A spectroscopic study on medium polarity in fluorous alcohol

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Abstract

The paper describes the polarities of three fluorous (F) aliphatic alcohols: perfluorinated *tert*-butanol (F-*t*-BuOH), *n*-butanol (F-*n*-BuOH), and *n*-heptanol (F-*n*-HepOH). For the purpose, we conducted absorption and fluorescence spectroscopies of coumarin 153 (C153) and 102 (C102) in three F and 13 non-fluorous (non-F) alcohols and determined their maximum energies: ν^a (absorption) and ν^f (fluorescence). We obtained linear relationships between the Stokes shifts of the dyes (i.e., ($\nu^a - \nu^f$)) and a medium polarity parameter for 13 non-F alcohols, $f(x)$: $f(x) = [(D_s - 1)/(2D_s + 1) - (n^2 - 1)/(2n^2 + 1)]$, where D_s and n were the dielectric constant and refractive index of a solvent, respectively. By comparing the Stokes shifts of the dyes in three F alcohols with those in 13 non-F alcohols (i.e., ($\nu^a - \nu^f$) vs. $f(x)$ plot), the D_s values in F-*t*-BuOH, F-*n*-BuOH, and F-*n*-HepOH were evaluated to be 2.7–3.9, 4.3–5.1, and 4.0–5.2, respectively, while those in the relevant non-F alcohols were 12.5, 17.5, and 12.9, respectively. Thus, the present experiments demonstrated that the polarities of these F alcohols were much lower than those of the relevant non-F alcohols.

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1. Introduction

Chemical synthesis and separation sciences based on fluorous solvents are expanding research areas known as fluorous biphase/triphase synthesis, fluorous liquid/liquid, solid/liquid extraction, and so forth [1–4]. The fundamental idea of the chemistry is a ''like dissolves like'' concept and a temperature dependent miscibility between fluorous (F) and common organic (non-F) solvents. In both cases, the chemistry is based on molecular interactions between an F solvent(s) and an F/non-F molecule(s). Although applications of the fluorous chemistry to synthetic reactions and separation sciences are very active research areas as mentioned above, physico-chemical properties of an F solvent and molecular-level solubilization behaviors between F and non-F liquids are still controversial. As an example, we found recently that, although perfluorohexane and *n*-heptane are mixed homogeneously above 41 °C as observed by naked eyes or under an optical microscope, Raman spectroscopic

imaging experiments of the mixture demonstrated that the two liquids were not mixed homogeneously at a molecular level [5].

Among various physico-chemical properties of an F solvent, its dielectric constant or polarity is one of the important fundamental parameters and has been studied among the decades. As an example, the Taft's π^* polarity indices of several fluorous alkanes have been estimated on the basis of a visible absorption solvatochromic shift of a probe molecule [6]. Freed et al. also reported the polarity indices (P parameter) of various F solvents on the basis of the absorption maximum wavelength of an organic dye [7,8]. These studies have demonstrated that an F solvent exhibits a very low polarity as compared to the relevant non-F solvent. For example, the P parameters of *n*-hexane and benzene (F/non-F) have been reported to be 0.00/2.56 and 4.53/6.95, respectively: less polar for a smaller P number [7]. The low polarity of an F solvent has been discussed in terms of the low polarizability of the solvent. In contrast to such characteristics, on the other hand, Freed et al. have also reported that the polarity of an F alcohol is higher than the relevant non-F alcohol; the P values of $CH_3(CH_2)_2CH_2OH$ and $CF_3(CF_2)_2CH_2OH$ are 7.62 and 9.76, respectively [7]. A

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visible absorption solvatochromic shift of a probe molecule is a very convenient method to evaluate a solvent polarity and, in practice, several solvent polarity parameters including those mentioned above have been employed in chemical researches [9,10]. In these empirical solvent polarity parameters, solvation-induced stabilization/destabilization of the ground state energy of a probe molecule is used as a measure of the medium polarity. In a fluorous medium, however, since solute (i.e., probe molecule)–solvent interactions might be different from those in non-F solution systems, discussion on a medium polarity by the absorption solvatochromic shift of a probe might not be necessarily warranted. In particular, high polarity nature of an F alcohol relative to that of the corresponding non-F alcohol is worth studying in some more detail for further advances in the researches of fluorous synthesis and separation sciences.

Another possible approach to evaluate a solvent polarity is the use of the Stokes shift of a probe molecule. A Stokes shift, defined by the difference between absorption and fluorescence maximum energies, is determined by solvent-induced stabilization/destabilization of both ground- and excited-state energies of a probe molecule and, thus, the contribution of specific solute–solvent interactions in the ground- and/or excited-states of the probe to the observed solvent polarity would be minimized. In practice, polarities in inhomogeneous systems such as in micelles, biomembranes, synthetic polymers, and so forth have been evaluated by the Stokes shift of a probe molecule [11]. In the present work, therefore, we studied absorption and fluorescence spectra of coumarin dyes (coumarine 153 and 102, see Scheme 1) in both F and non-F alcohols to evaluate the polarity in a fluorous alcohol. A coumarin dye shows in general absorption and strong florescence in the visible region, and the spectroscopic properties of the dye are known to be sensitive to a medium polarity. In the case of coumarin 153, furthermore, since the dipole moments in the ground- and singlet excited-states have been already reported [12], analysis of solvent effects on the Stokes shift of the dye would provide information about the solvent polarity. In the present paper, we report the absorption and fluorescence characteristics of two coumarin dyes in three F and 13 non-F alcohols. On the basis of these results, we evaluated the dielectric constants of three fluorous alcohols.
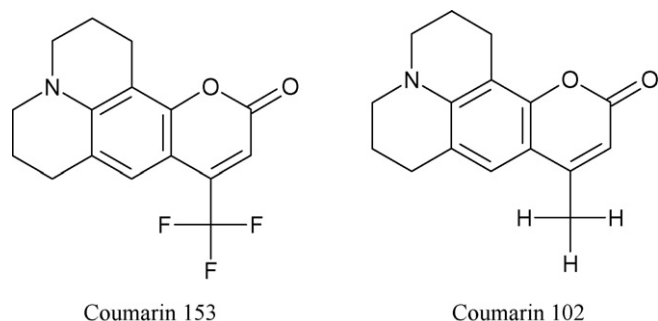
2. Results and discussion

2.1. General features of solvent effects on spectroscopic properties of coumarin dyes

Figs. 1 and 2 show absorption/fluorescence spectra of C153 and C103 in fluorous alcohols, respectively ((a), in F-t-BuOH, F-n-BuOH, and F-n-HepOH, upper panels), together with those in the relevant non-fluorous alcohols ((b), lower panels). Table 1 summarizes the spectroscopic data of the dyes in each solvent: absorption (ν^a) and fluorescence maximum energies (ν^f), and the full-width at half maximum (fwhm) of the spectrum. Table 1 also includes the dielectric constant (D_s) and refractive index of a solvent (n) [13].

The ν^a values of the dyes were dependent marginally on a variation of the fluorous (F) or non-fluorous (non-F) alcohol without a large change in the spectral band shape: see also the fwhm values in Table 1. As an example, ν^a of C153 in the F alcohol ranged in 22,800 (439 nm)–23,060 cm^{-1} (434 nm) (energy difference; $\Delta\nu^a = 260$ cm^{-1}, entries 1–3 in Table 1), while that in the non-F alcohol varied between 23,830 (420 nm) and 24,040 cm^{-1} (416 nm) ($\Delta\nu^a = 210$ cm^{-1}, entries 4–6 in Table 1). It is worth emphasizing that the ν^a value of C153 in each F alcohol is always lower in energy than that in the relevant non-F alcohol. Analogous behaviors with those of C153 were also observed for C102, though the absorption energy of C102 in a given medium was higher than that of C153. An increase in a medium polarity (D_s) often gives rise to a lower energy shift of the absorption spectrum of a probe molecule and, thus, to destabilization of the ground-state
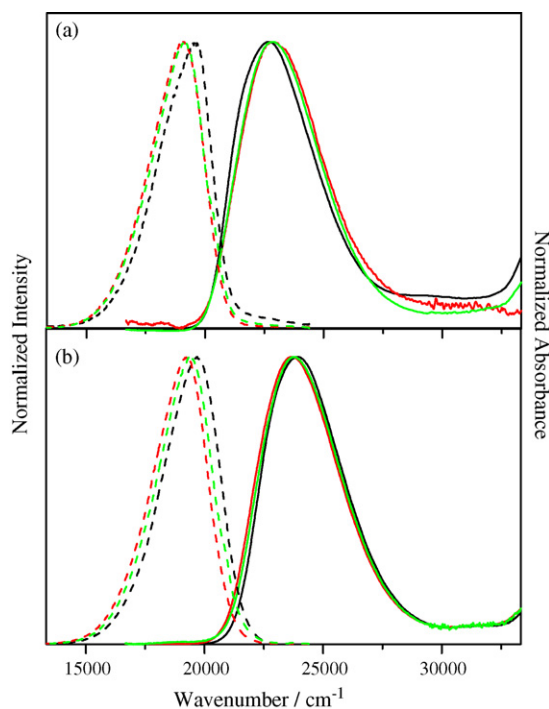

Fig. 1. Absorption (solid lines) and fluorescence (dotted lines) spectra of coumarin 153 in F-t-BuOH (black lines), F-n-BuOH (red lines), and F-n-HepOH (green lines) (a) and in the relevant non-fluorous solvents (b).

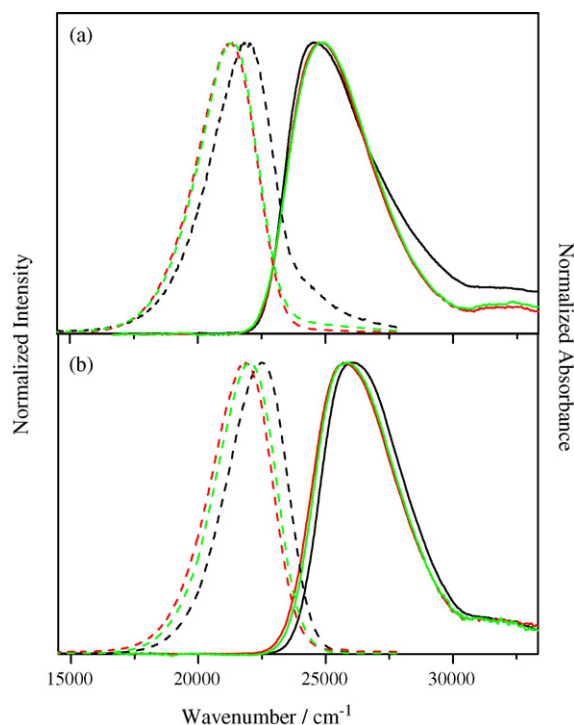Scheme 1. Structures of coumarin 153 and 102.

Coumarin 153

Coumarin 102

Fig. 2. Absorption (solid lines) and fluorescence (dotted lines) spectra of coumarin 102 in F-t-BuOH (black lines), F-n-BuOH (red lines), and F-n-HepOH (green lines) (a) and in the relevant non-fluorous solvents (b).

energy [9,10]. In the present case, since the change in D_s among three non-F alcohols is rather small ($D_s = 12.5–17.5$), a clear trend of the solvatochromic shift mentioned above has not been observed. However, as far as the comparison of the ν^a value between F and non-F alcohols is concerned, the lower energy shift of the absorption spectrum of C153 or C102 in the F

alcohol as compared to ν^a in the relevant non-F alcohol suggests that an F alcohol is more polar than the relevant non-F alcohol, which agrees quite well with the report by Freed et al. [7].

On the other hand, the fluorescence spectrum of C153 or C102 showed larger solvent effects as compared to the absorption spectrum. No clear spectral change with a variation of the medium was observed as seen in Figs. 1 and 2: see also the fwhm values in Table 1. The ν^f value of C153 in the F alcohol ranged in 18,670 (536 nm)–19,000 cm^{-1} (526 nm) (energy difference, $\Delta \nu^f = 330$ cm^{-1}), while those in non-F alcohols were in the range of 18,850 (531 nm)–19,310 cm^{-1} (518 nm) ($\Delta \nu^f = 460$ cm^{-1}). In good agreement with the results on the solvent shift of the absorption spectrum, the fluorescence spectrum in a given F alcohol was also shifted to the lower energy as compared to that in the relevant non-F alcohol: stabilization of the excited-state energy. However, it is worth noting that the fluorescence spectral shift in the non-F alcohols ($\Delta \nu^f = 460$ cm^{-1}) is larger than that in the F alcohols ($\Delta \nu^f = 330$ cm^{-1}), which is an opposite trend observed for the solvent effects on the absorption spectrum: $\Delta \nu^a(F) = 260$ and $\Delta \nu^a(non-F) = 210$ cm^{-1}. The results analogous to those of C153 were observed for C102 as well. These data demonstrate that perfluorination of a given alcohol gives rise to different effects on the ground- (ν^a) and excited-state energies (ν^f) of the dye and, thus, the discussion on the polarity of an F alcohol by the absorption spectral shift alone is not warranted. Table 1 also indicates that ν^f is sensitive to D_s of the non-F alcohol as compared to ν^a and, in the non-F alcohol, the lower energy shift of ν^f observed for C153 or C102 in the sequence of t-BuOH (19,310 or 22,180 cm^{-1}, respectively) < n-HepOH (19,040 or 21,750) < n-BuOH (18,850 or 21,570) agrees with the increasing order of D_s: t-BuOH ($D_s = 12.5$) < n-HepOH

Table 1
Solvent effects on spectroscopic parameters of C153 and C102

No.	Solvent	D_s[*]	n[**]	$f(x)$	Coumarin 153			Coumarin 102		
					ν^a (fwhm) ($\times 10^{-3}$/cm^{-1})	ν^f (fwhm) ($\times 10^{-3}$/cm^{-1})	$\Delta \nu^S$/cm^{-1}	ν^a (fwhm) ($\times 10^{-3}$/cm^{-1})	ν^f (fwhm) ($\times 10^{-3}$/cm^{-1})	$\Delta \nu^S$ (cm^{-1})
1	F-t-BuOH	–	1.3000[***]	–	22.80 (4.02)	19.00 (2.63)	3800	25.47 (4.06)	21.59 (2.87)	3880
2	F-n-BuOH	–	1.3000[***]	–	23.06 (4.13)	18.67 (2.67)	4390	25.14 (3.74)	21.01 (2.75)	4130
3	F-n-HepOH	–	1.3170[***]	–	23.00 (4.05)	18.73 (2.57)	4270	25.18 (3.80)	21.07 (2.72)	4110
4	t-Butanol	12.5	1.3877	0.251	24.04 (3.96)	19.31 (2.83)	4730	26.41 (3.73)	22.18 (2.78)	4230
5	n-Butanol	17.5	1.3993	0.263	23.83 (4.04)	18.85 (2.66)	4980	26.08 (3.76)	21.57 (2.81)	4510
6	1-Heptanol	12.9	1.4224	0.241	23.92 (4.00)	19.04 (2.69)	4880	26.16 (3.72)	21.75 (2.77)	4410
7	Benzyl alcohol	13.1	1.5404	0.206	23.26 (4.01)	18.60 (2.76)	4660	25.48 (3.68)	21.25 (2.56)	4230
8	1-Octanol	10.3	1.4295	0.226	24.03 (3.99)	19.16 (2.89)	4870	26.19 (3.73)	21.82 (2.72)	4370
9	1-Hexanol	13.3	1.4181	0.245	23.95 (4.03)	19.07 (2.81)	4880	26.20 (3.89)	21.72 (2.72)	4480
10	1-Pentanol	13.9	1.4100	0.249	23.92 (4.04)	19.02 (2.73)	4900	26.10 (3.74)	21.65 (2.69)	4450
11	3-Methyl-1-butanol	14.7	1.4071	0.253	23.94 (4.04)	19.03 (2.80)	4910	26.12 (3.74)	21.67 (2.68)	4440
12	1-Propanol	20.3	1.3856	0.274	23.85 (4.07)	18.87 (2.79)	4980	26.06 (3.79)	21.53 (2.67)	4530
13	Ethylene glycol	37.7	1.4318	0.275	23.29 (4.15)	18.15 (2.70)	5140	25.50 (3.75)	20.77 (2.73)	4730
14	2-Propanol	19.9	1.3752	0.277	23.94 (4.04)	19.04 (2.81)	4900	26.19 (3.74)	21.77 (2.66)	4420
15	Ethanol	24.6	1.3614	0.289	23.86 (4.13)	18.76 (2.85)	5100	26.06 (3.81)	21.41 (2.69)	4650
16	Methanol	32.7	1.3284	0.308	23.79 (4.17)	18.54 (2.75)	5250	25.94 (3.86)	21.10 (2.78)	4840
17	Chloroform	4.81	1.4429	0.149	24.10 (3.90)	20.14 (2.87)	3960	26.42 (3.95)	22.82 (2.96)	3600

[*] The dielectric constant of a solvent taken from ref. [13].
[**] The refractive index of a solvent taken from ref. [13].
[***] The data taken from ref. [15].

(12.9) < *n*-BuOH (17.5). Although the D_s values in the *F* alcohols are not known, both dyes in the *F* alcohols exhibited the fluorescence spectral shifts analogous to those in the non-*F* alcohol.

We conducted absorption and fluorescence measurements of the dyes in other 10 non-*F* alcohols (entries 7–16 in Table 1) to obtain the fundamental information about the solvent effects on ν^a/ν^f and, thus, to evaluate the polarity in the *F*-alcohol. Also, spectroscopic measurements of the dyes in CHCl$_3$ were conducted as a reference. The results in 11 solvents are included in Table 1. A close inspection of the data in 14 non-*F* solvents demonstrated that the spectroscopic shift of the dye could not be explained by the viscosity of a solvent (data are not shown here) and should be discussed in terms of the medium polarity parameters of D_s and/or *n*.

2.2. Solvent effects on Stokes shift

Table 1 indicates that the variation of the non-*F* alcohol brings about the ν^a change of the dye in the range of 23,260–24,040 cm^{-1} ($\Delta\nu^a = 780$ cm^{-1} for C153) or 25,480–26,410 cm^{-1} ($\Delta\nu^a = 930$ cm^{-1} for C102), while that gives rise to the ν^f shift of 18,150–19,310 cm^{-1} ($\Delta\nu^f = 1160$ cm^{-1} for C153) or 20,770–22,180 cm^{-1} ($\Delta\nu^f = 1410$ cm^{-1} for C102). Since both ν^a and ν^f values are under the influence of D_s and/or *n*, it is clear that the Stokes shift of the dye, defined by $\Delta\nu^S = (\nu^a - \nu^f)$, should be discussed to analyze the polarity in the alcohol instead of the solvent-induced ν^a shift. On the basis of the Onsager dielectric continuum model, the Stokes shift of a molecule is given by Eq. (1) [14],

$$\Delta\nu^S = \frac{2\Delta\mu^2}{hca^3}\left[\frac{D_s-1}{2D_s+1} - \frac{n^2-1}{2n^2+1}\right] = \frac{2\Delta\mu^2}{hca^3}f(x) \quad (1)$$

where $\Delta\mu$ is a dipole moment change upon the electronic transition of a molecule and *h*, *c*, and *a* are the Planck constant, the speed of light, and the Onsager radius of a molecule, respectively. The D_s and *n* values (n^2: optical dielectric constant) of a solvent are related to dipole orientation and electronic polarizability of a solvent molecule, respectively.

A Stokes shift of a molecule is originated from $\Delta\mu$ and/or geometrical distortion between the ground- and singlet excited-states of the molecule in a given medium with D_s and *n*. In the case of C153 and C102, the latter possibility is neglected owing to the rigid coumarin backbone structure [12] and, therefore, the Stokes shift of the dye should be responsible for $\Delta\mu$. In practice, the dipole moments of C153 in the ground- and singlet excited-states have been reported to be 5.63 and 9.51 D, respectively, as estimated by MNDO calculations [12]: $\Delta\mu \sim 3.9$ D. Since the dipole moment of C153 in the singlet excited-state is larger than that in the ground state, the larger solvent effects on ν^f as compared to those on ν^a seen in Table 1 are the reasonable consequence. On the basis of the $\Delta\mu$ value of C153, furthermore, Maroncelli and Fleming have reported that the (aprotic) solvent effects on the Stokes shift of C153 can be explained very well by the Onsager model [12] and, thus, by $f(x) = f(D_s) - f(n)$, where $f(D_s)$ and $f(n)$ represent the D_s and *n*
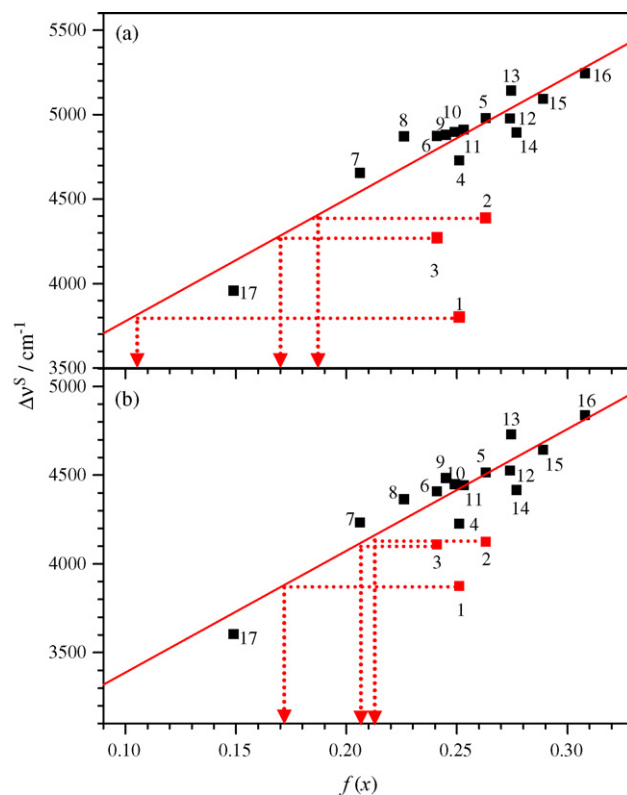

Fig. 3. The relationships between $f(x)$ and $\Delta\nu^S$ for coumarin 153 (a) and coumarin 102 (b). The numbering corresponds to that in Table 1.

terms in Eq. (1), respectively. Besides coumarin dyes, it has been also reported that linear relationships between $f(x)$ values and ν^a, ν^f, or $\Delta\nu^S$ have been observed for a variety of a compound and a solvent including alcohols [9,14].

Fig. 3 shows the relationships between $\Delta\nu^S$ and $f(x)$ for both C153 and C102: the $\Delta\nu^S$ and $f(x)$ values are included in Table 1. Since the $f(x)$ value was limited to 0.2–0.3 for the data in the non-*F* alcohols, we included the data in CHCl$_3$ (entry 17 in Table 1) for the following analysis. As seen in Fig. 3, the plots observed for both C153 ((a)) and C102 ((b)) were linear with the slope values (correlation coefficient, *R*) of 7230 ($R = 0.934$) and 6860 cm^{-1} ($R = 0.926$), respectively. Assuming the Onsager radius (*a*) of C153 to be 3.9 Å (based on the van der Waals volume of C153), the change in the dipole moment upon the electronic transition is estimated to be 6.5 D on the basis of the slope value in Fig. 3a. The value agrees very well with that of C153 determined by the slope of the $f(x)$ versus $\Delta\nu^S$ plot in aprotic solvents ($\Delta\mu = 6.0$ D, $a = 3.9$ Å) and is comparable to that calculated by MNDO calculations ($\Delta\mu = 4$ D) as mentioned above [12]. This indicates that the present solvent effects on $\Delta\nu^S$ are not influenced by a specific solute–solvent interaction. On the basis of the slope value of the plot, therefore, one can evaluate the polarity in the *F* alcohol.

2.3. Evaluation of polarity in fluorous alcohol

Assuming that the $f(x)$ values of the three *F* alcohols in Table 1 are identical with that in the relevant non-*F* alcohol, we

plotted the Stokes shifts of C153 and C102 in the F alcohols as shown in Fig. 3 (shown by closed red-squares). It is clear that the data of the dye in the F alcohols deviate largely from the corresponding linear relation between $f(x)$ and $\Delta \nu^S$, which indicates that the assumption made on $f(x)$ mentioned above is not appropriate. It is worth noting that since the n values in the three F alcohols have been reported (see Table 1) [15], we can evaluate the contribution of n to $f(x)$ in each F alcohol. Furthermore, it has been reported that effects of the hydrogen bonding interaction between a solute (i.e., naphthalimide derivative) and an F alcohol on the Stokes shift of the solute is very small; $\Delta \nu^S$ in methanol and 2,2,2-trifluoroethanol are 85 and 110 cm^{-1}, respectively [16], while the difference in $\Delta \nu^S$ between an F alcohol and the relevant non-F alcohol is 300–930 cm^{-1}. Therefore, the deviation of $\Delta \nu^S$ values observed for the three F alcohols from the linear relationship in Fig. 3a or b should be ascribed mainly to the difference in the D_s value between an F alcohol and the relevant non-F alcohol. On the basis of such discussions, we interpolated the $f(x)$ value corresponding to the observed $\Delta \nu^S$ value of the dye in a given F alcohol (red dotted arrows in Fig. 3) and evaluated the D_s value. The value (determined by the C153–C102 data) in F-t-BuOH, F-n-BuOH, or F-n-HepOH was 2.7–3.9, 4.3–5.1, or 4.0–5.2, respectively. The D_s value is much smaller than that in the non-F t-BuOH, n-BuOH, or n-HepOH: 12.5, 17.5, or 12.9, respectively [13]. The present results demonstrated that perfluorination of the alcohol decreases considerably the dielectric constant of the solvent, whose conclusion is opposite to the results on CF$_3$(CF$_2$)$_2$CH$_2$OH and (CF$_3$)$_2$CH$_2$OH reported by Freed et al. [6].

Barthel-Rosa and Gladysz have reported that the results on the absorption energy of a probe and, thus, the polarity in the F-alcohol shown by Freed et al. would be responsible for strong hydrogen bonding between the F alcohol and the probe molecule [8]. The solvatochromic probe employed by these authors is 9-(α-perfluoroheptyl-β,β-dicyanovinyl)julolidine, **1**; structure is shown in Scheme 2 [7]. The cyano groups in **1** might certainly undergo strong hydrogen-bonding with an alcohol. However, since the situation on the hydrogen-bonding interaction in an F-alcohol would be similar to that in a non-F alcohol, such effects might not be necessarily the reason for the polarity in the F alcohol. In practice, Demeter et al. have reported that the absorption maximum energy of a naphtha-limide derivative as a hydrogen bonding acceptor in methanol or 2,2,2-trifluoroethanol is 28,160 or 28,020 cm^{-1}, respectively [16]. It is worth emphasizing again that the ν^a value of C153 or C102 shows the lower energy shift in the present F alcohol series as compared to that in the corresponding non-F alcohol
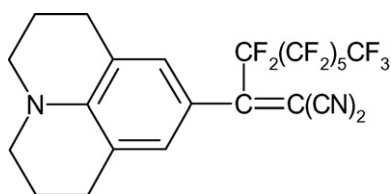
series, and this suggests the high polarity nature in the F alcohol. The absorption band shape and maximum energy of a probe molecule are governed by various factors such as medium polarity, viscosity, hydrogen-bonding ability, acidity/basicity, and so forth [9,10]. Therefore, we suppose that the discussion on a medium polarity based on an absorption solvatochromic shift alone will not be reliable enough and detailed analysis of the solvent effects on the Stokes shift is more appropriate to discuss a medium polarity. Since it is generally accepted that fluorous solvents are the less polar of any known liquids owing to high local symmetry and a lack of polarizability of the molecule itself [6–8,17], it is reasonable that any perfluorinated alcohols would be also less polar than the corresponding non-F alcohol.

Table 1 demonstrates that the $\Delta \nu^S$ value of C153 in F-t-BuOH, F-n-BuOH, or F-n-HepOH is smaller than that in the relevant non-F alcohol by 930, 590, or 600 cm^{-1}, respectively. In the case of a series of a non-F alcohol, an increase in $f(x)$ brings about the lower energy shift for both ν^a and ν^f, which implies destabilization and stabilization of the ground- and excited-state energies of the dye, respectively. Therefore, the Stokes shift indicates that the dye is less solvated in the F alcohol as compared to the corresponding non-F alcohol and, thus, the F alcohol is less polar than the non-F alcohol. It is worth noting that, although the D_s value in t-BuOH is the smallest among those in t-BuOH (12.5), n-BuOH (17.5), and n-HepOH (12.9), the $\Delta \nu^S$ change of C153 by solvent perfluorination is the largest in t-BuOH (930 cm^{-1}): small $\Delta \nu^S$ in F-t-BuOH. It suggests that the observed polarity in an F alcohol does not governed by bulk D_s and/or n alone. It has been reported that a gas solubility in an F solvent is dependent on the structure of the solvent, and a bulky F solvent shows a higher gas solubility owing to the presence of large cavities in the medium [17,18]. If this is the case, the coumarin dye should sit in the cavity in F-t-BuOH, which would imply poor solvation around the dye as compared to that in less bulky n-BuOH or n-HepOH. In particular, the presence of the perfluoromethyl group in C153 might also contribute to poor solvation, since the C102 dye having –CH$_3$ group shows almost comparable $\Delta \nu^S$ change by solvent perfluorination irrespective of the alcohol: 350, 380, or 300 cm^{-1} in t-BuOH, n-BuOH, or n-HepOH, respectively. Therefore, we suppose that such structural characteristics of the F alcohol will be also one of the possible reasons for the observed dielectric constant.

3. Conclusion

In the present study, we evaluated the polarity of three fluorous alcohols on the basis of the solvent effects on the Stokes shift of a coumarin dye. The absorption maximum energy of the dye in the F alcohol was lower than that in the relevant non-F alcohol and, thus, the F alcohol was suggested to be polar than the relevant non-F alcohol. This finding agrees with that report by Freed et al. [7]. However, the absorption and fluorescence maximum energies of the dye showed different medium polarity effects. By focusing on the Stokes shift of the

Scheme 2. Structure of **1**.

dye, we found that the polarity (D_s) in the *F* alcohol was much lower than that in the relevant non-*F* alcohols, which indicated that evaluation of a medium polarity by an absorption solvatochromic shift alone was not necessarily appropriate enough. It has been reported that a fluorous solvent is less polar than the corresponding non-*F* solvent [7,8]. As judged from the present findings, therefore, we conclude that a fluorous alcohol is also less polar than the relevant non-*F* alcohol, which provides information about further development of the fluorous chemistry.

4. Experimental

Coumarin 153 and 102 were purchased from ACROS ORGANICS (laser grade, 99%) and used as supplied. Perfluoro-*tert*-butanol (*F*-*t*-BuOH, 99%), 2,2,3,3,4,4,4-hepta-fluoro-1-butanol (*F*-*n*-BuOH, 98%, both supplied from Aldrich), and 1H,1H,7H-dodecafluoroheptanol (*F*-*n*-HepOH, 97%, ACROS ORGANICS) were used without further purification. Other non-fluorous solvents were the highest grade available from Wako Pure Chemical Industries Ltd. and used as supplied. Steady-state absorption and fluorescence spectroscopies were conducted by using a Hitachi UV-3300 spectrophotometer and a Hitachi F-4500 spectrofluorometer, respectively. All measurements were conducted at an ambient temperature.

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