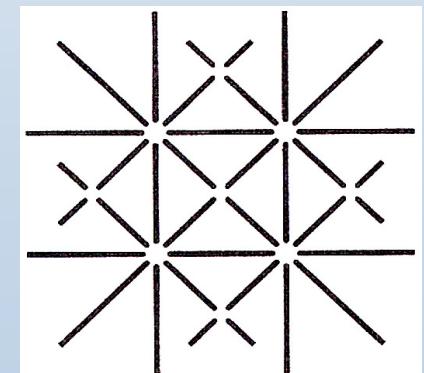


University of Utah, Salt Lake City

## A novel approach to the characterization of polar liquids

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University of Basel



September 15, 2003

# Background: Classical Clausius-Mosotti-Debye Equation

$$\frac{\epsilon - 1}{\epsilon + 2} * \frac{M}{\rho} = \frac{N_A}{3\epsilon_0} \left( \alpha + \frac{\mu_g^2}{3KT} \right)$$

- $\epsilon$  = quasi-static relative dielectric constant  
 $M$  = molecular weight  
 $\rho$  = density  
 $N_A$  = Avogadro number  
 $\epsilon_0$  = electric field constant in the vacuum  
 $\alpha$  = polarizability of the molecule  
 $\mu_g$  = dipole moment ( in the state of an ideal gas )  
 $K$  = Boltzmann constant  
 $T$  = temperature

# Validity of the classical Clausius-Mosotti-Debye Equation

Classical Clausius-Mosotti-Debye Equation  
is only valid for

- o the case of ideal gases and
- o for highly diluted solutions of a molecule with a permanent dipole moment in a liquid with no dipole moment such as water in 1,4-dioxane!

## Classical Clausius-Mosotti-Debye Equation

Is based on the Lorentz approach

- o i.e. what is the local electric field  $E_{\text{local}}$ , which feels a molecule at the center of a virtual cavity with a shape of a homogeneously polarized sphere.

The outside of the sphere is treated as a continuum

- o having macroscopic properties with  $\epsilon = \text{quasi-static relative dielectric constant}$ .

## The local electric field $E_{\text{local}}$

$$E_{\text{local}} = E_i + E - E_{\text{sph}}$$

$E_i$  = internal electric field, caused by the nearest neighbor interaction of molecules surrounding the molecule at the center of the sphere

$E$  = externally applied electric field

$E_{\text{sph}}$  = electric field caused by the charges at the surface of the virtual sphere (as a consequence of the surrounding polarized continuum).

## Internal electric field $E_i$

- In case of an ideal gas:  $E_i = 0$
- In case of a liquid or solid:  $E_i \neq 0$

Due to the close molecule-molecule interaction,  
which is not isotropic in all directions,  
i.e.  $E_i$  is not zero by canceling out!

## Modified Clausius-Mosotti-Debye Equation

$$\frac{\varepsilon - 1}{3 \frac{E_i}{E} + (\varepsilon + 2)} \frac{Mr}{\rho} = \frac{N_A}{3\varepsilon_0} \left( \alpha + \frac{\mu_g^2}{3KT} \right)$$

$E_i$  = internal electric field

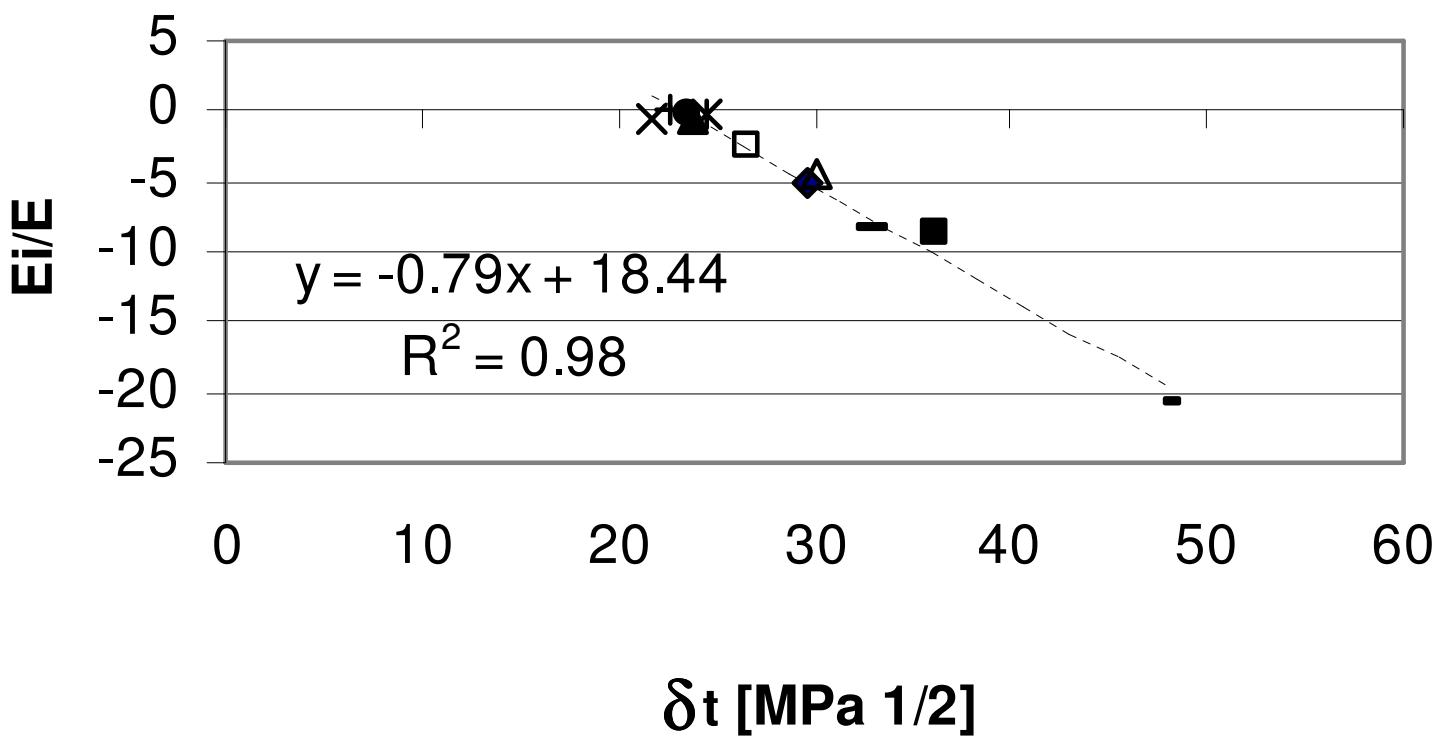
$E$  = externally applied electric field

- o Thus the unknown parameter  $E_i / E$  can be determined and used to characterize dense systems such as solids or liquids especially polar ones!
- o For  $E_i / E = 0$  the classical Clausius-Mosotti-Debye Equation results

# Towards a better understanding of the parameter $E_i/E$

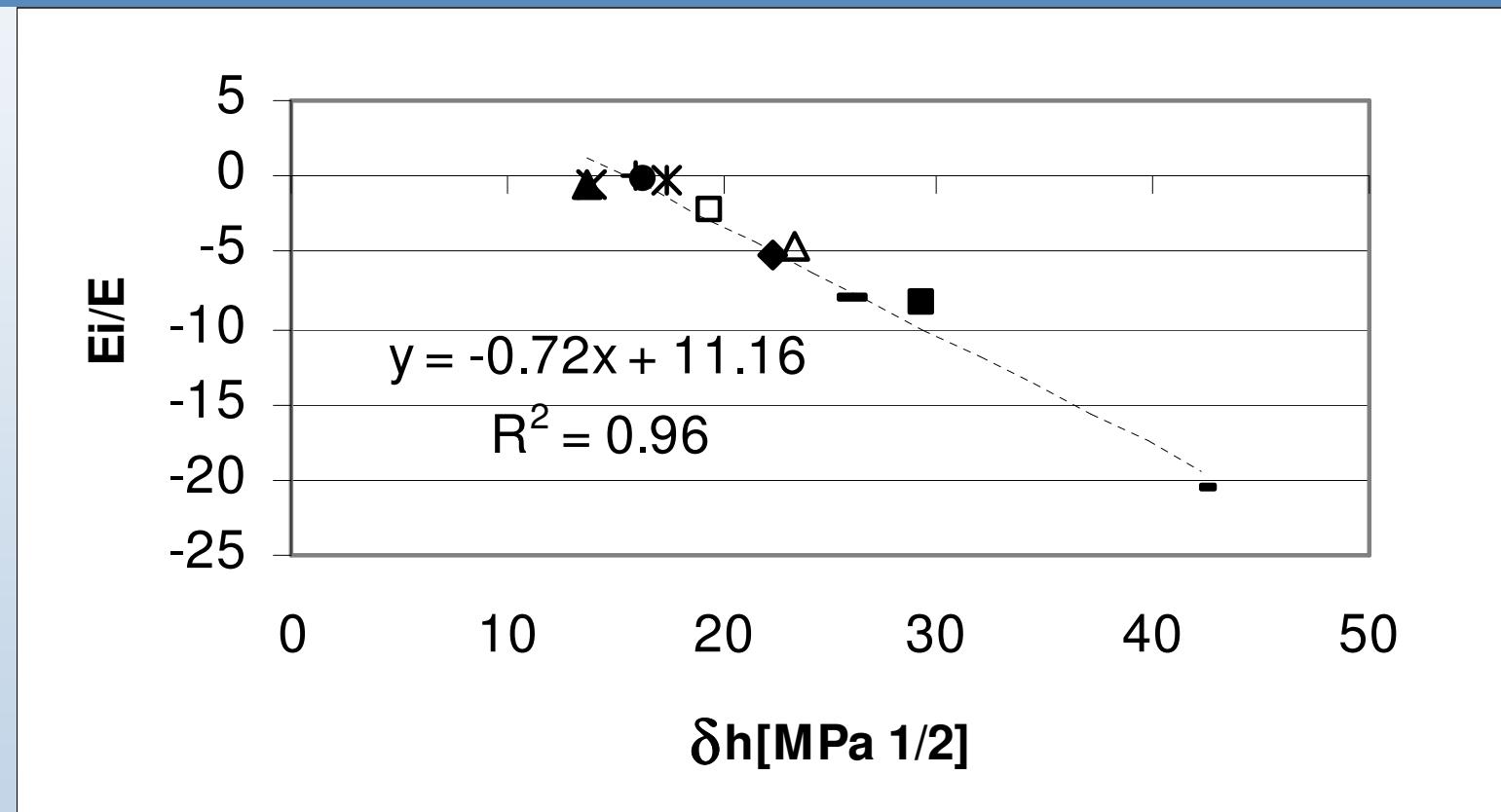
Substance	OH -groups	<sup>1)</sup> Ei/E- value	Number OH/vol	<sup>2)</sup> $\delta_t$ (MPa <sup>1/2</sup> )	<sup>2)</sup> $\delta_p$ (MPa <sup>1/2</sup> )	<sup>2)</sup> $\delta_h$ (MPa <sup>1/2</sup> )	<sup>2)</sup> $\delta_d$ (MPa <sup>1/2</sup> )	$(\delta_p^2 + \delta_h^2)^{1/2}$
Methanol	1	-5.190	0.025	29.600	12.300	22.300	15.100	25.470
Ethanol	1	-2.390	0.017	26.500	8.800	19.400	15.800	21.300
Benzylalcohol	1	-0.570	0.010	23.800	6.300	13.700	18.400	15.080
2-Methyl-1-butanol	1	-0.550	0.009	21.700	4.500	13.900	16.000	14.610
1-Propanol	1	-0.140	0.013	24.500	6.800	17.400	16.000	18.680
2-Propanol	1	-0.100	0.013	23.500	6.100	16.400	15.800	17.500
2-Methyl-1-propanol	1	0.170	0.011	22.700	5.700	16.000	15.100	16.980
Water	1.33	-20.620	0.074	47.800	16.000	42.30	15.600	45.220
1,2-Ethanediol	2	-8.210	0.036	32.900	11.000	26.000	17.000	28.230
1,2-Propanediol	2	-4.560	0.027	30.200	9.400	23.300	16.800	25.120
1,2-Butanediol	2	-3.110	0.022	n.a	n.a	n.a	n.a	n.a
Glycerol	3	-8.540	0.041	36.100	12.100	29.300	17.400	31.700

# $E_i/E$ values as a function of the total Hildebrand solubility parameter $\delta_t$ at 298.2K



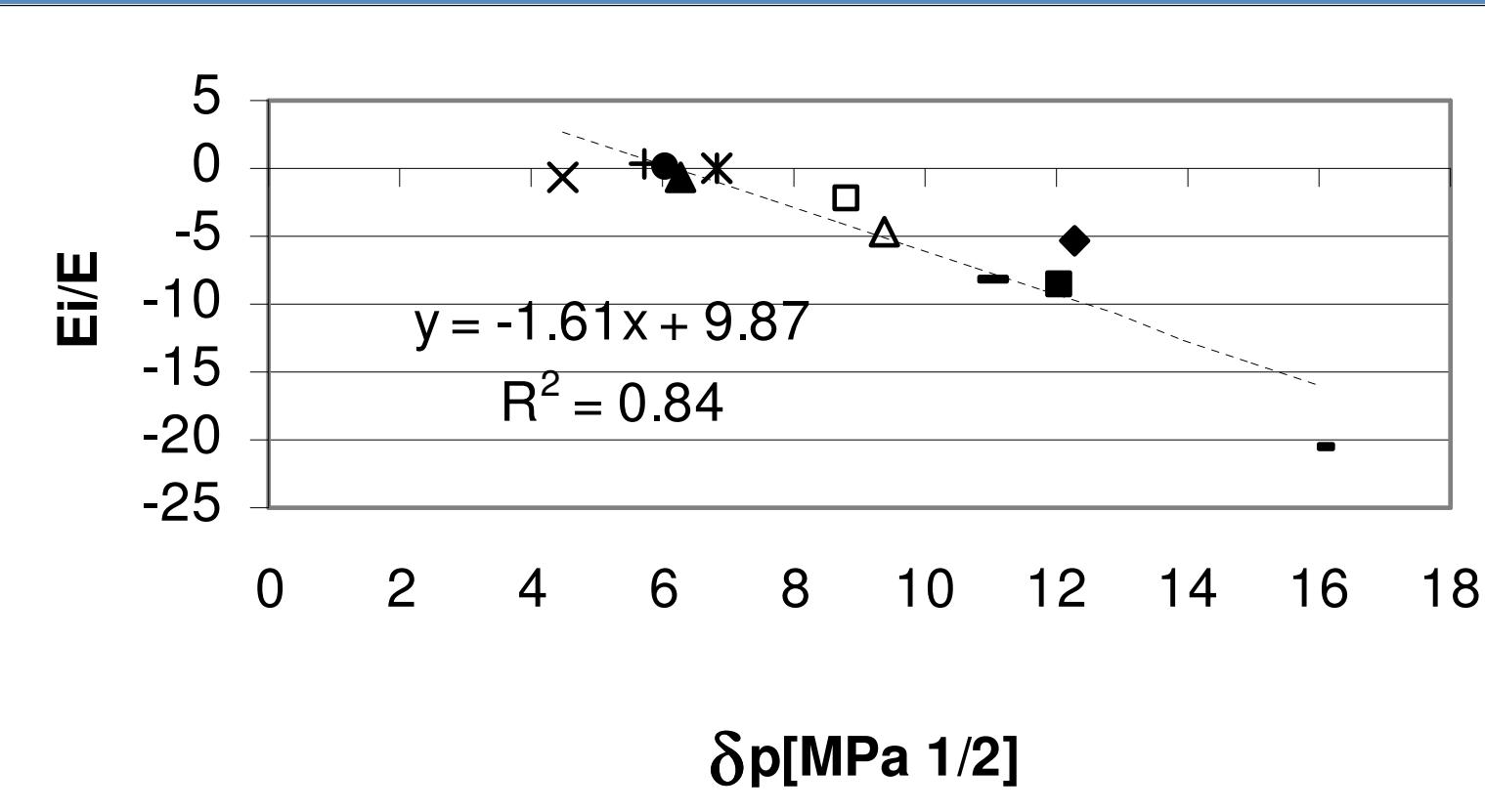
- ◆ Methanol   □ Ethanol   ♦ Benzylalcohol   × 2-methyl-1 butanol   ✕ 1-propanol   ■ glycerol
- + 2-methyl-1 propanol   – water   — 1,2-ethanediol   △ 1,2-propanediol   • 2-propanol

# $E_i/E$ values as a function of the partial Hanson solubility parameter $\delta_h$ at 298.2K



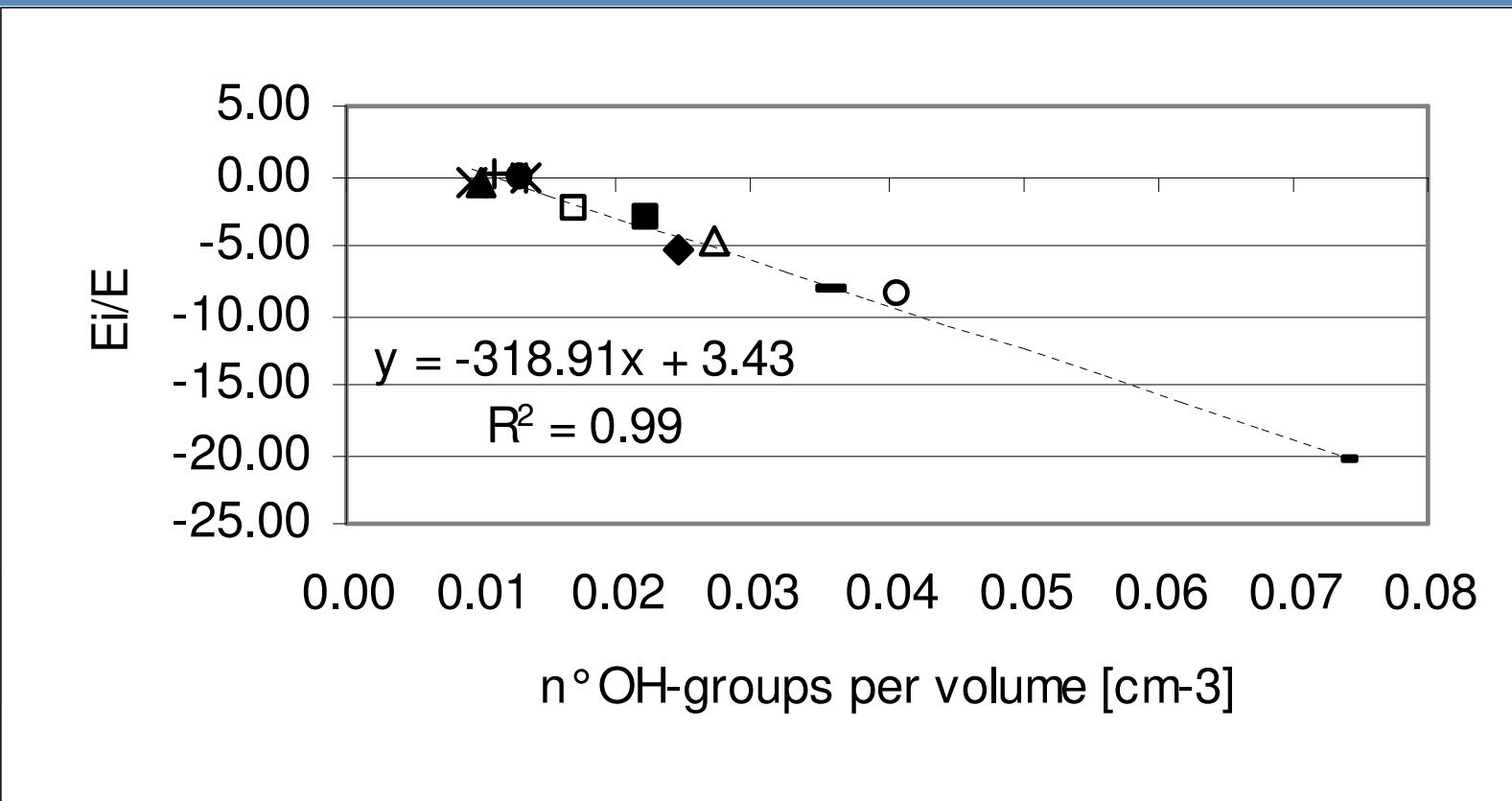
◆ Methanol □ Ethanol ♦ Benzylalcohol × 2-methyl-1 butanol ✕ 1-propanol ■ glycerol  
+ 2-methyl-1 propanol – water — 1,2-ethanediol △ 1,2-propanediol • 2-propanol

# $E_i/E$ values as a function of the partial Hanson solubility parameter $\delta_p$ at 298.2K

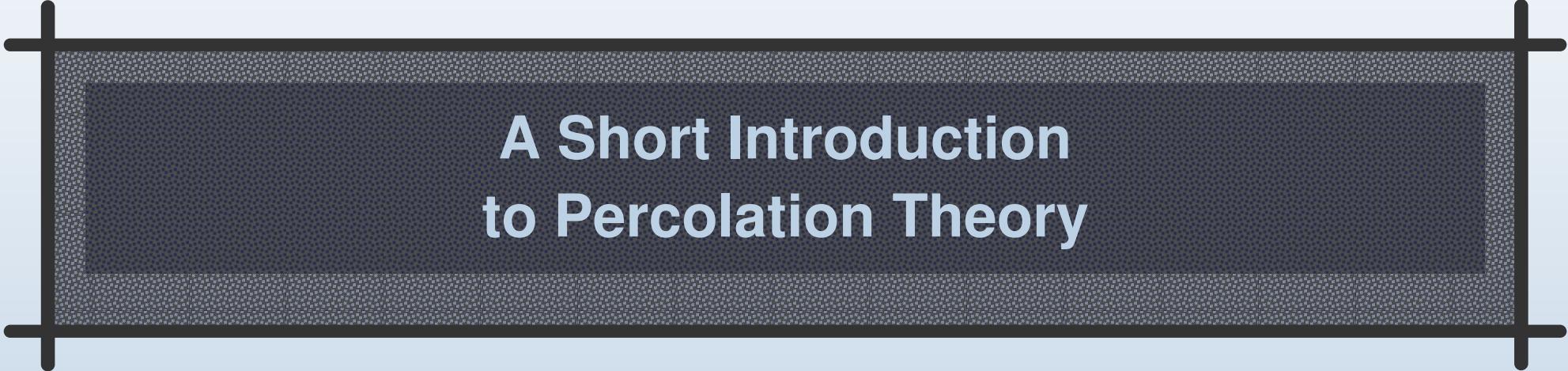


◆ Methanol   □ Ethanol   ♦ Benzylalcohol   × 2-methyl-1 butanol   ✕ 1-propanol   ■ glycerol  
 + 2-methyl-1 propanol   – water   — 1,2-ethanediol   △ 1,2-propanediol   • 2-propanol

# $E_i/E$ values as a function of the number of OH-groups per volume at 298.2 K



- ◆ Methanol □ Ethanol ♦ Benzylalcohol × 2-methyl-1 butanol ✂ 1-propanol
- 1,2-butanediol + 2-methyl-1 propanol – water — 1,2-ethanediol △ 1,2-propanediol • 2-propanol O glycerol



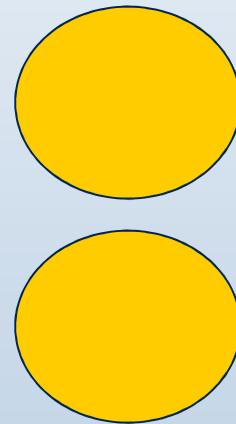
# A Short Introduction to Percolation Theory

Application of Percolation Theory



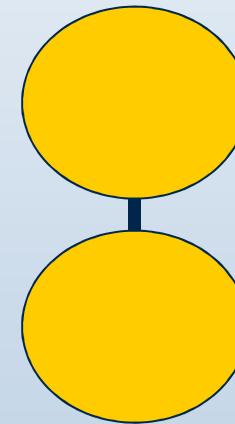
# Percolation

Site



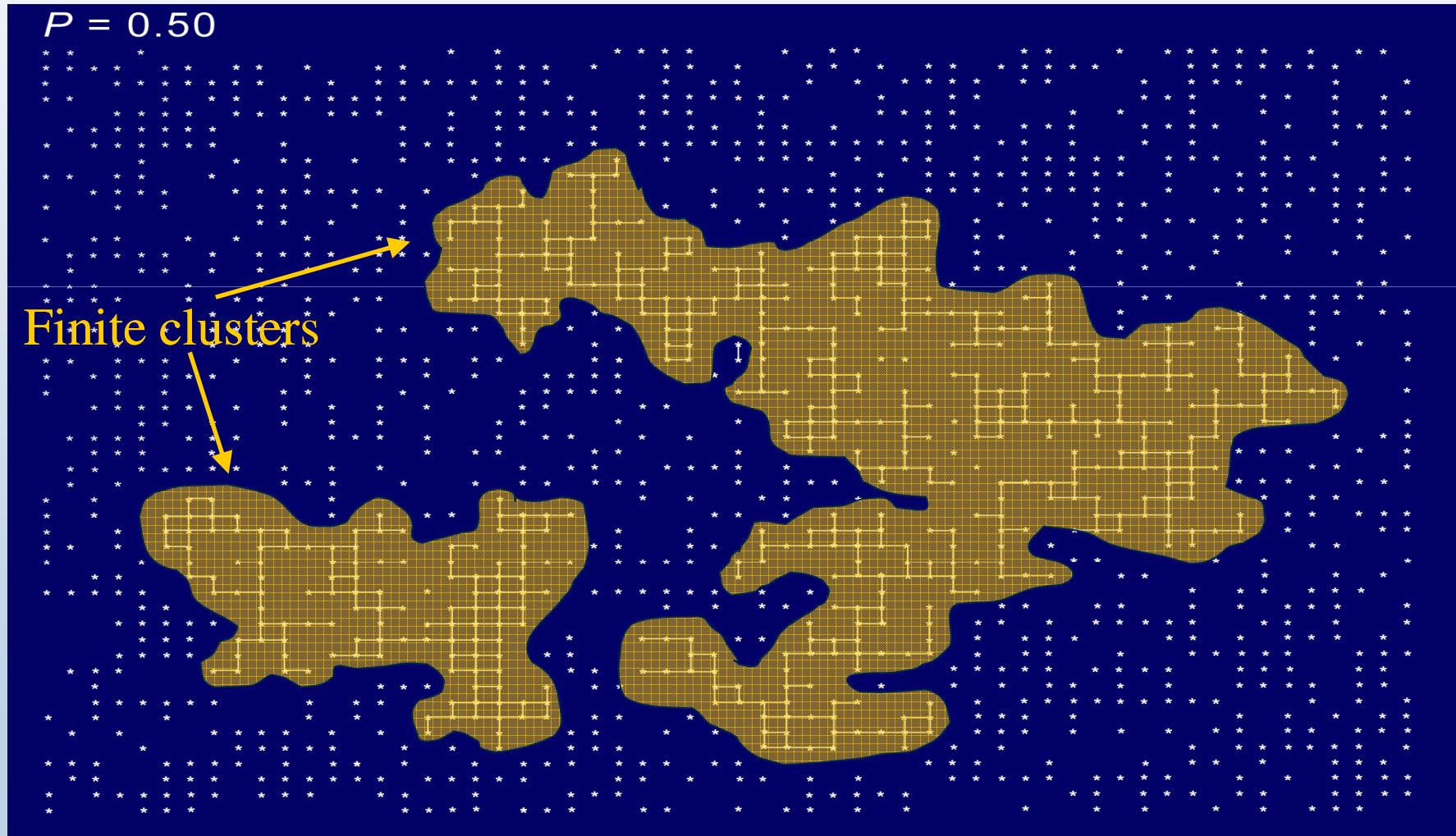
Cluster size = 2

Bond

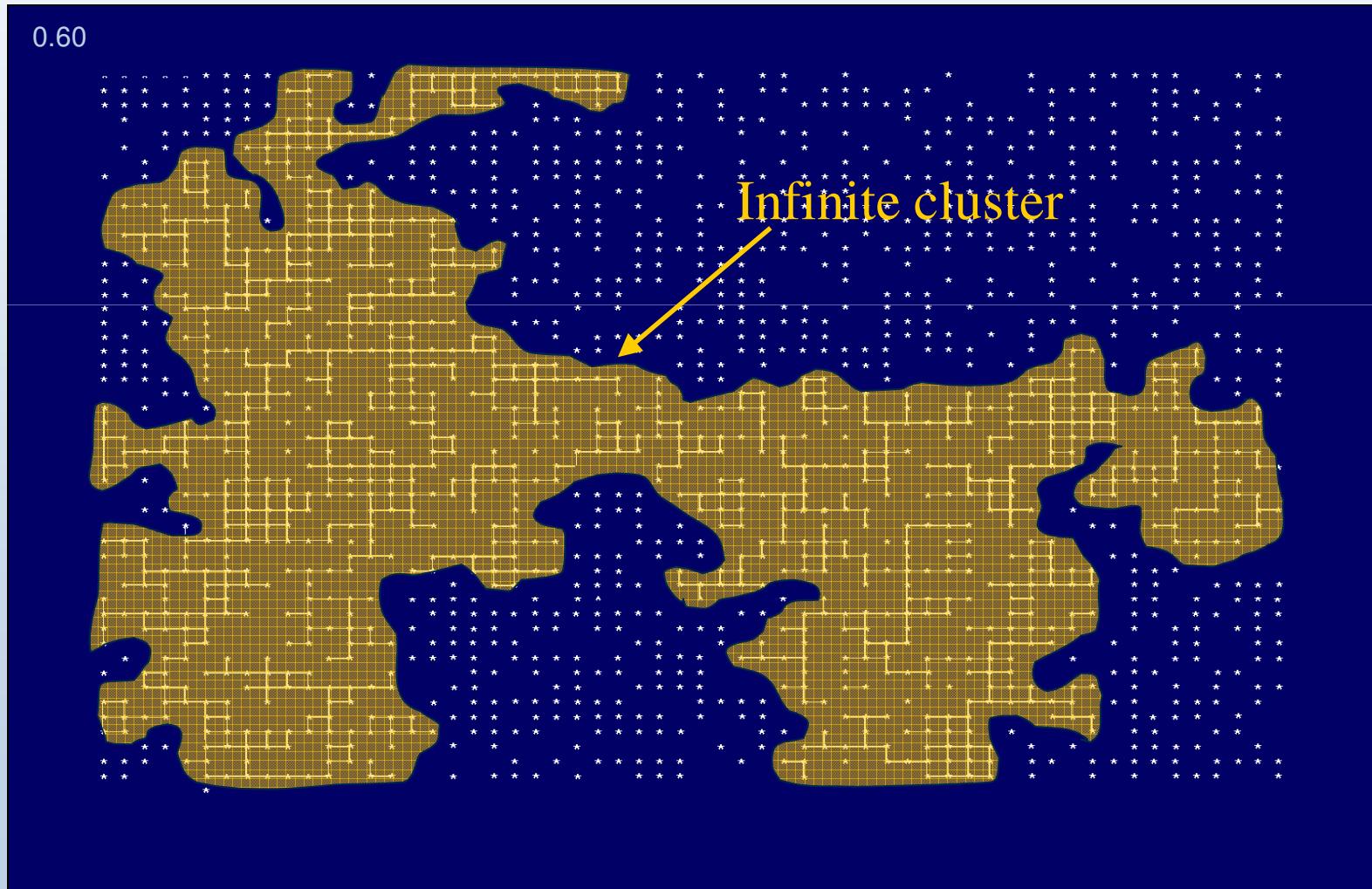


Cluster size = 1

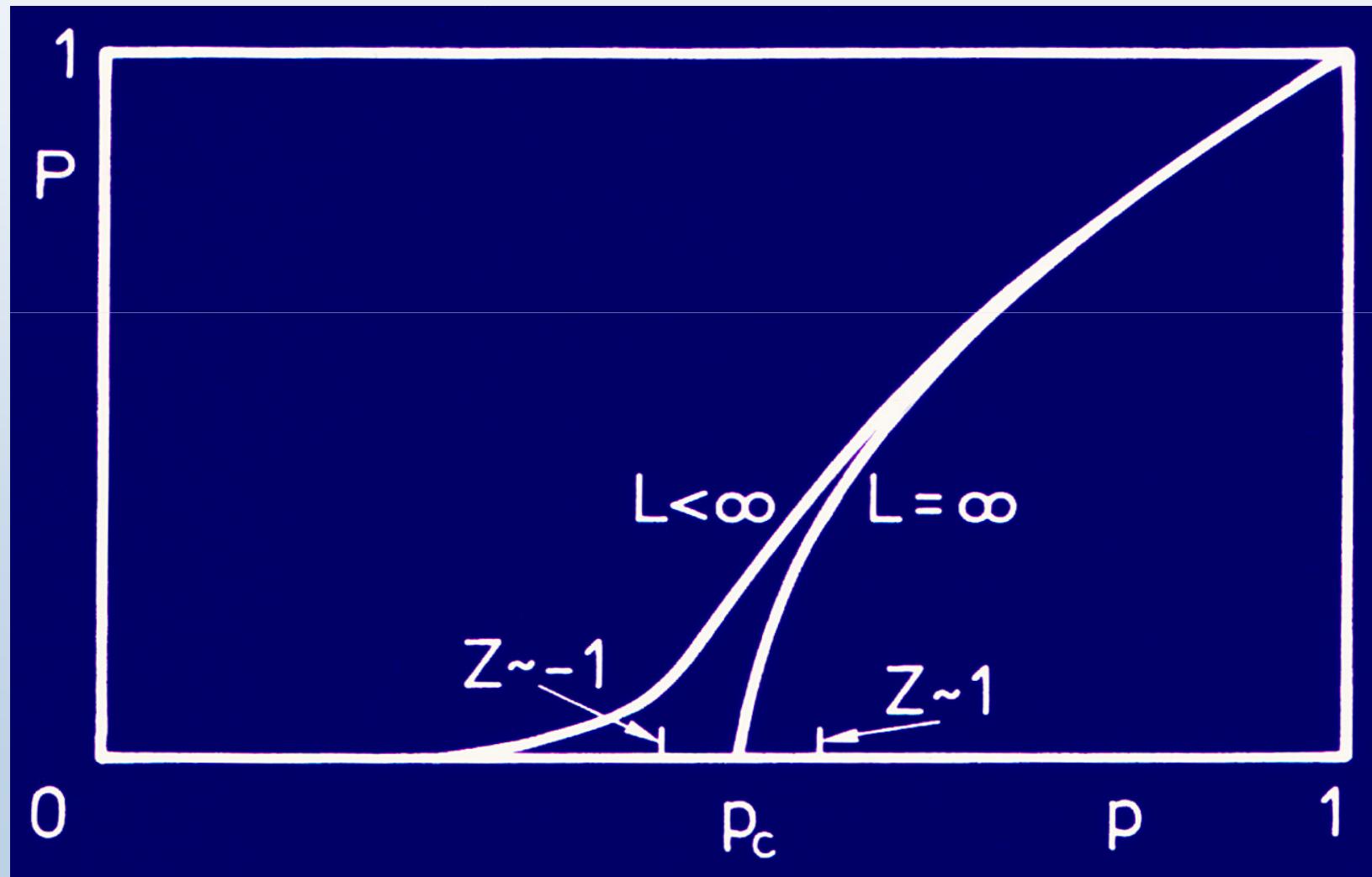
## 2-dimensional square lattice - occupation probability $p = 0.50$ - no infinite cluster



# 2- dimensional Square lattice occupation probability $p = 0.60$ - infinite cluster



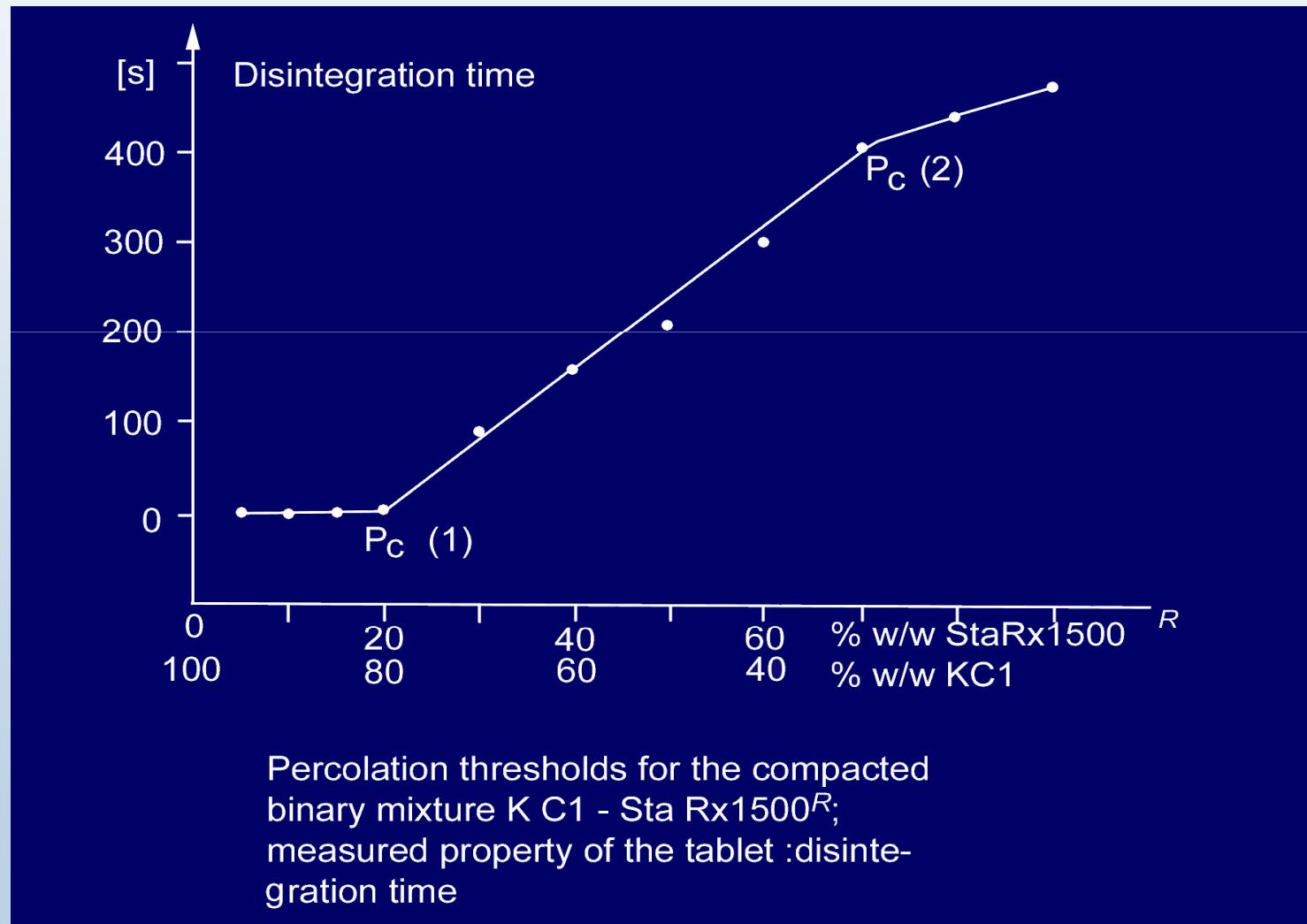
In practice: often no sharp percolation threshold due to finite size of a sample



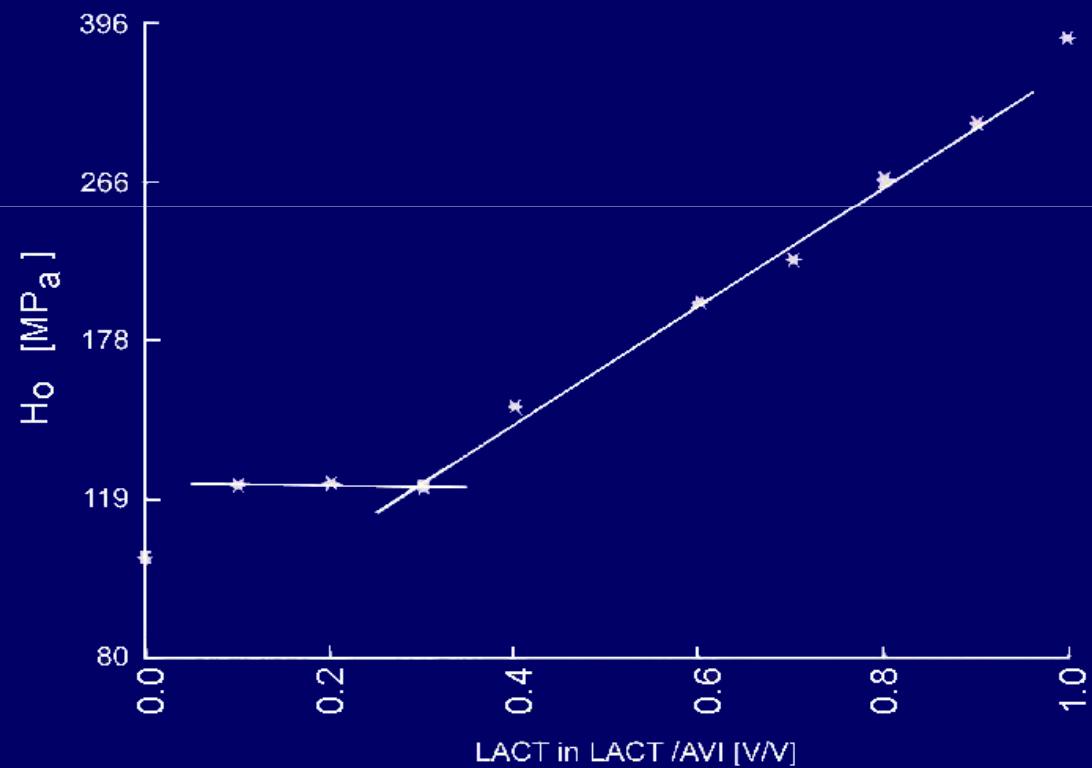
## Basic equation property X

- o Site occupation probability  $p$  with threshold  $p_c$
- o Basic equation: Property X
  - $X = S |p - p_c|q$
  - $S$  = scaling factor
  - $q$  = critical exponent
- o In 3 dimensions - 2 percolation thresholds!

# Tablet property: Disintegration time

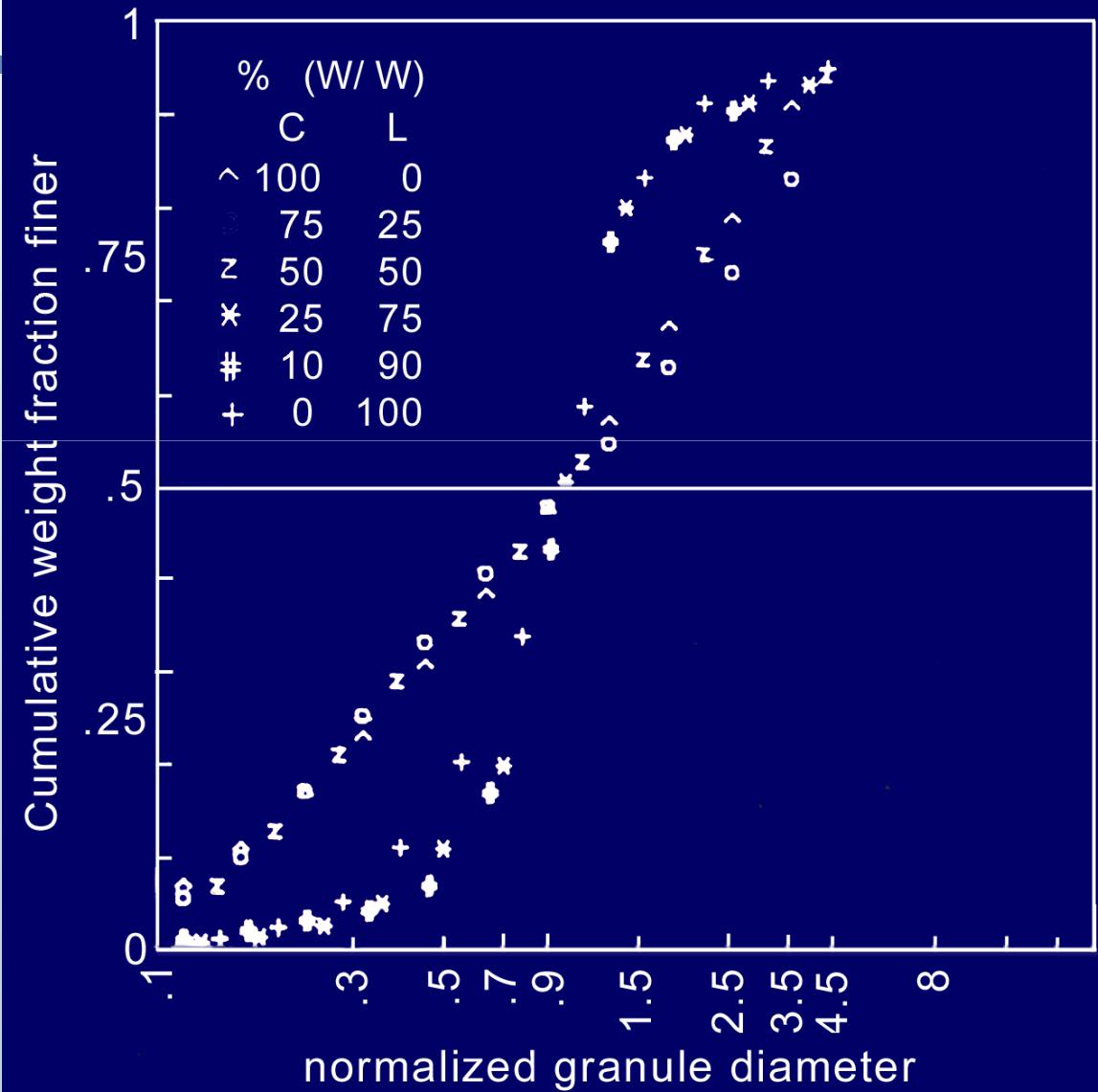


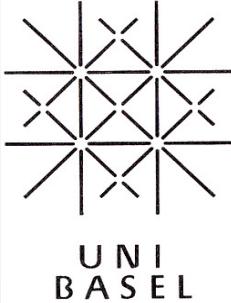
# Tablet property: Indentation Hardness Brisnell Hardness



# Granule Property

Normalized cumulative size distribution at  $\pi = 0.63$  for the binary mixture Corn starch (C) / Lactose (L)





# PERCOLATION THRESHOLDS

## For Site and Bond Percolation

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Lattice	Site	Bond
Honeycomb	0.6962	0.65271
Square	0.59275	0.50000
Triangular	0.50000	0.34729
Diamond	0.428	0.388
Simple cubic	0.3117	0.2492
BCC	0.245	0.1785
FCC	0.198	0.119

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## Mean Cluster Size $S$

$$S \text{ prop } |p - p_c|^{-\gamma}$$

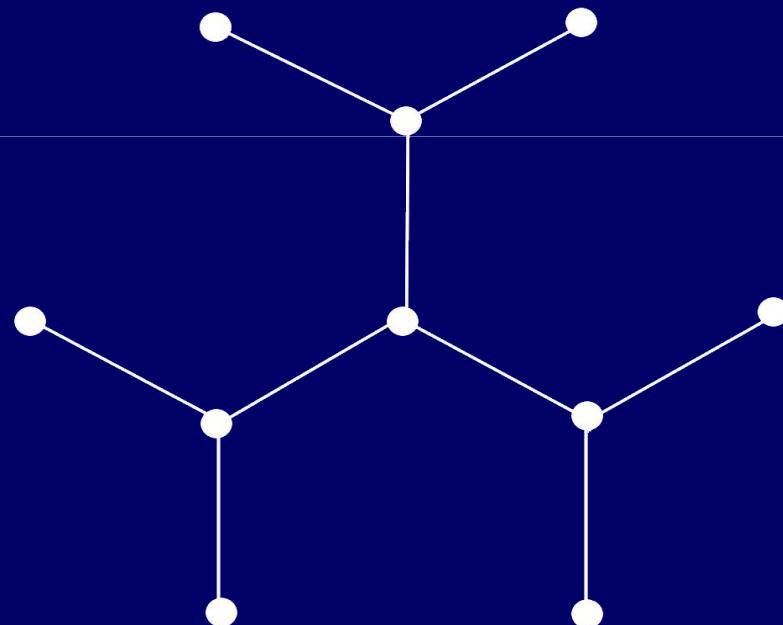
$p$  = site occupation

$p_c$  = percolation threshold

$\gamma$  = critical exponent

# Bethe – Lattice for problems with dimensions $\geq 6$

$$p_c = 1 / (z - 1)$$



Bethe Lattice with  $z = 3$

# Bethe Lattice – Approximation for lower dimensional problems $d < 6$

Bethe Lattice

Percolation Threshold  $p_c$

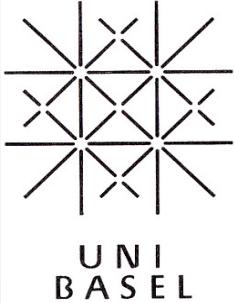
$$p_c = \frac{1}{z - 1}$$

$z$  = Coordination Number

# PERCOLATION THRESHOLDS

## For Site Percolation

Lattice type	$P_c$	z Coord. Number	Bethe Approx. $z \approx$
Diamond	0,43	4	3.3
Simple cubic	0,3116	6	4.2
BCC	0,246	8	5.0
FCC	0,198	12	6.0
Bethe	$1/(z-1)$	$z$	$z$



## Estimation of z

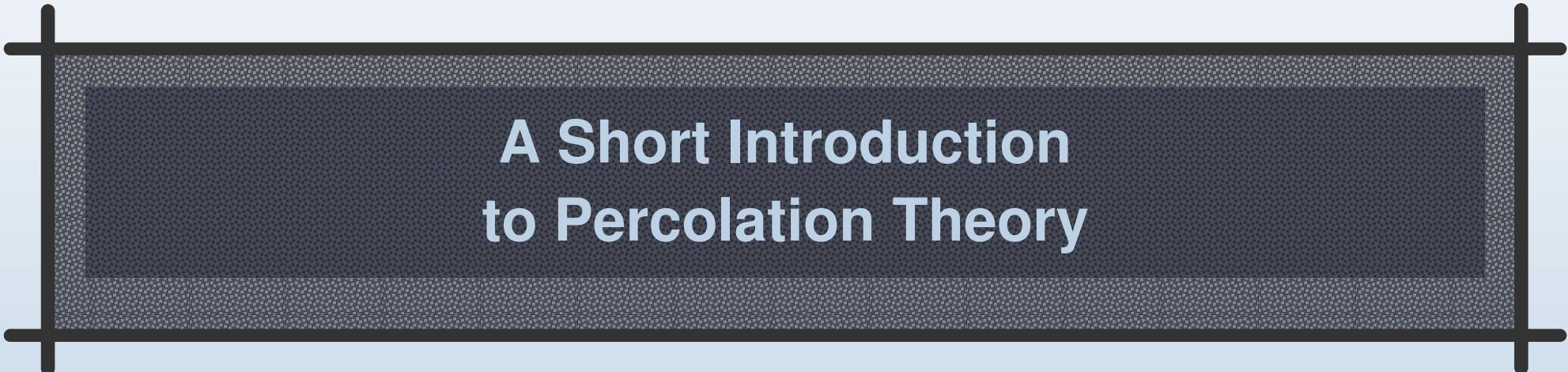
Powder - Systems

Coordination Number z

$z \gg p/e$  for  $0.25 < e < 0.5$

Are Liquids Nano-Powders?

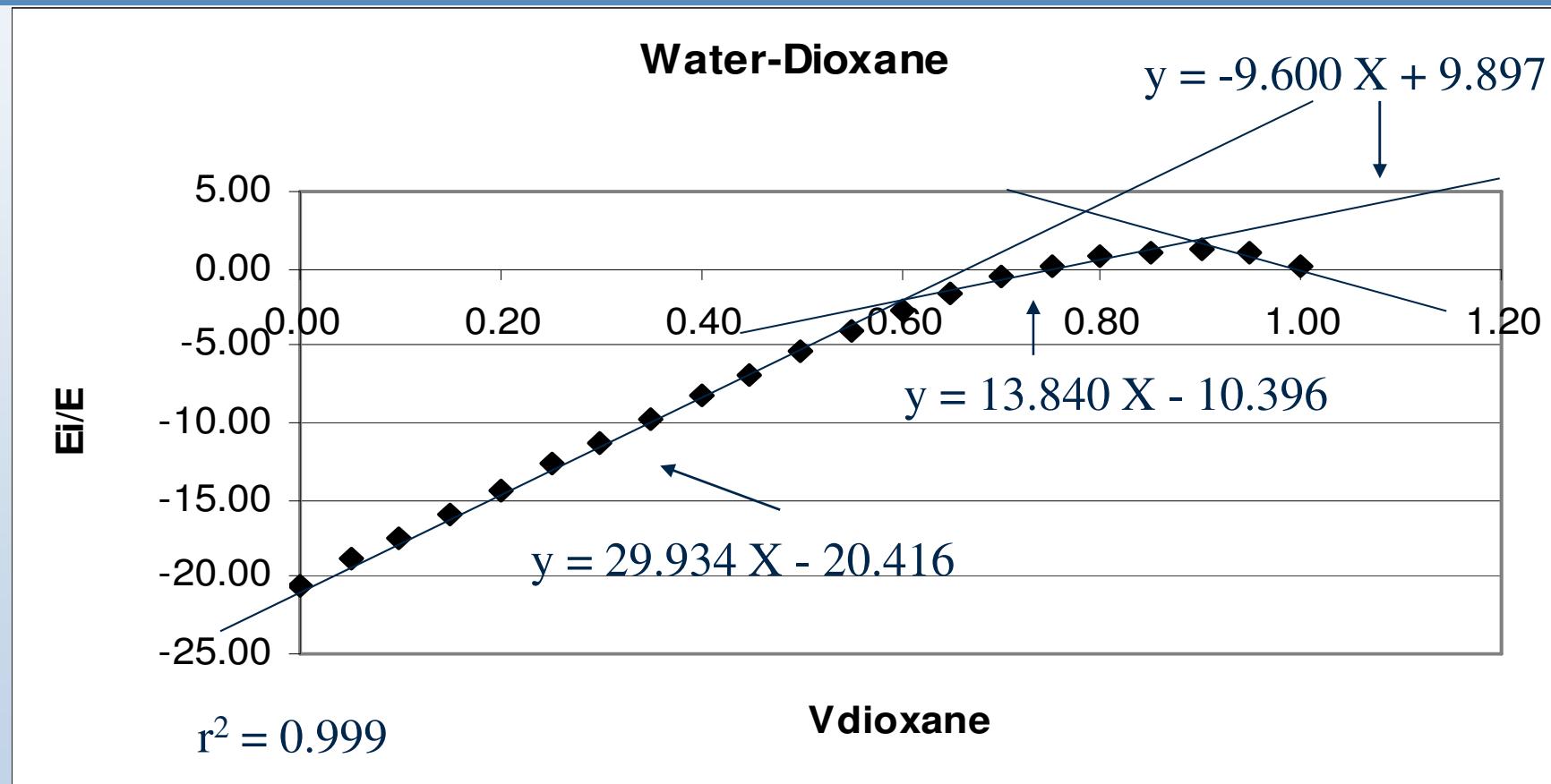
E N D   O F



A Short Introduction  
to Percolation Theory

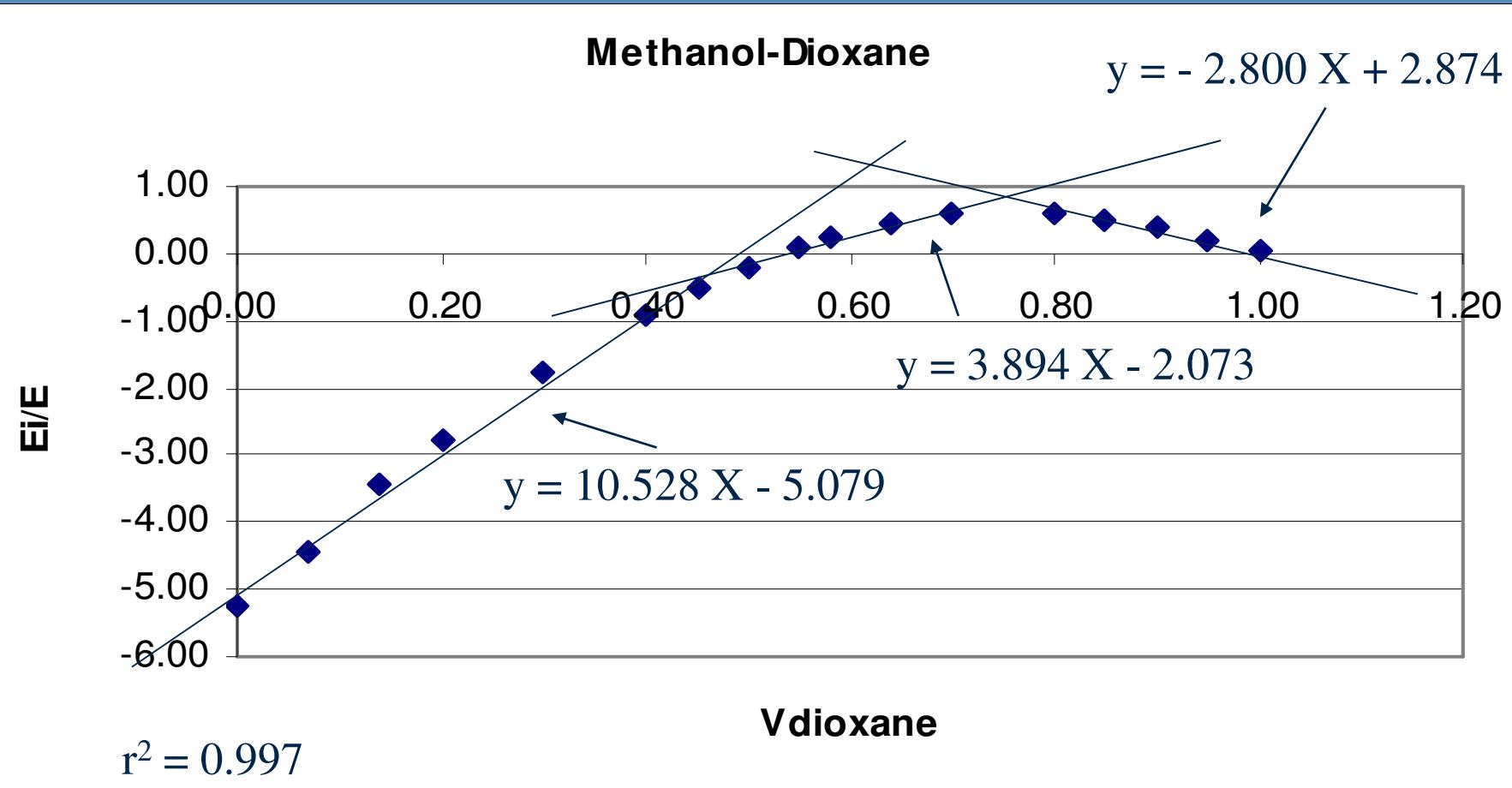


# $E_i/E$ values of the water-dioxane binary mixtures at 298.2 K. $p_c = 0.62$ or $0.86$ ?



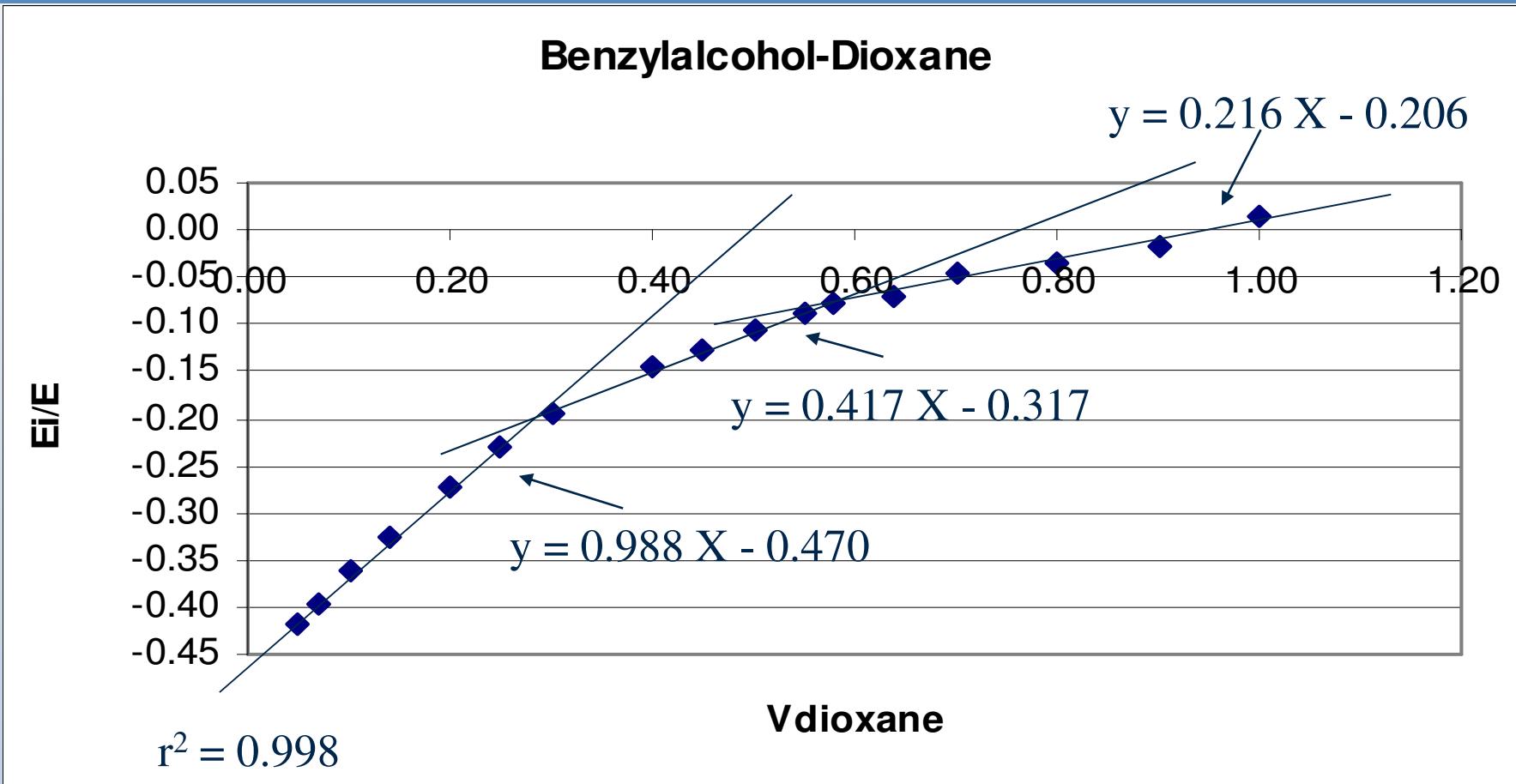
The intersections are located at ca. 62% and 86% (V/V) 1,4-dioxane

# $E_i/E$ values of the methanol-dioxane binary mixtures at 298.2 K    $p_{c(1)} \approx 0.45$    $p_{c(2)} \approx 0.74$



The intersections are located at ca. 45% and 74% (V/V) 1,4-dioxane

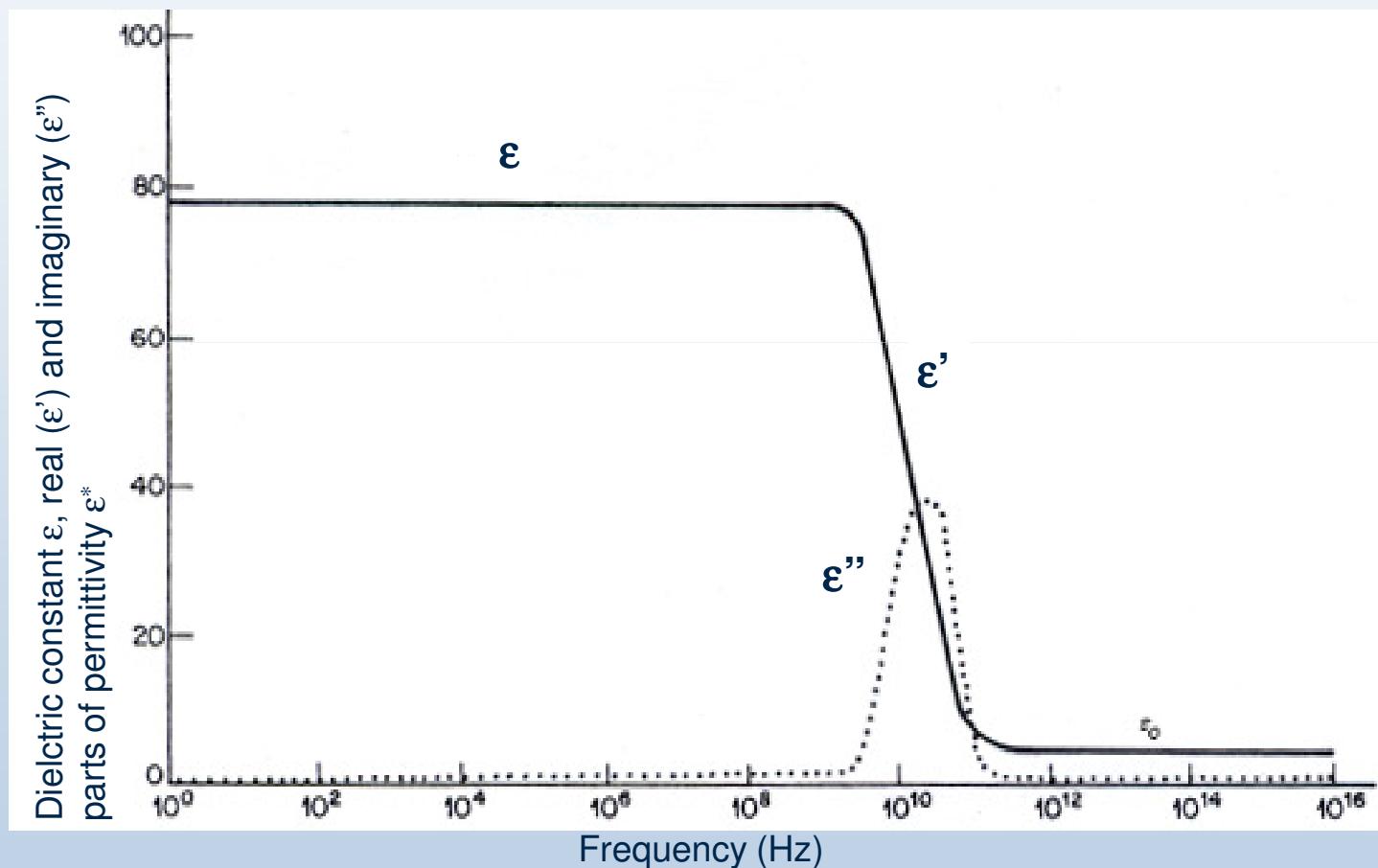
# $E_i/E$ values of the benzylalcohol-dioxane binary mixtures at 298.2 K    $p_{c(1)} \approx 0.27$    $p_{c(2)} \approx 0.55$



The intersections are located at ca. 27% and 55% (V/V) 1,4-dioxane.

# **Results of Broad Band Dielectric Spectroscopy**

# Dielectric permittivity of a polar substance as a function of frequency



(Decareau et al., 1985)

# The Debye equation for the complex dielectric permittivity $\epsilon^*$

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon - \epsilon_\infty}{1 + i\omega\tau}$$

The Debye can be splitted for the real ( $\epsilon'$ ) and imaginary part ( $\epsilon''$ ) of the complex permitivity:

$$\epsilon'(\omega) = \epsilon_\infty + (\epsilon - \epsilon_\infty) \frac{1}{1 + \omega^2\tau^2}$$

$$\epsilon''(\omega) = (\epsilon - \epsilon_\infty) \frac{\omega\tau}{1 + \omega^2\tau^2}$$

with  $\tau$  characteristic relaxation time

## Superposition of two Debye Equations

$$\varepsilon^*(\omega) = \varepsilon_\infty + (\varepsilon - \varepsilon_\infty) \left\{ \frac{l_1}{1 + i\omega\tau_1} + \frac{l_2}{1 + i\omega\tau_2} \right\}$$

i.e. we have two relaxation times  $\tau_1$  and  $\tau_2$

and two weights,  $l_1$  and  $l_2$

with  $l_1 + l_2 = 1$

## The Cole-Davidson relaxation behavior

Taking into account the real and imaginary part:

$$\epsilon'(\omega) = \epsilon_\infty + (\epsilon - \epsilon_\infty)(\cos \phi)^\beta \cos \beta\phi$$

$$\epsilon''(\omega) = (\epsilon - \epsilon_\infty)(\cos \phi)^\beta \sin \beta\phi$$

$$\phi = \arctan(\omega\tau_0)$$

$\beta$  = parameter describing the broadness of distribution

In case of  $\beta = 1$  the Cole-Davidson equation is identical with the Debye-equation.

# Superposition of the Debye-equation with the Cole-Davidson distribution function

$$\varepsilon'(\omega) = \varepsilon_\infty + (\varepsilon - \varepsilon_\infty) \left[ l_1 \left( \frac{1}{1 + \omega^2 \tau_1^2} \right) + l_2 ((\cos \phi)^\beta \cos \beta \phi) \right]$$

$$\varepsilon''(\omega) = (\varepsilon - \varepsilon_\infty) \left[ l_1 \left( \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} \right) + l_2 ((\cos \phi)^\beta \sin \beta \phi) \right]$$

$\phi = \arctan(\omega \tau_0)$

$\beta$  = parameter describing the broadness of distribution of the Cole-Davidson equation with the characteristic Cole-Davidson relaxation time  $\tau_0$

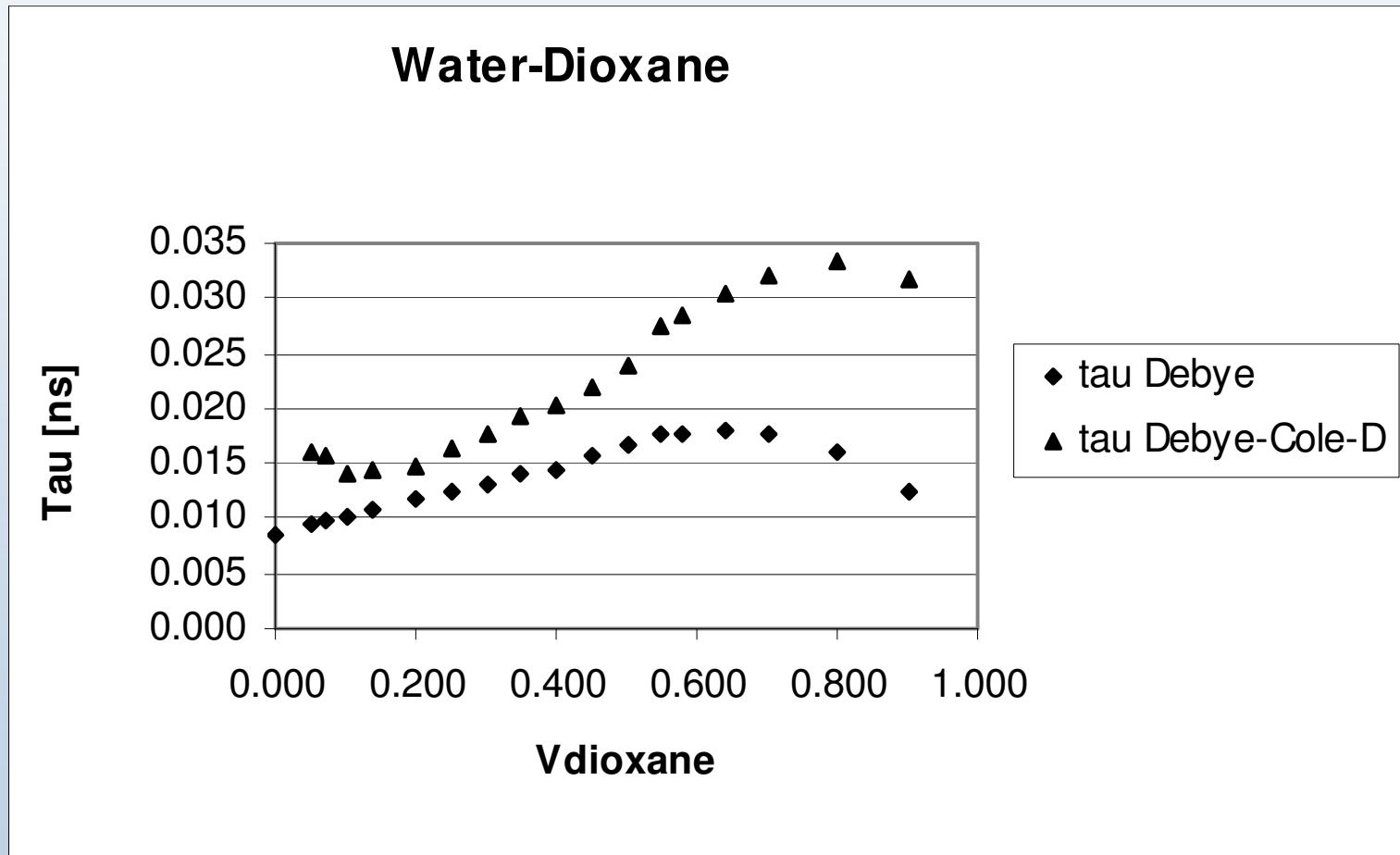
$\tau_1$  = characteristic (undisturbed) Debye relaxation time  
 (typically valid within a certain range of the binary mixture)  
 with two weights  $l_1, l_2$ , and  $l_1 + l_2 = 1$

# Physical properties of the solvents studied at room temperature / study of binary mixtures

	Dipole Moment [D]	MW [gmol-1]
<b>Methanol</b>	1.70	32.04
<b>Benzylalcohol</b>	1.71	108.14
<b>Water</b>	1.85	18.02
<b>1,4-Dioxane</b>	0.00	88.11

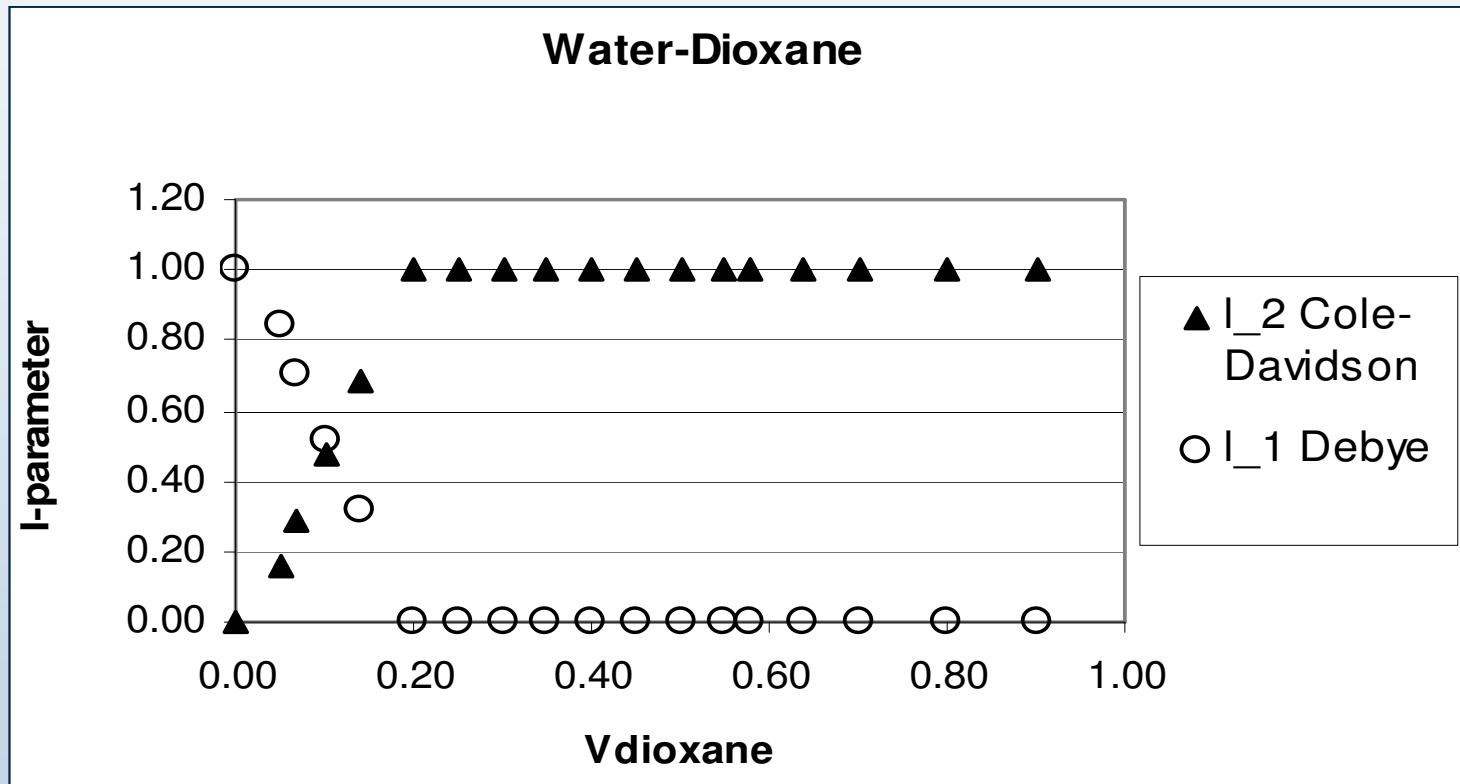
Broad band dielectric spectroscopy

# Two different models for the description of the relaxation behavior of the water dipole



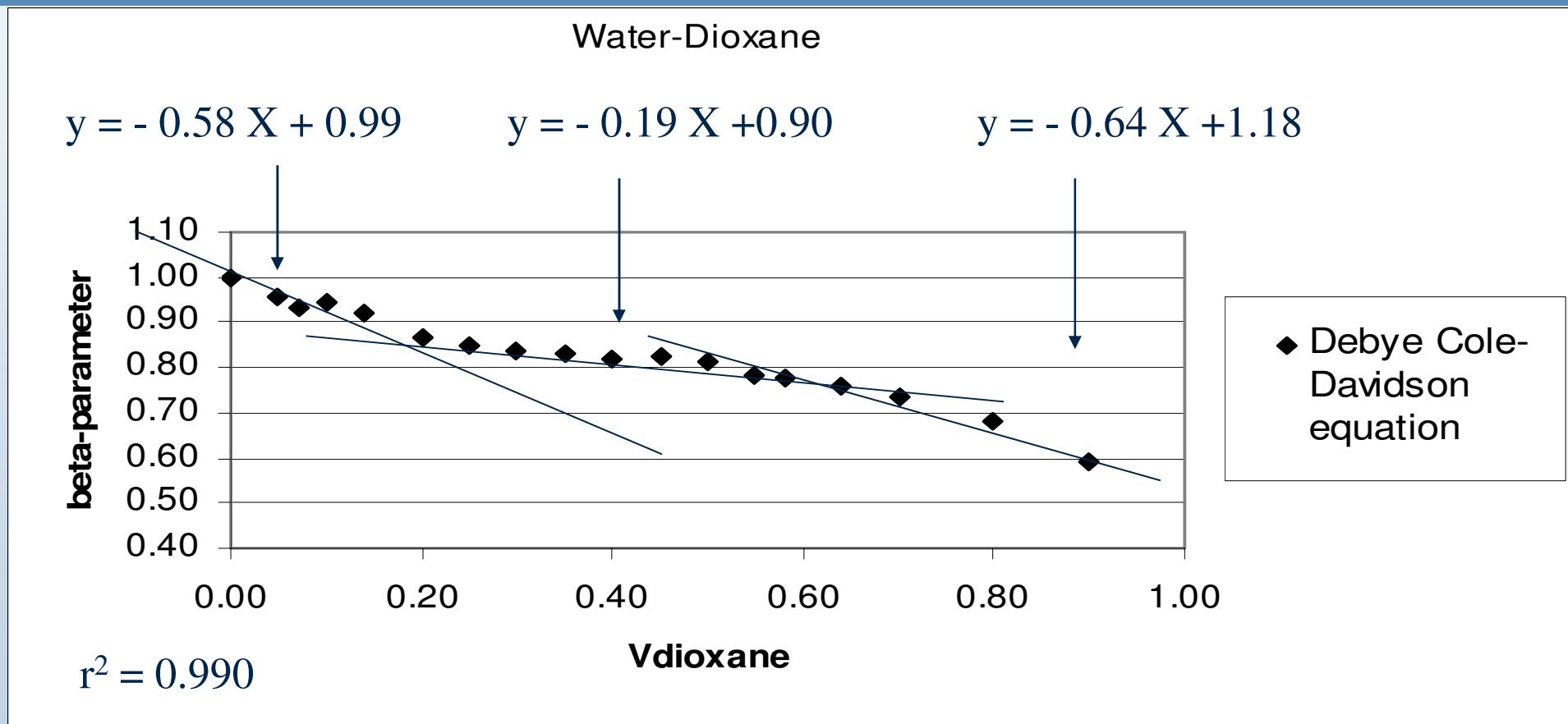
in 1,4-dioxane - water mixtures at 298.2 K

# Weight factor of relaxation time $p_{c(1)} \approx 0.20$



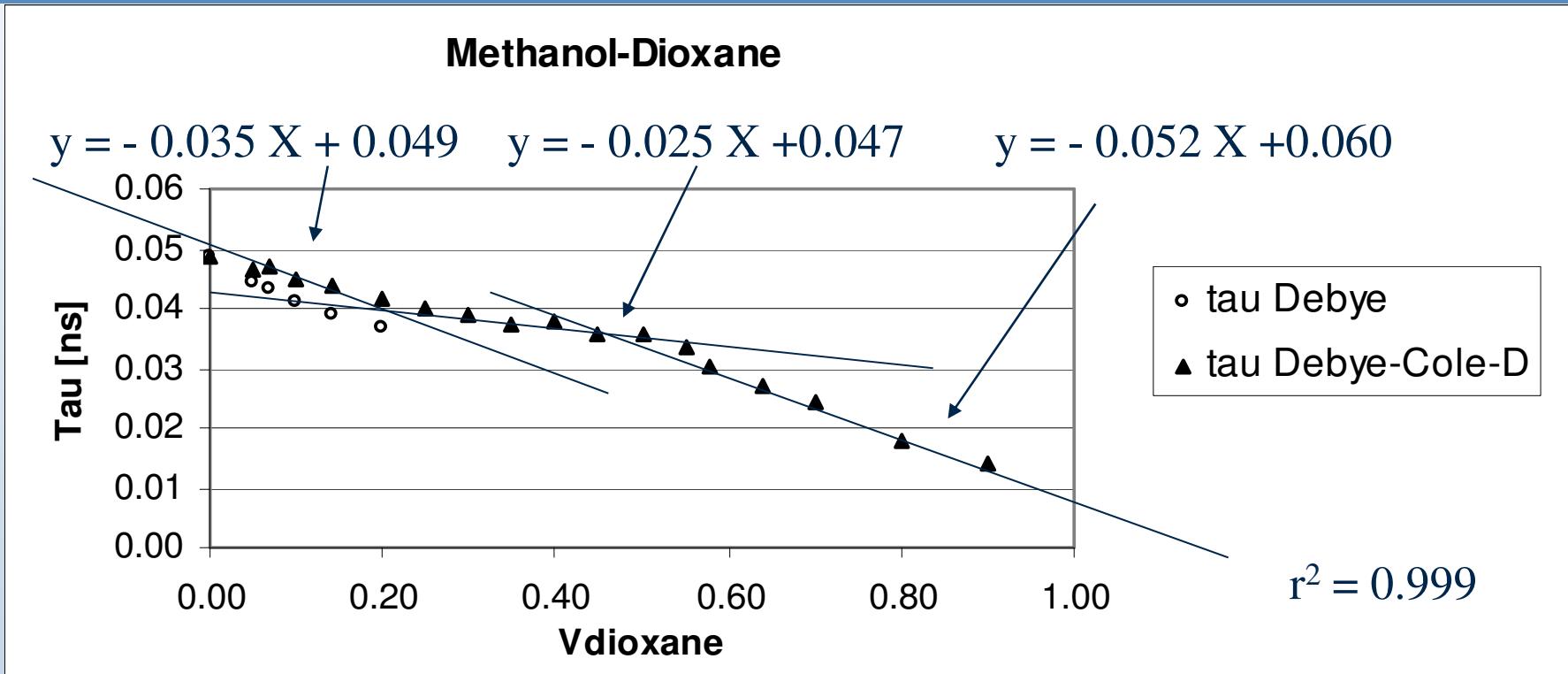
Weight factor of relaxation time (I-parameter: I<sub>1</sub>, I<sub>2</sub>) for water-dioxane binary mixtures at 298.2 K as a function of the volume fraction of dioxane (Vdioxane) calculated for with the superposition of one Debye equation (I<sub>1</sub>) and the Cole-Davidson equations function (I<sub>2</sub>).

# Skewness $\beta$ of the distribution of relaxation times



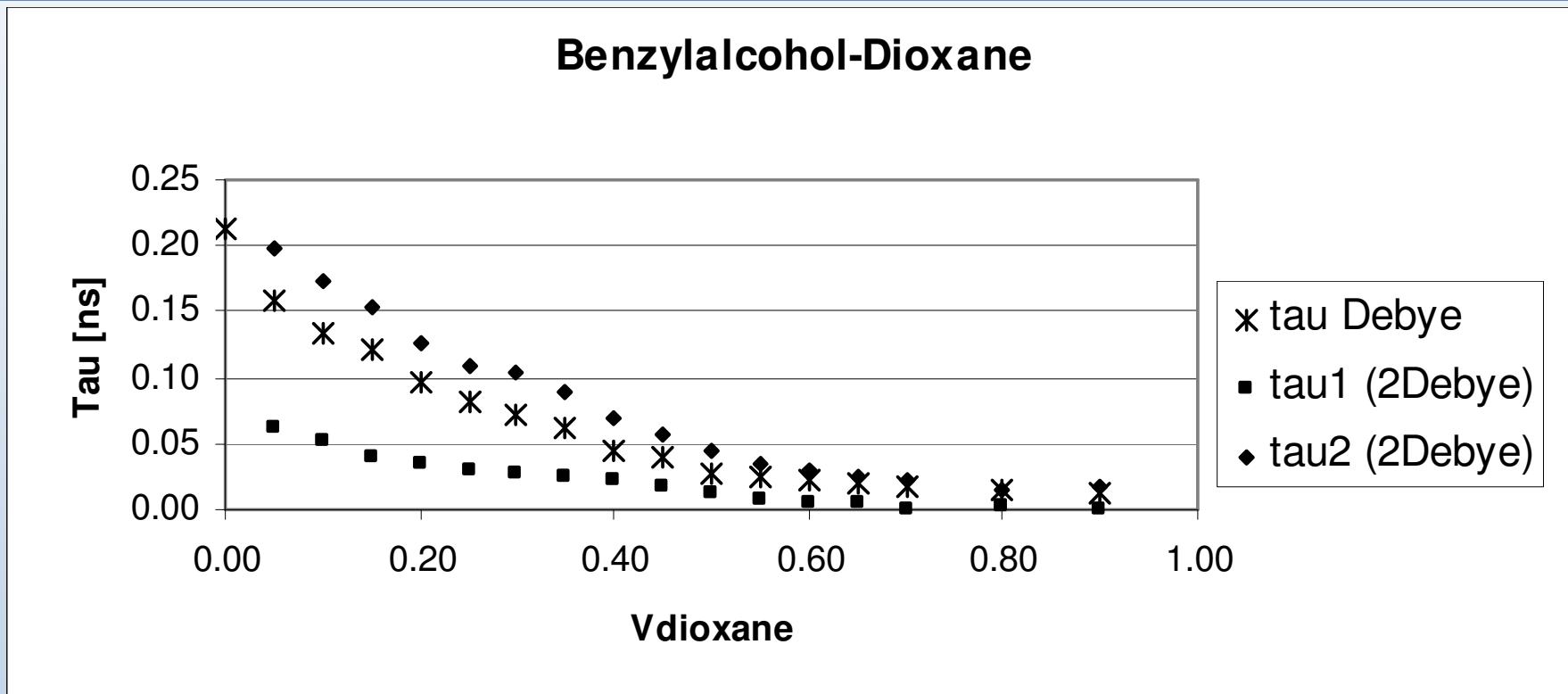
$$p_{c(1)} \approx 0.20 \quad p_{c(2)} \approx 0.60$$

# Relaxation behavior of the dipole of methanol



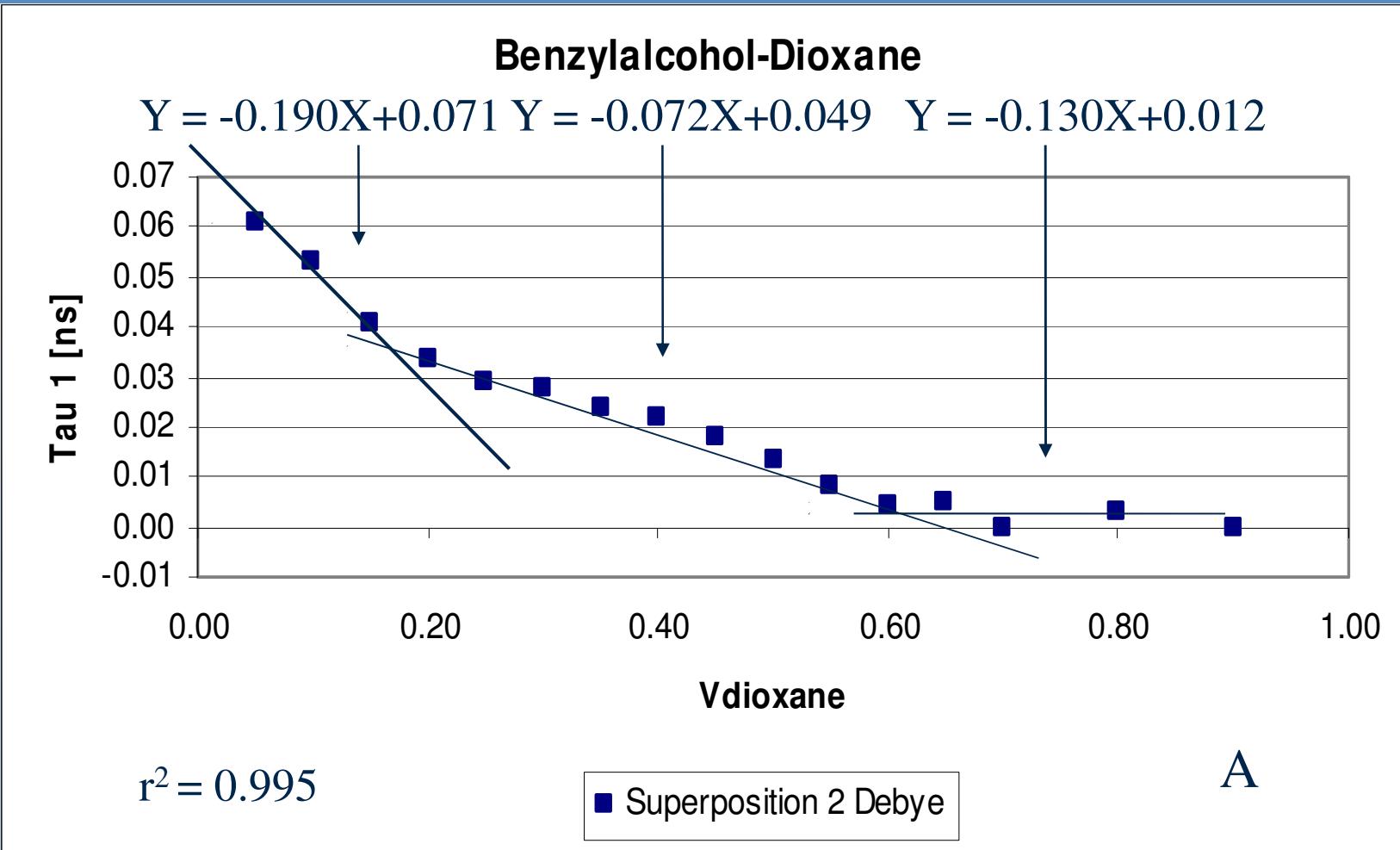
$$p_{c(1)} \approx 0.20 \quad p_{c(2)} \approx 0.45 ?$$

## Two different models

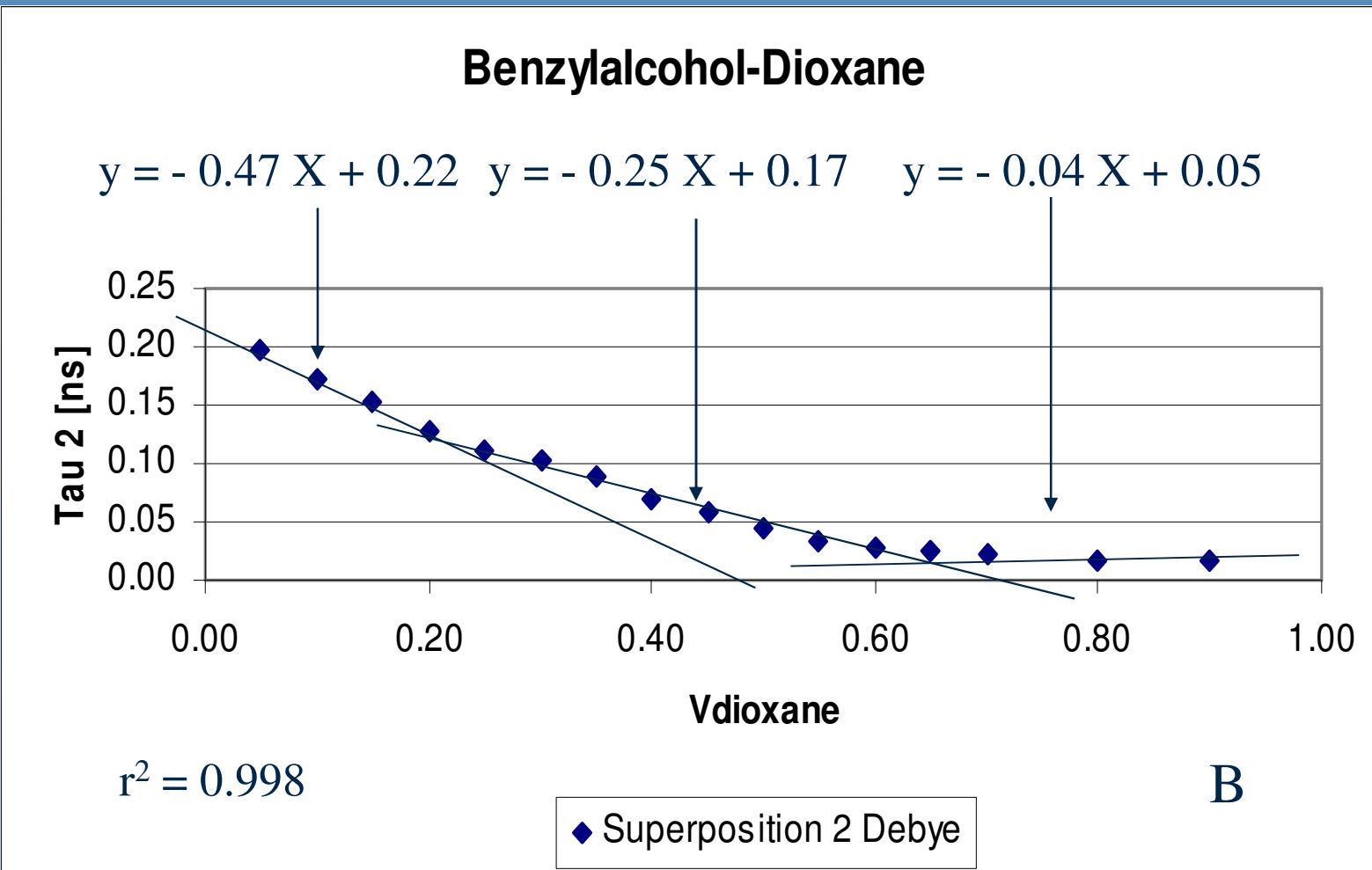


**Two different models to fit the relaxation time behavior  
for benzylalcohol-dioxane binary mixtures at 298.2 K  
as a function of the volume fraction of 1,4-dioxane**

# Bencylalcohol-Dioxane, $p_{c(1)} \approx 0.18$   $p_{c(2)} \approx 0.60$



## Bencylalcohol-Dioxane, $p_{c(1)} \approx 0.20$   $p_{c(2)} \approx 0.65$



**Thank you for your attention**  
**Best greetings from Basel**

