

FIG. 6. Dissection of activation enthalpy. Solvent dependence of activation ( $\Delta H^*$ ) and initial ( $\Delta \bar{H}_s^\ddagger$ ) and transition state ( $\Delta \bar{H}_s^\ddagger$ ) enthalpies at 50.25 °C.

less than 0.05 mol fraction alcohol. For this reason one cannot be dogmatic about concluding that the extremum in  $\Delta H^*$  is due to a corresponding extremum in the enthalpy behavior of the initial state  $\Delta \bar{H}_s^\ddagger$ . However, there is every indication in the limited data available at 0.05 and 0.075 mol fraction *t*-butyl alcohol that this may indeed be so.

In Figs. 4 and 5 the positions of minima in  $\Delta H^*$  and  $\Delta S^*$  appear to be pressure dependent and move to higher alcohol compositions as the pressure is increased. If the extremum in  $\Delta H^*$  is due to the difference in the structure making and breaking abilities of the initial and transition states, as Arnett has suggested (21), then this observation is not surprising. The application of pressure itself is known to influence the structure of aqueous binary solutions (22) and hence presumably the additional structural influence of solute molecules, such as benzyl chloride, would be expected to vary with pressure.

The concurrent shift of the position of the extremum in  $\Delta S^*$  is in keeping with the generally observed compensatory behavior of enthalpy

and entropy changes, but also suggests that the order-disorder phenomena which produce the observed extrema have their optimum effect at higher alcohol compositions at higher pressures.

#### The Pressure Derivatives of the Rate, $\Delta V^*$ and $\partial \Delta V^* / \partial P$

The volumes of activation obtained in this work are plotted against solvent composition in Fig. 7. The negative values of  $\Delta V_0^*$  are characteristic for solvolyses of alkyl halides in aqueous binary solvents (4-6). The negative sign corresponds to increased electrostriction of the kinetically important immediate solvent environment around the more polar transition state compared with the initial state (23-25).

The volume of activation is defined by eq. 17 and thus can be "dissected" in a similar manner to enthalpy. Values of  $\bar{V}^\ddagger$  were calculated from

$$[17] \quad \Delta V_0^* = \bar{V}^\ddagger - \bar{V}^g$$

the measured values of  $\Delta V_0^*$  and  $\bar{V}^g$ . The solvent dependences of these three parameters at 50.25 °C are shown in Fig. 8. It is apparent that the minimum in the behavior of the activation parameter,  $\Delta V_0^*$ , is primarily, but not exclusively, the result of a maximum in  $\bar{V}^g$  rather than in the extremum behavior of the transition state volume,  $\bar{V}^\ddagger$ , as a function of solvent composition.

The extremum behavior of  $\bar{V}^\ddagger$  of benzyl chlo-

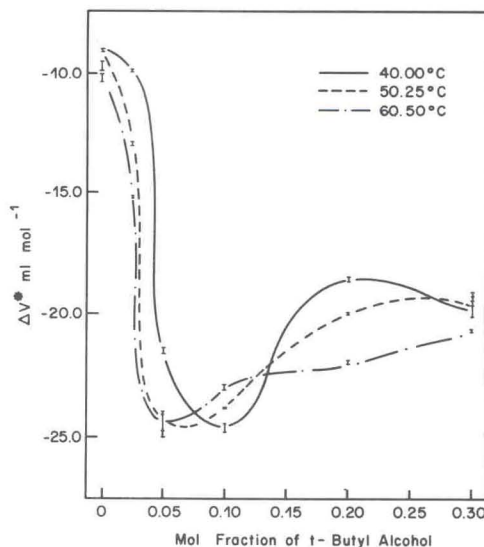


FIG. 7. Solvent dependence of activation volume at three temperatures.

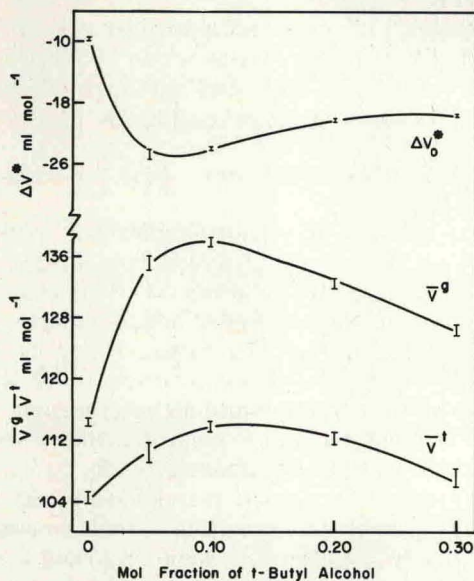


FIG. 8. Dissection of activation volume. Solvent dependence of activation ( $\Delta V_0^*$ ) and initial ( $\bar{V}^a$ ) and transition state ( $\bar{V}^T$ ) volumes at 50.25 °C.

ride in aqueous *t*-butyl alcohol is actually typical of several other non-electrolytes in aqueous alcohol mixtures. In aqueous ethyl alcohol, for example, benzyl fluoride, benzyl chloride and *p*-chloro benzyl chloride all pass through a maximum in  $\bar{V}^a$  near 0.3 mol fraction alcohol (26). These maxima occur at a solvent composition which has been suggested to possess minimum structuredness (27). If it is valid to draw an analogy between the behavior of the benzyl chloride initial state in aqueous ethyl alcohol and in aqueous *t*-butyl alcohol, then the maximum in  $\bar{V}^a$  in the latter solvent may indicate that the solvent possesses a minimum of structuredness at 0.1 mol fraction of alcohol. The observed minima in  $\Delta V_0^*$  in the 0.05–0.10 mol fraction alcohol region would then be largely attributed to solvent structural changes.

Since 0.1 mol fraction *t*-butyl alcohol corresponds to 30% alcohol by volume it is hardly surprising that relatively little water-like open structuredness remains in such a binary and hence non-electrostricting solutes such as benzyl chloride must displace solvent molecules on dissolution resulting in a maximization of partial molal volume of solution.

In Fig. 7 it is apparent that an increase in temperature from 40.00 to 50.25 °C causes the

minimum in  $\Delta V_0^*$  to move to a less alcoholic composition. Whether the further increase in temperature from 50.25 to 60.50 °C produces any further shift in the extremum is not conclusive. An increase in temperature also causes the minimum in the partial molal volume of *t*-butyl alcohol in aqueous *t*-butyl alcohol mixtures,  $\bar{V}_{t\text{-BuOH}}$ , to move to lower alcohol compositions (12). Since  $\bar{V}_{t\text{-BuOH}}$  presumably reflects the solvent structure, the parallel effect of temperature on the extremum in  $\Delta V_0^*$  and  $\bar{V}_{t\text{-BuOH}}$  strengthens the argument that this activation parameter reflects solvent structural changes.

Figure 9 illustrates the effect of solvent and temperature variation on  $\partial\Delta V^*/\partial P$  the second pressure derivative of the rate. The values of  $\partial\Delta V^*/\partial P$  are generally positive and exhibit a pronounced maximum at about 0.05 mol fraction of *t*-butyl alcohol.

The pressure dependence of  $\Delta V^*$  is defined by eq. 18. This dissection is analogous to the Arnett

$$[18] \quad \partial\Delta V^*/\partial P = \partial\bar{V}^T/\partial P - \partial\bar{V}^a/\partial P$$

*et. al.* (8) and Golinkin *et al.* (4) dissections of  $\Delta H^*$  and  $\Delta V_0^*$  respectively.

In pure water  $\partial\Delta V^*/\partial P$  is approximately zero indicating that the partial molal volumes of the initial and transition states responded similarly to pressure, *i.e.*  $\partial\bar{V}^T/\partial P \doteq \partial\bar{V}^a/\partial P$ . This appar-

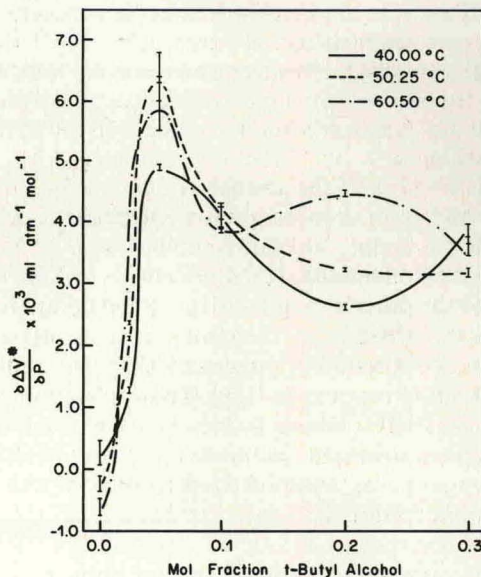


FIG. 9. Pressure dependence of activation volume as a function of solvent composition at three temperatures.