Surfactant for Pesticide Formulation.

Supplement Edition : ME Formulation

Japan Agro-Formulation Consulting Co.,Ltd. (J.A.C.)
SK. AgroThink (Shanghai) Corp.,

Shin-Ichi ITOH.

1. What is ME Formulation

1-1. Thermodynamically stable formulation.

Theoretically, ME is thermodynamically stable formulation, technical is solubilized in inside of micelle, so if there are no any thermodynamic change, formulation is stable, no separation, no appearance change observed. This is completely different from such as other EW, EC that are thermodynamically unstable.

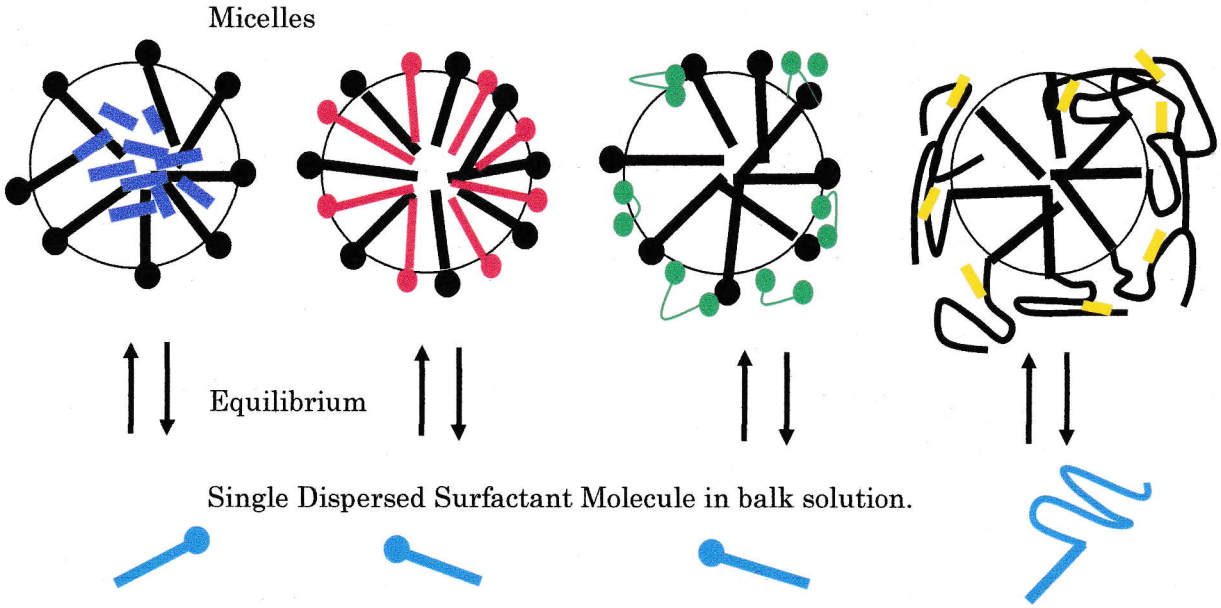


Fig.-1. Different Solubilization type.

1-2. Physical-Chemical property of ME

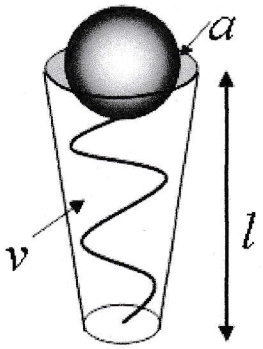
ME is Transparent, little bit viscous formulation. In this point of view, appearance looks very similar with other transparent formulation such as EC (EW, Emulsion), SL, these are essentially "Solution".

Because the size of Micelle is enough small, so formulation looks Transparent, but exactly the size of Micelle and its structure, Liquid Crystal structure are highly depend on a kind of Surfactant applied, dosage of its Surfactant. In Fig.-2, it shows different type of Liquid Crystal form which strongly related with Solubilization. Unfortunately proposed model surfactant is different from actually often used Surfactant for ME, but maybe we can understand essential solubilization difference by Micelle.

Actually for solubilization, HLB balanced Polyoxyalkylene arylpheny ether is often used because of bulky structure of Lipophilic part, and well solubilize organic TC.

Now we can understand ME is usually little bit viscous compare with other formulation such as EC, SL, this is because all TC is solubilized in Micelle inside, and micelle itself is essentially construct a kind of structure, and it will become a kind of

Liquid Crystal especially at stage of concentrated.



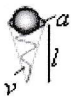
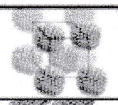
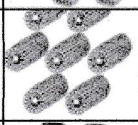
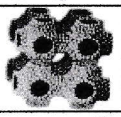
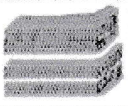
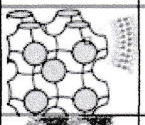
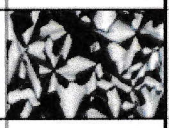
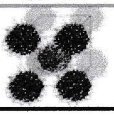
	溶存状態	充填パラメーター		会合構造	構造	記号	組織像
親水性	ミセル		$v/al \leq 1/3$		球 状	L_1	——
+			$1/3 < v/la \leq 1/2$		棒 状	L_1	——
曲率	液 晶		$v/al \leq 1/3$		キュービック	I_1	——
			$1/3 < v/la \leq 1/2$		ヘキサゴナル	H_1	
			$1/2 < v/al \leq 1$		キュービック	V_1	——
			$v/al \approx 1$		ラメラ	$L\alpha$	
			$1 \leq v/al$		キュービック	V_2	——
			$1 < v/al$		逆ヘキサゴナル	H_2	
			$1 < v/al$		キュービック	I_2	——
親油性	逆ミセル		$1 < v/al$		球状	L_2	——

Fig.-2 Liquid Crystal, Critical Packing Parameter

2. General Composition of ME and its Ingredients.

The ME composition is similar with other Water based formulation but dosage of Surfactant is rather big because of TC solubilization, also Co-surfactant / Co-solvent might be used, these might be a kind of Key for ME formulation.

High dosage of Surfactant will cause high cost and high Viscosity of formulation, so these difficulties must be solved by using Co-surfactant, Co-solvent, and these ingredients make ME formulation stable also.

Following Table shows general Composition of ME.

Table-1. General Composition of ME.

	Dosage (wt %)	Function
Technical	~ 40	Active Ingredient
Surfactant (solubilizer)	10 to 30	Solubilization, Emulsification
Co-Surfactant	5 to 20	Solubilization, Emulsification
Anti-freeze	3 to 5	Anti-freezing
Solvent	adequate	Solvent for TC, Compatible with Water & TC
Ion exchanged Water	Rest	Continuous phase

3. Ingredients of ME.

3-1. TC (Technicals) and Solvent.

Physically, Chemically quite different TC will be formulated in ME, and its dosage is also different in ME formulation.

Liquid TC is rather easily applied for ME but some time we need adequate Solvent for TC, because TC will easily crystalize at low temperature if there is no adequate solvent. So, primitive function of Solvent is to make TC liquid form at low temperature, and when we think about Solvent for TC, *log P* will be a one of Indicator for Solvent selection (*log P* : Kow Octanol partition coefficient), also we should pay attention for Density, Melting point, Water solubility etc.,

But at the same time such Solvent must be solubilized also, it means dosage of Solvent must be enough for TC, but it should be minimum volume in ME formulation. At the same time we need consider both affinity of Solvent to TC and Water.

Following Table-2 shows HLB of several solvent based on I/O Balance conception. I/O value is different from *log P* for TC, but its conception itself is quite useful to select solvent for ME formulation. The order of HLB for solvent which often used for ME, such as Cyclohexanone, NMP, BDG, Bu-OH including Anti-freeze such as EG, are listed in a Table clearly.

Again, important thing for Solvent selection for ME is, both affinity to TC, Water must be considered. Sometimes, different solvent combined to make stable ME.

Also about Anti-Freeze such as EG, it might be Hydrotrope (solubilizer), and make viscosity of ME lower. We need consider this point also.

Table-2. Inorganic-Organic Balance of Solvent.

Solvent Name	I / O	HLB (I / O x 10)	*Log P*
Kerosene	0.000	0.00	
Ethyl benzene	0.075	0.75	3.15
Xylene	0.094	0.94	3.12
Toluene	0.107	1.07	2.69
OME (Me-Oleate)	0.236	2.36	7.45
Methyl naphthalene	0.273	2.73	3.87
Cyclohexanone	0.625	6.25	0.81
BDG	0.875	8.75	0.30
n-C4H9-OH (n Bu-OH)	0.125	12.50	0.88
iso-C_4H_9-OH (iso Bu-OH)	0.143	14.30	0.80
NMP	1.450	14.50	0.38
PGM (Propylene glycol methyl ether)	1.710	17.10	-0.49
PG	4.000	40.00	-0.92
EG	5.000	50.00	-1.36
Glycerin	5.000	50.00	-1.76

3-2. Surfactant (Solubilizer).

ME is TC solubilized in Micelle, Water and Oil (TC) rather well balanced formulation, so generally Surfactant should have big solubilizing power and well balanced HLB. Following Table show general surfactant which used for ME formulation.

Table-3. Surfactant for ME.

Surfactant	HLB	I/Ox10	ION	Solubilization	Comment
SK-97DM		2.50	(C)	(M/B)	
SK-5935	4.30	6.08	N	(M/B)	Empirical HLB might be appropriate
SK-53CA		8.82	A	(M/B)	
SK-94S7	11.80	10.61	N	M	
SK-5218CP	13.00	11.56	N	B	I/O x 10 might be appropriate
SK-33SC	(12.00)	12.07	N-A	B	
SK-92FS1	15.00	13.54	N	B	It might be around 14.50
SK-5945	15.00	14.74	N	M/B	
SK-34SC	(15.00)	16.10	N-A	B	
SK-551		17.62	A	M	
SK-96		19.28	N	M	
SK-9702Q		22.50	C	S	Main component of SK-41CN

HLB : ( ), HLB of raw material Nonionic surfactant,

ION : N/ Nonion, A/Anion, N-A/Nonion modified to Anion, B/Betain, C/Cation, (C)/Amine

Solubilization : B/Big, M/B /Medium to Big, M/Medium, S/M /Small to Medium, S/Small

(M/B)/Medium to big in case together with Nonion, single is not water soluble

Just same as other formulation, ME must have formulation stability at high temperature and low temperature. When single use of Nonionic surfactant such as SK-5218CP only, sometime formulation will be cloudy at high temperature because of Cloud point of Nonionic surfactant. This is because, actually both Nonionic and Anionic Surfactant combined.

More concrete example might be as follows.

SK-5218CP single use → Replace (partly) to SK-33SC → SK-34SC

→ Combine SK-551

→ Solvent change to more strong Water affinity solvent

4. Production of ME

When formulation recipe is already finalized, in this case there is no special direction for production. But in case still formulation study needed, then production course should be highly systematized. Because to make solubilization completely, such systematic solubilization is highly required. Simply said,

1st step : TC should be dissolved into solvent (TC mixture).

Solvent should have more bigger solubility, need consideration about Water affinity (Solvent combination).

2nd step : TC mixture should be dissolved into Surfactant/Co-surfactant/Anti-freeze.

Mixture should be Transparent.

Surfactant dosage is bigger than other formulation such as SL, EC, EW.

3rd step : Water should be added dropwise into above mixture.

Water volume should be checked when formulation become cloudy. (even formulation become cloudy, sometimes, it will become transparent again because change of micelle structure)

When formulation cloudy at added Water volume is too small, Surfactant, Solvent, its dosage must be considered again.

To improve Cloudy situation, Water affinity of ingredient must be more higher.

4th step : Formulated ME estimation.

Not only Heat Stability, Cold Stability, Crystalization in Diluted emulsion must be checked. If Crystalization was founded, Dosage of Solvent should be increased, also Water affinity of solvent should be changed to more Hydrophobic.

Following Diagram show general direction for ME formulation study.

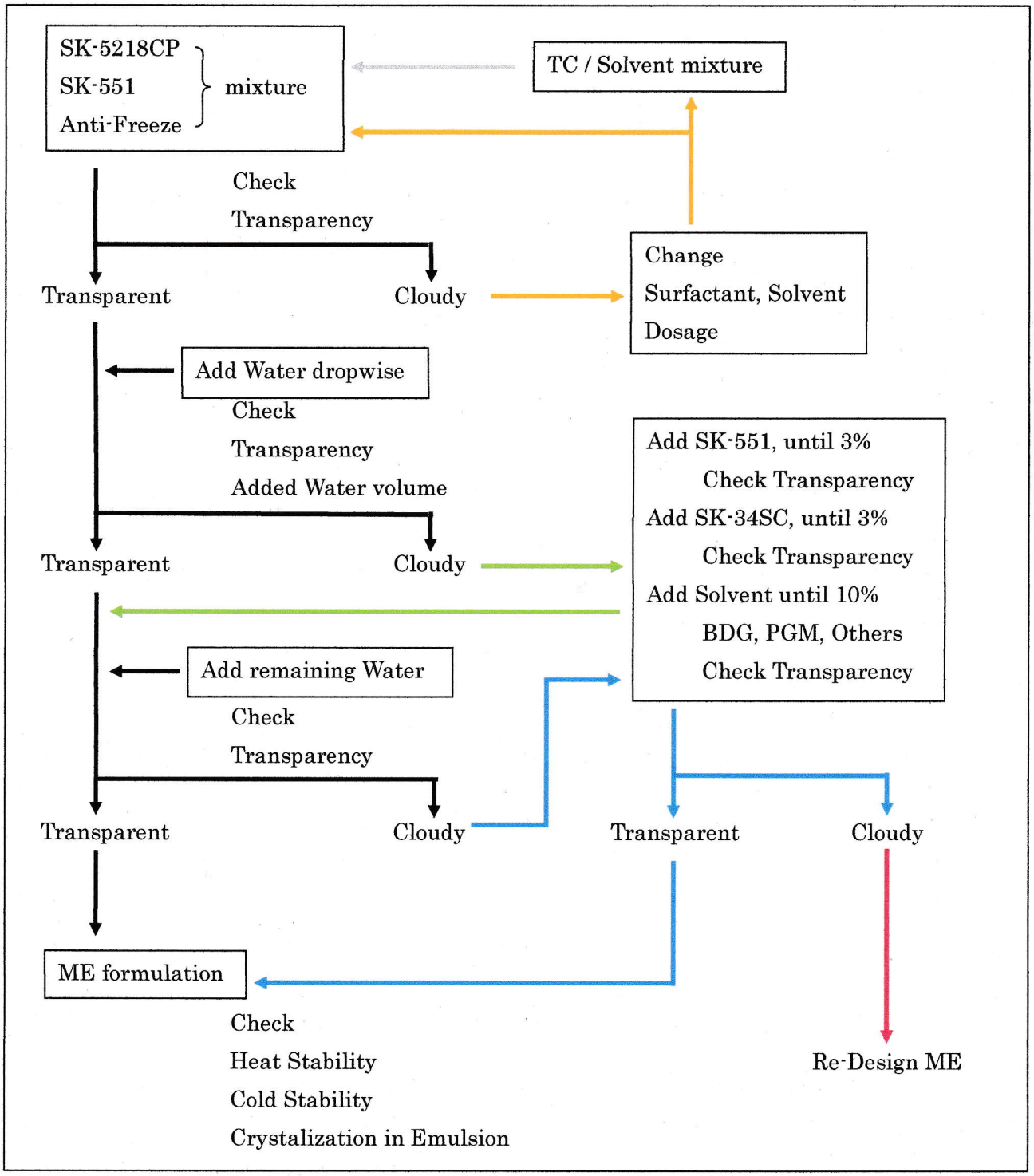


Fig. 3. ME formulation Study Direction.

5. Estimation of ME.

5-1. Cold Stability

Cold stability (Crystalization) highly depend on kind of Solvent. The solvent must has biggest solubility for TC (such solvent might be Polar solvent usually, then additional Co-solvent should be combined to avoid Crystalization in diluted emulsion).

5-2. Heat Stability

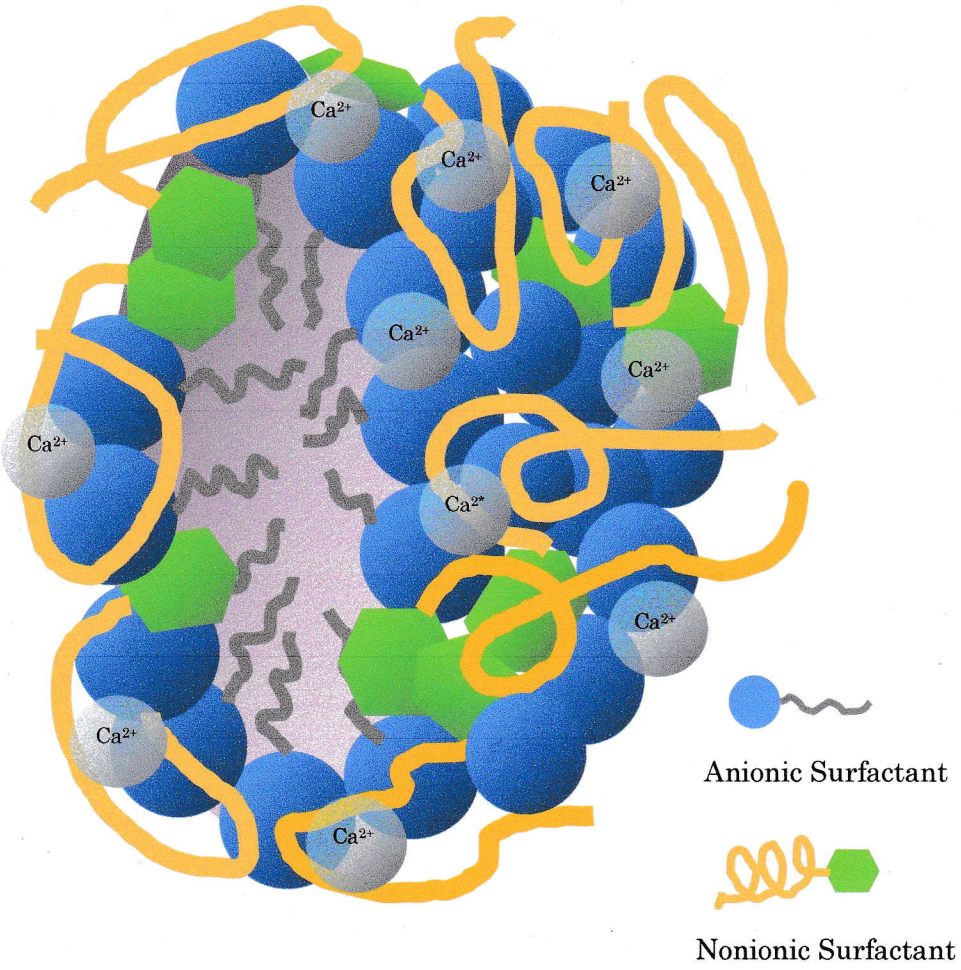
Heat Stability should be carried out at proper temperature (usually 54 Celsius).
If ME become cloudy at high temperature, then HLB of Solvent, Surfactant should be increased.

5-3. Crystalization in Diluted Emulsion.

When ME was diluted with Water for application, it will become Emulsion easily. And usually TC was no longer solubilized in micelle but become normal Emusion, so Crystal appeared in Emulsion.

To prevent this phenomena, Polarity of Solvent must be changed to more non-polar solvent. But in this case, Cold Stability of ME might have problem, so we need carefully select the solvent.

More actual concrete image of Micelle.



Illustrative Micelle Structure of Anionic, Nonionic Surfactant Mixture.

1. Micelle is composed with Calcium Alkylbenzene sulfonate / POE arylphenyl ether.
2. Micelle inside has Hydrophobic property because of Alkylbenzene and Aryl group.
3. Micelle surface composed with Hydrophilic POE chain, SO_3^{2-} part together with Counter ion Ca^{2+}.
4. There are Steric hindrance by POE chain and Electric double layer on Micelle surface.
5. Each surfactant Molecule is in Equilibrium state with Molecule which located in bulk water.