

Co-extraction and Concentration of Dyes into the Ionic Liquid Formed in an Aqueous Solution

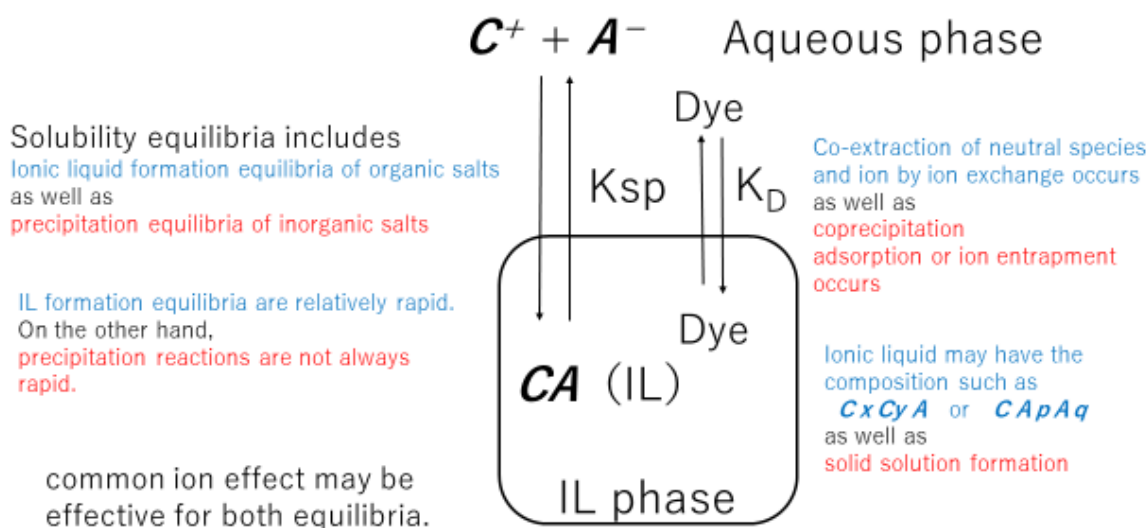
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The novel methodology of ionic liquid extraction of chemical species was investigated. To form the ionic liquid in an aqueous solution, 1-butyl-3-methylimidazolium chloride solution was added to the aqueous solution of a dye, then the solution of lithium bis(trifluoromethylsulfonyl)imide was added into the solution. Another phase of ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide appeared immediately. Some dyes such as ethyl violet, rhodamine B were simultaneously concentrated into the ionic liquid phase. On the other hand, fast green, new cocchine, tartrazin and some dyes were not extracted at all. The distribution behaviors of dyes were related to their chemical structures.

1. Introduction

The studies of the ionic liquids (ILs) have been developed in a few decades. Because of the character of vapourless and insoluble in water, ILs are required as the extraction solvents for the separation and concentration of the chemical compounds[1-3]. So far, almost all ILs were synthesized and purified, and then, used as the liquid-liquid extraction media. However, the costs of ILs are much more expensive than the usual organic solvents. Although, researchers seek to examine a lot of



Scheme1 Phenomena of hetero phase formation equilibria of IL comparing those of precipitation equilibria

combination of cations such as imidazoliums, pyridiniums or alkyl ammoniums ...etc and anions such as bis(trifluoromethylsulfonyl)imide ion, tetrafluoroborate ion and so many kinds of anions. Because, one of the advantage of the ILs as the solvents might be the variety of the chemical character changeable by means of substitute the part of the cation or of the anion. It is impossible to synthesize and purify so many kinds of ILs for each experiments.

As shown in scheme 1, ILs are insoluble salts like inorganic salts such as AgCl. If the cation and the anion were supersaturated over their solubility of the salt, ILs, organic liquid salts formed another phase in the aqueous solution, like the precipitation of an inorganic solid salts. Chemical reactions using the precipitation equilibrium shall be applicable for ILs formation equilibrium, because both are same hetero phase formation equilibria. Authors focused on the reaction of forming ILs in an aqueous solution. At same time, co-extraction (as well as the co-precipitation in the precipitation reaction) of some chemical organic species will be accompanied by the ILs formation reaction.

In this study, combination of 1-butyl-3-methylimidazolium [BMIm] chloride or 1-octyl-3-methylimidazolium [OMIm] chloride aqueous solution and the lithium bis(trifluoromethylsulfonyl)imide [NTf₂] solution were examined to form the ILs phase in the aqueous solution including dyes. Co-extraction behaviors of some dyes were examined. These compounds to form ILs are shown in Figure 1

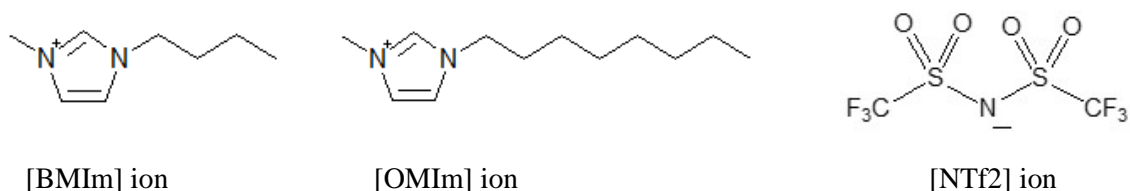


Figure 1. Structures of the cations and an anion forming the ILs in this study.

2. Experimental

2.1.1 Reagents to form ILs

Reagents for forming ILs were purchased as follows; 1-butyl-methylimidazolium [BMIm] chloride from Wako pure chemical, 1-methyl-3-n-octylimidazolium [OMIm] chloride from Tokyo Kasei Co., and lithium bis(trifluoromethylsulfonyl)imide [NTf₂] from Tokyo Kasei Co.. All reagents were more than 98% purity. The aqueous solution of 1 M [BMIm]Cl, [OMIm]Cl and Li [NTf₂] were diluted with a distilled water.

2.1.2 Dyes

Dyes used were acid red 52 (C₂₇H₂₉N₂NaO₇S₂) purchased from Wako pure chemical Co., ethyl violet (C₃₁H₄₂ClN₃ 0.5ZnCl₂) from Tesque Co., crystal violet (C₂₅H₃₀ClN₃) from Nacalai Tesque Co., Brilliant green (C₂₇H₃₄N₂O₄S) from Tesque Co., basic violet (C₂₄H₂₈ClN₃) from Tokyo chemical industry Co., malachite green (C₂₄H₂₅O₂N₂) from Wako pure chemical Co., methylene blue (C₁₆H₁₈N₃SCl) from Tesque Co., rose Bengal (C₂₀H₂Cl₄L₄Na₂O₅) from Wako pure chemical Co., rhodamine B (C₂₈H₃₁ClN₂O₃) from Wako pure chemical Co., erythrosine B (C₂₀H₆I₄Na₂O₅) from Wako pure chemical Co., phloxine B (C₂₀H₂Br₄Cl₄Na₂O₅) from Kishi Kasei Co., bromocresol green (C₂₁H₁₄Br₄O₅S) from Nacalai Tesque Co., bromocresol purple (C₂₁H₁₆Br₂O₅S) from Wako pure chemical Co., methyl red (C₁₅H₁₅N₃O₂) from Wako pure chemical Co., lithol rubine B (C₁₈H₁₂CaN₂O₆S) from Kishi Kasei Co., fluorescein (C₂₀H₁₂O₅) from Wako pure chemical Co., sunset yellow FCF (C₁₆H₁₀N₂Na₂O₇S₂) from

Wako pure chemical Co., bordeaux S ($C_{20}H_{11}N_2Na_3O_{10}S_3$) from Wako pure chemical Co., new coccine ($C_{20}H_{11}N_2Na_3O_{10}S_3$) from Wako pure chemical Co., tartrazine ($C_{16}H_{19}N_4Na_3O_9S_2$) from Wako pure Chemical Co., allura red AC ($C_{18}H_{14}N_2Na_2O_8S_2$) from Wako pure chemical Co., metacresol purple ($C_{21}H_{18}O_5S$) from Wako pure chemical Co., fast green ($C_{37}H_{34}N_2Na_2O_{10}S_3$) from Wako pure chemical Co., indigo carmine ($C_{16}H_8N_2Na_2O_8S_2$) from Wako pure chemical Co., brilliant blue ($C_{37}H_{34}N_2Na_2O_9S_3$) from Wako pure chemical Co.. Bromocresol green, bromocresol purple, metacresol purple, methylene blue, fluorescein, methyl red and tetrabromotetrachloro-fluorescein were dissolved with a small portion of 1 M (mol/dm^3) sodium hydroxide solution. Lithol rubin B was dissolved with diluted sulfuric acid. Other dyes were dissolved and diluted with distilled water.

2.2 Apparatus

Absorption spectra of the aqueous solution of dyes were measured by Hitachi U3310 spectrophotometer. The pH of an aqueous solution was measured by Toa DKK HM25R pH meter. Freeze drying machine was used to eliminate water in ILs by Eyla freeze dryer FD1000.

2.3 Procedure for the ionic liquid formation in an aqueous solution

The 1 M 1-butyl-3-methylimidazolium [BMIm] chloride solution and the 1 M lithium bis(trifluoromethylsulfonyl)imide [NTf₂] solution were added to the aqueous solution containing the 5×10^{-6} M dye, to be the concentration of [BMIm] ; 0.1 M and [NTf₂] ; 0.1 M in an aliquot (10 mL) of the solution. The solution were shaken with the mechanical shaker with 180 spm, and then centrifuged with 2000 rpm. As an IL phase appeared under the water phase, it was collected with the pipet and the concentration of the dye in the aqueous phase were determined spectrophotometrically. The weight of IL phase was determined after the collection and freeze-drying. The concentrations of [BMIm]Cl solutions and Li[NTf₂] solutions were changed, and the amount of the IL phase were measured.

3. Results and Discussion

3.1 Ionic liquid formation

The small volume of an IL phase appeared under the aqueous phase. In order to determine the weight of IL phase, it was collected and freeze dried and weighed. The aqueous solution containing 0.1 M [BMIm] and 0.1 M [NTf₂] in 10 mL formed the IL phase of 0.252 ± 0.0082 mL ($n=10$). As the concentration of [BMIm] and [NTf₂] increased up to 0.3 M, the volume of the IL increased lineally, and the line followed the calculated line considering the K_{sp} value of [BMIm] [NTf₂]. If a compound like malachite green were distributed and concentrated into the IL phase, concentration ratio would be 40 times as usual equal volume extraction.

3.2 Co-extraction of a dye into the IL

As shown in Figure 2, after adding the [BMIm] and [NTf₂] solution, IL phase of [BMIm] [NTf₂] was separated from the aqueous solution. The dye, ethyl violet was co-extracted into the IL phase. Table 1. shows percent extraction and the distribution ratio D of dyes between IL and aqueous solution.

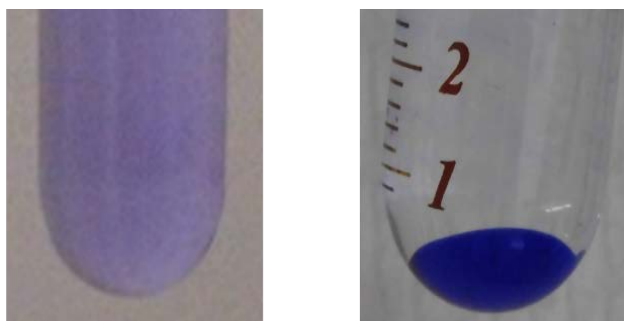


Figure 2. Photos of the solutions before and after the addition of [BMIm] and [NTf₂] into the ethyl violet solution.

Table 1 Distribution of dyes between water and IIs

	[BMIm][NTf2]			[OMIm][NTf2]		
	pH	%E	logD	pH	%E	logD
malachite green	8.00	99.7	4.16	7.39	98.9	3.37
methylene blue	8.01	99.4	3.85	7.33	97.1	2.95
crystal violet	8.00	98.7	3.47	7.40	99.2	3.52
basic violet	7.81	97.4	3.16	7.60	96.6	2.89
ethyl violet	8.03	96.9	3.09	7.35	97.4	3.01
brilliant green	8.10	94.4	2.82	7.38	99.4	3.64
rhodamine B	8.06	93.3	2.74	7.46	95.4	2.74
rose bengal	7.90	20.0	0.99	7.33	98.0	3.12
acid red	8.12	12.7	0.76	7.40	46.8	1.37
fast green FCF	8.06	3.3	0.13	7.47	4.2	0.23
bromocresol purple	9.75	0.7	-	9.63	5.3	0.17
erythrosine B	8.01	0.3	-	7.42	86.6	2.24
phloxine B	7.97	0.3	-	7.45	92.7	2.53
Br4Cl4-fluorecein	8.03	0.0	-	7.80	91.0	2.43
bromocresol green	9.76	0.0	-	9.73	41.6	1.28
methyl red	8.00	0.0	-	7.55	35.4	1.17
lithol rubine B	7.52	0.0	-	5.05	15.9	0.7
fluorecein	8.01	0.0	-	7.42	0.5	-
sunset yellow	8.15	0.0	-	7.47	0.0	-
bordeaux S	8.05	0.0	-	7.44	0.0	-
new cocchine	8.19	0.0	-	7.40	0.0	-
tartrazine	8.07	0.0	-	7.42	0.0	-
allura red	7.83	0.0	-	7.42	0.0	-
metacresol purple	10.89	0.0	-	10.47	0.0	-
indigo carmine	8.22	0.0	-	7.48	1.0	-
brilliant blue	8.05	0.0	-	7.38	0.0	-

The distribution ratio D is expressed as equation (1).

$$D = [\text{dye}]_{\text{IL}} / [\text{dye}]_{\text{aq}} \quad (1)$$

Where $[\text{dye}]_{\text{IL}}$ is the concentration of the dye in the IL phase, and $[\text{dye}]_{\text{aq}}$ is the concentration of the dye in the aqueous phase. The percent extraction % E of the dye is expressed as equation (2)

$$\%E = 100D / (D + (V_{\text{W}}/V_{\text{IL}})) \quad (2)$$

Where V_{W} is the volume of the aqueous phase, and V_{IL} is the volume of the IL phase.

As shown in Table 1, some dyes were well co-extracted into the IL phase for both case of the formation

of [BMIm][NTf₂] and [OMIm][NTf₂]. The structures of such dyes are shown in Figure 3.

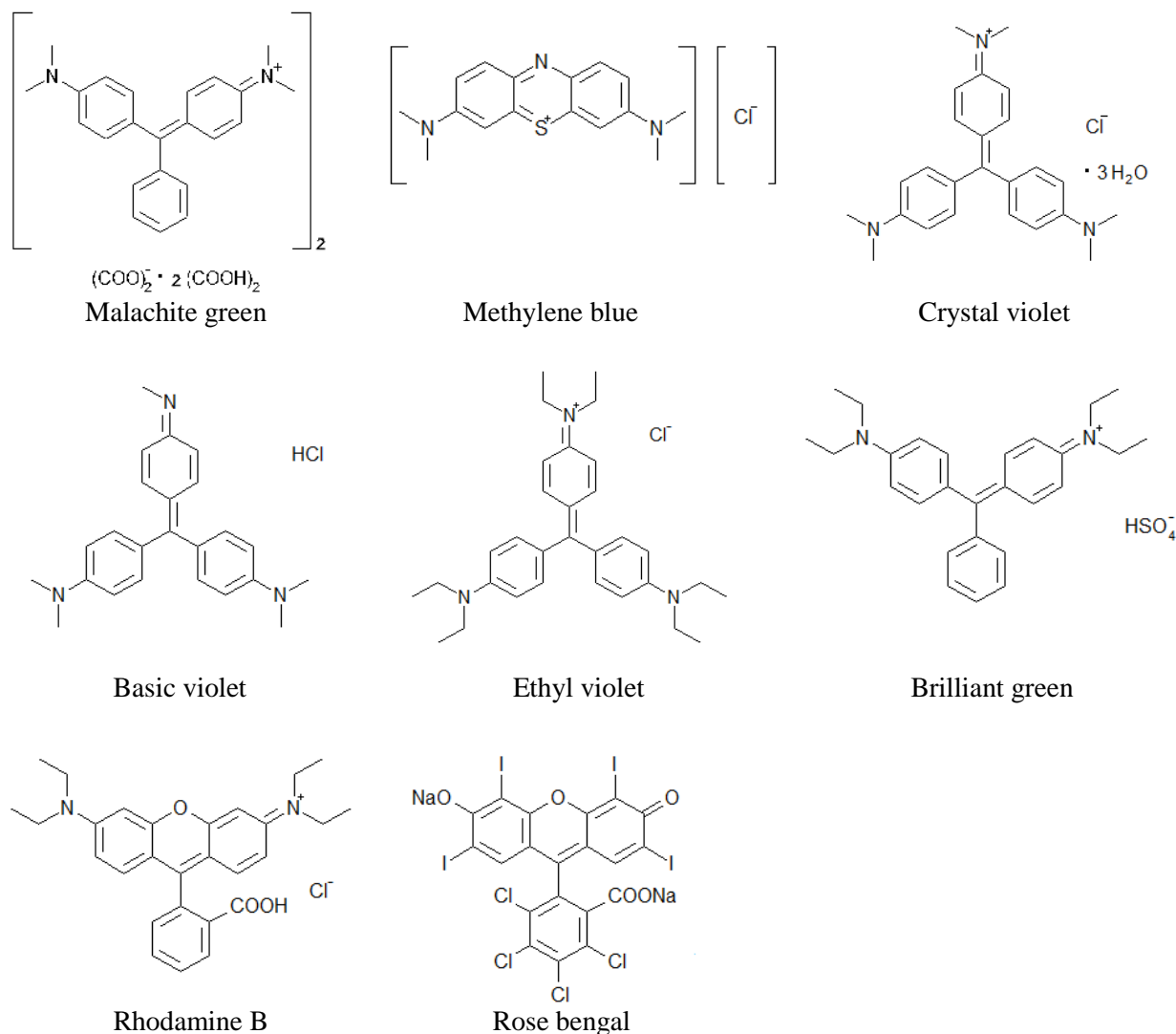


Figure 3. Chemical structures of dyes well co-extracted when the formation of both [BMIm][NTf₂] and [OMIm][NTf₂].

Those dyes have chemical structures which is hydrophobic and their cation center are on the nitrogen atoms seem to delocalized to aromatic rings with the exception of basic violet and rose bengal.

Because, the structure of protonated basic violet has similar structure to that of crystal violet, it may be co-extracted well. The difference of %*E*s between brilliant green and rhodamine B may be caused by the introduction of carboxyl group into the structure of brilliant green. In the case of formation of [BMIm][NTf₂], the values of %*E* are quite different. It is interesting to focus for the effect of the length of alkyl chains between the BMIm and OMIm for these two dyes. On the other hand, Figure 4 shows the structures of dyes which are well extracted with [OMIm][NTf₂], not extracted well with [BMIm][NTf₂]

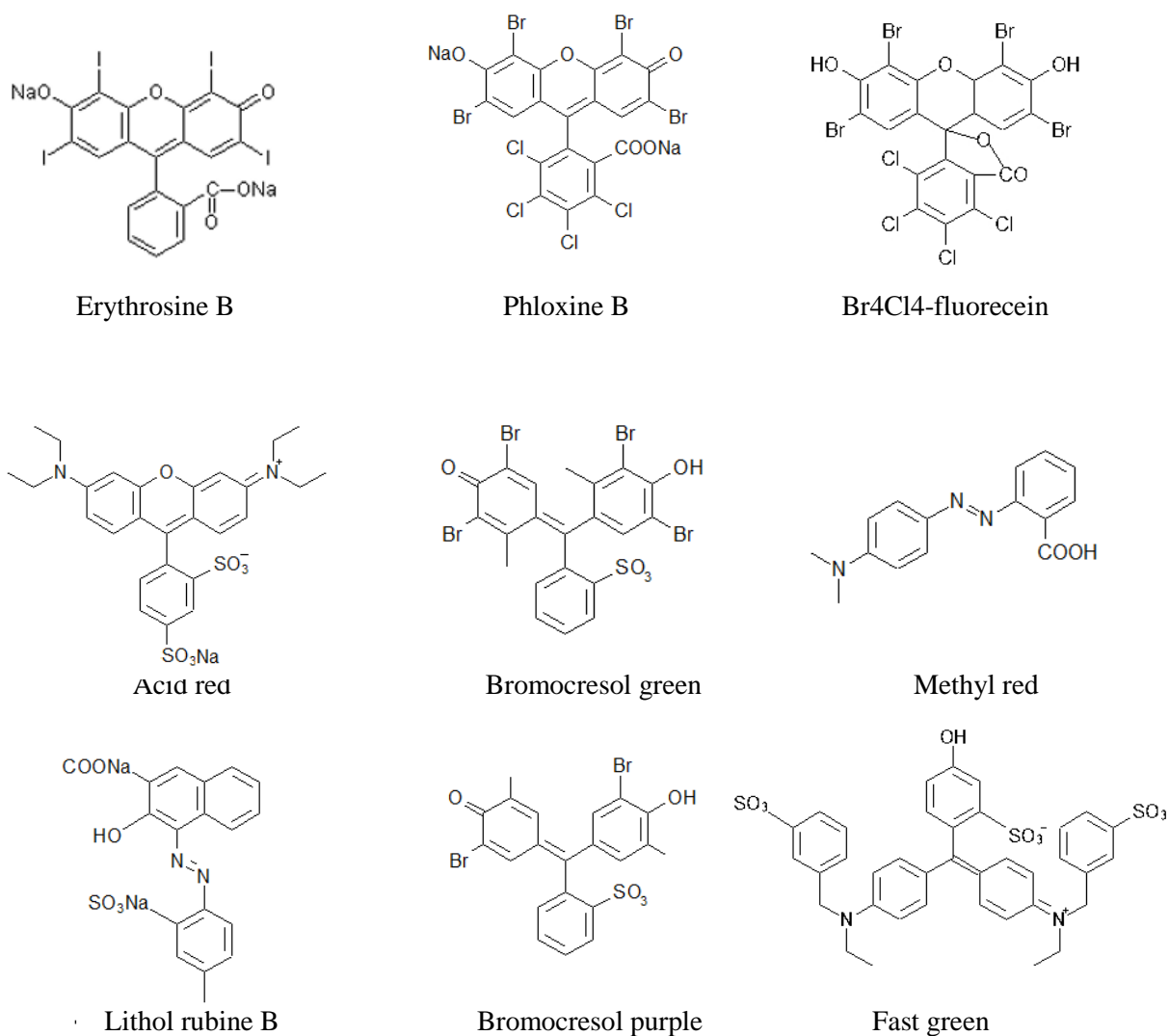


Figure 4. Chemical structures of dyes well co-extracted when the formation of [OMIm][NTf₂] not co-extracted well with [BMIm][NTf₂].

The results of Table 1 and the structures on Figure 4 indicate the importance of the alkyl chain length different between OMIm and BMIm on the co-extraction. Erythrosine B, phloxine B and Br₄Cl₄-fluorecein have hydrophobic part in their molecules. These dyes were co-extracted with [OMIm][NTf₂], however not co-extracted with [BMIm][NTf₂]. The dyes which have a sulfo group in their molecules, it is hard to be co-extracted with [BMIm][NTf₂] and even with [OMIm][NTf₂]. Lithol rubine, bromocresol purple and fast green not co-extracted with both ILs. Figure 5 shows the photograph of the fast green solution of high concentration when [BMIm][NTf₂] formed in the solution. It is clear the dye which have a few sulfo groups in the molecule are not co-extracted at all. Figure 6 shows the structures of dyes which are not co-extracted at all with both of [BMIm][NTf₂] and [OMIm][NTf₂]

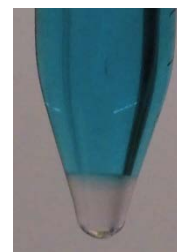


Figure 5. Fast green with IL

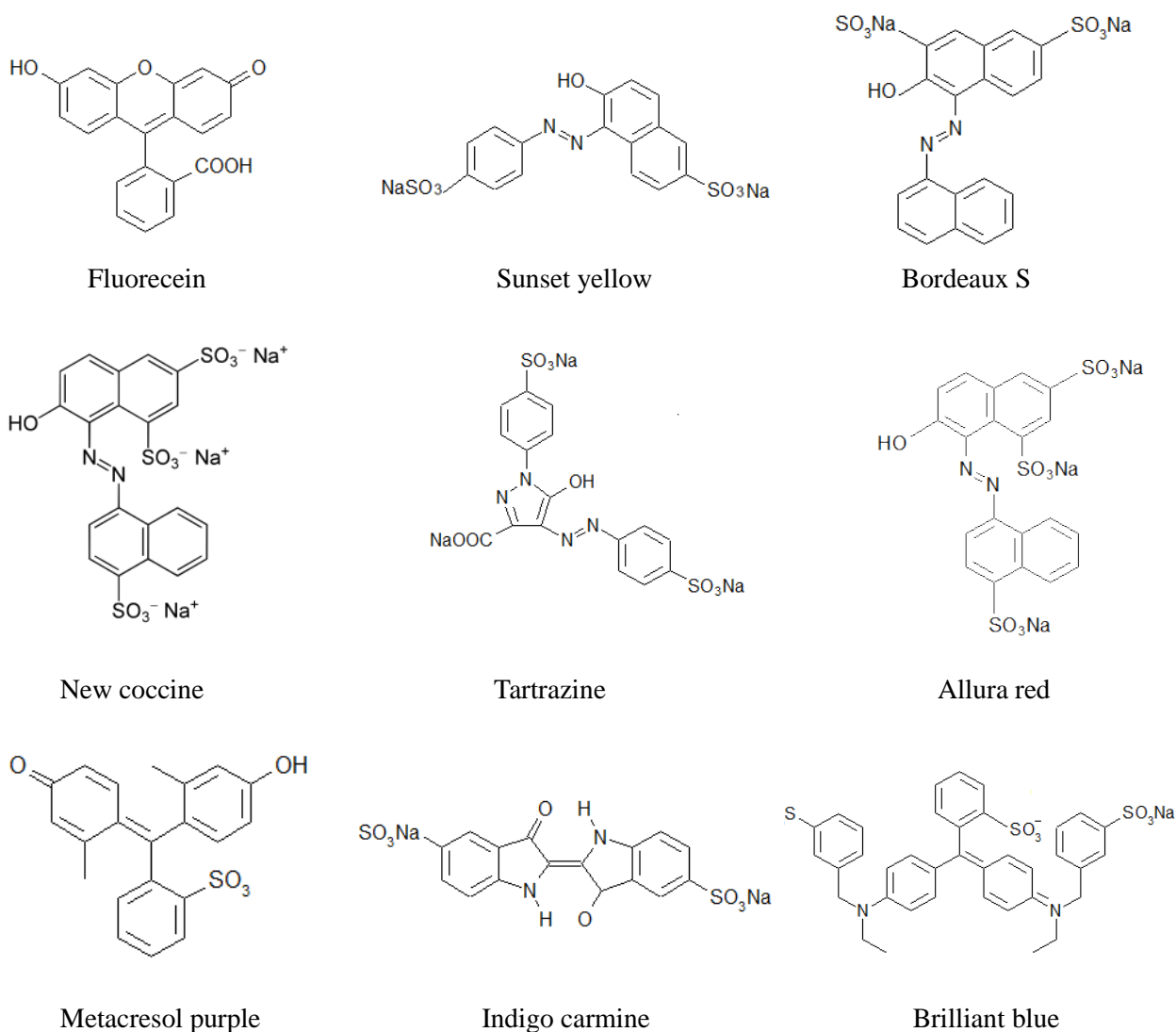


Figure 6. Chemical structures of dyes not co-extracted at all when the formation of [OMIm][NTf₂] and [BMIm][NTf₂].

Almost all dyes in Figure 6 are water soluble and have some hydrophilic groups such as hydroxyl, carboxyl and sulfo groups in their molecules. It seems, at least two hydrophilic groups in a molecule may be helpful to surround the dye by the water network which defend to move over the water-IL interface. It can be possible to separate between the dyes in Figure 4 and those in Figure 6. Further, it would be possible to concentrate the dye to determine the concentration by spectrophotometrically.

4. Conclusion

The methodology developed in this study for IL extraction might save the time of IL extraction, because it shortcuts the synthesis and purification of IL in as much as those processes were not necessary. Some of analytical method such as extraction spectrophotometry may be taken place with those methods. Further, the applications for the chemical processes such as separations of products during synthesis,

specific extraction of biomaterials in order to use a specific groups in the compartment cation or anion would be possible.

Acknowledgement

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