

$(\partial\Delta V^*/\partial P)_T$ undergoes parallel changes (30). The implication of all this is that solvent structure is playing a part in influencing this kinetic behavior. This has been illustrated in other studies (18, 19, 30). However, at present a quantitative estimate of the extent of this cannot be made.

It is worthwhile to mention that in all of those studies quoted in the previous paragraph involved aqueous-organic solvent mixtures. It is known that the structural nature of these systems is quite complex. This complexity is reflected in the kinetics in these systems. However, when the variation of activation volume with solvent is related to a change from one pure solvent to another (*e.g.* ethanol, methanol, etc.), Eckert and co-workers (31-33) have found that then the variation of ΔV^* with solvent can be explained on the basis of ion-dielectric theory. All of the solvents involved in these studies are structurally similar, so structural influences are ruled out and a less complicated behavior results.

One further conclusion worth mentioning here, is the fact that the contributions to the pressure dependence of the activation volume from quadrupole moments can be quite significant and cannot be ignored. The contribution from quadrupole moments is about equal to that from dipole moments, Table 2.

To summarize, we may say that although these calculations are not very refined mainly because of the rough estimates of the parameters involved, that ion-dielectric, as applied here, does afford a clearer understanding of the nature and origin of the pressure dependence of the activation volume. Valuable information about the transition state can also be extracted on this basis. However, it may be constantly borne in mind that the contribution to ΔV^* and $(\partial\Delta V^*/\partial P)_T$ arising from structural properties of the aqueous binary solvent must be considered.

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1. H. S. GOLINKIN, W. G. LAIDLAW, and J. B. HYNE. *Can. J. Chem.* **44**, 2139 (1966).
2. B. T. BALIGA and E. WHALLEY. *Can. J. Chem.* **48**, 528 (1970).
3. J. KOSKIKALLIO and E. WHALLEY. *Trans. Faraday Soc.* **55**, 813 (1959).
4. K. J. LAIDLAW and R. MARTIN. *Int. J. Chem. Kinet.* **1**, 113 (1969).
5. A. B. LATEEF and J. B. HYNE. *Can. J. Chem.* **47**, 1369 (1969).
6. B. T. BALIGA and E. WHALLEY. *J. Phys. Chem.* **73**, 654 (1969).
7. J. B. HYNE, H. S. GOLINKIN, and W. G. LAIDLAW. *J. Am. Chem. Soc.* **88**, 2104 (1966).
8. SIDNEY W. BENSON and JEROME A. BERSON. *J. Am. Chem. Soc.* **84**, 152 (1962).
9. CHEVES WALLING and DENNIS D. TANNER. *J. Am. Chem. Soc.* **85**, 612 (1963).
10. SIDNEY W. BENSON and JEROME A. BERSON. *J. Am. Chem. Soc.* **86**, 259 (1964).
11. E. WHALLEY. *Adv. Phys. Org. Chem.* **2**, 93 (1964).
12. M. G. EVANS and M. POLANYI. *Trans. Faraday Soc.* **31**, 875 (1935).
13. S. D. HAMANN. *Physicochemical effects of pressure*. Butterworths Scientific Publications, London, 1957.
14. E. WHALLEY. *J. Chem. Phys.* **38**, 1400 (1968).
15. E. WHALLEY. *Ber. Bunsenges. Phys. Chem.* **70**, 957 (1966).
16. A. L. TH. MOESVELD. *Z. Phys. Chem.* **105**, 455 (1923).
17. A. L. TH. MOESVELD and W. A. T DE MEESTER. *Verlag Gevone Vergader Afdell Natuurk. Ned. Akad. Wetenschap*, **36**, 827 (1927).
18. E. M. ARNETT, W. G. BENTRUDE, J. J. BURKE, and P. M. DUGGELBY. *J. Am. Chem. Soc.* **87**, 1541 (1965). E. M. ARNETT, P. McC. DUGGELBY and J. J. BURKE. *J. Am. Chem. Soc.* **85**, 1350 (1963). E. M. ARNETT, W. G. BENTRUDE, and P. McC. DUGGELBY. *J. Am. Chem. Soc.* **87**, 2048 (1965).
19. F. FRANKS and D. J. G. IVES. *Q. Rev.* **20**, 1 (1966).
20. DIGBY D. MACDONALD and J. B. HYNE. *Can. J. Chem.* **48**, 2494 (1970).
21. D. L. GAY and E. WHALLEY. *Can. J. Chem.* **48**, 2021 (1970).
22. B. B. OWEN, R. C. MILLER, C. E. MILLER, and H. L. COGAN. *J. Phys. Chem.* **65**, 2065 (1961).
23. E. A. MOELWYN-HUGHES. *Physical chemistry*, 2nd revised ed. Pergamon Press, N.Y., 1961, pp. 323, 331.
24. C. WALLING and H. S. SCHUGAR. *J. Am. Chem. Soc.* **85**, 607 (1963).
25. K. J. LAIDLAW and D. CHEN. *Trans. Faraday Soc.* **54**, 1026 (1963).
26. J. KISKIKALLIO and E. WHALLEY. *Can. J. Chem.* **37**, 783 (1959).
27. MOYRA J. MACKINNON, A. B. LATEEF, and J. B. HYNE. *Can. J. Chem.* **48**, 2025 (1970).
28. B. T. BALIGA and E. WHALLEY. *Can. J. Chem.* **43**, 1835 (1964).
29. B. T. BALIGA, R. J. WITHEY, and E. WHALLEY. *Trans. Faraday Soc.* **61**, 517 (1965).
30. H. S. GOLINKIN, I. LEE, and J. B. HYNE. *J. Am. Chem. Soc.* **89**, 1307 (1967).
31. R. A. GRIEGER and C. A. ECKERT. *Trans. Faraday Soc.* **66**, 2579 (1970).
32. C. A. ECKERT. *Ind. Eng. Chem.* **59**(9), 20 (1967).
33. J. R. MCCABE, R. A. GRIEGER, and C. A. ECKERT. *Ind. Eng. Chem. Fund.* **9**(1), 156 (1970).