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Colloidal aspects of beverages

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Colloidal aspects of beverages are important in relation to product appearance and stability. Attention is directed here towards the physicochemical principles underlying the turbidity of dispersions and the phase separation of polymer solutions. The relevance of these theories to the cloudiness of fruit drinks and the formation of tea cream is described.

INTRODUCTION

Most beverages—hot or cold, alcoholic or non-alcoholic—contain some dispersed entities of colloidal size. This has the consequence that the manufacture, storage and consumption of such products are all affected by considerations of colloid stability. Of course, the wide variety of beverage formulations makes it impossible to cover the subject comprehensively in a short review article. Perhaps all one can hope to do is to indicate the most important types of physicochemical phenomena that lead to potential instability in beverages, and illustrate the main factors controlling product quality and appearance with a few well-chosen examples. One aspect of appearance which is often considered to be especially important is the turbidity or cloudiness. This particular aspect will therefore be discussed in some detail.

As a class beverages have a few things in common. They are low-viscosity liquids; they consist predominantly of water; and the concentration of dispersed species is relatively low. This means that, unlike some other kinds of food colloids (e.g. margarine or mayonnaise), their stability is not determined by the structure or texture of the dispersion medium. Apart from this, of course, the main factors influencing appearance and stability are the same as those which apply to all food colloids (Dickinson & Stainsby, 1982; Dickinson, 1992).

A typical beverage consists of a dilute aqueous phase containing various dissolved species (salts, sugars, alcohol, caffeine, lipids, proteins, polyphenols, polysaccharides, etc.) into which may be dispersed various colloidal species (oil droplets, protein particles, etc.) as well as microscopic particles such as cell-wall fragments. The distinction between dissolved macromolecules and dispersed polymer aggregates is sometimes indistinct. In many beverages an important stability consideration is that high-molecular-weight species should remain soluble during the preparation or storage of the drink. In thermodynamic terms this implies that the aqueous continuous phase should remain a good solvent for the macromolecular solute over a specified range of conditions (temperature, alcohol content, pH, ionic strength, etc.).

Formation and stabilization of gas bubbles is a key aspect of the quality of many popular drinks (mineral water, beer, cappuccino, etc.). Important physicochemical phenomena involved here are the nucleation and growth of gas bubbles, the diffusion of gas between bubbles (disproportionation), and the rupture of thin films in a polyhedral foam (e.g. froth on a glass of beer). A noteworthy feature of a typical beverage foam is its transient character in comparison with other more permanent food foams like meringue or whipped cream. This transient character is primarily attributable to the relatively low concentration of surface-active species in many beverages, as well as to the high gas solubility in carbonated soft drinks. (This is another important topic, but there is not space to cover it here. For further information the reader is referred to articles by Prins (1987, 1988), Dickinson (1989) and Bamforth (1989).)

TYPES OF COLLOIDAL INSTABILITY

With any colloidal system the first step in trying to understand the source of the instability is to identify clearly the kind of physical process(es) involved. In beverages the following types of process can occur: creaming, sedimentation, phase separation, coacervation, flocculation, coagulation, coalescence and Ostwald ripening.

Creaming is the upward movement of particles (especially oil droplets) of lower density than the aqueous dispersion medium under the action of gravity. An unsightly manifestation of the creaming of flavour oil droplets in some fruit drinks is 'ringing' in the neck of the bottle after prolonged storage. The action of gravity on particles denser than the aqueous medium is known as sedimentation. The enhancement of sedimentation during processing is useful in the clarification of beverages, e.g. the fining of wines by addition of isinglass (purified fish collagen) or bentonite clay (Rankine & Emerson, 1963). Fast creaming or sedimentation is usually driven by flocculation, i.e. the coming together of particles or droplets to form aggregates under the influence of net attractive forces acting between them. Another term used to describe colloidal aggregation is coagulation. By convention, the particles in flocculated aggregates (flocs) are reversibly held together, whereas the process of coagulation leads to the irreversible separation of a coagulum (e.g. heat-denatured coagulated protein). Solid colloidal particles may coagulate or flocculate depending on the strength and range of the interparticle interactions. Creamed or flocculated liquid droplets may coalesce into bigger liquid droplets which are in turn more susceptible to creaming, flocculation and coalescence. When polymer solutions become unstable, what occurs is not so much particle aggregation as thermodynamic phase separation. Coacervation is the formation of a dense insoluble precipitate of phase-separating polymer molecules. The colloidal precipitate formed by black tea liquor as it cools (so-called 'tea cream') is a type of coacervate. Another way in which droplets or particles may grow is by Ostwald ripening, i.e. by mass transport of soluble dispersed phase material through the aqueous continuous phase. This is an appreciable phenomenon in some fruit oil emulsions used to flavour soft drinks due to the significant solubility of essential oils (e.g. limonene) in water. In contrast, for a dairy-based beverage such as milk or a cream liqueur, the process of Ostwald ripening of oil droplets is insignificant because of the negligible solubility of triglycerides in water. Further examples of these different kinds of instability may be found elsewhere (Mulder & Walstra, 1974; Darling & Birkett, 1987; Dickinson, 1992).

TURBIDITY OF BEVERAGES

Cloudiness arises from the scattering of light by dispersed particles or droplets of the size of the order of the wavelength of light (Farinato & Rowell, 1983). The turbidity of milk is due to light scattering by large protein particles (casein micelles) and small fat globules. The turbidity of citrus juices is due to a variety of dispersed particles containing proteins, polysaccharides and lipids (Scott *et al.*, 1965). In manufactured fruit-type beverages, the artificial cloud is derived from scattering by dispersed oil droplets of size 0·5–5 μm present at concentrations of *c.* 0·1 wt% in the final product. While optimization of cloud is usually achieved in practice on a trial and error basis (Preston, 1978), some useful insight into the key factors affecting the degree of cloudiness can be obtained from a consideration of the simple principles of light absorption and light scattering.

The amount of light absorbed by a dilute solution or dispersion is often expressed in terms of the optical density

$$\text{O.D.} = \log_{10}(I/I_0) = -\log_{10}T \qquad (1)$$

where I_0 is the incident light intensity, I is the transmitted intensity, and T is the optical transmittance:

$$T = \exp(-\tau L) \qquad (2)$$

In eqn (2), L is the optical path length and τ is the turbidity. The turbidity is proportional to the concentration C of dispersed particles. It also depends on the difference in refractive index between the particles and the medium, and on the particle size distribution $p(D)$ where D is the particle diameter. To eliminate the effect of particle concentration, it is convenient to work in terms of the specific turbidity τ/C. For a system of spherical particles of volume–surface mean diameter D_{32}, the specific turbidity is given by (Dobbins & Jizmagian, 1966)

$$\tau/C = 3Q_{av}/2\rho D_{32} \qquad (3)$$

where ρ is the density of the dispersed phase and Q_{av} is the average particle scattering efficiency:

$$Q_{av} = \int_0^\infty Q(D)p(D)D^2\mathrm{d}D \Big/ \int_0^\infty p(D)D^2\mathrm{d}D \qquad (4)$$

The quantity $Q(D)$ in eqn (4) is the scattering efficiency of a particle of diameter D; its value depends on the wavelength of the incident light, as well as on the refractive indices of the particle and the continuous phase (Kerker, 1969).

Figure 1 shows a plot of specific turbidity τ/C against mean diameter D_{32} for a dispersion of particles with a log-normal distribution as calculated by Hernandez and Baker (1991). (Note that these authors express particle concentration in units of g g^{-1}, which gives the

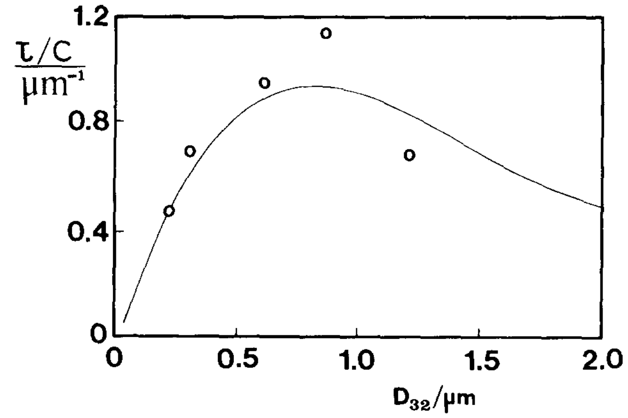

Fig. 1. Influence of particle size on the cloudiness of a dispersion. The specific turbidity τ/C (where C is the mass concentration expressed in units of g g^{-1}) is plotted against the average droplet diameter D_{32}: ——, theoretical prediction for a system with a log-normal particle size distribution; ○, experimental results for citrus oil-in-water emulsions. [Reproduced with permission from Hernandez & Baker (1991).]

specific turbidity in units of m^{-1}. When concentration is in g cm^{-3}, the specific turbidity is in the (more usual) units of $cm^2\ g^{-1}$ (Farinato & Rowell, 1983).) Scattering efficiences were calculated using the formula of van de Hulst (1957) assuming a wavelength of 650 nm and a refractive index appropriate to a citrus oil solution at 20°C. Also plotted in Fig. 1 are experimental data obtained spectrophotometrically at 650 nm for citrus oil-in-water emulsions prepared with gum arabic as the emulsifying agent. Good agreement is obtained between theory and experiment with a maximum specific turbidity at a mean particle size of *c.* 1 μm. A similar result was obtained by Goulden (1958) for diluted milk emulsions.

The light-scattering theory as applied to citrus oil clouding agents predicts that the maximum specific turbidity occurs at a mean particle size which is slightly greater than the wavelength of the light. For a given wavelength and droplet concentration, the predicted turbidity increases with increasing refractive index of the dispersed phase. This is supported by measurements of the optical density of citrus oil-in-water emulsions (Ray *et al.*, 1983). We note that the effective refractive index of the dispersed droplets is slightly different from that of the bulk dispersed phase due to the effect of the adsorbed emulsifier (e.g. gum arabic).

In the above it has been assumed that the only contribution to the optical density is from light scattering by suspended particles. For a coloured beverage, of course, there is a contribution also from light absorption. This needs to be taken into account (e.g. by using a coloured reference solution) when spectrophotometric methods are employed to monitor haze in cloudy juices and beverages. Another disadvantage of using a spectrophotometer is that it is insensitive to light scattered by very small particles ($\leq 0{\cdot}2\ \mu$m). For these reasons the opacity of beverages is often measured commercially using a nephelometer which compares the intensity of light scattered at 90° (±30°) with that of a standard suspension. However, readings from such an instrument may be disproportionately sensitive to small particles, giving high values for a fine suspension containing 'invisible' haze (i.e. haze not readily detected by the consumer's eye); the maximum scattering at 90° typically occurs at a mean particle size of *c.* 0·2 μm (Hernandez *et al.*, 1991). This problem can be overcome through the use of low-angle light-scattering instruments (Morris, 1987).

Any process that increases the number of particles of size $\sim 1\ \mu$m in a beverage will tend to increase the turbidity, whereas loss of micron-sized particles will lead to loss of cloudiness. In an emulsion any one or more instability processes (coalescence, Ostwald ripening, creaming, etc.) are likely to lead to a loss of cloud due to removal of micron-sized droplets from the main body of the sample. Enhancement of cloudiness in a polymer solution may be achieved by inducing limited phase separation. On the other hand, extensive phase separation usually leads to loss of cloud due to flocculation and subsequent sedimentation.

PHASE SEPARATION

The thermodynamic conditions for the phase separation of a polymer solution are conveniently described by the statistical theory of Flory and Huggins (Flory, 1953). The change in Gibbs free energy on forming a binary mixture of solvent (1) + polymer (2) at temperature T and pressure p is

$$\Delta G_{\text{mix}} = x_1\mu_1 + x_2\mu_2 - x_1\mu^\circ{}_1 - x_2\mu^\circ{}_2 \qquad (5)$$

where x_1 and x_2 are the mole fractions of the two components, μ_1 and μ_2 are their chemical potentials, and the superscript ° denotes the standard state. Whether the system exists at equilibrium as a one- or two-phase system depends on the curvature of the plot of ΔG_{mix} as a function of composition. The critical point at which the homogeneous solution becomes unstable with respect to phase separation occurs when the second and third derivatives of ΔG_{mix} with respect to composition are both zero. In the Flory–Huggins theory, the solvent chemical potential is given by

$$\mu_1 = \mu^\circ{}_1 + RT[\ln(1-\phi_2) - (1-m^{-1})\phi_2 + \chi_{12}\phi_2^2] \qquad (6)$$

where ϕ_2 is the polymer volume fraction, m is number of chain units, R is the gas constant, and χ_{12} is the Flory–Huggins parameter which defines the quality of the solvent for the polymer. In a good solvent ($\chi_{12} \approx 0$) the solute molecules distribute themselves more or less randomly throughout the uniform solution. In a poorer solvent ($\chi_{12} > 0$) the polymer molecules become more associated, and when χ_{12} exceeds a certain critical value $\chi^c{}_{12}$ the system separates into coexisting phases. The position of the critical point depends only on the molecular weight of the polymer:

$$\chi_{12}^c = (1 + m^{1/2})^2/2m\ , \ \phi_2^c = (1 + m^{1/2})^{-1} \qquad (7)$$

In the high-molecular-weight limit ($m \rightarrow \infty$), we have $\chi_{12}^c = \frac{1}{2}$ and $\phi_2^c = m^{-1/2}$.

In a ternary system of solvent (1) + polymer (2) + polymer (3) there are three different Flory–Huggins parameters to consider: χ_{12}, χ_{13} and χ_{23}. Now two kinds of phase separation are possible: (i) complex coacervation, where one phase consists predominantly of solvent and the two polymer components coexist together in the other phase, and (ii) thermodynamic incompatibility, where the two polymer components reside predominantly in separate solvent-rich phases. Which type of phase separation actually occurs in any particular situation depends primarily on the value of the polymer–polymer Flory–Huggins parameter χ_{23}. In terms of the molecular interactions, complex coacervation is associated with a net attraction ($\chi_{23} < 0$) between the two polymer components, and thermodynamic incompatibility is associated with a net repulsion ($\chi_{23} > 0$). The higher the polymer concentration(s), the lower is the absolute value of χ_{23} required for phase separation. In a ternary mixture with $m_2 = m_3 = 10^4$ and $\phi_1 \leq 0{\cdot}9$, phase separation takes place for $|\chi_{23}| \geq 0{\cdot}1$.

The Flory–Huggins theory is in principle applicable to any multicomponent polymer system which exhibits phase separation on cooling. An example of such a phase separation is the formation of tea cream on cooling a strong infusion of black tea (Bee *et al.*, 1987). At high temperature when the tea is made ($T \approx 95$°C, $\chi_{12} < \chi_{12}^{c}$) entropy of mixing effects predominate and the solutes remain solubilized in the aqueous phase. However, as the tea cools down, the energetic effects become more important, and phase separation occurs below a critical temperature of *c.* 60°C. Figure 2 shows an experimental phase diagram as determined by a combination of optical and electron microscopy (Rutter, 1971; Harbron *et al.*, 1989). The shape of the phase diagram is similar to the classical case of two liquids which mix at high temperatures but separate into two immiscible liquid phases on cooling below the (upper) critical solution temperature (Rowlinson, 1969).

Tea cream is a coloured precipitate which exists as stable colloidal particles rather than as a separate distinct bulk phase. The colloidal morphology depends on the tea solids concentration (Bee *et al.*, 1987). Dilute infusions ($\leq 0{\cdot}1$ wt %) produce macromolecular aggregates of size *c.* 50 nm, and at higher concentrations these tend to aggregate further to produce larger irregular clusters of size up to *c.* 1 μm. At solids contents of ≥ 5 wt % the cream consists of spherical droplets a few microns in diameter (Smith, 1968). On the basis of whether the tea cream particles are granular or spherical, the two-phase region of the phase diagram in Fig. 2 is divided into two sub-regions I and II. In chemical terms, tea cream is a complex mixture of many components with thearubigins, theaflavins and caffeine being the most predominant (Roberts, 1963). The major macromolecular components are the thearubigins with molecular weights probably lying in the range 10^3–10^4 Daltons. The heterogeneous nature of tea cream is indicated by the considerable temperature dependence of its solubility (Rutter & Stainsby, 1975).

The spherical droplets of tea cream exhibit a high level of stability with respect to flocculation and coalescence. Recent electrophoretic mobility and colloid coagulation studies (Harbron *et al.*, 1989) suggest that the mechanism of stabilization of the particles is predominantly electrostatic. Due to the presence of ionized acidic groups ($pK_a \sim 3$) the particles carry a net negative charge at the natural pH of tea infusions (pH $\approx$ 4·7). Electrostatic repulsion between the charged droplet surfaces protects the droplets from coagulation in accordance with the classical theory of the stability of lyophobic colloids (Verwey & Overbeek, 1948).

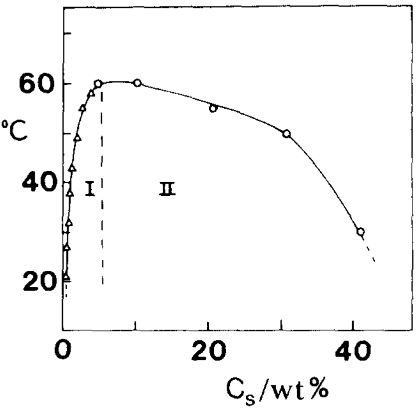

Fig. 2. Experimentally determined phase diagram for the separation of tea cream showing regions of (I) granular aggregates and (II) spherical droplets. Temperature T is plotted against solids concentration C_S: Δ, data of Rutter (1971); O, data of Harbron *et al.* (1991). [Reproduced with permission from Harbron *et al.* (1991).]

CONCLUDING REMARKS

The relevance of the principles of colloid science to the appearance and stability of beverages has been described. In particular, it has been shown how a consideration of the principles of light scattering from a dispersion of particles gives information relevant to the optimization of cloudiness in dilute citrus-oil flavour emulsions, and how the formation of tea cream can be understood in terms of the thermodynamics of phase separation. While the same physical principles are applicable to a wide range of systems, we must also recognize that distinct instability phenomena are associated with certain beverages because of the specific chemical components involved. One such example is the influence of ethanol or calcium ions on the properties of adsorbed casein layers which can have profound implications for the stability of cream liqueurs (Banks & Muir, 1988; Dickinson *et al.*, 1989). Another dairy-type example is the so-called 'feathering' of homogenized cream in hot coffee solutions due to the flocculation of casein-coated particles under the combined influence of high temperature and low pH. What each of these examples has in common is a change in texture and appearance of the beverage which can be attributed to some breakdown in colloid stability. The control of this instability requires an understanding of how changes in chemical composition can affect the physical processes involved.

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