

Fig. 7. Activation enthalpy versus pressure. 0.1 N Hg(NO<sub>3</sub>)<sub>2</sub>.

isotherms, and since the structure appears to vary radically with temperature, these values of activation enthalpy and entropy probably do not apply to any single isotherm.

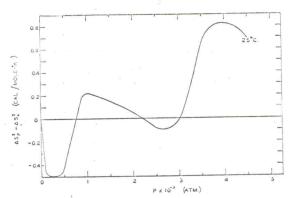


Fig. 8. Activation entropy versus pressure, 0.1 N Hg(NO<sub>3</sub>)<sub>2</sub>.

## NITRATE SOLUTIONS AT 25°C

The curve for the diffusion coefficients and activation volume ratios *versus* pressure for the nitrate solutions at 25°C are shown in Figs. 9 and 10, respectively

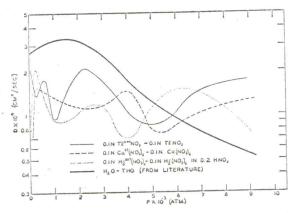


Fig. 9. Diffusion coefficients versus pressure, nitrate solutions at 25°C.

Figure 10 shows that the activation volume ratios asymptotically level at high pressure indicating the formation of a stable structure with motion in the interstices similar to that in the sulfate solutions. Further similarities between the nitrate solutions (Fig. 10) and the sulfate solutions (1) are readily apparent. The extreme values for the activation volume ratios are less for water indicating that molecular motion is generally more difficult in aqueous solutions, probably due to the large effective size of the ionic particles relative to those

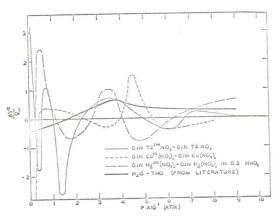


Fig. 10. Activation volume ratio versus pressure, nitrate solutions at 25°C.

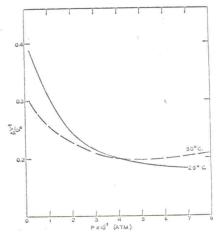


Fig. 11. Activation volume ratio versus pressure, 0.01 M HgCl<sub>2</sub> in n-butanol.

of water. Another noticeable feature is the relatively greater stability of the water structure toward pressure. A decrease in activation volume ratio occurs at lower pressure for the aqueous solution which indicates a local structural collapse at lower pressure than in the case of water.

The diffusional process in the nitrate solutions deviates more from water than in the sulfate solutions which indicates a larger influence of ionic interaction and degree of solvation on diffusion and a stronger pressure dependency on these two forces. At this time it is not

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