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Solvent Effect under High Pressure. III.[1] The Application of the Electrostriction Model to the Activation Entropy

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The expression which relates the activation entropies of the reactions measured in various solvents with the products of the coefficients of thermal expansion and the molar volumes of the respective solvents has been derived based on the concepts of the electrostriction theory. For three Menschutkin reactions and one acylation reaction linear correlations to be expected from the above expression have been found between the activation entropies and the products of the coefficients of thermal expansion and the molar volumes of the solvents. Moreover, the interrelation between the activation volumes and the activation entropies has been discussed based on this model.

Various attempts have been made to clarify the mechanism of how the solvent influences the rate of the reaction in solution. These attempts have used two alternative methods. One of which seeks out the quantitative relation between the experimental results and the various characteristics of the solvents.[2-6] The other is the method of applying empirically-determined solvent parameters.[7]

In a previous paper[1] the present authors have used an analytical expression which combined the activation volumes measured in various solvents with compressibilities of those solvents based on an electrostriction model.

As that relation has been proved to hold for two Menschutkin reactions,[1] the present authors have now tried to extend this model to an analysis of the dependence of an activation entropy of a reaction in a solution on the nature of the solvent.

In this paper the analytical expression proposed by the present authors will be compared with the experimental results of the various workers.

Discussion

In the previous paper[1] the following expression has been derived to describe the dependence of an activation volume on the compressibility of the solvent;

$$\Delta V_0^{\ne} = \{V_{\ne}-(\overline{V}_A^{\circ}+\overline{V}_B^{\circ})\}-Z\Delta PKV^{\circ} \qquad (1)$$

where $V_{\ne}$, $\overline{V}_A^{\circ}$, $\overline{V}_B^{\circ}$ and V° denote the molar volumes of an activated complex, the reactant A, the reactant B, and a solvent in its pure state and where Z, ΔP, and K denote the solvation number of an activated complex, an average pressure within a solvation shell of an activated complex, and the compressibility of the solvent, respectively.

As one example of the above relationship, the experimental results of $\Delta V_0^{\ne}$ measured by Hartmann *et al.*[8] are plotted against the value of KV° in Fig. 1.

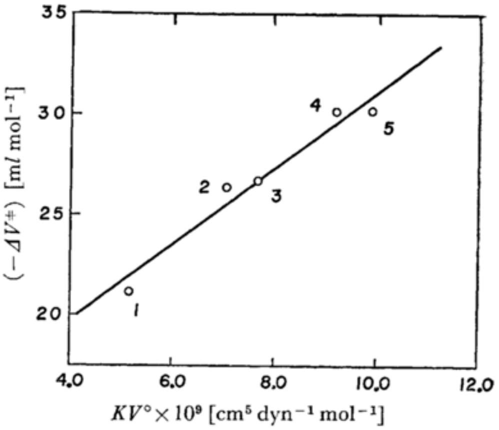

Fig. 1. Plot of $(-\Delta V^{\ne})$ measured in various solvents by Hartmann *et al.*[8] *vs.* KV°.
Reaction: ω-Bromoacetophenone+α-Picoline
Solvent 1: $PhNO_2$, 2: PhBr, 3: PhCl, 4: Acetone, 5: $PhCH_3$

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[1] Part II, Y. Kondo, M. Uchida and N. Tokura, This Bulletin, **41**, 992 (1968).

[2] A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill, New York (1962).

[3] J. D. Reinheimer, J. D. Harley and W. W. Meyers, *J. Org. Chem.*, **28**, 1575 (1963).

[4] H. G. Grim, H. Ruf and H. Wolf, *Z. Physik. Chem.*, **13**B, 301 (1931).

[5] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York (1941).

[6] J. B. Rossel, *J. Chem. Soc.*, **1963**, 5183.

[7] C. Reichardt, *Angew. Chem.*, **77**, 30 (1965).

[8] H. Heytmann, A. P. Schmidt and H. Hartmann, *Ber. Bunsen Ges. Physik. Chem.*, **70**, 444 (1966).

In order to derive the expression for the activation entropy, it would be suitable to adopt a procedure similar to that used in the preceding paper for deriving the activation volume.

We assume that in the vicinity of an ionic species in the solution the entropy of a solvent, $S_{\mathrm{solv}}{}^{\circ}$, is changed to $S_{\mathrm{solv}}{}'$ by the electrostatic influence caused by the ionic charge of the solute.

Then the total entropy, S_{t}, of the solution composed of N moles of a solvent and n moles of a solute may approximately be expressed, as follows;

$$S_{\mathrm{t}}=(N-nZ)S_{\mathrm{solv}}{}^{\circ}+ns_{\mathrm{s}}{}^{\circ}+nZS_{\mathrm{solv}}{}'+\Delta S_{\mathrm{cratic}} \quad (2)$$

where $S_{\mathrm{solv}}{}^{\circ}$, $s_{\mathrm{s}}{}^{\circ}$, $S_{\mathrm{solv}}{}'$, $\Delta S_{\mathrm{cratic}}$ and Z are the molar entropies of a free solvent, a pure solute and a solvated solvent, and a cratic entropy change on dilution and a solvation number, respectively.

Therefore, the partial molar entropy of a solute, $\bar{s}_{\mathrm{s}}$, is given by;

$$\bar{s}_{\mathrm{s}}=\left(\frac{\partial S_{\mathrm{t}}}{\partial n}\right)=s_{\mathrm{s}}{}^{\circ}+Z(S_{\mathrm{solv}}{}'-S_{\mathrm{solv}}{}^{\circ})+\Delta s_{\mathrm{cratic}} \quad (3)$$

In Eq. (3) the term $(S_{\mathrm{solv}}{}'-S_{\mathrm{solv}}{}^{\circ})$ indicates the entropy change which accompanies the transfer of a solvent molecule from the pure state under an atmospheric perssure into the ionic cosphere of a solute.

Practically, the change is produced by the electrostriction of a solvent molecule resulting from the electrostatic interaction of a solvent molecule with the ionic charge of a solute. However, at present we will estimate the value assuming that the entropy change is produced by exerting an external pressure on a solvent molecule.

Making use of the thermodynamical relation,[9] Eq. (4);

$$\left(\frac{\partial S}{\partial P}\right)_{\mathrm{T}}=-\left(\frac{\partial V}{\partial T}\right)_{\mathrm{P}} \quad (4)$$

and the coefficient of a thermal expansion, α, as defined by:

$$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)=\alpha \quad (5)$$

the entropy change caused by applying external pressure on a solvent molecule may be approximately given by;

$$\Delta S=-\alpha V^{\circ}(P-1)=-\alpha V^{\circ}\Delta P \quad (6)$$

where V° and P denote the molar volume of a pure solvent and the average pressure within the cosphere of an ionic solute.

The partial molar entropy of a solute can be obtained approximately by substituting Eq. (6) into Eq. (3):

$$\bar{s}_{\mathrm{s}}=s_{\mathrm{s}}{}^{\circ}-Z\Delta P\alpha V^{\circ}+\Delta s_{\mathrm{cratic}} \quad (7)$$

In the discussion of an activation entropy we have only to treat the entropy at an appropriately chosen standard state. Since the cratic entropy term is dependent only on the composition of the solution, not on the characteristics of the solvent, it makes an equal contribution to all the activation entropies based on the same standard state.

If we assume that the activated complex is of an ionic nature while the reactants are nonpolar, we would be able to use Eq. (7) as the entropy of the activated complex. Then the activation entropy for the bimolecular reaction is given by:

$$\mathrm{A}+\mathrm{B}\longrightarrow \mathrm{M}^{\neq}\longrightarrow \mathrm{Product}$$

$$\begin{aligned}\Delta S^{\neq}&=\{\overline{S_{\neq}}{}^{\circ}-(\overline{S_{\mathrm{A}}}{}^{\circ}-(\overline{S_{\mathrm{A}}}{}^{\circ}+S_{\mathrm{B}}{}^{\circ})\}\\&=S_{\neq}{}^{\circ}-(\overline{S_{\mathrm{A}}}{}^{\circ}+\overline{S_{\mathrm{B}}}{}^{\circ})+C-Z\Delta P\alpha V^{\circ} \quad (8)\end{aligned}$$

where C denotes the constant characteristic of the chosen standard state.

As the activation entropies measured in various solvents should be affected by the second term on the right hand side of Eq. (8), the linear relation may be expected to hold in the plotting of the activation entropies against the αV° values of the solvents. These plots are given in Figs. 2, 3, 4 and 5.[*1,*2]

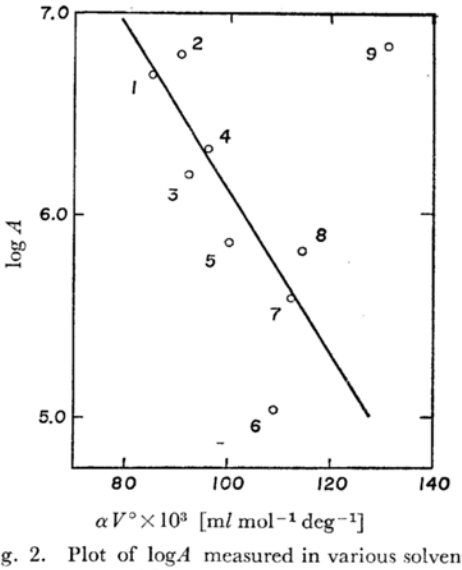

Fig. 2. Plot of log$A$ measured in various solvents by Grim *et al.*[4] *vs.* αV°.
Reaction: EtI + $\mathrm{Et_3N}$
Solvent 1: $\mathrm{PhNO_2}$, 2: PhCN, 3: PhI, 4: PhBr, 5: PhCl, 6: Bz, 7: PhF, 8: $\mathrm{PhCH_3}$, 9: Cyclohexane

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9) G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill, New York (1923); 2nd Ed., Revised by K. S. Pitzer and L. Brewer (1961).

[*1] The values of the density and the coefficient of the thermal expansion were calculated at 25°C by means of the polynominal equation in "The International Critical Tables" and by means of the differentiation of these with respect to the temperature.

[*2] In Figs. 2, 3, and 5, log A is used in place of an activation entropy where A was calculated by this equation:

$$k=A\exp(\Delta E^{\neq}/\boldsymbol{R}T)$$

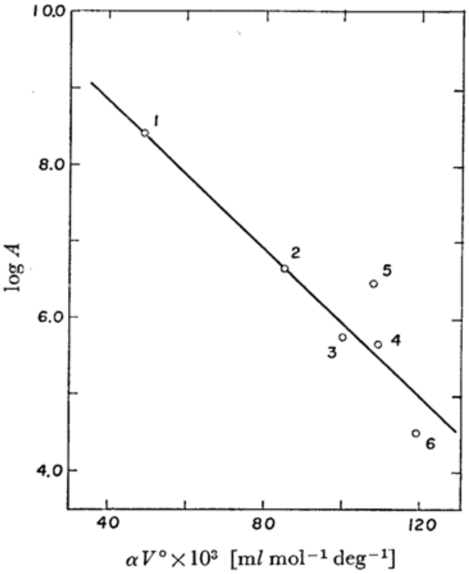

Fig. 3. Plot of log A measured in various solvents by Hartmann *et al.*10) *vs.* αV°.
Reaction: MeI + Pyridine
Solvent 1: MeOH, 2: $PhNO_2$, 3: PhCl, 4: Bz, 5: Acetone, 6: CCl_4

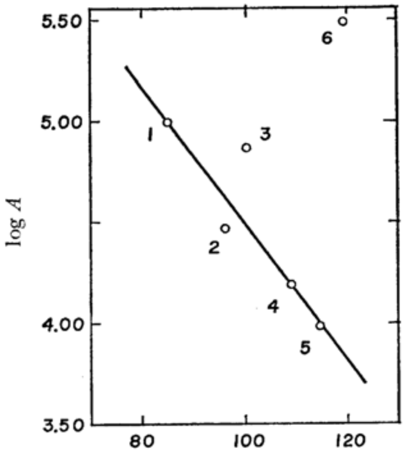

Fig. 5. Plot of log A measured in various solvent by Hinshelwood *et al.*11) *vs.* αV°.
Reaction: *m*-Nitroaniline + Benzoyl chloride
Solvent 1: $PhNO_2$, 2: PhBr, 3: PhCl, 4: Bz, 5: $PhCH_3$, 7: CCl_4

As is shown in these figures, approximately linear correlations have been found in all these examples in spite of the varieties of the solvent used. Moreover, the signs of the solpes of these plots are those to be expected from Eq. (8).

When we compare Eq. (8) with Eq. (1), we can see that the solpes of both these plots represent the values of $Z\Delta P$.

If the assumed model describes the reaction in a solution precisely, the values of $Z\Delta P$ obtained by the two methods should be equal to each other (Table 1).

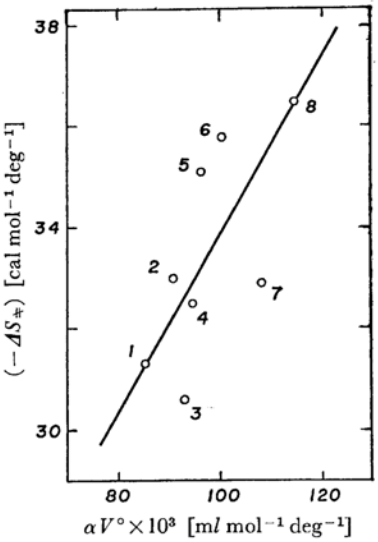

Fig. 4. Plot of $(-\Delta S^{\ddagger})$ measured in various solvents by Hartmann *et al.*8) *vs.* αV°.
Reaction: ω-Bromoacetophenone + α-Picoline
Solvent 1: $PhNO_2$, 2: PhCN, 3: Propionitrile
4: Cyclohexanone, 5: PhBr, 6: PhCl,
7: Acetone, 8: $PhCH_3$

TABLE 1. THE VALUES OF $Z\Delta P$ DERIVED BY THE TWO METHODS

	Reaction		
	$EtI+Et_3N$	MeI+ Pyridine	MeI+ α-Picoline
$Z\Delta P$ from $\Delta V_0^{\ddagger}$ (kg·cm^{-2})	2.6×10^3	2.6×10^3	1.9×10^3
$Z\Delta P$ from $\Delta S^{\ddagger}$ (kg·cm^{-2})	7.9×10^3	9.4×10^3	7.6×10^3

Though this equality does not hold accurately in these cases as is shown in Table 1, these values are of the same order for each example.

Previously Laidler and Chen12) reported a linear correlation between the activation volumes and the activation entropies for the alkaline hydrolysis of esters in an aqueous solution. Recently Hepler13) found a similar relation between the volume changes

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10) H. Hartmann, H. Kelm and G. Rinck, *Z. Physik. Chem. N. F.*, **44**, 335 (1965).

11) N. J. T. Pickles and C. N. Hinshelwood, *J. Chem. Soc.*, **1936**, 1353.

12) K. J. Laidler and D. Chen, *Trans. Faraday Soc.*, **54**, 1026 (1958).

13) L. G. Hepler, *J. Phys. Chem.*, **69**, 965 (1965). In the original formula Hepler considered the above relation to be based on the Maxwell equation: $(\partial S/\partial V)_T = (\partial P/\partial T)_v$. Thermodynamically, the following equation can be proved easily: $(\partial P/\partial T)_v = (\alpha/K)$ where K indicates the coefficient of an isothermal compressibility. Therefore Eq. (11) agrees with his opinion.

and the entropy changes for the acid dissociation reaction in a water solvent.

For the reaction in the single solvent the effect of changing reactants reveals itself in the activation entropy change upon the variation in $Z\Delta P$, for in our model the values of $Z\Delta P$ function as the measure of the development and the redistribution of the charge accompanying the formation of an activated complex.

Then, from Eq. (7) the following equation may be obtained:

$$\Delta\Delta S^{\neq} = -\alpha V^{\circ}\cdot\Delta(Z\Delta P) \tag{9}$$

Similarly, for the activation volume:

$$\Delta\Delta V_0^{\neq} = -KV^{\circ}\cdot\Delta(Z\Delta P) \tag{10}$$

By combining Eqs. (9) and (10), we obtain:

$$\Delta\Delta S^{\neq} = (\alpha/K)\Delta\Delta V^{\circ\neq} \tag{11}$$

This relation is similar not only that derived thermodynamically be Hepler,¹³⁾ but also to the alternative form of the observation by Laidler and Chen.12) Thus, it may be concluded that this model, based on the electrostriction theory, is applicable to the analysis of the activation volume and entropy for a reaction in a solution.