Diffusion Coefficients of Copper Sulfate in Water and Water in *n*-Butyl Alcohol

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The differential diffusivities of the two systems $CuSO_4$-H_2O and *n*-butyl alcohol–water have been measured at 25° C. by the diaphragm cell technique. The $CuSO_4$-H_2O data include a range of $CuSO_4$ concentrations from 0.35 *N* to 1.4*N* (saturation). The water–*n*-butyl alcohol concentration ranges were from pure *n*-butyl alcohol to a water concentration of 9.89 moles per liter (miscibility limit).

DIFFUSION COEFFICIENTS of $CuSO_4$ in water and water in *n*-butyl alcohol were measured by the diaphragm cell technique. The diaphragms consisted of porous glass disks with nominal pore size of 3 to 5 microns, 5.0 cm in diameter and 0.5 cm. thick. The cells were monted with the diaphragms in a horizontal position, with the lower compartment containing the denser solution. Both solutions were magnetically stirred with 1-inch Teflon covered stirring bars held at the ends of the cell, about 3 cm. from the diaphragm. The cells were immersed in a water bath maintained at 25 ± 0.1° C. Differential diffusion coefficients were calculated by the method outlined by Strokes (*5*). This technique is equivalent to assuming the differential diffusivity to be adequately represented by a polynomial in the concentration,

$$D = \sum_{i=0}^{N} a_i C^i$$

The a_i can be obtained from the measured integral coefficients (*2*). Once determined, the a_i permit the calculation of the differential diffusivity at any concentration with the range of the experimental data (including saturation).

At first measurements were attempted with the diaphragm in a vertical position. However, differences in the densities of the two solutions sets up unbalanced hydrostatic pressures in the two compartments. This results in natural convection bulk flow through the diaphragm from the dense to the light solution. The volume of less dense liquid (and thus its hydrostatic head) increases until a steady state is reached in which the pressure drop across the diaphragm at any point above its center is matched by an equal and opposite drop at a point equally distant below the center. This creates a steady-state circulation from the denser to the lighter solution below the diaphragm center and in the opposite direction above. A rough calculation for saturated $CuSO_4$ on one side and water on the other shows that the mass flux through a 5-micron pore caused by flow is of the order 100 times greater than that caused by diffusion. This effect is believed responsible for the observed tenfold increase of the measured diffusivity for this case above its actual value. This model offers a possible explanation for the high values of the diffusion coefficient that are observed when the diaphragm is inclined from the horizontal. Stokes (*4*) suggested that the coefficient increases as a quadratic function of the angle, whereas the bulk circulation model sketched here predicts that the coefficient will increase roughly as the logarithm of the sine of the angle.

Natural circulation should not be present in the horizontal diaphragm arrangement, since hydrostatic pressure gradients along the diaphragm surfaces are absent. However, the stirring of the liquids produces a rotational flow pattern in each compartment which can also result in position dependent pressure differences across the diaphragm. If the fluid adjacent to the diaphragm is in rotational motion, a pressure gradient of $r\rho\omega^2$ is created (r = radial position, ρ = fluid density, ω = rotational frequency). If the densities are different on the two sides of the diaphragm, a larger radial pressure gradient is set up in the denser solution than in the dilute solution. This will result in forced circulation from the concentrated to dilute solution at the periphery and return at the center. This effect was not significant for stirring speeds below 80 r.p.m., but it is believed to have been the cause of high observed diffusivities at higher spees. Below 80 r.p.m., the measured intergral coefficients were reproducible, independent of stirring speed, and agree satisfactorily with the measurements of other workers.

Differential diffusion coefficients for $CuSO_4$ in water at 25° C. are listed in Table I for concentrations from 0.35 moles/liter to saturation (1.404 molar). The precision of the

Table I. Diffusivity of Copper Sulfate in Water at 25° C.

Concn., Moles/Liter	Diffusion Coeff., Sq. Cm./Sec. × 10^6	Concn., Moles/Liter	Diffusion Coeff., Sq. Cm./Sec. × 10^6
0	8.50[a]	0.60	4.45
0.10	5.64[b]	0.80	4.24
0.20	5.37[b]	1.0	4.07
0.35	5.23[b]	1.2	3.95
0.35	4.95	1.404[c]	3.83
0.40	4.86		

[a] Nernst limiting value. [b] Based on reference 1. [c] Saturation.

Table II. Diffusivity of Water in *n*-Butyl Alcohol at 25° C.

Water Concn., Moles/Liter	Diffusion Coeff., Sq. Cm./Sec. × 10^6	Water Concn., Moles/Liter	Diffusion Coeff., Sq. Cm./Sec. × 10^6
0	5.62	6.0	3.14
1.0	5.18	7.0	2.88
2.0	4.66	8.0	2.63
3.0	4.15	9.0	2.39
4.0	3.76	9.89[a]	2.17
5.0	3.43		

[a] Saturation.

measurements was ±5%. For comparison, the earlier measurements of Eversole and others (*1*) and the Nernst limiting value are included in Table I. At 0.35 molar, the present data and those of Eversole and others differ by approximately 5%, which is approximatley the experimental error of the diaphragm cell measurements. A convenient empirical correlation of the differential diffusivities of $CuSO_4$ in water at 25° C. is:

$$D/D_0 = 1 - 0.52C^{1/5}; \qquad 0 \leqq C \leqq 1.4$$

Differential diffusion coefficients for water in *n*-butyl alcohol are listed in Table II. The precision of the measurements was ±6%. Randall, Longtin, and Weber have reported much larger diffusivities for this system (*3*). However, their data are almost certainly incorrect, since the values reported are two orders of magnitude greater than any other liquid diffusion coefficients in the literature.

LITERATURE CITED

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Water-Content Isotherms for a Sulfonic Acid–Styrene-Divinylbenzene, Cation-Exchange Resin at 110° and 130°C.

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Water-content isotherms were determined for Dowex 50W-X8 cation-exchange resin in the potassium form at 110° and 130° C. over a water vapor pressure range from 0 to 22 mm. of Hg using a carrier gas method.

SEVERAL investigators have published data on the water content of the sulfonated styrene-divinylbenzene, cation-exchange resins as a function of the partial pressure of water vapor present at temperatures of 25° and 50° C. (*1, 2, 4*). These studies have included such resin variables as ionic form and relative crosslinking. More recently, Wymore has shown that this water-holding property makes these resins promising desiccants (*5*). Use of the resins as desiccants will involve a cyclic process in which the resin takes on water at ambient temperatures from a liquid or gas stream and is then regenerated by stripping the water from it at a higher temperature. The efficiency of such a regeneration is dependent on the equilibrium water content of the resin as a function of the partial pressures of water vapor present at temperatures above 100° C. Since no such data have been published, the present work was carried out.

The work was limited to the potassium form of a cation-exchange resin of average crosslinkage, Dowex 50W-X8. The potassium form of the resin has been shown to be the most useful as a desiccant in that it combines stability, good equilibrium capacities, and good kinetic properties (*5*).

EXPERIMENTAL

A carrier gas method was used for the determination of the high temperature isotherms. A known amount of resin in a thermostated chamber was allowed to equilibrate with a flow of nitrogen containing a know partial pressure of water vapor. The weight of the resin at equilibrium was determined and the water content calculated. The water vapor content of the carrier gas was varied to obtain the isotherms over the desired range.

A sample of Dowex 50W-X8 resin in the 100 to 200 mesh size was used. This resin in the hydrogen form had an exchange capacity of 5.05 meq. H^+ per dry gram, and when fully swollen and centrifuged, contained 54.9% water. The resin was converted to the potassium form with an excess of potassium carbonate and thoroughly rinsed. The 100 to 200 mesh size was used to give faster equilibration times.

The experimental train had four major components. The gas supply system consisted of a cylinder of nitrogen with a flow-regulating valve and a rotameter. An average flow rate of 20 ml./min. was used.

The nitrogen stream was adjusted to the desired water-vapor level by passing it through two 250-ml. gas-washing bottles, each two-thirds filled with standardized sulfuric acid. The sulfuric acid was analyzed by titration of a weighed sample before it was placed in the saturator. As a check, a sample of the acid from the second gas-washing bottle was analyzed at the end of a run using a particular strength of acid. In all cases these two analyses agreed within experimental error. A mist knock-out chamber consisting of a gas-washing bottle filled with glass helices was used in series with the saturator bottles. All three of these bottles were completely immersed in a constant temperature bath which could be set at either 25° or 30° C. and held to ±0.1° C. The water vapor pressure in the nitrogen stream at a given temperature and sulfuric acid concentration was obtained from the literature (*3*).

The equilibration and weighing chamber was immersed in a constant temperature bath containing a silicone heat-exchange fluid. The gas entering passed through a spiral heat exchanger immersed in the bath before entering the equlibration chamber. The resin sample (about 0.5 gram) was placed in a small platinum dish and suspended in the