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Monitoring sedimentation processes by conductivity measurements

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Summary

A non-destructive method to determine the sedimentation behavior of water-continuous dispersed systems has been developed, which is based on conductivity measurement through the dispersion at different heights. Conductivities of sedimenting dispersions are interpreted in terms of dispersion dielectric theory, to convert the qualitative conductivity values into the quantitative volume fraction values of the dispersed phase. First applications are presented illustrating the possibilities in evaluating dispersion's sedimentation stability under normal gravitational field and at different temperatures, and also under centrifugal field. Collection of such profiles at appropriate time intervals allows sedimentation processes to be followed before they become apparent by visual means.

Introduction

The gravitational force acting on dispersed particles can lead to mass transport, providing there is a density difference between the dispersed and continuous phase. These changes in the volume fraction of the dispersed phase are a problem of widespread practical and theoretical interest. For instance, since pharmaceutical dosage forms have to be stored for a period of years, the formulation scientist must be able to guarantee their long-term stability in the shortest possible time. At a more fundamental level, the examination of the sedimentation behavior of dispersions offers a way of characterizing structure and interactions in concentrated dispersions (Buscall, 1990). Thus, there is a considerable need for techniques that reliably monitor the particle concentration in space and time.

As recently reviewed by Williams et al. (1990), non-intrusive and non-destructive X-ray, γ-ray, ultrasonic and microwave techniques have been developed, which allow such a detailed distribution determination of the dispersed phase. However, safety problems are encountered for the high-energy sources, and the methods based on ultrasonics and microwaves are relatively complex in operation, and also relatively cost intensive.

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An alternative technique was recognized in the use of conductivity measurements which seemed to be quite attractive to us due to the simple electronic measuring circuit and electrode structure. Moreover, as known from the studies of Quack et al. (1975) and Schambil et al. (1989), the time-related changes in the conductivities of o/w emulsions in the upper and the lower part of the test samples make it possible to draw qualitative conclusions about the stability of the systems.

In continuation of these promising findings, the major objective of the present study is to interpret conductivities of sedimenting dispersions measured at different heights in terms of dispersion dielectric theory, providing data conversion of the qualitative values of conductivity into the quantitative values of volume fraction of the dispersed phase. For this purpose the dielectric model of Bruggeman (1935) was reformulated. In order to prove experimentally the reliability of this model, with a sedimented dispersion the data conversion was compared with those obtained by two destructive methods (Karl-Fischer titration, spectrophotometry). Since Bruggeman's theory is based upon the assumption of spherically dispersed particles, it was reasonable to use data of an emulsion rather than those of a suspension where the dispersed particles are generally not spherical. In addition, to investigate a more real pharmaceutical emulsion, a non-ionic o/w emulsion was chosen containing no supporting electrolytes, i.e. a system with low conductivity. The second objective was to explore the applicability of this conductivity method for stability assessment under normal gravitational field, but different storage temperatures, and also under centrifugal fields.

Background of the Method

Many investigators searched for the relation between the volume fraction of the dispersed phase and the electrical conductivity as reviewed by Hanai (1968) and Clausse (1983). One of the most prominent equations is the one developed by Bruggeman (1935). Likewise, in this approximation the conductivity of the dispersion is a function of the constituent phases' conductivities and of the phase volume of the dispersed phase:

$$\frac{k - k_d}{k_c - k_d}\left(\frac{k_c}{k}\right)^{1/3} = (1 - \phi) \qquad (1)$$

where k, k_c and k_d are the conductivities of the dispersion, the dispersed phase and the continuous phase, respectively, and ϕ is the volume fraction of the dispersed phase. Since the conductivity of the dispersed phase is much lower than that of the continuous phase ($k_c \gg k_d$), Eqn 1 simplifies to:

$$\frac{k}{k_c} = (1 - \phi)^{3/2} \qquad (2)$$

Implicit in the derivation of Bruggeman (1935) is the assumption that an incremental (spherical) drop is added to an emulsion consisting of drops all smaller than the added drop. Therefore, Bruggeman's model is strictly applicable to systems only if a large range of particle sizes is present in the dispersion. This requirement of polydispersity is satisfied in virtually all real pharmaceutical dispersions. Accordingly, Bruggeman's model has been found to provide adequate agreement with experimental data for o/w emulsions at dispersed phase volume fractions between 0.1 and 0.8 (Hanai et al., 1960). Hanai's measurements were made on emulsions of a mixture of mineral oil, tetralin and carbon tetrachloride in 0.05 N potassium chloride aqueous solution, stabilized by approx. 1% of an equal-weight mixture of polysorbate 20 and sorbitane laurate or polyoxyl 31 cetyl ether. De la Rue and Tobias (1959) determined conductivities of suspensions of glass beads in $ZnBr_2$ solution with volume fractions less than 0.4. The glass beads were separated into six different size fractions, each with a broad size distribution. It was shown that the dependence between the conductivity of the dispersions and ϕ is represented very well by Eqn 2 for all investigated particle sizes. Furthermore, it was indicated that the conductivity of the dispersions depends on the volume fraction and the particle size distribution, but not on the mean particle size.

For the purpose of determining the volume fractions of sedimenting dispersions Bruggeman's Eqn 2 may be reformulated by equating the initial terms of the volume fraction and of the conductivities (ϕ_0, k_0, k_c) with the terms at some height x and after some time t ($\phi_{x,t}$, $k_{x,t}$, $k_{c,x,t}$):

$$\frac{k_0}{k_c}\frac{1}{(1-\phi_0)^{3/2}} = \frac{k_{x,t}}{k_{c,x,t}}\frac{1}{(1-\phi_{x,t})^{3/2}} \tag{3}$$

As long as $k_{c,x,t} = k_c$ for all x and t, which is a realistic assumption, Eqn 3 is solved for $\phi_{x,t}$ yielding Eqn 4

$$\phi_{x,t} = 1-(1-\phi_0)\left(\frac{k_{x,t}}{k_0}\right)^{2/3} \tag{4}$$

It is apparent that the term k_c is no longer contained in Eqn 4, i.e. the conductivity of the continuous phase does not need to be determined experimentally. However, one must be aware that a condition for the use of Eqn 4 is a non-changing conductivity of the continuous phase with height.

A serious problem, that enters into the application of Eqn 4, is the viscosity change of dispersions during storage due to aging effects. As stated by Walden's rule, in homogeneous liquids, the conductivity is inversely proportional to the viscosity. As also observed by Schambil et al. (1989), the conductivity of o/w emulsions is strongly influenced by viscosity changes, i.e. the higher the viscosity the lower the conductivity. Thus, the conductivity changes should be regarded mainly as a superposition of changes due to viscosity and of changes due to sedimentation of dispersed particles. Therefore, for the purpose of normalization, the term of the initial conductivity, k_0, in Eqn 4 is replaced by the average conductivity at each particular measurement time,

$$\langle k_t \rangle = 1/n \sum_{x=1}^{n} k_{x,t} \tag{5}$$

where n is the number of electrodes.

Despite the simplicity of the electrode constant determination with the help of solutions having known conductivity, this technique is plagued with an extreme workload for several conductivity cells each containing multiple electrode pairs. Assuming an initially homogeneous dispersion, an internal electrode constant, C_x, may be defined where the uncalibrated conductivity, k_{ref}, at one electrode and at time $t = 0$ serves as reference:

$$C_x = k_{x,t=0}/k_{\text{ref}} \tag{6}$$

With Eqn 6 the internally calibrated conductivities, $k^{\text{i}}_{x,t}$, are given as:

$$k^{\text{i}}_{x,t} = k_{x,t}/C_x \tag{7}$$

Since anything that disturbs the dispersion during the time required for the initial measurement can distort this internal calibration procedure, the initial homogeneity of the dispersion must carefully be adjusted.

With the approximations of Eqns 5 and 7, Eqn 4 may be expressed as

$$\phi_{x,t} = 1-(1-\phi_0)\left(\frac{k^{\text{i}}_{x,t}}{\langle k^{\text{i}}_t \rangle}\right)^{2/3} \tag{8}$$

which is now based on internally calibrated conductivities and their averaged conductivities at each measurement time, $\langle k^{\text{i}}_t \rangle$.

Materials and Methods

Materials

The following materials were all of pharmacopoeial quality: polysorbate 60 (Tween 60, ICI), sorbitan stearate (Span 60, ICI), caprylic/capric triglyceride (Myritol 318, Henkel), propylene glycol and benzyl alcohol (Merck). Sudan III (Siegfried, Zofingen, Switzerland) and dioxan (Fluka) was used as received. Demineralized water of specific conductance of about 1 μS/cm at 25 °C was used throughout the experiments.

Preparation of the emulsions

Two model o/w emulsion systems were tested whose formulae are given in Table 1. The mixing proportion of the surfactants corresponds to HLB

TABLE 1

Composition of the investigated o/w emulsions

Excipients	Emulsion A	Emulsion B
Polysorbate 60	1.56 g	1.56 g
Sorbitan stearate	1.44 g	1.44 g
Caprylic/capric triglyceride	30.0 g	30.0 g
Propylene glycol	5.0 g	5.0 g
Benzyl alcohol	1.0 g	1.0 g
Sudan III	7.5 mg	–
Water demineralized q.s. ad	100.0 g	100.0 g

10.0. The total surfactant amount is one tenth of the oil. Benzyl alcohol was added as preservative, and propylene glycol as co-preservative and humectant.

800 g emulsion were prepared in a 1 l laboratory vessel fitted with a stirrer and a homogenizer, and allowing working under vacuum. The oily phase consistent of caprylic/capric triglyceride and sorbitan stearate (and, in the case of emulsion A, Sudan III) was mixed and heated to about 70 ° C. The aqueous phase consisting of polysorbate 60, propylene glycol, benzyl alcohol and water was mixed, heated to about 70 ° C and added to the oily phase under stirring. After complete addition of the aqueous phase the coarse emulsion that formed was homogenized for 1 min and cooled to room temperature under constant stirring. The emulsion was stored in a 25 ° C chamber for 1 day to allow equilibration and was slightly stirred prior to further use.

Droplet size analysis

The droplet size analysis was performed using a laser diffraction technique (Malvern MasterSizer). The following procedure was adopted for the dilution step: about 1 ml of the emulsion was diluted with demineralized water to about 50 ml. Then about 0.5–1.0 ml of this dilution was placed in the receiver of the MasterSizer (50% stirring and pump intensity), until an extinction of about 0.2 ± 0.05 absorbance units was achieved. Using a 45 mm lens this diluted dispersion was immediately measured for 10 s.

Density measurement

In preparing the disperse systems, it is most convenient to add quantities of the two phases by weight, although one is ultimately interested in the volume fraction of the dispersed phase in the system. The initial volume fraction of the dispersed phase, ϕ_0, and the weight fraction of the dispersed phase, ϕ_w, are related through:

$$\phi_0 = \phi_w \frac{\rho_t}{\rho_d} \qquad (9)$$

where ρ_d and ρ_t are the densities of the dispersed phase and of the total dispersion. These densities were measured with a Paar Precision Density Meter (type DMA 50).

In emulsions A and B it is assumed that the lipophilic surfactant is completely dissolved in the dispersed phase and the hydrophilic surfactant in the aqueous phase. Furthermore, it is assumed that benzyl alcohol and propylene glycol are present in the aqueous phase only. With these approximations ϕ_w is equal to 0.3144 for both emulsions A and B.

Conductivity cells and measurements

The cells are constructed in such a way as to make possible the measurements of conductivity at different fixed positions. Details of the construction are given in Fig. 1 (cell A, 6 electrode pairs; cell B, 9 electrode pairs). The cells are constructed with plexiglass walls to enable also a visual study of the sedimentation process. The electrodes consist of stainless steel.

The main series of measurements was executed with the cell used for gravitational studies (Fig. 1A). The other cell (Fig. 1B) was designed to fit into the tube of a centrifuge (Heraeus-Christ, type JJ I KS). The distance between the rotor axis and the midpoint of the top electrode pair was 6.4 cm, and between the rotor axis and the midpoint of the bottom electrode pair 12.1 cm.

Conductivity was measured by using a Philips PW 9527 digital conductivity meter operating at a frequency of 4000 Hz. All measurements were performed with the cell constant set to 1.0 cm^{-1}, and without temperature compensation.

Karl-Fischer titration and spectrophotometry

For temperature equilibration the emulsion and three sedimentation cells of the type shown in Fig. 1A were put into a 45 ± 1 °C controlled temperature chamber. After thermal equilibration was achieved, the emulsion was gently stirred with a glass rod for approx. 3 min to ensure droplet homogeneity. The emulsion was filled into the cells, and again gently stirred to remove any air bubbles at the cell walls. The cover was closed, the initial conductivity at each height was determined immediately, and also after 7 days.

Directly after the 7-day conductivity measurements, samples are drawn off by layers with a syringe as carefully as possible. The samples, corresponding to the volumes between the electrode pairs at the different heights of the creaming cell, were gently stirred with a glass rod to ensure homogeneity, and further divided for the Karl-Fischer titration, and spectrophotometric determination.

To perform the Karl-Fischer titration, about 0.05–0.1 g of the sample, exactly weighed, were injected into the reaction chamber of the titrator (Metrohm type K-F Processor 658). The titration has been performed three-fold for each sample. The results are given directly in terms of weight fraction of water, $\phi_{w,x}(H_2O)$. From this value the weight fraction of dispersed phase, $\phi_{w,x(KF)}$, is calculated according to Eqn 10:

$$\phi_{w,x(KF)} = 1 - \phi_{w,x}(H_2O) \qquad (10)$$

For the spectrophotometric determination Sudan III was chosen as an indicator, since it is insoluble in water, moderately soluble in oil, and easily detectable spectrophotometrically. As known from separate studies, a concentration of 0.075 mg/g emulsion was sufficient to obtain a detectable dye concentration even with low weight fractions of dispersed phase, as may occur after creaming. The spectrophotometric measurements were performed by means of a Kontron Uvikon 820, using Hellma quartz cuvettes of 1 cm width, a single width band of 2.00 nm, and a peak detection sensitivity of 0.1%. The absorptions were measured at the peak maximum at 518 nm. The blank was obtained with about 2 g of emulsion B containing no Sudan III and dissolved in dioxan to a volume of 20.0 ml.

Amounts of about 2 g of the creamed emulsion samples were exactly weighed (W_x), and dissolved in dioxan to a volume of 20.0 ml. The measured

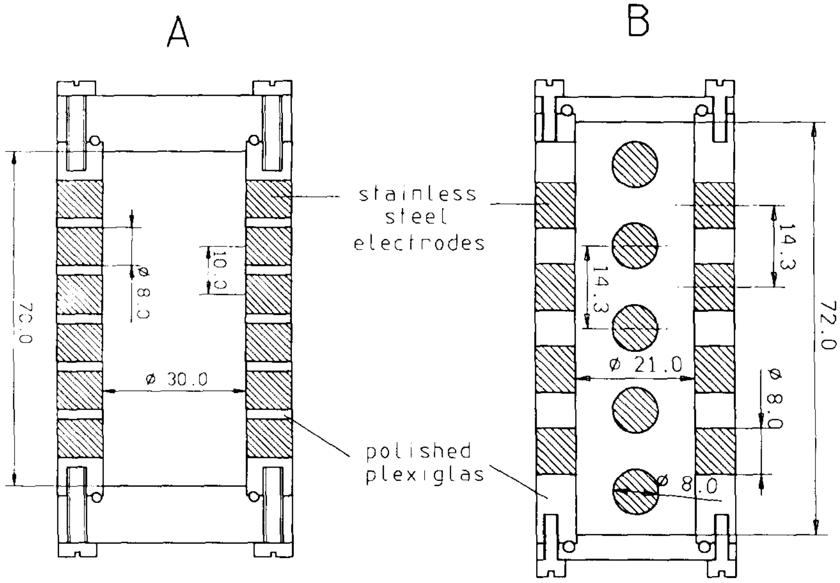

Fig. 1. Cross-sectional diagram of the conductivity cells for monitoring sedimentation processes of dispersions: (A) for determinations under gravitational field; (B) for determinations under centrifugal field.

TABLE 2

Volume fraction of dispersed phase of emulsion B at different temperatures

Temperature (°C)	ρ_t (g/ml)	ρ_d (g/ml)	ϕ [a]
5	0.99548	0.96381	0.3247
25	0.98669	0.94698	0.3276
45	0.97484	0.93041	0.3294

[a] Calculated according to Eqn 9 with $\phi_w = 0.3144$.

absorptions are given as A_x. The initially uncreamed emulsion A was treated in the same way with weight W_r and absorption A_r.

The weight fraction of dispersed phase at the different heights, $\phi_{w,x(PH)}$, was calculated according to

$$\phi_{w,x(PH)} = \phi_w \frac{W_r}{A_r} \frac{A_x}{W_x} \qquad (11)$$

As the mean value of three measurements the term W_r/A_r was determined to be 3.4742. With $\phi_w = 0.3144$, Eqn 11 becomes:

$$\phi_{w,x(PH)} = 1.0923 \frac{A_x}{W_x} \qquad (12)$$

Results and Discussion

Examination of the reformulated Bruggeman equation

Emulsion A was filled into three conductivity cells of the type in Fig. 1A and stored at 45 °C to accelerate the creaming. After 7 days, a not clearly separated region could be observed at the bottom of the cells. Thus, after this time, the conductivity at 45 °C was measured and afterwards the Karl-

TABLE 3

Volume fractions and weight fractions of dispersed phase determined with different methods (emulsion A, stored 7 days at 45 °C)

Electrode position (x)	Conductivity (μSi/cm)		Cell constant (C_x)	Calibrated conductivity ($k^i_{x,t=7}$)	$\phi_{x,t=7}$ [a]	$\phi_{w,x,t=7}$ [b]	Photometry $\phi_{w,x(PH)}$ [c]	Karl-Fischer $\phi_{w,x(KF)}$ [d]
	Initial	7 days						
1 (bottom)	61.04	90.92	1.000	90.92	0.187	0.179	0.141	0.227
2	63.72	83.49	1.044	79.98	0.254	0.242	0.239	0.310
3	64.72	80.13	1.060	75.57	0.281	0.269	0.268	0.337
4	64.30	76.18	1.053	72.32	0.302	0.288	0.292	0.364
5	63.61	63.72	1.042	61.15	0.376	0.359	0.370	0.437
6 (top)	57.17	26.99	0.937	28.82	0.622	0.594	0.612	0.673
1 (bottom)	56.58	85.24	1.000	85.24	0.187	0.178	0.136	0.225
2	58.85	77.39	1.040	74.40	0.257	0.246	0.235	0.312
3	60.60	75.51	1.071	70.50	0.284	0.271	0.264	0.344
4	60.31	72.12	1.066	67.66	0.303	0.289	0.287	0.362
5	59.77	61.18	1.056	57.91	0.372	0.355	0.341	0.416
6 (top)	52.93	25.52	0.935	27.28	0.620	0.591	0.593	0.665
1 (bottom)	58.92	87.53	1.000	87.53	0.191	0.183	0.130	0.212
2	60.96	79.67	1.035	77.00	0.258	0.246	0.236	0.311
3	60.08	74.38	1.020	72.94	0.284	0.271	0.262	0.340
4	61.05	72.48	1.036	69.95	0.304	0.290	0.288	0.363
5	59.05	60.18	1.002	60.05	0.371	0.354	0.339	0.407
6 (top)	52.41	25.89	0.890	29.11	0.612	0.584	0.601	0.659

[a] At 45 °C for all x: $\phi_{x,t=0} = \phi_0 = 0.3294$ (see Table 2).

[b] Calculated according to $\phi_{w,x,t} = \phi_{x,t}\,(\rho_d/\rho_t)$. At 45 °C with $\rho_d = 0.93041$ and $\rho_t = 0.97484$ (see Table 2), it follows that $\phi_{w,x,t} = 0.95442\phi_{x,t}$.

[c] Calculated according to Eqn 12.

[d] Calculated according to Eqn 10.

Fischer titrations and the spectrophotometric determinations were performed.

The initial mean volumetric droplet diameter of emulsion A was determined to be 2.08 μm and the droplet size did not change over the time scale of the creaming experiment.

All results are compiled in Table 3. For the internal calibration (Eqn 6), the electrode pair at the bottom, position 1, was taken as the reference, giving with Eqn 7 the calibrated conductivities and with Eqn 8 the volume fraction of dispersed phase at the six electrode positions. It should be mentioned that these calculations are invariant with regard to the position of the reference electrode, as can easily be proved.

In all three cells $\langle k^{\mathrm{i}}_{t=7} \rangle - \langle k^{\mathrm{i}}_{t=0} \rangle \sim 7\ \mu\mathrm{Si/cm}$, i.e. the mean conductivity increases after 7 days storage at 45 °C. The mean volume fraction of dispersed phase

$$\langle \phi_t \rangle = 1/n \sum_{x=1}^{n} \phi_{x,t} \tag{13}$$

is for $t = 7$ equal to 0.337 for all three cells, and is in good agreement with the initial volume fraction $\phi_0 = 0.329$. On the other hand, substituting $\langle k^{\mathrm{i}}_{t=7} \rangle$ by $\langle k^{\mathrm{i}}_{t=0} \rangle$ in Eqn 8 leads to $\langle \phi_{t=7} \rangle =$ 0.287, i.e. some dispersed phase disappeared from the cell, which is unreasonable. This comparison demonstrates the need and the justifiability of the approximation made in Eqn 5.

Although the investigated emulsion was consciously composed without supporting electrolytes, the reproducibility of the volume fractions of dispersed phase is very good with relative standard deviations at the six electrode positions between 0.23 and 1.34 with a mean of 0.75. The relative standard deviations of the weight fractions obtained with the Karl-Fischer titration are between 0.16 and 3.71 with a mean of 1.68, and those obtained spectrophotometrically are between 0.78 and 4.91 with a mean of 2.19.

Linear regression analysis between the weight fractions obtained with the two destructive methods (Karl-Fischer titration, spectrophotometry) showed, that these data are highly correlated (see Table 4, Eqn 14). The significant intercept can be explained with the content of water-soluble components (benzyl alcohol, propylene glycol, polysorbate 60) with an apparent weight fraction of 0.0756. These components are not detected with the Karl-Fischer titration and hence the values of $\phi_{\mathrm{w},x(\mathrm{KF})}$ are systematically overestimated. The deviation of the slope from unity may be explained by the magnitude of ϕ_{w} in Eqn 11. This value is estimated on the basis of the emulsion's composition. The precise distribution of the different components between the water and oily phases is not known, nor are the degree of micellar solubilization of the oil and the degree of solvation at the interphase (Bisal et al., 1990).

To compare the results of the conductivity procedure with those of the destructive methods, the volume fractions must be recalculated into weight fractions of dispersed phase. The calculation procedure is stated in Table 3 (footnote b). The fittings of the resulting data are presented in Fig. 2, and the respective linear regression equations are compiled in Table 4 (Eqns 15 and 16).

TABLE 4

Least-squares regression analysis of weight fractions of dispersed phase determined with different methods (emulsion A, stored 7 days at 45 °C) [a]

Eqn		r [b]	n
14	$\phi_{\mathrm{w},x(\mathrm{KF})} = 0.9565\ (\pm 0.0079) \cdot \phi_{\mathrm{w},x(\mathrm{PH})} + 0.0875\ (\pm 0.0027)$	0.9995	18
15	$\phi_{\mathrm{w},x(\mathrm{PH})} = 1.0997\ (\pm 0.0252) \cdot \phi_{\mathrm{w},x,t=7} - 0.0407\ (\pm 0.0088)$	0.9958	18
16	$\phi_{\mathrm{w},x(\mathrm{KF})} = 1.0537\ (\pm 0.0203) \cdot \phi_{\mathrm{w},x,t=7} + 0.0480\ (\pm 0.0070)$	0.9971	18

[a] $\phi_{\mathrm{w},x(\mathrm{KF})}$ is the weight fraction of dispersed phase obtained from Karl-Fischer titration, $\phi_{\mathrm{w},x(\mathrm{PH})}$ from spectrophotometry, and $\phi_{\mathrm{w},x,t=7}$ from the conductivity method.

[b] r is the correlation coefficient, and n the number of observations.

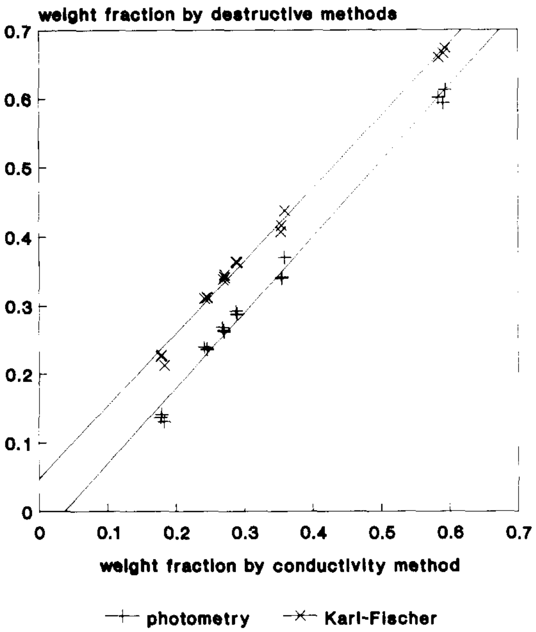

Fig. 2. Weight fractions of dispersed phase at different heights of emulsion A, stored for 7 days at 45 ° C: conductivity results vs the results of Karl-Fischer titration and spectrophotometry.

The agreement between the data obtained with the conductivity method and the two destructive methods is fairly good, but not perfect. The data obtained at the bottom electrodes of the cells may have same outlying character, which can be explained by the delicate sampling technique, but not by the destructive analytical methods themselves (see Eqn 14). Nevertheless, the slopes deviate slightly from unity. A source of error may again be seen in the estimation of the weight fraction of dispersed phase, ϕ_w, entering Eqn 8 via Eqn 9. Also, the term ρ_d in Eqn 9 is an apparent density of the dispersed phase, guessed from the emulsion's composition.

It is hard to say to what extent the agreement would be improved with a precisely known weight fraction. Interestingly, the agreement with the Karl-Fischer data containing no weight fraction estimate is better than that with the spectrophotometric data containing this term. Since this difficulty cannot be overcome, it is not possible to state whether other factors from the approximations contained in Bruggeman's equation and its reformulation are responsible for the trend of the conductivity method of slightly overestimating at low weight fractions and slightly underestimating at high weight fractions.

From a practical standpoint, the reformulated Bruggeman model (Eqn 8) may be considered as satisfactory, yielding information of good accuracy.

Applications to creaming stability assessment

Stress conditions normally employed to diagnose the creaming stability during preliminary formulation evaluation include elevated temperature and centrifugation. In a typical test program the emulsion should be stable for at least 60–90 days at 45 ° C, and 12–18 months at room temperature (Rieger, 1986). In addition, as indicated by Becher (1965), centrifugation at 3750 rpm in a 10 cm radius centrifuge for a period of 5 h would be equivalent to the effect of gravity for about 1 year. Both tests have to rely on visible signs of separation. A technique which is sensitive to small changes would be considerably useful in shortening the time needed for stability assessments. The conductivity method is evaluated under these aspects.

With emulsion B the creaming behavior was determined up to 71 days in cells of the type in Fig. 1A at 5 ° C (2 cells), 25 ° C (2 cells), and 45 ° C (3 cells). The densities and the respective volume fractions of dispersed phase, determined at 5, 25 and 45 ° C with emulsion B, are listed in Table 2. Using these values, the $\phi_{x,t}$ data are calculated as shown in Fig. 3A–C. For these graphical presentations, the height (in cm) is defined as the midpoint of each electrode.

At 5 ° C (Fig. 3A), no change in $\phi_{x,t}$ could be observed. With increased storage temperature the creaming is considerably accelerated as reflected in the $\phi_{x,t}$ profiles. The profiles conform with those expected for hindered creaming, i.e. the creaming velocity decreases with increasing volume fraction. However, diffusion is significant, smoothing at 45 ° C the discontinuity at the top. At 45 ° C (Fig. 3C), the creamed region at the top with $\phi > 0.60$ grows with time and is gradually compressed to a maximum ϕ of about 0.7, which changed little with time.

Visually, in the 5 ° C samples, no change could be observed. In the 25 and 45 ° C samples the base of the emulsion did not begin to clear optically with a very diffuse lower meniscus for approx. 6 and 10 days, respectively, although using the conductivity technique, creaming was detected within 1 day.

Emulsion B was centrifuged at 25 ° C in two cells of the type in Fig. 1B at 1000 and 2000 rpm for up to 4 h. As can be seen from the $\phi_{x,t}$ profiles (Fig. 3D and E), creaming is drastically accelerated. Due to the force field varying with the height, the $\phi_{x,t}$ profile at 2000 rpm and that at 25 ° C under gravitational field are similar, but

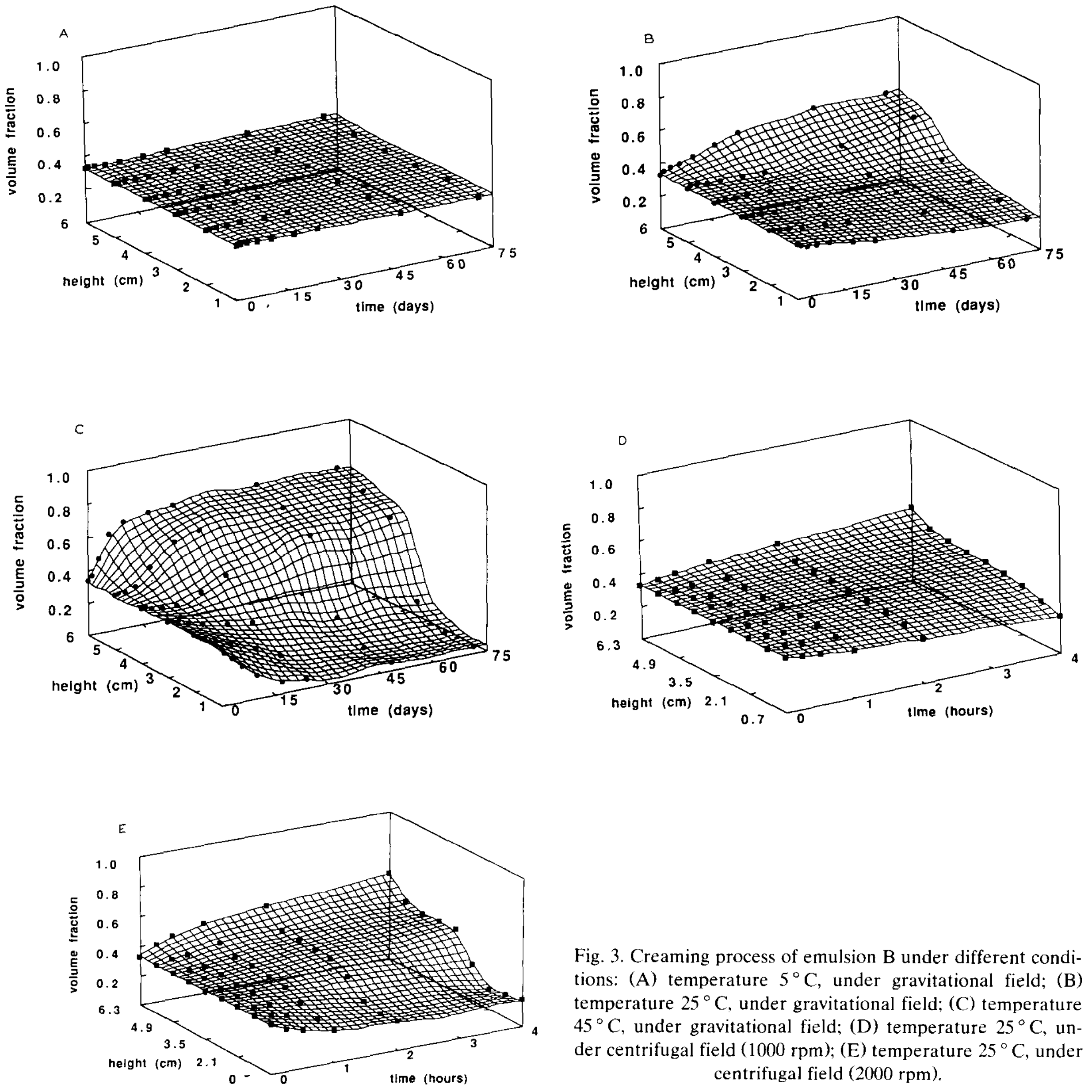

Fig. 3. Creaming process of emulsion B under different conditions: (A) temperature 5 ° C, under gravitational field; (B) temperature 25 ° C, under gravitational field; (C) temperature 45 ° C, under gravitational field; (D) temperature 25 ° C, under centrifugal field (1000 rpm); (E) temperature 25 ° C, under centrifugal field (2000 rpm).

not directly comparable. Visually, in the 1000 rpm samples, only slight changes at the bottom of the cell could be observed. In the 2000 rpm samples, the base of the emulsion began to clear optically with a very diffuse lower meniscus after 4 h centrifugation. Using the conductivity technique, creaming was detected at both speeds of rotation already after 15 min, the first measurement time.

With these few experiments the principal usefulness of the conductivity method may be illustrated. Particularly, the method may allow the phenomenological demonstration of the absence of creaming in screening experiments or quantitative stability predictions based on a kinetic analysis of the $\phi_{x,t}$ profile.

Conclusion

The dielectric model of Bruggeman (1935) was reformulated to monitor the volume fraction of the dispersed phase of sedimenting dispersions at different heights with time. The method has a large degree of model independence, only requiring a reasonable assumption of the initial volume fraction of dispersed phase. Compared with two destructive methods (Karl-Fischer, spectrophotometry) the conductivity method is capable of detecting sedimentation processes with a good accuracy, even for disperse systems of low conductivity. Due to its simple operational set-up the method is very rapid.

Although in the present study o/w emulsions were investigated, the conductivity method should principally be also applicable to aqueous suspensions to monitor settling events, as long as the conditions of Bruggeman's equation are fulfilled, i.e. spherical particles with polydispersed size distribution. For shapes other than spherical, Bruggeman's equation is generally not applicable, particularly when the particles are greatly elongated or when they contain cavities (De la Rue and Tobias, 1959).

Applications of this technique may include predictive testing of dispersions' stability and testing models relating the sedimentation behavior of dispersions to different formulation and also processing variables.

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