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EFFECT OF SOLVENTS ON SPECTRA UNDER HIGH PRESSURE. THE SOLVATOCHROMISM OF 1-ETHYL-4-CARBOMETHOXYPYRIDINIUM IODIDE (Z-VALUE)

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The charge-transfer absorption spectra of the title compound have been measured for seven solvents at 25°C over the pressure range 1-1960 kg/cm^2. The effect of the solvents on the shift of λ_{max} with pressure was remarkable in a series of alcohols. The λ_{max} for methanol and ethanol shifted to the red, while for the other alcohols it shifted to the blue. This may be one of the interesting behavior based on the hydrogen bonding between the solute and the solvents.

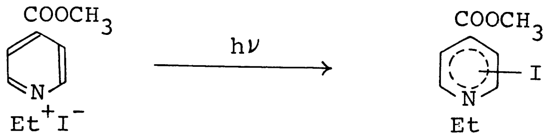
It is well known that the solvent polarity is one of the most important factors in determining the rate and therefore the selectivity of a chemical reaction. We have studied the relationships between reaction rates and solvent polarity under high pressure, and whether solvent polarity parameters proposed by several groups of workers$^{1)}$ can be employed in order to interpret reaction rates and mechanisms under high pressure. In a previous paper,$^{2)}$ it was reported that the solvent polarity parameter: E_T-value$^{3)}$ was available for the kinetic studies on Menschutkin reactions. In the present work, Kosower's Z-value which is an empirical scale of solvent polarity$^{4)}$ is determined at high pressures. In the course of the investigation, it was found that the charge-transfer absorption band of 1-ethyl-4-carbomethoxypyridinium iodide used as a standard indicator showed very interesting behavior in alcohols at high pressures. The absorption band shifted to the red for methanol and ethanol with increasing pressure, while for the other solvents it shifted to the blue. This means that the direction of the shift of the absorption band with pressure is dependent on the nature of solvent.

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

Z-values are sensitive to it. The details of the equipment have been reported previously.[5)]

The solvents used for the experiments were commercial guaranteed reagents for spectroscopy. Methanol, ethanol, and iso-propanol were dried with magnesium and distilled. The other solvents were used directly.

The Z-value is the following charge-transfer transition energy.



$$Z = h\nu = 2.859\times10^{5}/\lambda_{max} \text{ (in Å)} \qquad \text{kcal/mol}$$

Effects of pressure on the spectra of acetone solution are shown in Fig.1. The absorption peak shifts to shorter wavelength region (blue shift). The wavelengths of absorption maximum measured at 1, 1000, and 1960 kg/cm^2 pressure were observed at 434, 430, and 428 nm, respectively.

The Z-values and λ_{max} for a series of alcohols, N,N-dimethylformamide (DMF), and acetone at various pressures are listed in Table 1.

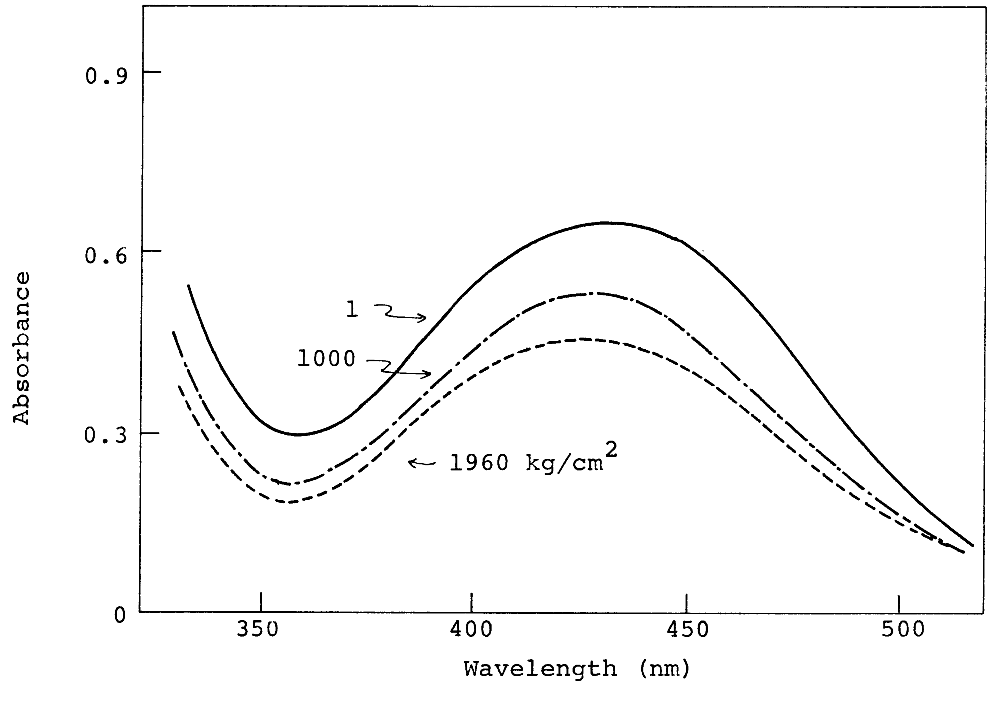


Fig. 1 Absorption spectra for acetone solution at 25°C

Table 1 The Z-values and the λ_{max} for a series of alcohols, N,N-dimethylformamide, and acetone at 25°C and various pressures

Pressure (kg/cm^2)		1	430	820	1170	1520	1960
MeOH	λ_{max}	343	345	347	347	349	349
	Z	83.39	82.81	82.44	82.35	82.11	82.10
EtOH	λ_{max}	359	360	361	361	361	360
	Z	79.64	79.46	79.35	79.24	79.31	79.38
iso-PrOH	λ_{max}	360	359	359	358	358	359
	Z	79.42	79.64	79.71	79.79	77.79	79.75
n-BuOH	λ_{max}	369	368	367	367	366	366
	Z	77.59	77.69	77.90	77.97	78.11	78.11
iso-BuOH	λ_{max}	369	368	367	367	366	366
	Z	77.41	77.69	77.83	77.97	78.11	78.22
DMF	λ_{max}	417	415	414	413	412	411
	Z	68.56	68.84	69.03	69.23	69.39	69.56
Acetone	λ_{max}	434	432	431	430	429	428
	Z	65.93	66.13	66.30	66.57	66.72	66.84

* These are the average values of three to five measurements.

* The values of λ_{max} are rounded to the nearest whole numbers.

* λ_{max} (in nm)

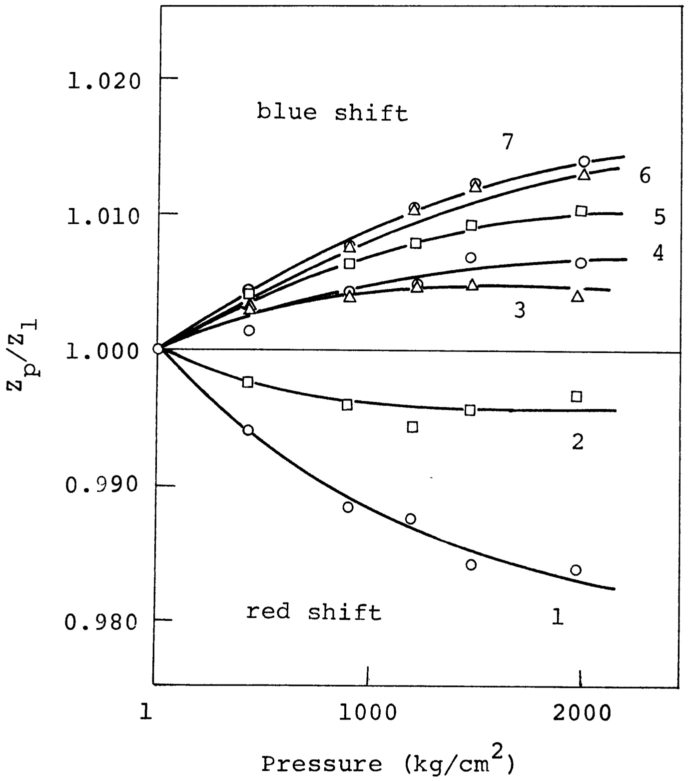


Fig.2 Pressure dependence of the relative Z-values for various solvents
1: MeOH, 2: EtOH, 3: iso-PrOH
4: n-BuOH, 5: iso-BuOH,
6: Acetone, 7: DMF

In order to compare the degree of the pressure effects on the Z-value of each solvent, the relative Z-values were plotted against pressure (Fig.2). The Z_p/Z_1 ratios become progressively greater as the number of carbon atoms in the alcohols increases, that is, there is a progressive shift from the red to the blue of the absorption band. The Z_p/Z_1 for methanol decreases with pressure. That for ethanol also decreases, however, it becomes constant at about 1000 kg/cm^2. On the other hand, for iso-propanol it initially increases and becomes constant at about 700 kg/cm^2. The values Z_p/Z_1 for the other solvents increase progressively.

The change in solvent polarity with pressure influences strongly the indicator with electric charges in ground state. Generally, the bulk solvent polarity increases with pressure, so that the ground state is stabilized and the transition energy increases with increasing pressure. This tendency was observed for acetone and N,N-dimethylformamide, however, the results for alcohols cannot be briefly explained because of the complicated interactions based on their hydrogen bonding to the solute. Fig.2 suggests that the interactions decrease with increasing the number of carbon atoms in the alcohols.

The molecular structure of the indicator is similar to that of the products of Menschutkin reactions between pyridine derivatives and alkyl halides. Therefore, we may expect that some information about the stability of the products and the nature of the activated complexes of Menschutkin reactions under high pressure can be obtained from the results of the pressure dependence of the Z-values.

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