to obtain by using extrapolating technique (extrapolations not accurate). For engineering uses, reliable methods for prediction and estimation of the viscosity of solutions over wide ranges of concentration, temperature, and pressure would be extremely valuable. Therefore, experimental data for the viscosity of aqueous systems at high temperatures and high pressures are needed to test predictions of theoretical models and improves them. However, measurements of the viscosity of aqueous salt solutions have so far been limited to rather narrow ranges of temperature, pressure, and concentration with less than satisfactory accuracy.

In this paper, we report new viscosity measurements for aqueous $Ca(NO_3)_2$ solutions over wide ranges of temperature, pressure, and composition using a capillary flow technique, which allows us to perform the accurate measurements at high temperatures and high pressures (Abdulagatov and Azizov).[1] The research presented in this paper is part of a continuing series of measurements of thermodynamic and transport properties of aqueous solutions at high temperatures and high pressures (Abdulagatov and Azizov,[1−6] Azizov and Akhundov,[7] Akhundov et al.[8,9]). A literature survey revealed that all previously reported viscosity data for aqueous $Ca(NO_3)_2$ solutions were performed at atmospheric pressure. There are no viscosity data for aqueous $Ca(NO_3)_2$ solutions as a function of pressure. Thus, the main objective of this work is to provide reliable experimental viscosity data for aqueous $Ca(NO_3)_2$ solutions at high temperatures (up to 573 K) and high pressures (up to 40 MPa).

Kuznezov et al.[10] reported viscosity data for $H_2O + Ca(NO_3)_2$ solutions for five solutions between (0.693 and 5.555) $mol \cdot kg^{-1}$ and four isotherms (288, 298, 308, and 318) K at atmospheric pressure. Measurements were made with a glass capillary viscometer. Authors claim the uncertainty in viscosity measurements is 0.3%. The same technique was used by Prozenko et al.[11] to measure the viscosity of $H_2O + Ca(NO_3)_2$ solutions in the temperature range from (283 to 363) K at a composition of 0.6771 $mol \cdot kg^{-1}$. The author claims that the uncertainty in viscosity measurements is 1.0%. Blinova et al.[12] measured densities and viscosities of $H_2O + Ca(NO_3)_2$ solutions at temperatures from (293 to 363) K for five compositions between (0.677

---

* To whom correspondence should be addressed. E-mail: ilmutdin@boulder.nist.gov. Fax: (303) 497-5224. Tel: (303) 497-4027.

† Russian Academy of Sciences.

‡ Azerbaijan State Oil Academy.

§ Present address: Physical and Chemical Properties Division, National Institute of Standards and Technology, 325 Broadway, Boulder, CO 80305.

10.1021/je049853n CCC: $27.50

Table 1. Experimental Viscosities, η, as a Function of Pressure and Temperature for Pure Water

	η/mPa·s								
p/MPa	294.46 K	318.60 K	359.40 K	395.73 K	448.31 K	486.79 K	527.16 K	567.60 K	597.56 K
1	0.9696	0.5910	0.3289						
10	0.9669	0.5924	0.3314	0.2290	0.1575	0.1279	0.1055	0.08843	
20						0.1293	0.1090	0.09231	0.08035
40	0.9605	0.5986	0.3380	0.2375	0.1630				0.08762
50						0.1369	0.1151	0.1009	0.09053

to 6.094) mol·kg^{-1}. Measurements were performed by means of a capillary method with an uncertainty of 1%. Ambrus et al.[13] reported the viscosity data for $H_2O + Ca(NO_3)_2$ solutions at low temperatures (from −83 to 25 °C) for four compositions.

Aseyev[14] represented available experimental viscosity data from the literature for $H_2O + Ca(NO_3)_2$ solutions by following the correlation equation

$$\log(\eta/\eta_0) = 1.486\omega + 0.00211(t/°C)\omega \qquad (1)$$

where η_0 is the viscosity of pure water at temperature t and ω is the mass fraction.

Experimental Apparatus and Procedures

The apparatus and procedures used for the viscosity measurements of the $H_2O + Ca(NO_3)_2$ solutions have been described in detail in previous papers[1,7,8,15] and were used without modification. Only essential information will be given here. The measurements were made using a capillary flow method which gives an uncertainty of 1.5% for the viscosity. The main parts of the apparatus consisted of a working capillary with extension tube, a high-temperature and high-pressure autoclave, movable and unmovable cylinders, electrical heaters, and a solid red copper block. The working capillary with an inside diameter of 0.3 mm and length of 216 mm was made from stainless steel (1 × 18H9T, 1 chrome-18 nickel-9 titanium). A capillary together with an extension tube was located in the high-temperature and high-pressure autoclave. The input and output sections of the capillary had conical extensions. The capillary tube was filled with mercury. When the movable cylinder was moved vertically at constant speed, the fluid flowed through the capillary. Both cylinders were supplied with two viewing windows that were made with plexiglass. The autoclave was placed in a solid red copper block. Two electrical heaters were wound around the surface of the copper block. To create and measure the pressure, the autoclave was connected with a dead-weight pressure gauge (MP-600) by means of a separating vessel. The mercury was used as a separating liquid. The mercury was in contact with the solution at room-temperature zone (see details in Abdulagatov and Azizov).[1] The uncertainty in pressure measurements was 0.05%.

The final working equations for this method are

$$\eta = U\tau\frac{\rho}{\rho_c}\left(1 - \frac{\rho_c}{\rho_{Hg}}\right)(1 + \alpha\Delta t)^3 - W\frac{\rho_c}{\tau}$$

$$U = \frac{g\pi R^4 \Delta H_0 \rho_{0,Hg}}{8LV_c}$$

$$W = \frac{mV_c}{8\pi L} \qquad (2)$$

where $R = 0.15091$ mm is the inner radius of the capillary, $L = (540.324 \pm 0.005)$ mm is the capillary tube length, τ is the time of flow, α is the linear expansion coefficient of the capillary material, Δt is the temperature difference between experimental temperature and room temperature, $m = 1.12$ is a constant, $\rho(p,T)$ is the density of the fluid under study at the experimental conditions (p,T), $V_c = 1.2182$ cm^3 is the volume of the unmovable (measuring) cylinder, ρ_c is the density of the fluid under study at room temperature and experimental pressure, $\Delta H_0 = (H_1 - H_2)/\ln(H_1/H_2)$, where H_1 and H_2 are the mercury levels at the beginning and ending of the fluid flowing, respectively, at room temperature and atmospheric pressure, ρ_{Hg} is the density of mercury at room temperature and experimental pressure, and $\rho_{0,Hg}$ is the density of mercury at room temperature and atmospheric pressure. Equation 2 was derived from Poisseuille's law with corrections for the temperature effects on the capillary sizes and mercury and sample densities at the experimental conditions (p,T) and entrance effects (acceleration of a fluid at the inlet and outlet) on the fluid.[1,7,8,15]

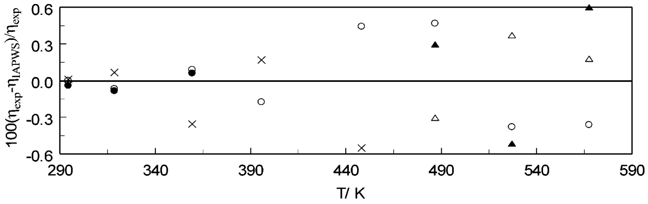

Figure 1. Percentage viscosity deviations, $\delta\eta = 100(\eta_{exp} - \eta_{cal})/\eta_{cal}$, of the experimental viscosities for pure water from the values calculated with IAPWS[16] formulation. ●, 1 MPa; ○, 10 MPa; △, 20 MPa; × , 40 MPa; ▲, 50 MPa.

Table 2. Experimental Viscosities, η, as a Function of Temperature and Molality for $H_2O + Ca(NO_3)_2$ Solutions at Atmospheric Pressure

	η/mPa·s at the following m/mol·kg^{-1}				
T/K	0.3210	0.6771	1.5230	2.6120	4.0620
298.15	0.963	1.051	1.384	1.954	3.256
323.15	0.599	0.660	0.852	1.204	1.928
348.15	0.419	0.466	0.596	0.837	1.297
358.15	0.371	0.415	0.530	0.741	1.134
368.15	0.334	0.374	0.480	0.664	1.006
373.15	0.314	0.340	0.450	0.622	0.937

The values of the parameters U and W can also be determined by means of a calibration technique. The volume of the unmovable cylinder V_c was determined using a weighing technique (Abdulagatov and Azizov).[1] This working eq 6, taking into account the acceleration of a fluid at the inlet and outlet, the variation of the geometrical sizes of the capillary with T and p, and the mercury and sample densities at the experimental conditions were varied with temperature and pressure.

For this method, the correct determination of the geometrical size of the capillary is very important, because, for example, parameter U in eq 6 is proportional to R^4. The average capillary radius was measured using a weighing technique (Abdulagatov and Azizov)[1] and by calibration (relative method) from the viscosity of a standard fluid (pure water) with well-known viscosity values (Interna-

Table 3. Experimental Dynamic Viscosities as a Function of Pressure, Temperature, and Molality of $H_2O + Ca(NO_3)_2$ Solutions

$m = 0.3207$ mol·kg^{-1}

	η/mPa·s at the following T/K														
p/MPa	299.20	308.60	322.41	340.80	357.62	375.81	396.40	418.20	437.43	461.81	480.23	503.74	524.82	546.54	562.72
5	0.9620	0.8153	0.6140	0.4661	0.3761	0.3088	0.2562	0.2169	0.1883	0.1609	0.1469	0.1320	0.1215	0.1093	0.1021
10	0.9630	0.8160	0.6150	0.4670	0.3775	0.3105	0.2578	0.2182	0.1896	0.1632	0.1484	0.1334	0.1228	0.1121	0.1043
20	0.9635	0.8170	0.6183	0.4691	0.3808	0.3145	0.2608	0.2203	0.1928	0.1666	0.1512	0.1360	0.1252	0.1153	0.1082
30	0.9640	0.8190	0.6210	0.4728	0.3840	0.3183	0.2635	0.2230	0.1952	0.1691	0.1540	0.1386	0.1278	0.1183	0.1115
40	0.9645	0.8203	0.6225	0.4750	0.3862	0.3198	0.2663	0.2258	0.1980	0.1719	0.1568	0.1415	0.1303	0.1210	0.1143

$m = 0.6771$ mol·kg^{-1}

	η/mPa·s at the following T/K														
p/MPa	299.80	312.41	324.50	338.73	354.19	373.78	399.27	423.50	446.79	463.48	482.72	505.80	527.31	552.13	571.31
5	1.0300	0.8162	0.6429	0.5229	0.4308	0.3492	0.2794	0.2320	0.1990	0.1801	0.1631	0.1471	0.1363	0.1227	0.1127
10	1.0303	0.8170	0.6454	0.5255	0.4330	0.3510	0.2812	0.2331	0.2006	0.1823	0.1654	0.1495	0.1378	0.1244	0.1143
20	1.0305	0.8188	0.6486	0.5303	0.4384	0.3555	0.2831	0.2364	0.2037	0.1856	0.1685	0.1525	0.1406	0.1282	0.1188
30	1.0309	0.8210	0.6520	0.5318	0.4394	0.3585	0.2863	0.2397	0.2072	0.1887	0.1716	0.1555	0.1435	0.1307	0.1228
40	1.0311	0.8230	0.6550	0.5350	0.4423	0.3615	0.2893	0.2428	0.2102	0.1918	0.1748	0.1586	0.1465	0.1347	0.1263

$m = 1.5235$ mol·kg^{-1}

	η/mPa·s at the following T/K														
p/MPa	298.20	310.41	321.70	335.41	357.62	373.20	395.23	420.69	441.32	464.49	481.70	504.92	525.34	549.71	570.70
5	1.3835	1.1071	0.8769	0.7034	0.5316	0.4523	0.3703	0.3062	0.2649	0.2319	0.2124	0.1920	0.1773		0.1488
10	1.3836	1.1083	0.8785	0.7051	0.5333	0.4539	0.3728	0.3080	0.2676	0.2336	0.2143	0.1937	0.1797	0.1626	0.1545
20	1.3840	1.1107	0.8825	0.7091	0.5378	0.4592	0.3770	0.3103	0.2713	0.2380	0.2186	0.1976	0.1830	0.1675	0.1596
30	1.3848	1.1129	0.8861	0.7146	0.5431	0.4630	0.3808	0.3147	0.2756	0.2422	0.2226	0.2015	0.1869	0.1720	0.1640
40	1.3859	1.1152	0.8902	0.7176	0.5454	0.4668	0.3849	0.3186	0.2795	0.2461	0.2265	0.2055	0.1907	0.1761	570.70

$m = 2.0310$ mol·kg^{-1}

	η/mPa·s at the following T/K														
p/MPa	298.80	308.70	324.51	342.22	361.80	377.79	394.50	416.80	432.52	459.80	481.40	504.23	526.83	547.35	574.23
5	1.6075	1.3470	0.9820	0.7600	0.5950	0.5015	0.4312	0.3615	0.3230	0.2703	0.2411	0.2198	0.2400	0.1843	0.1711
10	1.6080	1.3475	0.9830	0.7615	0.5978	0.5055	0.4362	0.3665	0.3275	0.2758	0.2463	0.2227	0.2045	0.1880	0.1745
20	1.6100	1.3510	0.9870	0.7660	0.6043	0.5136	0.4425	0.3720	0.3316	0.2811	0.2510	0.2272	0.2090	0.1932	0.1808
30	1.6110	1.3520	0.9922	0.7710	0.6102	0.5192	0.4468	0.3736	0.3355	0.2865	0.2565	0.2321	0.2131	0.1986	0.1859
40	1.6125	1.3555	0.9972	0.7755	0.6135	0.5222	0.4508	0.3790	0.3405	0.2908	0.2612	0.2366	0.2177	0.2031	574.23

$m = 2.6118$ mol·kg^{-1}

	η/mPa·s at the following T/K													
p/MPa	299.70	309.21	325.49	344.70	369.32	383.38	400.09	423.70	444.81	469.52	484.28	519.48	541.71	569.33
5	1.9070	1.6028	1.1546	0.8763	0.6501	0.4612	0.4851	0.4037	0.3483	0.3007	0.2786	0.2398	0.2184	0.1939
10	1.9072	1.6035	1.1560	0.8780	0.6522	0.4642	0.4870	0.4060	0.3502	0.3020	0.2800	0.2415	0.2205	0.1960
20	1.9075	1.6065	1.1620	0.8835	0.6600	0.5715	0.4925	0.4095	0.3558	0.3078	0.2855	0.2460	0.2260	0.2035
30	1.9080	1.6090	1.1680	0.8890	0.6682	0.5790	0.4975	0.4150	0.3612	0.3137	0.2912	0.2512	0.2320	0.2100
40	1.9090	1.6120	1.1740	0.8940	0.6705	0.5820	0.5030	0.4207	0.3662	0.3190	0.2965	0.2560	0.2370	0.2160

$m = 3.2815$ mol·kg^{-1}

	η/mPa·s at the following T/K														
p/MPa	299.20	314.30	327.60	339.52	358.41	376.20	398.72	420.42	442.13	461.51	481.31	502.73	524.51	556.21	572.80
5	2.5163	1.8626	1.4219	1.1828	0.9130	0.7465	0.5987	0.5000	0.4242	0.3732	0.3321	0.3040	0.2756	0.2400	0.2255
10	2.5170	1.8650	1.4240	1.1875	0.9190	0.7495	0.6020	0.5018	0.4280	0.3770	0.3380	0.3085	0.2783	0.2428	0.2342
20	2.5180	1.8710	1.4320	1.1940	0.9275	0.7590	0.6080	0.5090	0.4352	0.3838	0.3425	0.3108	0.2832	0.2500	0.2423
30	2.5200	1.8770	1.4390	1.2010	0.9340	0.7625	0.6160	0.5168	0.4422	0.3910	0.3508	0.3175	0.2892	0.2578	0.2490
40	2.5225	1.8850	1.4490	1.2100	0.9380	0.7680	0.6209	0.5208	0.4470	0.3965	0.3560	0.3225	0.2950	0.2640	572.80

$m = 4.0628$ mol·kg^{-1}

	η/mPa·s at the following T/K													
p/MPa	303.70	312.70	328.38	352.42	371.71	387.53	403.20	427.12	443.80	467.23	480.40	507.24	530.28	572.31
5	2.9479	2.4341	1.7443	1.2148	0.9653	0.8038	0.6919	0.5623	0.4992	0.4238	0.3939	0.3439	0.3126	0.2582
10	2.9490	2.4360	1.7480	1.2190	0.9680	0.8070	0.6940	0.5660	0.5010	0.4295	0.3975	0.3480	0.3152	0.2615
20	2.9520	2.4420	1.7570	1.2280	0.9740	0.8180	0.7020	0.5742	0.5085	0.4375	0.4055	0.3550	0.3215	0.2720
30	2.9540	2.4480	1.7670	1.2360	0.9780	0.8240	0.7108	0.5855	0.5170	0.4450	0.4130	0.3620	0.3290	0.2810
40	2.9560	2.4540	1.7770	1.2440	0.9820	0.8305	0.7180	0.5910	0.5240	0.4525	0.4205	0.3690	0.3355	0.2890

tional Association for the Properties of Water and Steam (IAPWS)[16] formulation). The values of the capillary radius determined with both weighing and by calibration techniques are 0.15091 mm and 0.15048 mm, respectively. In this work, we used the value of 0.15091 mm. The time of fluid flowing through the capillary τ was measured with a stopwatch with an uncertainty of less than 0.1 s (0.5%). An electromagnetic device was used to start and stop the

Table 4. Experimental Kinematic Viscosities as a Function of Pressure, Temperature, and Molality of $H_2O + Ca(NO_3)_2$ Solutions

	$10^6\ \nu/m^2{\cdot}s^{-1}$				
T/K	0.1 MPa	10 MPa	20 MPa	30 MPa	40 MPa
		$m = 4.9861\ mol{\cdot}kg^{-1}$			
298.55	3.1570	3.1580	3.1600	3.1618	3.1650
313.35	2.3040	2.3055	2.3070	2.3080	2.3108
334.15	1.5048	1.5060	1.5070	1.5080	1.5125
347.95	1.2400	1.2410	1.2418	1.2435	1.2450
369.85	0.9050	0.9065	0.9090	0.9125	0.9143
386.35		0.7442	0.7452	0.7490	0.7505
407.15		0.6105	0.6125	0.6148	0.6162
429.35		0.5090	0.5118	0.5140	0.5160
445.35		0.4510	0.4532	0.4565	0.4590
466.35		0.3868	0.3893	0.3933	0.3945
485.95		0.3525	0.3555	0.3585	0.3600
502.85		0.3295	0.3330	0.3350	0.3372
524.95		0.3029	0.3061	0.3090	0.3116
545.35		0.2819	0.2850	0.2908	0.2935
572.55		0.2566	0.2592	0.2700	0.2730
		$m = 6.0941\ mol{\cdot}kg^{-1}$			
298.25	4.3506	4.3520	4.3550	4.3570	4.3600
309.45	3.4100	3.4105	3.4125	3.4150	3.4180
329.35	2.1118	2.1125	2.1150	2.1170	2.1180
342.05	1.7289	1.7300	1.7320	1.7340	1.7360
360.65	1.2940	1.2952	1.2970	1.2990	1.3020
378.15		1.0132	1.0155	1.0178	1.0195
398.85		0.7815	0.7835	0.7860	0.7900
419.85		0.6473	0.6495	0.6520	0.6546
442.65		0.5283	0.5298	0.5320	0.5358
462.05		0.4440	0.4475	0.4496	0.4545
480.75		0.3978	0.4023	0.4050	0.4095
497.45		0.3734	0.3776	0.3808	0.3845
517.65		0.3440	0.3475	0.3514	0.3540
546.65		0.3092	0.3118	0.3155	0.3183
573.05		0.2856	0.2874	0.2898	0.2943

watch. All values of τ are averages of at least 5−10 measurements. At a temperature of 573 K, the minimal value of τ is 40 s.

Measurement uncertainties were associated with uncertainties that exist in measured quantities contained in working eq 2 used to compute the viscosity from experimental data. The viscosity was obtained from the measured quantities R^4, ΔH_0, L, V_c, τ, ρ_{Hg}, ρ_c, T, p, and m. The accuracy of the viscosity measurements was assessed by analyzing the sensitivity of eq 2 to the experimental uncertainties of the measured quantities. At the maximum measured temperature (573 K), the values of the root mean square deviations in the viscosity measurements was $\delta\eta = 2 \times 10^{-5}\ g{\cdot}cm^{-1}{\cdot}s^{-1}$. On the basis of the detailed analysis of all sources of uncertainties likely to affect the determination of viscosity with the present apparatus, the combined maximum relative uncertainty $\delta\eta/\eta$ in measuring the viscosity was 1.5% (see Abdulagatov and Azizov).[1] The relative systematic uncertainties Q_η/η was 0.001%. The experimental uncertainty in the mass fraction is estimated to be 0.014%.

The Reynolds (Re) number occurring during all measurements was less than the critical values ($Re_c = 300$).

As one can see from eq 2, to calculate the dynamic viscosity from measured quantities, the values of density of the solution under study at room temperature and experimental pressure ρ_c and density at the experimental conditions $\rho(p,T)$ are needed. For this aim, we used the density data reported by Akhundov et al.[9] for aqueous $Ca(NO_3)_2$ solutions at high temperatures (up to 573 K) and high pressures (up to 40 MPa).

As a check of the method and procedure of the measurements, the viscosity of pure water were measured from (294.46 to 597.56) K at pressures up to 50 MPa. Table 1 provides the present experimental viscosity data for pure water measured using the same experimental apparatus. These data were compared with values calculated from the IAPWS[16] formulation. The deviation plot is given in Figure 1. As one can see from the deviation plot (see Figure 1), the agreement between IAPWS[16] calculations and the present results along the isobars 1, 10, 20, 40, and 50 MPa is excellent. Deviation statistics for the present viscosity data for pure water and values calculated with IAPWS[16] formulation are as follows: AAD = 0.27%, bias = −0.05%, standard deviation = 0.32%, standard error = 0.06%, and maximum deviation = 0.59% (N = 25). The maximum deviation of 0.59% is found at the maximum temperature of 597.56 K and at the maximum pressure of 50 MPa. No systematic shape of the deviations was found for pure water (see Figure 1). This excellent agreement between the present data and IAPWS[16] calculations for pure water confirms the reliability and high accuracy of the measurements for $H_2O + Ca(NO_3)_2$ solutions and correct operation of the present instrument. This generally good agreement

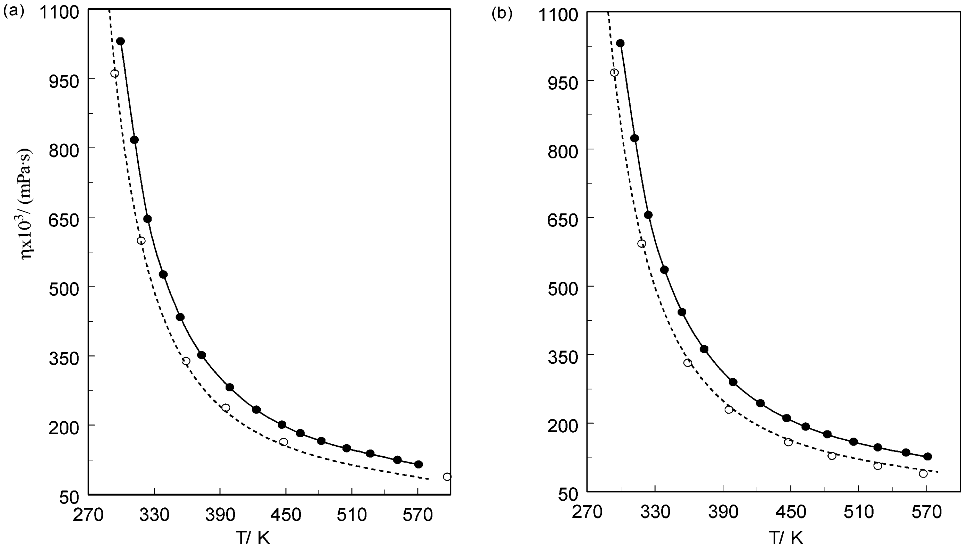

Figure 2. Measured values of viscosity of $H_2O + Ca(NO_3)_2$ solutions as a function of temperature along the two selected isobars for the composition of 0.6771 mol·kg⁻¹. (a) 10 MPa; (b) 40 MPa. ○, pure water (this work); dashed line, pure water (IAPWS).[16] The solid curve is a guide to the eye.

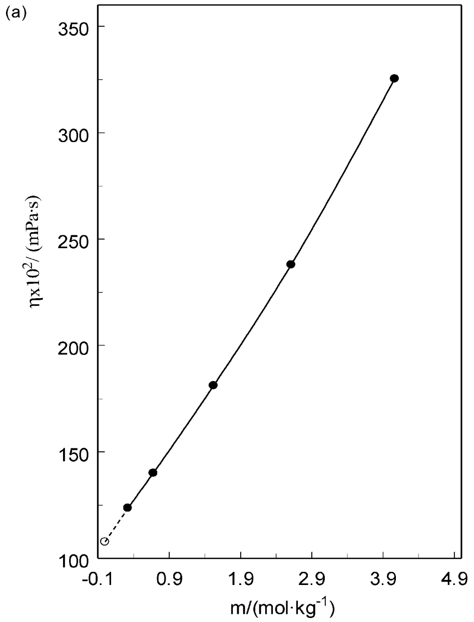

Figure 3. Measured values of viscosity of $H_2O + Ca(NO_3)_2$ solutions as a function of concentration along the two selected isobars for the isotherm of 523.15 K. (a) 10 MPa; (b), 40 MPa. ●, this work for solution; ○, pure water (IAPWS).[16] The solid curve is a guide to the eye.

provides some confidence in the experimental values of Tables 2−4.

Chemically pure $Ca(NO_3)_2$ and distilled water were used to prepare the solutions. The solutions at the desired concentration were prepared by gravimetric method, and the concentration was checked using the density at 20 °C by means of pycnometers with reference data.

Results and Discussion

The dynamic viscosity, η, measurements for aqueous $Ca(NO_3)_2$ solutions has been made in the temperature range from (298 to 573) K at pressures up to 40 MPa for compositions from (0.3207 to 4.0628) mol·kg^{-1}. This concentration range is sufficiently lower than the saturation concentration of $Ca(NO_3)_2$ in water. For example, at atmospheric pressure and at temperatures (298.15, 323.15, and 373.15) K, the values of the saturated concentrations are (8.42, 20.80, and 22.1) mol·kg^{-1}, respectively. Because of the lack of the density data for solution at high concentrations, we performed kinematic viscosity, $\nu = \eta/\rho$, measurements for two compositions (4.9861 and 6.0941) mol·kg^{-1}. The experimental temperature, viscosity, pressure, and composition values for the aqueous $Ca(NO_3)_2$ solutions are presented in Tables 2−4. Some selected experimental results for $H_2O + Ca(NO_3)_2$ solutions as an example of the present results are shown in Figures 2−4 in the $\eta-T$, $\eta-p$, and $\eta-m$ spaces together with values calculated from the IAPWS[16] formulation for pure water ($m = 0$). Figures 2−4 illustrate how viscosity changes with temperature, pressure, and concentration. The viscosity of solution considerably decreases with temperature (see Figure 2). For example, at constant pressures (10 and 40) MPa between temperatures (298 and 573) K, the viscosity of solutions changes by a factor of 10. Along isotherm 523 K and compositions between (0 and 4) mol·kg^{-1}, the viscosity changes by a factor of 7, while viscosity is barely affected (4% at pressures between 0.1 and 40 MPa) by pressure along the isotherms (see Figure 4). As Figure 4 shows, the viscosity of solution along constant composition and temperature increases linearly. To check the reproducibility of the experimental data, the measurements of the viscosity were performed at 5−10 times at the same selected temperature and pressure. The scattering of the experimental data is within of ±0.3%. All experimental viscosity data were obtained as a function of temperature at six isobars (0.1, 5, 10, 20, 30, and 40) MPa and seven compositions (0.3207, 0.6771, 1.5235, 2.0310, 2.6118, 3.2810, and 4.0628) mol·kg^{-1}. The present results for the viscosity of $H_2O + Ca(NO_3)_2$ solutions at atmospheric pressure (see Table 2) can be directly compared with experimental values reported in the literature. For example, parts a and b of Figures 5 and 6 contain the values of viscosity reported by Kuznezov et al.,[10] Blinova et al.,[12] and Prozenko et al.[11] and the data from ICT[17] together with the present results for selected isotherms (298.15 and 323.15) K and selected isopleths at atmospheric pressure. These figures include also the values of viscosity for $H_2O + Ca(NO_3)_2$ solutions calculated with the correlation eq 1 reported by Aseyev.[14] As one can see from parts a and b of Figures 5 and 6, the agreement between various data sets is satisfactory, except the data reported by Kuznezov et al.[10] Parts a and b of

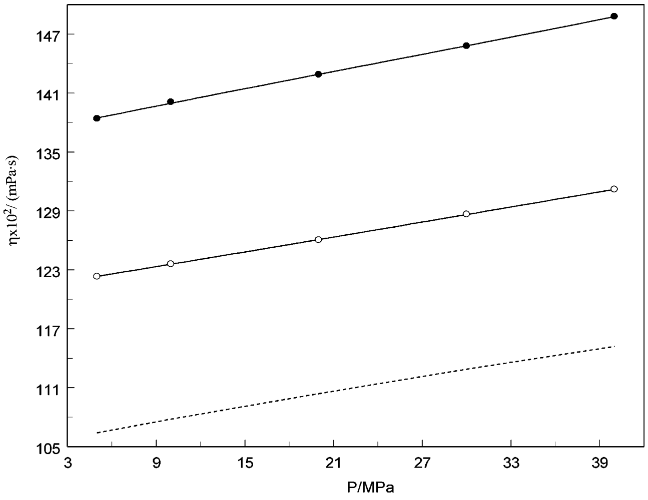

Figure 4. Measured values of viscosity of $H_2O + Ca(NO_3)_2$ solutions as a function of pressure along the two selected compositions for isotherm 523.15 K. ●, 0.6771 mol·kg^{-1}; ○, 0.3207 mol·kg^{-1}; dashed line, pure water (IAPWS).[16] The solid curve is ga uide to the eye.

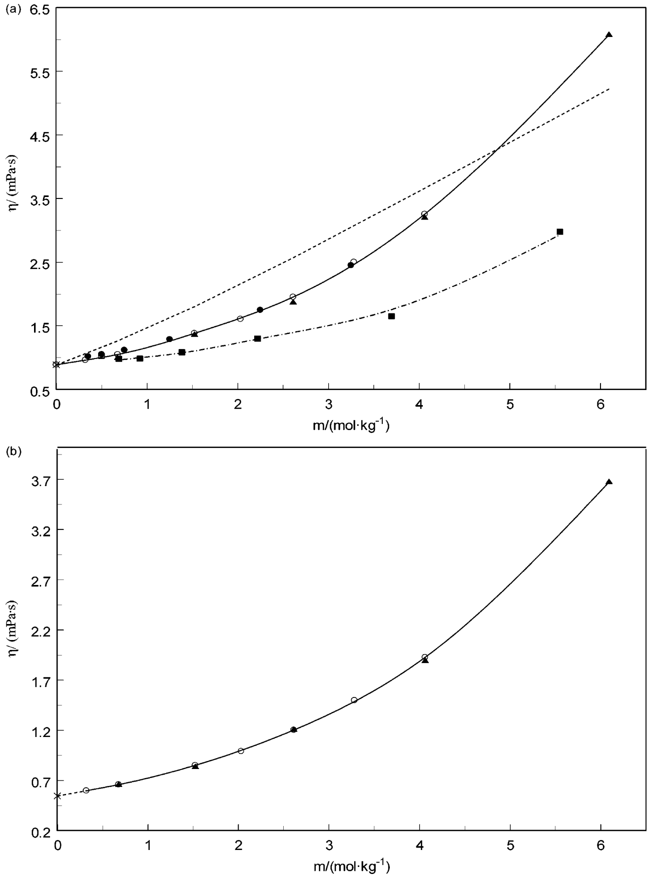

Figure 5. Comparison of the concentration dependence of the present viscosity results for $H_2O + Ca(NO_3)_2$ solutions with the data reported in the literature at atmospheric pressure and at selected temperatures of 298.15 K (a) and 323.15 K (b). ○, this work; ●, ICT;[17] ▲, Blinova et al.;[12] ■, Kuznezov et al.;[10] □, Prozenko et al.;[11] ×, IAPWS[16] (pure water); dashed line, calculated from correlation by Aseyev.[14] The solid curve is a guide to the eye.

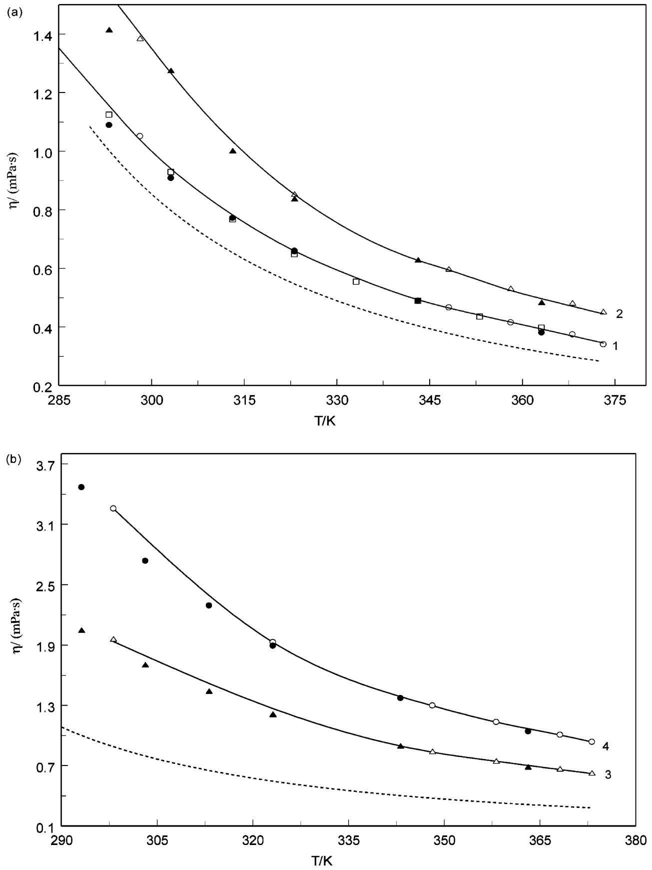

Figure 6. Comparison of the temperature dependence of the present viscosity results for $H_2O + Ca(NO_3)_2$ solutions with the data reported in the literature at atmospheric pressure and two various compositions. (a) 1, 0.6771 mol·kg^{-1}; 2, 1.5235 mol·kg^{-1}. (b) 3, 2.6120 mol·kg^{-1}; 4, 4.0620 mol·kg^{-1}. ○, this work; ●, Blinova et al.;[17] ▲, Blinova et al.;[12] □, Prozenko et al.;[11] △, this work; dashed line, IAPWS[16] (pure water). The solid curve is a guide to the eye.

Figures 5 and 6 illustrate that our data are consistent well with literature values at atmospheric pressure. Good agreement with AAD = 1.21% is found between present measurements and the data reported by Blinova et al.[12] The deviation is very close to their experimental uncertainty of 1% and uncertainty present results (1.5%). For these data, the maximum deviation (5%) is observed at a temperature of 303 K. Differences between our measurements and the data from ICT[17] are within 3−4%. The data reported by Prozenko et al.[11] agree with present viscosity values within 2.5%. At high temperatures, the agreement is good (deviation is 1−2%), while at low temperatures, the differences reached up to 4%. This agreement also confirms the reliability of the present measurements and its consistence with literature data.

Correlation

The results of the (η,p,T) measurements for $H_2O + Ca(NO_3)_2$ solutions for each measured composition were represented by the equation

$$\eta/\mathrm{mPa{\cdot}s} = A + B(t/°\mathrm{C}) + \frac{C}{(t/°\mathrm{C})} + \frac{D}{(t/°\mathrm{C})^{2.5}} \qquad (3)$$

where η is the viscosity of the solution in mPa·s and t is the temperature in °C. The pressure dependence of viscosity η for each measured compositions has been taken into account through the A, B, C, and D parameters as a linear function of the pressure p

$$\begin{aligned} A &= a_1 + a_2 p/\mathrm{MPa} \\ B &= b_1 + b_2 p/\mathrm{MPa} \\ C &= c_1 + c_2 p/\mathrm{MPa} \\ D &= d_1 + d_2 p/\mathrm{MPa} \end{aligned} \qquad (4)$$

This equation previously (Abdulagatov and Azizov[1] and Azizov and Akhundov[7]) was used to represent experimental

Table 5. Parameters a_{ij}, b_{ij}, c_{ij}, and d_{ij} of Eq 3 for $H_2O + Ca(NO_3)_2$ Solutions

m	a_1	a_2	b_1	b_2	c_1	c_2	d_1	d_2
0.3207	-0.0410×10^0	2.9422×10^{-4}	6.5710×10^{-5}	-8.3000×10^{-8}	3.6352×10^1	1.3670×10^{-3}	-1.3538×10^3	-1.2250×10^0
0.6771	-2.2167×10^{-2}	1.9710×10^{-4}	2.1170×10^{-5}	4.0320×10^{-7}	3.8329×10^1	8.6090×10^{-3}	-1.4142×10^3	-1.8707×10^0
1.5235	-0.4289×10^0	4.1528×10^{-4}	7.5110×10^{-5}	2.4000×10^{-8}	5.0180×10^1	-7.2930×10^{-4}	-1.8168×10^3	-0.7372×10^0
2.0310	-0.0665×10^0	5.0924×10^{-4}	1.1627×10^{-4}	-1.0608×10^{-7}	6.0160×10^1	-2.9907×10^{-4}	-2.2392×10^3	-1.2487×10^0
2.6118	-0.1058×10^0	4.4721×10^{-4}	1.7902×10^{-4}	3.0647×10^{-7}	7.3409×10^1	1.1209×10^{-2}	-2.7362×10^3	-3.0453×10^0
3.2815	-0.1919×10^0	1.1240×10^{-4}	3.2430×10^{-4}	1.4535×10^{-6}	9.6084×10^1	4.5189×10^{-2}	-3.4217×10^3	-5.9216×10^0
4.0628	-0.2832×10^0	6.3298×10^{-5}	4.6588×10^{-4}	1.9769×10^{-6}	1.2089×10^2	0.0602×10^0	-3.7887×10^3	-9.6620×10^0

viscosity data for pure water and aqueous $MgCl_2$, $BaCl_2$, and Li_2SO_4 solutions. Equation 3 describes the viscosity of pure water and $H_2O + Ca(NO_3)_2$ solutions with an accuracy of 0.7% and 0.6%, respectively, in the temperature range from (298 to 575) K and at pressures up to 40 MPa. The coefficients of eq 3 have been exclusively determined in order to minimize the mean quadratic deviation of the fitted experimental viscosity values. The derived values of the coefficients a_i, b_i, c_i, and d_i in eqs 4 for each studied solutions are given in Table 5. Equation 3 is valid in the temperature range from (298 to 575) K, at pressures up to 40 MPa.

Conclusion

Dynamic viscosities of seven (0.3207, 0.6771, 1.5235, 2.0310, 2.6118, 3.2810, and 4.0628) $mol \cdot kg^{-1}$ and kinematic viscosities of two (4.9861 and 6.0941) $mol \cdot kg^{-1}$ aqueous $Ca(NO_3)_2$ solutions have been measured in the liquid phase with a capillary flow technique. Measurements for solutions were made at four isobars (0.1, 5, 10, 20, 30, and 40) MPa. The range of temperature was from (298 to 573) K. The total uncertainty of viscosity, pressure, temperature, and concentration measurements were estimated to be less than 1.5%, 0.05%, 15 mK, and 0.014%, respectively. The reliability and accuracy of the experimental method was confirmed with measurements on pure water for three isobars (1, 10, 20, 40, and 50) MPa and at temperatures between (295 and 578) K. The experimental and calculated values of viscosity for pure water from IAPWS[16] formulation show excellent agreement within their experimental uncertainties (AAD = 0.27%). The correlation equation for viscosity of solutions was obtained as a function of temperature and pressure for each measured composition by a least-squares method from the experimental data. The AAD between measured and calculated values of viscosity for solution from this correlation equation was 0.6%. The measured viscosity values of solutions at atmospheric pressure were compared with the data reported in the literature by other authors. Good agreement (deviations within ±1.2 to 2.5%) is found between the present measurements and the data sets reported by other authors in the literature.

Acknowledgment

I.M.A. thanks the Physical and Chemical Properties Division at the National Institute of Standards and Technology for the opportunity to work as a Guest Researcher at NIST during the course of this research.

Literature Cited

(1) Abdulagatov, I. M.; Azizov, N. D. Viscosity for Aqueous Li_2SO_4 Solutions at Temperatures from 298 to 575 K and at Pressures up to 30 MPa. *J. Chem. Eng. Data* **2003**, *48*, 1549−1556.

(2) Abdulagatov, I. M.; Azizov, N. D. Thermal Conductivity of Aqueous $Sr(NO_3)_2$ and $LiNO_3$ Solutions at High Temperatures and High Pressures. *J. Chem. Eng. Data* **2004**, *49*, 688−704.

(3) Abdulagatov, I. M.; Azizov, N. D. *PVTx* Measurements for Aqueous $LiNO_3$ Solutions. *J. Chem. Thermodyn.* **2004**, *36*, 17−27.

(4) Abdulagatov, I. M.; Azizov, N. D. Experimental Vapor Pressures and Derived Thermodynamic Properties of Aqueous Solutions of Lithium Sulfate from 423 to 523 K. *Fluid Phase Equilib.* **2004**, *216*, 189−199.

(5) Abdulagatov, I. M.; Azizov, N. D. Densities and Apparent Molar Volumes of Aqueous $NaNO_3$ Solutions at Temperatures from 292 to 573 K and at Pressures up to 30 MPa. *J. Solution Chem.* **2003**, *32*, 573−599.

(6) Abdulagatov, I. M.; Azizov, N. D. *PVTx* Measurements and Partial Molar Volumes for Aqueous Li_2SO_4 Solutions at Temperatures from 297 to 573 K and Pressures up to 40 MPa. *Int. J. Thermophys.* **2003**, *24*, 1581−1610.

(7) Azizov, N. D.; Akhundov, T. S. Viscosity of Aqueous $MgCl_2$ and $BaCl_2$ Solutions at Temperatures from (293 to 573) K. *Russ. J. Phys. Chem.* **1997**, *71*, 1955−1959.

(8) Akhundov, T. S.; Iskenderov, A. I.; Zeinalova, A. B. Dynamic Viscosity of Aqueous $BaNO_3$ Solutions. *Izv. Vuzov, ser. Neft i Gas* **1991**, *5*, 64−66.

(9) Akhundov, T. S.; Akhmedova, I. N.; Tairov, A. D. Experimental Study of *PVT* and P_S-T_S Dependences of Aqueous $Ca(NO_3)_2$. *Izv. Vuzov, ser. Neft i Gas* **1989**, *9*, 55−56.

(10) Kuznezov, V. V.; Trostin, V. N.; Khrenova, A. A.; Krestov, G. A. Density, Viscosity, and Speed of Sound in Aqueous Solutions of Nitrates Mg, Ca, and Sr. *Izv. Vuzov, ser. Khimiya i Khimicheskaya Tekhnologiya* **1983**, *26*, 1507−1508.

(11) Prozenko, P. I.; Razumovskaya, O. N.; Ivleva, T. I. Properties of Solutions for Some Nitrates of One- and Two-Valence Metals. *Russ. J. Appl. Chem.* **1967**, *11*, 2576−2577.

(12) Blinova, M. B.; Sorina, G. A., Tsekhanskaya, Yu. V. Density and Viscosity of H_2O+$Ca(NO_3)_2$ System. *Russ. J. Appl. Chem.* **1978**, *2*, 466−476.

(13) Ambrus, J. H.; Moynihan, C. T.; Macedo, P. B. The Temperature Dependence of Viscosity and Conductivity of Concentrated Aqueous Calcium Nitrate Solutions. *J. Electrochem. Soc.* **1972**, *119*, 191−196

(14) Aseyev, G. G. *Electrolytes. Properties of Solutions. Methods for Calculation of Multicomponent Systems and Experimental Data on Thermal Conductivity and Surface Tension*; Begell-House Inc.: New York, 1998.

(15) Abdulagatov, I. M.; Rasulov, S. M. Viscosity of N-Pentane, N-Heptane and Their Mixtures within the Temperature Range from 298 K up to Critical Points at the Saturation Vapor Pressure. *Ber. Bunsen−Ges. Phys. Chem.* **1996**, *100*, 148−154.

(16) Kestin, J.; Sengers, J. V.; Kamgar-Parsi, B.; Levelt Sengers, J. M. H. Thermophysical Properties of Fluid H_2O. *J. Phys. Chem. Ref. Data* **1984**, *13*, 175−189.

(17) *International Critical Tables, Viscosity of Aqueous Solutions of Strong Electrolytes*; Bates, S. J., Baxter, W. P., Eds.; McGraw-Hill: New York, 1928; Vol. 3, pp 12−19.

Received for review April 9, 2004. Accepted June 21, 2004.

JE049853N