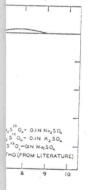


iffusion coefficients ctively, versus preswater and sulfuric

ween these sulfate e similarity is even and 0.1 N sodium potassium sulfate.

, it appears that e more rigid strucxception of the insodium sulfate and ial pressure range, creasing to a miniping off in the high

where D initially se in free volume. as so and does not ent with the initial ressure where D is in the value of D activation volume



olutions at 25°C.

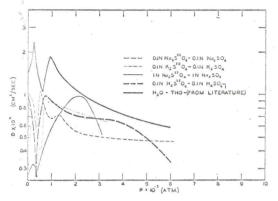


Fig. 16. Diffusion coefficients for sulfate solutions at 0°C.

ratio to relatively small values (Fig. 17). Inasmuch as the activation volume ratios are extreme and their variations are compressed in the pressure range below 1000 atmospheres, only the high pressure values are plotted. It is this portion of the curves that indicate the formation of similarly stable structures for water and sulfate solutions.

The conductivity data of Zisman⁷ on 0.01 N salt solutions (including Na₂SO₄) shows a maximum in the conductance at about 1000 atmospheres, followed by a

⁷ W. A. Zisman, Phys. Rev. 39, 151 (1932).

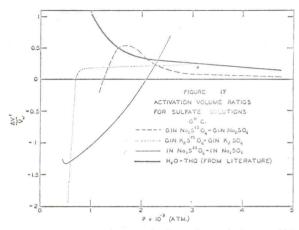


Fig. 17. Activation volume ratios for sulfate solutions at 0°C.

linear decrease. The lack of detailed structure may be due to the decreased concentration or to the lack of sensitivity of conductance.

R. B. Cuddeback would like to acknowledge assistance from the Shell Fellowship Committee and from the U.S. Atomic Energy Commission.

R. C. Koeller would like to acknowledge assistance from the Pan American Refining Corporation and the U. S. Atomic Energy Commission.

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 21, NUMBER 4

APRIL, 1953

The Effect of Pressure on Diffusion in Aqueous and Alcoholic Salt Solutions*

R. B. CUDDEBACK AND H. G. DRICKAMER Department of Chemistry, University of Illinois, Urbana, Illinois (Received August 26, 1952)

Diffusion coefficients have been measured as a function of pressure to 10 000 atmos for the following aqueous solutions:

0.1 N Hg(NO₃)₂ at 0°, 25°, 50°, 75°C,

0.1 N CaCl₂ at 25°, 50°C, 0.1 N Ca(NO₃)₂ at 25°C,

0.1 N TINO3 at 25°C,

and for 0.01 M HgCl2 in n-butanol at 25° and 50°C. The results are interpreted in terms of the activation volume, and compared with previous data on water and sulfate solutions.

IFFUSION coefficients have been measured as a function of pressure to 10 000 atmos in 0.1 Naqueous solutions of Hg(NO₃)₂ at 0°, 25°, 50°, and 75°C; CaCl₂ at 25° and 50°C; Ca(NO₃)₂ at 25°C; and TINO at 25°C. Measurements have also been made in a 0.01 M HgCl₂ in n-butanol solution.

In every case a radioactive tracer technique was used. The tracers (Hg²⁰³, Ca⁴⁵, Tl²⁰⁴) were obtained from Oak Ridge National Laboratory of the U.S. Atomic Energy Commission. The salts were of cp quality. The *n*-butanol was purchased from Eastman Kodak.

The experimental procedures, method of calculation of the diffusion coefficient, and the general theory have been previously discussed.1,2,3

The results are presented in Tables I-V and Figs. 1-5. These will be discussed under four headings; mercuric nitrate, comparison of nitrate isotherms, calcium chloride isotherms, and mercuric chloride-butanol isotherms.

¹ R. C. Koeller and H. G. Drickamer, J. Chem. Phys. 21, 267 (1953).

² R. C. Koeller and H. G. Drickamer, J. Chem. Phys. 21, 575 (1953).

³ Cuddeback, Koeller, and Drickamer, J. Chem. Phys. 21, 589 (1953)

^{*} This work was supported in part by the U. S. Atomic Energy Commission.