



Some Strange Effects of Alcohol...

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This talk is dedicated to my “old mate” and good friend

Tom Healy



**Many congratulations, Tom, on
being awarded the Rideal Medal !**

Sir Eric Rideal : 1890 - 1974



Introduction

- The thermodynamic & structural properties of alcohol – water mixtures in bulk exhibit unexpected behaviour, especially within the concentration range 0 to 0.3 mole fraction alcohol (x_A), e.g.
 - Minima in the partial molar volume & adiabatic compressibility
 - Maxima in the viscosity, excess heat capacity & ultrasound speed.
- At low x_A the water molecules tend to organise as low-density “cages” of longer-living H-bonds around the hydrophobic groups of the alcohol molecules
- The question is : what happens at a solid / alcohol-water solution interface ?
- Actually there is very little direct (experimental, theoretical or simulation) information, and more studies are required!
- I am going to tell you about a small contribution I made , many years ago, for my PhD (in Bristol) and postdoc (in Wageningen)....

Contents

Bristol

- Diffusion-controlled coagulation rate constants, critical coagulation concentrations of electrolytes and electrophoretic mobilities of **polystyrene latex particles** in mixtures of the lower n-alkanols and water .
- Composite adsorption isotherms, and wetting properties , of mixtures of the lower n-alkanols and water at the polystyrene / solution interface.

contact angle (θ_R) for water on PS is $\sim 82^\circ$ (see later)

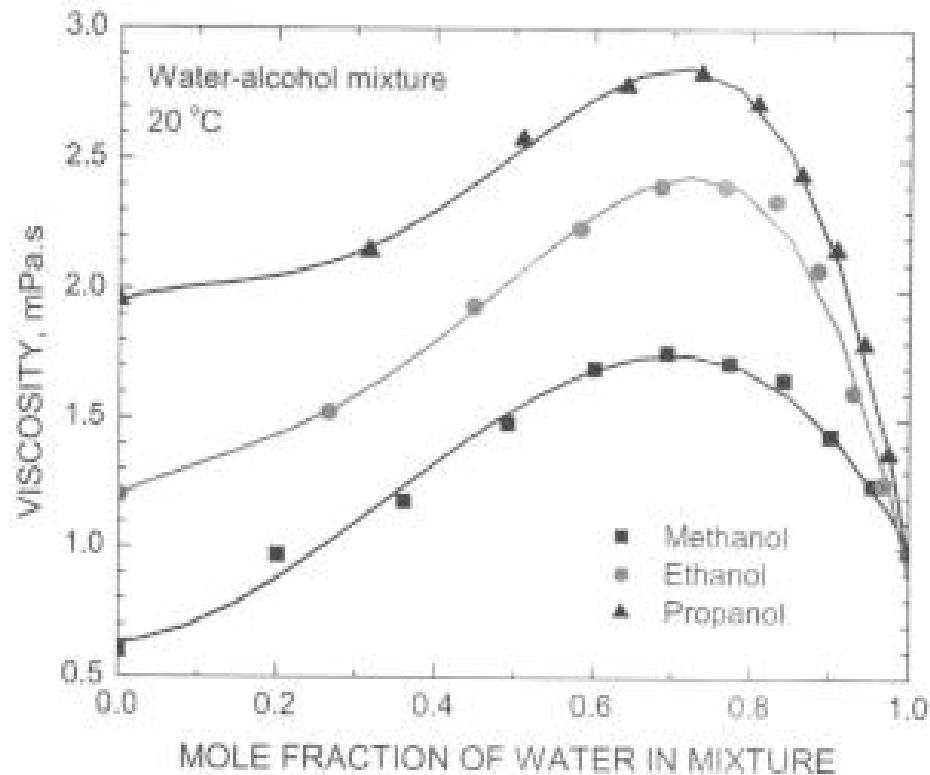
Wageningen

- critical coagulation concentrations of electrolytes and potentiometric titration data for **AgI particles** in mixtures of n-butanol and water

contact angle (θ_R) for water on AgI is $\sim 23^\circ$ at PZC (pAg 5.5), decreasing to $\sim 8^\circ$ at high $-ve$ & $+ve$ charge

Billett, Hough & Ottewill, J. Electroanal. Chem. 1976 74 107

Bulk viscosity of n-alkanol – water mixtures



Shear rate = 1000 s^{-1}
but Newtonian liquids
(*Rheolab* concentric cylinder
rheometer)

FIG. 1. Viscosity of binary mixtures of water-alcohols as a function of mole fraction of water in the mixture.

Normalised, diffusion-controlled coagulation rate constants ($k_0\eta$)

200 nm diam. PS latex particles in alcohol – water mixtures, plus $\text{Ba}(\text{ClO}_4)_2$ above the critical elec. conc. (c_c)

η is the *bulk* viscosity of the medium

Can we invoke the “Spielman” effect, i.e. an additional hydrodynamic drag on the particles as they approach, due to increased “structuring” in the liquid layer near the surface?

But how do we account for the urea data?!

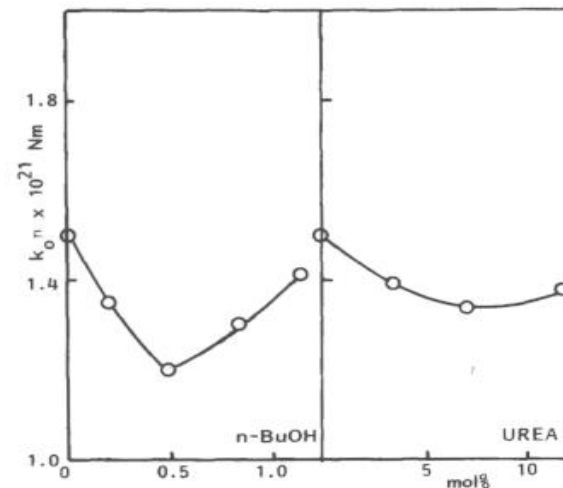
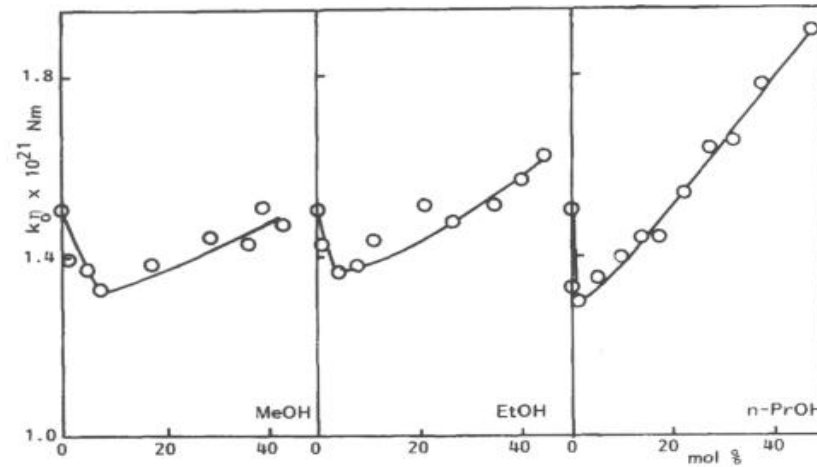


Fig. 2
 $k_0\eta$ values for latex A as a function of alkanol or urea concentration.

Vincent, *Adv. Colloid Interface Science* 1992 **42** 279-302 (from my PhD studies!)

Critical coagulation electrolyte concentrations (c_c)

Electrolyte = $\text{Ba}(\text{ClO}_4)_2$, pH 8

PS particles have surface $-\text{COO}^-$ groups

Ba^{2+} ions specifically adsorb to these sites.

$$c_c \sim \frac{\epsilon^3 \psi_d^x}{z^y A^2}$$

In limit high ψ_d : $x \rightarrow 0, y \rightarrow 6$

In limit low ψ_d : $x \rightarrow 4, y \rightarrow 2$

Could HO-R molecules preferentially adsorb onto the $-\text{COO}^-$ sites initially, partially displacing the Ba^{2+} ions?

This would lead to an (initial) increase in the Stern potential (ψ_d) and hence c_c

This should be reflected in the ζ potential data (if ζ is close to ψ_d)

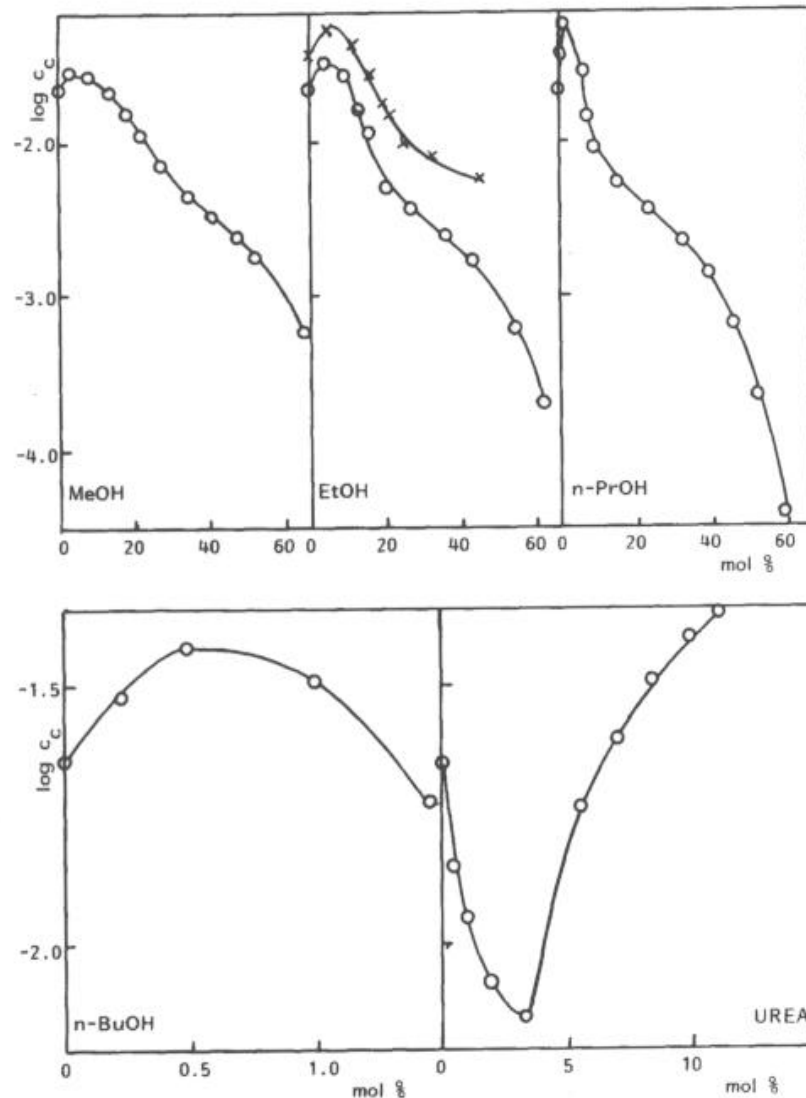
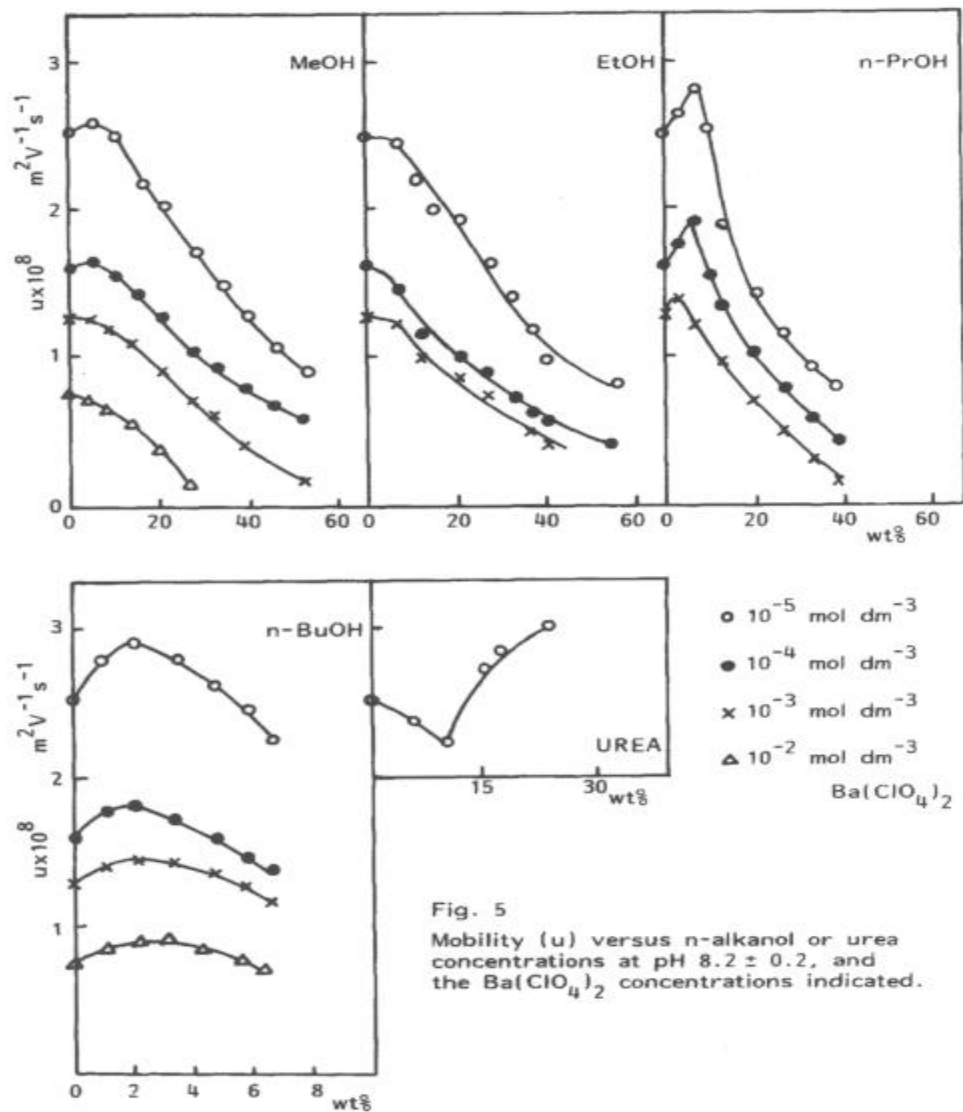


Fig. 4. $\log c_c$ versus n-alkanol or urea concentration.
 \circ , latex A 200 nm
 \times , latex B 100 nm

Electrophoretic mobilities (u)



Zeta potentials (ζ)

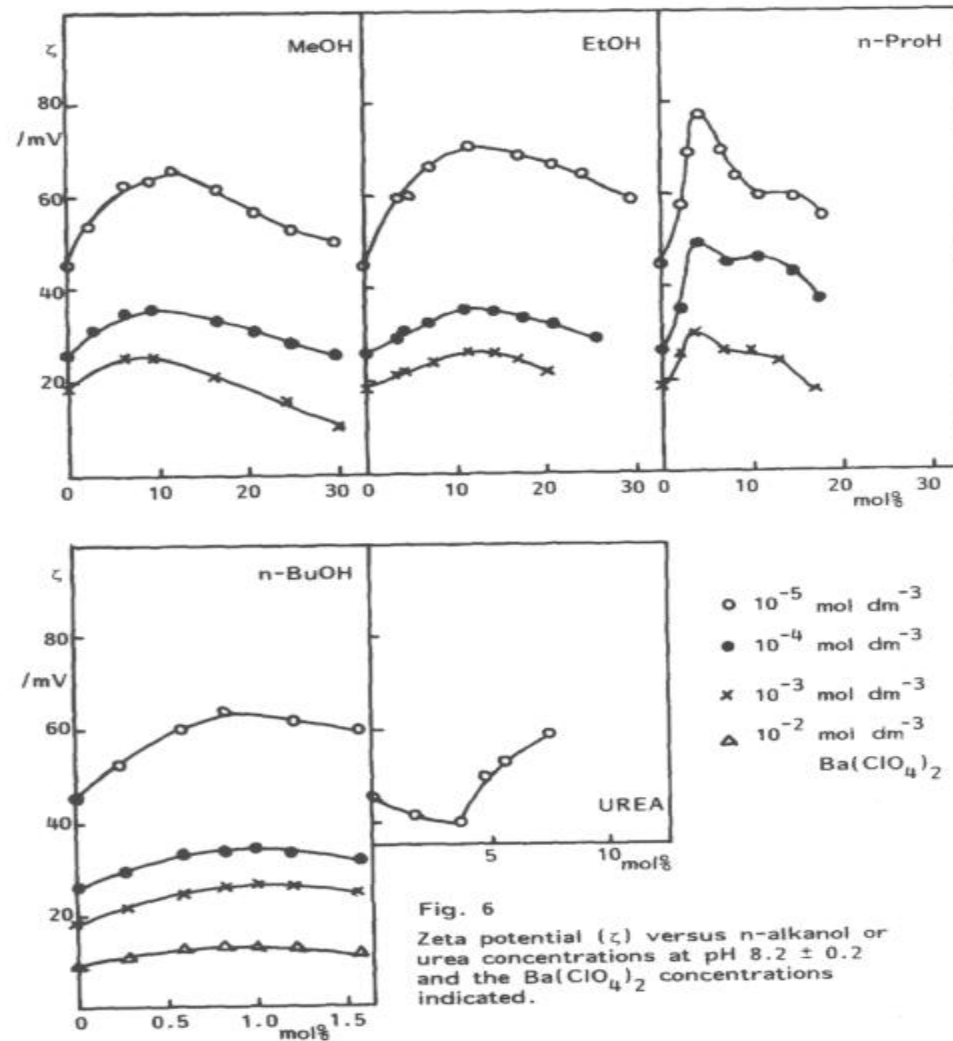


Fig. 6

Zeta potential (ζ) versus n-alkanol or urea concentrations at pH 8.2 ± 0.2 and the $\text{Ba}(\text{ClO}_4)_2$ concentrations indicated.

Wiersema, Loeb & Overbeek analysis used to calculate ζ from u .

Composite adsorption isotherms: ethanol and n-propanol at the polystyrene particle / aqueous solution interface

$(\Gamma^{\text{ex}} = n^0 \Delta x_A / m)$

Δx_A was determined by measuring the r.i. change in the bulk solution using a differential interferometer.

Note:

- 1) Initially the isotherms are low affinity.
- 2) At high x_A water is preferentially adsorbed!
- 3) The arrow is where $\theta = 0$

Ottewill & Vincent,
J. Chem.Soc., Farad.
Trans. 1, 1972 68
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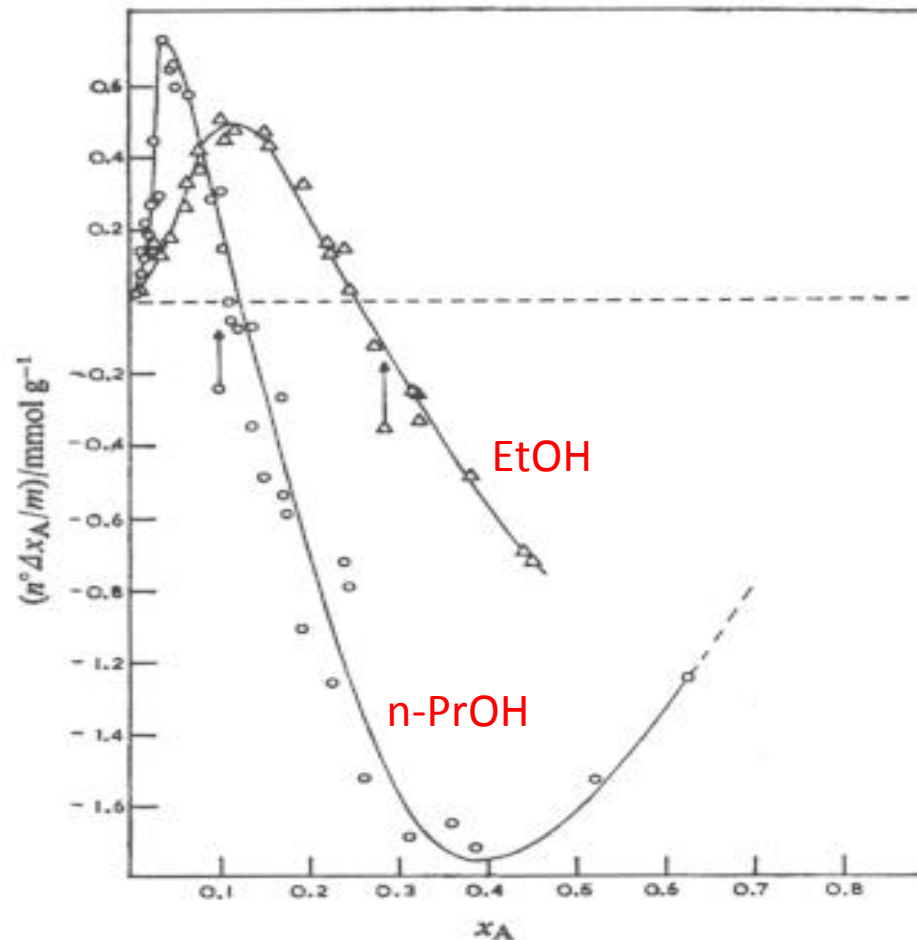


FIG. 1.—Composite isotherms for the adsorption of ethanol and propanol on to a polystyrene latex surface at 25°C: Δ , ethanol; \circ , n-propanol. \uparrow , mole fraction of alcohol at which receding contact angle became zero.

Composite adsorption isotherm: n-butanol at the polystyrene particle / aqueous solution interface

Again low affinity initially.

The saturation concentration of n-BuOH in water is at $x_A = 0.018$

Multilayer adsorption of n-BuOH is observed as this saturation concentration is approached.

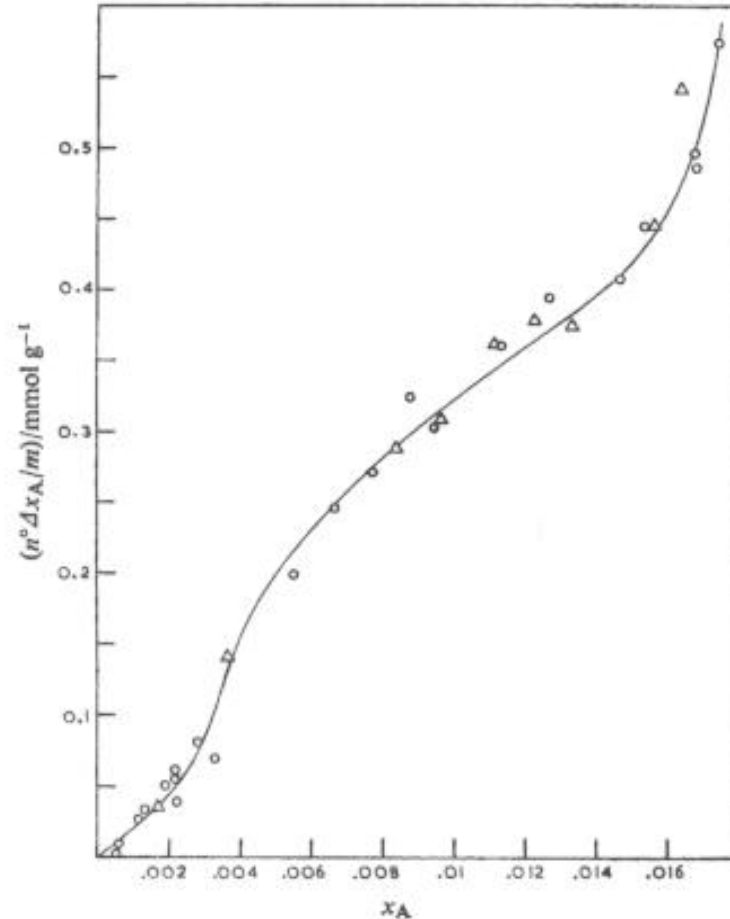


FIG. 3.—Isotherm for the adsorption of n-butanol on to a polystyrene latex surface at 25°C: ○, results obtained in the absence of electrolyte; △, results obtained in the presence of 1 % w/v barium perchlorate.

Comparison of adsorption of n-butanol on PS latex and “Graphon” particles

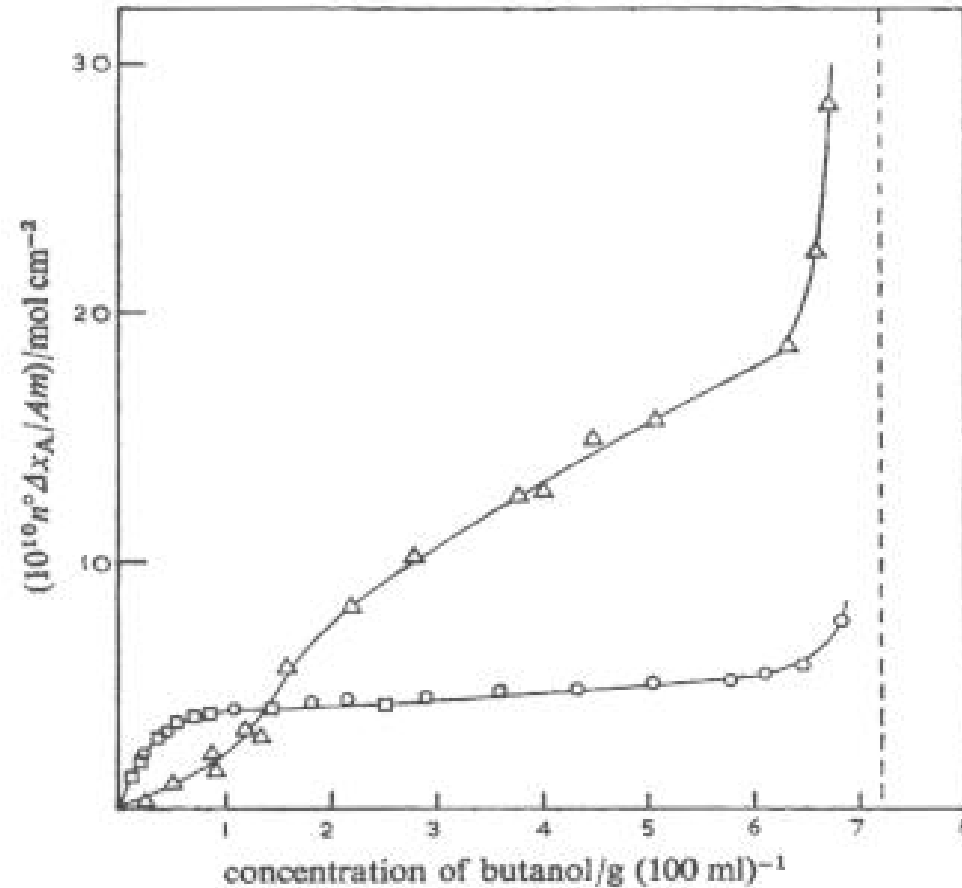
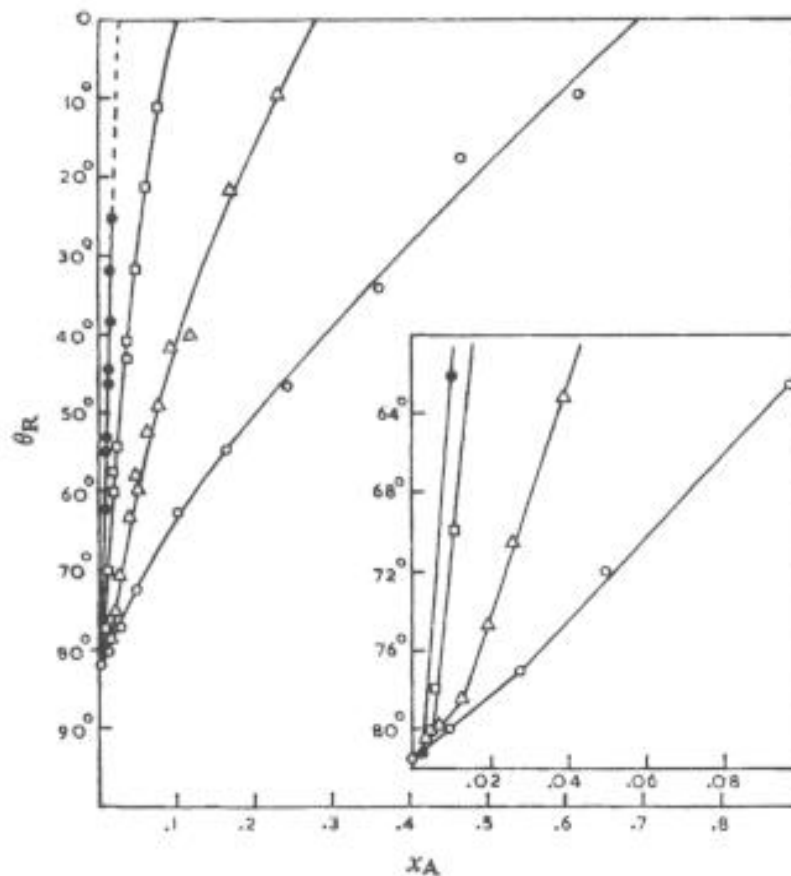


FIG. 6.—Comparison of the adsorption isotherms for n-butanol on a polystyrene latex surface, Δ , and on a Graphon surface, \circ , Hansen and Craig¹⁷; \square , Young, Chessick and Healy.¹⁸ \vdots , solubility limit of n-butanol in water.

a different one!

Wetting data: contact angle as a function of x_A

Films formed by dissolving PS latex particles in MEK, and casting on a microscope slide. Contact angle measured by the captive bubble technique.



For MeOH, EtOH and n-PrOH wetting is achieved ($\theta = 0$) when $\gamma_{LV} = 27 \pm 1$ mN m⁻¹ in each case. (See next slide)

For n-BuOH wetting is *not* achieved prior to the saturation concentration being reached.

Vincent later showed* that γ_S was :
55 ± 3 mN m⁻¹ for films formed from PS latex
46 ± 2 mN m⁻¹ for films formed from bulk PS (i.e. no COOH groups).

* *Ber. 6th Inter. Kongr.*

Grenzflächenactive Stoffe (Zurich), 1972 p 581.

FIG. 5.—Measurements of the receding contact angle on a polystyrene latex surface as a function of mol fraction of alcohol: ○, methanol; △, ethanol; □, n-propanol; ●, n-butanol.

Analysis of the wetting data

Young's equation:

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} = 1 \quad \text{when } \theta = 0$$

$$\begin{aligned} \text{So, } \gamma_{LV}(\text{crit}) &= \gamma_{SV} - \gamma_{SL} \\ &= [\gamma_S - \Pi_{SV}] - [(\gamma_S^{1/2} - \gamma_{L(S)}^{1/2})^2 - I_{SL}] = 27 \text{ N m}^{-1} \\ &\quad \downarrow \\ &\quad \text{(Fowkes)} \end{aligned}$$

Hence, one obtains γ_S , if one can estimate the 3 unknown quantities (in red)

$\gamma_{L(S)}$ for a monolayer of alkanol molecules in contact with the solid is ~ the surface tension (γ_{LV}) of the *pure* alkanol.

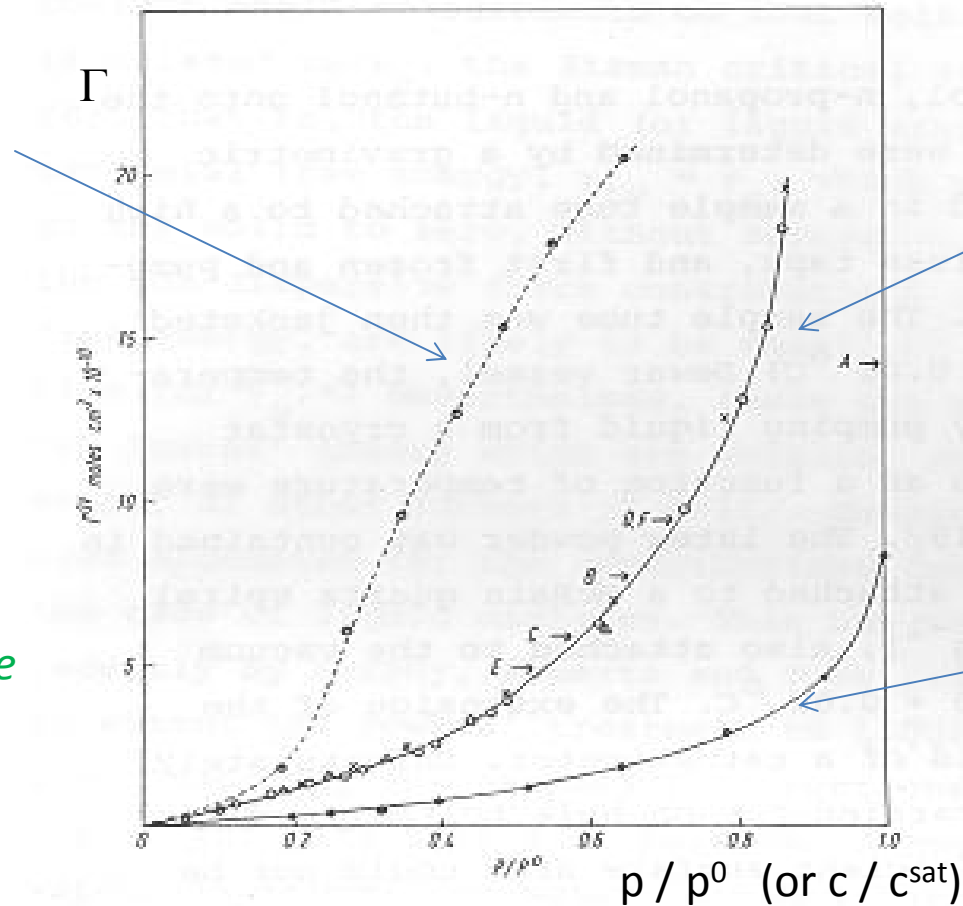
I_{SL} is very small (~ 0) for a monolayer of alkanol tails in contact with the PS surface.

Π_{SV} can be obtained from the *vapour* adsorption isotherms for the alkanol on PS and use of the Gibbs adsorption equation.

Vapour adsorption isotherms

n-BuOH at **SL**
interface
(see before)

Vincent,
Ber. 6th Inter.
Kongr.
Grenzflächenactive
Stoffe (Zurich),
1972 p 581.



X = EtOH
 Δ = n-PrOH
O = n-BuOH

All at **SV** interface
(all 3 alkanols wet PS)

Water at **SV** interface
(does *not* wet PS)

Isotherms obtained gravimetrically using a calibrated McBain spiral quartz spring, and a temperature bath to control the vapour pressure of the alkanol or water.

NB the congruence of the 3 vapour adsorption isotherms for EtOH, n-PrOH and n-BuOH (so Π_{sv} is the same for all 3)

Comparison with AgI: effect of n-BuOH on c_c

monovalent counter ions pl 6.5

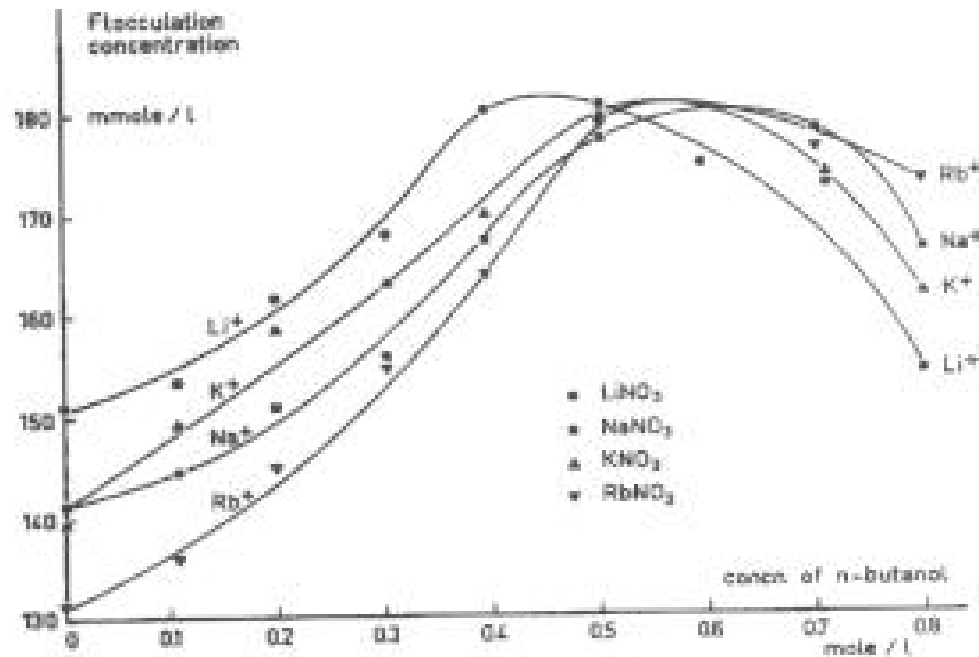


FIG. 1. Stability of a AgI sol in the presence of n-butanol. Sol concentration 2×10^{-4} mole/l. pI = 6.5, $T = 20^\circ\text{C}$. Monovalent counterions.

Vincent, Bijsterbosch and Lyklema, *J. Colloid Interface Sci.*, 1971 **37** 171

divalent counter ions

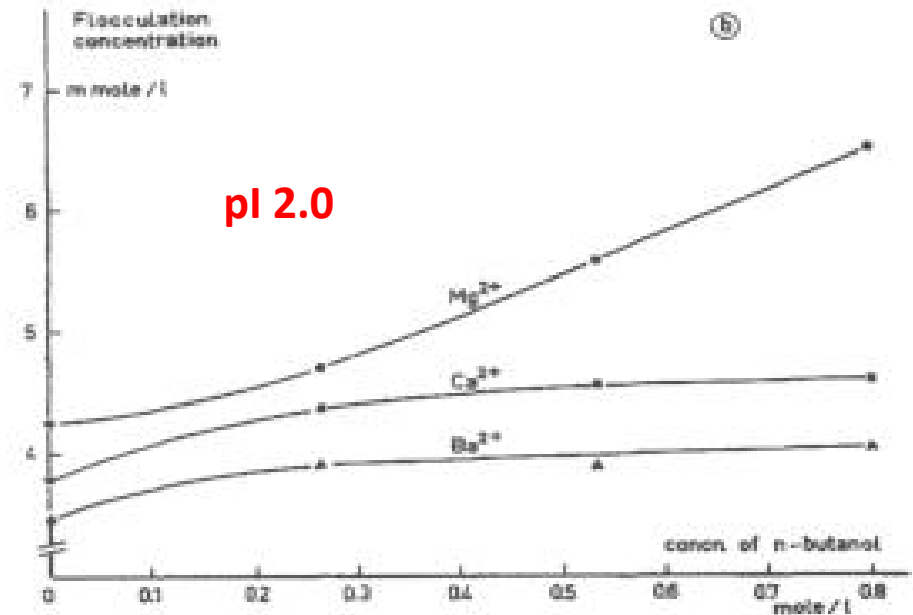
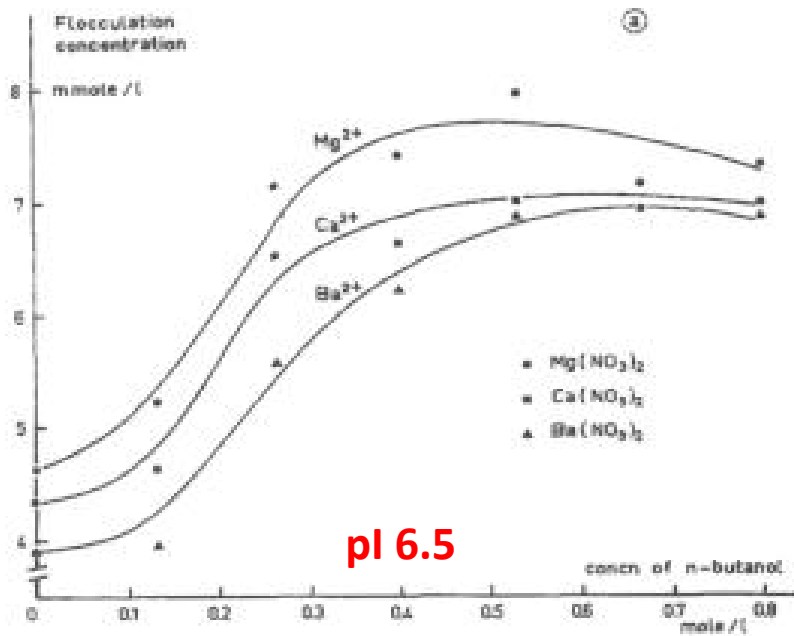


FIG. 2. Stability of a AgI sol in the presence of n-butanol. Sol concentration 2×10^{-4} mole/l. $T = 20^\circ\text{C}$. Bivalent counterions. (a) pI = 6.5; (b) pI = 2.0.

Estimation of σ_s as a function of BuOH concentration

$$\sigma_0^- = \sigma_s^+ + \sigma_d^+ + \sigma_d^-$$

From potentiometric titration data

From ψ_d , estimated from c_c values

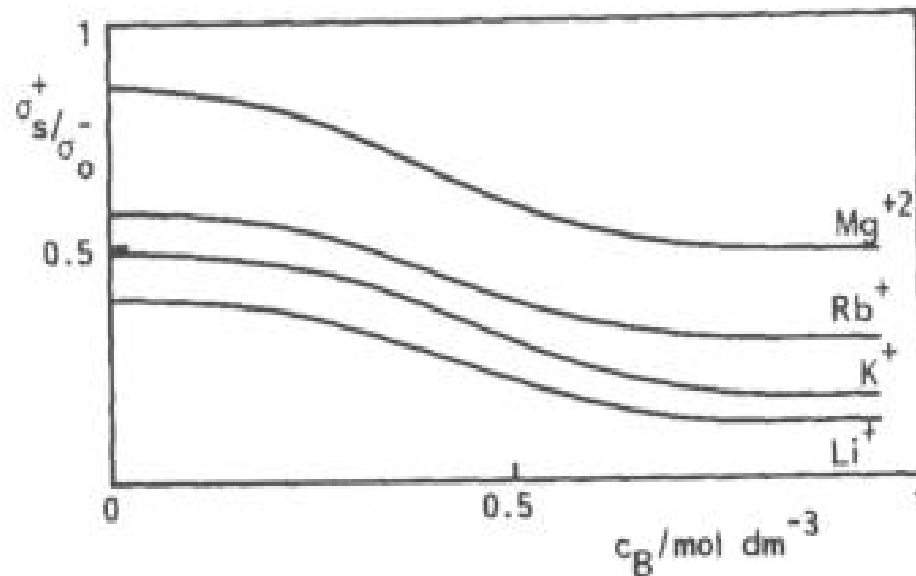


Fig. 8. Relative specific adsorption for various counter-ions at the AgI/soln. interface, as a function of BuOH concentration (c_B). $\text{pI}=6.5$ [16]

Conclusions (or rather Conjectures!) regarding Alkanol Adsorption

- PS and AgI particles behave rather similarly in that, at low concentrations of n-alkanols in water, there is strong competition between the alkanol molecules and specifically adsorbed counter-ions, leading to partial displacement of the counter ions. Could this perhaps be due to a relatively strong dipole-ion interaction between the –OH groups of the alkanol molecules and the COO⁻ or I⁻ groups on the surface? Note that the orientation of the ROH molecules at these surface sites would then be -OH group down, hydrophobic tail group out in solution.
- For PS at least (no similar data are available for AgI) the composite isotherms show that, at low alkanol concentrations, the adsorption of the n-alkanol molecules is low affinity (unlike on more strongly hydrophobic “Graphon”). Maybe this reflects the strongly competitive adsorption with the counter-ions on the COO⁻ surface sites referred to above? Also, recall that at these low alkanol concentrations the protruding tails of the alkanol molecules are strongly hydrated with water “cages”, so maybe their adsorption on the hydrophobic regions of the PS surface (between the COO⁻ groups) is somewhat restricted sterically, until the alkanol concentration is high enough to begin to destroy these water cages. Then adsorption becomes more favourable.
- Eventually a monolayer of n-alkanol molecules does form (presumably now mostly tails down). In the case of n-butanol (limited solubility) this grows into a multilayer. For EtOH and n-PrOH, on the other hand, this monolayer now renders the PS surface hydrophilic, and water becomes preferentially adsorbed at high alkanol concentrations. Correspondingly, the PS surface is water wetted in these regions.

And finally, the real excuse for choosing this title for my lecture:

Another strange effect of alcohol....



**RACI Colloid Conference
Coogee Beach, Sydney
Feb 2005...**



So congratulations again Tom, and many thanks for being such a good mate and mentor for so long...