

tron on  $V^{4+}$  occupies the  $d_{xy}$  orbital that has  $\pi$  symmetry with respect to the bridging V–O bonds, and electron trapping occurs at high temperatures since the extent of V–O–V  $\pi$  bonding is low as a result of the  $125^\circ$  bridge bond angle.<sup>4,7</sup> The same argument may be applied to our system. However, since the V–O–V bridge bond is  $158^\circ$  for this complex<sup>8</sup> and the extent of V–O–V bonding is relatively large, electron transfer will be facilitated.

We have shown that temperature variation of the polycrystalline EPR spectrum of  $\alpha$ -1,2,3-[H<sub>2</sub>PV(IV)V<sub>2</sub>W<sub>2</sub>O<sub>40</sub>]<sup>5-</sup> can be explained qualitatively and that the large V–O–V bridge bond angle is responsible for facile electron transfer in this complex. More information may be obtained from EPR spectra of this complex at temperatures below 100K and from simulation of the spectra at various temperatures. Also needed is a better analysis of the dependence of electron transfer rate on the V–O–V bridge bond angle.

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## A Thermodynamic Consideration on the DBC–Bivalent Cation Complexes in Some Nonaqueous Solvents

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In the previous paper the stability constants of the complexes formed between dibenzo-18-crown-6(DBC) and alkaline earth metal cations in dimethyl sulfoxide(DMSO), dimethyl formamide(DMF), and acetonitrile(AN) at 25°C were reported<sup>1</sup>. The results were interpreted in terms of ion-cavity radius ratio concept, solvent donocity, and solvation of the cations with little obviosity.

However, little attention has been paid to the thermodynamic consideration on the complexation of the crown ether type ligands in the nonaqueous solvents. In this work the stability constants of the DBC–bivalent cation complexes at two more different temperatures, 35°C and 40°C, were measured by the same methods described in the previous paper and are shown in Table 1. The enthalpy and entropy contribution to the free energy of binding for DBC were calculated from Van't Hoff equation are given in Table 2. The results showed that complex formation of DBC is enthalpic in origin<sup>2,3</sup>. For all the bivalent cations complexation in the

basic solvents is favorable from enthalpic point of view with either unfavorable for Ca<sup>2+</sup> and Sr<sup>2+</sup> or favorable but low entropic contribution for Ba<sup>2+</sup>. In spite of the facts that the charge density of Ca<sup>2+</sup> is the largest among the cations, and that complex formation involves replacement of the solvent molecules by a single DBC molecule, the overall entropy of the complexation processes is negative. Apparently Ca<sup>2+</sup> and Sr<sup>2+</sup> ions act as structure breakers in the basic solvents and formation of the DBC–bivalent cation complexes results in an overall increase of organization in the solution<sup>4</sup>.

X-ray crystallographic studies also showed the cavity of the 18-crown-6 type ligands to be celliptical in the uncomplexed state, but nearly circular in the complex<sup>5,6</sup>. The significant conformational change followed by the change of ligand solvation might play an important role for the decrease in the entropy. Higher charge density of Ca<sup>2+</sup> ( $Z^2/r = 10.3$ )<sup>7</sup> than that of Ba<sup>2+</sup> (7.6) may be attributed to it. It is also probable that the difference in solvation of the ligand in the different sol-

Table 1. Stability constants (log K) of the DBC complexes in AN, DMF, and DMSO at various temperatures

Solvents Salts	AN			DMF			DMSO		
	CaI <sub>2</sub>	SrI <sub>2</sub>	BaI <sub>2</sub>	CaI <sub>2</sub>	SrI <sub>2</sub>	BaI <sub>2</sub>	CaI <sub>2</sub>	SrI <sub>2</sub>	BaI <sub>2</sub>
25°C*	2.30	3.36	3.50	2.17	3.18	3.38	1.76	2.83	3.20
35°C	1.93	3.18	3.40	1.52	3.15	3.28	1.13	2.52	3.16
40°C	1.67	3.03	3.37	1.08	2.92	3.23	0.83	2.34	3.14

\*Values from reference 1.

**Table 2. Enthalpy and Entropy Contribution to the Binding of Alkaline Earth Metal Cations by DBC at 25°C**

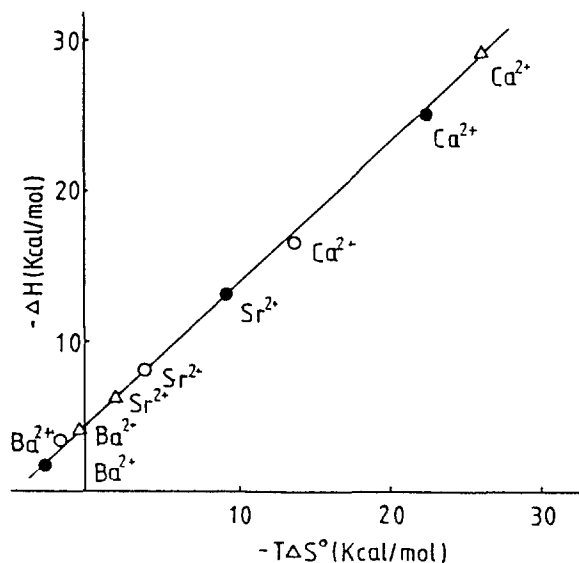
Solvent	Cation	$-\Delta H^\circ$ (Kcal mol <sup>-1</sup> )	$T\Delta S^\circ$ (Kcal mol <sup>-1</sup> )
AN	Ca <sup>2+</sup>	16.9	-13.7
	Sr <sup>2+</sup>	8.39	-3.82
	Ba <sup>2+</sup>	3.04	1.72
DMF	Ca <sup>2+</sup>	29.3	-26.3
	Sr <sup>2+</sup>	6.25	-1.93
	Ba <sup>2+</sup>	4.04	0.55
DMSO	Ca <sup>2+</sup>	25.1	-22.7
	Sr <sup>2+</sup>	13.1	-9.26
	Ba <sup>2+</sup>	1.62	2.78

vent affects the magnitude of  $T\Delta S^\circ$ .

To look at this phenomenon more closely, correlation between  $\Delta H^\circ$  and  $-T\Delta S^\circ$  for the systems is drawn in Figure 1 which revealed compensation effect.<sup>8</sup> Highly favorable enthalpy contribution and large but negative entropy contribution result in the smaller stability constants of Ca<sup>2+</sup> complexes than those of Ba<sup>2+</sup> complexes in the solvents used. As for Ba<sup>2+</sup> complexes having relatively low  $-\Delta H^\circ$  values, fitting of the metal ion into the cavity is of great importance. The relatively low  $-\Delta H^\circ$  and  $-T\Delta S^\circ$  of Ba<sup>2+</sup> complexes reflect its soft character and its weak structure breaking effect in the basic solvents.

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**Figure 1.** Correlation between  $\Delta H^\circ$  and  $T\Delta S^\circ$  for alkaline earth metal cation-DBC complexes in AN( $\circ$ ), DMF( $\Delta$ ), and DMSO( $\bullet$ ).

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## Applicability of Dual Substituent Parameter Equation to S<sub>N</sub>2 Reaction

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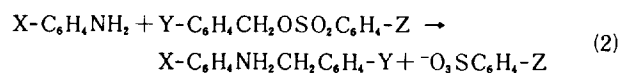
Recently various dual substituent parameter(DSP) equations have been proposed for analyses of substituent effects on rates and equilibria in terms of polar( $\rho_{pol}$ ,  $\sigma_{pol}$ ) and resonance( $\rho_r$ ,  $\sigma_r$ ) components.<sup>1-5</sup> All the DSP equations have basically the same form, (1)

$$\log(k/k_o) = \rho_{pol} \sigma_{pol} + \rho_r \sigma_r + B \quad (1)$$

where B is a constant. The polar component is variously expressed as inductive( $\rho_i$ ,  $\sigma_i$ )<sup>6,7,10</sup> or field effect( $f/F$ )<sup>6,14</sup> term.

In this report we examine applicability of four major DSP equations, Yukawa-Tsuno-Jencks(YTJ),<sup>8,9</sup> Taft,<sup>10-13</sup> Swain-Lupton(SL)<sup>14</sup> and Afanas'ev<sup>15</sup> correlation, to S<sub>N</sub>2 reactions by

applying the equations to rate data for reactions of benzyl benzenesulfonates with anilines,(2).<sup>16-18</sup>



where X = *p*-CH<sub>3</sub>O, *p*-CH<sub>3</sub>, H, *p*-Cl, *m*-NO<sub>2</sub>

Y = *p*-CH<sub>3</sub>, H, *p*-Cl, *p*-NO<sub>2</sub>

Z = *p*-CH<sub>3</sub>, H, *p*-Cl, *m*-NO<sub>2</sub>

Application of the four DSP equations to the rate data of reaction (2) gave the results summarized in Table 1. Correlation coefficients for the multiple linear regression of the calculated