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
SOLUBILITY OF Capa[®] 6500 IN ORGANIC SOLVENT

INTRODUCTION

Polycaprolactone Capa[®] 6500 is a highly crystalline polyester. The ease with which it crystallises means that its solubility is limited in many solvents which would dissolve similar amorphous polyesters.

The solubility of polycaprolactone in a solvent can be predicted to some extent by the functional groups in the solvent.

Solubility is particularly promoted by the presence of:

(i)	Aromatic rings	
(ii)	halogens	-Cl + -Br
(iii)	nitro groups	-NO ₂
Other groups increasing solubility are:		
(iv)	carboxyl	-CO ₂ H
(v)	carbonyl	-C=O
(vi)	ether	-O-
(vii)	olefin	-C=C-

Alkyl groups -R, and hydroxyl groups -OH diminish solubility. Solubility can be seen to be progressively reduced, proceeding up a homologous series, eg. formates dissolve Capa[®] 6500 more easily than acetates. Methyl esters are better solvents than ethyl esters.

Mixed solvent systems are less predictable. For instance, the addition of 5-20% (preferably 5-10%) of an alcohol such as n-butanol will improve the solubility of Capa[®] 6500 in Xylene.

TEST PROCEDURE

Three grams of Capa[®] 6500 was shaken with 30 grams of the solvent in question at room temperature (Typically 20°C), in a flask shaker. If soluble, agitation was continued until solution was complete or until a definite residue was left.

Insoluble materials were heated until solution occurred. The resultant solutions were allowed to cool to ambient temperature and stored at least two weeks or until significant precipitation occurred, whichever was the shorter.

The solvents were classified as follows:

- (i) solvent dissolving Capa[®] 6500 at ambient temperature.
- (ii) solvents partially dissolving Capa[®] 6500 at ambient temperatures, leaving a residue which dissolves on heating to yield a stable solution.
- (iii) solvents partially dissolving Capa[®] 6500 at ambient temperatures, leaving a residue which dissolves on heating and precipitates on prolonged storage at ambient temperatures.
- (iv) solvents which do not significantly dissolve Capa[®] 6500 at ambient temperatures, but which dissolve Capa[®] 6500 on heating to yield a stable solution.
- (v) solvents which do not dissolve Capa[®] 6500 at ambient temperatures, but which dissolve it on heating only for precipitation to occur when the solution cools.
- (vi) solvents which do not dissolve Capa[®] 6500 both with and without heating.

As a general rule, it can be taken that if Capa[®] 6500 is soluble at a level of 10% the solvent will be capable of dissolving Capa[®] 6500 to form a stable solution at higher levels. The critical factor is most likely to be one of solution viscosity rather than compatibility.

The results for Capa[®] 6500 will probably hold true for Capa[®] 6400 in most cases.

The solubility of Capa[®] 6500 is particularly sensitive to temperature in some classes of solvent, notably xylenes and some esters. Some of these solvents are denoted with an asterisk in section (A) of the results. Higher or lower ambient temperatures may alter the solubility accordingly.

The results are treated in two ways:

- Solubility of Capa[®] 6500 in different chemical types of solvent.
- Classification of solvents according to their efficiency of dissolving Capa[®] 6500. The six categories defined above are used.

Solubility of Capa[®] 6500 in different classes of solvent

1. **Aliphatic and Cycloaliphatic Hydrocarbons**

Polycaprolactone was found to be insoluble (both hot and cold) in the following:

40° - 60° Petroleum ether
100° -120° Petroleum ether
Shellsol T
cyclohexane
methyl cyclohexane

2. **Unsaturated Hydrocarbons**

Unsaturation increases the affinity of a hydrocarbon for polycaprolactone.

The following were tried:

Di isobutylene	-	insoluble
Cyclohexene	-	insoluble cold, soluble hot, solutions stable for a few days, recipitation eventually occurring.
Dipentene (a terpene)	-	insoluble cold, soluble hot, precipitation on cooling.

3. **Aromatic Hydrocarbons**

Polycaprolactone is soluble in aromatic hydrocarbons. Substitution of alkyl groups tends to reduce solubility. This becomes noticeable with xylene and ethyl benzene.

(i) Soluble cold

Benzene
Toluene
Styrene
methyl naphthalene
Chlorobenzene
Nitrobenzene
Cresol (mixed isomers)

(ii) Partially soluble cold, soluble hot, forms stable solutions

o-xylene (soluble in warm weather)
m-xylene

(iii) Partially soluble cold, soluble hot, precipitates on cooling

p-xylene	(solutions stable a few days)
xylene mixed isomers	(solutions stable a few days)
ethyl benzene	(solutions stable a few days)

(iv) Insoluble cold, soluble hot, precipitates on cooling

Shellsol A
Psuedo Cumene
Tetrahydronaphthalene

4. **Halocarbons**

Polycaprolactones are completely soluble in most chlorinated solvents.

(i) Soluble cold

Dichloromethane
Chloroform
Carbon Tetrachloride (slow to dissolve without heat)
1,2 Dichloroethane
1,1,1 Trichloroethane
1,2 Dichloroethylene
Trichloroethylene
1,2 Dichloropropane
Chlorobenzene
O-dichlorobenzene
Bromobenzene

(ii) Insoluble cold, partially soluble hot, precipitates on cooling

Tetrachloroethylene

5. **Alcohols**

Polycaprolactone is insoluble in most alcohols. Some alcohols will dissolve Capa[®] 6500 on heating but precipitation occurs immediately on cooling. The presence of other functional groups may improve solubility.

(i) Soluble Cold

Benzyl alcohol

(ii) Insoluble cold, soluble hot, precipitates on cooling

n-butanol
2-ethyl hexanol
cyclohexanol
Butyl digol
Ethyl digol
2-ethoxy ethanol
2-butoxy ethanol
Dipropylene glycol
Polypropylene glycol (400 MW)
Allyl Alcohol
Diacetone Alcohol

(iii) Insoluble cold, partially soluble hot, precipitates on cooling

Polyethylene glycol (400 MW)

(iv) Insoluble hot and cold

methanol
ethanol
isopropanol
ethane diol
digol
glycerol

6. Esters

Polycaprolactone will only dissolve in most esters if heat is applied. In most instances, precipitation occurs on cooling within an hour. The larger the alkyl groups in the constituent acids and alcohols are, the poorer will be the solvent action of the ester.

(i) Soluble cold

methyl benzoate
methyl acetate (may require heat in cold weather)
ethyl formate (may require heat in cold weather)

(ii) Partially soluble cold, soluble hot, stable solution

n-butyl formate

(iii) Insoluble cold, soluble hot, stable solution

ϵ -Caprolactone
Benzyl Benzoate

(iv) Insoluble cold, soluble hot, precipitates on cooling

Ethyl acetate (solution stable 2 days)
butyl acetate
2-ethoxy ethyl acetate
amyl acetate
methyl cyclohexyl acetate
ethyl acetoacetate
n-amyl formate
n-butyl propionate
di-ethyl carbonate
diethyl adipate
dimethyl phthalate
di-n butyl phthalate
 γ -butyrolactone
triethyl phosphate

7. Ketones

The behaviour of ketones is similar to that of esters.

(i) Soluble cold

Cyclopentanone
acetophenone
acetyl acetone

(ii) Partially soluble cold, soluble hot, stable solution

Cyclohexanone

(iii) Partially soluble cold, soluble hot, slow precipitation on cooling

Acetone
Ethyl methyl ketone

(iv) Insoluble cold, soluble hot, precipitation on cooling

methyl cyclohexanone (solution stable some weeks)
isobutyl methyl ketone
methyl n-propyl ketone
methyl isoamyl ketone
methyl n-hexyl ketone
diethyl ketone
diacetone alcohol
isophorone

8. Ethers

(i) Soluble cold

1:4 dioxan
Tetrahydrofuran

(ii) Insoluble cold, soluble hot, precipitates on cooling

Dimethyl digol (stable some hours)
2-ethoxy ethanol
2-butoxy ethanol
ethyl digol
butyl digol
dipropylene glycol
Polypropylene glycol 400

(iii) Insoluble hot and cold

diethyl ether
di-isopropyl ether
digol

9. Miscellaneous

(i) Soluble cold

formic acid
acetic acid
pyridine
nitromethane

(ii) Partially soluble cold, soluble hot, stable solution

propionic acid

(iii) Insoluble cold, soluble hot, precipitates on cooling

Dimethyl formamide (stable several days)
Dimethyl acetamide
Dimethyl sulphoxide

(iv) Insoluble hot and cold

carbon disulphide

10. Monomers

(i) Soluble cold

Styrene
 α -methyl styrene
penton (bis 33 chloromethyl oxetane)

(ii) Partially soluble cold, soluble hot, stable solution

Vinyl acetate
methyl acrylate
methyl methacrylate
acrylic acid

(iii) Insoluble cold, soluble hot, precipitates on cooling

di-allyl phthlate
di n-butyl fumarate
di n-butyl maleate

11. Mixtures

(i) Soluble cold

xylene/isopropanol	9:1
xylene/isopropanol	4:1
xylene/butanol	9:1
xylene/butanol	9:1
xylene/butanol	4:1

(ii) Partially soluble cold/soluble hot, stable solution

xylene/n-pentanol	4:1
ethyl acetate/methyl ethyl ketone	1:1

(iii) Insoluble hot and cold

Shellsol T/n-butanol 4:1

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FREEDOM FROM PATENT RESTRICTIONS SHOULD NOT BE ASSUMED

Soluble Cold	Partially Soluble Cold Soluble Hot, Stable Solution	Partially Soluble Cold Soluble Hot, Partial Precipitation	Insoluble Cold Soluble Hot, Stable Solution	Soluble Hot, Precipitation on Cooling	Insoluble Hot and Cold
Benzene	o-xylene	p-xylene	Caprolactone	Cyclohexene	40-60 pet. ether
Toluene	m-xylene	xylene mixed isomers	Benzyl Benzoate	dipentene	100-120 pet.ether
chlorobenzene	n-butyl formate	acetone		Shellsol A	Shellsol T
dichlorobenzene	cyclohexanone	methyl ethyl ketone		Pseudo cumene	cyclohexane
nitrobenzene	vinyl acetate	ethyl benzene		tetrahydronaphthalene	methyl cyclohexane
Cresols	methyl acrylate			tetrachloroethylene	di isoutylene
methyl naphthalene	methyl methacrylate			n-butanol	methanol
dichloromethane	acrylic acid			2-ethyl hexanol	ethanol
chloroform	propionic acid			butyl digol	isopropanol
carbon tetrachloride	xylene/n-pentanol 4:1			ethyl digol	ethane diol
1,2 dichloroethane	ethyl acetate/MEK 1:1			2-ethoxy ethanol	digol
1,1,1 trichloroethane				dipropylene glycol	glycerol
1,2 dichloroethylene				propylene glycol	di ethyl ether
trichloroethylene				allyl alcohol	di isopropyl ether
1,2 dichloropropane				diacetone alcohol	polyethylene glycol
Benzyl alcohol				ethyl acetate	carbon disulphide
methyl benzoate				n-butyl acetate	Shellsol T/ n-butanol 4:1
methyl acetate				amyl acetate	
ethyl formate				2-ethoxyethyl acetate	
cyclopentanone				methyl cyclohexyl acetate	
acetophenone				ethyl acetoacetate	
acetyl acetone				n-amyl formate	
1,4 dioxan				n-butyl propionate	
tetrahydrofuran				diethyl carbonate	
formic acid				di ethyl adipate	
acetic acid				dimethyl phthalate	
pyridine				dibutyl phthalate	
nitromethane				-butyrolactone	
styrene				triethyl phosphate	
α -methyl styrene				methyl cyclohexanone	
bis33chloromethyl oxetane				methyl n-propyl ketone	
xylene/isopropanol 9:1				methyl isobutyl ketone	
xylene/isopropanol 4:1				methyl isoamyl ketone	
xylene/butanol 19:1				methyl n-hexyl ketone	
xylene butanol 9:1				diethyl ketone	
xylene butanol 4:1				isophorone	
				dimethyl digol	
				dimethyl formamide	
				dimethyl acetamide	
				dimethyl sulphoxide	
				diallyl phthalate	
				di n-butyl fumarate	
				di n-butyl maleate	
				2-butoxy ethanol	
				polypropylene glycol	