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Diffusion Coefficient of Ammonium Perchlorate in Concentrated Aqueous Solutions between 20 and 30 °C

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The diffusion coefficient of ammonium perchlorate was measured in aqueous solutions close to saturation in the temperature range 20–30 °C. A restricted-diffusion method was used in which concentration profiles were measured by using holographic interferometry.

The limited number of published data concerning the diffusivities of dissolved species generally presents a problem for the prediction of mass-transfer rates in dissolution and crystallization processes. In particular, for the case of crystallization, if it is necessary to take into account the step in which solute molecules are integrated into the crystal lattice, as well as the process of diffusive transfer, this step can often have a decisive influence.

In the present work we give the results of measurements of the diffusion coefficient of ammonium perchlorate in aqueous solutions close to saturation, data which are useful for studying the crystallization of this salt. For this purpose we have adopted a restricted-diffusion technique in which the progress of the diffusion was observed by optical means by using the holographic interferometry.

Prediction of Diffusion Coefficients of Concentrated Electrolyte Solutions

The theoretical or empirical methods for estimating diffusion coefficients of electrolyte solutions are generally much less satisfactory than those available for nonelectrolyte systems. The diffusion phenomenon is rendered much more complex in electrolyte solution because of the ionic dissociation and the forces which thus arise between the ions, whether solvated or not.

In the case of concentrated electrolyte solutions, the theory of Onsager and Fuoss (*1*) forms the basis of the existing correlations. Even though the experimental data often show a satisfactory agreement with the predictions of their theory, it remains true, nevertheless, that for most systems it is inconvenient to use because most of the required data concerning quantities such as the activity coefficients, ionic mobilities, or degree of solvation are still hard to find. Thus, except for the few systems for which the properties just noted are available, the theoretical or empirical methods of prediction are inapplicable and the only solution possible is to measure the diffusion coefficient experimentally.

In the particular case of ammonium perchlorate in aqueous solution, the physicochemical data necessary for studying its crystallization are too few in number; this led us to measure the diffusion coefficient experimentally at concentrations close to saturation in the temperature range 20–30 °C.

Experimental Method

In this work we have made use of a restricted-diffusion method in which two solutions of different concentrations are superposed in a cell of finite height. The diffusion is allowed to proceed until the concentration changes at the two ends of the cell begin to become significant. From that point on, the concentration profile in the cell is recorded at regular intervals. The measurement of the development of this profile with time makes it possible to calculate the diffusion coefficient.

This technique was originally suggested by Onsager and was first applied by Harned and French (*2*) to dilute electrolyte solutions in which the concentration difference was measured by a conductimetric method. Newman and Chapman (*3*) have shown that the results obtained from these measurements give the differential diffusion coefficient at the final average concentration. They also showed that by use of optical interferometry to measure the concentration profiles, it was possible to generalize the method and apply it to concentrated electrolyte solutions for which the solution resistance is too low for conductimetric measurements to be used.

The same procedure was applied by Sanchez et al. (*4*) and by Sanchez and Clifton (*5*) to the case of binary mixtures of organic liquids. In their work, as in the present case, the concentration profiles were measured by using real-time holographic interferometry.

It should be remembered that holographic interferometry differs from traditional interferometric techniques in that the reference cell is replaced by a hologram which records the optical properties of the cell in an initial reference state (i.e., one in which it is filled with a liquid of uniform composition and of refractive index close to that of the solutions used in the subsequent measurements). The major advantage of this technique is that it allows the use of an observation cell of lesser optical quality; since the interferogram represents a comparison of two different states of the same cell, any slight imperfections in the structure of the cell are eliminated by difference (*6*). In the present work, a standard photometric cell (1 cm × 1 cm × 4 cm) was used, clamped in a metal holder thermostated to within 0.1 °C.

The interface between the two solutions of different concentration was formed by first filling the cell to half its height with the denser of the two solutions. Then the second solution was carefully added through a hypodermic needle, the point of which was kept at the level of the free surface of the liquid throughout the filling operation. A steady flow rate was obtained by using a small, variable-speed peristaltic pump. As the holographic technique was operated in real time, the interferometer image could be observed continually via a video system so as to ensure that the interface being formed was sufficiently distinct and that no convection currents had been set up. In actual fact, the restricted-diffusion method does not require that the initial interface be perfectly sharp, so the superposition procedure used here is quite adequate. When the cell had been completely filled, it was sealed to prevent evaporation of the solution.

Method of Calculating the Diffusion Coefficient

The diffusion coefficient can be determined from the observations of restricted diffusion by using the following relationship (*7*):

$$\frac{d}{dt}\ln\,(x_{a/6} - x_{5a/6}) = -\pi^2 D/a^2 \qquad (1)$$

where a is the height of the cell, and $x_{a/6}$ and $x_{5a/6}$ are the

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Table I. Diffusion Coefficients of Ammonium Perchlorate in Aqueous Solutions Close to Saturation

expt no.	temp, °C	solubility, kg/kg of soln	initl concn of soln, kg/kg of soln		av concn, kg/kg of soln	10^9D, $m^2\ s^{-1}$
1	20	0.17941	0.15804	0.17773	0.16789	1.47
2	22	0.18769	0.16773	0.18760	0.17767	1.50
3	25	0.19993	0.17734	0.19791	0.18783	1.75
a	25	0.19993				1.3
4	27	0.20795	0.18778	0.20788	0.19783	1.83
5	30	0.21978	0.19794	0.21783	0.20789	2.16
6	30	0.21978	0.17753	0.19794	0.18773	2.05
a	35	0.23901				1.55
b	35	0.23901				2.60

[a] Values given by Ayerst and Phillips (*10*). [b] Extrapolated from our experimental values by using Arrhenius' law.

concentrations observed at one-sixth and five-sixths of the cell height, respectively, in the interferogram recorded at time t.

The difference in concentration, $\Delta x = x_{a/6} - x_{5a/6}$, can be readily determined from each interferogram. Over the narrow range of concentration used in each measurement, the refractive index n of the solution varies linearly with the concentration x, so that

$$\Delta n = k(x_{a/6} - x_{5a/6}) = k\Delta x \qquad (2)$$

Also, the number of fringes N between any two points on the interferogram is proportional to the difference in refractive index between the points:

$$N = e\Delta n/\lambda \qquad (3)$$

where e is the optical path length and λ is the wavelength of the light source (here λ = 632.8 nm). Thus, we have

$$\Delta x = N\lambda/ek \qquad (4)$$

If this relationship is substituted into eq 1, we have

$$\frac{d}{dt} \ln N = -\pi^2 D/a^2 \qquad (5)$$

Thus, if ln N is traced as a function of time, a straight line is obtained whose slope is $-\pi^2 D/a^2$, where D is the differential diffusion coefficient at the final average concentration.

Experimental Results

The diffusion coefficient of ammonium perchlorate in aqueous solutions close to saturation was determined at five temperatures in the range 20–30 °C. Also, at 30 °C the diffusion coefficient was measured at two concentrations differing in mass fraction of solute by 0.02, so that the variation of diffusivity with concentration could be examined. The experimental results are shown in Table I. We have also shown in this table the solubility of the salt at each temperature, which was calculated from the following relationship (*8*):

$$100x = 9.924 + 0.5745\theta + 0.001123\theta^2 \qquad (6)$$

Previously published measurements show that the refractive index really does vary linearly with concentration in the range of concentration considered here (*8*, *9*):

$$n = 1.33250 + 7.9 \times 10^{-2}x' - 1.6 \times 10^{-4}(\theta - 20) \qquad (7)$$

Each diffusion measurement was performed with two solutions whose solute mass fractions and refractive indices differed by 0.02 and 0.00160, respectively. The imprecision in our measurements has been estimated at 0.6% approximately.

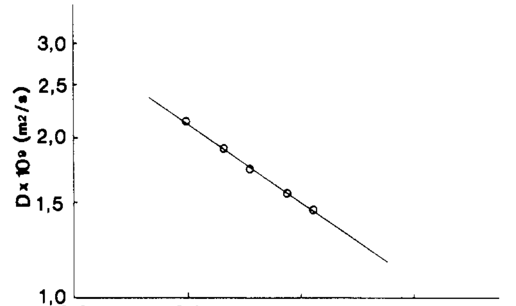

Figure 1. Diffusion coefficient of ammonium perchlorate in concentrated aqueous solution vs. temperature.

In Table I we have also given some previously published values (*10*) of the diffusion coefficient.

Discussion

Influence of Solution Concentration on Diffusivity. Our results show an increase of about 5% in the diffusion coefficient for an increase in mass fraction of solute of 0.02. Newman and Chapman (*3*) have shown however that such variations of diffusivity with concentration have no influence on the results obtained by the restricted-diffusion method and that the diffusivities obtained really are the correct values for the differential diffusion coefficient at the final average concentration.

Influence of Temperature. It is customary to correlate data on rate processes by means of Arrhenius' law. In our case, this may be written

$$D = A \exp(-E/RT) \qquad (8)$$

The activation energy E of the diffusion process can thus be determined from the slope of the graph of ln D as a function of $1/T$. Figure 1 shows that our results fit this law quite well. The values of the parameters A and E in eq 8 have the following values

$$A = 1.90 \times 10^{-4}\ m^2\ s^{-1}$$

$$E = 28684\ J\ mol^{-1}$$

so that

$$D = 1.90 \times 10^{-4} \exp(-3450/T)$$

Comparison of the Results with Those Previously Published. The only published data which we have been able to find concerning the diffusivity of ammonium perchlorate in aqueous solution are those of Ayerst and Phillips (*10*). The differences between our values and the data published by these authors are considerable; it should be noted, however, that these authors do not state under what experimental conditions their measurements were made.

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Glossary

a	height of the observation cell, m
A	constant in the Arrhenius law, m^2 s^{-1}
D	diffusion coefficient, m^2 s^{-1}
e	optical path length, m
E	activation energy (Arrhenius law), J mol^{-1}
k	constant in eq 2
n	refractive index
N	number of fringes
R	ideal gas constant, J K^{-1} mol^{-1}
t	time, s
T	temperature, K
x	mass ratio of the solution, kg of solute/kg of water
x'	mass fraction of solute, kg of solute/kg of solution
λ	wavelength of laser light, m
θ	temperature, °C

Registry No. Ammonium perchlorate, 7790-98-9.

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Vapor Pressure Measurement of Tetralin at Reduced Pressures

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The vapor pressure of Tetralin was measured over the pressure range of 0.40–32.5 kPa, i.e., the temperature range of 330.80–437.13 K. The results were fitted to Chebyshev polynomials and the Miller and Antoine equations, the percent root mean square deviations of which were estimated as 0.22, 0.29, and 0.33, respectively.

Introduction

To measure vapor–liquid equilibrium and vapor pressure at reduced pressure, we constructed a new equilibrium still. In this work the vapor pressure of Tetralin (1,2,3,4-tetrahydronaphthalene) has been measured at 0.40–32.5 kPa, because there have been only a few data on the vapor pressure at reduced pressures: the six values by Herz and Schuftan (*1*) in 1922, the three by Linder (*2*) in 1931, the three by Lagrange et al. (*3*) in 1971, the four by Nasir et al. (*4*) in 1980, and the four by Katayama and Watanabe (*5*) in 1980. Some of these are not precise.

Recently Tetralin has been employed as a reagent for the liquefaction of coal.

Experimental Section

Material. Commercial-grade Tetralin was distilled in a wetted wall column with 1-m length and 10-mm i.d. at 1.3 kPa. The intermediate distillate used for this work was monitored by measuring the change in the refractive indexes of each 10-mL distillate.

The purity of the Tetralin was estimated to be 99.8% by gas chromatography with Porapak-s as described in the previous paper (*5*). The refractive index and the density of the Tetralin at 25.0 °C have already been determined previously (*5*) as 1.5383, compared with the literature value 1.539 19 (*6*), and 963.6 kg/m^3, compared with the literature value 963.24 kg/m^3 (*7*).

Apparatus and Procedure. The experimental apparatus was set up as in Figure 1. The equilibrium still is made of Pyrex glass, and its cylinder is 400 mm high with a 70-mm i.d. The funnel of the Cottrell pump does not entirely cover the liquid surface so that discharged vapor can ascend not only through the Cottrell tube but also from the outside of the funnel. The still is designed to decrease the pressure drop between the surface and the condenser sections.

The measurement and the control of pressure were carried out with a Multi-Range Model 157/100 pressure standard from Texas Instruments Inc. Its accuracy is ±0.002 kPa for the 35–10-kPa range and ±0.001 kPa for the 10–0.40-kPa range. The accuracy of pressure control on operation was found to be within ±0.000 03 kPa for the 35–1-kPa range, and within ±0.0004 kPa for the 1–0.40-kPa range. Since the pressure below 0.40 kPa could not be controlled well, the vapor pressures below this pressure were not measured.

Mercury thermometers with immersion lines marked 18 cm from the bulb end, which consisted of three sets of graduation from 40 to 100, 100 to 150, and 150 to 200 °C, were used. They have been calibrated in 10 °C intervals by Watanabe Keiki Seisakusho Co., Ltd., Tokyo. Their accuracies are within ±0.04 K.

The McLeod gage in Figure 1 was employed only when the zero counter (calibration) of the Bourdon capsule was to be determined.

About 120 mL of a sample was poured into the bottom of the still through the stopper 11. The circulation of vapor was carried out at the rate of 40 drops/min for 2 h. The outside wall of the still was held at 3 K below the boiling point. Since the Tetralin is polymerized by heating as described previously (*5*), a fresh sample was used after every three measurements.

Results and Discussion

The vapor pressure data of Tetralin are presented in Table I. The data are also plotted in Figure 2 including a comparison with values from the literature. The data are in good agreement with the literature in the pressure range between 32 and 5 kPa, but are somewhat smaller than quoted values below 5 kPa. The values of Nasir et al. (*4*) are larger than the others.

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