Density, Surface Tension, and Refractive Index of Aqueous Ammonium Oxalate Solutions from 293 K to 333 K

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Density d, surface tension γ, and refractive index n of ammonium oxalate aqueous solutions of concentrations up to saturation have been measured in the temperature range between 293 K and 333 K. The results of d, γ, and n are fitted as functions of solution concentration. It was found that the first- and second-order equations relating these quantities with solution concentration can satisfactorily be used to describe the data.

Introduction

During the determination of the mechanism of crystal growth and the modeling of the formation of solute clusters in solutions, knowledge of some of the physical properties (for example, solubility, density, viscosity, and surface tension) of solutions of substances to be grown under given growth conditions are frequently required (Fredericks et al., 1994; Sangwal, 1994; Polak and Sangwal, 1995, 1996). Moreover, for the growth of large-sized crystals of good quality, the solution supersaturation is controlled by continuosly monitoring one or more of its physical properties (Mullin, 1972). Density and refractive index are among the properties frequently used for controlling solution supersaturation during a growth run. Consequently, investigation of the physical properties of solutions is an area of continued interest (Ananikyan et al., 1985; Szewczyk and Sangwal, 1988; Fredericks et al., 1994).

Recently, the authors investigated (Mielniczek-Brzóska and Sangwal, 1994; Sangwal et al., 1996) the kinetics and the mechanism of growth of ammonium oxalate monohydrate $(NH_4)_2C_2O_4{\cdot}H_2O$. However, until now reliable data are available only on its temperature dependence of solubility (Söhnel and Novotny, 1985). Although there are some data on the temperature dependence of the density, these values are primarily for undersaturated solutions (Söhnel et al., 1984). No data have been reported on refractive index and surface tension. Therefore, it was thought worthwhile to investigate the density, the surface tension, and the refractive index of ammonium oxalate solutions from the lowest possible concentration of 0.08 M up to saturation in a temperature range between 293.15 K and 333.15 K.

Experimental Section

Ammonium oxalate aqueous solutions were prepared using analytically grade 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 hydration and absorbed water was removed by drying the salt in an oven at 353 K for 72 h. The time and temperature of dehydration of the compound were estimated by using thermogravimetric tests. The dehydrated material was first used to prepare saturated solutions at particular temperatures in the range between 293.15 K and 333.15 K, employing the solubility data from the literature (Söhnel and Novotny, 1985). Other concentrations, down to the lowest concentration of 0.08 M, were prepared in volumetric flasks by diluting the saturated solution with double-distilled water. The uncertainty in the compositions of the solutions prepared from the reported solubility data was esimated to be ±1.5%.

The experimental density d_m of the solutions was determined with a modified hydrostatic balance by weighing a 10-cm^3 float in air and in the desired solution with an accuracy of $\pm 1 \times 10^{-8}$ kg. Taking into account the air density and capillary action, the corrected experimental values of the density d were obtained from the relation: $d/\mathrm{kg{\cdot}m^{-3}} = d_m + 0.0002d_m + 1.2$. The density values were reproducible to ± 0.1 kg·m^{-3}.

Refractive index measurements were made by using a Carl Zeiss Jena immersion refractometer. The reproducibility in the refractive measurements was $\pm 2 \times 10^{-5}$.

Surface tension data were obtained using the stalagmometric method. The stalagmometer consisted of a capillary of 2.85 mm internal diameter, surrounded by a closed cylindrical glass-thermostat with circulating water in it. The water supply to this glass thermostat was made from an external thermostat whose temperature could be maintained constant within ±0.01 K. Surface tension γ was calculated from the formula: $\gamma = (dN_{H_2O}F/d_{H_2O}NF_{H_2O})\gamma_{H_2O}$, where d and d_{H_2O} are the densities of the solution and water, respectively, N and N_{H_2O} are the numbers of drops of solution and water, respectively, F and F_{H_2O} are factors that depend on the stalagmometer foot and the volume of solution drop, and γ_{H_2O} is the surface tension of water. The

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Table 1. Experimental Densities d for Aqueous Ammonium Oxalate Solutions

	$10^{-3}d$/kg·m^{-3}								
$10^{-3}c$/mol·m^{-3}	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K	328.15 K	333.15 K
0.00	0.998 01	0.996 75	0.995 64	0.994 26	0.992 33	0.990 54	0.988 37	0.985 99	0.983 53
0.08	1.002 61	1.001 34	1.000 22	0.998 62	0.996 81	0.995 14	0.992 88	0.990 45	0.987 89
0.16	1.007 15	1.005 89	1.004 69	1.003 13	1.001 32	0.999 48	0.997 36	0.994 96	0.992 14
0.20	1.009 55	1.008 13	1.006 88	1.005 39	1.003 50	1.001 74	0.999 59	0.997 09	0.994 43
0.24	1.011 85	1.010 28	1.008 99	1.007 60	1.005 78	1.003 97	1.001 82	0.999 29	0.996 60
0.28	1.014 07	1.012 50	1.011 28	1.009 75	1.007 99	1.006 18	1.004 03	1.001 43	0.998 77
0.36	1.018 29	1.016 93	1.015 72	1.014 21	1.012 42	1.010 61	1.008 57	1.005 85	1.003 10
0.38		1.017 89	1.016 72	1.015 30	1.013 48	1.011 71	1.009 75	1.007 35	1.005 08
0.42		1.020 10	1.018 88	1.017 46	1.015 60	1.013 89	1.011 94	1.009 41	1.007 24
0.44			1.019 95	1.018 59	1.016 63	1.015 01	1.012 84	1.010 20	1.007 52
0.48			1.022 14	1.020 89	1.018 83	1.017 20	1.014 92	1.012 43	1.009 68
0.51				1.022 42	1.020 53	1.018 93	1.016 72	1.013 98	1.011 25
0.55				1.024 58	1.022 61	1.020 95	1.018 83	1.016 24	1.013 45
0.59					1.024 72	1.023 20	1.020 99	1.018 25	1.015 59
0.63					1.026 78	1.025 37	1.023 11	1.020 41	1.017 74
0.67						1.027 54	1.025 31	1.022 54	1.019 82
0.72						1.030 18	1.027 99	1.025 24	1.022 56
0.76							1.030 13	1.027 21	1.024 66
0.81							1.032 79	1.029 95	1.027 36
0.85								1.031 96	1.029 49
0.91								1.035 19	1.032 68
0.96									1.035 45
1.02									1.038 51

Table 2. Experimental Surface Tension γ for Aqueous Ammonium Oxalate Solutions

	$10^{3}\gamma$/J/·m^{-2}								
$10^{-3}c$/mol·m^{-3}	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K	328.15 K	333.15 K
0.00	72.75	71.97	71.18	70.38	69.56	68.74	67.91	67.05	66.18
0.08	73.09	72.34	71.54	70.61	69.80	69.03	68.22	67.34	66.50
0.16	73.38	72.61	71.88	70.99	70.19	69.38	68.50	67.68	66.82
0.20	73.62	72.81	72.04	71.14	70.31	69.53	68.71	67.76	66.93
0.24	73.79	72.99	72.19	71.25	70.53	69.69	68.82	67.99	67.13
0.28	73.98	73.17	72.36	71.54	70.64	69.81	68.98	68.09	67.27
0.36	74.27	73.47	72.66	71.74	70.91	70.19	69.25	68.41	67.55
0.38		73.57	72.75	71.84	71.03	70.27	69.39	68.51	67.65
0.42		73.69	72.85	72.02	71.15	70.31	69.50	68.66	67.77
0.44			72.90	72.08	71.25	70.42	69.65	68.74	67.87
0.48			73.14	72.24	71.40	70.54	69.75	68.88	68.00
0.51				72.41	71.59	70.73	69.83	69.04	68.15
0.55				72.61	71.68	70.90	70.02	69.16	68.25
0.59					71.90	71.03	70.19	69.33	68.44
0.63					72.07	71.15	70.32	69.42	68.57
0.67						71.30	70.46	69.60	68.71
0.72						71.50	70.62	69.75	68.94
0.76							70.79	69.94	69.09
0.81							70.99	70.12	69.29
0.85								70.24	69.40
0.91								70.54	69.66
0.96									69.86
1.02									70.04

water surface tension was taken from the *Handbook of Chemistry and Physics* (Lide, 1996/97). The accuracy of the method used was estimated to be $\pm 10^{-4}$ J·m^{-2}. During the measurements, the temperature of the solutions was maintained constant with an accuracy of ±0.01 K. The temperature of the solutions was controlled by a conventional mercury thermometer.

All the above measurements were made three times for the solution of a given concentration at a particular temperature. From these measurements, the average values were calculated and used for the analysis.

Results

The results of the density d, the surface tension γ, and the refractive index n measurements for solutions in the temperature range investigated are given in Tables 1−3. Figure 1 illustrates an example of the dependence of density d on concentrations of the salt at different temperatures. The tables and the figure show that the density, the refractive index, and the surface tension at a particular temperature increase with an increase in the concentration of the salt, while at a particular salt concentration they decrease with an increase in solution temperature.

Our values of the density of solutions agree very well with the data reported by Söhnel et al. (1984). However, in contrast to their data, which are extrapolated for concentrated solutions, we report here the precisely measured experimental data.

The dependence of density, surface tension, and refractive index of solutions in the range of concentration from 0.08 M to saturation at a given temperature may be described by the conventional equations (Horvath, 1985)

$$d/\text{kg}\cdot\text{m}^{-3} = d_0 + A_1 c/c_0 + A_2 (c/c_0)^2 \tag{1}$$

$$\gamma/\text{J}\cdot\text{m}^{-2} = \gamma_0 + A_3 c/c_0 \tag{2}$$

$$n = n_0 + A_4 c/c_0 \tag{3}$$

Table 3. Experimental Refractive Index *n* for Aqueous Ammonium Oxalate Solutions

$10^{-3}c$/mol·m^{-3}	*n*								
	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K	328.15 K	333.15 K
0.00	1.333 00	1.332 54	1.331 96	1.331 44	1.330 64	1.329 93	1.329 41	1.328 22	1.327 55
0.08	1.334 86	1.334 39	1.333 78	1.333 25	1.332 34	1.331 74	1.331 03	1.330 13	1.329 19
0.16	1.336 66	1.336 17	1.335 66	1.334 94	1.334 02	1.333 49	1.332 93	1.331 74	1.330 83
0.20	1.337 58	1.337 11	1.336 54	1.335 94	1.335 10	1.334 43	1.333 51	1.332 77	1.331 93
0.24	1.338 53	1.337 96	1.337 51	1.336 68	1.335 90	1.335 13	1.334 43	1.333 50	1.332 50
0.28	1.339 48	1.338 87	1.338 30	1.337 73	1.336 77	1.336 20	1.335 36	1.334 32	1.333 40
0.36	1.341 19	1.340 70	1.340 20	1.339 25	1.338 53	1.337 92	1.337 07	1.336 24	1.335 39
0.38		1.341 08	1.340 62	1.339 79	1.339 06	1.338 42	1.337 49	1.336 58	1.336 05
0.42		1.341 94	1.341 42	1.340 55	1.339 94	1.339 14	1.338 42	1.337 77	1.336 74
0.44			1.341 87	1.340 92	1.340 39	1.339 79	1.338 80	1.338 11	1.337 15
0.48			1.342 59	1.341 83	1.341 28	1.340 55	1.339 67	1.339 06	1.337 92
0.51				1.342 47	1.341 79	1.341 12	1.340 43	1.339 75	1.338 61
0.55				1.343 35	1.342 78	1.341 98	1.341 35	1.340 58	1.339 52
0.59					1.343 46	1.342 82	1.342 28	1.341 23	1.340 58
0.63					1.344 48	1.343 71	1.343 01	1.342 17	1.341 19
0.67						1.344 70	1.343 98	1.342 89	1.342 28
0.72						1.345 64	1.344 81	1.344 21	1.343 28
0.76							1.345 52	1.345 12	1.344 06
0.81							1.346 76	1.345 94	1.345 15
0.85								1.347 00	1.345 91
0.91								1.348 36	1.347 13
0.96									1.348 25
1.02									1.349 69

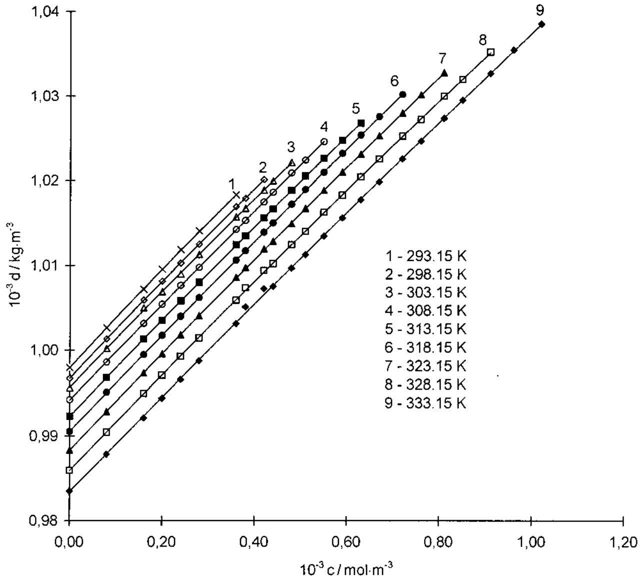

Figure 1. Plots of the dependence of density of aqueous ammonium oxalate solutions on concentration in the temperature range between 293.15 K and 333.15 K. The solid lines represent the least-squares fits according to eq 1. The constants are given in Table 4.

Table 4. Coefficients and Standard Deviations of Equation 1 at Different Temperatures

T/K	d_0	A_1	$-A_2$	σ/kg·m^{-3}
293.15	997.96	59.32	7.42	0.09
298.15	996.75	57.82	5.39	0.04
303.15	995.67	56.68	3.25	0.05
308.15	994.22	55.92	1.17	0.05
313.15	992.96	56.99	3.47	0.04
318.15	990.56	56.32	1.72	0.04
323.15	988.35	56.86	2.52	0.07
328.15	985.97	56.42	2.66	0.11
333.15	983.48	55.57	1.64	0.25

Table 5. Coefficients and Standard Deviations of Equation 2 at Different Temperatures

T/K	$10^3\gamma_0$	10^3A_3	$10^3\sigma$/J·m^{-2}
293.15	72.74	4.30	0.03
298.15	71.98	4.13	0.02
303.15	71.23	3.94	0.03
308.15	70.33	4.03	0.04
313.15	69.52	3.97	0.03
318.15	68.76	3.83	0.03
323.15	67.92	3.80	0.02
328.15	67.05	3.80	0.03
333.15	66.19	3.79	0.02

Table 6. Coefficients and Standard Deviations of Equation 3 at Different Temperatures

T/K	n_0	A_4	$10^4\sigma$
293.15	1.333 02	0.023	0.40
298.15	1.332 58	0.022	0.40
303.15	1.332 04	0.022	0.90
308.15	1.331 54	0.022	0.80
313.15	1.330 62	0.022	0.80
318.15	1.330 01	0.022	0.80
323.15	1.329 35	0.022	1.20
328.15	1.328 31	0.022	1.30
333.15	1.327 16	0.023	3.00

where d_0, γ_0, n_0, A_1, A_2, A_3, and A_4 are constants and $c_0 = 10^3$ mol·m^{-3} The values of these constants and the standard deviations of the best fit of the data by the above equations, estimated by the least-squares method, are given in Tables 4−6. The tables show that the values of d_0, γ_0, n_0, A_1, and A_3 decrease but those of A_2 increase with increase in temperature, while that those of A_4 are practically temperature-independent. The constants d_0, γ_0, and n_0 correspond to the density, the surface tension, and the refractive index of water at a given temperature, respectively. Our values of d_0, γ_0, and n_0 for most cases show average deviations of about 0.02% from the reported values of these parameters, but in no case differ by more than 0.07%, 0.07%, and 0.03%, respectively, from the values reported in the handbook (Lide, 1996/97). The deviations of our zero-concentration values of d_0, γ_0, and n_0 from those values reported in the handbook imply measurement uncertainties of 0.2 kg·m^{-3}, 10^{-5} J·m^{-2} and 2.6×10^{-4}, respectively. These implied measurement uncertainties for d_0 and n_0 are more than our experimental values, but that for γ_0 is lower than the experimental one.

The dependences of A_1, A_2, and A_3 on temperature were analyzed according to the first-, second-, and third-order polynomial equations. It was found that the following equations describe these dependences satisfactorily:

$$A_1 = 80.16 - 1.74(T/\mathrm{K} - 273.15) + 4.18 \times 10^{-2}(T/\mathrm{K} - 273.15)^2 - 3.30 \times 10^{-4}(T/\mathrm{K} - 273.15)^3 \quad (4)$$

$$A_2 = -36.69 + 2.34(T/\mathrm{K} - 273.15) - 5.25 \times 10^{-2}(T/\mathrm{K} - 273.15)^2 + 3.80 \times 10^{-4}(T/\mathrm{K} - 273.15)^3 \quad (5)$$

$$A_3 = 4.43 \times 10^{-3} - 10^{-5}(T/\mathrm{K} - 273.15) \quad (6)$$

As mentioned above, A_4 is practically independent of temperature.

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