

Emulsions and Emulsification: Status and Future Challenges

Shaffiq Jaffer, Procter and Gamble

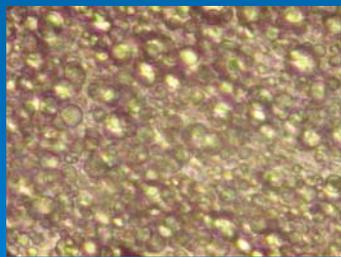
Alvin Nienow, University of Birmingham

Emulsion Definition

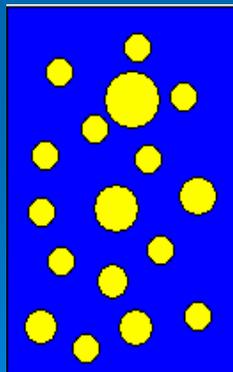
- The combination of two immiscible (or partially Miscible) phases that is made up of at least one phase dispersed in the other
 - Defn: Immiscible: Two liquids that have a non zero interfacial tension when they are in contact:

$$\sigma > 0 \text{ N/m or J/m}^2$$

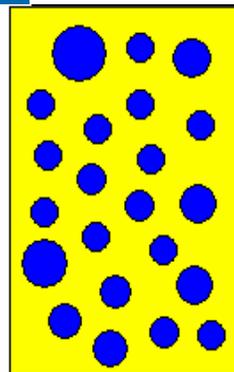
Emulsion Types



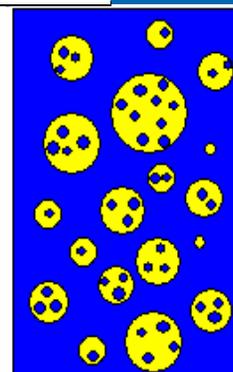
Oil/ water



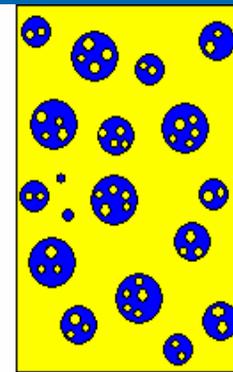
O/W



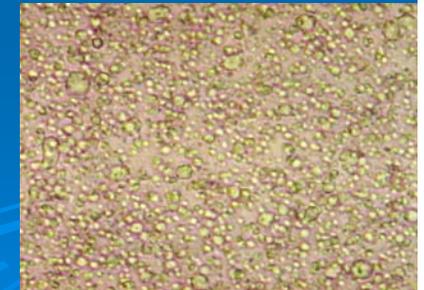
W/O



W/O/W



O/W/O



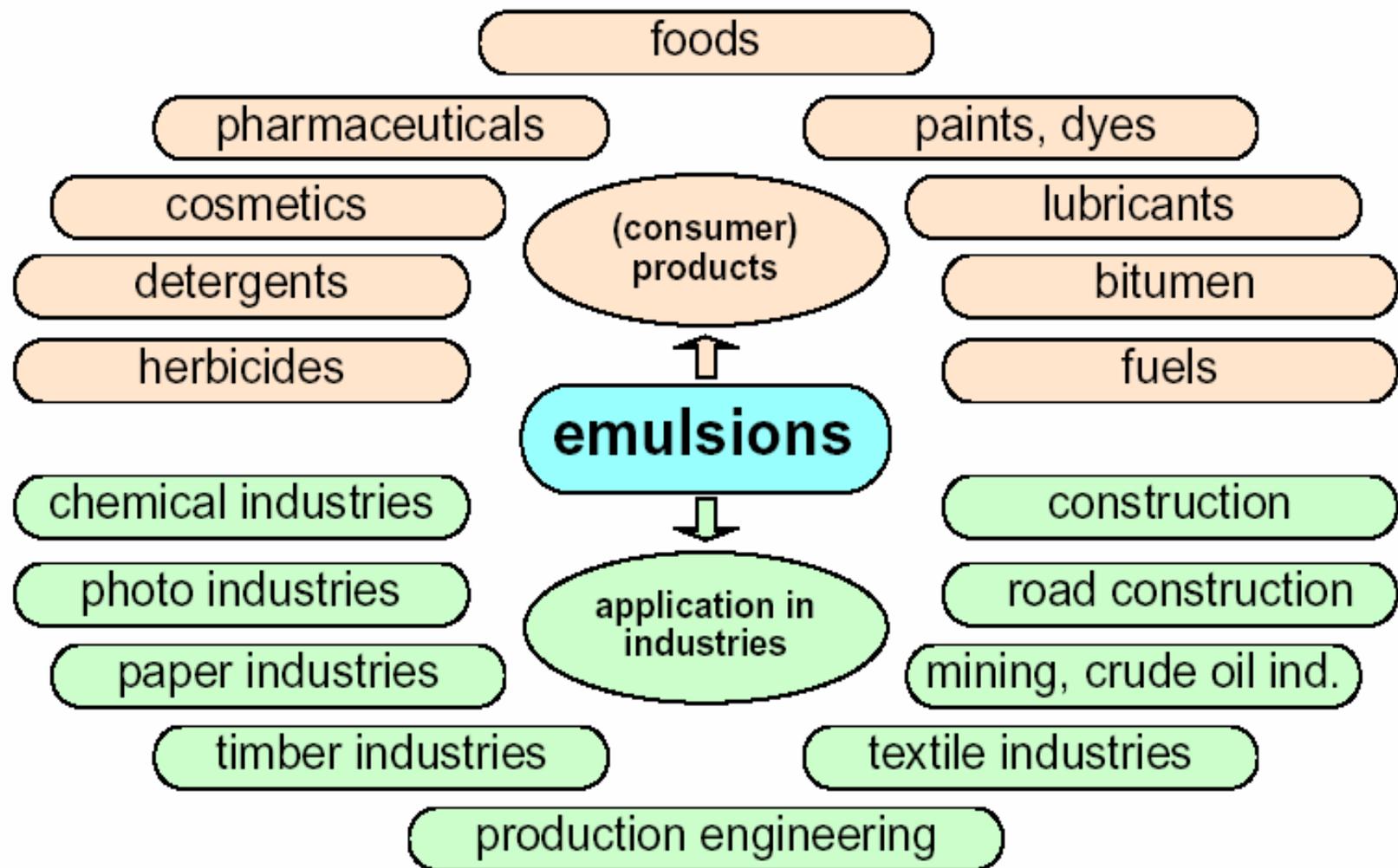
Water / Oil

Multiple Emulsions

Definition

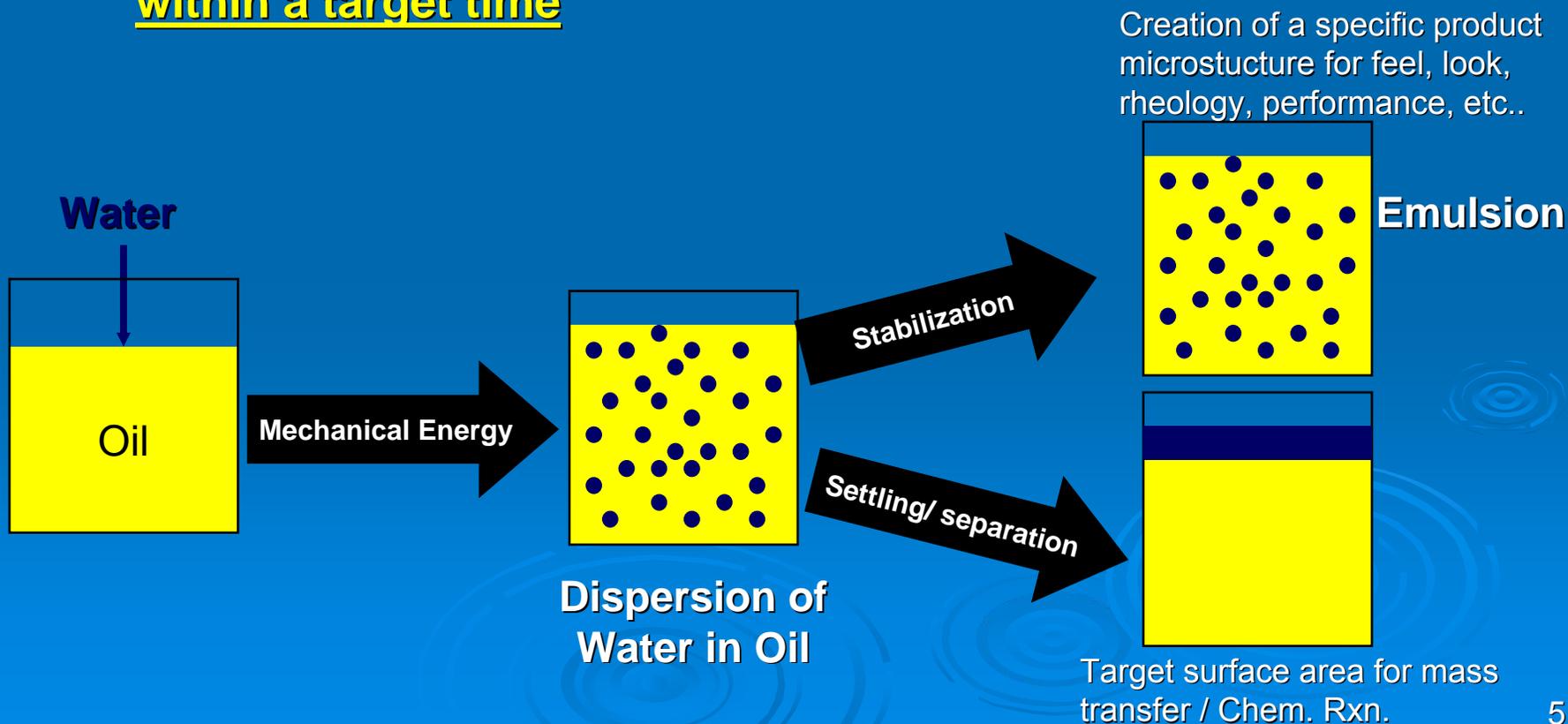
- Emulsions may be thermodynamically stable and may form spontaneously (micro-emulsions)
- Most emulsions are in a metastable state and therefore depend on the state variables (temperature and composition) and the preparation method (equipment / hydrodynamics and process method)

Products and industrial applications



Emulsification

- What is Emulsification?
 - The process by which one phase is broken up, dispersed and distributed in a second immiscible or partially miscible
- Process Objective:
 - Produce high interfacial area between two immiscible fluids within a target time



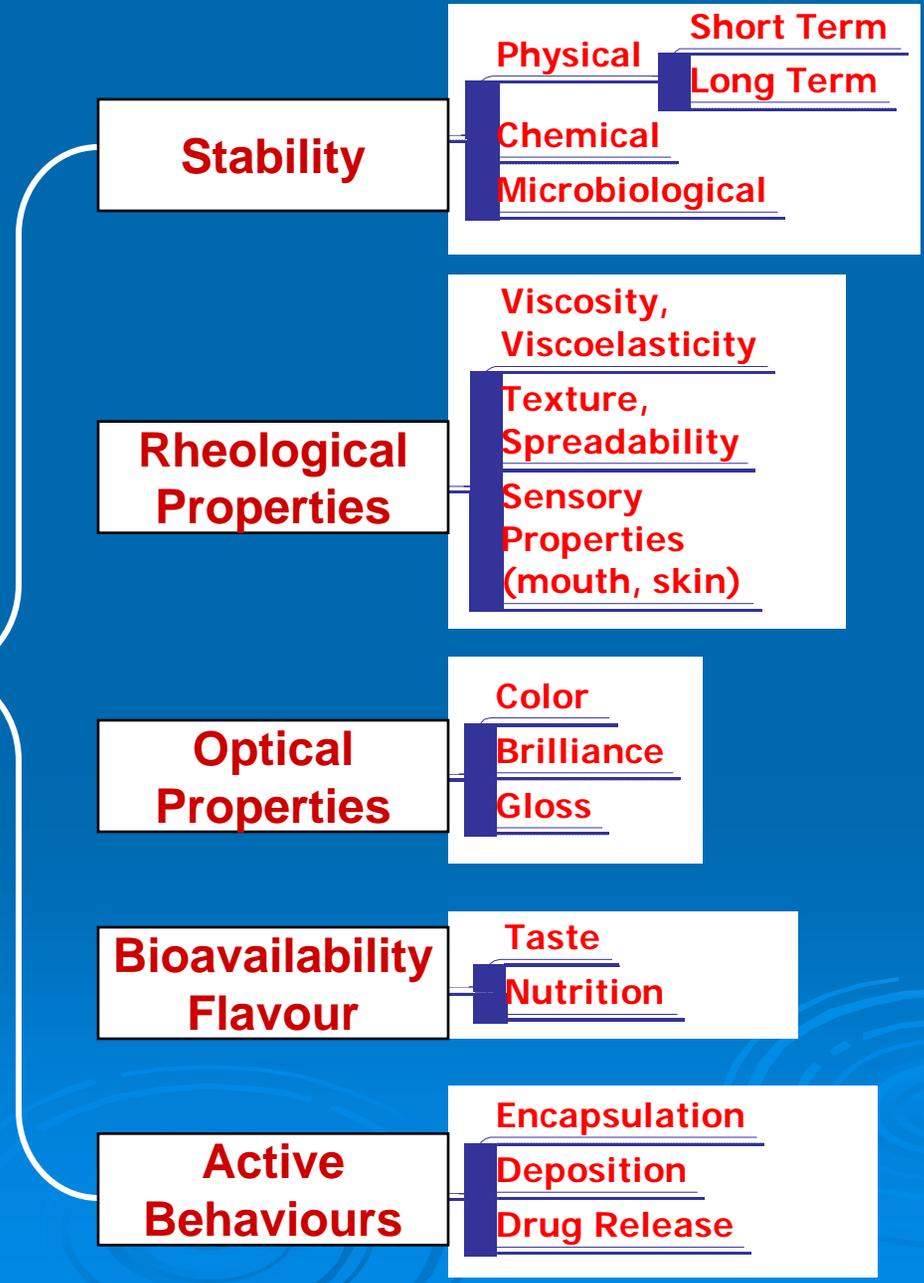
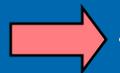
Emulsion Objectives

Average Drop Size

Drop Size Distribution

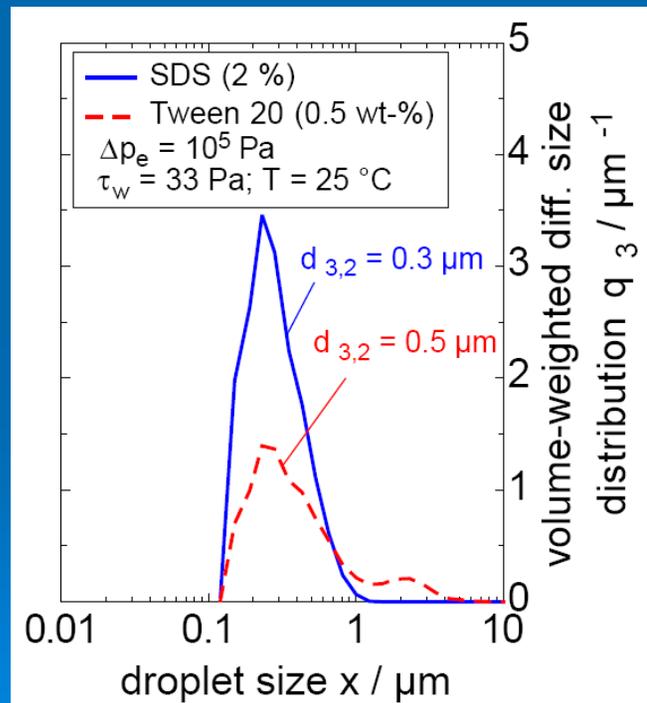
Emulsifiers, Surfactants, Stabilizers

Material Properties



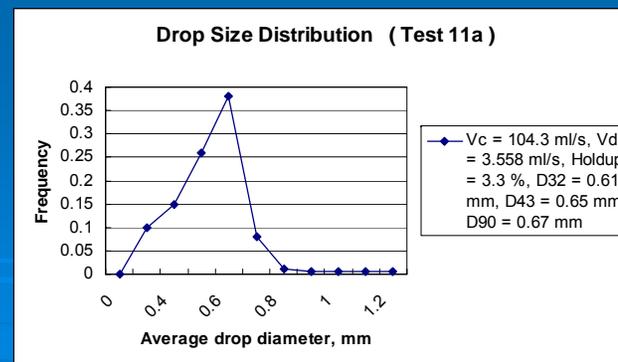
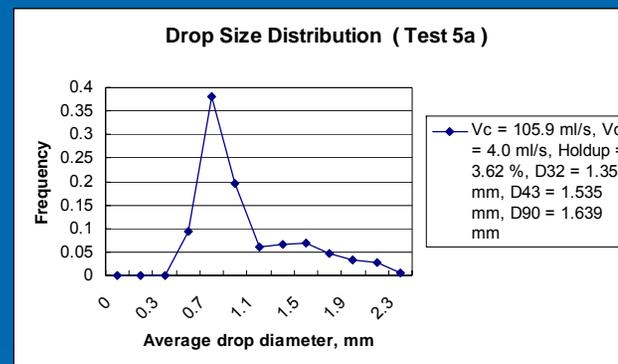
Emulsion distributions - rarely ideal in real systems!

- Not ideal in real systems and hardly ever the same across scales



High Pressure Homogenizer

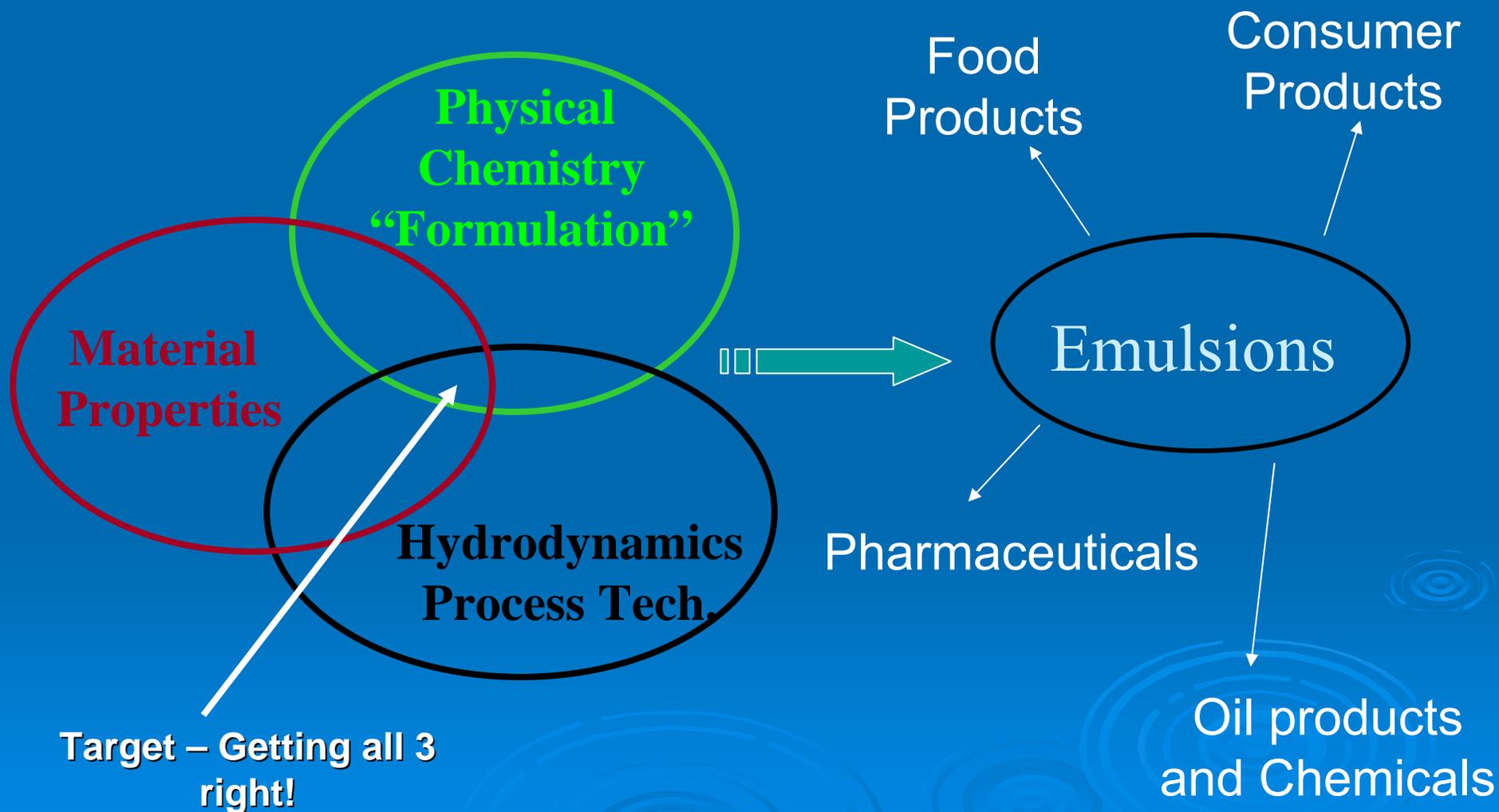
Schubert 2000



Static Mixer – Laminar Flow

Rao et al. (2007)

The Paradigm of Emulsions and Emulsification



Turbulent and Laminar Emulsification

The State-of-the-Art is well set out in the excellent chapter by Leng and Calabrese in “Handbook of Industrial Mixing; Science and Practice”, (Eds. E.L Paul, V.A Atiemo-Obeng and S.M. Kresta), 2003.

However, discussion mainly for turbulent flow and anomalies/questions still exist even at the most basic level

Questions about the Basic Drop Size Equation at Low Concentrations of Dispersed Phase (non-coalescing?)

The Basic Equation

Application of Kolmogoroff's theory of local, homogeneous isotropic turbulence: (Hinze, 1955)

- Resisting breakage - interfacial tension, σ (N/s) and dispersed phase viscosity, μ_d (Pas)
- Causing breakage - local specific energy dissipation rate, ε_T (W/kg or $\text{m}^2 \text{s}^{-3}$)
- **For low μ_d** , breakage continues on passing through $(\varepsilon_T)_{\max}$ until all drops $< (d_p)_{\max}$,

$$(d_p)_{\max} \propto (\varepsilon_T)_{\max}^{-0.4} (\sigma / \rho_c)^{0.6}$$

Davies (1985) correlated drop sizes from a whole range of devices at low concentrations this way

Only for geometrically-similar systems on scale-up, can one assume

$$(\varepsilon_T)_{\max} \propto \bar{\varepsilon}_T = P / \rho V \propto P_o N^3 D^5 / T^3 \propto N^3 D^2$$

$$\text{so } d_{32} / D \propto (\rho_c N^2 D^3 / \sigma)^{-0.6}$$

In general, however,

Since $(\varepsilon_T)_{\max} = \Phi \bar{\varepsilon}_T$ where the mean specific energy dissipation rate, $\bar{\varepsilon}_T = P_o N^3 D^5 / (\pi / 4) T^3$ if $H=T$ and P_o is the power number

Assuming $(d_p)_{\max} \propto d_{32}$, then:

$$d_{32} / D \propto (\rho_c N^2 D^3 / \sigma)^{-0.6} (P_o \Phi D^3 / T^3)^{-0.4}$$

or

$$d_{32} / D = A We_D^{-0.6} \text{ where } A = f(P_o, D/T, \Phi)$$

Thus, A should depend on impeller type (Φ , P_o) and impeller to tank diameter ratio (D/T) but not on scale

Experimental Evidence-Nearly All Early Literature Rushton Impellers

Drop Size Distribution in Agitated Liquid-Liquid Systems

AIChE Journal

September, 1967

HSIAO TSUNG CHEN and STANLEY MIDDLEMAN

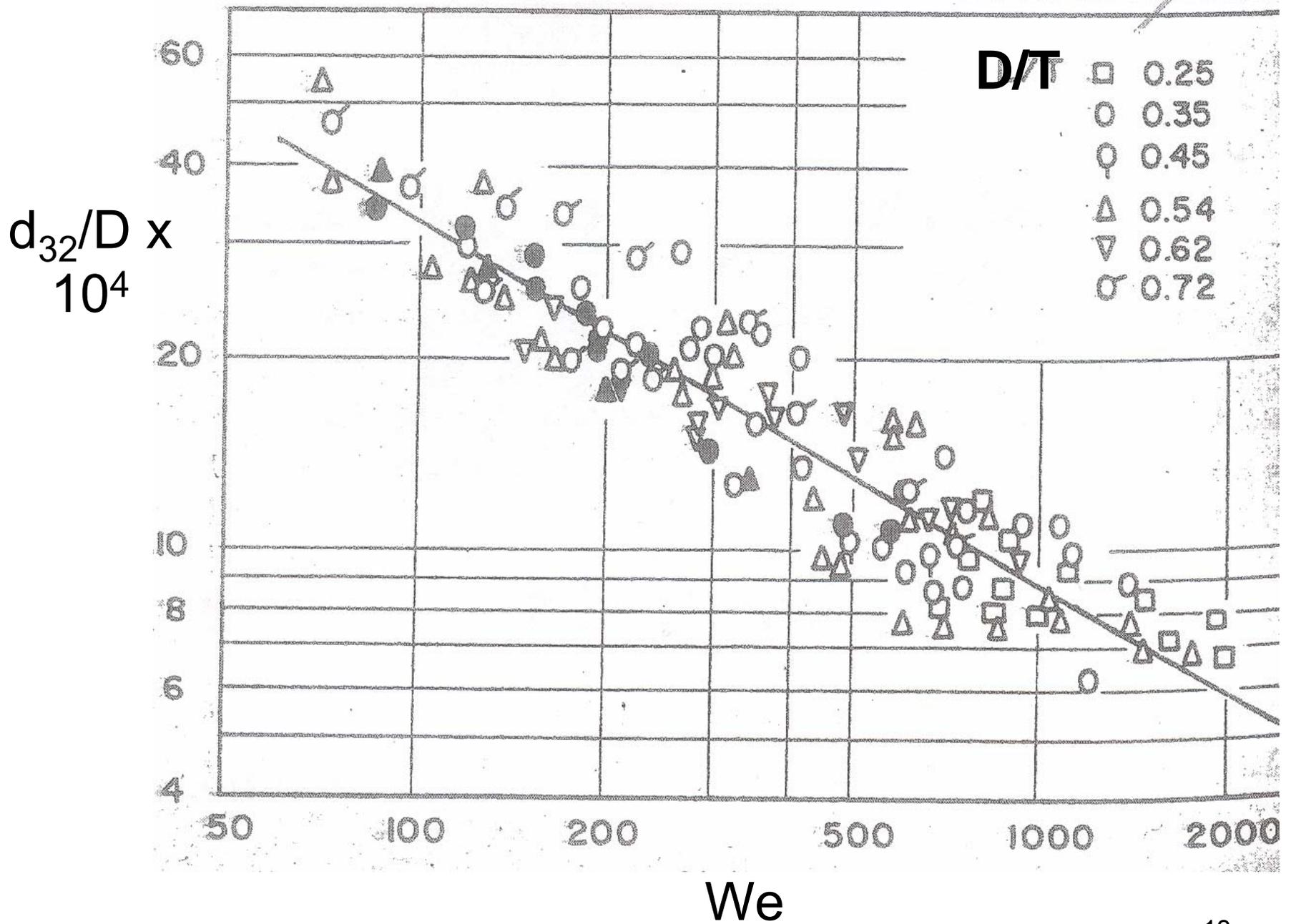
University of Rochester, Rochester, New York

Used large number of impeller sizes (2, 3, 4, 5 and 6 inches) in many (4, 6, 10, 12 and 18 inch diameter) tanks. Gave D/T ratios on results graph most of which cannot be obtained from these sizes of impeller and tank!

Correlation for all D/T ratios:

$$d_{32}/D = 0.053 We^{-0.6}$$

Quoted in Handbook



Can't use to test theory!

Seven years after Chen and Middleman

EFFECT OF IMPELLER GEOMETRY ON DROP BREAK-UP IN A STIRRED LIQUID-LIQUID CONTACTOR

Chemical Engineering Science, 1974, Vol. 29, pp. 345-348.

D. E. BROWN and K. PITT†

Table 1. Impeller dimensions **Rushton turbines**

Impeller No.	D	W	L_b	W/D	D/T	N_p	Nt_c
1	0.10	0.025	0.0315	0.25	0.33	5.8	12.3
2	0.10	0.050	0.0315	<u>0.50</u>	0.33	<u>9.3</u>	7.8
3	0.15	0.0375	0.0475	0.25	<u>0.50</u>	5.8	3.1

Standard

Deep blades

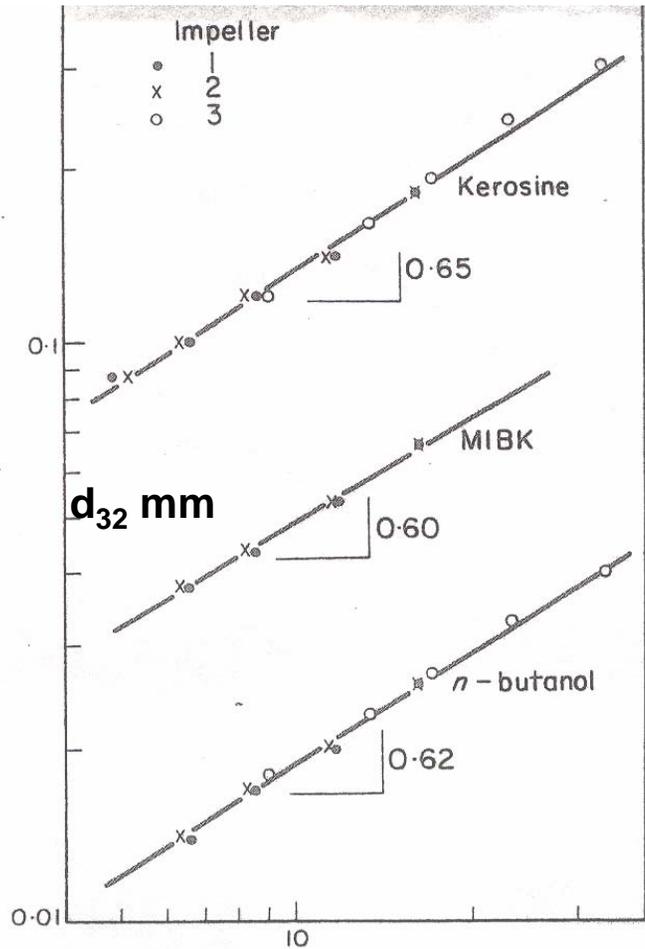
Big D/T

Table 3. Drop size measurements, circulation times and energy input **Three organics in water**

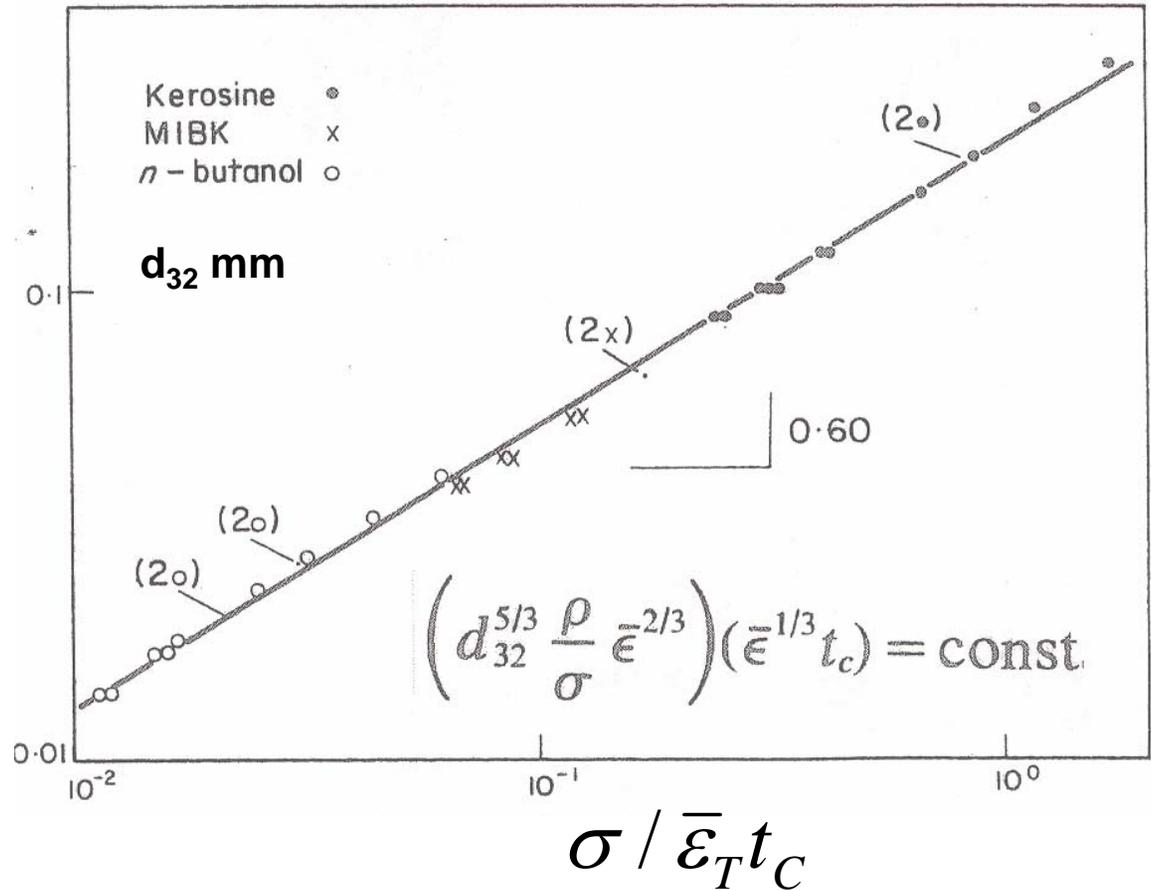
Speed Impeller (rpm)	t_c	$\bar{\epsilon}$	Sauter mean diameter (mm)		
			kerosene	M.I.B.K.	<i>n</i> -butanol

Tabled Results- Perfect for Testing

Complex Model Based on Estimated Circulation Time (t_c) through Impeller

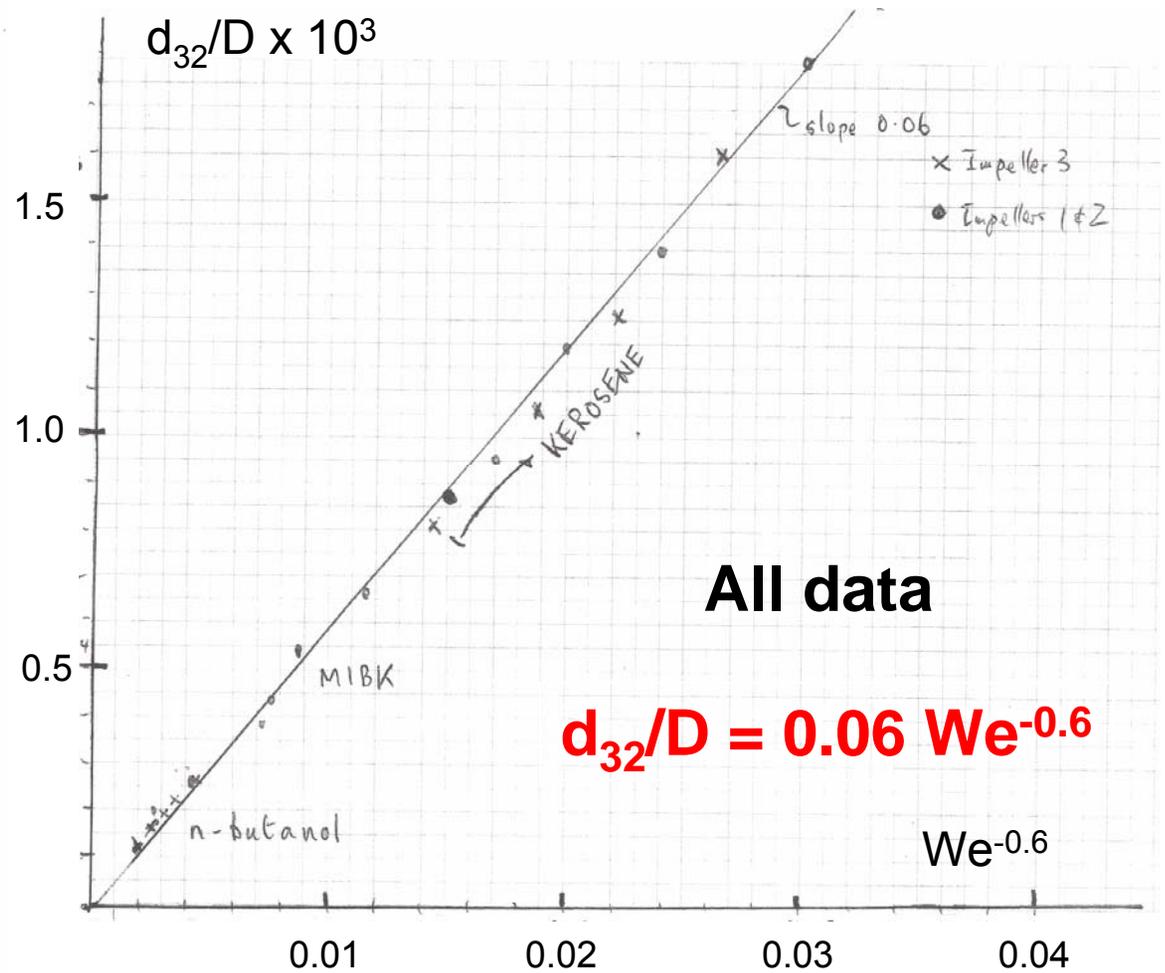
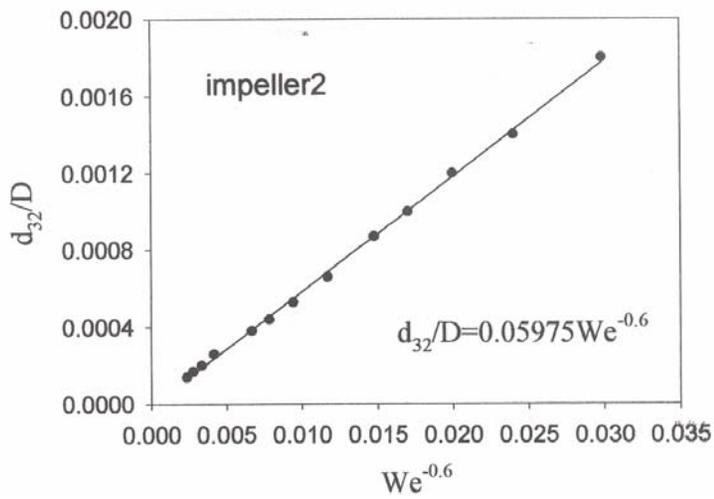
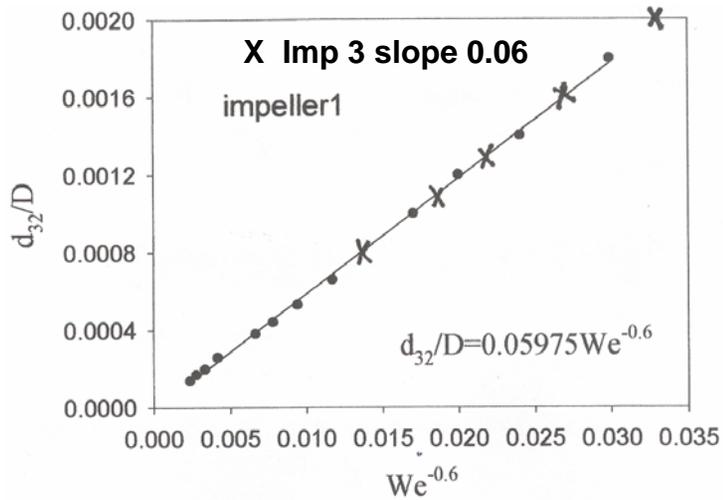


Effect of Impeller Geometry



Overall Correlation

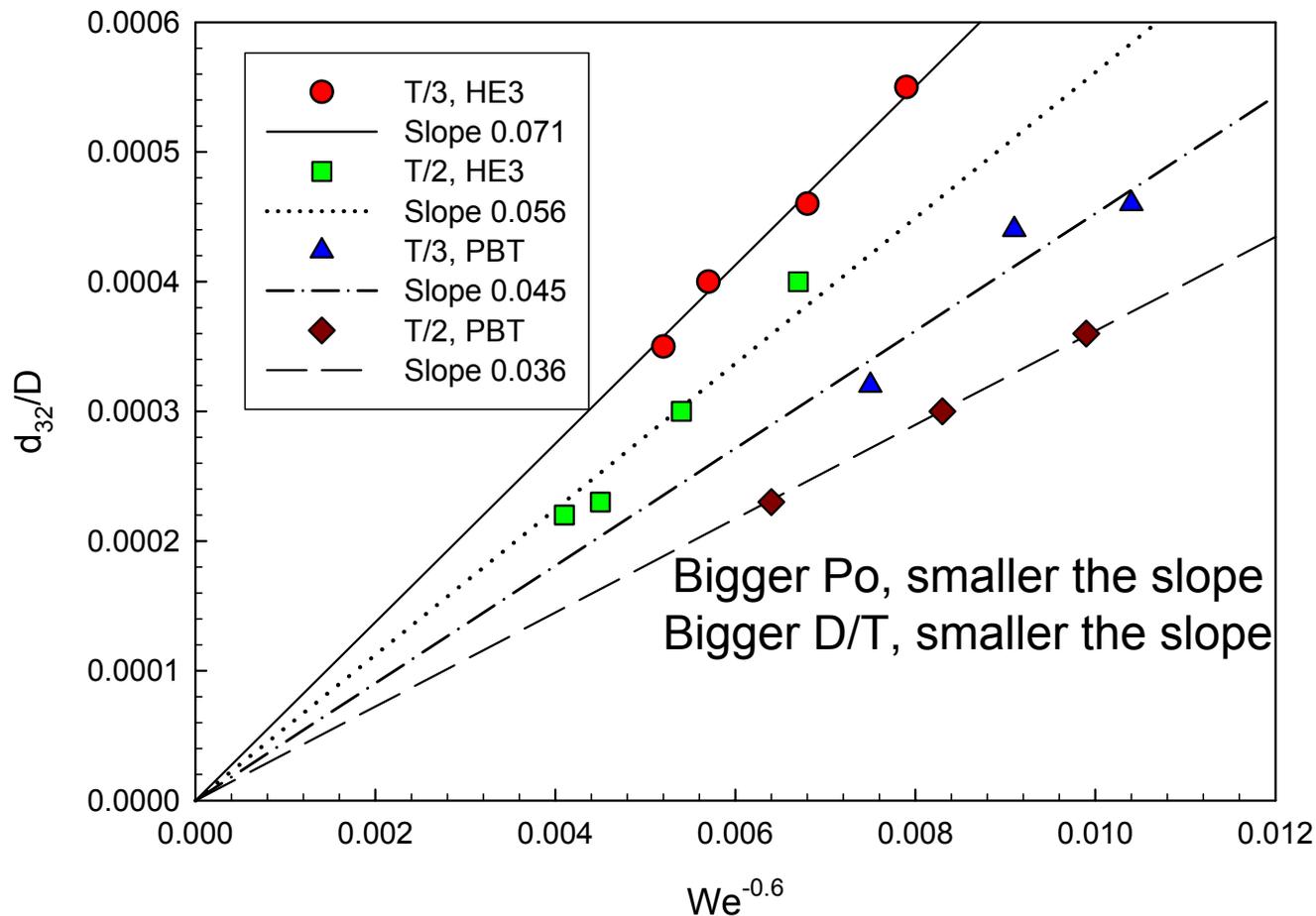
Remarkable fit to earlier correlation. Why produce a new one?



FMP Data- with Thanks (see Nienow, Adv.Coll. Int. Sci. 108-109, (2004), 95)

$$d_{32} / D = A We_D^{-0.6} \quad \text{where } A \propto \left(P_o \Phi D^3 / T^3 \right)^{-0.4}$$

If Φ is const., for same D/T , $A \propto P_o^{-0.4}$;
 $[P_o_{HE3}/P_o_{PBT}]^{-0.4} = \sim 1.9$; ratio of slopes, ~ 1.6



Measurement and Analysis of Drop Size in a Batch Rotor-Stator Mixer

Richard V. Calabrese, Michael K. Francis*, Ved P. Mishra and Supathorn Phongikaroon

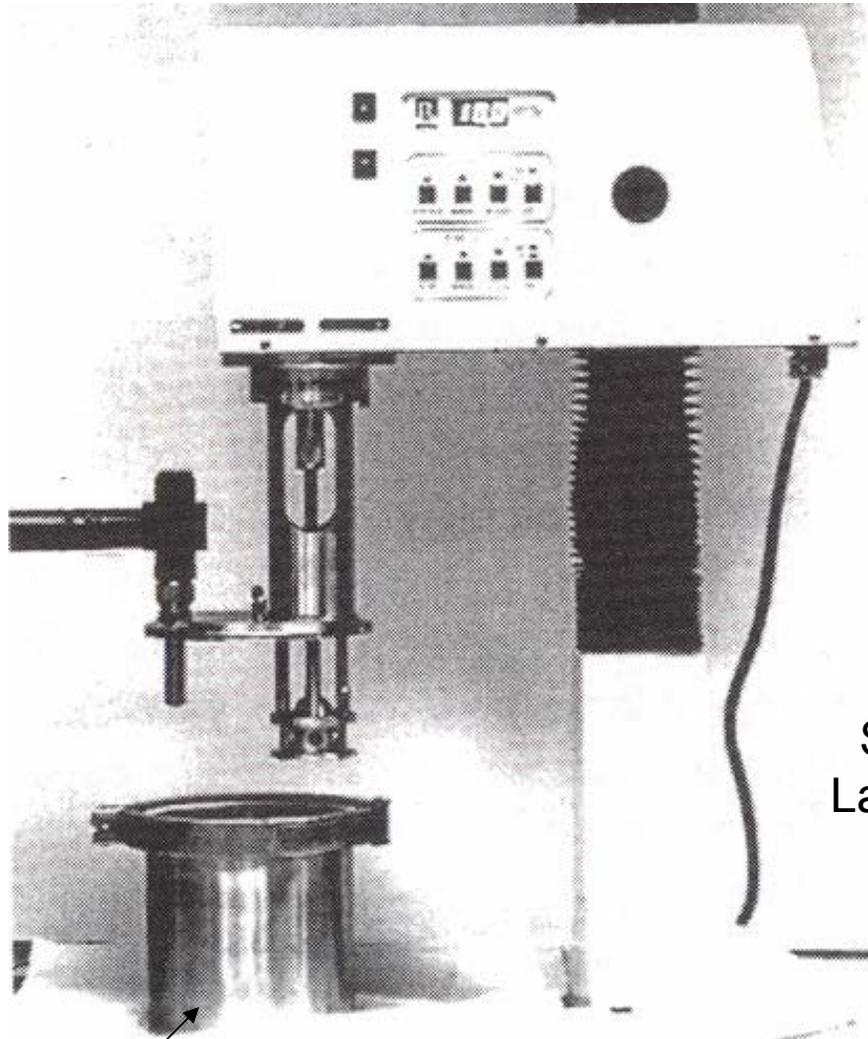
Department of Chemical Engineering, University of Maryland,
College Park, MD 20742-2111 USA

Figure 6 is a plot of d_{32} / D versus Weber No. The data are well fit by

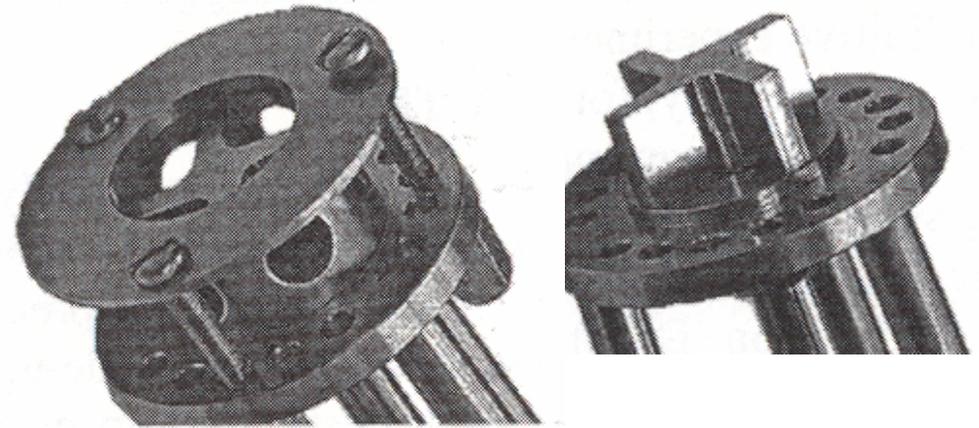
$$d_{32} / D = 0.40 We^{-0.58} \quad (9)$$

It therefore appears that Eq. (3) correctly scales the data and that breakage, like in turbine stirred tanks, is due to drop interactions with inertial subrange eddies. For a Rushton turbine, Chen and Middleman (1967) reported $d_{32} / D = 0.45 We^{-0.57}$, a strikingly similar result.

Later corrected to 0.040 and .0.045



2.5 L stainless steel-air excluded



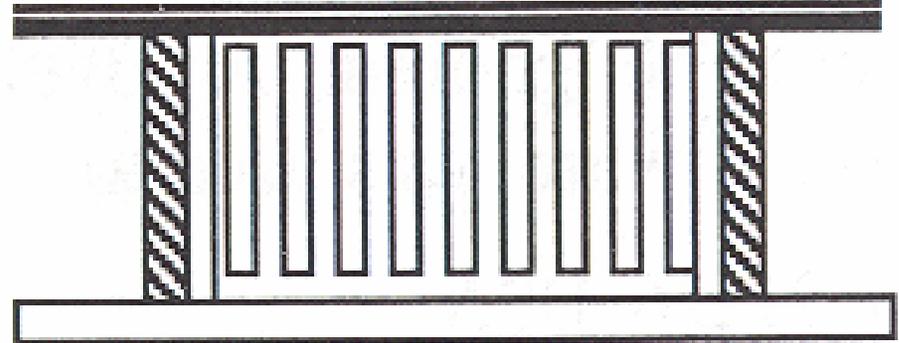
Close-up of 'Disintegrating' Stator Head

Diagram of Slotted Stator Head:

Rotor $D = 3.4$ cm;

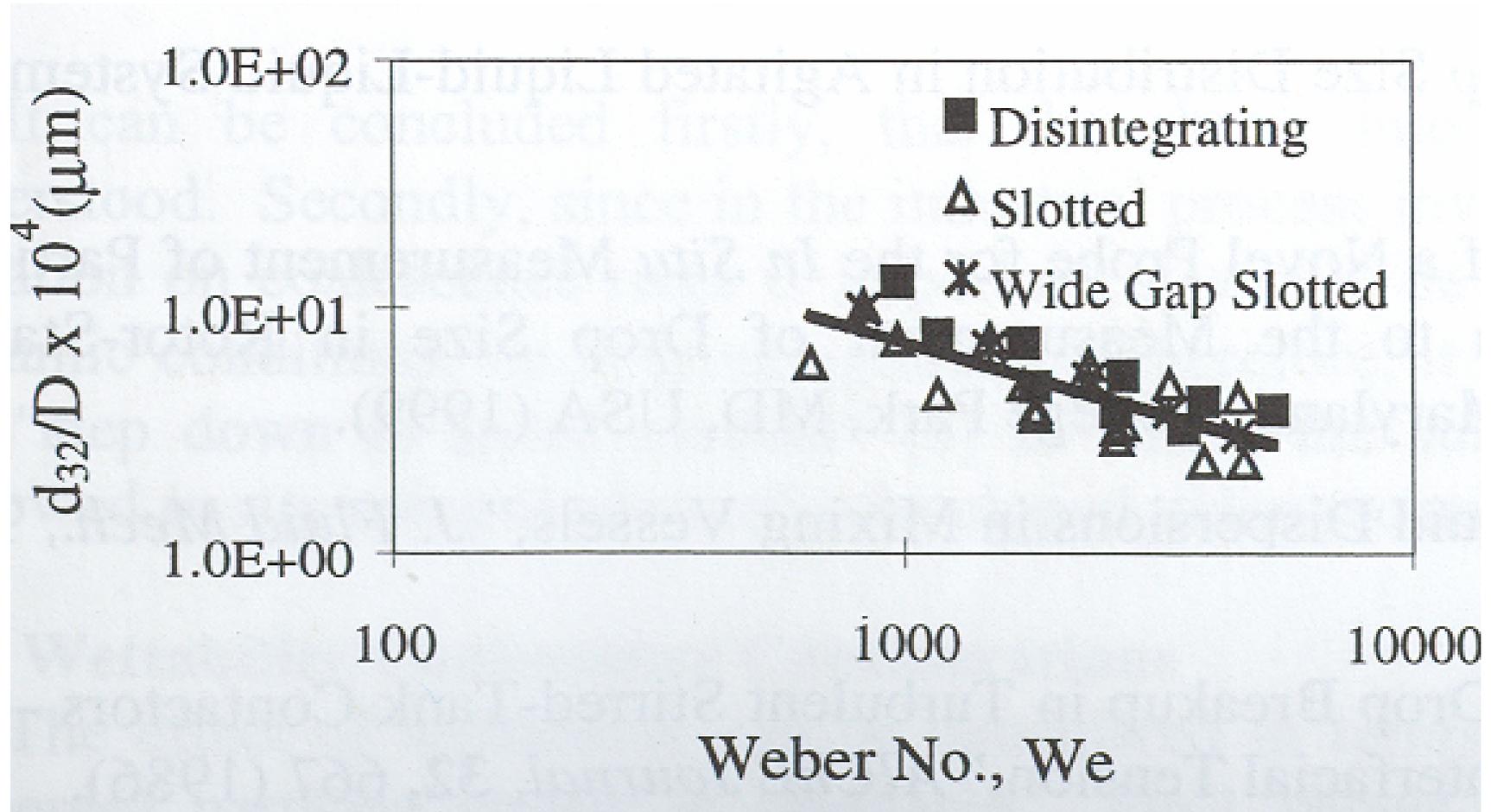
Standard stator, $D_s = 3.5$ cm; gap, $\delta = 0.5$ mm

Large stator, $D_s = 3.6$ cm; $\delta = 1.0$ mm (wide gap)



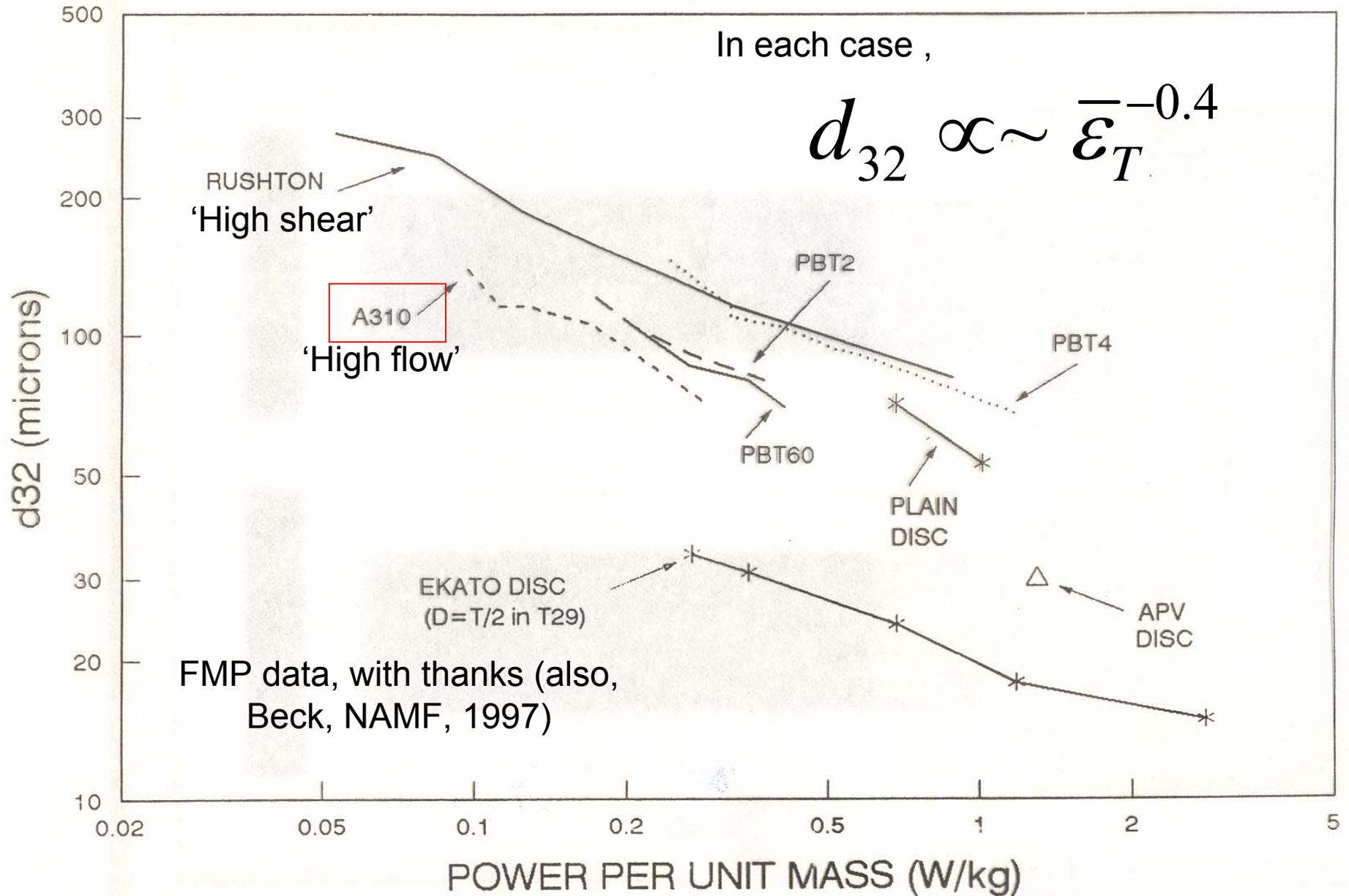
Ross Model ME 100LC Batch Rotor Stator Mixer

Weber Number Correlation: Incorporates Physical Properties

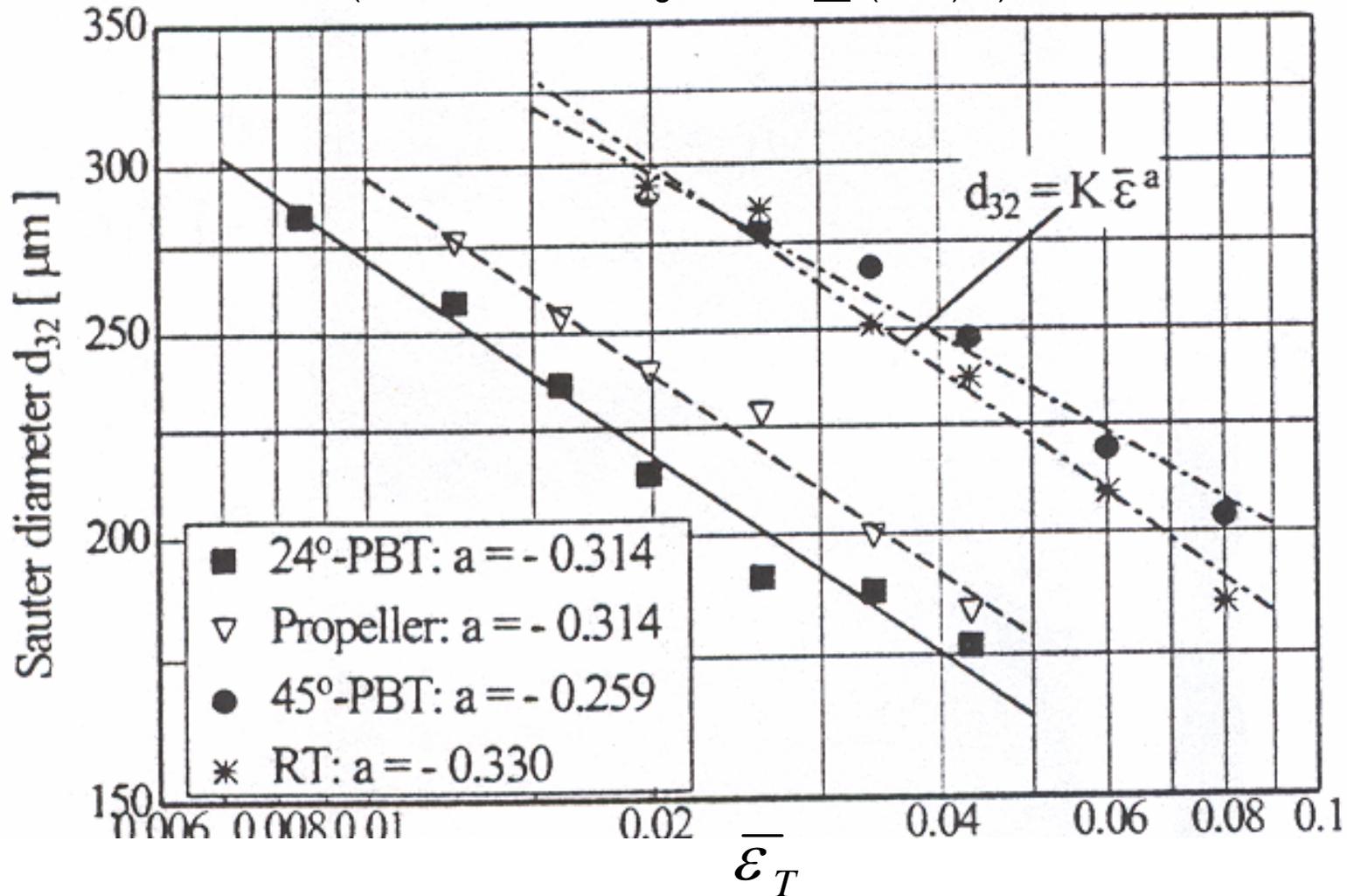


Considering geometrical differences, it is indeed surprising for turbulent, inertial regime that overall equation recommended is $d_{32}/D = 0.044 We^{-0.6}$

Little on other impellers in Handbook



Surfactant to inhibit coalescence; 400 mPas silicone oil
 (Wille et al, Chem Eng Technol. 24, (2001), 2)

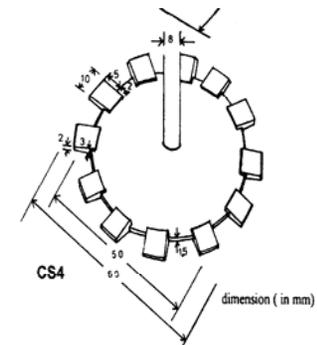
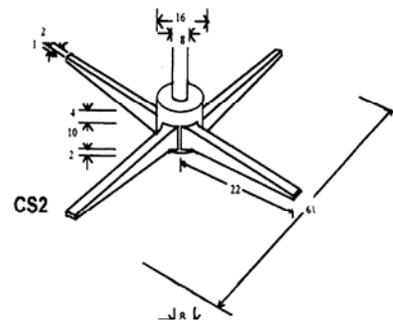
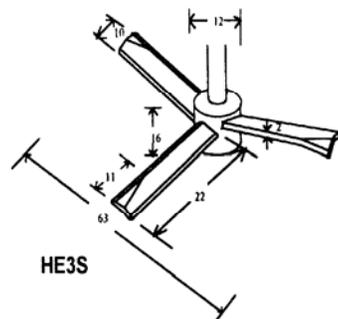
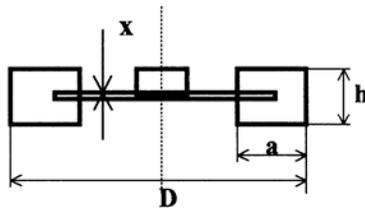


Slope doesn't fit basic theory of -0.4 BUT at same $\bar{\epsilon}_T$
 low Po , 'low shear' impellers give smaller drops than RT ²²

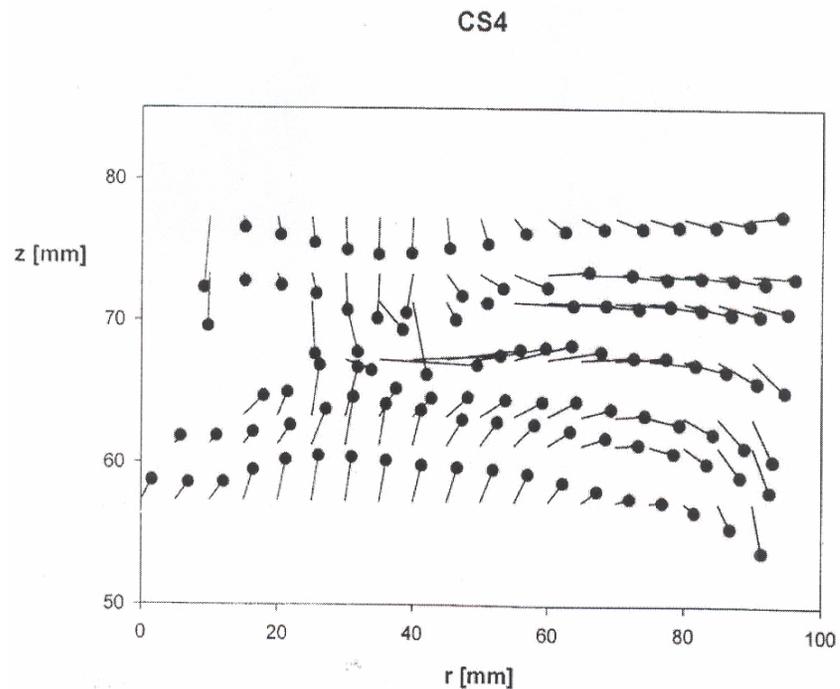
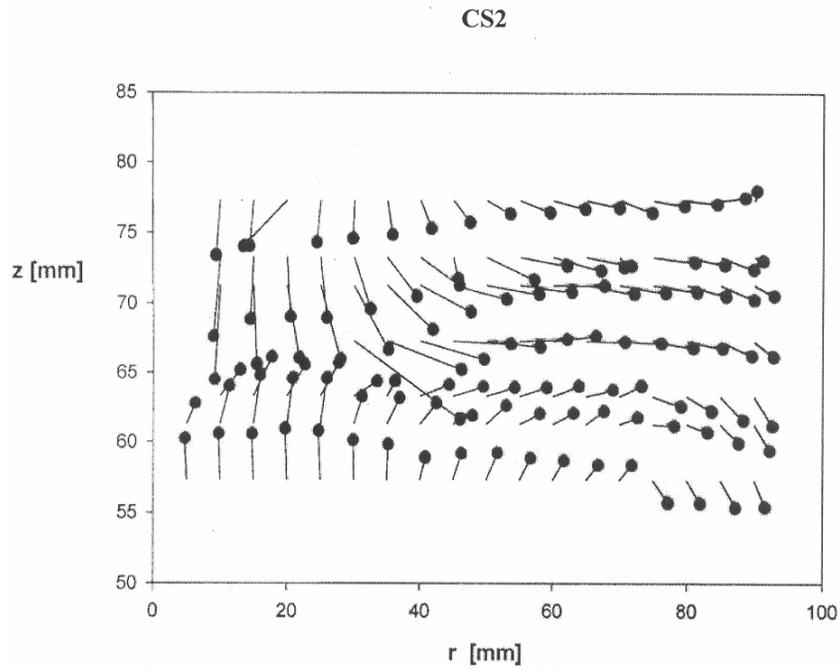
Another Comparison of Impellers

(Pacek *et al.*, Chem Eng Sci, 54, (1999), 4211)

- Four impellers:
 - Rushton Turbine ($Po = 5$, $Fl = 0.8$) - 'High Shear'
 - Chemineer HE3 ($Po = 0.3$, $Fl = 0.6$) - 'High Flow'
 - Chemineer CS2 & CS4 ($Po = 0.3$, $Fl = 0.06$) - 'Ultra high shear'



Note: D all the same and Po equal for HE3, CS2 and CS4



Fl =

0.04

to

0.14

LDA measurements to give Fl for the 2 Chemshear impellers (unpublished data-Birmingham, value depends on precisely where plane of integration is put)

Fl

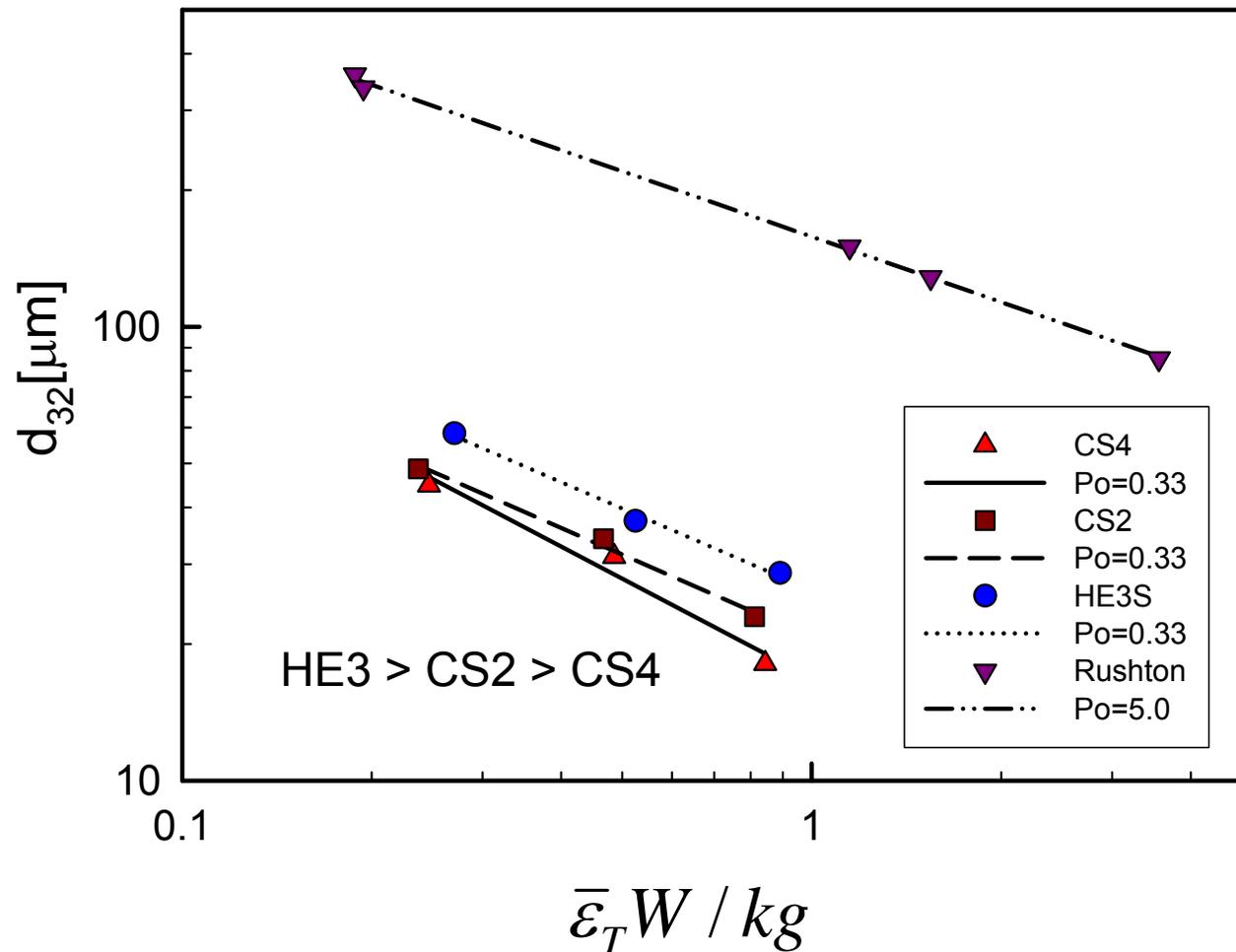
0.04

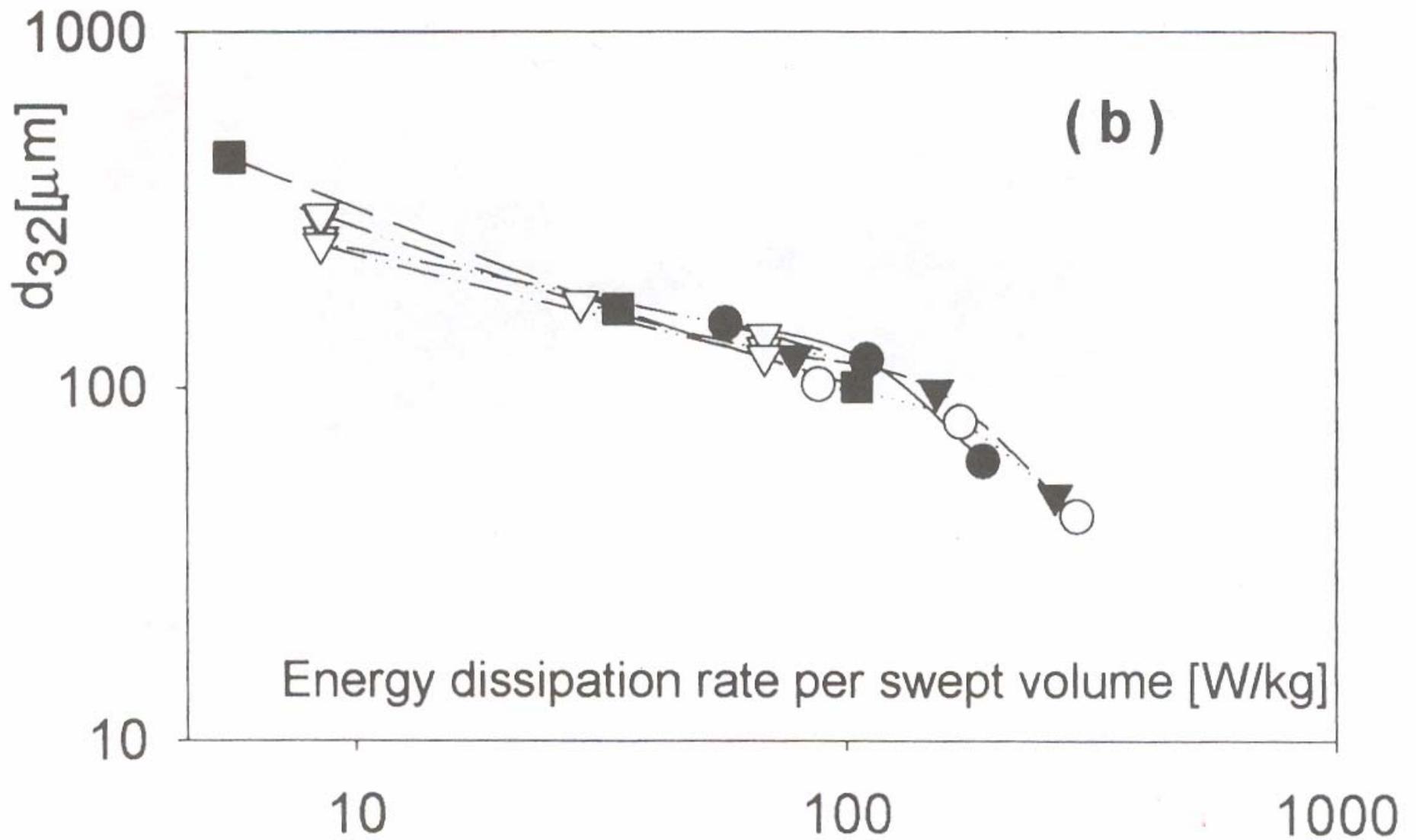
to

0.10

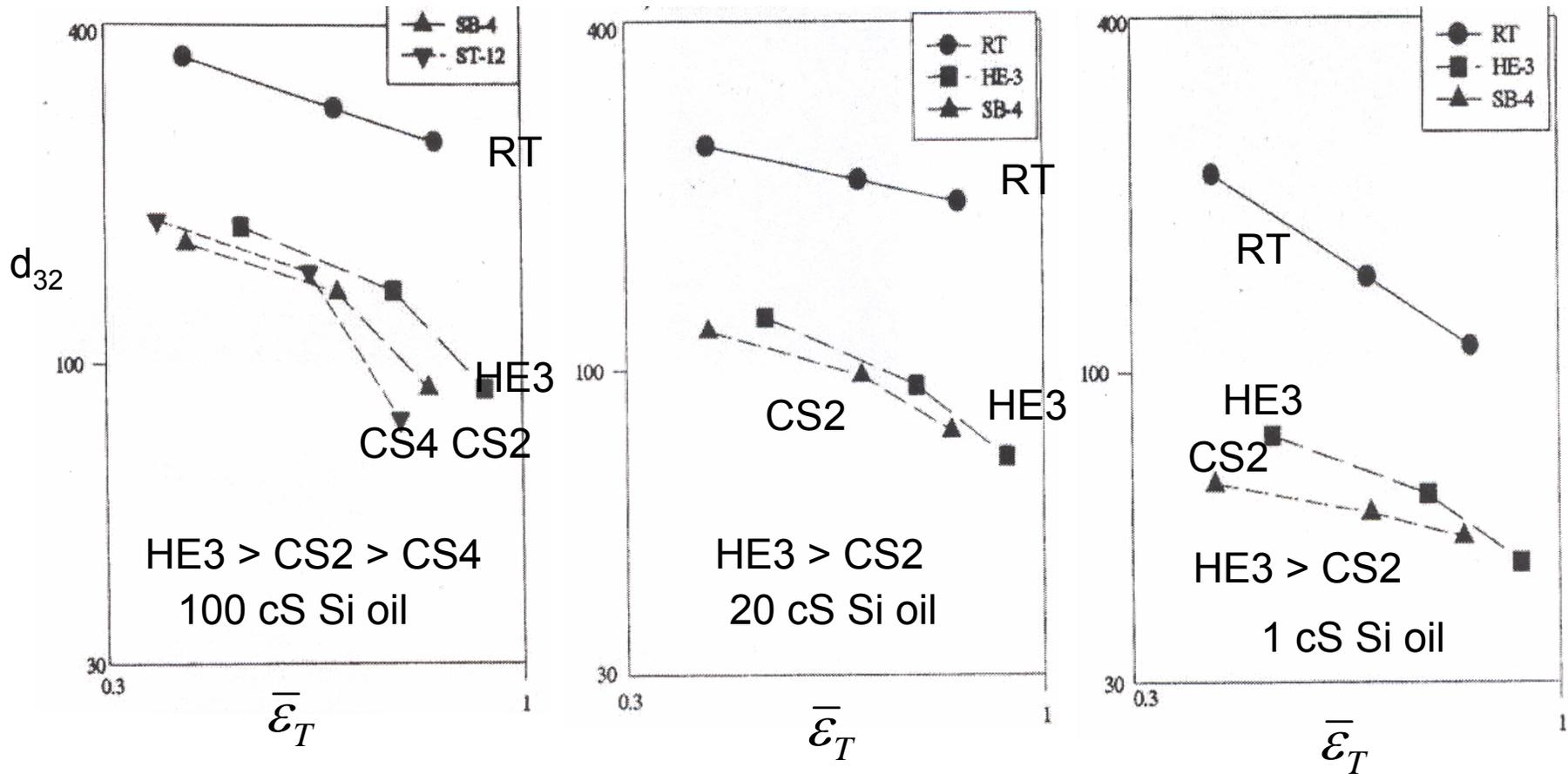
Results

All low Po impellers give approx. equivalent smaller drop sizes than the Rushton turbine.(1% sunflower oil; 55mPas)





Sauter mean diameter as function of energy dissipation rate /swept volume for 5% sun flower oil



Same impellers with silicone oil:

Lower viscosity, smaller drops; HE3 \approx 'Chemshear' \ll RT

Potential for improved flow and same drop size using HE3 type impellers compared to 'Chemshear'

(Unpublished data – Birmingham)

Time to Produce Equilibrium d_{32} following Handbook

(or Smit, Euro Mixing Conf, 1994)

Depends on number of circulations through impeller, Flow no, FI;

$$t_c = V / F I N D^3$$

In same vessel, V , at same $\bar{\varepsilon}_T$ and D , $N \propto Po^{-1/3}$, so that

$$t_c \propto Po^{1/3} / FI$$

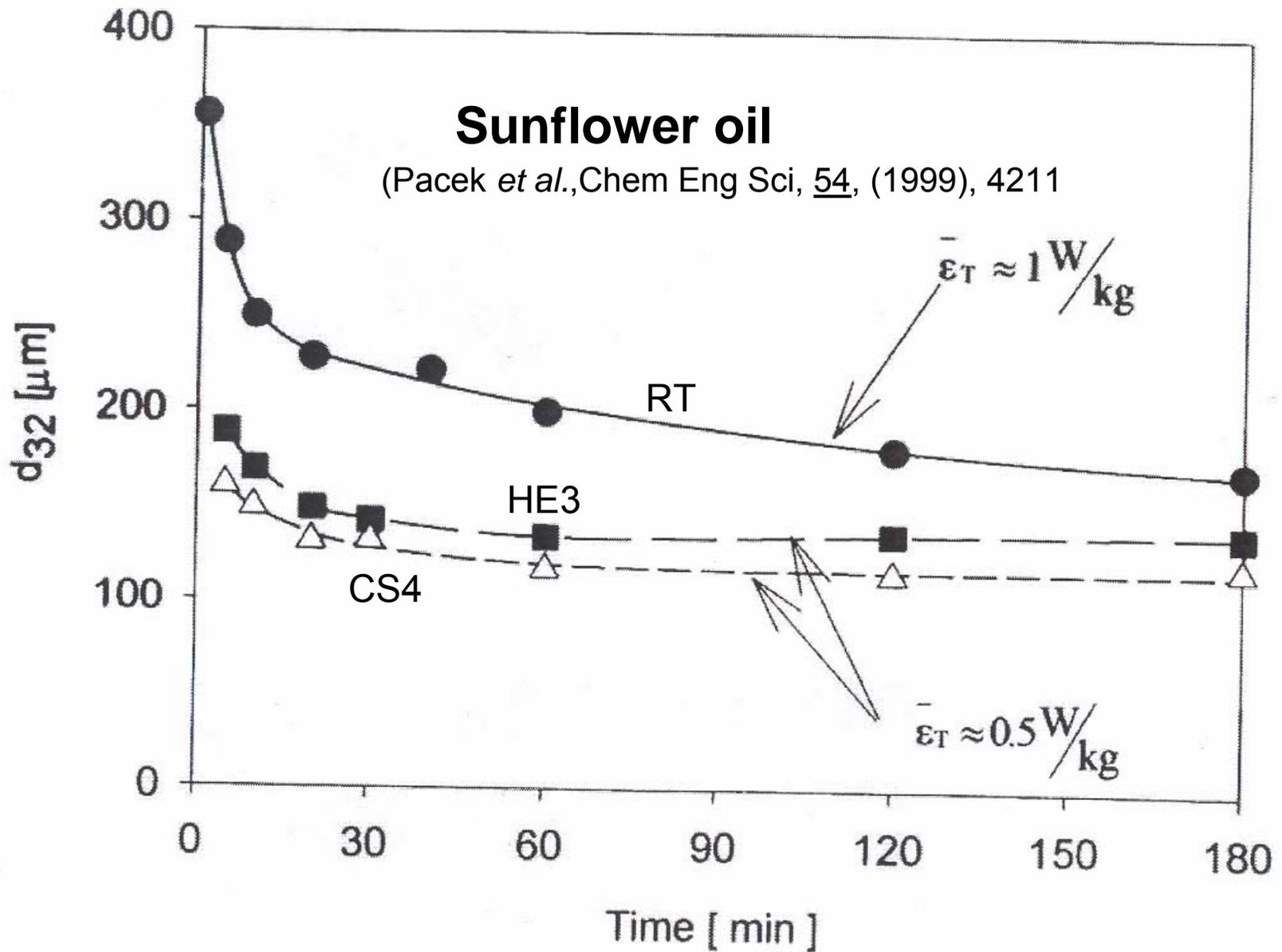
Thus for RT used here, $(t_c)_{RT} \propto 5^{1/3}/0.8$ and $(t_c)_{HE3} \propto 0.3^{1/3}/0.6$

and time to equilibrium for RT, $(t_c)_{RT} \approx 2 (t_c)_{HE3}$

However, $(t_c)_{CS2} \approx (t_c)_{CS4} \propto 0.3^{1/3}/0.06$ so that

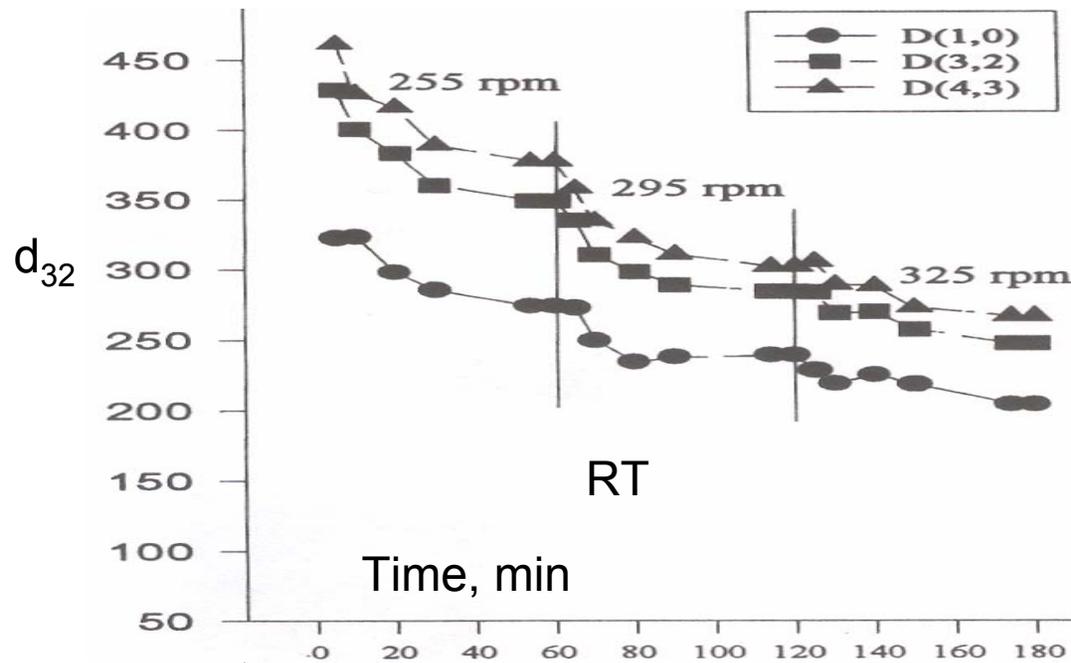
$$(t_c)_{CS2} \approx (t_c)_{CS4} \gg (t_c)_{HE3}$$

Experiments show $(t_c)_{HE3} \approx (t_c)_{CS2} \approx (t_c)_{CS4} < (t_c)_{RT}$

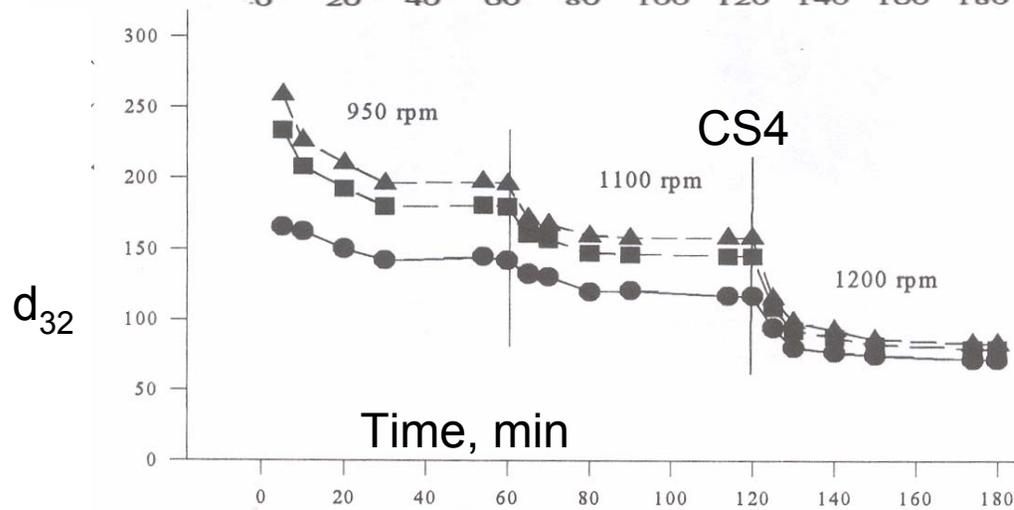


Similar result with Ekato saw-tooth impeller (Beck, FMP and NAMF, 1997)

100cS Si oil



**Chemshear CS4 (FI ≈ 0.6)
as fast or faster to
equilibrium as Rushton**



Unpublished data, Birmingham

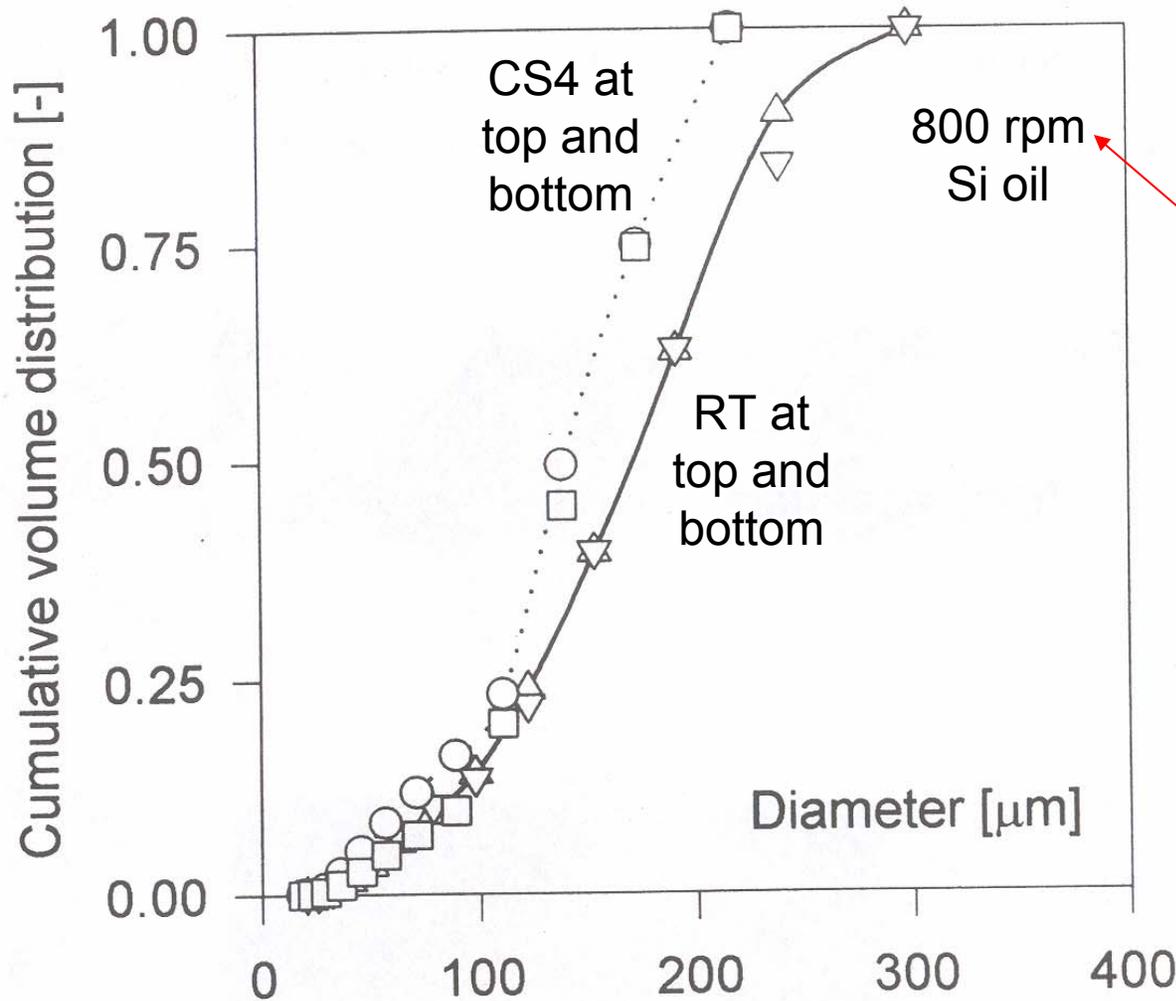
Recommended scale-up in Handbook to give equal drop sizes is equal $\bar{\varepsilon}_T$

- Classic theory as above suggests geometric similarity and equal $\bar{\varepsilon}_T$
- However, many experiments since Konno et al., 1982 (Okufi *et al.*, 1990; Zhou and Kresta, 1998; Collander, 2000 (in very short time because high concentration and coalescence repressed by surfactant); Schulze *et al.*, 2000), all show smaller drop sizes at equal $\bar{\varepsilon}_T$
- Scale-up at about constant tip speed ($\sim \mathbf{ND}$)
- Explained by intermittency

Intermittency (Baladyga *et al.*, 2001)

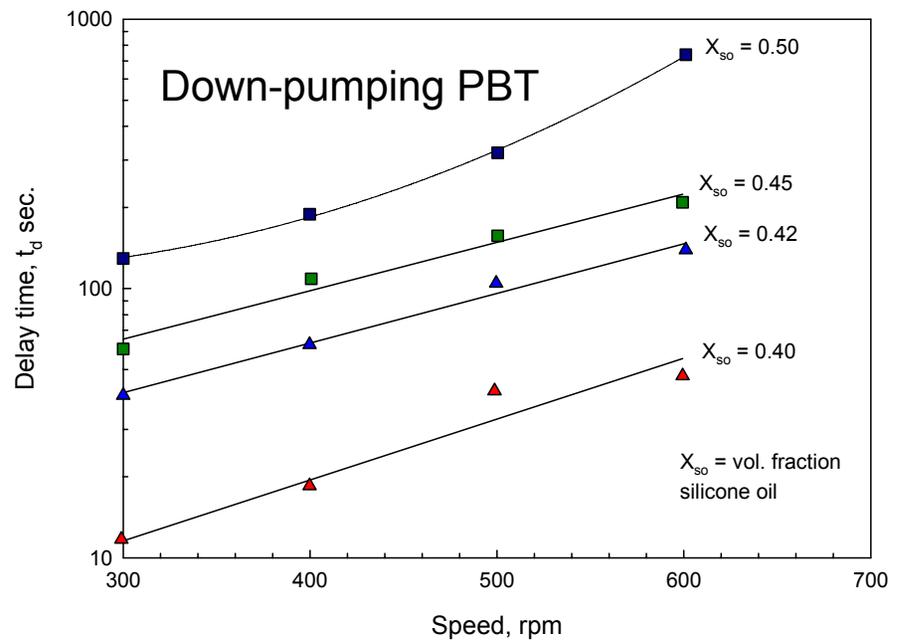
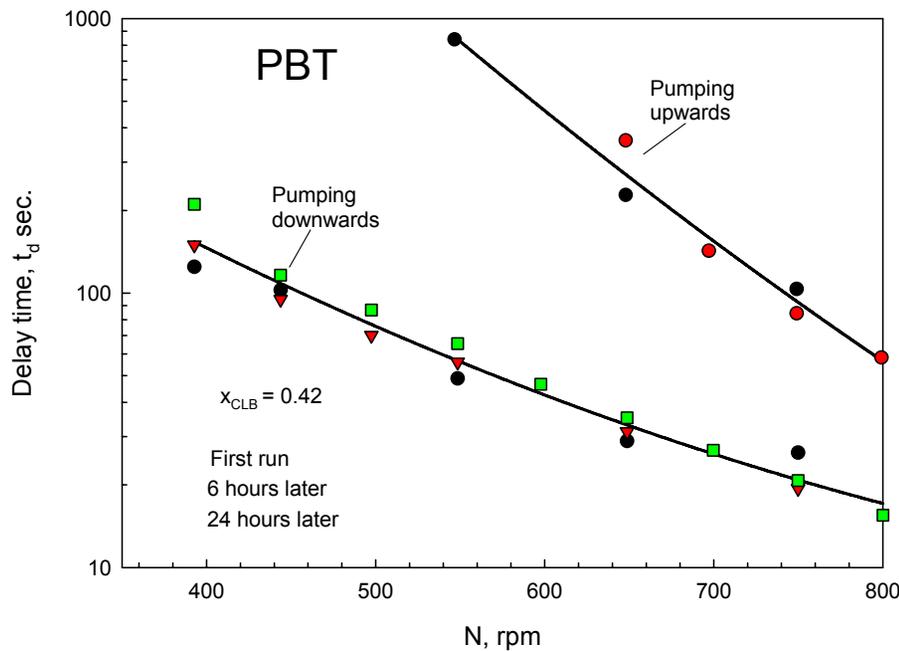
- $\varepsilon_T / \bar{\varepsilon}_T = f(\text{space and time(intermittency)})$
- It is always higher than average (typically 20 times) near the impeller and less (~ 0.1) well away from it. However, at any point, there are temporal deviations from the average, so that occasionally near the impeller, values of 40 may be found. The greater the scale (Re no.), the higher the possible deviation from the average, This leads to:
- $ND^{0.93} = \text{const.}$ or $N \propto D^{-1}$, i.e., const. tip speed

Handbook quotes Sprow (Chem Eng Sci., 22, (1967), 435) that due to drop coalescence at higher concentrations, different sizes and functionalities at impeller and elsewhere.



Pacek *et al.*, (Chem Eng Sci, 54, (1999), 4211) with Si oil; and Pacek and Nienow (Trans I Chem E (A), 73, (1995), 512) with heavily coalescing chlorobenzene, unlike Sprow, found same drop sizes same everywhere

Coalescence: All theories in the Handbook use local ε_T but large Scale Flow Structures may be important. For example, at high concentrations, the time, t_d , it takes for a water-in-oil dispersion to invert to an oil-in-water depends on the rate of break-up relative to coalescence. At the same $\overline{\varepsilon}_T$, t_d depends on the direction of pumping with a pitched blade turbine and the density of the dispersed phase relative to the continuous.



$\rho_d (H_2O) < \rho_c (CLB)$, $N \uparrow$, coalescence in trailing vortex \uparrow , $t_d \downarrow$

$\rho_d (H_2O) > \rho_c (SO)$, $N \uparrow$ centrifuge out of vortex, coalescence \downarrow , $t_d \uparrow$

Nienow, Adv.Coll. Int. Sci. 108-109, (2004), 95)

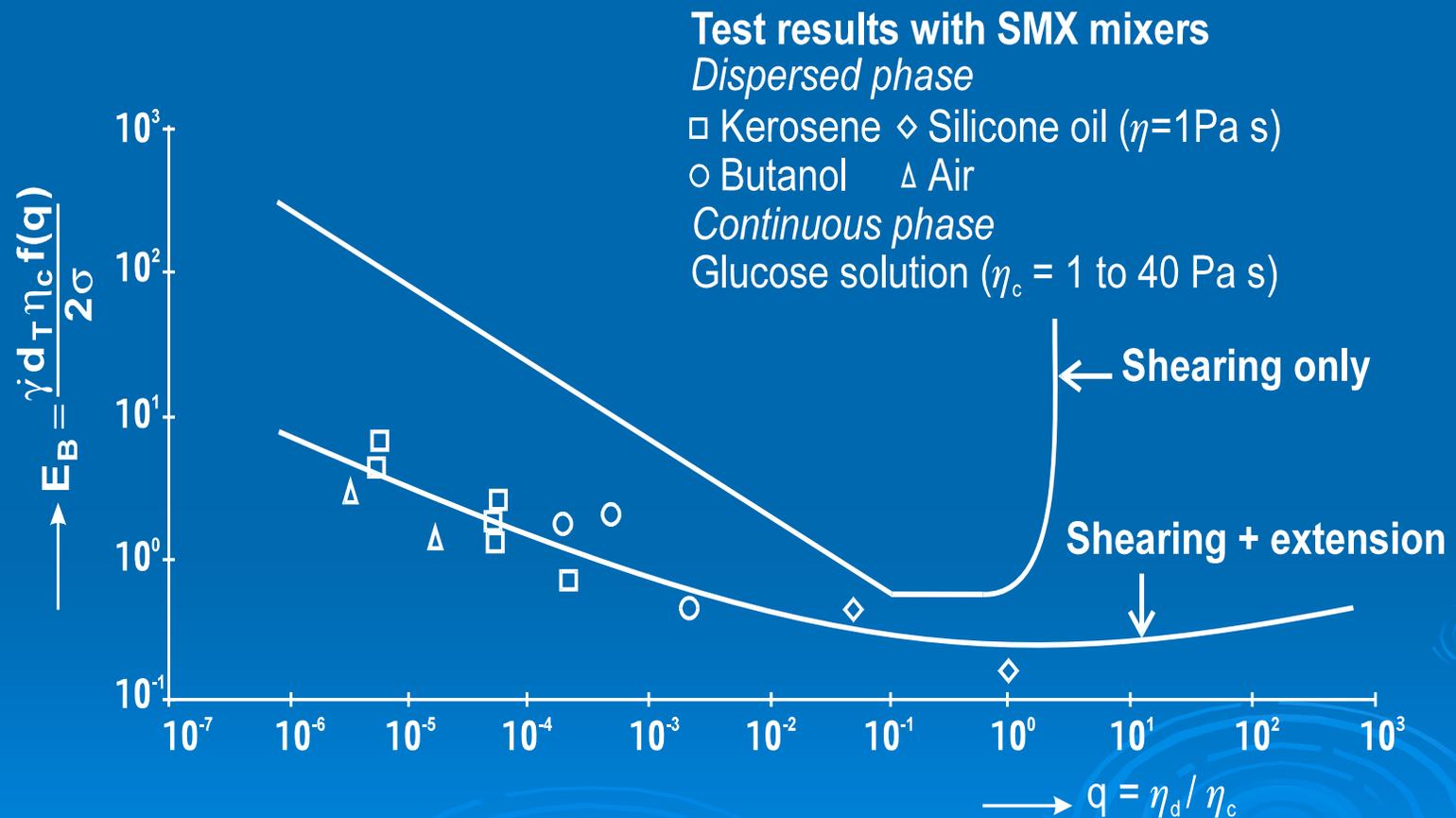
Laminar Emulsification

- Resisting breakage - interfacial tension, σ (N/s) and dispersed phase viscosity, μ_d (Pas)
- Causing breakage - local deformations rates, shear and elongation
- Deformation (stretching) in laminar or steady flow characterized by, Ca , Capillary No

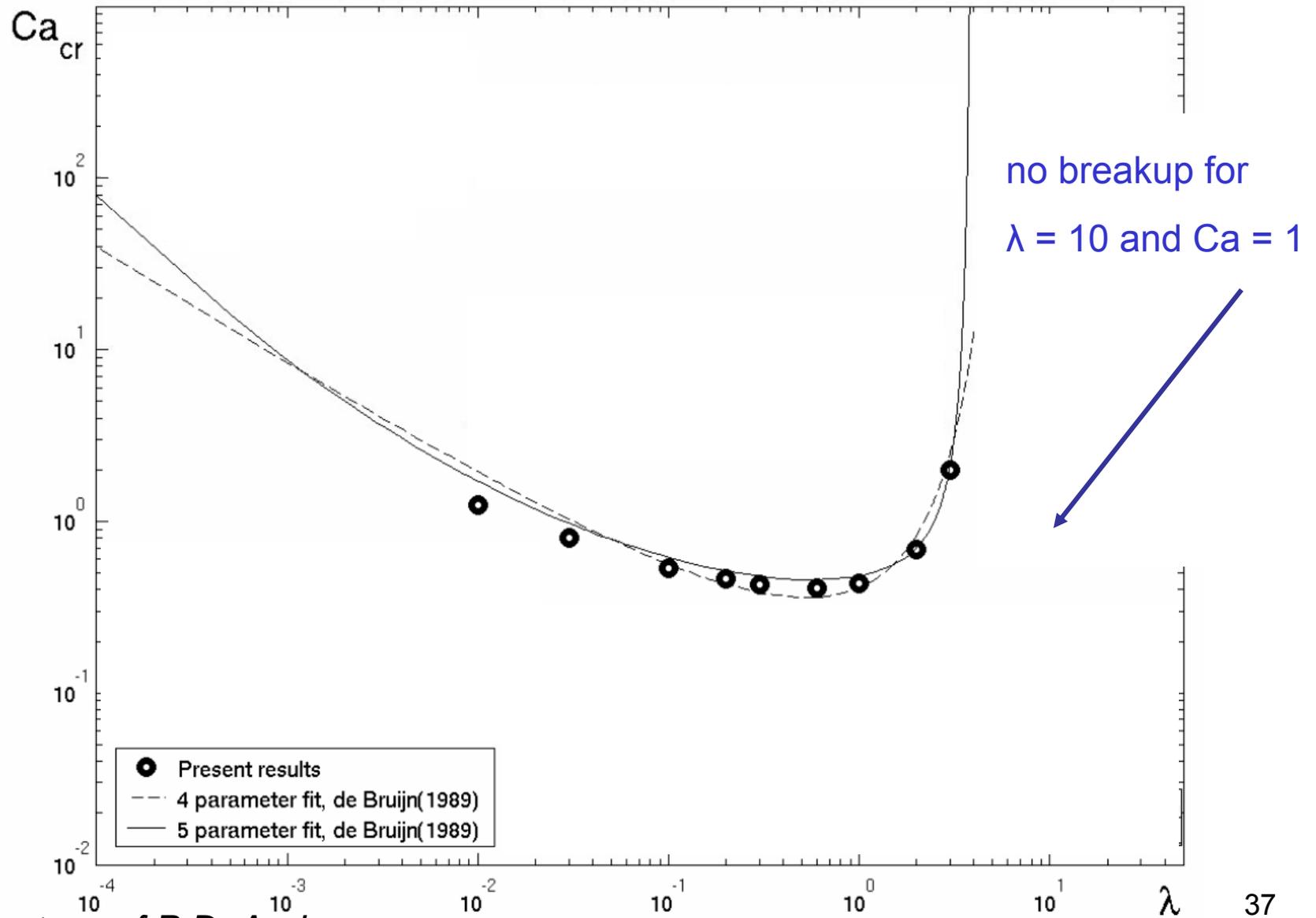
$$Ca = \frac{\mu_c \dot{\gamma} d}{\sigma} = \frac{\text{Viscous Stresses}}{\text{Surface Forces}}$$

$$\mu_R = \mu_d / \mu_c$$

Critical Shear or Extensional Rates



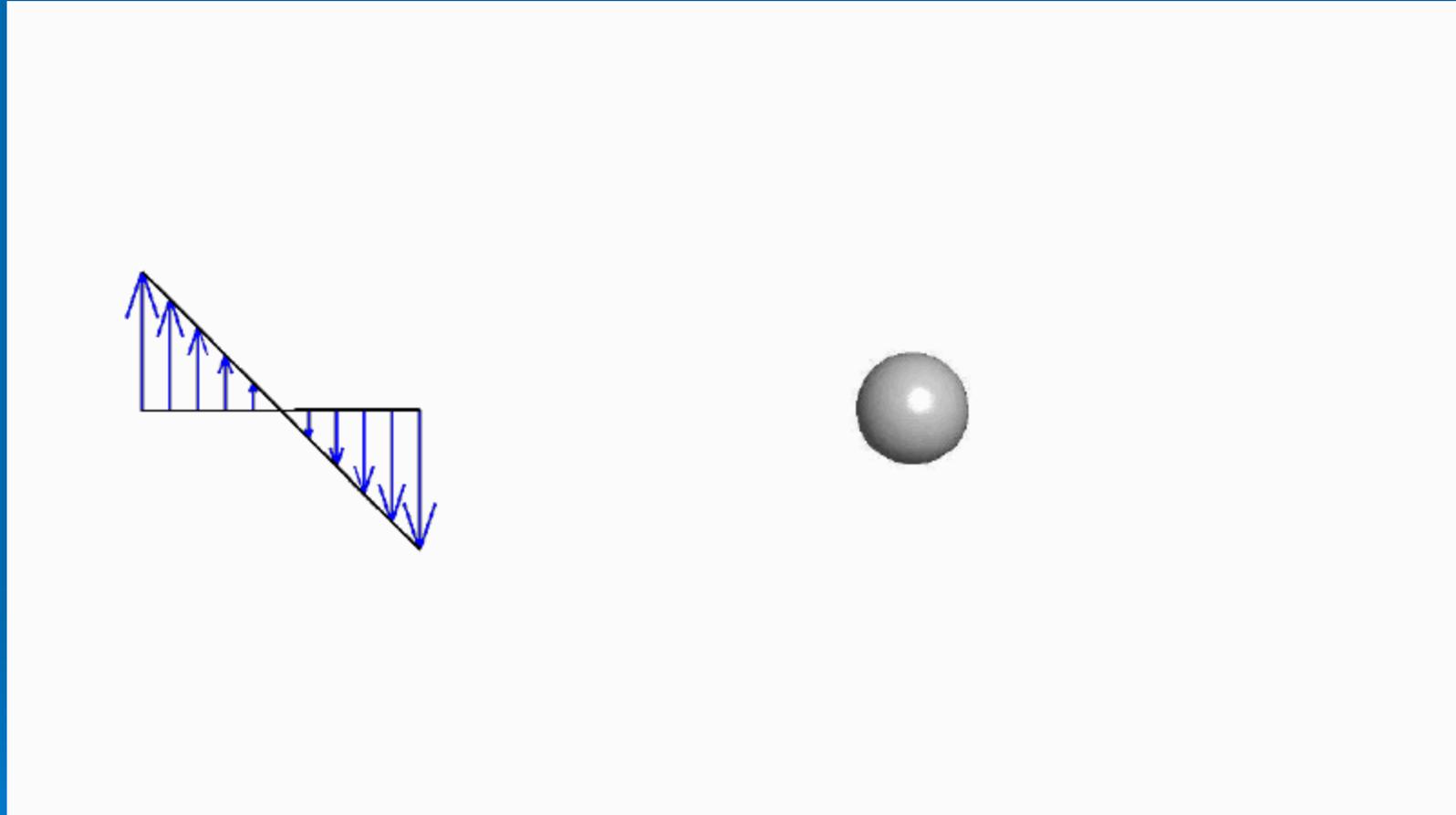
Modeling Drop Breakup (Grace curve)



Courtesy of P.D. Anderson

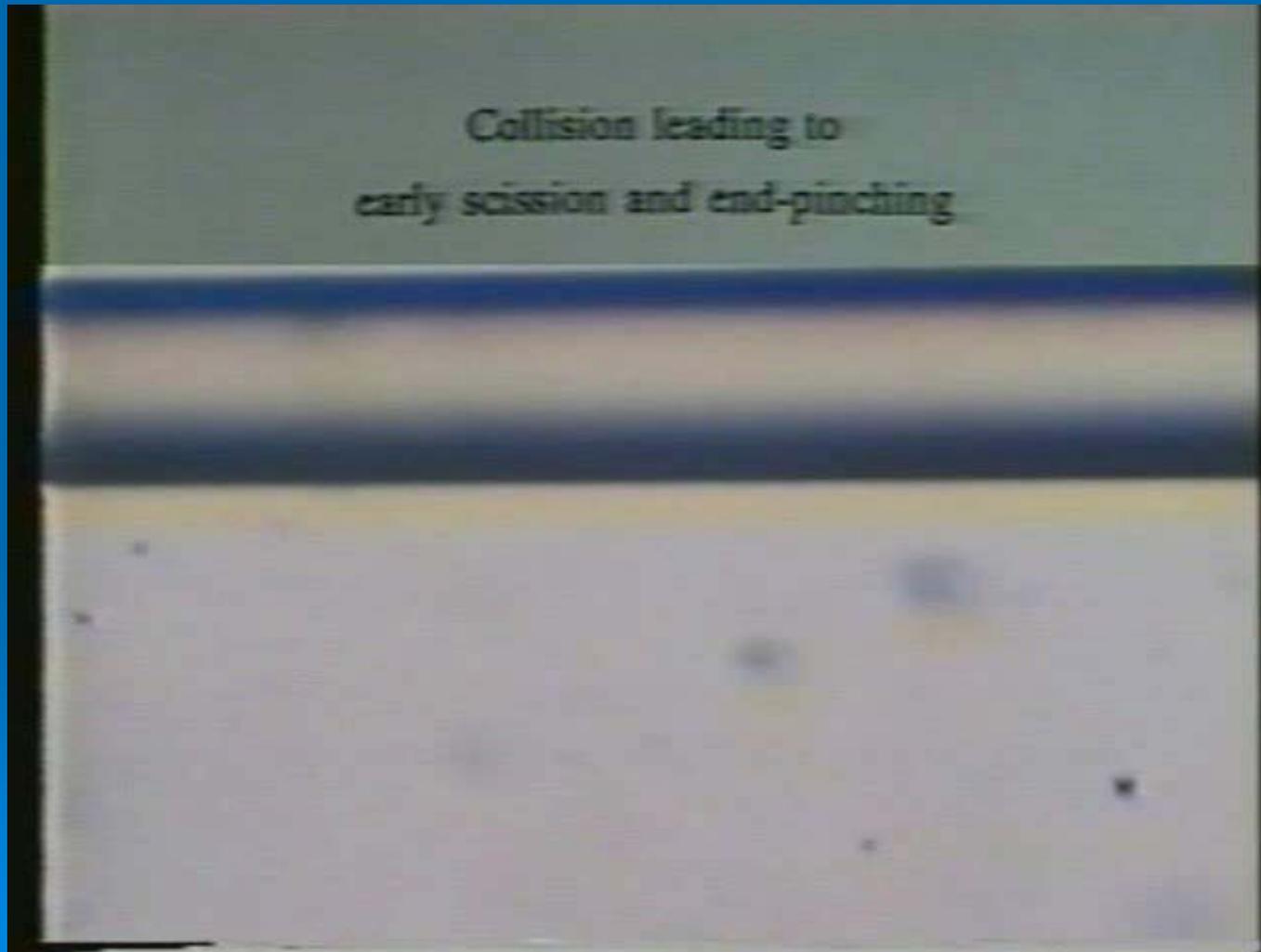
Grace Curve Applicability

(Rotating flow field)

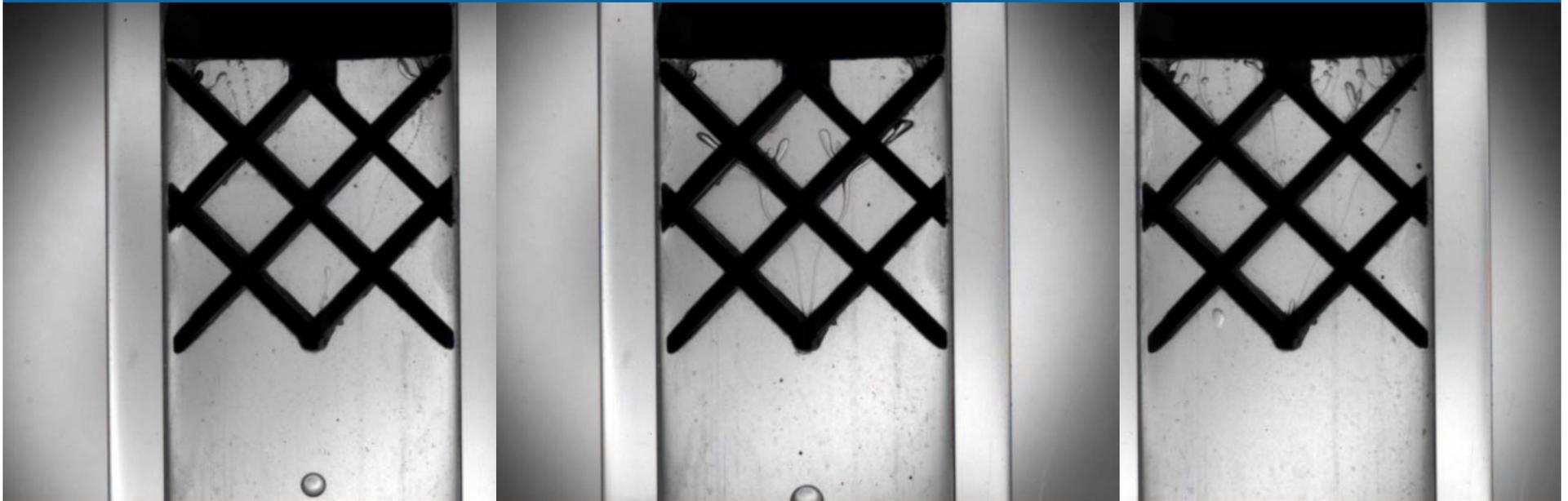


$$\lambda = 10 \text{ and } Ca = 1$$

Emulsions – always many drops around! How do they impact drop breakup?



Breakup above critical condition (S.Liu, A.N. Hyrmak and P.E. Wood)



A

B

C

Flow condition and property:

$\mu_c = 615 \text{ cP}$, $\mu_d = 98.4 \text{ cP}$, $\rho_c = 1364 \text{ Kg/m}^3$, $\rho_d = 960 \text{ Kg/m}^3$, $\sigma = 0.036 \text{ N/m}$,

$\mu_d / \mu_c = 0.16$, $V = 0.0466 \text{ m/s}$, diameter of tube = 15.8 mm, $Re = 1.64$.

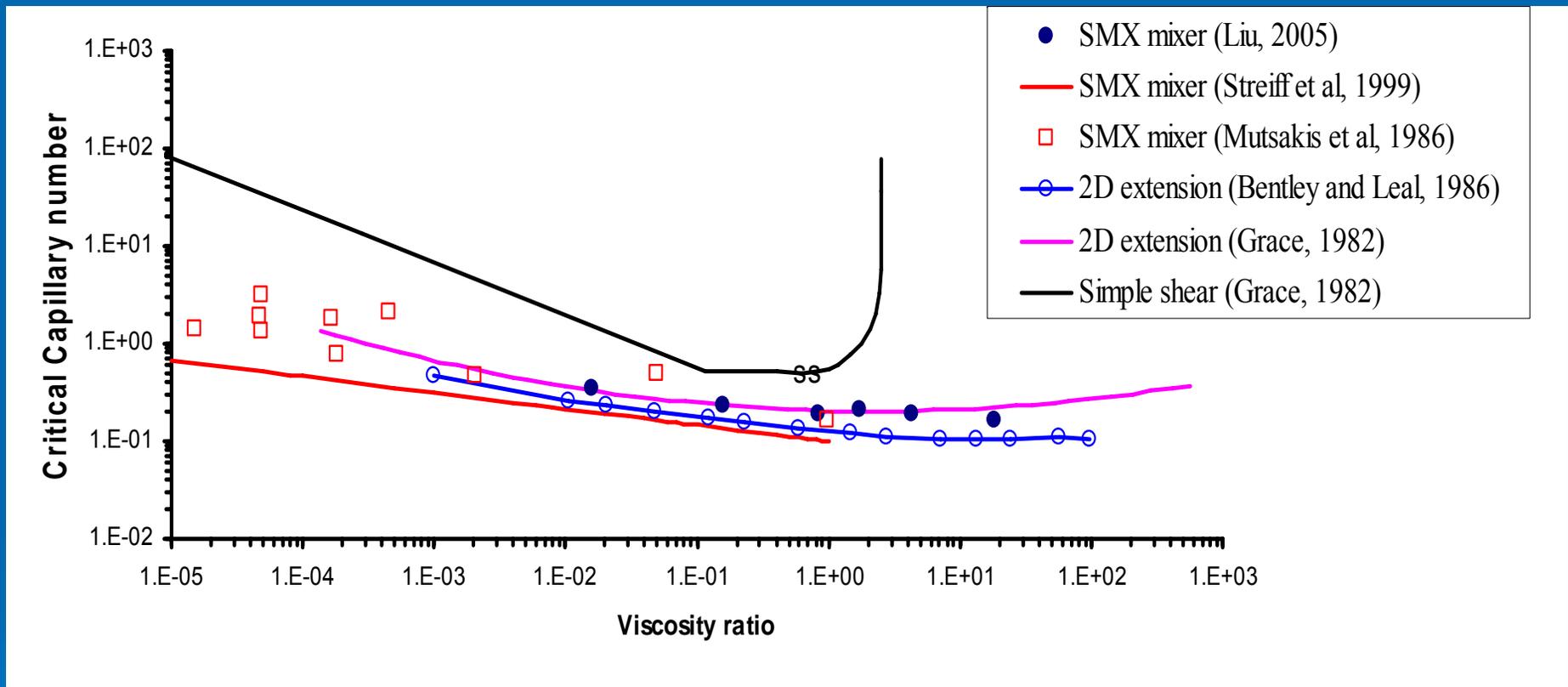
Average strain rate = 176 s^{-1} , critical $Ca = 0.24$, $d_{max} = 0.16 \text{ mm}$

initial diameter of drop: $d_A = 1.297 \text{ mm}$, $d_B = 1.66 \text{ mm}$, $d_C = 2.335 \text{ mm}$

Initial capillary number: $Ca_A = 1.95$, $Ca_B = 2.50$, $Ca_C = 3.72$

d_{max} after six elements: $d_{maxA} = 0.418 \text{ mm}$, $d_{maxB} = 0.454 \text{ mm}$, $d_{maxC} = 0.413 \text{ mm}$

Maximum drop diameter d_{max}



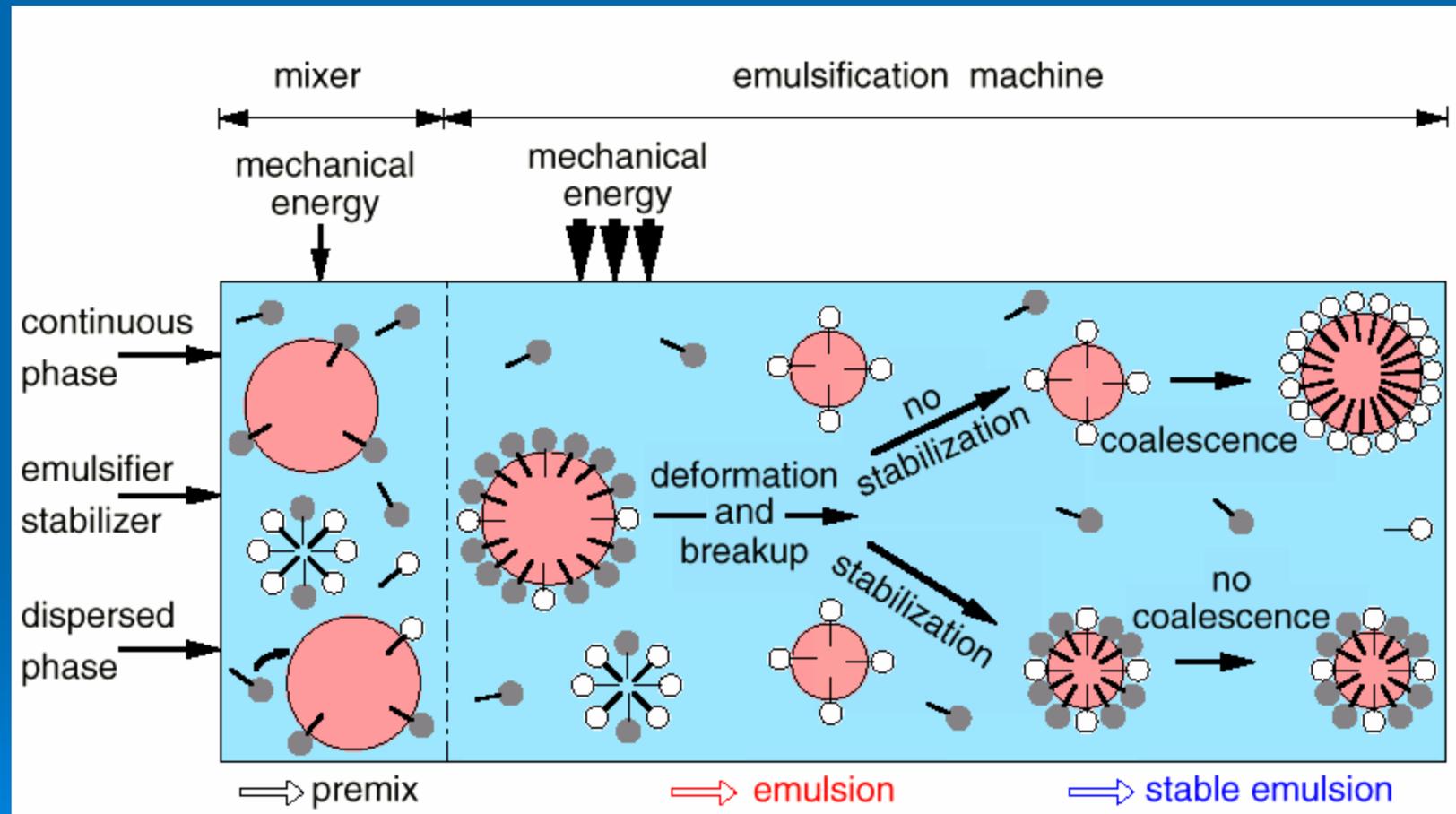
S. Liu (2005) results are calculated based on drops impacting a cross point.

Grace Curve applicable except when..

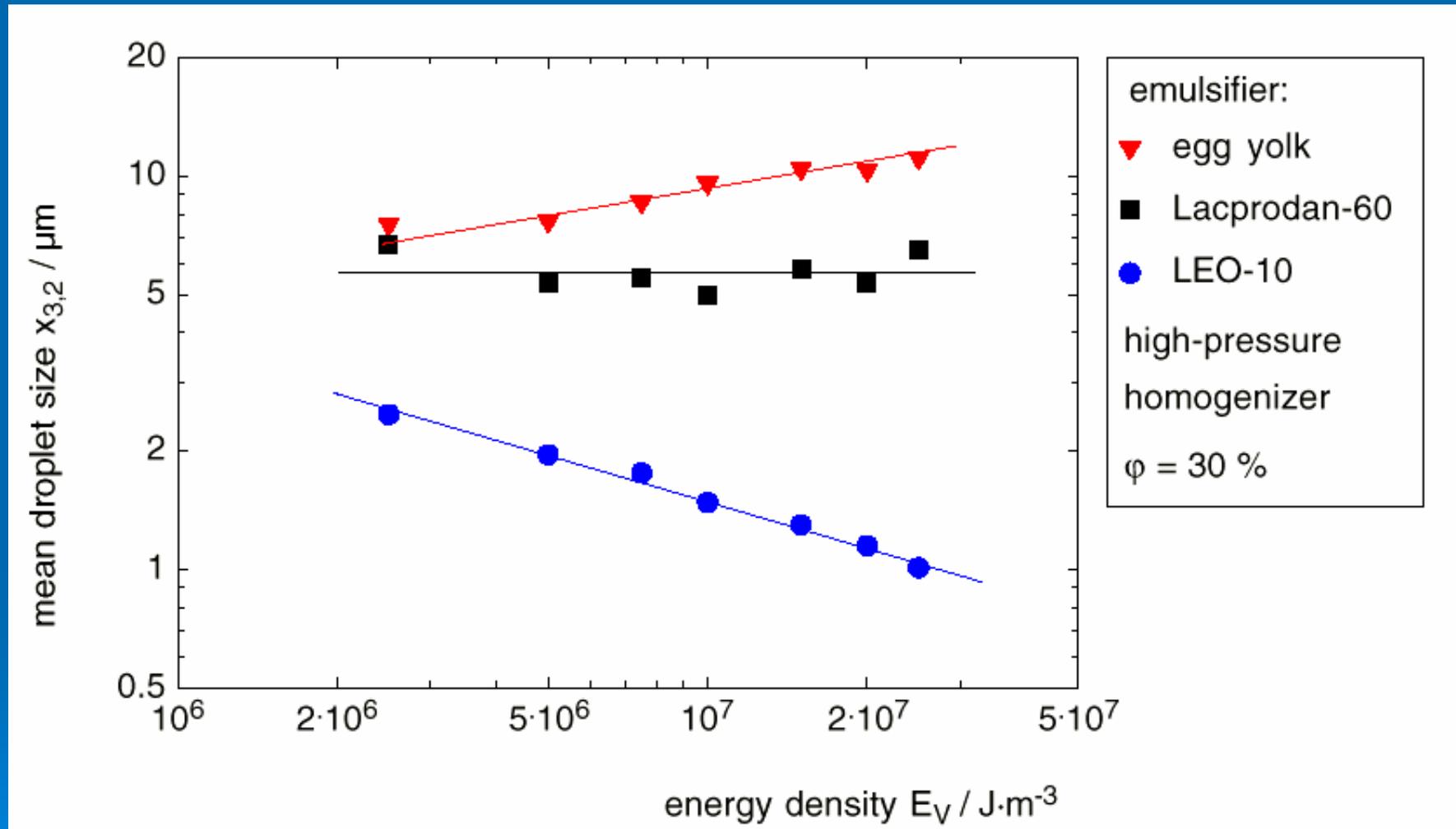
- 1. the initial drop is not spherical
- 2. the orientation of the flow changes
- 3. startup effects are present
- 4. drop are confined by nearby walls
- 5. interfacial tension gradients present: surfactants, or temperature effects
- 6. presence of other drops nearby or interacting
- 7. any transient flow behavior

Surfactants and Emulsification

Dispersion and Stabilization of Emulsions



Influence of Emulsifier Properties on Droplet Size



Surfactant Effects – 2D Elongation Flow drop breakup

Videos from Han Meijer's Research Group –
Eindhoven University (tue.mtl.nl)

[Eindhoven University -1](#)

[Eindhoven University – 2](#)

[Eindhoven University - 3](#)

Surfactant Effects – Rotor Stator

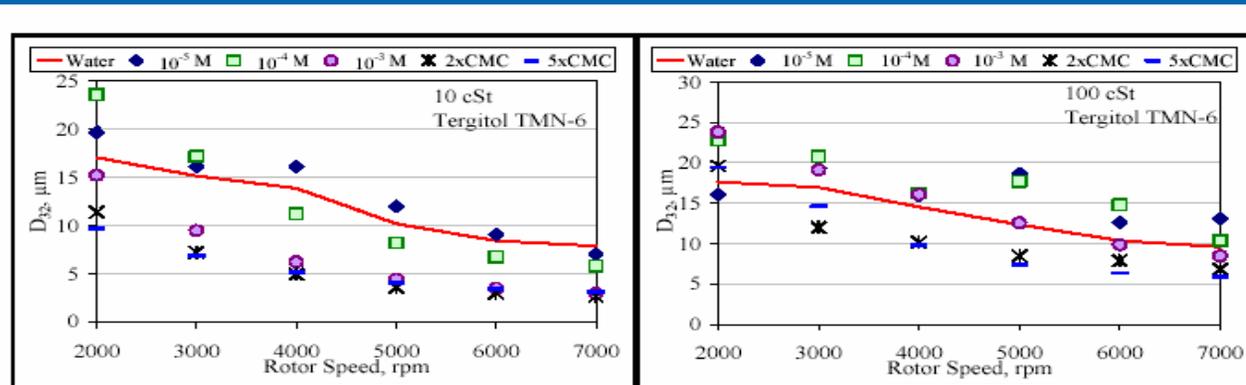


Fig. 10. D_{32} against rotor speed for 10 (left) and 100 cSt (right) silicone oils at all Tergitol TMN-6 concentrations. Continuous line: same oil in clean water. M = mol/l

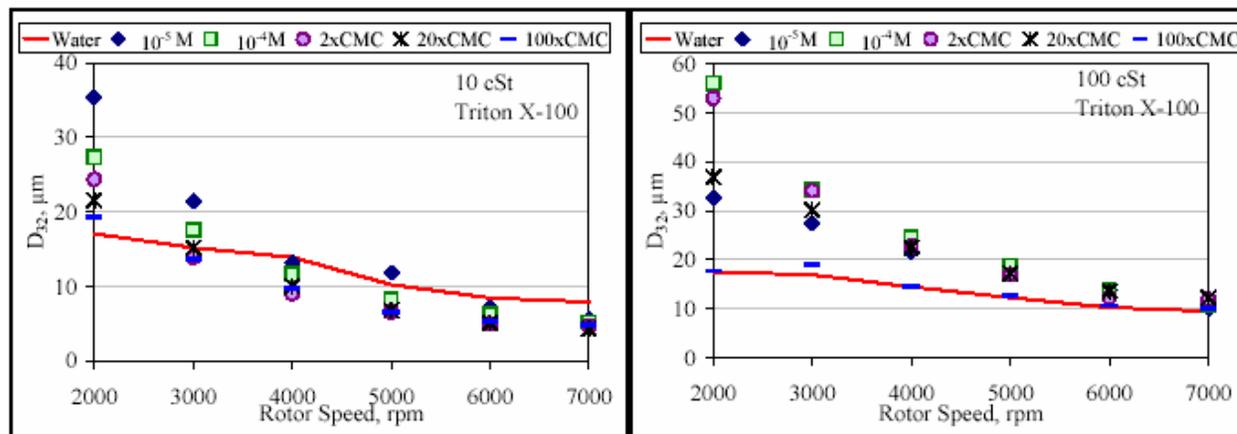
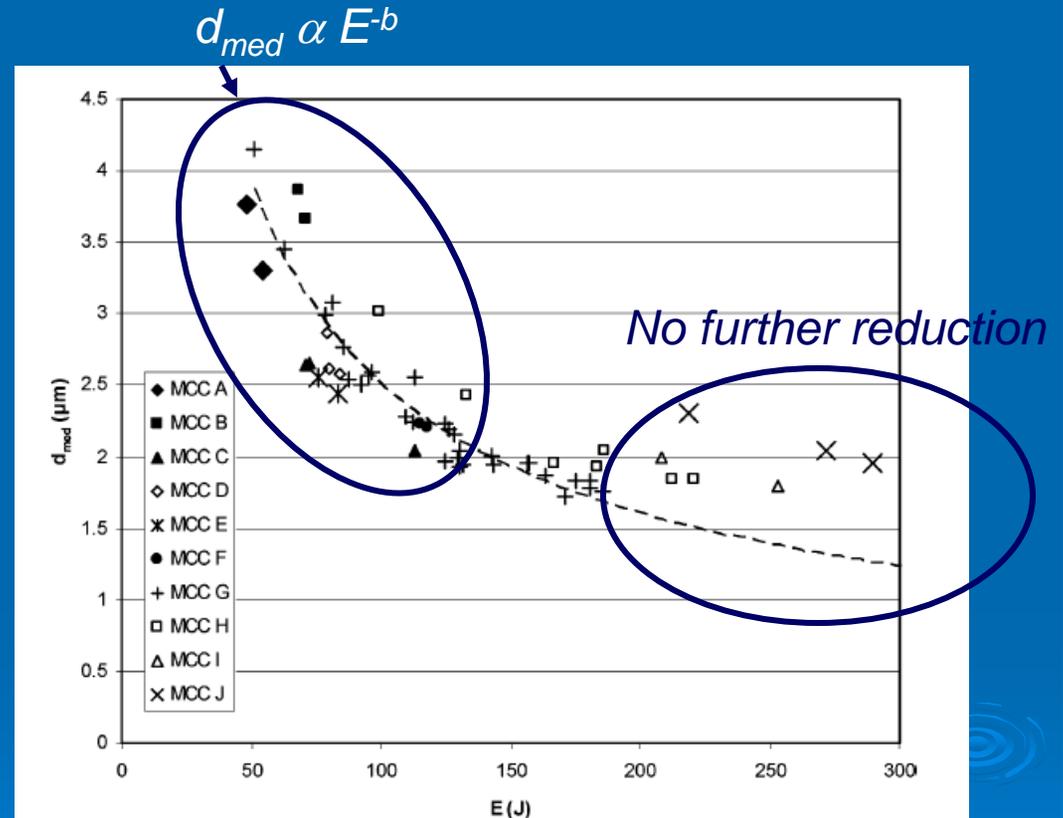


Fig. 11. D_{32} against rotor speed for 10 (left) and 100 cSt (right) silicone oils at all Triton X-100 concentrations. Continuous line: same oil in clean water. M = mol/l

Kinetics in Bitumen Emulsions

10 Static Mixer Configurations

MCC						
A	H		H	SMX		SMX
B	SMX	SMX		H	H	H
C	H	H	H	H	SMX	SMX
D		SMX		SMX		SMX
E	SMX	SMX	SMX			
F	H		H	SMX	SMX	SMX
G	H	H	H	SMX	SMX	SMX
H	H	H	SMX	SMX	SMX	SMX
I	H	SMX	SMX	SMX	SMX	SMX
J	SMX	SMX	SMX	SMX	SMX	SMX



Gingras et al., *Ind. Eng. Chem. Res.*
 2007, 46, 2618-2627

IKA Dispax Rotor Stator Results

- H. Shubert has shown in general for RS

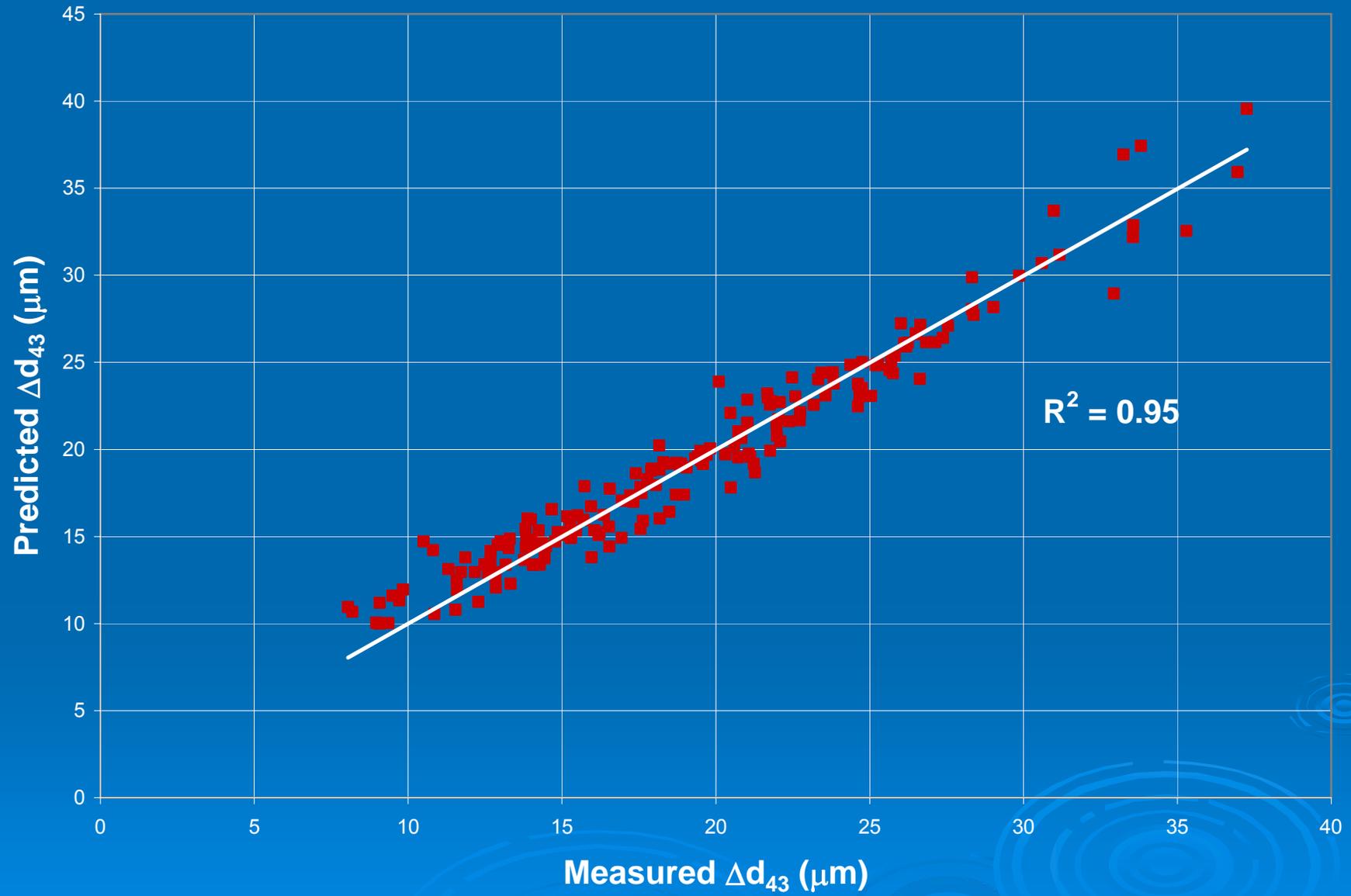
$$d_{32} \propto E_v^{-0.35} t^{-0.3}$$

- Where $E_v = \text{Energy/volume} = \rho v^2$

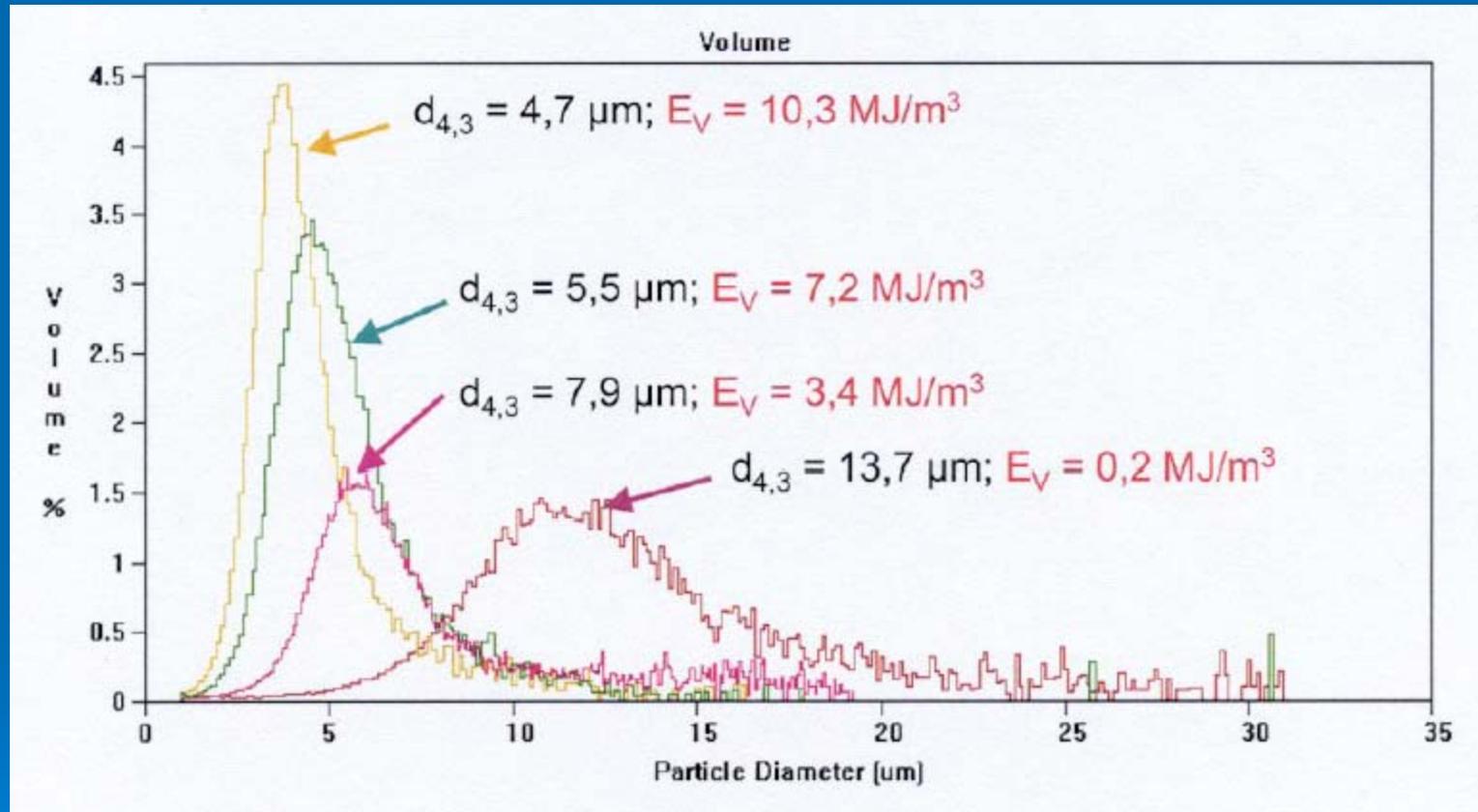
- P&G found (with surfactants present)

$$\frac{\Delta d_{43}}{d_o^{1.3}} \propto E_v^{0.3} t^{0.3}$$

IKA Dispax Rotor Stators



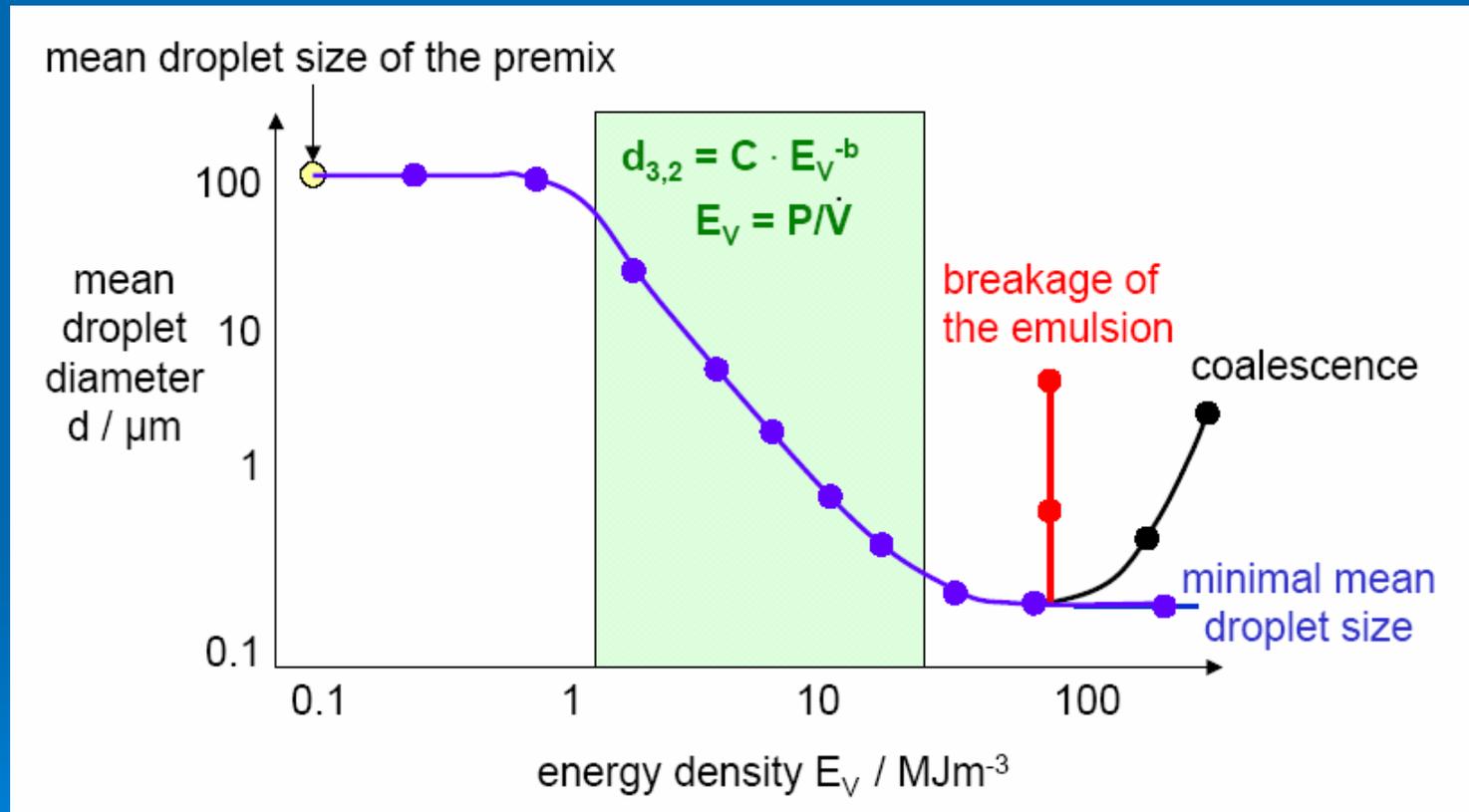
Energy dissipation ... Limits?...



The higher the energy input, the smaller the particle size, but there is a limit!

Energy dissipation... Limits?

More and more Energy is not equivalent to smaller droplets



This is very typical of surfactant containing products – formulated products

Explanations for this behaviour

- Coalescence vs breakup rates different
- Interfacial rheology – additional resistance
- Rates of adsorption / desorption of surfactants at interface – dynamic interfacial tension
- Unstable interfaces due to non-even concentrations of surfactant

Physical Chem + hydrodynamics

- Little research on understanding the interaction between the Physical Chem + hydrodynamics
- Very little design guidelines- trial and error and DOE ends up dominating in formulation chemistry (20+ ingredients) development

In the end ... Takeaways....

1. Questions and inconsistencies that need to be addresses in turbulent flow
2. No real correlations and limited data exist for laminar emulsification in mixing equipment
3. Need better studies incorporating material props, phys chem. and hydrodynamics

Questions?