

possible to say which forces (free volume, structural arrangement, degree of solvation, or ionic interaction) are responsible for the various maxima and minima in the diffusion coefficient curves. If the sudden initial decrease in D for 0.1 N thallous nitrate is discounted, then the nitrate curves display remarkable similarity. The diffusion coefficients pass through a maximum in the low pressure range (200–600 atmospheres), another in the intermediate pressure range (2000–4000 atmospheres) and rise to a final peak in the range 6000–10 000 atmospheres. There are, of course, corresponding minima for D and maxima and minima for the activation volume ratio. These effects are somewhat compressed for the 0.1 N mercuric nitrate solution.

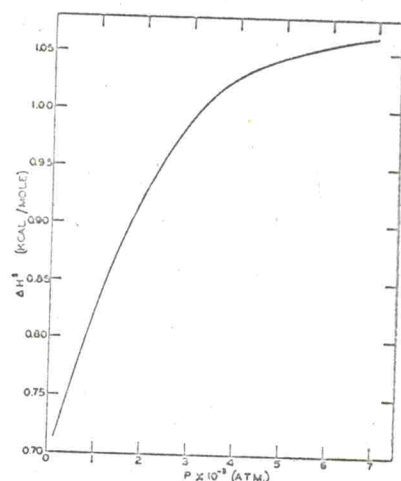


Fig. 12. Activation enthalpy versus pressure, 0.01 M $HgCl_2$ in n -butanol, 37.5°C.

CALCIUM CHLORIDE

The plot of diffusion coefficient versus pressure for 0.1 N $CaCl_2$ is shown in Fig. 2. The results show qualitatively the same variations exhibited by the other aqueous solutions. The rather low values at high pressure for this relatively small molecule indicate how little the diffusion rate depends on the ionic volume.

MERCURIC CHLORIDE IN n -BUTANOL

The diffusion coefficients are plotted versus pressure in Fig. 5. Figures 11, 12 and 13 are plots of activation volume ratio, activation enthalpy, and activation entropy, respectively, versus pressure. The pressure variation of D is very regular and the value of D , which is always higher at 50°C, decreases by a factor of 50 from atmospheric pressure to 8500 atmospheres at 50°C and 7000 atmospheres at 25°C. The relatively high value of the activation volume ratio at the initial pressure indicates that a high degree of distortion and local expansion accompany the activation process. The rapid decrease of activation volume ratio upon increased compression in the low pressure range indicates a more ordered arrangement of the n -butanol medium. The

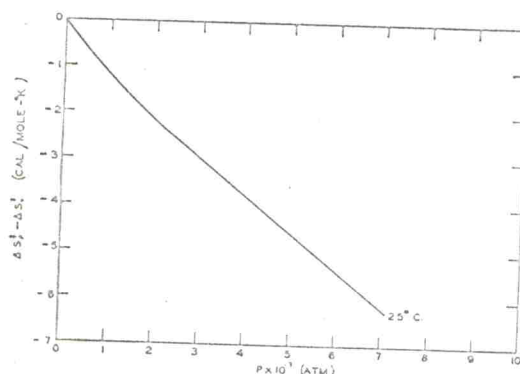


Fig. 13. Activation entropy versus pressure, 0.01 M $HgCl_2$ in n -butanol, 25°C.

decrease in activation entropy shows that a preferred orientation is developing in the n -butyl alcohol solution. In this same region the activation enthalpy increases.

At high pressure the activation volume asymptotically levels at values comparable to those for the aqueous solutions but at higher values than those for other organic solutions.^{2,3} This trend in activation volume, the continual decrease in activation entropy, and the decreasing rate of increase of the activation enthalpy imply the formation of a more ordered and stable configuration through which molecular motion occurs.

It is evident that the butyl alcohol provides an essentially normal organic medium for motion even for an inorganic salt. $HgCl_2$ is probably almost entirely undissociated in the alcoholic solution.

From the work done on salt solutions it is possible to draw the following conclusions:

1. Molecular motion in aqueous solutions appears to be a combination of several effects: those which govern motion in water, the effects of pressure on the ionic interaction, and on the effects of solvation.
2. At high pressure a similarly stable structure develops for the water and aqueous solutions.
3. A definite similarity in the variation of diffusion coefficient with pressure exists among the curves in any set of comparative isotherms.
4. With the exception of a short range of pressure on a few isotherms, the diffusion coefficient for water is higher than for the salt solutions.
5. The structure of the aqueous salt solutions appears to be less stable towards pressure than water.
6. The extreme values of the activation volume ratio are smaller than those for aqueous salt solutions, indicating a smaller activation volume effect for water.
7. The diffusion of molecular salts in butyl alcohol is quite normal and gives no evidence of association or other unusual structure.

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