Current Opinion in Colloid & Interface Science 20 (2015) 215–226

Contents lists available at ScienceDirect

Current Opinion in Colloid & Interface Science

journal homepage: www.elsevier.com/locate/cocis

Laser Doppler Electrophoresis applied to colloids and surfaces

I.M. Tucker [a],*, J.C.W. Corbett [b], J. Fatkin [b], R.O. Jack [b], M. Kaszuba [b], B. MacCreath [b], F. McNeil-Watson [b]

[a] *Unilever Research & Development Port Sunlight, Quarry Rd East, Bebington, Wirral CH63 3JW, UK*
[b] *Malvern Instruments Ltd., Grovewood Road, Malvern, Worcestershire WR14 1XZ, UK*

ARTICLE INFO

Article history:
Received 2 June 2015
Received in revised form 10 July 2015
Accepted 11 July 2015
Available online 26 July 2015

Keywords:
Laser
Doppler
Electrophoresis
Colloid
Mobility
Zeta potential
Surface
Scattering
Emulsion
Medical
Acoustophoresis

ABSTRACT

The colloidal state is often taken for granted and yet it surrounds us in both home and in the workplace. Coating technologies, drug delivery systems, cleaning and personal care formulations all rely on discrete well controlled physical properties at several distance scales in order to derive the desired product performance, and are reliant on an in-depth knowledge of the surface of interest. Techniques such as dynamic light scattering and Laser Doppler Electrophoresis are readily available to the experimenter who can perform a measurement without the need for in-depth knowledge of the technique and is finding ever-increasing applications. Although the actual means of determining mobility using LDE has not changed much, these are exciting times in that good instrumentation and sample environment, together with high quality method development all combine in a robust platform enabling new science and stronger engagement with industry. In this review, we report on the current state of the application of LDE, both in standard and advanced formats. There is the alliance of LDE and neutron scattering to study polymer surfactant interactions, advances in the measurement of protein electrokinetics, novel approaches to the study of surface zeta potential, and progress towards measurements in high concentration dispersions are all reported and discussed. We also report on recent advances where industrial applications in-line have resulted in cost savings and reduced environmental impact. It is our observation that industrial and academic users are asking questions which require the fundamentals of the instrumentation and its capabilities and limits to be better communicated and understood, and this has resulted in a doubling of the number of publications featuring LDE to ~1300 over the last several years. Particular areas of growth are biomedical, drug delivery, fast moving consumer goods, engineered nanoparticles, toners and printing technology.

1. Introduction

The colloidal state is often taken for granted and yet it surrounds us in both home and in the workplace. Coating technologies, drug delivery systems, cleaning and personal care formulations all rely on discrete well controlled physical properties at several distance scales in order to derive the desired product performance. Techniques such as dynamic light scattering (DLS) [1] and Laser Doppler Electrophoresis (LDE) [2] are available in many laboratories and are used in quality control and production environments routinely to the point where the underpinning science is easily overlooked, that is, until something goes wrong. The advent of modern equipment such as the Brookhaven Nanobrook series [3] and Malvern Zetasizer Nano series [4] instruments, both of which have "Microsoft style" graphical user interfaces, renders these instruments readily available to the experimental scientist be they chemist, physicist or biologist without any need to understand either the physics of the instrumentation nor the precise physical chemical conditions required to achieve a decent result. Modern instrumentation is quick, convenient and reliable, therefore these instruments are also present in many R&D and QC organisations where the focus is more on product quality and material consistency rather than obtaining fundamental understanding of the colloids or surfaces under investigation. However, with a little thought and understanding, both DLS and LDE techniques can be used as a powerful means of advancing knowledge and developing new technologies. It is the aim of this review article to cast these methods, particularly LDE, colloquially termed "zeta potential measurement" in a more suitable light, demonstrating both the application of the technique in "standard manner" and also highlighting advances and exciting developments in the area in order to encourage their use as part of the research methods portfolio as well as extending their application outside of the laboratory.

1.1. Background

The measurement of electrophoretic mobility relies on being able to determine the velocity of a charged particle moving under an applied external electric field. A full description may be found in references [1–4] and only the minimal basis on which the technique is founded is

---

* Corresponding author. Tel.: +44 0151 641 1784; fax: +44 0151 641 1800.
E-mail address: ian.tucker@unilever.com (I.M. Tucker).

http://dx.doi.org/10.1016/j.cocis.2015.07.001
1359-0294/

described herein. The zeta potential and electrophoretic mobility are related by the Henry equation, i.e.

$$U_E = \frac{2\varepsilon\zeta F(\kappa a)}{3\eta} \quad (1)$$

where U_E is the mobility, ζ is the zeta potential, η is the viscosity of the fluid, $F(\kappa a)$ is the Henry function and κ is the inverse of the Debye screening length. Depending on the size of the colloid and the supporting electrolyte conditions the prefactor, $F(\kappa a)$, of either 1.0 or 1.5 applies depending on the size of the particle and the solution electrolyte conditions (as these govern the Inverse Debye screening length, κ). Under phase analysis light scattering the frequency shift associated with the electrophoretic motion is derived from Fourier transform of the transient Moiré fringe, that is;

$$\Delta v = 2U_e \frac{\sin(^{\theta}/_{2})}{\lambda} \quad (2)$$

and this is the basis of LDE.

2. Highlights of LDE application

2.1. Examples of applications in scattering

In the area of neutron scattering, studies of surfactant adsorption at interfaces have progressed from the model hydrophobic air liquid interface to surfaces which are closer to real life. In particular two groups have independently pioneered the study of adsorption at the oil water interface, one using neutron reflectivity and the other using contrast variation combined with small angle scattering (SANS). In the former case, Zarbakhsh et al. have developed an approach using spun coated thin hexadecane layers cast onto a prepared silicon single crystal and then arranged a modified liquid solid neutron reflectivity approach [5]. Surfactant adsorbs onto the thin oil film from the aqueous solution which is in intimate contact with the oil. In this work Zarbakhsh has remarked that the different interfaces have slightly different properties and that the buried oil water interface has a different structure to that at the external surface in contact with the aqueous solution [6]. In contrast Staples, Penfold & Tucker have devised an approach using an emulsion where the oil emulsion core is neutron refractive index matched to the solvent [7]. The scattering then only arises from the hydrogenous shell of the surfactant which is adsorbed at the emulsion oil water interface. By careful choice of phase volume and control of the particle size being careful to minimise polydispersity, and be below the minimum Q vector of the SANS experiment, sufficient surface area can be generated to render the experiment viable with around 0.4 m^2 of surface available for adsorption. It is here that the techniques of dynamic light scattering and Laser Doppler Electrophoresis find a role. Firstly in the experiment, the concentration of emulsifier, SDS, was varied from 1.2 mM up to 18 mM and beyond in order to determine the point at which free micelles coexisted with the emulsion droplets. Over this concentration range it was important to ensure that the emulsion particle size distribution and polydispersity remained invariant. The data in Fig. 1 below confirm that the hydrodynamic radius of the emulsion remains invariant over the range of SDS concentrations studied [8]. At the time of the original article the measurement of zeta potential was less straightforward than it is nowadays, and consequently it is only recently that a comparison between the adsorbed amount of surfactant and the variation in surface charge density has been made.

Fig. 2 shows that the surface charge density, calculated using a Gouy–Chapman approach using the experimentally derived Zeta potential values mirrors the surfactant adsorbed amount. Although this is in one sense intuitive this work serves to exemplify how surfactant stabilised emulsions can be manipulated whilst still maintaining sufficient surface charge so as to preserve colloidal stability.

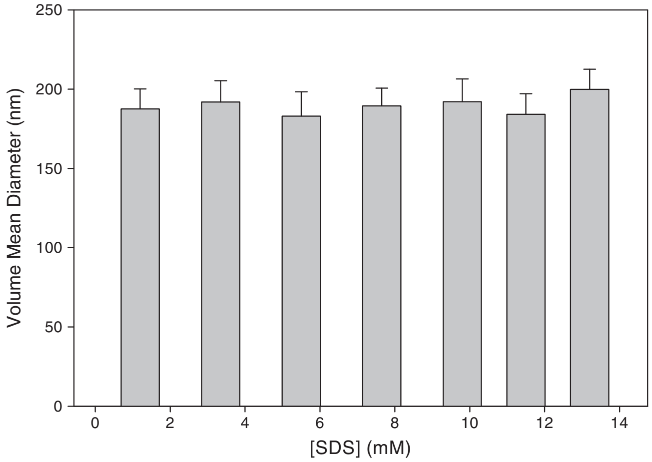

Fig. 1. The variation in emulsion hydrodynamic diameter with addition of surfactant, SDS, via the water continuous phase. The free micelle CMC is 11.6 mM under these circumstances [8].

Furthermore in a subsequent study involving the competitive adsorption of oppositely charged polyelectrolyte and surfactant at the oil water interface, Tucker et al. were able to determine the adsorption of the polymer at this interface and also the aggregation state of the emulsion particles where bridging took place between polymer and adjacent particles. They observed that the zeta potential measurements were very sensitive to changes in polymer adsorption, whilst the SANS revealed that the adsorbed amount of SDS remained invariant [8]. Recently this approach has been used to study the adsorption of novel polysorbate surfactants at the oil water interface [9] where control of surface charge was used as a criteria to create a stable emulsion where the surface was in part covered by an “invisible (deuterium labelled) SDS” surfactant at a trivial level as far as the surface was concerned but a non-trivial level in terms of the surface specific charge which provided the physical stability of the base emulsion. With a full description of the counter-ion activity this approach may enable electrochemical approaches to studying surfactant adsorption at interfaces other than those requiring ion-selective electrodes [10].

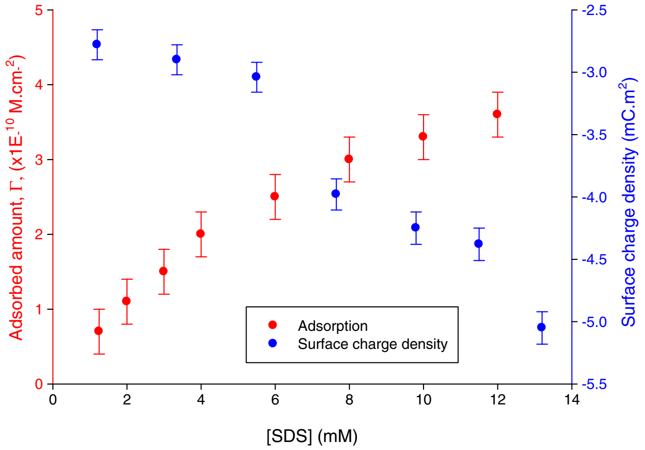

Fig. 2. The variation in SDS adsorption and surface charge density with solution composition surface charge density.
Reproduced from data in reference [8] with permission.