

The Effect of Temperature and High Pressure on Intermolecularly Induced Optical Activity

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Abstract

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The effects of temperature and high pressure on the magnitude of the induced circular dichroism of the $n-\pi^*$ bands of the achiral solutes *trans*-azobenzene, 2-adamantanone, and ethylene trithiocarbonate in the chiral solvents (S)-propylene carbonate and (-)-bornyl acetate have been examined over the temperature range 25° to 70°C and over the pressure range 0.1 to 300 MPa. The dependence of the magnitude of the induced circular dichroism on the relative intermolecular solute-solvent distance was calculated from the relative changes in densities of the solvents with temperature and pressure and was shown to fall off as R^n where $n \approx -6$ for three of these solutions in agreement with theoretical predictions. The solution of *trans*-azobenzene in (-)-bornyl acetate was exceptional showing a much larger and therefore unlikely distance dependence. The signs of the induced circular dichroism were found to be independent of the sign of the natural circular dichroism of the lowest energy band of the chiral solvent contrary to predictions on current theoretical models.

Introduction

Based on our earlier experimental work [1, 2] on induced circular dichroism (ICD) [3] of achiral solutes, *A*, in chiral solvents, *C*, Craig et al. [4], Schipper [5, 6], and Mason [7] have proposed theoretical descriptions of the ICD phenomenon based on two different models: (1) a "locked-up" model in which *A* and *C* form a complex with fixed mutual orientation of *A* and *C*, and (2) a model of an unassociated and randomly oriented collisional complex of *A* and *C* in which the coupling of *A* to *C* is entirely due to van der Waals' forces.

On model (1) the magnitude of the induced rotatory strength was considered to be proportional to $(R_{AC})^{-2}$ or $(R_{AC})^{-3}$ where the centers of *A* and *C* are separated by R_{AC} [4, 7], and in model (2) to be proportional to $(R_{AC})^{-6}$ [5, 7]. It was also proposed on model (2) that the sign of *ind* $\Delta\epsilon$ should be the same as for the natural circular dichroism of the lowest energy band of *C*, $\Delta\epsilon_C$.

We have now examined the effects of temperature and high pressure on the magnitude of *ind* $\Delta\epsilon$ arising from *A*, with different molecular rigidities, dissolved in *C* which are non-associating [8] and have analyzed our results to test features of the two theoretical models described above.

Experimental

The synthesis and purification of (S)-propylene carbonate were described previously [8]; $[\alpha]_D^{25} - 1.7^\circ$ (c0.92, ethanol); ORD: positive plain curve below 395 nm (undil., 1×10^{-4}); CD: positive below 220 nm with no maximum (undil., 1×10^{-4}). (-)-Bornyl acetate (Aldrich Chemical Company, Cat. No. B 5520-3) was partially

crystallized from the melted sample and the crystals were recovered by decantation. This procedure was repeated until the UV and CD spectra of the melted sample showed no further change; $[\alpha]_D^{25} - 46.7^\circ$ (undil., 1×10^{-3}); ORD: negative plain curve to 250 nm (undil., 1×10^{-3}); CD: $\Delta\epsilon_{\max}$ (cyclohexane) at 216 nm $+0.209 \text{ M}^{-1} \text{ cm}^{-1}$; UV: λ_{\max} (MeCN) 208 nm, ϵ_{\max} 56.2; λ_{\max} (cyclohexane) 210 nm ϵ_{\max} 61.7. Ethylene trithiocarbonate and 2-adamantanone were recrystallized to constant melting points from ethanol; *trans*-azobenzene was a zone-refined product of purity >99% (Aldrich, Gold Label) and was used without further treatment.

The design and operation of the high pressure circular dichrometer cell have been described [9]. The CD and ORD spectra were run in Vancouver on a JASCO J20 circular dichrometer-spectro-polarimeter fitted with a thermostated sample compartment maintained within $\pm 0.1^\circ$ by an external circulating bath. The compressions and thermal coefficients of expansion of the solvents were determined at Uppsala pycnometrically according to Andersson [10].

Results

The variations of the densities of the chiral solvents with pressure and temperature, measured over the ranges 0-3 000 atm and 298 to 343 K, could be well described by the Tait equation for pressure, $k = C \log_{10} (B+P)/(B+1)$, and by a polynomial of the second degree for temperature, $\rho = A + BT + CT^2$. The pressure constants for (S)-propylene carbonate were $B = 1\,625 \text{ atm.}$, $C = 0.2014$ and for (-)-bornyl acetate were $B = 1\,350 \text{ atm.}$, $C = 0.1955$ and the temperature constants were $A = 2.0087$, $B = -4.1554 \times 10^{-3}$, $C = 4.8352 \times 10^{-6}$ and $A = 0.27676$, $B = 5.4676 \times 10^{-3}$, $C = -1.0395 \times 10^{-5}$, respectively.

The effects of pressure and temperature on the magnitude of the induced circular dichroism, *ind* $\Delta\epsilon$, are shown in Figs. 1 and 2 respectively for *trans*-azobenzene in (-)-bornyl acetate (*ind* $\Delta\epsilon(+)$ at 450 nm, plot A) and in (S)-propylene carbonate (*ind* $\Delta\epsilon(-)$ at 445 nm, plot B), of ethylene trithiocarbonate in (-)-bornyl acetate (*ind* $\Delta\epsilon(-)$ at 455 nm, plot C), and of 2-adamantanone in (S)-propylene carbonate (*ind* $\Delta\epsilon(+)$ at 298 nm, plot D).

The total absorbance of the solutions was followed throughout the experiments by recording the voltage applied to the photo-multiplier in the circular dichrometer and showed no detectable change with either temperature or pressure. We have previously shown [2] that $\Delta\epsilon$ of a conformationally rigid naturally optically active compound does not change significantly with increasing pressure.

Discussion

The achiral solutes were selected to have well-isolated $n-\pi^*$ bands of different intensities and a wide range of molecular

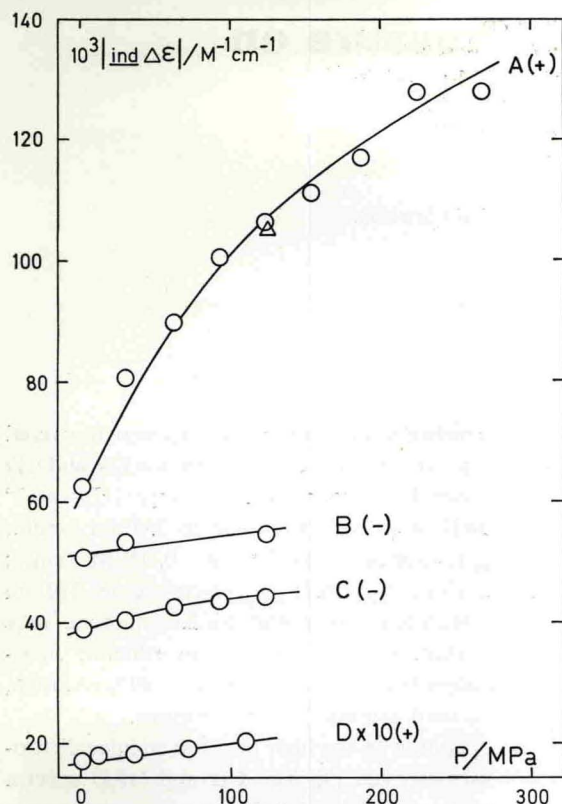


Fig. 1. The effect of high pressure on the magnitude of the induced circular dichroism of (A) *trans*-azobenzene in (–)-bornyl acetate $\text{ind}\Delta\epsilon(+)$ at 450 nm, (B) *trans*-azobenzene in (S)-propylene carbonate $\text{ind}\Delta\epsilon(-)$ at 445 nm, (C) ethylene trithiocarbonate in (–)-bornyl acetate $\text{ind}\Delta\epsilon(-)$ at 455 nm, (D) 2-adamantanone in (S)-propylene carbonate $\text{ind}\Delta\epsilon(+)$ at 298 nm. The triangle indicates a measurement made during depressurization.

structures and conformational flexibilities. The chiral solvents were selected to be transparent in the $n-\pi^*$ electronic frequency range, conformationally well-defined, non-associating, and liquid over the temperature and pressure ranges of interest (298 to 343 K, 0.1 to 300 MPa).

We have varied R_{AC} by changing the temperature at constant pressure and by varying the pressure at constant temperature.

The relative change in the distance between solute and solvent molecules, R_{AC} , was calculated as $R_P^T/R_{0.1}^{298} = (\rho_P^T/\rho_{0.1}^{298})^{-1/3}$. Also the

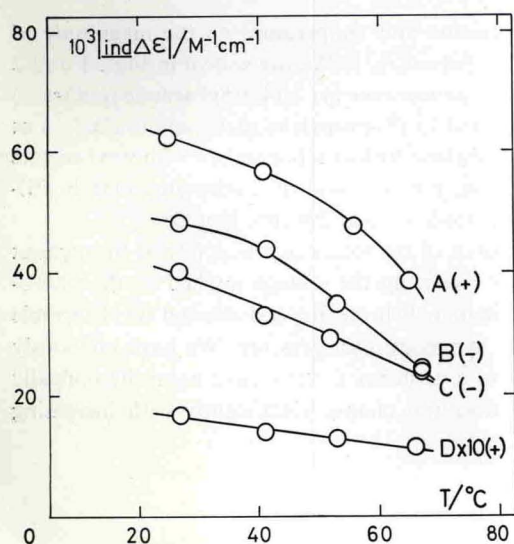


Fig. 2. The effect of temperature on the magnitude of the induced circular dichroism of A in C. For details see Fig. 1.

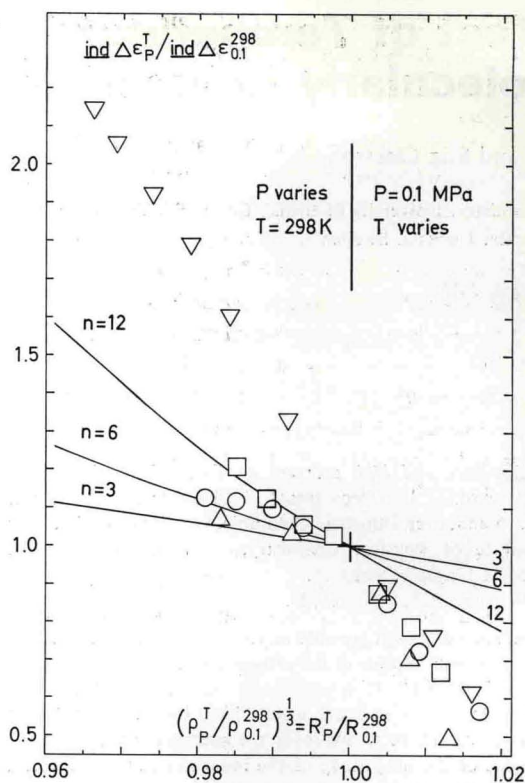


Fig. 3. Plot of normalized induced circular dichroism versus normalized solute-solvent distances. The symbols refer to the solutions described in Fig. 1 as follows: $\nabla = A$, $\Delta = B$, $\circ = C$, $\square = D$. The power law relationship $\text{ind}\Delta\epsilon_{\text{norm}} = (\text{normalized distance})^n$ is represented by the plotted lines.

effect of the relative intermolecular distance, $R_P^T/R_{0.1}^{298}$ upon the induced circular dichroism, $\text{ind}\Delta\epsilon$, was calculated in terms of the relative values, $\text{ind}\Delta\epsilon_P^T/\text{ind}\Delta\epsilon_{0.1}^{298}$ (Fig. 3).

According to the normalized data of Fig. 3, although the relative induced circular dichroism of each AC solution showed a characteristic dependence on the relative intermolecular distance, the distance dependences for three solutions were rather similar and corresponded to $\text{ind}\Delta\epsilon$ falling off as $(R_{AC})^n$ with n greater than 3 but less than 12.

The unreasonably large apparent distance dependence of $\text{ind}\Delta\epsilon$ for the solution of *trans*-azobenzene in (–)-bornyl acetate, under pressure variation (Fig. 3), seems to indicate a specific, pressure-sensitive interaction between these compounds. Since the distance dependence under temperature variation, and under both temperature and pressure variation for *trans*-azobenzene in (S)-propylene carbonate solution, fits well with those of the conformationally more rigid solutes, the large pressure effect on $\text{ind}\Delta\epsilon$ cannot be attributed solely to a pressure effect in the molecular conformation of *trans*-azobenzene. It should be noted that this pressure effect was reversible.

Since we know the variation of the normalized values of both $\text{ind}\Delta\epsilon$ (Fig. 3) and the solvent densities with both temperature and pressure, it is straightforward to calculate the variation of $\text{ind}\Delta\epsilon_{\text{norm}}$ with temperature for a system where volume is kept constant. In such a system an increase in temperature must, of course, lead to an increase in pressure and increase of these two parameters will have opposite effects on the $\text{ind}\Delta\epsilon_{\text{norm}}$ values.

For the four solutions studied the values of $[\partial(\text{ind}\Delta\epsilon_{\text{norm}})/\partial T]_V$ were in the range $-(1-2)10^{-2} \text{ K}^{-1}$. This shows that there is an energy term in addition to the distance dependence involved in the interaction of A with C. This is also evident from the fact