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The surface tension measurements were made by Joseph P. Reardon of the Laboratory for Chemical Physics, U. S. Naval Research Laboratory.

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Specific Gravity, Viscosity, and Solubility for Aqueous Nickel Sulfate Solutions

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Specific gravity and viscosity of aqueous nickel sulfate solutions have been measured over the temperature range 20–60°C for concentrations up to and above saturation. The solubility of the α-hexahydrate of nickel sulfate has been measured over its equilibrium temperature range (31.2–53.3°C). Data obtained in the present work are compared with those from earlier workers.

This work was done in connection with a study on the crystallization of nickel sulfate from aqueous solution, and a governing purpose was to investigate possible ways of determining simply and rapidly but precisely the concentrations of given nickel sulfate solutions, above and below saturation. Some data existed prior to this work but they covered only parts of the range of interest. In particular, no previous measurements could be traced of specific gravities in the supersaturated region. Also, existing data on viscosity and solubility were not in good agreement.

REAGENTS

All experiments were made using Lot No. 36060 of "Baker analyzed" reagent-grade nickel sulfate α-hexahydrate from J. T. Baker Chemical Co. (Phillipsburg, NJ). This reagent meets ACS specifications, and the manufacturer's actual lot analysis for Lot 36060 is shown in Table I. The reagent was used without further treatment.

The α-hexahydrate is the normal commercial form of nickel sulfate (prepared by crystallization from solution between 31.2 and 53.3°C). Unlike the efflorescent heptahydrate (crystallizing below 31.2°C), the α-hexahydrate was stable in ordinary atmospheres at room temperature, neither losing nor gaining water appreciably even through months of exposure.

Table I. Manufacturer's Actual Lot Analysis for Lot 36060

Assay ($NiSO_4 \cdot 6H_2O$)	99.3%
Insoluble matter	0.002%
pH of 5% solution at 25°C	3.8
Chloride (Cl)	0.0005%
Nitrogen compounds (as N)	0.002%
Substances not precipitated by $(NH_4)_2S$	0.10%
Cobalt and manganese (as Co)	0.002%
Copper (Cu)	0.0005%
Iron (Fe)	0.0005%

The water was distilled from a still in which distillate contacted only borosilicate glass and Teflon. Its specific resistance was not less than 0.4 MΩ-cm. Dissolved air was always boiled out immediately before use.

SPECIFIC GRAVITY

Method. The specific gravity bottle method (*3*) was used. The bottles were approximately 25 cm^3 in volume and had previously been calibrated precisely using distilled water. Solutions were prepared by weighing appropriate amounts of nickel sulfate α-hexahydrate and distilled water to the nearest milligram on an analytical balance and mixing (with heating if necessary) to dissolve. Any evaporation loss during dissolving was made up immediately prior to pouring the solutions into the bottles. All weighings were corrected for air buoyancy. Concentrations were expressed as wt % real hexahydrate, despite the fact that the manufacturer's assay for $NiSO_4 \cdot 6H_2O$ on the real hexahydrate was less than 100%. As shown later, the influence of hexahydrate purity variations on the properties studied cannot be large at a purity level of 99% or better. The estimated limits of error on the concentration of solutions prepared by this weighing method were ±0.01 wt % hexahydrate.

A Haake Bros. (Karlsruhe, W. Germany) Model FT water bath was used and the temperature within it measured by a Hewlett Packard (Palo Alto, CA) Model 2801 A quartz thermometer. When we allowed for bath-temperature fluctuations and the calibration error of the thermometer, the limits of error on the temperature of the bottles were ±0.03°C.

By repeating the bottle-temperature equilibration and weighing steps on the bottle and contents but at successively higher temperatures, specific gravities at all temperatures could be obtained from just one filling of the bottle for each concentration.

In the supersaturated region, nucleation and crystallization of the solutions were always dangers, but by working reasonably fast, measurements could be made without appreciable nucleation on solutions supercooled by up to 10°C. To estimate repeatability, two runs were made on the same batch of solution for each concentration. To estimate reproducibility, two batches of solution made to the same concentration were run in a few cases. To estimate the effect of reagent purity on specific gravity, a few measurements were made on solutions made with nickel sulfate α-hexahydrate from a different lot (No. 38934) which had a manufacturer's assay for $NiSO_4 \cdot 6H_2O$ of 99.0 wt %, as opposed to 99.3 wt % for lot 36060.

RESULTS AND DISCUSSION

Table II presents the original specific gravity results. Each reported value is the mean of the values from two runs on the same batch of solution. These duplicate results never differed by more than 0.0003 and in most cases differed by not more than 0.0002. Their pooled estimated standard deviation was 0.00009. The mean specific gravities from the runs on duplicate batches of solution never differed by more than 0.0002 so there were no significant between-batch differences.

There were no significant differences of specific gravity between solutions with the same concentration and temperature but prepared from the different lots of nickel sulfate having different purities.

By least-squares fitting, the equation

$$\text{sp gr}_4{}^t = 1.00229 + (0.6236 \times 10^{-2})c + (0.2311 \times 10^{-4})c^2 + (0.1608 \times 10^{-6})c^3 - (0.0135 \times 10^{-2})t - (0.0296 \times 10^{-4})t^2 - (0.0470 \times 10^{-4})ct + (0.0493 \times 10^{-8})c^2t^2 \quad (1)$$

in which c is the solution concentration in wt % hexahydrate and t is the temperature in degrees centigrade, fitted the reported data with no statistically significant lack of fit throughout the ranges of temperature and concentration considered, namely 20–60°C and 0–60 wt % hexahydrate. The standard error of estimate of sp $\text{gr}_4{}^t$ from the equation was 0.00017.

Of course in fitting a single equation throughout the whole range of concentration, it is assumed that the curves of specific gravity against concentration have no abrupt changes of slope. An abrupt change might be expected, for instance, at the point of saturation. However there was no evidence for such a change in slope.

The results from this work compared with those from previous work show good agreement (present values higher by not more than 0.4%) with the values given in the International Critical Tables (*11*) for solutions of concentrations 1–30 wt % hexahydrate at temperatures near 20°C, and good agreement (present values lower by not more than 0.7%) with the values of Gelbach and Louderback (*5*) for solutions of concentrations 1–48 wt % hexahydrate at 25°C. There is poorer agreement (present values higher by not more than 2.8%) with the values of Dobrokhotov (*4*) for solutions of concentrations between 28 wt % hexahydrate and saturation at temperatures of 20–60°C. (Dobrokhotov also reported specific gravities at temperatures between 60° and 100°C.) Dobrokhotov reported preparing his solutions, by weighing, from nickel sulfate containing 60.4 wt % anhydrous $NiSO_4$. Since the expected limits on wt % anhydrous $NiSO_4$ in the solid are 55.1 and 58.9, corresponding to pure heptahydrate and pure hexahydrate, respectively, Dobrokhotov's figure may itself be in error and may have led in turn to errors in his concentration calculations. With the values of Alamelu and Suryanarayana (*1, 9*) for solutions of concentrations up to 47 wt % hexahydrate between 30° and 60°C, there is good agreement (present values lower by not more than 0.3%) at concentrations up to 36 wt % hexahydrate, but then there is a rapid divergence above 36 wt % hexahydrate, so that at 47 wt % hexahydrate the present values are higher by 4.0%.

VISCOSITY

Method. Cannon-Fenske viscometers were used to find the kinematic viscosities (*2*) and these were multiplied by the appropriate smoothed specific gravity values from Equation 1 (the numerical difference between specific gravity values and absolute density values in g/cm³ is only 0.003% and therefore quite negligible here) to obtain the absolute viscosities. The viscometers were size 50 and had been calibrated using distilled water. Solutions were prepared in the same way as for specific gravity except that evaporation losses were not made up, so it is estimated that the concentrations may be up to 0.1 wt % hexahydrate in error. A Precision Scientific Co. (Chicago, IL) "Temp-Trol" viscometer bath was used and the temperature within it again measured by the quartz thermometer, this combination giving limits of error of ±0.03°C on the temperature of the viscometers.

By repeating the timings on the same viscometer but at successively lower temperatures, viscosities at all temperatures could be obtained from just one filling of the viscometer for each concentration, the variations in sample volume with temperature being negligible. The same duplication procedures were used as for the specific gravity experiments.

Table II. Original Specific Gravity Results

(Aqueous nickel sulfate solutions)

The first column contains standard values of sp $\text{gr}_4{}^t$ for pure water (*12*). Entries underlined are in the supersaturated region

	c Wt % hexahydrate									
t, °C	0.00	10.00	20.00	30.00	40.00	50.00	52.50	55.00	57.50	60.00
20.00	0.9982	1.0622	1.1317	1.2080	1.2919	1.3838				
25.00	0.9971	1.0609	1.1299	1.2060	1.2899	1.3815	1.4061			
30.00	0.9957	1.0591	1.1281	1.2039	1.2876	1.3791	1.4037	1.4287		
35.00	0.9941	1.0572	1.1259	1.2016	1.2852	1.3767	1.4012	1.4262		
40.00	0.9922	1.0553	1.1237	1.1994	1.2827	1.3742	1.3988	1.4238	1.4497	
45.00	0.9902	1.0531	1.1214	1.1969	1.2802	1.3716	1.3962	1.4211	1.4471	
50.00	0.9881	1.0509	1.1190	1.1944	1.2775	1.3689	1.3935	1.4184	1.4444	1.4705
55.00	0.9857	1.0485	1.1164	1.1917	1.2748	1.3661	1.3907	1.4157	1.4417	1.4679
60.00	0.9832	1.0460	1.1138	1.1889	1.2721	1.3633	1.3879	1.4128	1.4389	1.4650

Table III. Viscosity Results

(Aqueous nickel sulfate solutions)

For each concentration and temperature, the top figure is the kinematic viscosity in centistokes and the bottom one the absolute viscosity derived from it, in centipoises, except in the case of the first column, which lists standard values for the kinematic and absolute viscosities of pure water (*12*, *13*). Entries which are underlined are in the supersaturated region

	c Wt % hexahydrate									
t, °C	0.00	10.00	20.00	30.00	40.00	50.00	52.50	55.00	57.50	60.00
20.00	1.004	1.223	1.562	2.130	3.178	5.290				
	1.002	1.299	1.768	2.573	4.105	7.321				
25.00	0.893	1.084	1.380	1.872	2.756	4.503	5.194			
	0.890	1.150	1.560	2.258	3.554	6.221	7.303			
30.00	0.801	0.971	1.234	1.655	2.416	3.898	4.462	5.290		
	0.798	1.028	1.392	1.993	3.110	5.377	6.264	7.558		
35.00	0.724	0.876	1.109	1.473	2.137	3.398	3.871	4.569		
	0.719	0.926	1.249	1.770	2.746	4.679	5.424	6.517		
40.00	0.658	0.795	1.000	1.321	1.903	2.983	3.380	3.963	4.600	
	0.653	0.839	1.124	1.584	2.441	4.100	4.728	5.643	6.668	
45.00	0.602	0.726	0.910	1.194	1.709	2.645	2.983	3.481	4.026	
	0.596	0.764	1.021	1.429	2.188	3.628	4.165	4.947	5.825	
50.00	0.553	0.666	0.832	1.085	1.540	2.360	2.648	3.088	3.556	4.121
	0.547	0.700	0.931	1.296	1.967	3.231	3.690	4.381	5.136	6.060
55.00	0.511	0.614	0.764	0.990	1.399	2.119	2.367	2.753	3.160	3.639
	0.504	0.644	0.853	1.180	1.783	2.895	3.292	3.898	4.555	5.342
60.00	0.475	0.569	0.704	0.906	1.274	1.911	2.121	2.458	2.810	3.215
	0.467	0.595	0.784	1.077	1.620	2.606	2.944	3.473	4.043	4.710

RESULTS AND DISCUSSION

Table III presents the original kinematic viscosity results and the absolute viscosities derived from them. Each value is calculated from the mean of two timings on the same sample. These timings never differed by more than 0.3%. The mean timings from runs on duplicate batches of solution never differed by more than 0.7%. The contributions from viscometer calibration constants and from solution densities to the imprecision in the absolute viscosities were negligible. Full statistical treatment of the results was difficult because of the nonlinear dependence of viscosity on concentration and temperature, but because the main difference in duplicates was between batches, the standard error was estimated from the mean range of the means from duplicate batches, giving a value of 0.5% for the standard error and hence 3 σ limits on viscosity of ±1.5%.

Results from this work compared with those from previous work show good agreement (present results higher by less than 1%) with the values of Wagner (*10*) for solutions of concentration up to 12 wt % hexahydrate at 25°C, poorer agreement (present results mostly lower; maximum deviation 20% of present value) with the values of Sri Rama Rao (*8*) for supersaturated solutions of concentrations 56.55 and 53.72 wt % hexahydrate at temperatures between 30° and 60°C, and very poor agreement (present values higher by not more than 50% of present value) with the values of Alamelu and Suryanarayana (*1*) for solutions of concentration up to 47 wt % hexahydrate at temperatures between 30° and 60°C. Alamelu and Suryanarayana's absolute viscosity values would be increased by not more than 4% if they were recalculated using the specific gravity values from the present work, but this would do little to reduce the 50% difference between them and the present absolute viscosity values.

SOLUBILITY

Method. This was basically as outlined by Mullin (*7*). A solution (250 grams) in a 250-cm³ Erlenmeyer flask with a ground glass stopper was immersed in the Haake Bros. Model FT water bath. An excess of α-hexahydrate crystals (size about 800 μ) was added and the mixture stirred for 24 hr at about 100 rpm by a magnetic stirrer. After an hour's settling time, two samples were then taken with a warmed pipet fitted with a stainless steel 400-mesh screen, their specific gravities found at the temperature of saturation (the specific gravity bottles being held in the same water bath), and hence their concentrations obtained via Equation 1. The remaining mixture was then stirred for another 12 hr, after which the sampling procedure was repeated.

As with the specific gravity experiments, the limits of error on the temperature were ±0.03°C.

At each temperature, the saturation point was approached from both supersaturated and undersaturated states. The initial solutions were of such concentrations that they were saturated at about 4°C above or below the test temperature.

To estimate the effect of reagent purity on solubility, one run was also made in which both the seed crystals and the crystals used to prepare the solution were from Lot 38934, which had an assay for $NiSO_4 \cdot 6H_2O$ of 99.0 wt %, as opposed to 99.3 wt % for Lot 36060.

After each run, the seed crystals were filtered off, washed of solution with methanol, rinsed with benzene, dried, and examined under a low-power microscope. In all cases they had retained the characteristic green-blue color and bipyramidal shape of the α-hexahydrate.

RESULTS AND DISCUSSION

The solubility results are given in Table IV, both as the specific gravity measurements on the saturated solutions and as the saturation concentrations derived from these via Equation 1. The specific gravities of the two samples taken at the same time never differed by more than 0.0002, and the mean specific gravities of pairs of samples taken during the same run after 24 hours and after 36 hours of stirring never differed by more than 0.00025. A grand mean of these two was calculated for each run, and for the runs at the same

Table IV. Original Solubility Results

(Aqueous nickel sulfate solutions)

Temp, t°C	Sp gr_4^t of soln satd at t°C	Satn concn c_t* wt % hexahydrate derived from Eq 1
32.00	1.4013	52.35
35.00	1.4093	53.30
40.00	1.4233	54.95
45.00	1.4379	56.63
50.00	1.4534	58.38
53.00	1.4629	59.43

temperature on initially supersaturated and initially undersaturated solutions, these grand means never differed by more than 0.0002. The final reported specific gravity at saturation is the simple mean of all eight measurements at each temperature. The simple pooled estimated standard error (standard deviation of the mean) was 0.00004, this estimate then incorporating errors due to the different times of sampling and to different initial concentrations as well as to the specific gravity measurements themselves.

No significant effect was found of reagent purity differences on specific gravity at saturation.

The saturation concentrations derived from the final reported specific gravity values using Equation 1 have an estimated standard error of 0.006 wt % hexahydrate, giving 3 σ limits of ± 0.02 wt % hexahydrate.

By least-squares fitting, the equation

$$c_t^* = 43.1726 + 0.2559\,t + 0.0009611\,t^2 \qquad (2)$$

in which t is the temperature in degrees centigrade and c_t^* is the saturation concentration of the solution at t°C in wt % hexahydrate, fitted the data with no statistically significant lack of fit over the range of temperature considered, namely 32–53°C. The standard error of estimate of c_t^* from the equation was 0.009 wt % hexahydrate.

The solubility results from this work were compared with those from previous work. Linke (*6*) reviewed work up to 1958, commenting that there was only fair agreement (differences of 1–3%) between the results of several individual workers, but presenting a set of "most probable" values. The present results are in good agreement with these values for the temperature range 32–53°C (difference of 0.6% at 53°C but less than 0.4% in the range 32–50°C), thereby helping to confirm Linke's estimated values.

Since Linke's review, Alamelu and Suryanarayana (*1*) have published solubility figures higher than those in this work by not more than 1.2% in the range 32–53°C. However, doubt is cast on their data, at least at the lower end of the temperature range, by their failure to report confirmation of the identity of the solid phase in their solubility tests, particularly as they report that their original reagent solid was the heptahydrate rather than the α-hexahydrate. Linke reports that metastable solubilities in which the solid phase remains as heptahydrate can be achieved at up to 40°C.

CONCLUSION

Specific gravity measurements do afford a suitable method for determining the concentration of nickel sulfate solutions (specific gravity measurements with a standard error of 0.00004 giving a concentration value with a standard error of 0.006 wt % hexahydrate), and the method has been applied to the determination of saturation concentration. The use of viscosity measurements for determination of concentration was discounted largely because of the excessive sensitivity of viscosity to temperature variations.

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