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Density and Viscosity of Undersaturated, Saturated, and Supersaturated Aqueous Ammonium Oxalate Solutions from 287 K to 325 K

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Experimental data on the density, *d*, and viscosity, η, of ammonium oxalate aqueous solutions in the range of undersaturation and supersaturation are reported for solutions of saturation concentrations, c_s, between 0.36 M and 0.75 M. It was found that the temperature dependence of *d* for solutions of different saturation concentrations may be described by a first-order equation while that of η may be described by an Arrhenius-type relation. Moreover, for solutions of particular saturation concentrations, c_s, both *d* and η linearly increase with supersaturation.

Introduction

Data on the physical properties of concentrated aqueous solutions of various compounds are useful in monitoring a crystal growth run and provide information about the nature of entities (ions, molecules, or large clusters) involved during growth (Mullin, 1972; Sangwal, 1994; Fredericks et al., 1994). However, the available experimental data mainly deal with low concentrations (Szewczyk et al., 1988; Söhnel and Novotny, 1985; Söhnel et al., 1984), and data for superaturated solutions are sparse (Khamskii, 1975; Szewczyk et al., 1985).

Recently, the authors (Frej et al., 1998) reported experimental data on density, surface tension, and refractive index for dilute aqueous ammonium oxalate solutions. However, until now no data have been published for its supersaturated solutions. In this paper data on the density and viscosity of concentrated aqueous solutions of ammonium oxalate in the range of undersaturation and supersaturation are reported.

Experimental Section

Aqueous ammonium oxalate solutions were prepared using analytically pure compound (impurities: 0.015% SO_4, 0.001% Cl, 0.001% Pb, and 0.0005% Fe/III) produced by Polish Chemical Reagents, Gliwice, Poland. The dehydration of salt was realized by drying the material in an oven at 353 K for 72 h. These conditions of dehydration of the compound were estimated on the basis of thermogravimetric tests, which revealed no further weight loss of the sample dried for longer durations and higher temperatures. Using the solubility data from the literature (Söhnel and Novotny, 1985), saturated solutions were prepared from dehydrated material for selected temperatures in the range between 293.15 K and 320.15 K. The concentration c_s of the saturated solutions varied from 0.36 M to 0.75 M. For the preparation of the solutions, double-distilled water was used. The uncertainty in the composition of the prepared solutions was estimated to be ±1.5%.

The experimental data on density d_m were obtained using a modified hydrostatic balance composed of a 10 cm^3 float and an analytical balance. The float was weighed in the air and in the specimen solution at a particular temperature with an accuracy of $\pm 1 \times 10^{-8}$ kg. Taking into account the air density and the capillary action, the corrected experimental values of the density *d* were calculated from the expression $d/\text{kg}\cdot\text{m}^{-3} = d_m/\text{kg}\cdot\text{m}^{-3} + 0.0002 d_m/\text{kg}\cdot\text{m}^3 + 1.2$. The reproducibility in the data on density was $\pm 0.01\ \text{kg}\cdot\text{m}^{-3}$.

The viscosity was determined with Höppler's B_3-type viscometer. The time *t* for the falling of the ball in a given solution at a particular temperature was determined with an accuracy of ±0.01 s. The viscosity was calculated from the relation $\eta = kt(d_k - d_r)$, where *k* is the ball constant at a particular temperature and d_k and d_r are the densities of the ball and the solution, respectively. The constant *k* of the ball, a function of temperature, was determined from measurements of the time of falling of the ball in water at different temperatures and was calculated from the formula $k = \eta_0/t(d_k - d_0)$, where η_0 and d_0 are the viscosity and the density of water at a given temperature. The viscosity and density of water were taken from the *Handbook of Chemistry and Physics* (Lide, 1996/97). The reproducibility in the viscosity measurements was $\pm 10^{-7}$ Pa·s.

Measurements of density and viscosity were made for each saturated solution starting from a temperature 5 K above the saturation temperature T_s (undersaturation range) to the temperature of onset of nucleation (supersaturation range). During measurements the solutions were cooled at a rate of 4 K/h and the measurements were made at temperature intervals of 0.5 K. The temperature of the cooled solutions was measured with a mercury thermometer with an accuracy of ±0.01 K. The density and viscosity values tested were derived from the average values of three measurements.

Results

The experimental data on density, *d*, and viscosity, η, for undersaturated, saturated, and supersaturated solutions are presented in Tables 1 and 2. The values of the density and viscosity for the saturated solutions are underlined in the tables. The tables show that density and viscosity for solutions in the concentration range between 0.36 M and 0.75 M increase with a decrease in the temperature both above and below the saturation temperature.

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Table 1. Densities of Undersaturated, Saturated, and Supersaturated Ammonium Oxalate Aqueous Solutions

	10^{-3} d/kg·m^{-3} at the following 10^{-3} c_s/mol·m^{-3} values									
T/K	0.753	0.700	0.646	0.598	0.553	0.508	0.465	0.429	0.392	0.356
325.15	1.02833									
324.65	1.02851									
324.15	1.02865									
323.65	1.02871									
323.15	1.02899									
322.65	1.02921									
322.15	1.02942	1.02621								
321.65	1.02970	1.02682								
321.15	1.03004	1.02722								
320.65	1.03016	1.02733								
320.15	1.03047	1.02756								
319.65	1.03082	1.02778								
319.15	1.03099	1.02792	1.02494							
318.65	1.03102	1.02810	1.02543							
318.15	1.03116	1.02830	1.02554							
317.65	1.03128	1.02850	1.02578							
317.15	1.03137	1.02877	1.02615							
316.65	1.03156	1.02891	1.02624							
316.15	1.03169	1.02906	1.02638	1.02501						
315.65	1.03183	1.02925	1.02662	1.02517						
315.15	1.03196	1.02945	1.02685	1.02553						
314.65	1.03210	1.02965	1.02700	1.02573						
314.15	1.03224	1.02972	1.02721	1.02594						
313.65	1.03237	1.02994	1.02743	1.02612						
313.15	1.03251	1.03010	1.02760	1.02633	1.02385					
312.65	1.03265	1.03027	1.02775	1.02657	1.02419					
312.15		1.03044	1.02785	1.02672	1.02433					
311.65		1.03061	1.02825	1.02689	1.02454					
311.15		1.03078	1.02846	1.02711	1.02476					
310.65		1.03095	1.02865	1.02734	1.02492					
310.15		1.03112	1.02883	1.02771	1.02515	1.02253				
309.65			1.02903	1.02787	1.02522	1.02272				
309.15			1.02924	1.02807	1.02541	1.02299				
308.65			1.02944	1.02828	1.02560	1.02322				
308.15			1.02965	1.02836	1.02588	1.02339				
307.65			1.02985	1.02868	1.02609	1.02369				
307.15				1.02889	1.02624	1.02376	1.02136			
306.65				1.02911	1.02654	1.02393	1.02171			
306.15				1.02932	1.02675	1.02405	1.02193			
305.65				1.02954	1.02695	1.02425	1.02207			
305.15				1.02975	1.02708	1.02444	1.02222			
304.65				1.02996	1.02720	1.02460	1.02235			
304.15				1.03018	1.02736	1.02478	1.02251	1.02003		
303.65					1.02762	1.02490	1.02265	1.02015		
303.15					1.02781	1.02507	1.02282	1.02031		
302.65					1.02800	1.02521	1.02303	1.02045		
302.15					1.02819	1.02535	1.02322	1.02061		
301.65					1.02838	1.02555	1.02339	1.02074		
301.15					1.02857	1.02572	1.02357	1.02087	1.01754	
300.65						1.02584	1.02373	1.02112	1.01770	
300.15						1.02598	1.02384	1.02121	1.01781	
299.65						1.02615	1.02399	1.02136	1.01801	
299.15						1.02631	1.02415	1.02159	1.01816	
298.65						1.02646	1.02433	1.02178	1.01826	
298.15							1.02446	1.02189	1.01840	1.01633
297.65							1.02459	1.02212	1.01853	1.01656
297.15							1.02471	1.02225	1.01867	1.01679
296.65							1.02489	1.02242	1.01881	1.01695
296.15							1.02504	1.02248	1.01898	1.01707
295.65							1.02519	1.02258	1.01910	1.01720
295.15								1.02282	1.01924	1.01733
294.65								1.02295	1.01936	1.01744
294.15								1.02310	1.01950	1.01755
293.65								1.02324	1.01967	1.01768
293.15								1.02339	1.01972	1.01779
292.65								1.02354	1.01984	1.01789
292.15								1.02368	1.02002	1.01800
291.65									1.02015	1.01816
291.15									1.02027	1.01828
290.65									1.02040	1.01829
290.15									1.02052	1.01848
289.65									1.02065	1.01858
289.15										1.01869
288.65										1.01880
288.15										1.01892
287.65										1.01903
287.15										1.01914

Table 2. Viscosities of Undersaturated, Saturated, and Supersaturated Ammonium Oxalate Aqueous Solutions

	η/mPa·s at the following $10^{-3}c_s$/mol·m^{-3} values								
T/K	0.753	0.700	0.646	0.598	0.553	0.508	0.465	0.429	0.392
325.15	0.6419								
324.65	0.6489								
324.15	0.6565								
323.65	0.6673								
323.15	0.6681								
322.65	0.6770								
322.15	0.6791	0.6741							
321.65	0.6873	0.6827							
321.15	0.6942	0.6921							
320.65	0.6994	0.6930							
320.15	0.7070	0.6969							
319.65	0.7121	0.7021							
319.15	0.7166	0.7097	0.6980						
318.65	0.7225	0.7174	0.7087						
318.15	0.7277	0.7257	0.7164						
317.65	0.7335	0.7308	0.7231						
317.15	0.7399	0.7396	0.7278						
316.65	0.7444	0.7430	0.7353						
316.15	0.7505	0.7492	0.7421	0.7213					
315.65	0.7559	0.7565	0.7494	0.7340					
315.15	0.7610	0.7666	0.7566	0.7397					
314.65	0.7668	0.7774	0.7635	0.7524					
314.15	0.7725	0.7826	0.7717	0.7582					
313.65	0.7782	0.7881	0.7771	0.7677					
313.15	0.7834	0.7933	0.7835	0.7741	0.7443				
312.65	0.7897	0.7991	0.7916	0.7805	0.7513				
312.15		0.8060	0.7995	0.7869	0.7565				
311.65		0.8112	0.8087	0.7952	0.7710				
311.15		0.8181	0.8150	0.8028	0.7762				
310.65		0.8227	0.8217	0.8104	0.7820				
310.15		0.8297	0.8283	0.8167	0.7927	0.7894			
309.65			0.8353	0.8256	0.7986	0.8009			
309.15			0.8412	0.8314	0.8087	0.8085			
308.65			0.8489	0.8390	0.8157	0.8167			
308.15			0.8559	0.8467	0.8271	0.8250			
307.65			0.8622	0.8536	0.8316	0.8307			
307.15				0.8618	0.8374	0.8404	0.8282		
306.65				0.8700	0.8462	0.8518	0.8382		
306.15				0.8751	0.8563	0.8551	0.8497		
305.65				0.8852	0.8620	0.8640	0.8592		
305.15				0.8922	0.8722	0.8766	0.8663		
304.65				0.9004	0.8811	0.8837	0.8740		
304.15				0.9105	0.8894	0.8919	0.8854	0.8480	
303.65					0.8978	0.9034	0.8944	0.8621	
303.15					0.9067	0.9110	0.8957	0.8742	
302.65					0.9161	0.9162	0.9071	0.8843	
302.15					0.9237	0.9270	0.9166	0.8940	
301.65					0.9294	0.9371	0.9299	0.9042	
301.15					0.9357	0.9472	0.9401	0.9150	0.9096
300.65						0.9574	0.9490	0.9251	0.9243
300.15						0.9669	0.9617	0.9328	0.9351
299.65						0.9768	0.9706	0.9424	0.9453
299.15						0.9856	0.9820	0.9525	0.9603
298.65						0.9932	0.9984	0.9663	0.9682
298.15							1.0061	0.9728	0.9781
297.65							1.0156	0.9848	0.9903
297.15							1.0270	0.9962	0.9991
296.65							1.0378	1.0082	1.0141
296.15							1.0492	1.0216	1.0233
295.65							1.0624	1.0331	1.0364
295.15								1.0412	1.0462
294.65								1.0529	1.0592
294.15								1.0655	1.0716
293.65								1.0775	1.0817
293.15								1.0901	1.0954
292.65								1.1033	1.1068
292.15								1.1185	1.1206
291.65									1.1348
291.15									1.1526
290.65									1.1681
290.15									1.1797
289.65									1.1876

The data on the dependencies of density, d, and viscosity, η, on measurement temperature T for various solutions saturated at a particular temperature were correlated in the ranges of undersaturation and supersaturation by the conventional equations (Horvath, 1985)

$$d/\mathrm{kg{\cdot}m^{-3}} = A + B(T/\mathrm{K}) \tag{1}$$

$$\log(\eta/\mathrm{mPa{\cdot}s}) = A_1 + B_1/(T/\mathrm{K}) \tag{2}$$

where A, B, A_1, and B_1 are constants. The values of these

Table 3. Coefficients and Standard Deviations of Eq 1 for Undersaturated and Supersaturated Solutions

$10^{-3}c_s$/mol·m^{-3}	A/kg·m^{-3}	$-B$/kg·m^{-3}·K^{-1}	δ/kg·m^{-3}
0.753	1143.96	0.3552	0.20
0.700	1143.54	0.3623	0.07
0.646	1153.59	0.4023	0.06
0.598	1160.39	0.4281	0.05
0.553	1145.27	0.3875	0.06
0.508	1125.77	0.3323	0.07
0.465	1118.86	0.3167	0.04
0.429	1114.21	0.3097	0.05
0.392	1098.61	0.2690	0.03
0.356	1085.45	0.2309	0.03

Table 4. Coefficients and Standard Deviations of Eq 2 for Undersaturated and Supersaturated Solutions

$10^{-3}c_s$/mol·m^{-3}	$-A_1$/mPa·s	B_1/mPa·s·K	$10^2\delta$/mPa·s
0.753	2.3778	712.15	0.20
0.700	2.5352	762.06	0.18
0.646	2.5788	774.30	0.13
0.598	2.5813	773.01	0.18
0.553	2.6577	792.68	0.15
0.508	2.6777	799.23	0.09
0.465	2.8309	844.58	0.12
0.429	2.8973	860.48	0.11
0.392	2.9347	872.06	0.10

Table 5. Coefficients and Standard Deviations of Eq 3 at Different Temperatures of Saturation

T_s/K	C/kg·m^{-3}	D/kg·m^{-3}	δ/kg·m^{-3}
296.15	1019.01	0.07	0.03
299.15	1021.89	0.08	0.03
302.15	1023.32	0.10	0.04
305.15	1024.44	0.10	0.03
308.15	1025.99	0.12	0.08
311.15	1027.25	0.15	0.08
314.15	1027.19	0.15	0.05
317.15	1028.76	0.12	0.04
320.15	1030.75	0.08	0.03

Table 6. Coefficients and Standard Deviations of Eq 4 at Different Temperatures of Saturation

T_s/K	C_1/mPa·s	D_1/mPa·s	$10^3\delta$/mPa·s
296.15	1.0200	0.7719	3.78
299.15	0.9559	0.6644	2.27
302.15	0.9242	0.6783	2.81
305.15	0.8733	0.6072	1.95
308.15	0.8249	0.5163	1.54
311.15	0.8054	0.4939	1.21
314.15	0.7726	0.4977	1.92
317.15	0.7407	0.4535	2.92
320.15	0.7090	0.3815	1.14

constants and standard deviations estimated by the least-squares method are collected in Tables 3 and 4.

Table 3 shows that, both for undersaturated and supersaturated solutions, the values of the constant A have a general tendency to increase while those of B tend to decrease with increasing saturation concentration for $c_s < 0.65 \times 10^3$ mol·m^{-3}. For solutions of saturation concentrations $c_s > 0.65 \times 10^3$ mol·m^{-3}, the values of A and B practically remain constant, probably due to some reorganization and change in the solution structure, since no nucleation was observed during the measurements. Table 4 shows that, in the range of both undersaturation and supersaturation, the values of constant A_1 increase while those of B_1 decrease with increasing saturation concentration of the solutions. Moreover, the dependence of density and viscosity on the supersaturation of the solutions may be described by the first-order equations

$$d/\mathrm{kg{\cdot}m^{-3}} = C + D\sigma \tag{3}$$

$$\eta/\mathrm{mPa{\cdot}s} = C_1 + D_1\sigma \tag{4}$$

where C, D, C_1, and D_1 are constants and σ is the supersaturation of the solution at a given temperature. The supersaturation σ of the solution was calculated from the usual formula $\sigma = (c - c_0)/c_0$, where c_0 is the concentration of the saturated solution and c is the concentration of the supersaturated solution at a given temperature. Here the concentrations c and c_0 are expressed in mole fractions. The values of the constants C, D, C_1, and D_1 are listed in Tables 5 and 6.

Tables 5 and 6 show that, with increasing saturation temperature T_s, the values of C increase while those of D remain practically constant. However, both C_1 and D_1 have a decreasing trend with increasing saturation temperature T_s.

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