Effect of Manufacturing Variables on the Viscosity of Aqueous Di(Hydrogenated Tallowalkyl) Dimethyl Ammonium Chloride

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ABSTRACT

The viscosity of aqueous di(hydrogenated tallowalkyl)dimethyl ammonium chloride (DHTDMAC) dispersions is affected by manufacturing variables such as the temperature of dispersion, electrolyte content, and stirring speed. These effects are rationalized by an analogy between DHDMAC dispersions and those of phospholipids, the disperse phase of which can have a vesicular structure.

INTRODUCTION

The use of aliphatic amines and their derivatives as surfactants has grown considerably since their commercial introduction in the late nineteen thirties.

The substantivity to the surface of common materials such as cellulose, keratin, minerals and metals has generated widespread application in areas such as mineral flotation, corrosion inhibition, fertilizer anticaking, bitumen emulsification and detergency (1). The largest single application, however, is the use of di(hydrogenated tallowalkyl)dimethyl ammonium chloride (DHTDMAC) as household fabric softener. This application usually involves the addition of an aqueous dispersion of the quaternary ammonium compound to laundered fabrics during the final rinsing operation (2-4). Although other materials such as dialkyl imidazolines are sometimes used DHTDMAC has received the widest acceptance. It is usually supplied as a 75% solution in isopropanol. The world consumption of DHTDMAC for this use is currently estimated to exceed 75,000 t.p.a.

The advantages derived from the use of fabric softener have been described previously, and it is not the purpose of this paper to discuss fabric softener performance but to direct attention to an important feature of the retail dispersion, its physical appearance.

A typical domestic rinse cycle fabric softener formulation is an approximately 5-10% w/w aqueous dispersion of DHTDMAC together with color and perfume. Optical brighteners, viscosity modifiers, and dispersion aids may also be included. An important physical property of such a dispersion is its viscosity. This should be sufficiently high for easy application, but not so high as to prevent pouring from a retail container, or rapid dispersion in water.

Although DHTDMAC is practically insoluble in water, it readily forms aqueous dispersions which exhibit non-Newtonian behavior at normal use concentrations. The apparent viscosity of these dispersions can vary widely according to the choice of manufacturing conditions such as: temperature of manufacture; shear conditions during manufacture; the presence of small amounts of ionic or nonionic materials. In this paper we describe the effect of added electrolyte and of homogenization on the viscosity of aqueous DHTDMAC dispersions and postulate that the disperse phase exists as multiwalled vesicles with a considerable amount of water entrapped within the vesicle walls. The result of the work is to allow the effect of manufacturing variables to be rationalized in terms of a simple model.

EXPERIMENTAL

The DHTDMAC used for all experiments was Arquad 2HT/75, which is a 75% solution of Arquad 2HT in aqueous isopropanol. The chemical composition of Arquad 2HT is reported to be 90% DHTDMAC with minor amounts of hydrogenated tallowalkyltrimethyl ammonium chloride and tris(hydrogenated tallowalkyl) methyl ammonium chloride (5). The hydrogenated tallowalkyl chain distribution is: hexadecyl 31%; octadecyl 59%; and octadecenyl 5%.

Unless otherwise stated, aqueous dispersions were prepared by adding molten Arquad 2HT/75 (m.pt 35-45 C) to stirred distilled water at 65 C. Stirring was by an anchor stirrer driven by a constant speed motor for low shear conditions and by a Silverson laboratory homogenizer (turbine type) for high shear conditions.

Homogenization of dispersions which had been prepared under low shear conditions was conducted with a hand homogenizer (low pressure homogenization) or an APV model ISM8BA homogenizer (high pressure homogenization).

Data in Table II were obtained from experiments in which dispersions were prepared in two stages. A 10% active dispersion containing the reported sodium chloride content was prepared under low shear conditions (NaCl added to the water prior to dispersion). This dispersion was allowed to cool to room temperature and subsequently diluted to 5% by the addition of an equal volume of cooled water containing the appropriate concentration of sodium chloride.

Conductivity measurements were made at 20 C with a Rank microelectrophoresis cell using direct currents of less than 500 microamperes.

Viscosity was measured with a Brookfield RVT viscometer using a spindle speed of 100 revs. min^{-1} in all measurements in order to minimize variation due to shear thinning.

Dialysis was performed on a 7.5% active dispersion containing 0.1% sodium chloride (added to the water before dispersion of the DHTDMAC) using a Viscose-Cellulose tube (Visking).

Phase volumes were measured with a Coulter Counter, Industrial Model D. This machine allows the number of particles (Δn) of a specific volume of electrolyte to be counted. By assuming the average volume ($\overline{V}$) for these particles, the total volume in this size range $\Delta n . \overline{V}$ is calculated. By accumulating these volumes over the whole size range, the total volume of disperse phase $\Sigma\ (\Delta n)\ \overline{V}$ is obtained.

RESULTS

Temperature of Dispersion Manufacture

DHTDMAC disperses slowly in stirred hard or deionized water at room temperature to produce a highly viscous gelatinous mass. The effect of the temperature of the dispersion during manufacture on the eventual viscosity of the dispersion is shown in Fig. 1. From this it is apparent

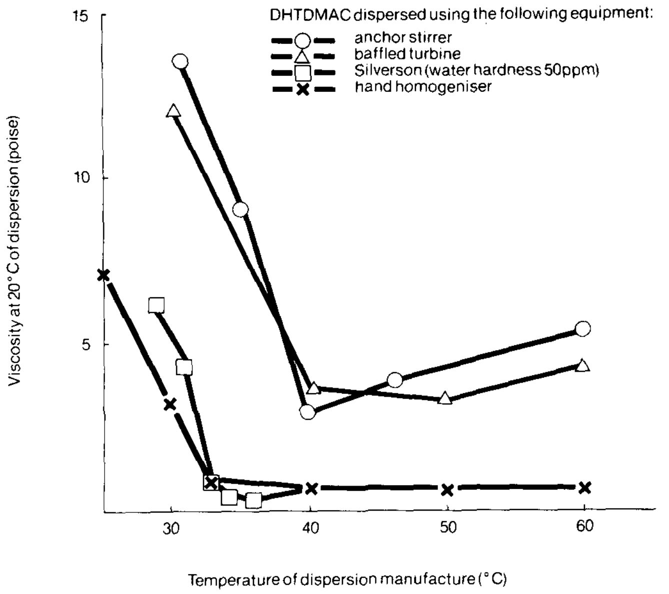

FIG. 1. Effect of Shear and Temperature of manufacture on aqueous DHTDMAC dispersion viscosity.

that a minimum viscosity is obtained from dispersion at 40 C, and that the viscosity increases rapidly as the temperature of manufacture is reduced below this value.

Shear during Dispersion Manufacture

The qualitative effect of shear during dispersion manufacture on final dispersion viscosity is shown by a comparison of dispersions prepared by (a) slow speed stirring with an anchor stirrer, (b) high speed stirring using a turbine stirrer, (c) low pressure homogenization using a hand homogenizer, (d) high pressure homogenization using a Manton-Gaulin type laboratory homogenizer. The results are summarized in Table I from which it is apparent that increased shear during dispersion manufacture at temperatures above 40 C causes decreased viscosity of the resultant dispersion. Homogenization at ambient temperature, however, leads to increased viscosity. For example, the viscosity of a dispersion prepared by low speed stirring increased from 130 cps to 630 cps following hand homogenization at 25 C.

Effect of Sodium Chloride on Dispersion Viscosity — One Stage Dispersion Preparation

The effect of low concentrations of sodium chloride is to reduce dispersion viscosity, and the magnitude of reduction is dependent on the point of salt addition during the manufacturing process. Addition of sodium chloride to a cooled 5% dispersion yielded a material which was less viscous than one prepared with an equivalent amount of salt added prior to dispersion manufacture (Fig. 2). Conductivity measurements showed that the dispersions prepared by the latter process were less conducting (Fig. 3), implying that not all of the sodium chloride was in the continuous phase.

Effect of Sodium Chloride on Dispersion Viscosity — Two Stage Dispersion Preparation

Commercially, DHTDMAC dispersions are frequently prepared in two stages. This process was simulated by preparing a 10% dispersion which was subsequently diluted to 5% with water.

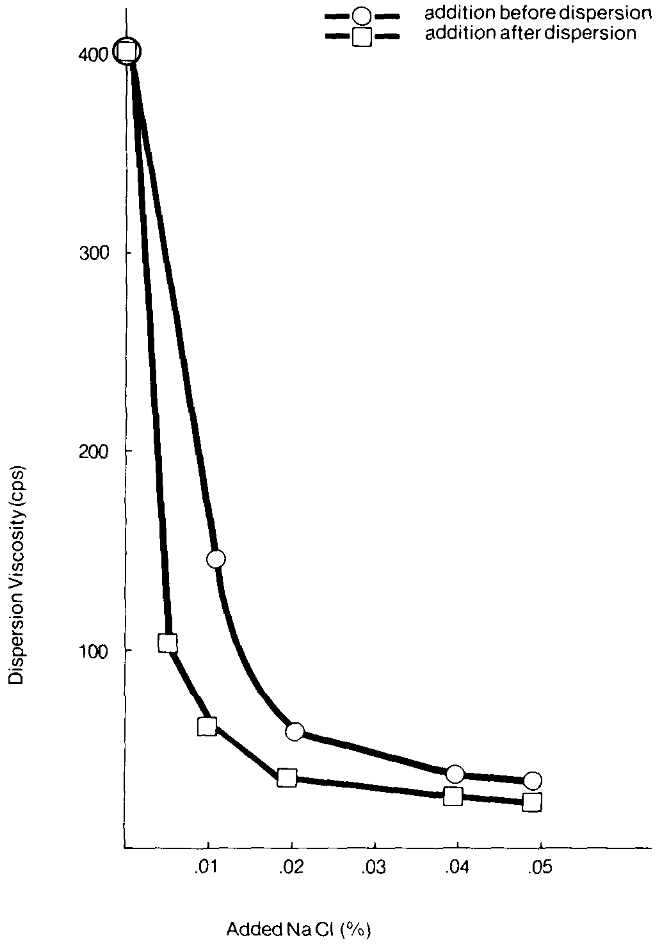

FIG. 2. Effect of added sodium chloride on aqueous DHTDMAC dispersion viscosity.

TABLE I

Effect of Shear upon the Viscosity of Aqueous DHTDMAC Dispersions

Method of Dispersion[a]	Activity %	Viscosity (cps[b])
Low speed stirring	5	670
Low speed stirring	7.5	965
Low speed stirring	10	2,420
High speed stirring (Silversun)	5	70
Hand homogenization[c]	5	44
Hand homogenization[c]	7.5	51
Hand homogenization[c]	10	190
High pressure homogenization[c]		
at 1,500p.s.i.	10	272
at 3,000p.s.i.	10	93
at 4,750p.s.i.	10	84
at 6,000p.s.i.	10	83

[a] Temperature of dispersion manufacture. = 65 C.
[b] Measured at 20 C.
[c] After premixing by low speed stirring.

Ten percent dispersions of DHTDMAC were prepared using 0.05% NaCl at 70 C. To the hot dispersion, an equal volume of cool water was added and the temperature noted. The viscosity was measured after allowing the dispersion to cool, and monitored over a period of several days. The results are illustrated in Fig. 4, which described the viscosity behavior for various dilution temperatures. Changes of viscosity with time are more pronounced when dilution occurs at low temperature, and a plot of final viscosity against dilution temperature (Fig. 5) shows a rather sharp change in behavior between 30 and 40 C. The viscosity of a sample which had been diluted at low temperature rose upon storage at ambient temperature, but subsequent heating to 60 C caused an irreversible reduction.

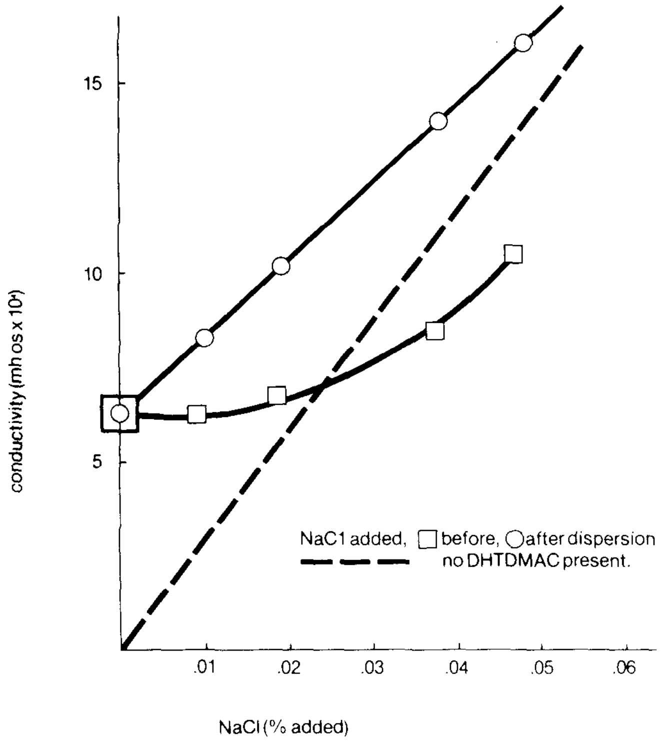

FIG. 3. Effect of added sodium chloride on DHTDMAC dispersion conductivity.

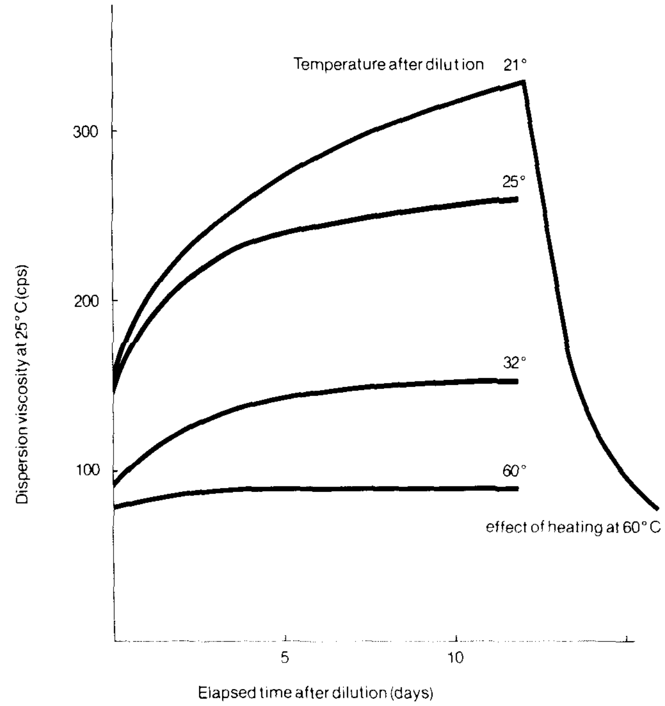

FIG. 4. Changes in the viscosity of aqueous DHTDMAC dispersions on dilution.

A second set of experiments shows the effect of changing the point of salt addition during the two stage process. Table II indicates that the greater the difference in salt concentration before dilution and after dilution the larger is the increase in viscosity on storage.

Effect of Other Additives on Dispersion Viscosity

Other additives, both electrolytes and uncharged molecules, have a similar effect on viscosity to that of sodium chloride. Figure 6 describes the effect of sodium sulphate, sodium chloride, and sucrose on the viscosity of a 5% active dispersion of DHTDMAC. In all cases the additive was added to the cold dispersion after manufacture. In Fig. 7 the same data are replotted, with concentration of the additive expressed in terms which allow a comparison of osmotic effects, i.e. gm-ions per litre for the electrolytes, gm-moles per litre for sucrose. The similar curves obtained when the concentrations are expressed in these terms are a strong support for the osmotic mechanism for viscosity reduction given in the Discussion. The reduction in viscosity caused when nonelectrolytes such as sucrose, glucose, and urea are added after dispersion manufacture is, however, temporary. After storage for one month at room temperature, the viscosity of dispersions which had been

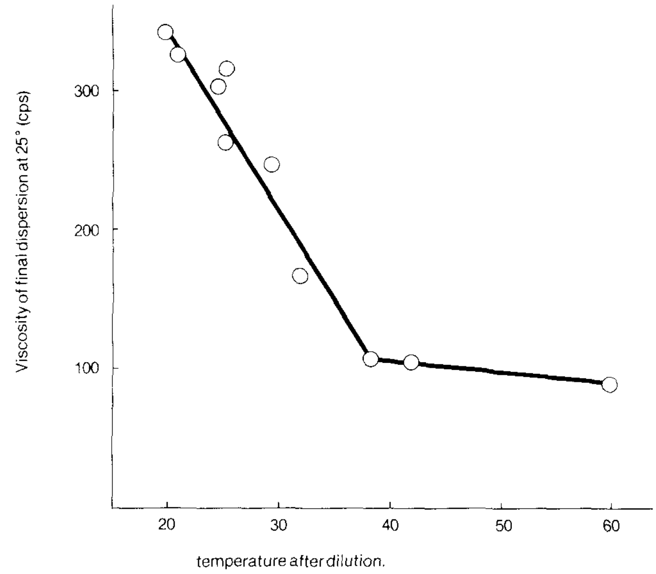

FIG. 5. Effect of dilution temperature on the final viscosity of aqueous DHTDMAC dispersions.

TABLE II

Two-stage Dispersion Manufacture: Effect of Point of Addition of Salt during Manufacture[a]

Salt content[b] before dilution w/w %	Salt content[b] after dilution w/w %	Viscosity of 5% dispersion after dilution: Immediately	After 1 day	After 2 days	After 14 days	After 21 days	After 42 days
0	0	220	320	390	585	740	790
0.02	0.010	262	490	590	790	975	1080
0.04	0.020	225	495	570	795	965	1050
0	0.005	76	81	83	112	120	128
0.02	0.015	134	164	170	222	260	256
0.04	0.025	180	252	240	328	385	372

[a] Dilution temperature 25 C; final DHTDMAC activity = 5%.
[b] Not including salt arising from the Arquad 2HT/75.

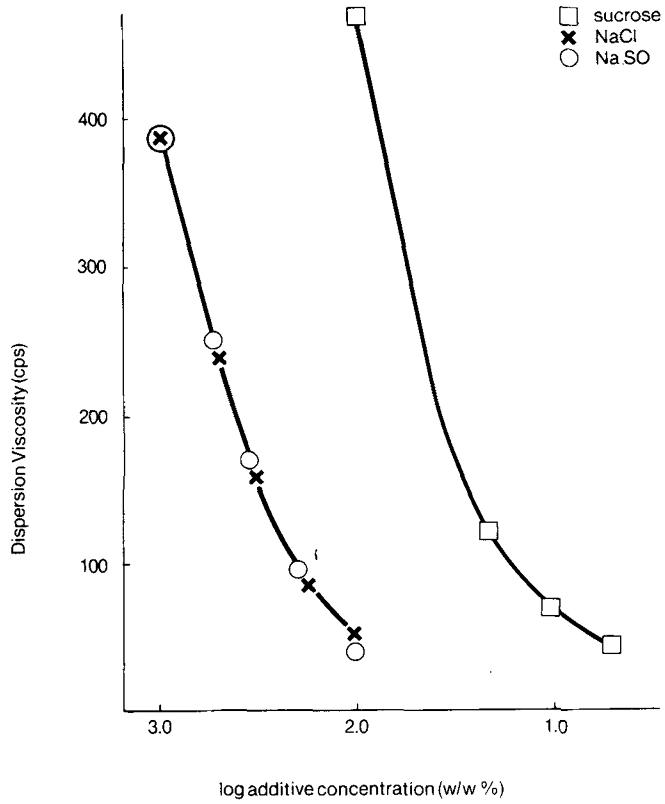

FIG. 6. Effect of additives on the viscosity of aqueous DHTDMAC dispersions.

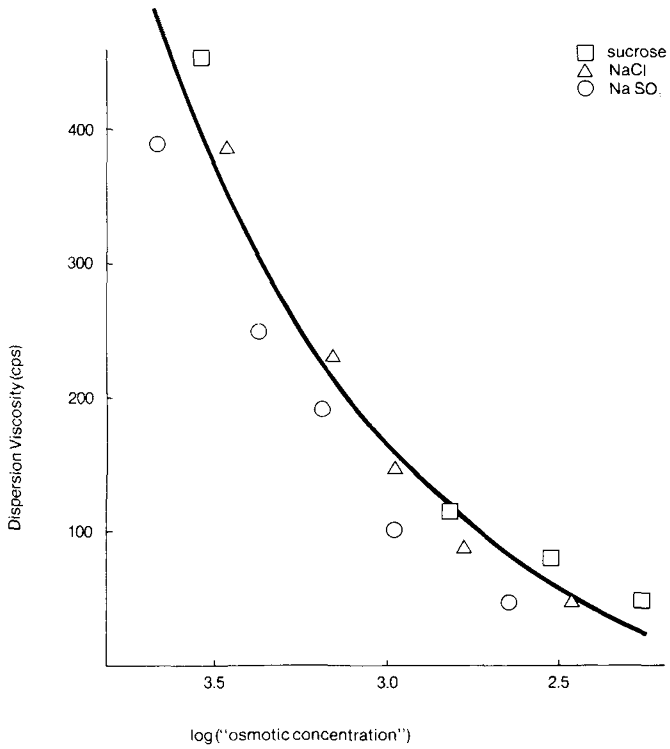

FIG. 7. Effect of additives on the viscosity of aqueous DHTDMAC dispersions, plotted so that osmotic effects can be compared (see text).

treated with nonelectrolytes rose almost to the level of untreated material, whereas dispersions treated with electrolytes still had low viscosity.

Dialysis

Dialysis is a method whereby electrolytes such as sodium chloride and small nonelectrolytes can be separated from larger molecules. Dialysis of a DHTDMAC dispersion caused a large increase in viscosity.

Phase Volume Measurement

The phase volume of the disperse phase was measured using a Coulter Counter and was found to be several times greater than the volume of DHTDMAC present. The difference between ϕ and % DHTDMAC appears to be a function of dispersion salt content (Fig. 8). There are reservations concerning this method of determining phase volume since Coulter Counter measurements are made in electrolyte solutions, but this observation gives some indication that the disperse phase volume ϕ is higher than the volume of DHTDMAC present.

DISCUSSION

The above observations can be rationalized by a model based on an analogy with phospholipid dispersions which have been extensively studied. Liquid crystalline phases of phospholipids and water occur in which lipid bilayers alternate with water layers (Fig. 9), and this structure is partially preserved in aqueous dispersions where the disperse phase consists of "multiwalled vesicles," comprised of lipid bilayer structures enclosing large amounts of water (6). We suggest that DHTDMAC dispersions contain similar structures. There are energetic grounds for supposing that surfactants with two long hydrocarbon chains may favor bilayer structures (7). Analogies drawn between phospholipid dispersions and DHTDMAC dispersions throw considerable light on the behavior of the latter, and the following is a summary of some of the former's most relevant properties.

(i). Because of the large amount of water enclosed within the bilayer structure, the true disperse phase volume is much greater than the volume of lipid and the viscosities of the dispersions are likewise higher than expected.

(ii). The viscosity of lecithin suspensions is markedly reduced by ultrasonic irradiation due to the expulsion of water from the disperse phase (8).

(iii). The spacing of the bilayers in the liquid crystaline phase varies with electrolyte concentration since it depends on the repulsion between the head groups in adjacent bilayers. Thus, the amount of enclosed water will tend to be reduced at high salt concentrations, causing a lowering of the disperse phase volume and the viscosity.

(iv). Bilayers are practically impermeable to inorganic ions below a critical temperature corrosponding to the "melting point" of the disperse phase (9).

(v). Unlike inorganic ions, water (10) is able to penetrate the bilayer so that a difference in electrolyte concentration inside and outside the disperse phase leads to osmotic swelling or shrinking of the lipid phase (11-13) with an associated increase or decrease in viscosity. A similar osmotic mechanism has been proposed to explain change in the viscosity of bitumen emulsions, the viscosity of which increases on standing as water is drawn into the bitumen phase by "trapped salts" (14).

We suggest that DHTDMAC can form similar vesicle structures to those observed for phospholipids in aqueous dispersion. The exact nature of these structures is not critical to the model. The basis of the model is that the disperse phase does not consist solely of DHTDMAC, but contains large amounts of water and electrolyte. Manufacturing variables can affect the relative amounts of DHTDMAC, water and electrolyte in the disperse phase, leading to changes in phase volume and hence viscosity. The conductivity measurements on dispersions confirm that the

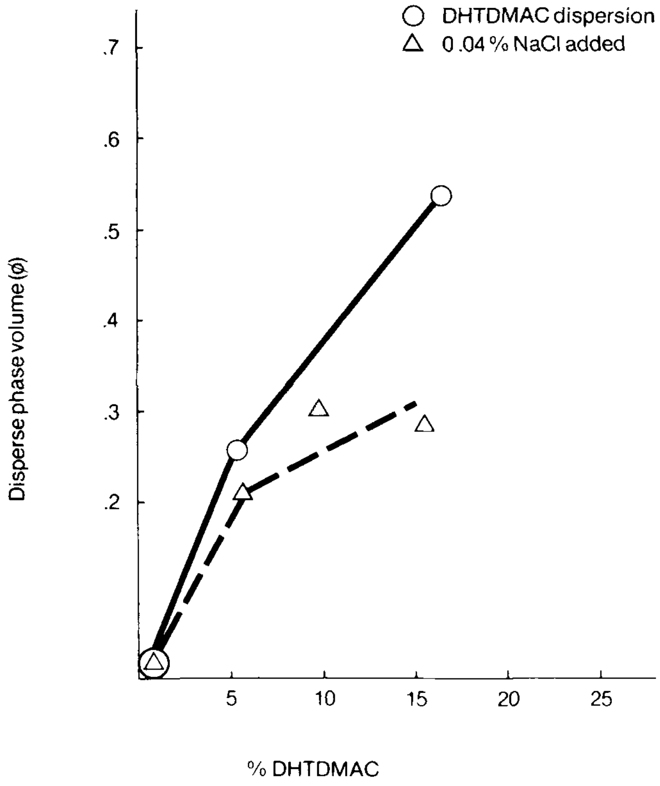

FIG. 8. Disperse Phase volumes of DHTDMAC dispersions with and without added salt.

disperse phase may entrap electrolyte. The Coulter Counter results also suggest large amounts of water in the disperse phase.

Manufacture of dispersions under high shear would be expected to reduce particle size. The associated decrease in viscosity (Table I) is not predicted by current theories relating particle size and viscosity at constant disperse phase volume (15), as has been noted previously (16). It is, however, analogous to the expulsion of water from the phospholipid vesicles by ultrasonic irradiation. Less water encapsulation associated with small particle size would give lower phase volumes at a particular DHTDMAC concentration and hence lower viscosity.

The results given in Results Section (3), (4), (5), (6) and (7) are consistent with a model where osmotic imbalance between the disperse and continuous phase can lead to swelling or shrinkage of the disperse phase due to osmotic transfer of water. Slow viscosity increases are associated with higher salt content in the disperse phase than the continuous phase (Table II). The effect of dilution temperature in two stage dispersion manufacture is consistent with a "melting-point" of DHTDMAC between 30 and 40 C. Above this temperature free exchange of both water and electrolyte is possible, leading to an equilibrated state.

An alternative explanation for the effect of electrolyte could be that changes in the double layer thickness may affect the clumping of DHTDMAC particles in the dispersion. Added elctrolyte would reduce the double layer thickness, leading to "tighter" clumps which enclose less water. This would lead to lower apparent viscosity at low shear rate where clumps move as single particles. Clumping certainly occurs in DHTDMAC dispersion, since viscosity is strongly dependent on shear rate, implying that clumps are being broken up at high shear. The reduction in viscosity caused by nonelectrolytes such as sucrose (Fig. 6 and 7) argues strongly against this mechanism, as do the temperature and dilution effects shown in Fig. 5 and Table II. If the reduction in viscosity caused by additives were primarily through an effect on the electrical double layer, sodium sulphate, with a doubly charged anion, it would have a much greater effect on viscosity of the cationic DHTDMAC emulsion than either sodium chloride or sucrose. That the viscosity reduction caused by the addition of nonelectrolytes such as sucrose is temporary whereas that which is caused by electrolytes is not, indicates that the membrane is less permeable to the latter. This is possibly due to the lower solubility of ionic materials in DHTDMAC. The results shown in Fig. 6 and 7 indicate that when additives are introduced after dispersion is complete, the resulting reduction in viscosity is due to an osmotic effect. When additives are present during dispersion, the reduction in viscosity may be due to a reduction in the double layer thickness which allows closer packing of the DHTDMAC bilayers in the surfactant mesophase.

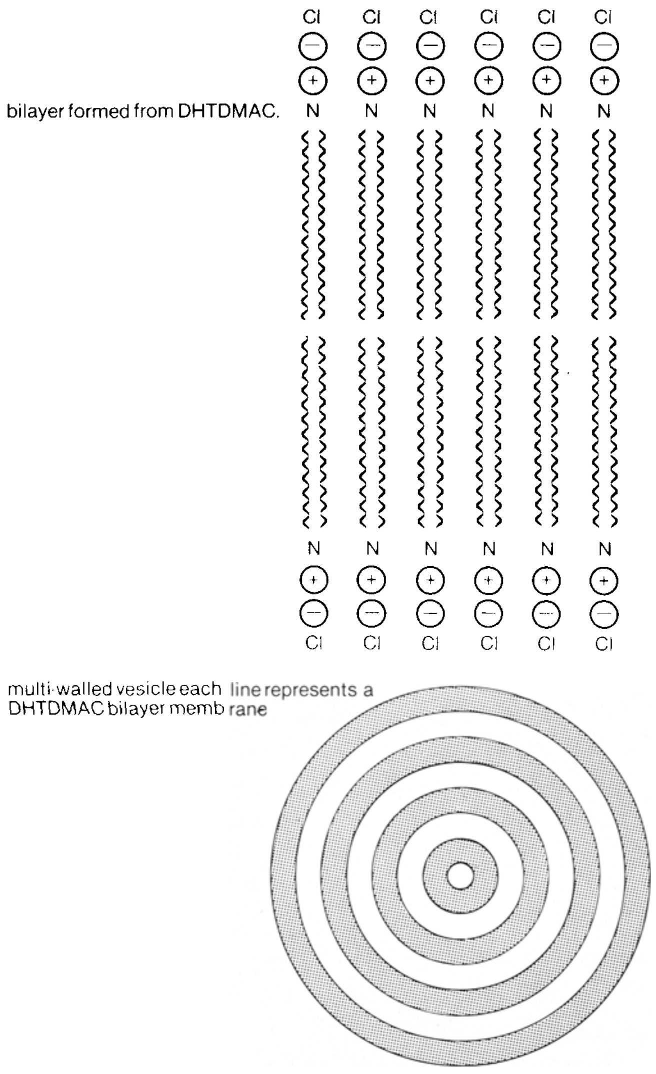

FIG. 9. Schematic representation of DHTDMAC bilayer and multiwalled vesicle.

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