

that there is a marked change in slope for all four plots in Fig. 3 at the point where the normalized volume is unity and the change-over occurs from varying pressure to varying temperature in order to change the volume.

It was earlier established by one of us [8] that the sign of  $ind\Delta\epsilon$  for achiral aliphatic ketones dissolved in (S)-propylene carbonate is dependent on the molecular point group to which the ketone belongs, being positive for ketones with near- $C_{2v}$  symmetry and negative for those with lower symmetry. From the data in Figs. 1 and 2 it is also evident that the sign of  $ind\Delta\epsilon$  is independent of the sign of  $\Delta\epsilon_C$  for the lowest energy transition in C in other AC systems. Thus while (-)-bornyl acetate in cyclohexane solution shows a positive  $\Delta\epsilon_C$  value at 216 nm and generates a positive  $ind\Delta\epsilon$  in *trans*-azobenzene at 450 nm, it also gives rise to a negative  $ind\Delta\epsilon$  in ethylene trithiocarbonate at 455 nm. While the lowest energy electronic absorption band of pure propylene carbonate lies below 200 nm and has not yet been defined, the trend of the CD spectrum of the undiluted (S)-isomer was positive at the wavelength limit of the dichrometer ( $\sim 209$  nm) imposed by increasing absorption, and this chiral solvent generated positive and negative  $ind\Delta\epsilon$  in 2-adamantanone (298 nm) and *trans*-azobenzene (445 nm) respectively as shown in Figs. 1 and 2.

We have also observed [11] that whereas  $ind\Delta\epsilon$  from ethylene trithiocarbonate is negative in both (-)-bornyl acetate (at 455 nm) and (S)-propylene carbonate (at 445 nm) and is positive from 2-adamantanone in both solvents,  $ind\Delta\epsilon$  from other  $n-\pi^*$  solutes can have opposite signs in these two solvents.

We must conclude therefore that the sign identity between  $\Delta\epsilon_C$  and  $ind\Delta\epsilon$  proposed on model (2) does not hold for the AC systems used here. On the other hand, the magnitude of  $ind\Delta\epsilon$  for aliphatic ketones in (S)-propylene carbonate was shown to be independent of the ketone polarizability, permanent dipole moment, density, and steric hindrance to approach to the carbonyl group [8]. It is therefore evident that model (1) which does not require identity of the signs of  $ind\Delta\epsilon$  and  $\Delta\epsilon_C$ , does not apply to these systems. The relatively low values of  $[\alpha]_D$  for the two chiral solvents used here also rules out the macroscopic Lorentz radiation field of the solvents as the source [7, 12] of the observed  $ind\Delta\epsilon$ .

#### Acknowledgements

We thank Professor C. A. McDowell for his continued interest and the National Research Council of Canada and the Swedish Natural Science Research Council for financial support.

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