

Fluorous Biphasic System of C₉F₁₈ and Its Use in Esterification*

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Abstract Some apolar organic solvents is miscible with perfluorous nonene to form fluoruous biphasic systems. Perfluorous nonene could be used as a green solvent in equimolar esterification of carboxylic acids with alcohols without removal of water or ester formed. Perfluorous nonene made the esterification equilibrium to move right and the yields of esterification to enhance in different degrees as compared with that in the absence of perfluorous nonene. After esterification perfluorous nonene is easy to be recovered and recycled.

Keywords perfluorous nonene, fluoruous biphasic system, esterification, green solvent

1 INTRODUCTION

The use of perfluorocarbons as reaction media in Green and Sustainable Chemistry and homogeneous catalysis was a topic of growing interest. In particular, the value of the fluoruous phase-separation and fluoruous catalysis immobilization was well recognized, and the concept was extended and developed by Horváth in 1994[1,2], known as fluoruous biphasic system (FBS)[3—6], which included a fluoruous phase containing a preferentially fluoruous soluble reagent or catalyst and an organic phase not dissolved in the fluoruous phase at room temperature. Perfluoroalkane, perfluorodialkyl ether or perfluorous trialkylamine are colorless, nontoxic, apolar, which could be used in many organic reactions as fluoruous phase such as heat transfer, refluxing and separating low boiling components[7], but too expensive to be used largely in industry. In order to reduce the cost, perfluorous nonene (PFN) was found a relatively cheap perfluorous solvent which could form FBS with some organic solvents and be used in green esterification.

2 EXPERIMENTAL

2.1 Preparation of PFN

PFN was a mixture of hexafluoropropene trimer [99.5% C₉F₁₈, colorless liquid, bp 105—115°C, fp 75°C, *d* 1.83], synthesized from hexafluoropropene by the method described in the literature[8]. KF (0.005mol) was used as catalyst in combination with 18-crown-6 (0.001mol), *N,N*-dimethylformamide (DMF 30ml) was used as solvent and the oligomerization was conducted at 90°C for 1h. PFN was produced with the selectivity of about 90%. Analytical-grade hexane, cyclohexane, heptane, tetra-chloromethane, ethyl ether, *n*-butanol, phenylformic acid, ethyl acetate, formic acid, acetic acid, benzene, toluene and *n*-propionic acid were purchased from the Shanghai Reagent Factory. Chemical-grade *n*-propanol, *n*-buteric acid and *n*-caprylic acid were purchased from Hangzhou Reagent Company.

2.2 Preparation of FBS

A test tube of 50ml added with equal volume of

organic solvent and PFN was put in a SC-15 digital super thermostat. The system was shaken by hand to mix, heated to and maintained at the specified temperature in turn. Temperature was recorded when the mixture became a homogeneous phase. Then the homogeneous phase was cooled to room temperature, PFN phase and organic phase were separated automatically. Each phase was sampled and analyzed by gas chromatography (GC).

2.3 Esterification

A 250ml flask was added with acid (0.1mol) and alcohol (0.1mol). Concentrated H₂SO₄ (98%, 1ml) was added as catalyst. When esterification was carried out in FBS, PFN (0.3mol) was added. The mixture was stirred magnetically and heated to refluxing for from 1 to 3h, then cooled to room temperature. PFN was separated itself from the reaction mixture as the lower layer, and could be reused directly in next runs without any purification. The organic layer was washed with water to neutrality, rectified and analyzed by GC.

2.4 GC analysis

The composition analysis of FBS and products was made with a gas chromatograph GC-14B (Shimadzu Corporation, Kyoto, Japan), equipped with a flame ionization detector (FID) and an OV-17 capillary column (3m long and 3mm outside diameter). The chromatographic conditions were as follows: injector temperature 250°C, detector temperature 250°C, column temperature 200°C. The concentration of compounds was given by the 2010 chromatography workstation according to the area of each chromatograph.

3 RESULTS AND DISCUSSION

3.1 Fluorous biphasic system

Little was known about the PFN as fluoruous solvent in FBS. It was found that some organic solvents could form FBS with PFN. The organic solvents would be alkanes (such as hexane, cyclohexane, heptane,

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chloroform, tetrachloromethane), ethers (such as dioxane, tetrahydrofuran, ethyl ether), alcohols (such as ethanol, propanol, butanol), acids (such as formic acid, acetic acid), aromatics (such as benzene, toluene, xylene, chlorobenzene, nitro-benzene) and other solvents (such as ethyl acetate, DMF, acetone, acetonitrile). The experimental results revealed that apolar PFN was completely immiscible with H₂O and common polar solvents such as acid, alcohol, chloroform, but had certain solubility in some apolar solvents and solvents of lower polarities as shown by the data in Table 1. PFN was immiscible with apolar solvents at room temperature, but could mix with them to form a homogeneous phase at elevated temperature.

Table 1 Initial temperature of mutually soluble FBS in organic solvents

Solvent	<i>T</i> , °C
ethyl ether	25.8
hexane	35.4
tetrachloromethane	53.6
heptane	54.8
ethyl acetate	65.4
cyclohexane	74.0

When FBS was cooled to room temperature, the mutual soluble solvents were separated two phases, the upper phase was organic phase and the lower phase was PFN. Each phase was analyzed (Table 2). The results showed that FBS did not separate fully at room temperature. There was amount of organic solvents in PFN. It was very important that PFN lost little in organic solvents such as cyclohexane and toluene.

3.2 Esterification in FBS

Esterification was one of the most important industry processes. Equimolar esterification of acid and alcohol was preferred. To enhance the yield of esterification, the water or ester formed had to be removed. Catalysts could accelerate esterification. An esterification process took the advantage of a mild catalyst, diphenylammonium triflate (DAPT)[9] in which equimolar alcohol reacts with acid in toluene without removing water to form the corresponding ester in excellent yield, generally 90%. It was reported[10]

that equimolar condensation of both reagents in the presence of hafnium and zirconium salts under azeotropic dehydration. Gacem and Jenner[11] used DAPT in the esterification of sterically hindered acids and alcohols in fluorous media (FC-77[®]), but poor yields were obtained. Other esterification of equimolar acid and alcohol in FBS were reported[12] to achieve good yield in the presence of a fluorous ponytail catalyst, Yb[C(SO₂C₈F₁₇)₃]₃. In this work, the application of PFN for the esterification of equimolar acid and alcohol in the presence of a common catalyst, H₂SO₄, was investigated.

Polar acids and alcohols did not dissolve in PFN, but the product esters could form FBS with PFN. The results of esterification of acids (formic acid, acetic acid, propionic acid, butyric acid, caprylic acid and phenylformic acid) with alcohols (*n*-propanol, *n*-butanol) by a conventional method (without PFN) and in PFN were listed in Table 3. The refluxing temperatures in PFN were lower in different degree than the traditional esterification. It was very important and useful to reduce energy consumption. The yields of esterification in PFN increased, most of which were good (No.3) or excellent (No.2, No.4—No.8). Although some yields were not good enough (No.1 and No.10), they increased by 78.1 % and 88.8 % respectively. It was found that the yield in the mixture solvent of benzene/PFN was lower than that by the conventional method by 8.6 % when phenylformic acid reacted with *n*-propanol in benzene (No.11). But if the reaction took place in the mixture solvent of toluene/PFN, the yield increased by 36.0 % (No.12) compared with that in toluene.

The esterification is a reversible process. Much excessive acid or alcohol is used to make the equilibrium-controlled reaction to move forward and to raise the yield. Another way is to remove produced ester or water in time. PFN does not mix with acids or alcohols to form FBS, but so do it with esters. When PFN is added in esterification systems, there are two phases, PFN phase with produced ester dissolved and organic phase containing acid and alcohol, so that the yield of the esterification can increase to beyond the equilibrium. Propyl benzoate and the solvent, benzene, were with low solubility in PFN, even lower than that of the reactant acid and alcohol, making the equilibrium to move left and the yields to decrease. But

Table 2 Contents of PFN and organic solvents in two phases of FBS

Organic solvents	<i>K</i> ^①	Fluorous phase		Organic phase	
		PFN, %	Organic solvent, %	PFN, %	Organic solvent, %
ethyl ether	1 : 1	56.9	43.0	13.1	86.4
tetrochloromethane	1 : 1	87.7	11.7	20.8	79.2
hexane	1 : 1	70.1	29.1	6.25	93.6
heptane	1 : 1	78.8	21.1	3.51	96.3
cyclohexane	1 : 1	64.0	35.9	1.16	98.7
ethyl acetate	1 : 1	89.0	11.0	4.79	94.7
toluene	4 : 1	81.4	18.5	0.37	99.1

① $K = V(\text{PFN})/V(\text{organic solvent})$

Table 3 Results of esterification in PFN and by conventional method

No.	Ester	Conventional esterification		Esterification in PFN		t_{reaction} , h	$\Delta \text{yield}^{\text{③}}$, %	ΔT , °C
		T_{reflux} , °C	yield', %	T_{reflux} , °C	yield'', %			
1	<i>n</i> -propyl formate	80	33.8	73	60.2	3	78.1	-7
2	<i>n</i> -butyl formate	95	76.3	85	96.6	3	26.6	-10
3	<i>n</i> -propyl acetate	94	60.7	81	76.7	1.5	26.4	-13
4	<i>n</i> -butyl acetate	104	71.5	80	98.8	1	38.2	-24
5	<i>n</i> -propyl propionate	109	74.0	93	86.8	3	17.3	-16
6	<i>n</i> -butyl propionate	110	66.5	95	85.7	2	28.9	-15
7	<i>n</i> -propyl butyrate	119	81.4	98	99.2	3	21.9	-21
8	<i>n</i> -butyl butyrate	126	79.0	101	94.8	2	20.0	-25
9	<i>n</i> -propyl caprylate	112	55.9	109	80.8	2	44.5	-3
10	<i>n</i> -butyl caprylate	120	38.3	109	72.3	2	88.8	-11
11	<i>n</i> -propyl benzoate ^①	108	67.6	86	61.8	3	-8.6	-22
12	<i>n</i> -propyl benzoate ^②	108	72.0	86	97.9	3	36.0	-22

① Benzene was added as solvent. ② Toluene was added in esterification in PFN. ③ $\Delta \text{yield} = (\text{yield}'' - \text{yield}') / \text{yield}' \times 100\%$, $\Delta T = T_{\text{reflux}}'' - T_{\text{reflux}}$

toluene could dissolve the product, ester, and be miscible with PEN to form FBS, which made esterification equilibrium to move right.

3.3 Recycle of PEN

Decantation separation of reaction mixture after esterification made PEN easily isolated and recovered. The average percent recovery of PEN was about 96.3% within 5 runs (Table 4). 4% of PEN used had to be complemented for a next run. PFN was recycled directly without any purification. The yields of product had even a little increase after first runs.

Table 4 Reusing of PEN for equimolar esterification of propionic acid with *n*-butanol (95°C, 2h)

Run	Percent recovery, %	Yield of ester, %
1	97.7	85.7
2	94.6	86.8
3	95.6	87.8
4	95.1	84.6
5	98.7	87.0

4 CONCLUSIONS

PFN and apolar organic solvents such as hexane, cyclohexane, heptane, ethyl ether, tetrachloromethane, toluene *etc.* could form FBS at elevated temperature. When esterification of equimolar organic acid and alcohol took place, addition of PFN made the esterification equilibrium to move right and the yield of esterification enhanced in different degree as compared with that without PFN. After esterification, PFN was easy to be recovered and recycled.

Comparing to conventional esterification, equimolar esterification of organic acids and alcohols in FBS provided higher yields without removing any water or ester produced during the reaction. PFN can be recovered easily by decantation and recycled di-

rectly without any purification, and the reaction temperature declined in different degree and those are seemingly promising in green organic synthesis

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