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Density, Viscosity, Vapor Pressure, and Hydrogen Solubility of Aqueous $MnSO_4$ Solutions

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Densities, viscosities, vapor pressures, and hydrogen solubilities of aqueous manganous sulfate solutions were measured at temperatures from 20 to 80 °C. The concentration of $MnSO_4$ varied from 0.5 to 3.5 g-mol/L. As the electrolyte concentrations are high, the solubility data do not follow the empirical Sechenov equation for salting out. The temperature dependency is not very pronounced particularly for the higher concentrated solutions.

Density, viscosity, and vapor pressure were measured in aqueous manganous sulfate solutions. In addition, the solubility of hydrogen in such solutions was determined. The data were needed for a study of the ortho-para-H_2 conversion in liquid phase which is catalyzed by transition-metal ions with unpaired electrons. It is, however, believed that the measured quantities are of broader interest. The concentration of $MnSO_4$ was varied from 0.5 to 3.5 g-mol/L and the temperature range was 20-80 °C.

Density

The densities of the solution were measured by pycnometry taking into account volume changes of the pycnometer at the higher temperatures. Thus the error is about ± 0.001 g/cm^3. It was found that the temperature dependency of the density of all solution follows the same law which can be expressed by

$$\delta_{c,t} = \delta_{c,20} - (0.53 \times 10^{-3})(t - 20)$$

The densities ($\delta_{c,20}$) of the various solutions for $t = 20$ °C are given in Table I.

Viscosity

An Ubbelohde viscosimeter was used to measure the viscosities. The data were evaluated with consideration of Hagenbach and Couette's corrections. From the measured kinematic viscosities and the densities, the dynamic viscosities were obtained which are presented in Table II. The mean relative error is less than ±0.3%.

An Arrhenius-type equation is commonly used to describe the temperature dependency of the viscosity. A plot of log η vs. $1/T$ does, however, not give one straight line. The data points can only be described by two straight lines. The cross points of these lines are between 35 and 50 °C depending on the concentration of $MnSO_4$.

Vapor Pressure

Vapor pressures were determined with an osmometer (Knauer, Berlin). This was calibrated by various electrolyte solutions of known vapor pressures. The reproducibility of Δp was better than 1%. The measured vapor pressure reductions $\Delta p = p_{H_2O} - p_L$ are given in Table III. Plots of log Δp vs. $1/T$ for each concentration of $MnSO_4$ yield parallel lines with a slope of 1850 K. From the intercepts the dependency on the $MnSO_4$ concentration can be evaluated. This leads to the following expression

$$\log \Delta p = -(1.85 \times 10^3)/T + 5.82c^{0.131} \qquad (1)$$

This equation describes the measured data of Δp within 1%. The vapor pressure data were needed to calculate the solubilities of H_2.

Table I. Densities ($\delta_{c,20}$, g/cm^3) of Aqueous $MnSO_4$ Solutions at 20 °C

0.5 g-mol/L	1.0 g-mol/L	1.5 g-mol/L	2.0 g-mol/L	2.5 g-mol/L	3.0 g-mol/L	3.5 g-mol/L
1.069	1.138	1.207	1.269	1.330	1.394	1.452

Table II. Dynamic Viscosities of Aqueous $MnSO_4$ Solutions (in mPa s)

c, g-mol/L	viscosity						
	20 °C	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C
0	1.002	0.798	0.653	0.546	0.467	0.405	0.355
0.5	1.344	1.069	0.874	0.732	0.607	0.530	0.459
1.0	1.872	1.481	1.196	0.988	0.820	0.711	0.609
1.5	2.693	2.099	1.665	1.376	1.130	0.966	0.825
2.0	3.903	2.980	2.338	1.908	1.566	1.321	1.139
2.5	5.832	4.413	3.392	2.693	2.256	1.874	1.589
3.0	8.943	6.632	5.029	3.862	3.219	2.682	2.283
3.5	14.13	10.37	7.713	5.863	4.693	3.918	3.293

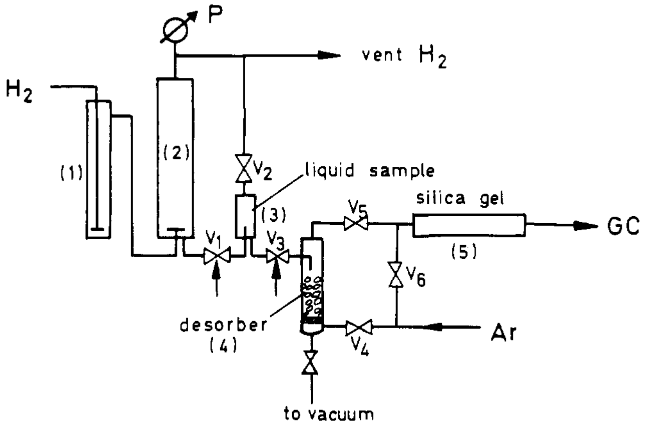

Figure 1. Schematic setup for the determination of H_2 solubilities.

Hydrogen Solubility

As the solubility of hydrogen is rather small, particularly at higher temperatures, a gas chromatographic technique was used. The experimental setup is outlined in Figure 1. Hydrogen (purity 99.9%) was taken from a cylinder and saturated with vapor by bubbling through the $MnSO_4$ solution (1). The vapor-saturated hydrogen was then sparged in $MnSO_4$ solution in column (2). After about 1 h, equilibrium was established. When valve V_1 was opened, solution flowed in tube (3) of known volume (about 10 cm^3). Parts (1), (2), and (3) were jacketed and maintained at the same temperature by means of a

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Table III. Vapor Pressure Reduction $\Delta p = p_{H_2O} - p_L$ (in Torr) of Aqueous $MnSO_4$ Solutions

	Δp									
c, g-mol/L	20 °C	25 °C	30 °C	37 °C	40 °C	45 °C	50 °C	60 °C	70 °C	80 °C
0.5	0.10	0.13	0.16	0.20	0.25	0.30	0.38	0.56	0.84	1.20
1.0	0.35	0.44	0.56	0.72	0.86	1.1	1.3	2.1	3.0	4.2
1.5	0.7	0.88	1.1	1.35	1.7	2.1	2.6	3.9	5.8	8.0
2.0	1.2	1.5	1.9	2.4	3.0	3.7	4.5	6.8	9.8	13.8
2.5	1.8	2.2	2.8	3.4	4.3	5.4	6.6	9.6	14.0	20.0
3.0	2.5	3.1	4.0	4.9	6.2	7.6	9.4	14.1	20.5	28.5
3.5	3.5	4.3	5.5	6.8	8.6	10.8	13.2	20.0	29.0	40.0

Table IV. Bunsen Absorption Coefficients of H_2 in $MnSO_4$ Solutions (Given Are Values of $10^2\alpha$)[a]

	$10^2\alpha$					
c, g-mol/L	20 °C	30 °C	40 °C	50 °C	60 °C	80 °C
0	1.820	1.700	1.640	1.610	1.600	1.600
0.5	1.672	1.508	1.429	1.342	1.302	1.236
1.0	1.339	1.212	1.141	1.141	1.072	1.108
1.5	1.002	0.945	0.867	0.856	0.835	0.920
2.0	0.725	0.696	0.690	0.686	0.690	0.782
2.5	0.515	0.524	0.573	0.585	0.592	0.631
3.0	0.375	0.399	0.427	0.464	0.462	0.477
3.5	0.304	0.312	0.330	0.352	0.339	0.352

[a] Data for water are taken from ref 1.

through-flow thermostat. The liquid sample was then introduced into the desorber (4) which was evacuated before and heated to a temperature about 10–30 °C higher than in column (2). Under these conditions the hydrogen desorbed almost completely. The rest of the H_2 was desorbed by stripping with carrier gas (argon, purity 99.8%). The gas flow was dried on silica gel (5) and introduced to the gas chromatograph (Perkin-Elmer, F 116 E). Peaks without tailing were obtained on a 2-cm column filled with molecular sieve 5A at 50 °C and a heat conductivity detector. The method was calibrated with H_2 and H_2/Ar mixtures at different temperatures, respectively. Thus the same range of hydrogen solubilities as found in the $MnSO_4$ solutions could be covered in the calibration. For the hydrogen solubility in water the data reported by Seidell and Linke (*1*) were used. Each determination was carried out five times. The reproducibility was usually better than 1%. After each series of measurements with a certain $MnSO_4$ solution, runs with water were carried out for calibrating and checking the method.

From the measured peak area and the calibration curve, the volume of hydrogen V_G^0 reduced to 0 °C and 760 torr was obtained. Therefrom the solubility is calculated by

$$\alpha = \frac{V_G^0}{V_L} \frac{760}{760 - p_L} \tag{2}$$

α is the Bunsen absorption coefficient the value of which presents the gas volume in cm^3 (at 0 °C and 760 torr) dissolved per cm^3 of solution at an gas partial pressure of 760 torr. V_L is the sample volume of liquid and p_L is the vapor pressure of the solution ($p_L = p_{H_2O} - \Delta p$, Δp given in Table III). The Bunsen coefficients are given in Table IV (as $10^2\alpha$ values). From repeated measurements the mean relative error was obtained. It is about 2% for the solutions with low $MnSO_4$ concentrations (1 g-mol/L) and increases to about 4% for the solution with 3.5 g-mol/L of $MnSO_4$.

As expected, the solubility decreases considerably with increasing $MnSO_4$ concentration. But the data do not follow the empirical Sechenov relation for salting out. The temperature dependency is not so pronounced. The H_2 solubility decreases with increasing temperature only for the low concentrated solutions, while for the higher concentrated solutions a slight increase of α is observed.

Literature Cited

(1) Seidell, A.; Linke, W. F. "Solubilities of Inorganic and Metalorganic Compounds"; Van Nostrand: Princeton, N.J., 1958; Vol. I.

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