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Solvent Effects under High Pressure. II.[1] Determination and Applications to Kinetic Studies of the E_T-Value at High Pressures

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The E_T-value was determined for eight solvents at 25 °C over the pressure range 1—1,960 kg/cm^2. They increase with pressure; the pressure dependence is affected by the nature of the solvents. It was also found that there is a linear relationship between the pressure coefficient of E_T and that of the logarithm of the rate constant of a Menschutkin reaction: $\ln k = a + bE_T$. On the basis of this relationship, an equation was derived in which the volume of activation $\Delta V^{\neq}$ is represented by the pressure coefficient of E_T; the effect of solvents on $\Delta V^{\neq}$ is discussed by making use of this equation.

One of the most important factors in determining the rate of a chemical reaction is the choice of solvent. This becomes more important and complex for reactions under high pressure.

Frequently, solvent polarity is represented by its dielectric constant. However, this is a macroscopic measure of a solvent response to an electric field. For the analysis of chemical reactions it is necessary to know the microscopic situation, the solute-solvent interaction, at the active point in which reaction occurs. It seems impossible to express adequately all the interactions between solute and solvent molecules by using a single physical parameter of a solvent. The problem of the correlation has therefore been tackled empirically. A standard reaction or dye is chosen, and the significant parameters of the reaction or the dye are observed as the solvent is changed. These parameters may be rate constants for the reaction or spectral shifts of the dye, and they have been used as measures of solvent polarity and have been correlated with reaction rate. Various empirical measures of solvent polarity have been proposed in order to rank the ionizing power of solvents more accurately;[2,3] these avoid the need to understand fully the complexities of molecular interactions in solution.

Most polarity parameters useful at atmospheric pressure are not available at high pressure, because there are generally extraneous factors which completely shield the effects of the changes of solvent polarity with increasing pressure in either the standard reaction or the spectral shifts of the standard dye being investigated. The determination of the parameters would then be meaningless. Therefore, the effects of the change of solvent polarity with pressure on reaction rate must be studied by using an adequate polarity parameter. The so-called E_T-value proposed by Dimroth *et al.*[4] is defined as the transition energy of the solvatochromic absorption band of *N*-(4-hydroxy-3,5-diphenyl-phenyl)-2,4,6-triphenylpyridiniumbetaine (Scheme 1). This can be determined for many solvents, and one can get a direct insight into solute-solvent interactions, since the microscopic transition energy of an electron is measured. In addition, the E_T-value bears a good linear relationship to many other solvent polarity parameters. For these reasons, we adopted the E_T-value as a parameter to study the pressure dependence of the solvent polarity, and evaluated it for the kinetic studies at high pressure. It was consequently concluded that at least for Menschutkin reactions the E_T-value can be used as a convenient solvent polarity parameter under high pressure.

The pressure coefficients of the E_T-value were applied to the investigation of the solvent effects on the volumes of activation $\Delta V^{\neq}$. For Menschutkin reactions, an extensive study of the influence of the solvent on the $\Delta V^{\neq}$ has been made by Gonikberg and his collaborators.[5] As a general tendency concerning these reactions, the solvation term of $\Delta V^{\neq}$ is large and negative for solvents whose compressibilities are high and whose dielectric constants increase greatly with pressure. The reason for this is as follows. Since the transition state is partially ionic, the volume of the solvation shell will be decreased due to the electrostriction of the surrounding solvent molecules. The contraction becomes larger if the solvent used has a higher compressibility. However, there are numerous exceptions to this analysis based on the changes in compressibility or dielectric constant with pressure, especially, since the relationship between $\Delta V^{\neq}$ and the pressure-dependence of the dielectric constant is extremely complex.[6,7] So we attempted to analyze the solvent effects on $\Delta V^{\neq}$ by using the E_T-value, and $\Delta V^{\neq}$ was correlated with the pressure dependence of the E_T-value.

Experimental

Materials. Commercial nitrobenzene of special grade was purified as noted in the literature.[8] The other solvents used, commercial spectro grade, were used withot purification.

The standard indicator, *N*-(4-hydroxy-3,5-diphenyl-phenyl)-2,4,6-triphenylpyridiniumbetaine, used for the determination of the E_T-value, was synthesized according to the method described in the previous paper.[1] The betaine was recrystallized from a methanol–water mixture (1 : 1); mp 207—280 °C.[4,9] (Found: C, 83.58; H, 5.26; N, 2.61%).

Apparatus. Figure 1 illustrates a part of the Drickamer-type high pressure equipment used, with optical windows, for the determination of the E_T-value. This is modified to circulate water through the jacket around the equipment from a thermostat in order to keep the temperature constant (25 °C); the E_T-value is very sensitive to temperature. A sample solution in a cylindrical quartz cell with path length of 10 mm is separated with mercury from the *n*-hexane used as a pressure transmitting medium. When the absorption spectra are measured at high pressures, attention must be paid to the mercury pushed into the cell with pressure so as not block the light.

The pressure was measured with a Bourdon gauge con-

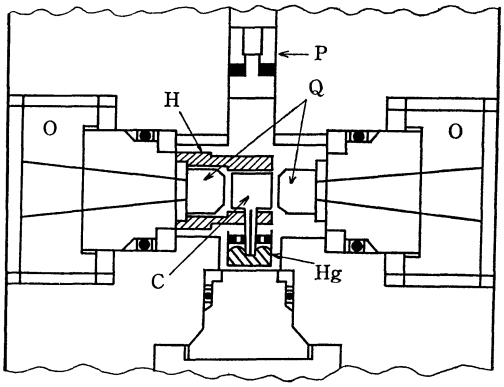


Fig. 1. Equipment for high pressure spectroscopic studies.
O: window plug Q: quartz window C: cell
H: cell holder P: high pressure piston

nected to the manual pump; it was calibrated by a manganin resistance gauge.

The area ratio of the pistons of the intensifier is 1 : 25. This indicates that the pressure ratio of the low pressure section to that of the high pressure must theoretically be equal to the reciprocal of the ratio of the pistons. However, the actual pressure measured in the high pressure section was lower than the theoretical value by about 20% due to friction between the packing and the piston cylinder.

The spectra were measured by means of Hitachi Model-139 Spectrophotometer. The details of the arrangement were described in the previous paper.[10]

Procedure. The quartz cell containing a sample solution of adequate concentration was set on a holder in the equipment, and then *n*-hexane was poured into it. This was allowed to stand for a few hours until the temperature of the system became 25 °C; it was then attached to the spectrophotometer. First the wavelength of the absorption maximum was measured at atmospheric pressure employing sensitivity values which had been determined relative to blank (100% transmittance) at each wavelength and at each pressure prior to the measurement of the absorption band. The described pressure was applied for about one hour, and then the measurement was carried out. The procedure for the measurement under high pressure is similar to that under atmospheric pressure.

Results

The betaine is a chemically stable indicator. It was confirmed that the betaine does not react with the mercury used to separate the sample solution from the pressure transmitting *n*-hexane, and its absorbance did not change with time. Also, the wavelength of absorption maximum (λ_{max}) was the same as before compression.

The position of λ_{max} at atmospheric pressure is very sensitive to the nature of the solvents, for example, the difference between the λ_{max} of methanol (516 nm) and that of acetone (675 nm) was about 160 nm. Pressure effects on the spectra were also observed, as shown for a methanol solution in Fig. 2. The absorption peak for this solution shifted to the shorter wavelength region (blue shift) with increasing pressure. The wavelengths of the absorption maximum at 1, 820, and 1,960 kg/cm² pressure were observed at 516, 512, and 508 nm, respectively. Similarly, such a blue shift with pressure was found in all other solvents used. The E_T-value can be calculated from the values of λ_{max} (in nm) with the following equation.

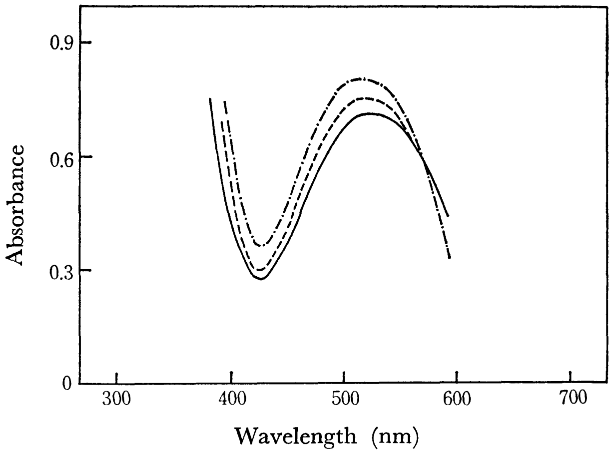


Fig. 2. Absorption spectra of the betaine in methanol at 25 °C and various pressures.
——: 1 kg/cm², – – – –: 820 kg/cm², —·—·: 1960 kg/cm²
The absorbance at high pressures is not corrected for the contraction of the solvent.

$$E_T = h\nu = 2.859\times 10^4/\lambda_{max} \quad \text{kcal/mol}$$

The E_T-values and the λ_{max} for each solvent at various pressures are summarized in Tables 1 and 2. The error range in λ_{max} is ±1∼±2 nm, depending on the solvent. The E_T-values for benzene, nitrobenzene, and a benzene-nitrobenzene mixture (0.6 mole fraction of nitrobenzene) at 25 °C cannot be determined at or above 1,000 kg/cm² pressure since these solvents freeze under these conditions. Although the betaine was only slightly soluble in benzene, the measurement of the λ_{max} was possible. The E_T-value for benzene determined at atmospheric pressure was larger than the value in the literature,[4] while that for nitrobenzene was smaller, and those for the other solvents were in agreement. As a general tendency, the rate of increase of the E_T-value with respect to pressure decreases with increasing pressure. In order to compare the relative changes of the E_T-values with pressure, $(E_T)_P/(E_T)_1$ was plotted against pressure for each solvent as shown in Figs. 3 and 4. The curves are evidently dependent on the nature of the solvents; however, the differences between the solvents are small in our pressure range. This behavior is distinct from that of the *Z*-value, another solvent polarity parameter proposed by Kosower.[11,12]

For each solvent one can culculate the slope $(\partial E_T/\partial P)_T$. This term has the dimension of volume; in the case of iodide ion, it has in fact been considered the volume change upon excitation.[13]

TABLE 1. E_T-VALUE AND λ_{max} FOR A SERIES OF ALCOHOLS AND ACETONE AT 25 °C AND VARIOUS PRESSURES

Pressure (kg/cm²)		1	430	820	1170	1520	1960
MeOH	λ_{max}	516	513	512	510	509	508
	E_T	55.41	55.69	55.84	56.06	56.17	56.28
EtOH	λ_{max}	551	549	547	545	544	542
	E_T	51.89	52.11	52.32	52.49	52.59	52.72
iso-PrOH	λ_{max}	591	588	586	584	583	581
	E_T	48.38	48.61	48.81	48.94	49.06	49.19
iso-BuOH	λ_{max}	583	581	579	578	577	576
	E_T	49.04	49.21	49.38	49.46	49.55	49.64
Acetone	λ_{max}	675	672	670	668	666	665
	E_T	42.39	42.54	42.67	42.82	42.91	42.99

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), E_T (in kcal/mol).

TABLE 2. E_T-VALUE AND λ_{max} FOR NITROBENZENE, 0.6 MOLE FRACTION OF NITROBENZENE MIXTURE, AND BENZENE AT 25 °C AND VARIOUS PRESSURES

Pressure (kg/cm²)		1	200	400	610	780
Nitrobenzene	λ_{max}	690	689	688	687	686
	E_T	41.45	41.51	41.56	41.62	41.68
0.6 mole fraction of	λ_{max}	699	698	697	696	695
nitrobenzene mixture	E_T	40.90	40.96	41.02	41.08	41.14
Benzene	λ_{max}	815	813	812	811	810
	E_T	35.10	35.17	35.21	35.28	35.32

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), E_T (in kcal/mol).

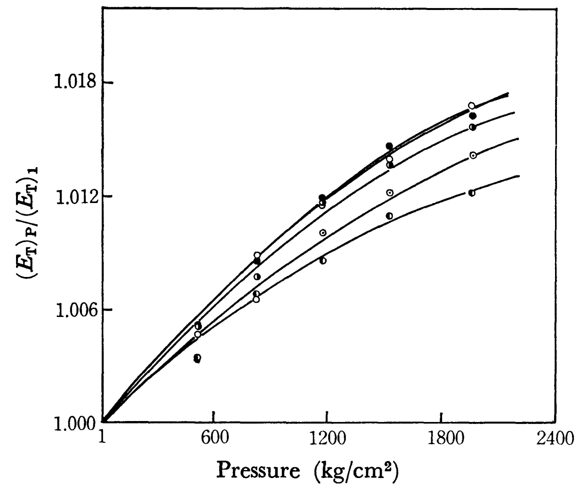


Fig. 3. Pressure dependence of the relative E_T-values for a series of alcohols and acetone at 25 °C.
○: *iso*-PrOH ●: EtOH ◑: MeOH ⊙: Acetone ◐: *iso*-BuOH

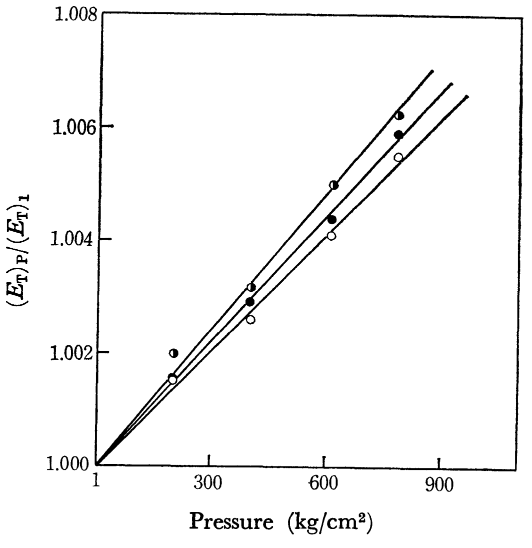


Fig. 4. Pressure dependence of the relative E_T-values for benzene, 0.6 mole fraction of nitrobenzene mixture, and nitrobenezne at 25 °C.
◐: Benzene ●: 0.6 mole fraction mixture ○: Nitrobenzene

Before the evaluation of $(\partial E_T/\partial P)_T$ from a set of E_T-values, the functional dependence of E_T-value on pressure must be established. The following two functions were checked by the least mean squares method.

$$E_T = A + BP \tag{1}$$

$$E_T = A + BP + CP^2 \tag{2}$$

It was concluded that the linear Eq. (1) was well suited for benzene, nitrobenzene and the benzene-nitrobenzene mixture which were measured over a small pressure range; the second-order polynomial (2) gives an adequate description for the other solvents. The constants A, B, and C in the above two equations were evaluated by using a computer programmed least mean squares technique; they are listed in Table 3. One can evaluate $(\partial E_T/\partial P)_T$ by differentiating the linear and quadratic expressions with respect to pressure:

Table 3. The constants A, B, and C in Eqs. (1) and (2), standard deviation, and the pressure coefficient of E_T

	$A\times 10^{-1}$ (kcal/mol)	$B\times 10^{4}$ (kcal/mol)/(kg/cm^2)	$C\times 10^{7}$ (kcal/mol)/(kg/cm^2)^2	$S.D.\times 10^{2}$	$(\partial E_T/\partial P)_T$ (cm^3/mol)
MeOH	5.542	6.662	−1.113	2.2	28.4
EtOH	5.188	6.139	−0.9515	1.2	26.2
iso-PrOH	4.838	5.865	−0.8907	0.5	25.0
iso-BuOH	4.904	4.595	−0.7782	1.0	19.6
Acetone	4.238	4.209	−0.5502	1.5	17.9
Nitrobenzene	4.145	2.891		0.4	12.3
0.6 mole fraction mix.	4.090	3.045		0.3	13.0
Benzene	3.510	2.795		0.6	11.9

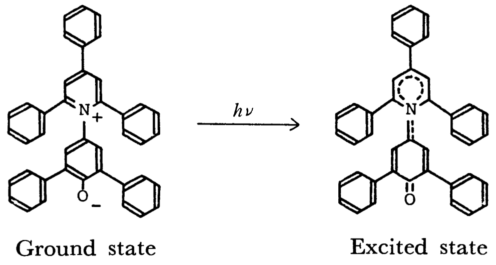
$$(\partial E_T/\partial P)_T = B \text{ or } (B + 2CP) \qquad (3)$$

The values of $(\partial E_T/\partial P)_T$, together with standard deviations, are summarized for each solvent at atmospheric pressure in Table 3. The order of the quantity of $(\partial E_T/\partial P)_T$ for each solvent almost corresponds to that of E_T. As there is some scatter in the data shown in Figs. 3 and 4, the values $(\partial E_T/\partial P)_T$ as estimated from the slopes in the figures are not necessarily consistent with those calculated from Eq. (3).

Although the physical meaning of the $(\partial E_T/\partial P)_T$ cannot be interpreted strictly, owing to insufficient information about the excited state, the experimental results suggest that the ground state interaction between the ionic solute and the surrounding solvent molecules is stronger in a more polar solvent, and consequently that the overall volume contraction of the solvation shell becomes greater.

Discussion

Pressure Dependence of E_T-value. In the visible region, the betaine shows a large hypsochromic effect with an increase in solvent polarity; *i.e.*, the wavelength of the absorption maxima shifts toward the blue with increasing solvent polarity. This is apparently due to the disappearance of the electric charges of the betaine when it is excited, together with intramolecular charge transfer as shown in Scheme 1.[14] These phenomena have been often observed in n→π* transitions.[15]



Scheme 1

The changes of E_T with pressure are due to the shifts of the energy levels in ground and excited states; however, precise information about the pressure dependence of the shifts of these levels cannot be obtained. A solute molecule, which in its ground state is in equilibrium with the surrounding solvent molecules that form its solvation shell, should be stabilized in the solution with increasing solvent polarity. According to the Franck-Condon principle an optical transition occurs within a time far shorter than the period of nuclear motions, and hence the molecule in the excited state (Franck-Condon state) is momentarily surrounded by a solvent shell whose size and orientation are those appropriate to the ground state. In the Franck-Condon state the solvation shell is unstable, because the dipole moment of the solute becomes small compared with that in the ground state, and the solute-solvent interactions become likewise smaller. Therefore, the more stable the ground state is, the more unstable is the excited state, owing to the increase in solvent polarity with pressure. The matter described above may be expressed qualitatively by Fig. 5. The energy level of the excited state rises with pressure, and on the contrary, that of the ground state falls. The slope of the curve may be dependent on the nature of the solvent. In the figure, the slopes have been selected arbitrarily for illustrative purposes.

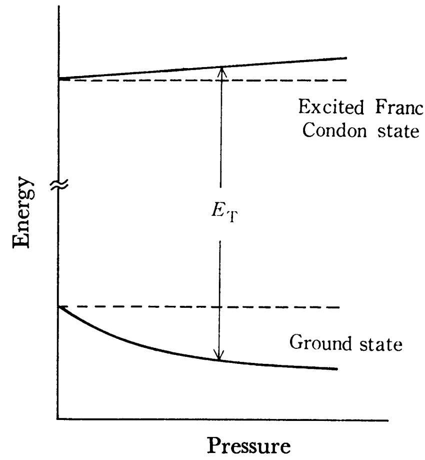


Fig. 5. Diagramatic representation of changes in ground and excited state energies for the betaine in a solvent as a function of pressure.

Correlation of Rate Constants with E_T-values. There are some examples of good linear relationship between E_T-values and logarithms of rate constants at atmospheric pressure. For example, as described in the previous paper,[1] the Menschutkin reaction of 3,5-lutidine with ethyl iodide in benzene-nitrobenzene mixtures shows good linearity. These relationships provide a valuable means of estimating the effect of solvents on the rate of chemical reactions, and of confirming abnormal solvent effects on reaction rates

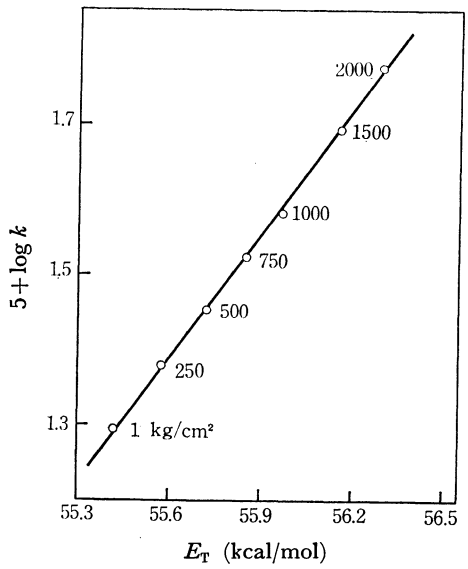


Fig. 6. A plot of log *k* *vs.* E_T for the Menschutkin reaction of pyridine with methyl iodide in methanol at various pressures.

or electronic transition. The reaction between pyridine and methyl iodide in six solvents (carbon tetrachloride, benzene, methanol, chlorobenzene, acetone, and nitrobenzene)[6] has a linear relationship, except for methanol, which is the only protic solvent. This means that the degree of solute-solvent interaction for methanol is different from that of the aprotic solvents.

We now discuss whether the E_T-value can also be employed for kinetic studies at high pressures. In order to investigate the linear relationship at high pressures, the logarithms of rate constants[6] of the reaction between pyridine and methyl iodide were plotted against the E_T-values with respect to four kinds of solvents (benzene, nitrobenzene, methanol, and acetone), up to 2,000 kg/cm². Figure 6 shows a plot of log *k* *vs.* E_T-value for methanol at various pressures. It is obvious that there is a good, linear relationship between them. Similar good linearity was observed in the plots for the other three solvents.[16] This relationship can be expressed in terms of the following linear equation.

$$\ln k = a + bE_T \tag{4}$$

The constants *a* and *b* were determined by means of the least mean squares method for each solvent; they are summarized in Table 4. The value of *a* becomes progressively larger as the E_T-value of the solvent increases, whereas the value of *b* becomes smaller.

Table 4. The constants *a* and *b* in Eq. (4) for various solvents

	Methanol	Acetone	Nitro-benzene	Benzene
a	−74.06	−99.69	−107.5	−144.3
b (mol/kcal)	1.186	2.192	2.439	3.824
E_T at 1 kg/cm²	55.41	42.39	41.45	35.10

By the use of the empirical equation (4), the volume of activation $(\partial E_T/\partial P)_T$. $\Delta V^{\neq}$ can be correlated with $(\partial E_T/\partial P)$.

According to the transition state theory[17] the volume of activation $\Delta V^{\neq}$ for a reaction is related to the pressure dependence of the rate constant by Eq. (5).

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^{\neq}}{RT} \tag{5}$$

If one differentiates Eq (4) with respect to pressure, one obtains

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = b\left(\frac{\partial E_T}{\partial P}\right)_T + E_T\left(\frac{\partial b}{\partial P}\right)_T \tag{6}$$

The following equation can be obtained from the Eqs. (5) and (6) by assuming $(\partial b/\partial P)_T = 0$ in our pressure range.

$$\Delta V^{\neq} = -bRT(\partial E_T/\partial P)_T \tag{7}$$

In order to discuss Eq. (7), the Menschutkin reaction of pyridine with methyl iodide has been chosen as an example; it has been cited in the case of discussing the linear relationship between ln *k* and E_T-value at high pressures. Table 5 lists both of the volumes of activation $\Delta V^{\neq}$, one calculated from the pressure dependence of *k* (Eq. (5)), and one evaluated using the values of $(\partial E_T/\partial P)_T$ and the constant *b* in Eq. (4) (summarized in Tables 3 and 4, respectively). By comparing these volumes of activation, it can be found that they appear to be in fairly good agreement. This means that the assumption, $(\partial b/\partial P)_T = 0$, is valid and further the experimental equations (1), (2), and (4) are also adequate expressions. Eq. (7) shows that $\Delta V^{\neq}$ can be correlated with two components, *b* and $(\partial E_T/\partial P)_T$ representing the polarity effects of solvents. The *b* defined by Eq. (4) represents the sensitivity of rate constants to changes of solvent polarity.

Table 5. Comparison of the volumes of activation calculated from Eq. (7) with those obtained by Hartmann *et al.*[6]

	Methanol	Acetone	Nitro-benzene	Benzene
$\Delta V^{\neq}$ a) (cm³/mol)	−22.6	−28.8	−19.7	−31.9
$\Delta V^{\neq}$ b) (cm³/mol)	−21.6	−25.2	−19.3	−29.2

a) Hartmann's data. b) The values calculated from Eq. (7).

In order to discuss the solvent effects on the $\Delta V^{\neq}$ by means of Eq. (7), the solvent dependence of $\Delta V^{\neq}$, $(\partial E_T/\partial P)_T$ and *b* was compared with respect to the four solvents shown in Table 4, and it was found that there is a correlation between these values and the nature of the solvent, except for the case of nitrobenzene. The absolute values of $\Delta V^{\neq}$ and *b* become large in the order of methanol, acetone, and benzene, whereas that of $(\partial E_T/\partial P)_T$ becomes smaller in the same order. So far as these solvents are concerned, it seems that the contribution of *b* to the changes of $\Delta V^{\neq}$ with the nature of the solvent is greater than that of $(\partial E_T/\partial P)_T$.

As described above, the solvent effect on $\Delta V^{\neq}$ was discussed on the basis of the values of $(\partial E_T/\partial P)_T$ and b; however, at the present stage a more detailed discussion about the correlation between the $\Delta V^{\neq}$ and the corresponding $(\partial E_T/\partial P)_T$ cannot be given due to the unavailability of suitable kinetic data. The problem of solvation at high pressures is very complex, and mechanisms depend on reaction and solvent used. Therefore, the procedures mentioned here are severely limited; however, they may furnish a guide to studies of solvent effects on the volume of activation.

The authors are indebted to Prof. W. J. le Noble for his valuable comments.

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