

(CH<sub>3</sub>)<sub>2</sub>SO-CF<sub>3</sub>CH<sub>2</sub>OH Adducts in 1,2-Dichloroethane  
Calorimetric Determination of Formation Constants and Enthalpies of  
Hydrogen-Bonding Adducts between Dimethyl Sulfoxide and  
2,2,2-Trifluoroethanol in 1,2-Dichloroethane

Honoh Suzuki, Shin-ichi Ishiguro\*

(Received 20 May, 1988)

Department of Electronic Chemistry, Tokyo  
Institute of Technology at Nagatsuta, 4259  
Nagatsuta, Midori-ku, Yokohama 227

An on-line controlled calorimeter has been devised and used for measuring heats of adduct formation of dimethyl sulfoxide (DMSO) with 2,2,2-trifluoroethanol (TFE) in 1,2-dichloroethane (DCE) at 25°C. The observed heats were well explained in terms of the formation of two adducts, (dmsO)(tfe) and (dmsO)(tfe)<sub>2</sub>, and their formation constants and enthalpies were simultaneously determined. For the formation of the 1:1 adduct, the formation constant was appreciably smaller and the enthalpy was less negative in DCE than in CCl<sub>4</sub>, implying that DMSO is more strongly solvated in polar DCE than in nonpolar CCl<sub>4</sub>.

## 1. Introduction

Molecular complexes in solution have been extensively studied by UV-visible, IR and NMR spectroscopic techniques<sup>1-3</sup>), but relatively less by calorimetry<sup>4,5</sup>), owing to difficulties in precise calorimetric measurements and in the analysis of data. A recent development in calorimetric techniques combined with electronic computers allows us to use this method for studying various types of solution equilibria. We have so far carried out a series of calorimetric studies on complexation equilibria between some transition metal (II) ions and halide ions in non-aqueous solvents<sup>6</sup>). A combination of an automatic calorimetry system for obtaining precise calorimetric data and a high-speed computer for the simultaneous determination of the formation constants and enthalpies by analyzing the data has been successful in these studies.

In this paper we report a calorimetric study on adduct formation equilibria of dimethyl sulfoxide (DMSO) with 2,2,2-trifluoroethanol (TFE) in 1,2-dichloroethane (DCE) at 25°C.\* TFE is known to be a strong electron acceptor (the acceptor number  $A_N = 53.5^7$ ), but a very weak donor (the donor number  $D_N \sim 0$ )<sup>8</sup>). DMSO has a stronger donicity ( $D_N = 29.8$ ) but a weaker electron-accepting ability ( $A_N = 19.3$ ) than TFE<sup>9</sup>). Besides, both DMSO and TFE are polar molecules with dipole moments  $14 \times 10^{-30}$  C m<sup>10</sup>) and  $6.8 \times 10^{-30}$  C m<sup>11</sup>), respectively.

\*  $t/^\circ\text{C} = T/\text{K} - 273.15$ 

IR studies revealed the formation of a hydrogen-bonding adduct between DMSO and TFE in CCl<sub>4</sub><sup>12,13</sup>). The thermodynamic parameters for the 1:1 DMSO-TFE adduct thus determined in DCE are compared with those in CCl<sub>4</sub>. We also describe in some detail the on-line controlled calorimetry system used and the procedure for a nonlinear least-squares analysis of calorimetric data.

## 2. Experimental

### 2.1 Reagents

All chemicals used were of reagent grade. Dimethyl sulfoxide (DMSO) was refluxed with CaH<sub>2</sub>, distilled at 60°C and 0.7 kPa, and then stored over molecular sieve 4A 1/16. Water content of DMSO was less than 160 ppm by Karl Fischer test. 2,2,2-Trifluoroethanol (TFE) was first treated with potassium carbonate, and then distilled at 73.6°C and atmospheric pressure before use. 1,2-Dichloroethane (DCE) was refluxed with molecular sieve 4A 1/16, and then distilled at 83.5°C and atmospheric pressure. All test solutions were prepared in a dry box over P<sub>2</sub>O<sub>5</sub>. No ionic medium was added to the solutions.

### 2.2 Measurements

Calorimetric measurements were carried out with a twin-type calorimeter (Tokyo Riko) regulated at 25.0°C with a precision of 0.003°C. Two Teflon-coated stainless steel vessels were inserted into an aluminium block, and the

temperature difference between the sample and reference vessels was measured with thermistors. Signals from the thermistors were amplified and monitored by using a digital multimeter TR6861 (Advantest) with an accuracy ±0.02%. The initial test solution (50 cm<sup>3</sup>) was placed in the vessel filled with dry nitrogen gas and isolated from moisture with a drying tube. The arrangement within the vessel is illustrated in Fig. 1. A couple of thermistors, a heater, a cooler and a

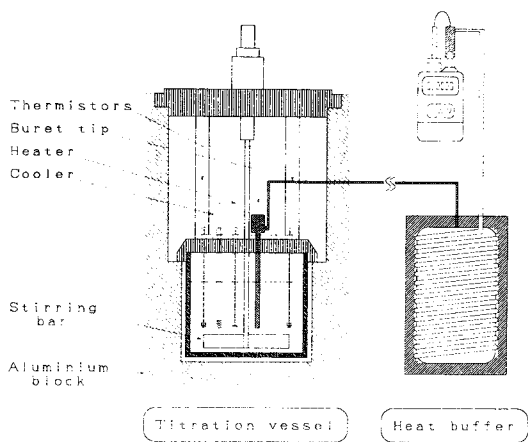


Fig. 1 Reaction vessel arrangement for calorimetric titrations.

buret tip are dipped in each solution. By the use of the two thermistors in each vessel, the temperature changes could be measured with an error of ±0.03 mK. The titrant solution (0.5-2.5 cm<sup>3</sup>) was introduced into the vessel through a heat buffer by using an autoburet (Kyoto Electronics) with an accuracy ±0.003 cm<sup>3</sup>.

A block diagram for the data acquisition and calorimeter control systems is shown in Fig. 2.

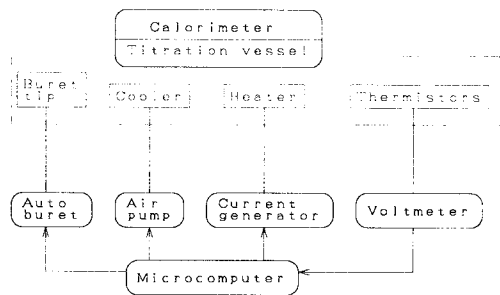


Fig. 2 Block diagram of the on-line controlled calorimetry system.

In nonadiabatic conditions, temperature rises by an exothermic reaction, and then falls when the evolution of heat becomes small. A profile of temperature changes at each titration point is shown in Fig. 3, which consists of four regions (a)-(d): (a) temperature rises by the

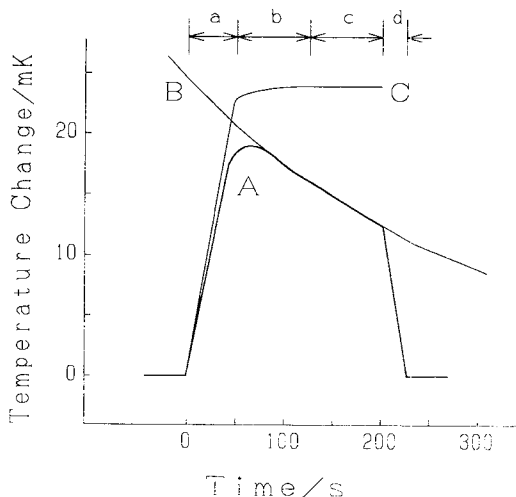


Fig. 3 Profile of temperature changes at one titration point. (A) An observed curve. (B) A calculated exponential decay curve. (C) A hypothetical curve to be obtained in adiabatic conditions.

addition of an aliquot of titrant; (b) with a weak evolution of heat, temperature begins to fall; (c) without an evolution of heat, temperature decreases exponentially to approach a thermal equilibrium; and (d) the vessel is cooled or heated to attain an equilibrium temperature  $T_o$  quickly.

The temperature change  $\theta(t) = T(t) - T_o$  measured every second in the regions (a)-(c) is expressed by Eq. 1 according to Newton's law of cooling:

$$d[(C_{p0} + C_p V) \theta(t)]/dt = \tilde{q}(t) - \lambda \theta(t) \quad (1)$$

where  $C_{p0}$ ,  $C_p$ ,  $V$ ,  $\tilde{q}(t)$  and  $\lambda$  denote the heat capacity of the blank vessel, the volumetric heat capacity, volume of the solution, the heat evolved per unit time and the heat-transfer coefficient, respectively. The total heat  $q_{obsd}$  is thus calculated by integration.

$$q_{\text{obsd}} = \int_0^t \tilde{q}(\tau) d\tau$$

$$= (C_{p0} + C_p V)\theta(t) + \int_0^t \lambda\theta(\tau) d\tau \quad (2)$$

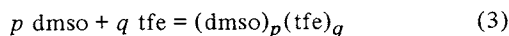
The parameters  $C_{p0} + C_p V$  and  $\lambda$  have been determined with a standard heater before each titration. Temperature changes calculated from  $q_{\text{obsd}}/(C_{p0} + C_p V)$ , shown by line C in Fig. 3, should become constant in the region (c) where the reaction is completed and no heat evolved. This constancy assures that the measurements of the temperature changes and the analysis of data have been satisfactorily carried out. An electrical calibration showed that the heat was calculated from Eq. 2 with a maximum error of  $\pm 0.5\%$ . In the present systems  $q_{\text{obsd}}$  ranged from 0.3 to 2.0 J with an uncertainty of  $\pm 0.015$  J.

The observed heats were further corrected for heats of dilution of the titrant, which had been determined by separate experiments. The major part of observed heats of dilution (0.2-0.4 J) may be due to the partial self-association of solute molecules in the titrant. The titrant solution is thus diluted to result in the dissociation of the self-associated molecules to monomers, since the concentration of the solute in the test solution was low throughout the measurements, as will be discussed in a later section. Heats of dilution may also involve the contributions arising from a small temperature difference between the sample and titrant solutions, and from the change in the liquid-vapor equilibrium upon titration. The former was found to be small (less than 0.05 J), and the latter was completely negligible (0.0007 J) according to Raoult's law.

Enthalpy of neutralization in aqueous solution has previously been measured and was in good agreement with the literature values<sup>14</sup>.

### 2.3 Data Analysis

Calorimetric data obtained were analyzed by assuming complexation equilibria as follows:



$$\beta_{pq} = [(\text{dmsso})_p (\text{tfe})_q] / [\text{dmsso}]^p [\text{tfe}]^q \quad (4)$$

Total concentrations of DMSO and TFE at each titration point,  $C_{\text{DMSO}}$  and  $C_{\text{TFE}}$ , respectively,

are expressed as

$$C_{\text{DMSO}} = [\text{dmsso}] + \sum p\beta_{pq} [\text{dmsso}]^p [\text{tfe}]^q \quad (5)$$

$$C_{\text{TFE}} = [\text{tfe}] + \sum q\beta_{pq} [\text{dmsso}]^p [\text{tfe}]^q \quad (6)$$

We assumed that the activity coefficients of the species were practically kept constant over the concentration range examined in this work. Distribution of the species in solution can be calculated with Eqs. 4-6, if  $\beta_{pq}$ 's are given.

The reaction heat  $q_{i,\text{calcd}}$  at the  $i$ th titration point is calculated from the overall formation constants  $\beta_{pq}$  and the enthalpies  $\Delta H_{\beta_{pq}}^0$  of the species  $(\text{dmsso})_p (\text{tfe})_q$ :

$$q_{i,\text{calcd}} = - \sum \Delta H_{\beta_{pq}}^0 (V_i \beta_{pq} [\text{dmsso}]_i^p [\text{tfe}]_i^q - V_{i-1} \beta_{pq} [\text{dmsso}]_{i-1}^p [\text{tfe}]_{i-1}^q) \quad (7)$$

Formation constants and enthalpies of the postulated complexes were simultaneously determined<sup>15</sup> by minimizing the error-square sum  $U = \sum (q_{i,\text{obsd}} - q_{i,\text{calcd}})^2$  with a least-squares program MQCAL. The optimization process of MQCAL is described in Fig. 4. The main iterative procedure

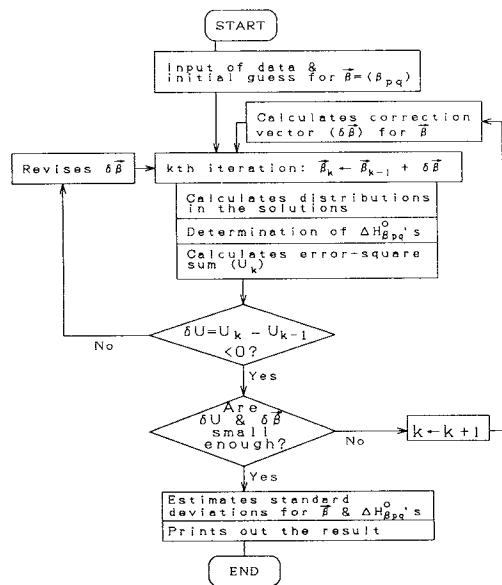


Fig. 4 Flow diagram of optimizing process of MQCAL.

in MQCAL searches for a suitable set of formation constants, expressed as a vector  $\vec{\beta} = (\beta_{pq})$ , according to an algorithm proposed by Marquardt for a nonlinear optimization process.<sup>16)</sup> At the  $k$ th iteration, a correction vector  $\delta\vec{\beta}$  is estimated and a new vector,  $\vec{\beta}_k = \vec{\beta}_{k-1} + \delta\vec{\beta}$ , is assumed. After the calculation of the distributions of species at all the titration points by using  $\vec{\beta}_k$ , the enthalpies  $\Delta H_{\beta pq}^{\circ}$ 's are readily optimized by a normal linear least-squares method, because  $q_{i, \text{calcd}}$  in Eq. 7 is expressed as a linear combination of enthalpies. The error-square sum  $U_k$  is then calculated. If  $U_k < U_{k-1}$ ,  $\vec{\beta}_k$  is accepted to be used for a next iteration. If  $U_k > U_{k-1}$ ,  $\delta\vec{\beta}$  is revised and another  $\vec{\beta}_k$  is proposed. The iterative cycle will be finished when both  $U_k$  and  $\vec{\beta}_k$  become practically unchanged ( $|\delta U/U| < 10^{-4}$ ,  $|\delta\beta_{pq}/\beta_{pq}| < 2.3 \times 10^{-4}$ ).

### 3. Results and Discussion

Titration were performed in two ways; (i) a DMSO solution (15-50 mmol dm<sup>-3</sup>) was titrat-

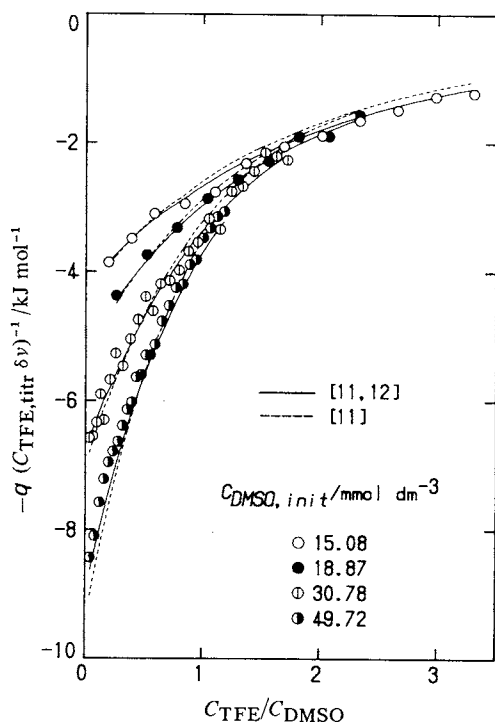


Fig. 5 Calorimetric titration curves of dimethyl sulfoxide (DMSO) solutions titrated with a 0.1 mol dm<sup>-3</sup> 2,2,2-trifluoroethanol (TFE) solution in 1,2-dichloroethane at 25°C. Initial concentrations of DMSO,  $C_{\text{DMSO}, \text{init}}$ , are given.

ed with a 0.1 mol dm<sup>-3</sup> TFE solution, and (ii) a TFE solution (24-56 mmol dm<sup>-3</sup>) was titrated with a 0.1 mol dm<sup>-3</sup> DMSO solution. Titration curves thus obtained are shown in Figs. 5 and 6,

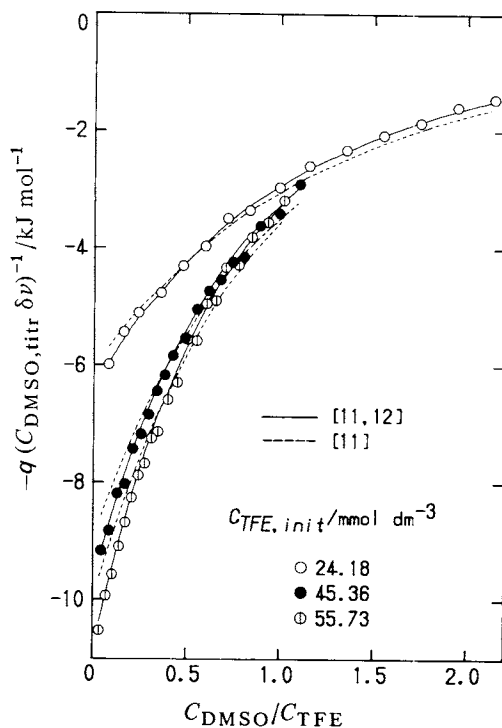


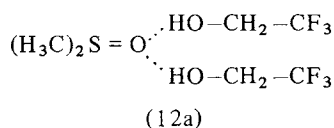
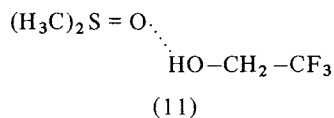
Fig. 6 Calorimetric titration curves of 2,2,2-trifluoroethanol (TFE) solutions titrated with a 0.1 mol dm<sup>-3</sup> dimethyl sulfoxide (DMSO) solution in 1,2-dichloroethane at 25°C. Initial concentrations of TFE,  $C_{\text{TFE}, \text{init}}$ , are given.

respectively. In Fig. 5 we plotted the normalized enthalpy of reaction  $-q(C_{\text{TFE}, \text{titr}} \delta v)^{-1}$  against the concentration ratio,  $C_{\text{TFE}}/C_{\text{DMSO}}$ , where  $q$ ,  $\delta v$ ,  $C_{\text{TFE}}$  and  $C_{\text{DMSO}}$  represent the heat evolved, the volume of the titrant added, and the total concentrations of TFE and DMSO in the sample solution, respectively, at each titration point, and  $C_{\text{TFE}, \text{titr}}$  is the total concentration of TFE in the titrant. An analogous plot is made in Fig. 6.

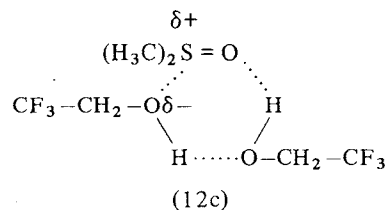
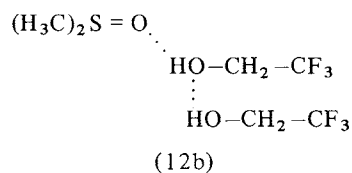
The self-association of DMSO molecules owing to the dipole-dipole interaction<sup>17)</sup>, and that of TFE molecules owing to the formation of hydrogen bonds<sup>18)</sup>, have been suggested by IR measurements in CCl<sub>4</sub>. The formation constants of the dimers were reported to be 0.9 mol<sup>-1</sup>

dm<sup>3</sup> for DMSO<sup>17)</sup> and 0.65 mol<sup>-1</sup> dm<sup>3</sup> for TFE<sup>18)</sup> in CCl<sub>4</sub>. In DCE, although the corresponding values are not reported, the self-association of DMSO and TFE may also occur to some extent. However, we expect that the extent of self-association may be similar or even smaller in DCE than in CCl<sub>4</sub>, considering the larger dielectric constant and acceptor number of the former solvent ( $\epsilon = 10.1$ ,  $A_N = 16.7$ ) than those of the latter ( $\epsilon = 2.2$ ,  $A_N = 8.6$ )<sup>8)</sup>. Then, for both DMSO and TFE the extent of dimerization may be less than 5% of the total concentration in the DCE solutions examined. Therefore we did not take into account these species in the course of the analysis.

DMSO has two lone-pairs on the oxygen atom which are capable of forming hydrogen bonds with TFE molecules. Therefore the following structures, (11) and (12a), are likely as the hydrogen-bonding 1:1 and 1:2 adducts between DMSO and TFE molecules, respectively:



Other types of structure, (12b) and (12c), might also be plausible for the 1:2 adduct, as has been suggested for the 1:2 analogue of sulfoxides with phenol in toluene by an IR study:<sup>19)</sup>



These three structures for the 1:2 adduct are not distinguishable in the calorimetric study, how-

ever.

In the course of the least-squares analysis, formation of not only these species but also other species were assumed. Table 1 summarizes the results of the formation constants and

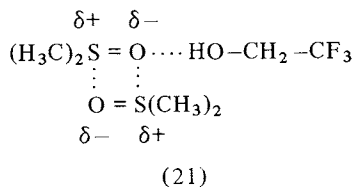
Table 1 Formation Constants,  $\log(\beta_{pq}/\text{mol}^{1-p-q} \text{dm}^3(p+q-1))$ , and Enthalpies,  $\Delta H_{\beta_{pq}}^0/\text{kJ mol}^{-1}$ , for the Reaction,  $p(\text{CH}_3)_2\text{SO} + q\text{CF}_3\text{CH}_2\text{OH} = ((\text{CH}_3)_2\text{SO})_p(\text{CF}_3\text{CH}_2\text{OH})_q$ , in 1,2-Dichloroethane at 25°C.

Case (pq)	(11)	(11,12)	(11,21)
$\log \beta_{11}$	1.23 (0.10)	1.28 (0.09)	1.13 (0.08)
$\log \beta_{12}$	-	1.86 (0.50)	-
$\log \beta_{21}$	-	-	1.33 (1.14)
$\Delta H_{\beta_{11}}^0$	-20.1 (2.7)	-18.1 (2.4)	-24.7 (3.3)
$\Delta H_{\beta_{12}}^0$	-	-23 (17)	-
$\Delta H_{\beta_{21}}^0$	-	-	32 (109)
$\chi^2$	0.563	0.182	0.184
$R^b$	0.054	0.031	0.031

The values in parentheses refer to three standard deviations. For the analysis 126 experimental points were used. a) Error-square sum. b) Hamilton R factor.

enthalpies obtained for the three sets of adducts which gave relatively small values of the Hamilton R factor.

In the case (11) assuming formation of the 1:1 adduct only, the curves calculated with the best-fit parameters considerably deviate from the experimental points (the broken lines in Figs. 5 and 6). This implies that not only the 1:1 adduct but also some other species coexist in the solution. In the case (11, 12) assuming the formation of (dms)(tfe)<sub>2</sub> in addition to the 1:1 adduct, the calculated curves well reproduce the experimental points (the solid lines in Figs. 5 and 6). The Hamilton R factor for the case (11, 12) is 3.1%, which is appreciably smaller than that for the case (11) (5.4%). The case (11, 21) assuming the 1:1 adduct and (dms)<sub>2</sub>(tfe) resulted in a similar value of the R factor to that of the case (11, 12). However, the formation of (dms)<sub>2</sub>(tfe) with such a structure as



may be ambiguous in dilute solutions, if we take into account the weak dipole-dipole interaction between DMSO molecules within the structure. Thus we propose the case (11, 12) in Table 1.

It is noted that the formation of (dmsO)(tfe)<sub>2</sub> has been also suggested in CCl<sub>4</sub> by IR spectroscopy<sup>12</sup>).

The formation constant  $\beta_{11}$  and enthalpy  $\Delta H_{\beta_{11}}^{\circ}$  of formation of (dmsO)(tfe) obtained in DCE may be compared with those in CCl<sub>4</sub>. Karjalainen and Ruostesuo obtained the values  $\beta_{11} = 148 \text{ mol}^{-1} \text{ dm}^3$  ( $\log \beta_{11} = 2.17$ ) and  $\Delta H_{\beta_{11}}^{\circ} = -23.1 \text{ kJ mol}^{-1}$  in CCl<sub>4</sub> at 25°C by IR measurements<sup>13</sup>). Sherry and Purcell obtained the values  $\beta_{11} = 141 \text{ mol}^{-1} \text{ dm}^3$  ( $\log \beta_{11} = 2.15$ ) and  $\Delta H_{\beta_{11}}^{\circ} = -26.2 \text{ kJ mol}^{-1}$  in CCl<sub>4</sub> at 24°C by calorimetry<sup>20</sup>). In DCE, the  $\log \beta_{11}$  value (1.28) is significantly smaller and the  $\Delta H_{\beta_{11}}^{\circ}$  value (-18.1 kJ mol<sup>-1</sup>) is less negative than the corresponding values in CCl<sub>4</sub>. A similar conclusion has been obtained for the adduct formation of DMSO with phenol in DCE and CCl<sub>4</sub><sup>2</sup>). The dipole-dipole interaction of DMSO with solvent molecules may be larger for DCE than for CCl<sub>4</sub>, since DCE is a polar solvent (dipole moment is  $6.1 \times 10^{-30} \text{ C m}$ )<sup>21</sup>) but CCl<sub>4</sub> is not. In addition, the electron-accepting ability of DCE ( $A_N = 16.7$ ) is larger than that of CCl<sub>4</sub> ( $A_N = 8.6$ )<sup>8</sup>). Consequently, DMSO molecules may be more strongly solvated in DCE than in CCl<sub>4</sub>. On the other hand, the dipole moment of TFE is relatively small, and the donicities of DCE and CCl<sub>4</sub> are weak ( $D_N \sim 0$ )<sup>8</sup>), so that TFE molecules may be solvated weakly in both solvents. The solvation of DMSO-TFE adducts is also expected to be weak, since the polar sites are no longer exposed to the solvent molecules. The adduct formation between DMSO and TFE in DCE thus requires more energy to break the interaction between DMSO and DCE, and thus a smaller formation constant and a less negative enthalpy in DCE than those in CCl<sub>4</sub> may result.

We are grateful to the Institute for Molecular Science in Okazaki for a financial support for the construction of the calorimetry system.

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