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RECEIVED for review January 26, 1972. Accepted May 9, 1972. This work was supported by the U.S. Department of the Interior, Office of Water Resources Research, A-012 TN, and the Petroleum Research Fund, American Chemical Society. Computing time was donated by the University of Tennessee computing center which has been generously supported by the National Science Foundation.

Solubility of Oxygen in Selected Organic Solvents

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The solubility of oxygen was measured in four organic liquids of high dielectric constant at 25°C by the method of Morrison and Billett. The measurements, expressed as Bunsen coefficients, were γ-butyrolactone 0.0499, propylene carbonate 0.0153, dimethyl sulfoxide 0.0342, and *N*-nitrosodimethylamine 0.0605. No salting-in or salting-out effects were observed in $LiClO_4$ (up to 1*M*) solutions in the first two solvents. The data were correlated with the liquids' surface tensions using the Uhlig cavity model.

The solubility of oxygen was measured in four organic solvents of high dielectric constant as part of an investigation of the oxygen electrode in aprotic electrolytic solutions. The four organic solvents were dimethyl sulfoxide, *N*-nitrosodimethylamine, propylene carbonate, and γ-butyrolactone. Their dielectric constants are given. In the last two solvents, the solubility was also measured in $LiClO_4$ solutions (up to 1*M*) to determine any salt effects.

APPARATUS AND MATERIALS

The apparatus and method of Morrison and Billett were employed (*5*). In this method, gas saturation is achieved by the liquid's flowing in a thin film down a spiral column which, in our apparatus, consisted of six turns of 10-mm glass tubing with an equivalent length of 1.8 m. A flow rate of 2-3 ml/min was maintained and, in a typical run, 100 ml of saturated liquid was collected. The reproducibility of this method is ±0.5% and, according to Morrison and Billett, the results are slightly low. For example, they reported a Bunsen coefficient of 0.0280 for

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Table I. Solubility of Oxygen in Organic Liquids

(25 ± 0.5°C)

Liquid	Dielectric constant	α
γ-Butyrolactone	39	0.0499 ± 0.0025
Propylene carbonate	64.4	0.0153 ± 0.0004
Dimethyl sulfoxide	48	0.0342 ± 0.0008
N-nitrosodimethylamine	53.0	0.0605 ± 0.0020

Table II. Solubility of Oxygen in $LiClO_4$ Solutions

Solvent	Concn, $LiClO_4M$	α
γ-Butyrolactone	0.00	0.0499
	0.20	0.0513
	0.45	0.0531
	0.60	0.0495
	0.80	0.0513
Propylene carbonate	0.00	0.0153
	0.50	0.0140
	0.50	0.0150
	1.00	0.0150
	1.00	0.0160

O_2 in water at 25°C as compared with an accepted value of 0.0285 (*1*). On the other hand, the method does not have the disadvantage of yielding high values because of supersaturation, enhanced in viscous organic liquids of the type investigated here.

Dimethyl sulfoxide (MX 1458), γ-butyrolactone (BX 2185), and propylene carbonate (PX 1705) were obtained from Matheson, Coleman and Bell; *N*-nitrosodimethylamine (ZF 622) from City Chemical Co. The organic liquids were purified and degassed by fractional distillating under reduced pressure through a Nester-Faust spinning band fractionation column, a center cut of 40% of the 1-liter initial volume being taken for the experiment. The receiver for the distillation unit also served as the reservoir for the solubility apparatus. When electrolyte solutions were prepared, the anhydrous $LiClO_4$ was placed on a sintered glass frit in the distillation unit above the receiver flask. The purified solvent flowed through and dissolved the salt (readily soluble in the liquids studied). With our method and apparatus, a Bunsen absorption coefficient of 0.0275 was obtained (average of six determinations) for O_2 in water at 25°C, compared with the value of 0.0280 (*5*) and the accepted value of 0.0285.

RESULTS

The solubilities of O_2 in the four liquids are reported in Table I in terms of the coefficient

$$\alpha = \frac{V_g}{V_s} \cdot \frac{273.15}{T}$$

where V_g is the volume of O_2 absorbed in a volume V_s of liquid. Each value represents the average of four determinations, and the average deviation is noted. Whereas the Morrison and Billett method has a reported reproducibility of ±0.5%, the precision of the results reported in Table I varies from 2.3-5.0%. There are few solubility determinations available in the literature for these liquids. Dymond (*3*) reports a value for dimethyl sulfoxide at 25°C and 1-atm partial pressure. When we assume ideal gas behavior and adherence to Henry's law, an absorption coefficient of 0.0432 is calculated from his data. The value reported in Table I is 21% lower. The solubility of O_2 in $LiClO_4$ solutions in γ-butyrolactone and propylene carbonate is given in Table II. Over the concentration range investigated, there is no salting-in or salting-out effect, and the variation appears to be random. The implication is that oxygen does not solvate in these solutions to any extent and that the dielectric constant of the electrolytic solution is not altered to any extent. An attempt was made to correlate the solubility data with the surface tension of the solvent following Uhlig's cavity model (*8*). The expression

$$\log \alpha = \frac{-4\,\pi r^2 \sigma + E}{2.303\,kT}$$

relates α, the absorption coefficient, to σ, the surface tension, to E, the interaction energy of solute and solvent, and to r the radius of the oxygen molecule and was used in the present treatment. The radius, r, was taken as 1.45×10^{-8} cm and k, the Boltzmann constant, as 1.3805×10^{-16} erg K^{-1}. Uhlig derived this equation with log γ, the Ostwald coefficient of solubility, and used a value for E of 110 cal/mol for O_2 at 20°C in various organic liquids. In the present treatment, a value for E of −262 cal/mol was used which makes the treatment semiempirical. The surface tensions of the liquids were measured with a Cassel tensiometer by the maximum bubble pressure method (*6*). The values agree reasonably well with literature values for *N*-nitrosodimethyl amine (*9*), propylene carbonate (*4*), and dimethyl sulfoxide (*2*), with any differences being attributed to the purification procedures. Calculated values for the absorption coefficients are compared with the observed values in Table III. The agreement is probably as good as could be expected considering the simplicity of the model used in the calculation, the exception being the solubility in propylene carbonate which is lower than expected. Schläpfer et al. (*7*) plotted the surface tensions of a number of organic liquids against the log γ for oxygen and found a uniform linear plot for 26 liquids with the exception of glycerin and ethylene glycol. The implication is that the simple relationship does not hold too well for the hydroxylated compounds. The structure of propylene carbonate is such as to suggest oxygen bonding and perhaps accounts for the similar behavior. However, the electrolyte experiments do not suggest any unusual solvation behavior that would explain the deviations. It is concluded that the solubility of oxygen in these organic liquids is related to the surface tension but that the function is more complicated than that given above.

Table III. Calculation of Solubility from Surface Tension Data

Liquid	σ, 20°C[a], dyn/cm	$(-d\sigma/dT)$	σ, 25°C[b]	α, calcd	α, obsd
γ-Butyrolactone	43.9 ± 0.2	0.1	43.4	0.0397	0.0499
Propylene carbonate	40.8 ± 0.1	0.1	40.3	0.0484	0.0153
Dimethyl sulfoxide	45.1 ± 0.1	0.118	44.5	0.0370	0.0342
N-nitrosodimethyl amine	38.4 ± 0.3	0.108	37.9	0.0564	0.0605

[a] Measured. [b] Calculated.

ACKNOWLEDGMENT

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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Received for review January 28, 1972. Accepted April 3, 1972. Work supported by the U. S. Army Mobility Equipment Research and Development Center, Fort Belvoir, VA, under contract No. DA 44-009-AMC-1386(T).

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