

The Orthogonality of the Selectivity Space in Reversed-Phase Thin-Layer Chromatography

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Solvation Parameter Model

$$SP = c + eE + sS + aA + bB + W$$

System Constant	Solute Descriptor	Interaction
v	V	Cavity formation Dispersion
e	E	Electron lone pair
s	S	Dipole-type
a	A	Solvent HBB-solute HBA
b	B	Solvent HBA-solute HBB



Solute Descriptors

- V is McGowan's Characteristic Volume
- E is the excess molar refraction
- S is the solute dipolarity/polarizability
- A is the effective solute hydrogen-bond acidity
- B is the effective solute hydrogen-bond basicity

System Maps

Solvent

Methanol

2-Propanol

2,2,2-Trifluoroethanol

Acetonitrile

Acetone

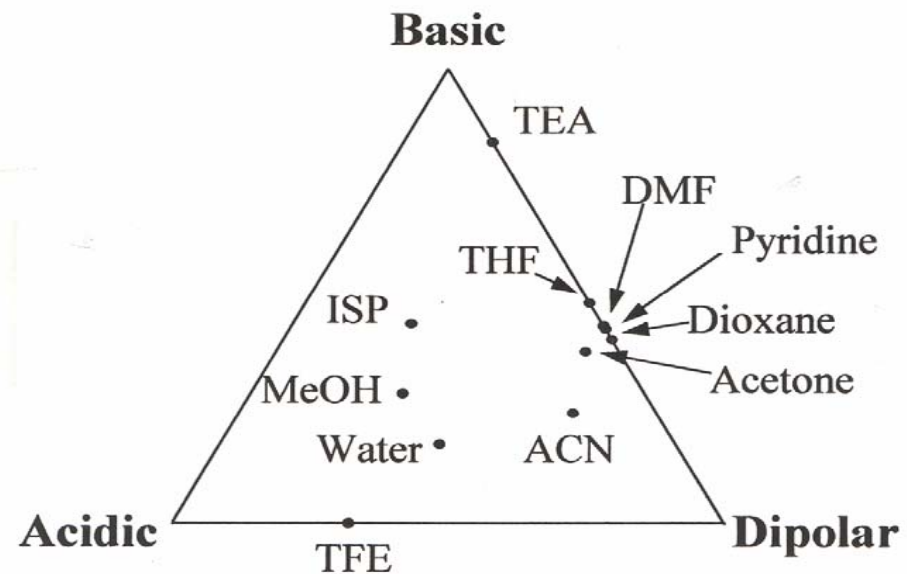
Dimethylformamide

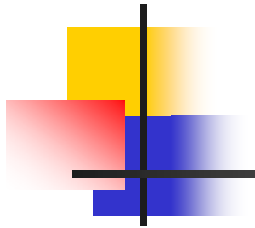
Pyridine

Stationary Phase

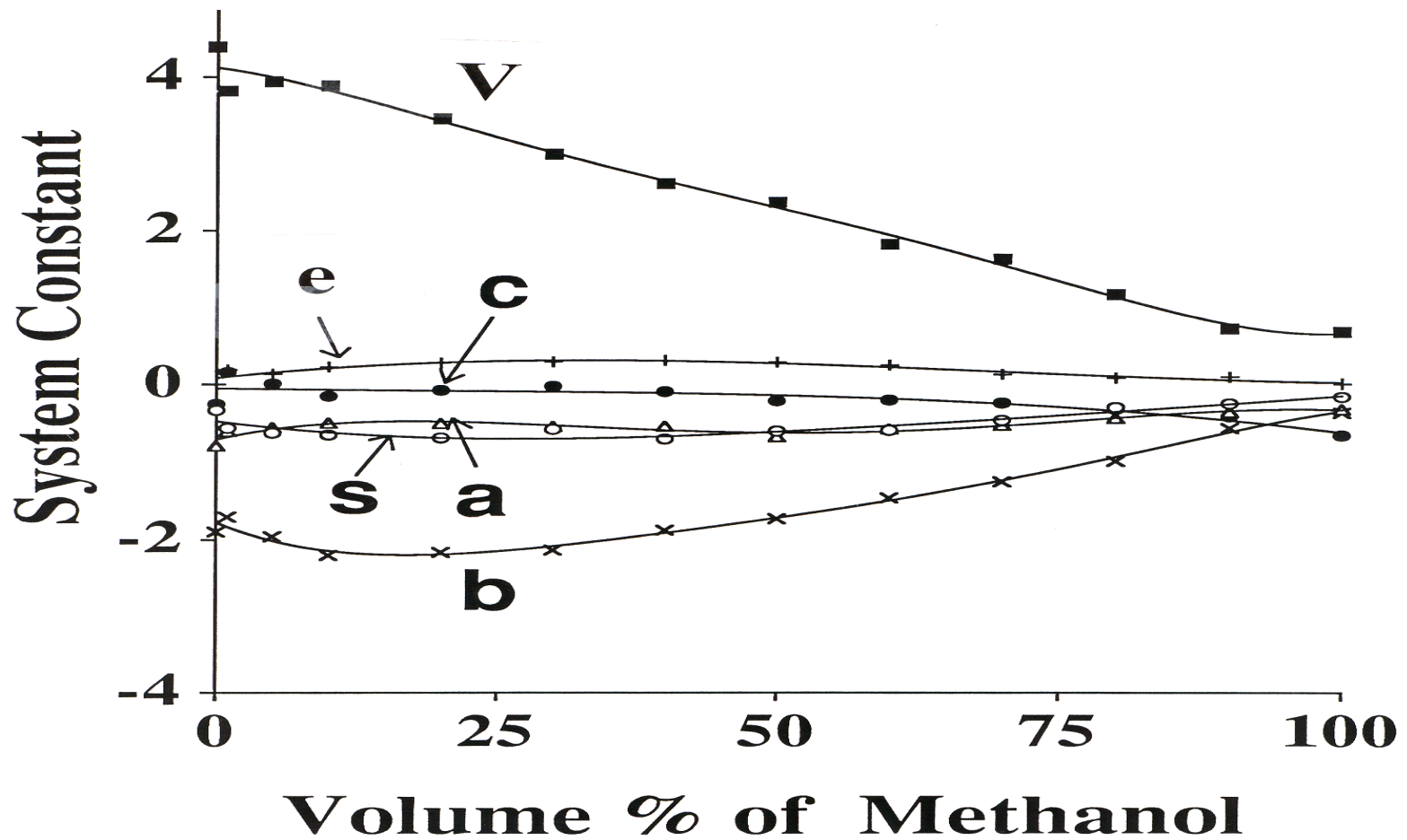
Octadecylsiloxane

Cyanopropylsiloxane





System Map





D-Parameter

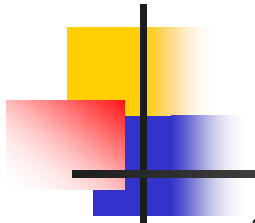
Euclidean distance in hyperspace

$$\sqrt{[(e_1 - e_2)^2 + (s_1 - s_2)^2 + (a_1 - a_2)^2 + (b_1 - b_2)^2 + (v_1 - v_2)^2]}$$

1=reference solvent (water)

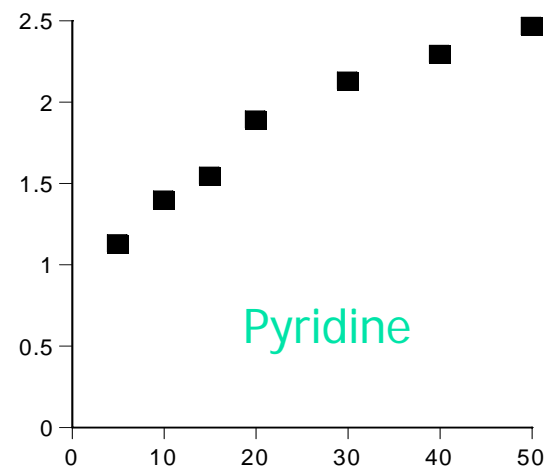
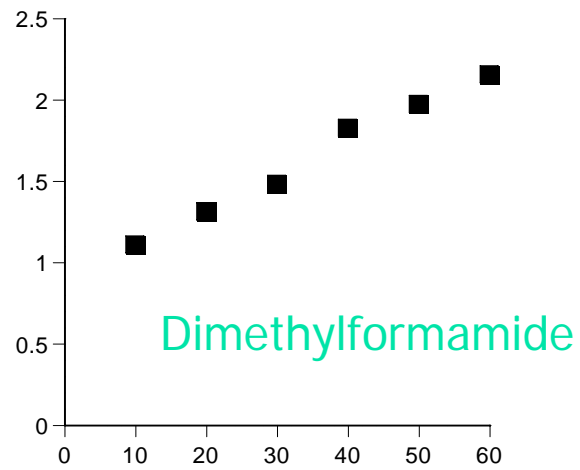
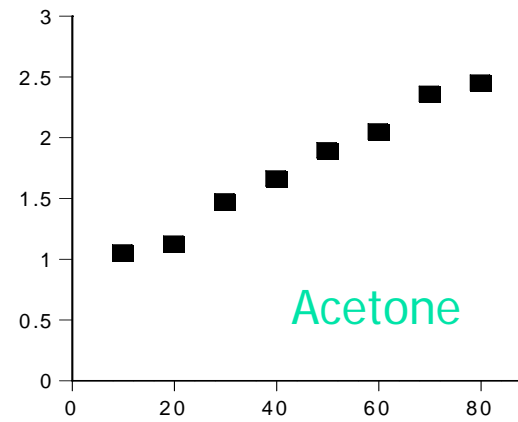
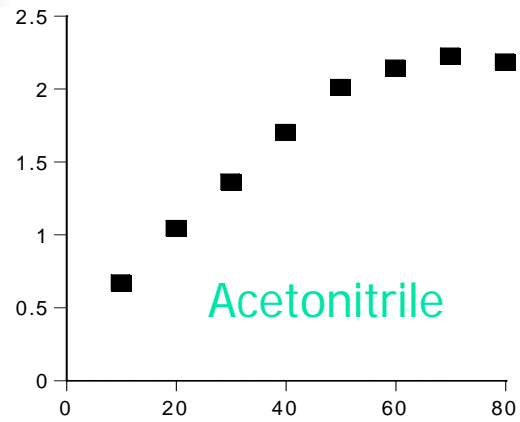
2=binary or higher order solvent mixture

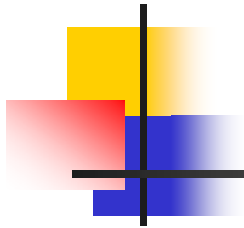
A measure of the chemical similarity of separation systems



D-Parameter

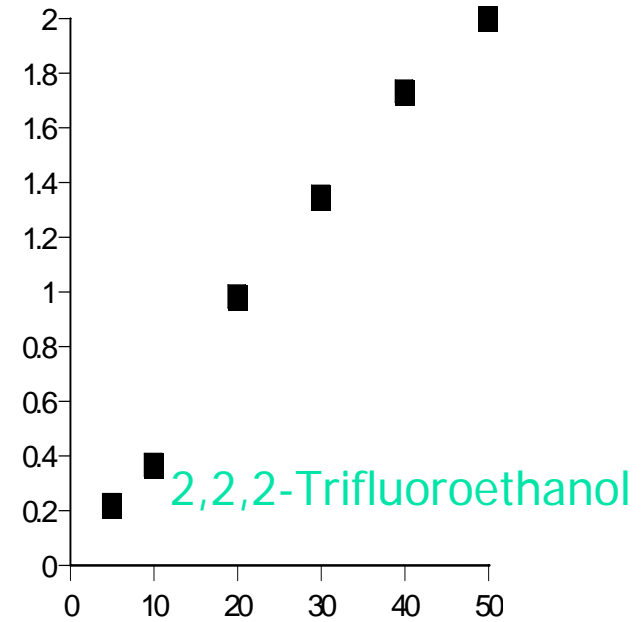
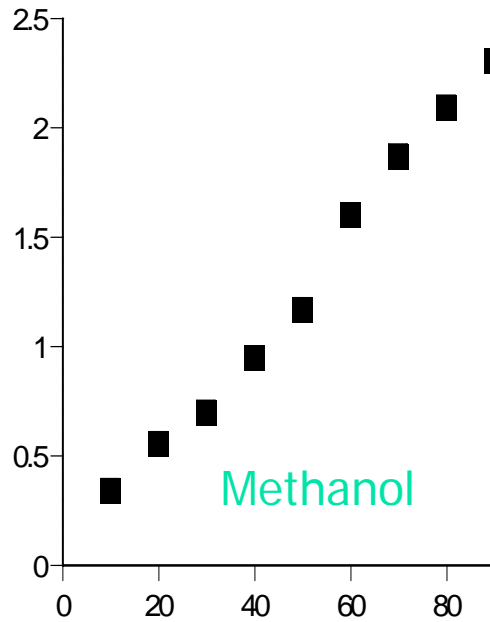
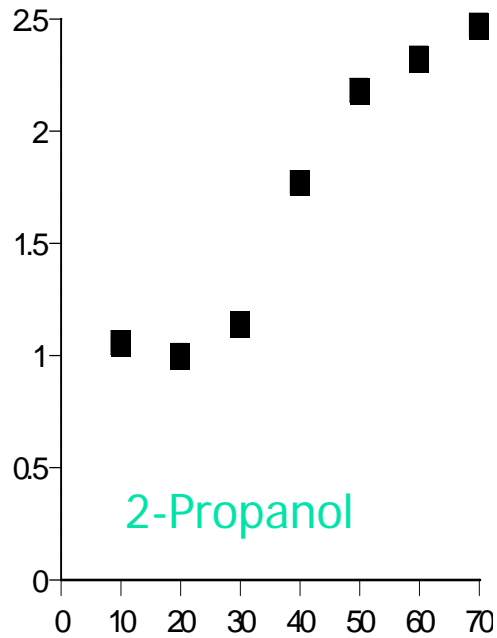
RP-18WF

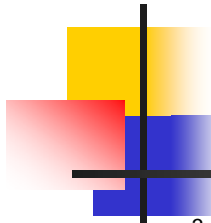




D-Parameter

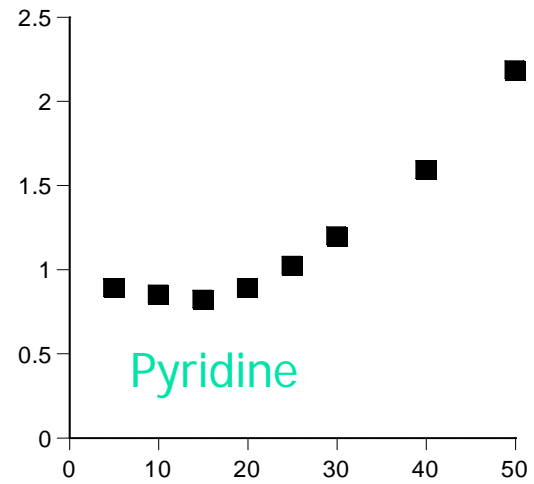
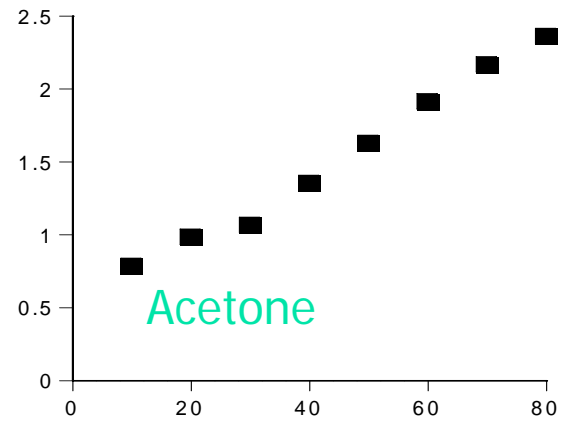
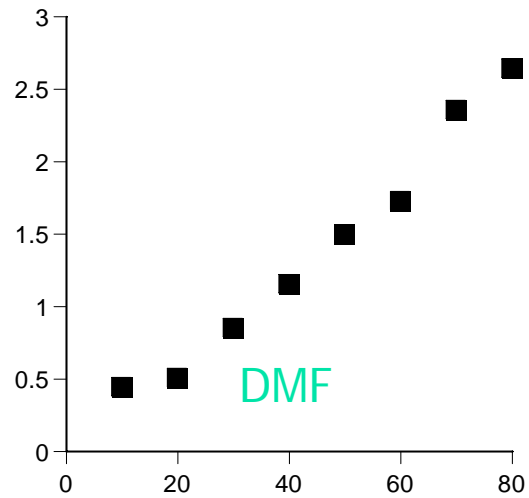
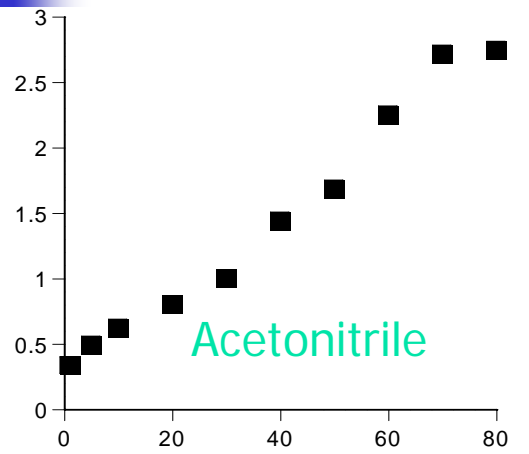
RP-18WF



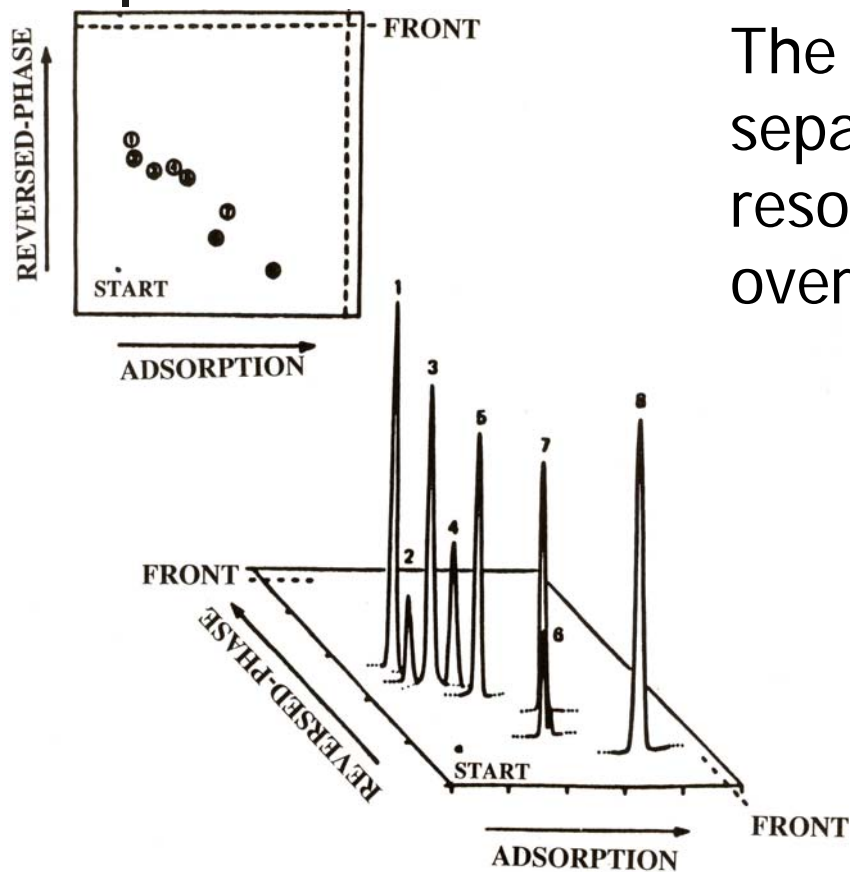


D-Parameter

CN-WF



TWO DIMENSIONAL TLC



The realization of a more efficient separation system implies that the resolved sample should be distributed over the entire surface

This can be achieved only if the selectivity of the separation mechanism is complementary in the orthogonal direction



Zone Capacity (Practical)

Development	Dimensions	Zone Capacity
Capillary controlled flow	1D	10-14
Forced flow	1D	40-50
Capillary flow (AMD)	1D	40-80
Capillary controlled flow	2D	≈ 100
Forced flow	2D	≈ 1500
Capillary flow (AMD)	2D	≈ 1500-6000



Cos θ

Conversion of the system constants to vectors allows identification of systems in which the dependent variables are expected to be correlated

Any other system with a new set of system constants is represented as another vector in hyperspace separated by an angle the magnitude of which depends on the difference in the system constants



Cos θ

$$\frac{(e_1 e_2 + s_1 s_2 + a_1 a_2 + b_1 b_2 + v_1 v_2)}{[\sqrt{(e_1^2 + s_1^2 + a_1^2 + b_1^2 + v_1^2)}][\sqrt{(e_2^2 + s_2^2 + a_2^2 + b_2^2 + v_2^2)}]}$$

A measure of the likely correlation of R_F values in the compared separation systems

Cos $\theta = 1$ (high correlation)

Cos $\theta = 0$ (systems are orthogonal)



Comprehensive GC

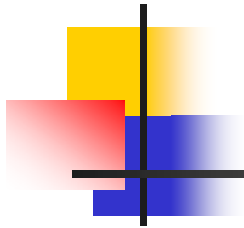
$\text{Cos } \theta$

	SPB-Octyl	DB-1
HP-5	0.83	0.99
DB-17	0.62	0.86
DB-210	0.30 (73°)	0.63
PEG	0.26 (75°)	0.63 (52°)
BPX90	0.22 (78°)	0.62 (51°)



Cos θ Binary Solvents

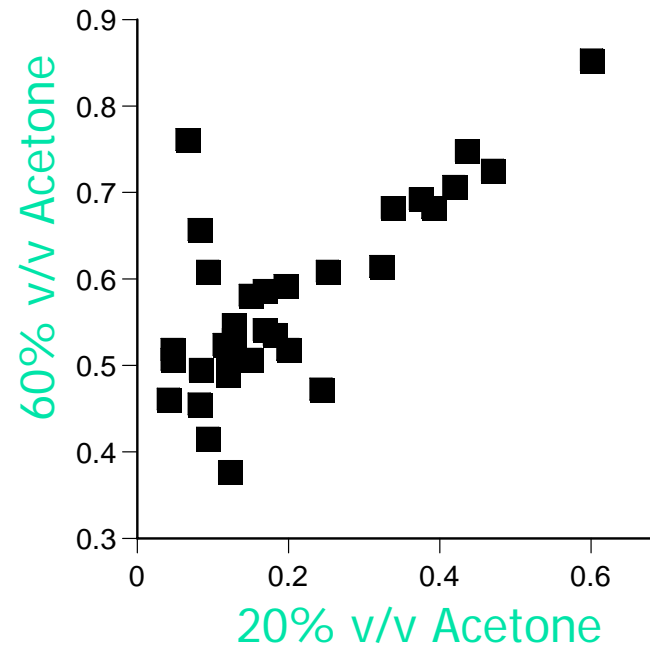
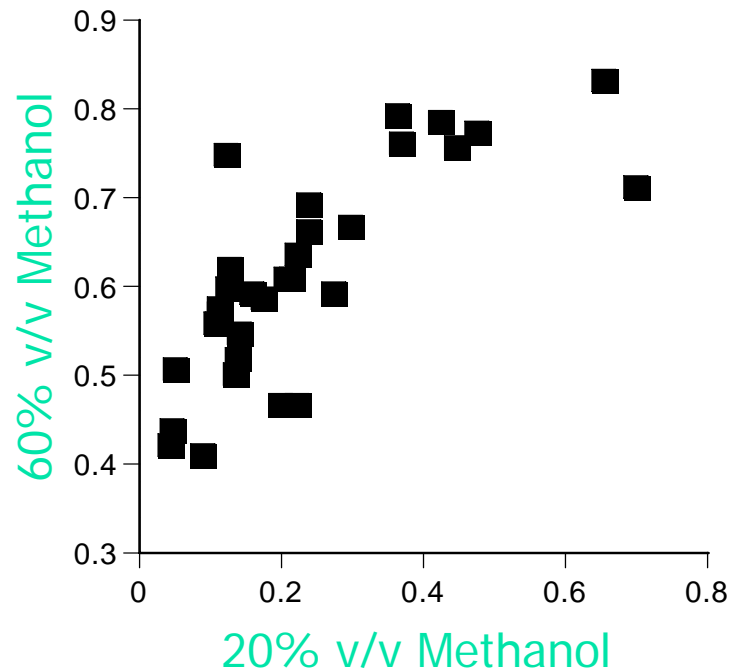
(%v/v)	Cos θ (CN Layer)			
	MeOH	ACN	Acetone	Pyridine
10	0.998	0.976	0.965	0.930
20	0.990	0.949	0.934	0.845
30	0.986	0.942	0.879	0.818
40	0.971	0.934	0.847	0.779
50	0.970	0.933	0.802	0.740
60	0.952	0.930	0.792	
70	0.946	0.931	0.784	



2D-TLC

Binary Solvent Systems

Cyano Layer





Recommended Systems RP-18w

Solvent 1 Water

Solvent 2

50%(v/v) Pyridine

90%(v/v) Acetone

50%(v/v) Acetone

30%(v/v) Pyridine

70%(v/v) 2-Propanol

40%(v/v) DMF

Cos θ

0.740 (42°)

0.748 (42°)

0.748 (37°)

0.802 (35°)

0.883 (28°)

0.885 (27°)

Solvent 1 10%(v/v) Acetone

Solvent 2

90%(v/v) Acetone

80%(v/v) Acetonitrile

50%(v/v) Pyridine

70%(v/v) 2-Propanol

50%(v/v) 2,2,2-TFE

Cos θ

0.767 (40°)

0.858 (31°)

0.886 (28°)

0.902 (26°)

0.922 (23°)



Recommended Systems CN F

Solvent 1 Water

Solvent 2

90%(v/v) Methanol

80%(v/v) Acetonitrile

80%(v/v) DMF

70%(v/v) 2,2,2-TFE

70%(v/v) Acetone

Cos θ

0.326 (71°)

0.428 (65°)

0.452 (63°)

0.494 (60°)

0.882 (28°)

Solvent 1 10%(v/v) Methanol

Solvent 2

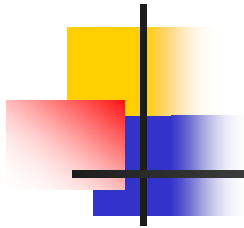
80%(v/v) Acetonitrile 0.437 (64°)

70%(v/v) 2-Propanol 0.446 (64°)

80%(v/v) DMF 0.461 (63°)

70%(v/v) 2,2,2-TFE 0.504 (60°)

70%(v/v) Acetone 0.922 (26°)



2D-TLC

Binary Solvent Systems

Cyano Layer

