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(Citation)

Analytical Sciences, 37(12):1783-1787

(Issue Date)

2021-12

(Resource Type)

journal article

(Version)

Version of Record

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(URL)

<https://hdl.handle.net/20.500.14094/90008888>



A Theoretical Approach to the Fluorophilicity of Ions *via* the Gibbs Energy of Ion Transfer at the Fluorous Solvent/Water Interface

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The non-Bornian solvation model has been applied to a theoretical consideration of the Gibbs free energy for the transfer of fluorinated anions, non-fluorinated cations, and non-fluorinated anions at the 2*H*,3*H*-decafluoropentane (DFP)/water (W) and 1,2-dichloroethane (DCE)/W interfaces. According to our previous experimental results, the fluorinated anions are more stable in DFP than DCE, while the non-fluorinated cations and anions are less stable in DFP. To understand this characteristic feature of DFP, energy decomposition analyses have been performed for the *hypothetical* transfer of ions at the DFP/DCE interface. In conclusion, the characteristics of DFP as a fluorous solvent should be explained in terms of the higher repulsive interaction of the solvent molecule with ions, particularly with non-fluorinated ions.

Keywords Gibbs free energy of ion transfer, fluorous solvent/water interface, non-Bornian solvation model, energy decomposition

(Received June 7, 2021; Accepted July 7, 2021; Advance Publication Released Online by J-STAGE July 16, 2021)

Introduction

The term “fluorous” was first introduced by Horváth and Rábai, as the analogue to the term “aqueous”, meaning dissolve in fluorocarbon solvents.¹ However, it should be noted that fluorocarbons are hardly miscible not only with water but also with common organic solvents such as toluene, acetone, and methanol.^{2–4} Thus, “fluorous” cannot be considered simply as “non-aqueous”. Regarding the affinity of fluorinated compounds to fluorous solvents, Gladysz and Emnet⁵ have emphasized: despite the “like dissolves like” paradigm, it is misleading to view fluorous solvents as capable of highly attractive or repulsive intermolecular interactions. Rather, they facilitate what might be viewed as a “molecular xenophobia” —the separation of non-fluorous molecules capable of stronger intermolecular interactions from fluorous molecules capable of only feeble ones.

In previous papers,^{6–9} our group reported the applicability of a fluorous solvent, DFP (2*H*,3*H*- or 1,1,1,2,3,4,4,5,5,5-decafluoropentane), as a non-aqueous solvent for liquid-liquid electrochemistry. Using the polarized DFP/water (W) interface, the apparent or formal Gibbs energies¹⁰ ($\Delta_{\text{tr}}G_{\text{W} \rightarrow \text{O}}^{\circ}$) for the transfer of various ions including fluorinated anions from W to O (=DFP) were determined voltammetrically or potentiometrically. The values of $\Delta_{\text{tr}}G_{\text{W} \rightarrow \text{O}}^{\circ}$ were then compared with those from W to non-fluorinated organic solvents such as nitrobenzene (NB) and 1,2-dichloroethane (DCE). It was suggested that the fluorophilicity of ions should be a physical property incompatible with lipophilicity as well as hydrophilicity.⁷ Previous authors^{11,12}

successfully proposed some empirical models for predicting the fluorophilicity of neutral solutes as the natural logarithm of partition coefficient ($\ln P$) in fluorous biphasic systems, *e.g.*, the perfluoro(methylcyclohexane)/toluene system. Nevertheless, there has been no clear interpretation of fluorophilicity based on intermolecular interactions.

In this study, we have applied the non-Bornian solvation model^{13,14} to study the effects of fluorine atoms of fluorinated solvents or ions on interfacial ion-transfer processes. In the theoretical analysis with the non-Bornian model, the solvation energy of an organic ion is evaluated using the local electric field on the ion’s minute surface (E_i with $i = 1, 2, 3, \dots$), which can be obtained through DFT calculation. By multivariate regression analyses with the experimental data, the semi-empirical equations have been obtained for rather accurate evaluation of the standard Gibbs energy ($\Delta_{\text{tr}}G_{\text{W} \rightarrow \text{O}}^{\circ}$) for ion transfer (the mean absolute errors were 2–3 kJ mol^{–1} for the NB/W¹³ and DCE/W¹⁴ interfaces). In this study, a similar approach has been taken with regard to the experimentally determined formal Gibbs energies ($\Delta_{\text{tr}}G_{\text{W} \rightarrow \text{O}}^{\circ}$) for the transfer of fluorinated and non-fluorinated ions at the DFP/W and DCE/W interfaces. However, the experimental $\Delta_{\text{tr}}G_{\text{W} \rightarrow \text{O}}^{\circ}$ would be affected by ion-pairing in the non-aqueous phase, being somewhat different from the corresponding $\Delta_{\text{tr}}G_{\text{W} \rightarrow \text{O}}^{\circ}$, as described previously.⁷ Therefore, we cannot make a meticulous discussion using $\Delta_{\text{tr}}G_{\text{W} \rightarrow \text{O}}^{\circ}$, because of scarce information on ion-pairing equilibria in water-saturated DFP as well as DCE. However, since the ion-pairing effect is possibly a secondary one, it seems significant to apply the non-Bornian model to $\Delta_{\text{tr}}G_{\text{W} \rightarrow \text{O}}^{\circ}$ by simply assuming $\Delta_{\text{tr}}G_{\text{W} \rightarrow \text{O}}^{\circ} = \Delta_{\text{tr}}G_{\text{W} \rightarrow \text{O}}^{\circ}$. In fact we could obtain valuable information for understanding the characteristic intermolecular interactions of fluorous molecules.

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Table 1 Experimental and theoretical values of $\Delta_{tr}G_{W \rightarrow DFP}^{\circ}$ and $\Delta_{tr}G_{W \rightarrow DCE}^{\circ}$ (in kJ mol^{-1}) for the transfer of fluorinated anions at the DFP/W and DCE/W interfaces (25°C)

Ion	$\Delta_{tr}G_{W \rightarrow DFP}^{\circ}$			$\Delta_{tr}G_{W \rightarrow DCE}^{\circ}$			$\Delta_{tr}G_{DCE \rightarrow DFP}^{\circ a}$
	Exp.	Theor. ^b	Diff.	Exp.	Theor. ^b	Diff.	Exp.
(1) BF_4^-	10.9 ^c	17.3	-6.4	9.4 ^c	6.7	2.7	1.5
(2) PF_6^-	0.4 ^d	1.1	-0.7	-0.8 ^d	4.8	-5.6	1.2
(3) CF_3COO^-	25.5 ^c	22.0	3.5				
(4) $\text{C}_2\text{F}_5\text{COO}^-$	18.8 ^e	15.7	3.1	21.8 ^e	20.4	1.4	-3.0
(5) $\text{C}_3\text{F}_7\text{COO}^-$	13.8 ^e	11.2	2.6	18.1 ^e	16.3	1.8	-4.3
(6) $\text{C}_4\text{F}_9\text{COO}^-$	8.6 ^e	7.4	1.2	15.2 ^e	13.1	2.1	-6.6
(7) $\text{C}_5\text{F}_{11}\text{COO}^-$	4.4 ^e	3.5	0.9	11.1 ^e	10.2	0.9	-6.7
(8) $\text{C}_6\text{F}_{13}\text{COO}^-$	-2.0 ^e	-0.4	-1.6	7.0 ^e	7.1	-0.1	-9.0
(9) $\text{C}_7\text{F}_{15}\text{COO}^-$	-7.0 ^e	-4.1	-2.9	1.8 ^e	4.3	-2.5	-8.8
(10) $\text{C}_8\text{F}_{17}\text{COO}^-$	-12.3 ^e	-7.9	-4.4	-2.5 ^e	1.4	-3.9	-9.8
(11) $\text{C}_8\text{F}_{17}\text{SO}_3^-$	-17.0 ^f	-23.7	6.7	-11.5 ^f	-17.6	6.1	-5.5
(12) $(\text{CF}_3\text{SO}_2)_2\text{N}^-$	-12.9 ^e	-12.8	-0.1	-7.5 ^c	-6.6	-0.9	-5.4
(13) $(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}^-$	-20.9 ^e	-20.9	0.0	-13.7 ^c	-12.8	-0.9	-7.2
(14) $(\text{C}_3\text{F}_7\text{SO}_2)_2\text{N}^-$	-30.6 ^c	-28.6	-2.0	-19.9 ^c	-18.8	-1.1	-10.7

a. For the hypothetical transfer of ions at the DFP/DCE interface. b. Obtained from Eq. (2) with the coefficients shown in Table 2. c. From Ref. 7. d. Remeasured by the previous method.⁷ e. From Ref. 9. f. From Ref. 8.

Experimental Data

Table 1 shows the values of $\Delta_{tr}G_{W \rightarrow DFP}^{\circ}$ and $\Delta_{tr}G_{W \rightarrow DCE}^{\circ}$ that were previously reported for 14 fluorinated anions⁷⁻⁹ (however, the data for an anion, 2, have been revised). The corresponding values for 12 non-fluorinated cations⁷⁻⁹ and 16 non-fluorinated anions^{7,9} are shown in Tables S1 and S2 (Supporting Information).

Calculation Methods

DFT calculations were performed using the Gaussian09 program package. Using the B3LYP hybrid DFT method with the 6-311++G(2d,p) basis set, geometries of ions in vacuum were optimized and partial atomic charges were computed by three different methods, Mulliken,¹⁵ Merz-Kollman,^{16,17} (MK), and natural population analysis¹⁸ (NPA). The numerical sums in a regression equation {e.g., $\sum S_i$, $\sum_{E_i \leq \xi} S_i E_i$, etc. in Eq. (2); see below} were then obtained by the previously reported subprogram.¹³ In the subprogram, E_i can be obtained on the van der Waals (vdW) surface of an ion and on the solvent-accessible surface^{19,20} (SAS) being apart from the vdW surface by 0.14 nm (=the radius of water molecule). Finally, multivariate regression analyses on Eq. (2) or (3) (see below) were performed with the experimental ion-transfer energies using Microsoft Excel 2010.

Results and Discussion

As described above, the following discussion has been presented by assuming $\Delta_{tr}G_{W \rightarrow O}^{\circ} = \Delta_{tr}G_{W \rightarrow O}^{\circ}$ ($O = \text{DFP}$ and DCE). In Fig. 1, we have plotted the experimental values of $\Delta_{tr}G_{DCE \rightarrow DFP}^{\circ}$ ($= \Delta_{tr}G_{W \rightarrow DFP}^{\circ} - \Delta_{tr}G_{W \rightarrow DCE}^{\circ}$) against those of $\Delta_{tr}G_{W \rightarrow DCE}^{\circ}$ for the three different ion groups (see also Tables 1, S1, and S2 for the values of $\Delta_{tr}G_{DCE \rightarrow DFP}^{\circ} = \Delta_{tr}G_{DCE \rightarrow DFP}^{\circ}$). Almost all the fluorinated anions show negative $\Delta_{tr}G_{DCE \rightarrow DFP}^{\circ}$ values regardless of whether they are hydrophilic (with positive $\Delta_{tr}G_{W \rightarrow DCE}^{\circ}$ values) or hydrophobic (with negative ones). This shows that the fluorinated anions should be more stable in DFP than DCE.

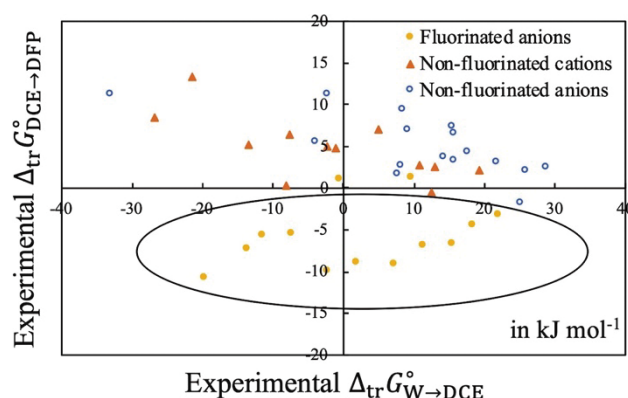


Fig. 1 Plots of $\Delta_{tr}G_{DCE \rightarrow DFP}^{\circ}$ against $\Delta_{tr}G_{W \rightarrow DCE}^{\circ}$ for three different ion groups: fluorinated anions, non-fluorinated cations, and non-fluorinated anions. The plots for almost all of the fluorinated anions are included in the region indicated by an ellipse.

For the transfer of 24 non-fluorinated anions at the DCE/W interface, we previously obtained¹⁴

$$\Delta_{tr}G_{W \rightarrow O}^{\circ} = \Delta A \sum S_i + \Delta B \sum_{E_i \leq \xi} S_i E_i + \Delta C \sum_{E_i \leq \xi} S_i E_i^2 + \Delta B_+ \sum_{E_i > 0} S_i E_i + \Delta C_+ \sum_{E_i > 0} S_i E_i^2 + \Delta B_- \sum_{\xi_- < E_i < 0} S_i E_i + \Delta C_- \sum_{\xi_- < E_i < 0} S_i E_i^2. \quad (1)$$

The first term on the r.h.s. of this equation is proportional to the ionic surface area ($\sum S_i$), which is originated from the so-called cavity formation energy, though being influenced by E_i -independent terms of the short-range ion-solvent interactions. The second and third terms represent the contributions from the much negatively charged surfaces with $E_i \leq \xi_-$ (threshold value). Such surfaces are selectively hydrated in the O phase¹³ and their effects are included in the two terms. The fourth and fifth terms represent the contributions from positively charged surfaces with $E_i > 0$. The respective terms are mainly due to ion-dipole (Coulomb) and ion-induced dipole (polarization) interactions. In a similar manner, the last two terms show the contributions from moderately negatively charged surfaces with $\xi_- \leq E_i \leq 0$.

An equation similar to Eq. (1) was also obtained for 26 non-fluorinated cations.¹⁴

The seven coefficients (ΔA , ΔB^* , ΔC^* , ΔB_+ , ΔC_+ , ΔB_- , and ΔC_-) in Eq. (1) were previously determined with appropriate precision as adjusting parameters in multiple regression analysis; In this study, however, we could not obtain any set of statistically significant coefficients by using Eq. (1), because the number of data (*i.e.*, 14 for fluorinated anions; 12 for non-fluorinated cations; 16 for non-fluorinated anions) is small for a relatively large number of coefficients, namely seven. So, the number of coefficients was reduced from seven to four by omitting the second-order terms in E_i (*i.e.*, $\Delta C^* \sum S_i E_i^2$, $\Delta C_+ \sum S_i E_i^2$, and $\Delta C_- \sum S_i E_i^2$). Satisfactory regression results were then obtained for all the three ion groups. The regression equations obtained for the DFP/W and DCE/W interfaces are expressed as:

For both fluorinated and non-fluorinated anions:

$$\Delta_{tr} G_{W \rightarrow O}^\circ = \Delta A \sum S_i + \Delta B^* \sum_{E_i \leq \xi_-} S_i E_i + \Delta B_- \sum_{\xi_- < E_i < 0} S_i E_i + \Delta B_+ \sum_{E_i > 0} S_i E_i. \quad (2)$$

For non-fluorinated cations:

$$\Delta_{tr} G_{W \rightarrow O}^\circ = \Delta A \sum S_i + \Delta B^* \sum_{E_i \geq \xi_+} S_i E_i + \Delta B_+ \sum_{0 < E_i < \xi_+} S_i E_i + \Delta B_- \sum_{E_i < 0} S_i E_i. \quad (3)$$

In the present analysis with these equations, we investigated the performance of regression analysis in all combinations of three different atomic groups (Mulliken, MK, and NPA) and two different molecular surfaces (vdW and SAS). Additionally, in the respective six combinations, the value of ξ_- or ξ_+ was optimized for each ion group in the DFP/W and DCE/W systems (note that the ξ -values are dependent on the nature of non-aqueous solvent and the sign of ion charge;¹³ although the values might be independent of whether the ion is fluorinated or not, they were tentatively optimized for each ion group separately). As a result, the best overall performance was obtained when using the combination of MK-vdW, although slightly better performances were obtained for other combinations in a few individual cases (*e.g.*, the combination of NPA-vdW for fluorinated anions). In the following discussion, the combination of MK-vdW is commonly used in order to compare the energy values of the respective terms in regression equations. In Table 2, the optimized coefficients in Eq. (2) (where $\Delta_{tr} G_{W \rightarrow O}^\circ$ is in kJ mol⁻¹, S_i in nm², E_i in V nm⁻¹) and the performance of regression analyses are shown for the transfer of fluorinated anions at the DFP/W and DCE/W interfaces. Similar data are provided in Tables S3 and S4 (Supporting Information) for the transfer of non-fluorinated cations and anions. As shown in these tables, the mean absolute errors (MAE's) in the regression analyses are 2.0 – 3.9 kJ mol⁻¹, which correspond to the error of 20 – 40 mV in the standard ion-transfer potential, $\Delta_\phi^W \phi^\circ$ ($= \Delta_{tr} G_{W \rightarrow O}^\circ / F$). Since the typical experimental error in voltammetric measurements is 10 – 20 mV, it has been suggested that the non-Bornian solvation model is available for accurate and reliable estimation of $\Delta_{tr} G_{W \rightarrow O}^\circ$ in the O/W systems studied.

Next, in order to clarify the characteristic feature of the fluorinated solvent, DFP, we performed an energy decomposition analysis for the Gibbs energy of the *hypothetical* transfer of an ion from DCE to DFP ($\Delta_{tr} G_{DCE \rightarrow DFP}^\circ$), which was calculated from the difference of the theoretical values of $\Delta_{tr} G_{W \rightarrow DFP}^\circ$ and $\Delta_{tr} G_{W \rightarrow DCE}^\circ$ being given by Eq. (2) or (3). In this calculation, however, the ξ_- or ξ_+ value for each ion group was chosen to give better accuracy on average from the values obtained for the DFP/W and DCE/W systems (*i.e.*, $\xi_- = -30$ V nm⁻¹ for fluorinated anions; $\xi_+ = 18$ V nm⁻¹ for non-fluorinated cations;

Table 2 Optimized coefficients in Eq. (2) and performance of regression analyses for the transfer of fluorinated anions at the DFP/W and DCE/W interfaces^a (25°C)

Coefficient	DFP/W		DCE/W	
	Optimized	SD ^b	Optimized	SD ^b
ΔA	-12.1	3.4	-8.67 (-10.1) ^c	3.14 (3.37) ^c
ΔB^*	-2.78	0.28	-3.64 (-2.81)	0.37 (0.31)
ΔB_-	-0.733	0.201	-0.749 (-0.469)	0.182 (0.199)
ΔB_+	-1.15	2.31	-1.57 (0.947)	1.98 (2.241)
ξ_- (V nm ⁻¹)	-30		-34 (-30)	
n^d	14		13	
R^{2e}	0.956		0.946 (0.941)	
MAE (kJ mol ⁻¹)	2.6		2.3 (2.4)	

a. Using the combination of MK-vdW.

b. Standard deviations.

c. The values in parentheses were obtained by using $\xi_- = -30$ V nm⁻¹.

d. Number of data.

e. Square of the correlation coefficient.

$\xi_- = -9$ V nm⁻¹ for non-fluorinated anions). Thus, $\Delta_{tr} G_{DCE \rightarrow DFP}^\circ$ could be decomposed into four terms in a similar manner as shown by Eq. (2) or (3):

For both fluorinated and non-fluorinated anions:

$$\Delta_{tr} G_{DCE \rightarrow DFP}^\circ = \Delta A \sum S_i + \Delta B^* \sum_{E_i \geq \xi_-} S_i E_i + \Delta B_- \sum_{\xi_- < E_i < 0} S_i E_i + \Delta B_+ \sum_{E_i > 0} S_i E_i. \quad (4)$$

For non-fluorinated cations:

$$\Delta_{tr} G_{DCE \rightarrow DFP}^\circ = \Delta A \sum S_i + \Delta B^* \sum_{E_i \geq \xi_+} S_i E_i + \Delta B_+ \sum_{0 < E_i < \xi_+} S_i E_i + \Delta B_- \sum_{E_i < 0} S_i E_i. \quad (5)$$

Tables S5 – S7 (Supporting Information) show the energy values for the respective terms (denoted by ΔA , ΔB^* , ΔB_- , and ΔB_+) together with the total energy, $\Delta_{tr} G_{DCE \rightarrow DFP}^\circ$ (denoted by ΔG). It has been found from the tables that the ΔA -term is negative for fluorinated anions, while it is positive for non-fluorinated cations and anions. This is also graphically presented in Fig. 2, where the results of energy decomposition are shown for three representative ions: **(9)** C₇F₁₅COO⁻, **(17)** Pr₄N⁺, and **(41)** Ph₄B⁻. Though the error bars (standard errors) are relatively large, the probability that the ΔA -term is negative is 67% for **9**, while the probability that the ΔA -term is positive is 88% for **17** and 83% for **41**. As also seen in Fig. 2, the sign of the ΔA -term coincides with the sign of ΔG , suggesting that the ΔA -term should be the principal factor that determines the stability of fluorinated and non-fluorinated ions in DFP or DCE. In the following, we will discuss the ΔA -term in more detail.

By taking the difference between the optimized ΔA -coefficients in $\Delta_{tr} G_{W \rightarrow DFP}^\circ$ and $\Delta_{tr} G_{W \rightarrow DCE}^\circ$ (in Tables 2, S1, and S2), we have estimated the coefficient of the ΔA -term of $\Delta_{tr} G_{DCE \rightarrow DFP}^\circ$ as $\Delta A = -2.1$, 3.0, and 4.5 kJ nm⁻² mol⁻¹ for fluorinated anions (with $\xi_- = -30$ V nm⁻¹), non-fluorinated cations (with $\xi_+ = 18$ V nm⁻¹), and non-fluorinated anions (with $\xi_- = -9$ V nm⁻¹), respectively. According to the previous papers,^{13,14} the coefficient of the ΔA -term ($\Delta A \sum S_i$) for $\Delta_{tr} G_{DCE \rightarrow DFP}^\circ$ is given by

$$\Delta A = A^{DCE} - A^{DFP}, \quad (6)$$

with

$$A^{DCE} = N^{DCE} \zeta_0^{DCE} - N^{DCE} U_{EX}^{DCE} - \gamma_1 - \gamma_2^{DCE}, \quad (7)$$

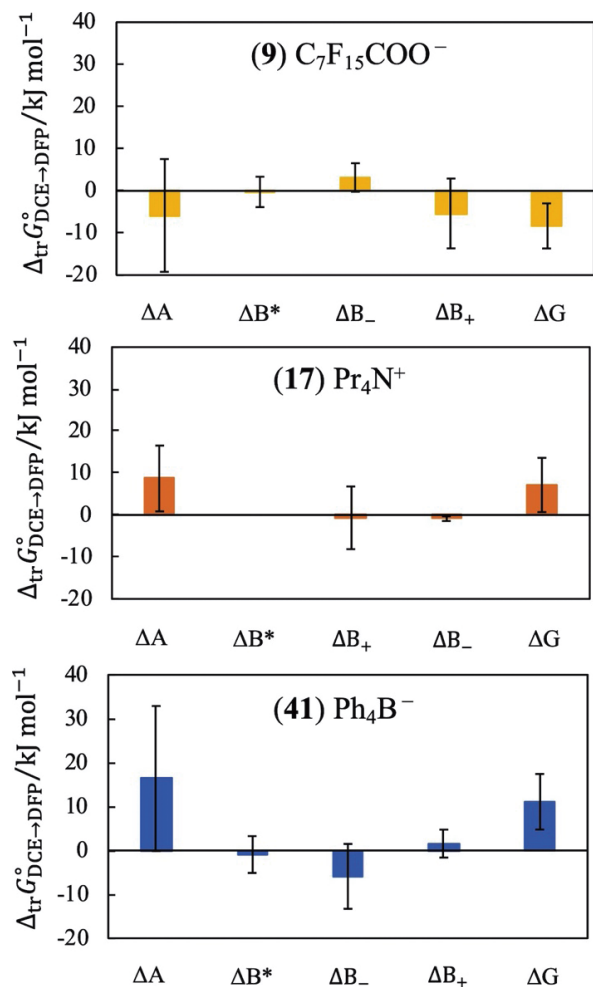


Fig. 2 Energy decomposition of $\Delta_{tr}G^{\circ}_{DCE \rightarrow DFP}$ for three representative ions: (9) $C_7F_{15}COO^-$, (17) Pr_4N^+ , and (41) Ph_4B^- . Error bars show the standard errors.

$$A^{DFP} = N^{DFP}\zeta_0^{DFP} - N^{DFP}U_{EX}^{DFP} - \gamma_1 - \gamma_2^{DFP}, \quad (8)$$

where N^{DCE} and N^{DFP} are the number of primary solvent molecules (DCE and DFP, respectively) in the unit surface area of an ion. The first term on the r.h.s. of Eq. (7) or (8) comes from the charge transfer (CT) between the ion and solvents in its vicinity, and ζ_0^{DCE} or ζ_0^{DFP} is the E_i -independent term of the CT interaction energy. Since we know that the CT interaction is usually not very significant, we will omit the relevant terms in the following equations. The second term in Eqs. (7) and (8) comes from the so-called exchange term (U_{EX}^{DCE} or U_{EX}^{DFP}), which represents the energy for the repulsion between an ion and a solvent molecule, more physically, for the short-range repulsion due to the overlap of electron distribution of the ion with that of the solvent, as described in detail in the previous *ab initio* SCF studies.^{21,22} Equations (7) and (8) also include parameters, γ_1 are γ_2^O (with $O = DCE$ or DFP), which are the “hypothetical” surface tension of an ion in vacuum and the surface tension of solvent O with its own vapor, respectively. Then, substituting Eqs. (7) and (8) into Eq. (6) yields

$$\Delta A = (\gamma_2^{DFP} - \gamma_2^{DCE}) + (N^{DFP}U_{EX}^{DFP} - N^{DCE}U_{EX}^{DCE}). \quad (9)$$

Here, the difference, $\gamma_2^{DFP} - \gamma_2^{DCE}$, can be estimated at 25°C from

the literature values^{23,24} of γ_2^{DFP} ($= 14.1 \text{ mN m}^{-1}$) and γ_2^{DCE} ($= 31.75 \text{ mN m}^{-1}$) as $\gamma_2^{DFP} - \gamma_2^{DCE} = -17.65 \text{ mN m}^{-1}$; however, when comparing with ΔA evaluated per mole, the value of $\gamma_2^{DFP} - \gamma_2^{DCE} = -10.6 \text{ kJ nm}^{-2} \text{ mol}^{-1}$ should be used. Using the above-estimated ΔA -values, the second term of Eq. (9) is then estimated as $(N^{DFP}U_{EX}^{DFP} - N^{DCE}U_{EX}^{DCE}) = 8.5, 13.6,$ and $15.1 \text{ kJ nm}^{-2} \text{ mol}^{-1}$ for the respective ion groups. Thus, this term is usually positive, but relatively small for the fluorinated anions.

Regarding N^{DFP} and N^{DCE} , we may perform the following estimation: The densities of DFP (MW: 252.05) and DCE (MW: 98.96) are 1.58 and 1.246 g cm^{-3} , respectively, at 25°C.⁷ Accordingly, the molar densities are 6.27 and $12.59 \text{ mmol cm}^{-3}$ for the respective solvents. Namely, the molar density of DFP is about half that of DCE. Considering this as well as the above-estimated values of $N^{DFP}U_{EX}^{DFP} - N^{DCE}U_{EX}^{DCE}$ we can conclude $U_{EX}^{DFP} > U_{EX}^{DCE}$ for all the ion groups. In this manner, DFP is more repulsive to ions than DCE. We would like to add that this is more pronounced when the ions are not fluorinated. Therefore, non-fluorinated ions are less stable in DFP than DCE (cf. Fig. 1).

Thus, the exchange term (U_{EX}) was found to be larger for non-fluorinated anions in fluororous solvents. In order to interpret this from a quantum chemical point of view, we have attempted to perform preliminary calculations of the intermolecular interaction energies of CF_4-CH_4 , CF_4-CF_4 , and CH_4-CH_4 using the Gaussian09 program. At this point, however, we have not yet obtained a clear picture of U_{EX} supporting our conclusion. The study is currently in progress.

Conclusions

The non-Bornian solvation model has been successfully applied to understand the characteristic feature of DFP, that is, the lower ability of solvation for ions. This can be ascribed to the higher repulsive interaction of DFP molecules with ions. Since fluorinated ions have less repulsion with DFP, their solubility in DFP is expected to be higher. Thus, the characteristics of DFP as a solvent should be explained not by the paradigm “like dissolves like” but rather, by “unlike does not dissolve unlike”, or, in terms of not the attractive but repulsive intermolecular interactions. This is in line with the previous authors’ view⁵ cited in the Introduction.

Supporting Information

Tables for the experimental and theoretical values of $\Delta_{tr}G^{\circ}_{W \rightarrow DFP}$ and $\Delta_{tr}G^{\circ}_{W \rightarrow DCE}$ for non-fluorinated cations and anions, their optimized coefficients and performance of regression analyses, and the energy decomposition of $\Delta_{tr}G^{\circ}_{DCE \rightarrow DFP}$ for the three different ion groups, and a figure reprinted from the Graphical Index.

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