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EFFECT OF PRESSURE ON THE SOLVENT POLARITY PARAMETER: E_T-VALUE

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Effect of pressure on the E_T-values for four kinds of solvents has been investigated at 25°C over the pressure range 1 - 1960 kg/cm^2. The E_T-values for the solvents studied increased with pressure. Their pressure dependence was affected by the nature of solvents and the detectable differences between them existed in our pressure range. The relation of the E_T-values to the reaction rates under high pressure has been discussed in brief.

One of the most important factors in determining the rate and therefore mechanism of chemical reaction is the polarity of solvent. A discussion of solvent effect must begin with a brief description of the solvents themselves and an account of the various ways in which they can be classified. Perhaps the simplest of all classifications can be made in terms of solvent dielectric constant. However it represents a single macroscopic characteristic of solvent and cannot express adequately all the interactions between solute and solvent molecules. Therefore some empirical parameters of solvent polarity to understand the complexities of molecular interactions in solution have been proposed by several groups of workers in recent years$^{1,2)}$.

The E_T-values proposed by Dimroth and Reichard are a measure of solvent polarity which probably covers a greater range of solvents than any of the others$^{3)}$. This was obtained by determining the molar transition energy, E_T (kcal/mol), for the solvatochromic band in the spectrum of a 2,4,6-triphenyl-N-(3,5-diphenyl-4-oxy-phenyl)-pyridinium betaine (Fig. 1) in a solvent. They give a good correlation with other empirical parameters of solvent polarity$^{4)}$. Since this compound is soluble in a variety of solvents, the E_T-values are experimentally useful to make an estimation of solvent polarity.

An accumlation of knowledge of the characteristics of solvent molecules around active sites under high pressure is necessary in order to study the effect of pressure on the chemical reaction in solution. The present investigation was undertaken to evaluate the pressure dependence of the E_T-values.

The E_T-values were determined for the solvatochromic band in the spectrum of a pyridinium betaine by using the following equation.

$$E_T = h\nu = 2.859\times10^5/\lambda_{max}(\text{in } \mathring{A}) \quad (\text{kcal/mol})$$

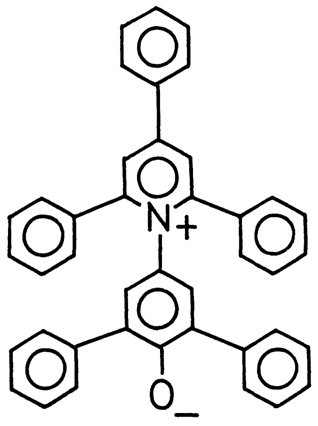

Fig. 1

The high pressure equipment with optical window for the measurement of spectroscopy was modified to circulate the water through the jacket around the equipment from thermostat in order to keep the temperature constant because the E_T-values are very sensitive to it. The details of the apparatus have been reported previously$^{5)}$.

Nitrobenzene was purified in the usual way. The other solvents were commercial guaranteed reagents for spectroscopy.

The dipole moment of pyridinium betaine in excited state is smaller than that in ground state ($\mu_E < \mu_G$) and the absorption peak shifts to shorter wavelength with increasing solvent polarity (negative solvatochromism).

Effects of pressure on the spectra of acetone solution are shown in Fig. 2. The absorption peak shifts to shorter wavelength region (blue shift). The values of maximum wavelength of the absorption measured at 1, 820 and 1960 kg/cm^2 pressure were observed at 675, 670, and 665 nm, respectively.

Similar spectra have been obtained for the other solvents. The increase of the absorbance is caused by the increasing concentration due to compression. The dependence of the E_T-values for benzene, nitrobenzene, ethanol (99.5-%) and acetone on pressure is shown in Figs. 3 and 4. The E_T-values for benzene and nitrobenzene increased by 0.22 and 0.23 kcal/mol,respectively with increasing pressure from 1 to 780 kg/cm^2 and the E_T-values for acetone and ethanol (99.5-%) were observed to increase by 0.60 and 0.83 kcal/mol, respectively, when the solutions were

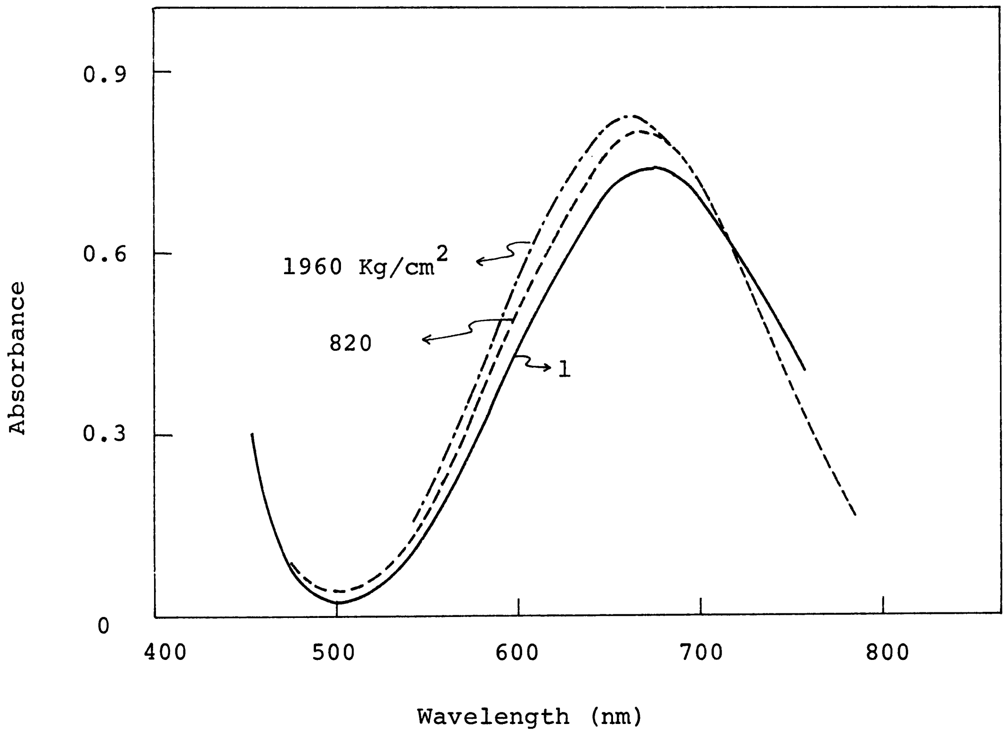

Fig. 2 Absorption spectra for acetone solution at 25°C

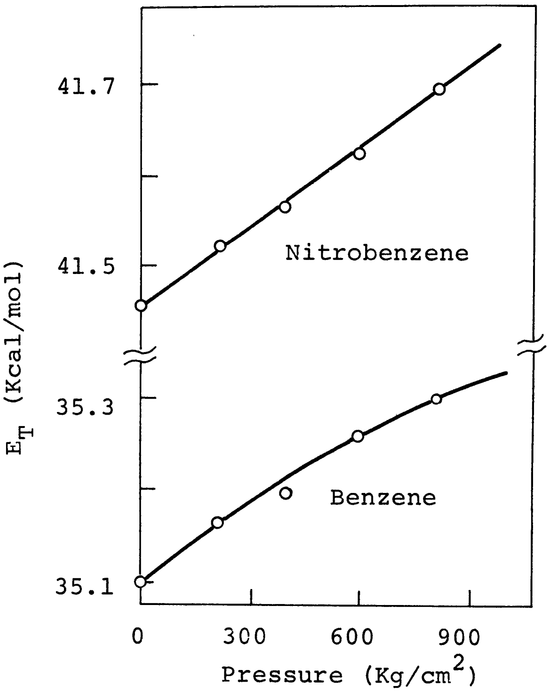

Fig. 3 Pressure dependence of E_T for nitrobenzene and benzene

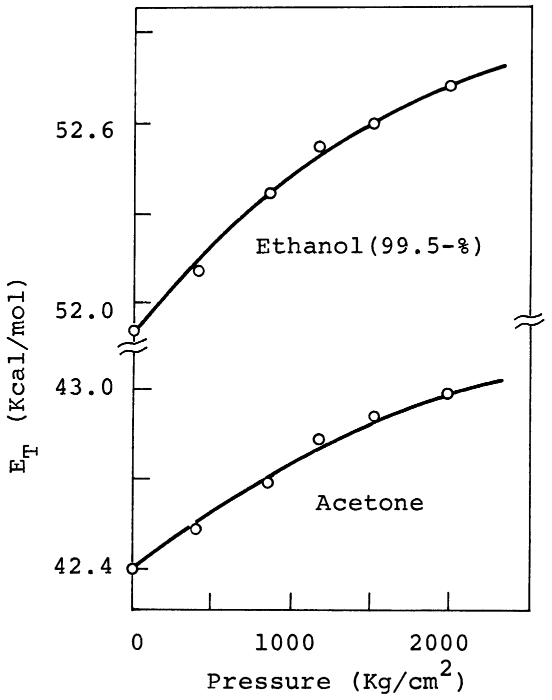

Fig. 4 Pressure dependence of E_T for ethanol(99.5-%) and acetone

pressurized at 1960 kg/cm^2. The measurements for benzene and nitrobenzene over 1000 kg/cm^2 pressure were unsuccessful at 25°C due to freezing. The freezing temperatures of benzene and nitrobenzene at 1000 kg/cm^2 have been reported as 33.7 and 27.9°C, respectively[6]. It has been found in Figs. 3 and 4 that the E_T-values increase with pressure but the degrees of increasing gradually decrease as a general tendency. The degrees of increasing were not independent of solvent and the definite differences between them were observed in our pressure range. In conclusion, the polarities of the solvents used in our experiment increased with pressure.

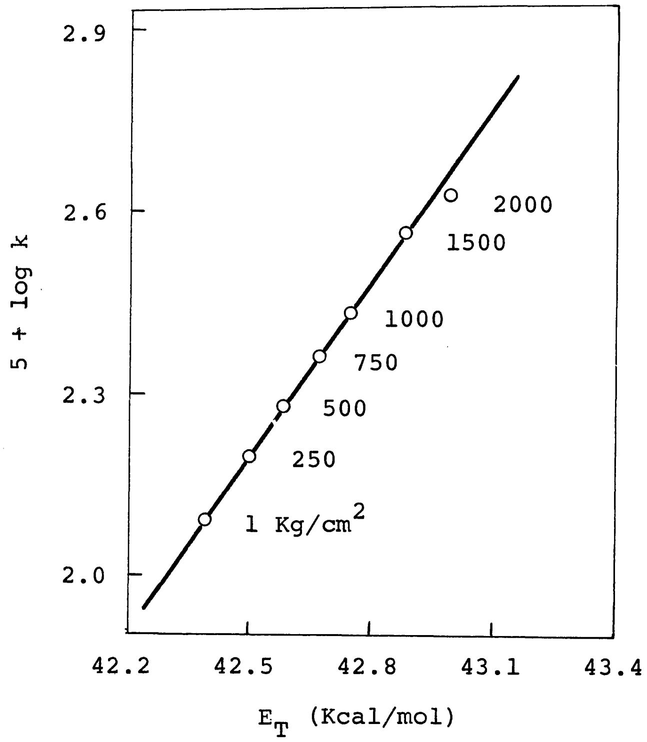

Fig. 5 A plot of log k vs. E_T for the Menschutkin reaction in acetone at various pressures

As shown in Fig. 5, comparison of the E_T-values with the rates of the Menschutkin reaction of pyridine with methyl iodide in acetone[7] revealed linear relation between the E_T-values and logarithms of the rate constants under high pressure. The expression, $\log k = a + bE_T$, is available for the kinetic studies on this reaction under high pressure.

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