A New Solution to Emulsion Liquid Membrane Problems by Non-Newtonian Conversion

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Emulsion liquid membrane separation processes remain excessively vulnerable to one or more of four major problems. Difficulties lie in developing liquid membranes that combine high levels of both stability and permeability with acceptably low levels of swelling and ease of subsequent demulsification for membrane and solute recovery. This article provides a new technique for simultaneously overcoming the first three problems, while identifying physical indications that the proposed solution may have little adverse effect on the fourth problem (demulsification) and may even alleviate it. Numerous benefits of optimized conversion of the membrane phase into suitable non-Newtonian form are identified, their mechanisms outlined, and experimental verifications provided. These include increased stability, retained (or enhanced) permeability, reduced swelling, increased internal phase volume, and increased stirrer speeds. The highly favorable responsiveness of both aliphatic and aromatic membranes to the new technique is demonstrated.

Introduction

Surfactant-stabilized emulsion liquid membrane processes constitute an emerging separation technology that has repeatedly been shown to be highly suited for such diverse separation processes as metal recovery or removal from dilute aqueous solutions (Gutknecht et al., 1986; Bart et al., 1986; Mikucki and Osseo-Asare, 1986a-c), separations in the food industry (Etuk and Murray, 1990), removal of organic bases and acids from water (Baird et al., 1987; Wang and Bunge, 1990), separation of hydrocarbons (Plucinski and Szust, 1988; Gupta et al., 1990), and pharmaceutical separations (Itoh et al., 1990; Thien et al., 1988). Some excellent recent reviews of the field include those by Frankenfeld and Li (1987), Noble and Way (1987), and Araki and Tsukube (1990).

Unsupported or emulsion liquid membrane systems are shown in Figures 1 and 2. Briefly, an aqueous phase is dispersed under high agitation as very small droplets (about 1–10 μ) in an oil phase containing a surfactant to stabilize the emulsion. The emulsion itself is then dispersed under more gentle agitation as globules (0.1–3 mm) in a third aqueous (external) phase, which contains a solute for removal into the small droplets inside the emulsion globules. This occurs across the intervening oil phase which is referred to as a liquid membrane, because of its selective barrier function. The solute concentration gradient across the membrane is maintained usually by a "trapping" reagent in the internal phase, which reacts with the solute to give a product that is insoluble in the membrane liquid. In some cases "carrier" agents are added to the membrane to solubilize the solute and facilitate its transfer across the membrane. Systems without and with carrier agents have been called Type 1 and Type 2 systems, respectively (Frankenfeld and Li, 1987).

The external phase and the emulsion are then allowed to separate, and the emulsion is broken by electrical or other means to allow recovery of the membrane phase and of the solute.

Problems and Objectives

Unfortunately, despite widespread recent activity, most such processes today remain excessively vulnerable to one or more of four major problems; this may be stated as the current inability to develop an emulsion liquid membrane with an acceptably low level of *swelling* combined with high levels of both *stability* and *permeability* and ease of subsequent *demulsification* for membrane and solute recovery (Nakashio et al., 1988).

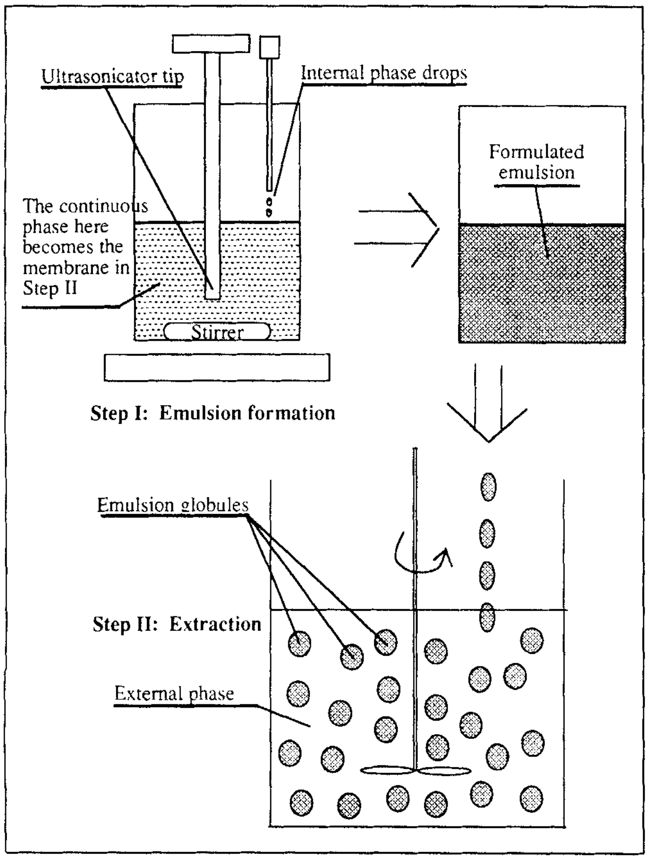

Figure 1. Experimental procedure for emulsion liquid membranes.

This article offers a solution to the first three of these problems, while existing knowledge (Hsu and Li, 1985; Nakashio et al., 1988) suggests that, in the operating range proposed, this solution may have little adverse effect upon the fourth problem (demulsification), and may even alleviate it.

An increase in volume of the emulsion globules is usually observed during the solute extraction step, due to the incorporation of some of the external phase solvent—or external phase itself—into the globules. This "swelling" constitutes a serious problem (Frankenfeld and Li, 1987; Itoh et al., 1990) because it increases the volume of emulsion to be handled, reduces the solute concentration in the swollen internal phase, increases the membrane breakage, and increases the agitation required to disperse the emulsion. Swelling mechanisms include three separate processes of external solvent permeation (osmosis) on the one hand (Itoh et al., 1990), and entrainment and secondary emulsification of this solvent on the other (Kinugasa et al., 1989). In this regard, several workers (Kinugasa et al., 1989; Tsuboi et al., 1987) have shown that substantial entrainment and secondary emulsification of the external phase solvent into the emulsion is dramatically suppressed by the presence of electrolytes in the external phase. The effect may be related to the well-known reduction in coalescence rate for droplets in agitated liquid-liquid systems caused by electrolytes dissolved in the continuous phase (Calderbank, 1967). In any event, one object of the present study is to achieve a significant reduction in the swelling problem.

A recurring stability problem has been the breakage of the membrane under the agitation conditions prevailing during the solute extraction step. This membrane instability permits leakage of the internal phase—and its acquired solute—into the external phase, thus nullifying some of the solute separation already achieved. Attempts to remedy this *either* by adding more stabilizing surfactant *or* by increasing the viscosity of the membrane phase both result in substantial reduction in solute permeability through the membrane and hence a reduction in extraction rate. This arises in the former case because of increased mechanical and adsorptive barriers to transfer at the interfaces between the membrane and the internal and external phases caused by the adsorbed extra surfactant (Garner and Skelland, 1956). Also, interfacial chemical reactions—as with the trapping reagent—are slowed down (Nakashio et al., 1988). In addition, swelling mechanisms D_2, D_3, and D_4 (described later) and Figure 6b all show that the swelling problem is made worse by merely increasing the surfactant content. Alternatively, increasing the Newtonian membrane viscosity decreases the molecular diffusivity of the solute through it, as predicted by the Eyring-Stokes-Einstein equations (Skelland, 1985). This explains the reduction in extraction rate found with increasing membrane viscosity (such as Kataoka et al., 1989). Typical of many recent pronouncements on the magnitude of this problem (Frankenfeld and Li, 1987; Noble and Way, 1987; Chan and Lee, 1987; Haggin, 1990) is the following latest assessment by Abou-Nemeh and van Peteghem (1992): "...the emulsion stability is the 'Achilles heel' of the process....the problem ...has not been solved yet, and no solution is apparent in the foreseeable future."

The difficulty was succinctly expressed by Frankenfeld and Li (1987), who reiterated the widely accepted "...need for

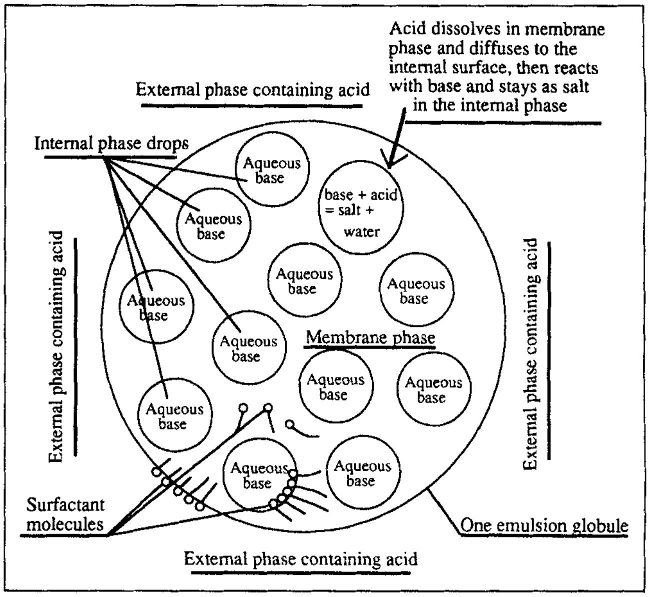

Figure 2. A single emulsion globule in the extraction of acids by emulsion liquid membranes in which the membrane phase is a hydrocarbon oil.

tradeoffs between extraction rate and emulsion stability in nearly all liquid-membrane processes." Another object of this article is to eliminate this seemingly indispensable tradeoff.

The demulsification of a water-in-oil emulsion having a given water content and specific surfactant is influenced by three physical characteristics of the emulsion, according to Hsu and Li (1985). These are the internal or disperse phase droplet size, the surfactant concentration, and the oil viscosity. They found that the ease of coalescence is a very sensitive function of droplet size and reduction in emulsion (internal) droplet size greatly reduces the ease of coalescence. Demulsification was also found to be more difficult with increasing surfactant concentration. (In this connection, Nakashio et al. (1988) explored a variety of surfactants. They showed that (a) the surfactant giving the most stable emulsion liquid membrane was also the one most easily demulsified by an electrical coalescer; (b) the structure of the hydrophilic head group in the surfactant strongly affects demulsification by an electrical coalescer; and (c) Span 80—used here—provided the second-most-easily-demulsified emulsion of the four surfactants they studied.) The coalescence of the smallest drops into larger drops, and the settling of the latter towards the oil/water coalescing interface, are both facilitated by reduction in the oil viscosity. However, according to Hsu and Li (1985), oil viscosities below about 10 cp will not notably impair the performance of an electric coalescer. For higher oil viscosities, they suggest heating the coalescer contents. The problem is considered further below.

An interesting observation was made by Nakashio et al. (1988), who found that an aliphatic (membrane) solvent, n-heptane, gives better results than an aromatic solvent, toluene, regarding the breakup and swelling of the water-in-oil emulsion. This is consistent with Kinugasa et al. (1989), who reported that a liquid membrane consisting of aliphatic hydrocarbons becomes more stable with increasing number of carbon atoms, while one consisting of toluene has very low mechanical strength. Both aliphatic and aromatic solvents were therefore selected for the present study, with the object of improving the performance of *both* types of membrane.

A Multifaceted Solution

Elimination of the tradeoff between membrane stability and permeability

The seeming inevitability of a sacrifice in membrane permeability in exchange for increasing its stability was overcome by Skelland (1993), by exploiting a 30-year-old finding in the field of non-Newtonian fluid mechanics. This is that molecular diffusivities of solutes in *dilute* polymer solutions are essentially unchanged by the substantial increase in "apparent viscosity" (Skelland, 1967) caused by small amounts of dissolved polymer. Hopper (1964), for instance, found that the "apparent viscosity" of cyclohexane increased more than a hundredfold when it contained up to 4 wt. % of dissolved polyisobutylene and yet the diffusivity of benzoic acid in these solutions differed only slightly from that in pure cyclohexane. Others (Metzner, 1965; Astarita, 1965; Ponter and Davies, 1966; Barlage, 1969) found actual *increases* in solute diffusivity in spite of increasing apparent viscosity of these non-Newtonian systems as polymer concentration increased. This remarkable contrast with Newtonian systems (a category to which previous membrane phases belonged) is accounted for in terms of facilitation of solute transport by an internal structure resulting from the dissolved polymer (Osmers and Metzner, 1972).

It will become evident that conversion of the liquid membrane into suitable non-Newtonian form by dissolution of proper amounts of an appropriate polymer will resolve several of the current problems in liquid membrane technology (Skelland, 1993).

When converting membrane phases to suitable non-Newtonian form, however, it is necessary to ensure that the polymer concentration is near or below C^*, the critical value at which interaction and overlapping of polymer molecules begin. This avoids obstruction of the diffusing solute by any significant polymer entanglement effects within the solution. A correlation of C^* in terms of known quantities for certain types of polymer solutions has been obtained by Skelland and Meng (1996).

Further benefits of appropriate non-Newtonian conversion of the membrane phase on stability, permeability, swelling, internal phase volume, stirrer speeds, and so on, may be identified as follows.

Benefits of conversion of the membrane phase into suitable non-Newtonian form

(*A*) *Stability* of the membrane against rupture or breakage during the extraction step is increased by the following three factors:

(1) The smaller droplets of internal phase obtained because of the *low* apparent viscosity of the non-Newtonian membrane during the emulsification stage (Hanna and Larson, 1985). Such low "viscosities" are brought about by the high shear rates used in emulsification, as shown in Figure 5. That such smaller drops enhance stability is indicated by Lissant (1974) and Hsu and Li (1985). They also increase the total internal interface and hence the mass-transfer rate during extraction (Hanna and Larson, 1985).

(2) The *high* apparent viscosity of the non-Newtonian membrane under the low shear rates used during the subsequent dispersion of the emulsion in the external phase, in conformity with Figure 5, provides further stability enhancement. This stabilizing effect of increased "viscosity" results from increased resistance to globule deformation and membrane breakage by pressure and shearing forces, and is in accordance with the findings of Frankenfeld et al. (1976), Yang and Rhodes (1980), Terry et al. (1982), and Calabrese et al. (1986).

(3) So-called "depletion" and "steric" forms of polymeric stabilization of the emulsion are also provided by the dissolved polymer (Heller and Pugh, 1954; Napper, 1983; Pirma, 1992).

(*B*) *Permeability* of the membrane by the transferring solute is essentially retained at its high value through the pure solvent—and may even be enhanced, in spite of the substantial increase in apparent viscosity due to the dissolved polymer at concentrations near or below C^*. This exploits the remarkable distinction between these non-Newtonian membranes and Newtonian fluids, as described earlier. Examples of such simultaneous enhancement of membrane stability with retained—or enhanced—permeability appear in Figures 10–14 and 16.

(*C*) *Transfer enhancement by surfactant reduction* follows because of the lower concentrations of stabilizing surfactant permitted by the stabilizing effects of the dissolved polymer. This not only removes some of the resistance to solute transfer across the phase interfaces offered by the adsorbed surfactant (Garner and Skelland, 1956), but also lessens the retarding effect of the surfactant on the chemical reaction rate (as with the trapping reagent) at these interfaces (Nakashio et al., 1988). Reduced surfactant is also known to promote the subsequent electrostatic demulsification (Hsu and Li, 1985).

(*D*) *Swelling* problems are reduced by a diminution in four of the following five swelling mechanisms, the first two of which were identified by Kinugasa et al. (1989) and the remaining three by Itoh et al. (1990):

(1) Entrainment of the external phase in the emulsion globules

(2) Secondary emulsification of the entrained solvent, due to excess surfactant in the primary emulsification

(3) Encapsulation of the external solvent by reversed micelles of surfactant

(4) Solvation of the surfactant by the external solvent

(5) Solvation of the transferring solute by the external solvent

The high apparent viscosity of the membrane caused by the dissolved polymer at the low shear rates prevailing during extraction will diminish the first mechanism (entrainment), while the next three must be reduced because of the lower surfactant content permitted as described under *C* above. This is exemplified by measurements of the swelling of an internal phase (aqueous NaOH) in its emulsion with a mixture of isoparaffins (Soltrol 220) containing 4% of surfactant Span 80, in an agitated external water phase in Figures 9i and 9ii. The dissolution of 2% of polybutadiene (avg. mol. wt. 940,000) in the membrane phase of Figure 9i reduced the swelling after 10 min of agitated contact plus 5 min of settling from 373.5% to 139%, that is, a 2.7-fold reduction, presumably by curtailing mechanism D_1—and hence D_2—above. Simultaneous reduction in surfactant concentration from 4% to 2% (Figure 9ii) then gave a total reduction in swelling from 373.5% to 50.2%, that is, a 7.4-fold reduction, presumably by diminishing mechanisms D_1 to D_4. Leakage rates were very low throughout, mostly below 2%/h.

(*E*) *Increased volume fraction of the internal phase* (*phi*) *in the emulsion* is made possible by the polymeric stabilization described here. This will: (1) increase the total internal interface; (2) reduce the thickness of the membrane; and (3) increase the capacity of the internal phase for transferred solute.

Items 1 and 2 above both increase the mass-transfer rate. The feasibility of this proposition is proved by Figures 9ii and 9iii, for the system outlined under *D* above. Thus in Figure 9ii, for a constant Span 80 content of only 2%, phi (vol. fraction of internal phase) of 0.2, an agitation rate of 300 rpm, and no dissolved polymer, the leakage rate was about 13%/h. This increased threefold in Figure 9iii to about 38%/h when phi was increased to 0.4. However, the latter leakage rate was then reduced to about 3%/h in Figure 9iii upon dissolution of 2% of polybutadiene (M.W. 940,000) in the oil phase, that is, a 12.7-fold reduction in leakage, and with swelling as low as 25% after 10 min of contact plus 5 min of settling.

As a separate benefit, subsequent electrostatic demulsification is known to be facilitated by increasing phi (Hsu and Li, 1985).

(*F*) *Increased agitator speeds during extraction* are permissible because of polymeric stabilization of the membrane. This increases the rate of solute transfer through the external phase (Skelland and Moeti, 1990), as well as the total surface area of the emulsion globules by reducing their size (Hong and Lee, 1985). Both factors increase the mass-transfer rate, while maintaining adequate stability, as shown by Figures 11 and 12.

Electrostatic demulsification of emulsions containing non-Newtonian membranes has not been studied. However, the following observations may be made regarding the three relevant emulsion characteristics identified earlier (Hsu and Li, 1985), namely, *internal drop size*, *surfactant concentration*, and *oil viscosity*.

The apparent viscosity of the non-Newtonian membrane phase decreases substantially under the high shear rates used for emulsification, as shown by Figure 5. This enables formation of internal phase drops that are smaller than would correspond to the higher apparent viscosity at or near zero shear rate (Hanna and Larson, 1985). However, the apparent viscosity at high shear does not fall as low as that of the solvent without dissolved polymer. The internal phase drops are accordingly still not as small as would be obtained in the absence of polymer. The effect of non-Newtonian conversion on the *internal drop size* is therefore strongly in the direction of promoting electrostatic demulsification, according to Hsu and Li (1985).

The use of non-Newtonian additives allows the *surfactant concentration* to be substantially reduced (to half or less in Figures 9i and 9ii and Figures 12 to 14). Hsu and Li (1985) contend that this also facilitates demulsification.

Some of our best results on membrane stability and transfer rates from non-Newtonian conversion were achieved with Soltrol 220 membranes containing polyisobutylene (M.W. 1.25 million) at concentrations of 0.5%, for which the membrane viscosity near zero shear rate was 10.7 cp (mPa·s) (Figure 12); and with polybutadiene (M.W. 0.94 million) at concentrations of 0.25 and 0.5%, for which the membrane viscosities near zero shear rate were 5.3 and 7.0 cp (mPa·s), respectively (Figure 13). Successful results were also obtained using toluene membranes containing polystyrene (M.W. 280,000) at concentrations of 1 and 2%, for which the membrane viscosities near zero shear rate were 1.98 and 4.17 cp (mPa·s), respectively. All of these *oil viscosities* are too low to significantly impair the performance of an electric coalescer operating at ambient temperature, according to Hsu and Li (1985).

Furthermore, item E above (increasing the volume fraction of the internal phase) has been shown by Hsu and Li (1985) to increase the recovery rate of the internal aqueous phase by electrostatic demulsification.

The effects of any "steric" or "depletive" polymeric stabilization of the emulsion (Piirma, 1992) upon electrostatic demulsification is a subject for further study, but evidently there are indications that the proposed non-Newtonian conversion may not adversely affect the problem of demulsification and might even alleviate it. Indeed, demulsification problems should be further reduced if advantage is taken of the combined effects of electric and centrifugal forces, as in the new "spinning electrostatic coalescer," developed by P. Bailes (Butcher, 1994). It should also be remembered that in some applications recovery of the membrane phase and solute are unnecessary, rendering demulsification irrelevant. This would be the case, for example, in: (a) artificial kidney applications; (b) treatment for drug overdose; and (c) the slow release of enzymes or drugs in biological systems, all of which are outlined by Frankenfeld and Li (1987).

It will be appreciated that judicious selection from among these benefits may be indicated in a given case.

Experimental Work

Materials

The aromatic membranes were made from certified A.C.S. grade toluene supplied by Fisher Scientific, and the aliphatic membranes contained Soltrol 220, an isoparaffinic oil (a mixture of C_{13}–C_{17} hydrocarbons) with a flash point of 222°F (106°C), provided by Phillips Petroleum Company. The adjustment of the viscosity in Newtonian fluid systems was achieved with addition of either S500N or S100N, both of which are neutral hydrocarbon oils—Newtonian fluids with higher viscosity, provided by Exxon Company. The physical properties of the oils used are listed in Table 1. The solute was certified A.C.S. benzoic acid (Fisher), the internal phase was 0.5N NaOH (NF/FCC from Fisher), and deionized water was used throughout. The surfactant was Span 80 (sorbitan monooleate) from Emulsion Engineering. Four different polymers were used for conversion of the membranes to non-Newtonian form, namely: polyisobutylene (PIB) EL-100 (avg. mol. wt. 1.25 million) from Exxon; polybutadiene (PBD) (avg. mol. wt. 0.94 million) from Polymer Scientific; polystyrene (LPS) (avg. mol. wt. 280,000) from Scientific Polymer Products; and polystyrene (HPS), (avg. mol. wt. 0.942 million) from Pressure Chemical. Use of these polymers was partly necessitated because the last two have inadequate solubility in Soltrol 220 (Brandrup and Immergut, 1975).

Procedures

The essential process steps when using polymer are summarized as follows:

(1) (Oil + surfactant + polymer) + low shear (high "viscosity") agitation → membrane phase.

(2) (Membrane phase + internal phase) + high shear (low "viscosity") agitation → water-in-oil emulsion.

(3) (Emulsion + external phase) + low shear agitation → globule formation + extraction.

Details are given below:

Membrane Preparation. The solutions of polymer in toluene or Soltrol 220 were prepared by dissolving small pieces while stirring. Addition of S500N and S100N could be achieved by simple mixing. The membrane phase was made by mixing the proper amount of Soltrol 220 oil, either S500N or S100N, and concentrated polymer solution, as well as Span 80. The apparent viscosity of the resulting membrane phase at or near zero shear rate was measured with a Brookfield viscometer Model RV. The internal phase was 0.5 N aqueous sodium hydroxide.

Table 1. Physical Properties of the Oils Used

Property	Soltrol 220	S100N	S500N
Boiling point, °F	450–550	~ 520	~ 620
Specific Gravity 60/60°F	0.809	0.86	0.88
Molec. Wt. (Avg.)	NA	370	500
Viscosity, cp (100°F)	3.7	36.9	197.5
Viscosity, cp (Exp., 295 K)	4.2	38.2	230

SI Conversion: °C = (°F − 32)/1.8; mPa·s = cp × 1

Emulsion Preparation. According to Frankenfeld (1992), reproducible and effective emulsion preparation is somewhat delicate—as confirmed here; it will accordingly be described in some detail. While stirring the membrane phase magnetically, the internal phase was slowly added using two fillings of a 10-mL pipet. The mixture was simultaneously emulsified with an XL-2020 Ultra-sonicator (Heat Systems, Inc.). The machines' energy output was fixed on 20% because of the use of a mini-tip, and the emulsifying program was run as "3-s-on and 2-s-off" so that the change in the emulsion temperature was not significant. Total emulsifying time was usually 5 min. The emulsion volume (total volume of membrane phase and internal phase) in every experiment was fixed at 100 mL, and it was made in a 200-mL Pyrex No. 1060 beaker. The latter was surrounded by a bath of water at 20°C to a height equal to that of the emulsion for added temperature control. The density and viscosity of the emulsion were immediately measured, the latter using a Brookfield concentric cylinder rotary viscometer, Model RV, with a UL adapter.

Extraction Equipment. The external phase (one L of water containing 500 ppm of benzoic acid) was contained for acid extraction in a cylindrical, flat-bottom, glass vessel, with a diameter of 110 mm and height of 150 mm. Four radial baffles, each 10 mm wide, were placed at 90° intervals to prevent vortex formation. A six flat-blade turbine impeller with diameter of 76.4 mm was centrally mounted in the vessel since this type of impeller showed the best dispersion performance for uniform mixing (Skelland and Lee, 1978). The experimental Agitator Model ELB (Bench Scale Equipment Company) was used to mix the liquids. The unit was equipped with a 1/4-hp (0.19-kW) drive motor, and provided an infinitely-variable output speed of 0–18 rps. The speed control was calibrated directly in rpm with a tachometer, and the extraction vessel was located in a water bath to maintain the temperature at 298 K.

For the extraction of benzoic acid, the conductance of the continuous phase was measured by an electrical conductivity cell constructed from two 7-mm-dia. glass capillary tubes 21 cm in length, both parallel and side by side, each containing 15 mm of 20-gage platinum wire exposed at one end. A glass bead was placed at the tip of the platinum wires to prevent them from moving in the turbulent flow field. The platinum wire was spot welded to a nickel-copper wire which ran the length of the capillary tube. The cell constant was determined to be 0.821/cm. The cell was connected to a conductivity meter (Model 32, Yellow Spring Instrument Co.) and the output was then recorded by a strip chart recorder (Fisher Recordall Series 5000).

Extraction Procedure. The relationship between solute concentration in the external phase and the conductance was calibrated before the study. The effect of the dispersed phase on the conductance reading of the continuous phase was allowed for by the well-known Maxwell equation (Skelland and Kanel, 1992).

After agitation was established the emulsion was poured in rapidly, and the transfer of benzoic acid out of the external phase and across the membrane in the emulsion globules was followed via the electrical conductivity cell. The leakage was followed quantitatively in separate experiments in which deionized water initially constituted the external phase. Leakage of NaOH from the internal to the external phase was determined by change in electrical conductivity of the external phase with time, in accordance with the expression:

$$L, \% = 100\,\frac{[\mathrm{NaOH}]_c V_c}{[\mathrm{NaOH}]_{io} V_{io}} \tag{1}$$

where V_c is the volume of the external (continuous) phase, considered constant; V_{io} is the initial volume of the internal phase; $[\mathrm{NaOH}]_c$ is the molar concentration in the continuous phase; and $[\mathrm{NaOH}]_{io}$ is the initial molar concentration in the internal phase.

Swelling of the emulsion was determined after 10 min of agitated contact with the external phase, followed by 5 min of undisturbed disengagement of the emulsion globules from the external phase by settling. This required measurement of the emulsion density at the end of settling, for use with the emulsion density measured before dispersion, using an expression for swelling corrected for leakage, derived and summarized later below.

Results

Emulsion and membrane viscosities

Boyadzhiev and Elenkov (1966) and Skelland and Kanel (1992b) have shown that at the low volume ratios of disperse (emulsion) phase to continuous phase used here the dominant transfer mechanism occurs during free travel of the drops (globules) around the vessel, and not during drop breakage or coalescence. However, during such free travel of the globules, their interior is essentially stagnant because of the combination of high interfacial tension between the organic membrane and the surrounding aqueous phase, the high concentration of surfactant in the membrane, and the small size of the globules (Garner and Skelland, 1956; Davies and Rideal, 1963; Skelland and Moeti, 1990; Skelland and Kanel, 1992b; Skelland, 1992). This is consistent with many mathematical modelings of the process, which invariably analyze only the motionless, unsheared interior of each globule (Ho et al., 1982; Bunge and Noble, 1984; Lorbach and Hatton, 1988). For this reason, the higher membrane and emulsion "viscosities" exhibited as shear rates within the globules approach zero are of special interest during the extraction stage. These result in stabilized membranes *without* loss of permeability due to the non-Newtonian benefits described earlier.

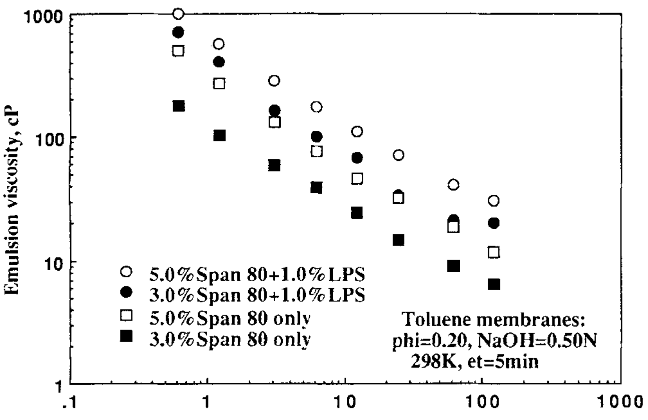

Figure 3. Viscosity of toluene emulsions vs. shear rate.

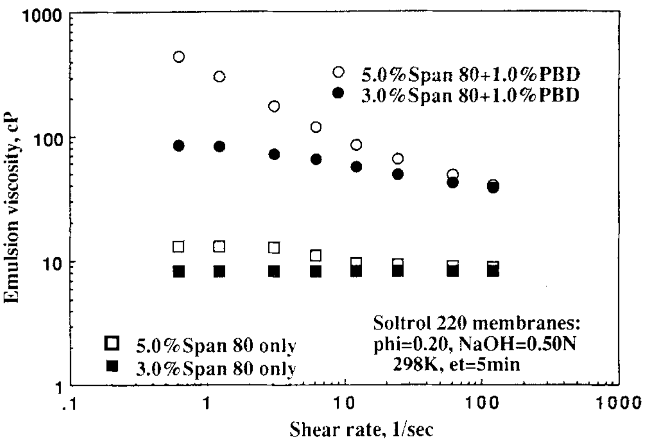

Figure 4. Viscosity of Soltrol 220 emulsions vs. shear rate.

Accordingly, the non-Newtonian character and higher apparent viscosities of the emulsions in the lower ranges of shear rate are presented in Figures 3 and 4. In contrast, the transformation of membrane viscosities to much lower values at the high shear rates generated by the ultrasonicator during emulsification are illustrated by Figure 5.

The emulsions consisted of an aqueous NaOH solution dispersed in oil containing surfactant with or without polymer; their viscosities were measured in a concentric cylinder viscometer over the shear rate range of 0.6 to 120 s^{-1}. The toluene-based emulsions show substantial non-Newtonian behavior even in the absence of dissolved polymer, in contrast to the emulsions based on Soltrol 220. The former emulsions exhibit much higher viscosities at very low shear rates than those seen in the Soltrol emulsions when polymer is absent. This difference between the two emulsions evidently diminishes greatly in the presence of dissolved polymer.

The membrane component Soltrol 220 is Newtonian and has a viscosity of 4.2 cp at 295 K. Addition of about 3% of PIB increased its apparent viscosity at (or near) zero shear rate by about 200-fold. Comparable results were obtained with PBD. The increase in viscosity resulting from blending with Newtonian oils S500N or S100N, however, was more gradual with increase in concentration. The fact that the apparent viscosities of our non-Newtonian membranes will diminish greatly under the high shear rates produced by the XL-2020 ultrasonicator is clear from Figure 5. This shows flow curves for some of the membrane phases (Soltrol 220 plus additives), as obtained from Bueche's equation (Bueche, 1954; Middleman, 1968, pp. 147, 178). The Middleman reference shows characteristics for PBD solutions that are comparable to those for PIB, where Bueche's equation was in reasonable agreement with the relevant data.

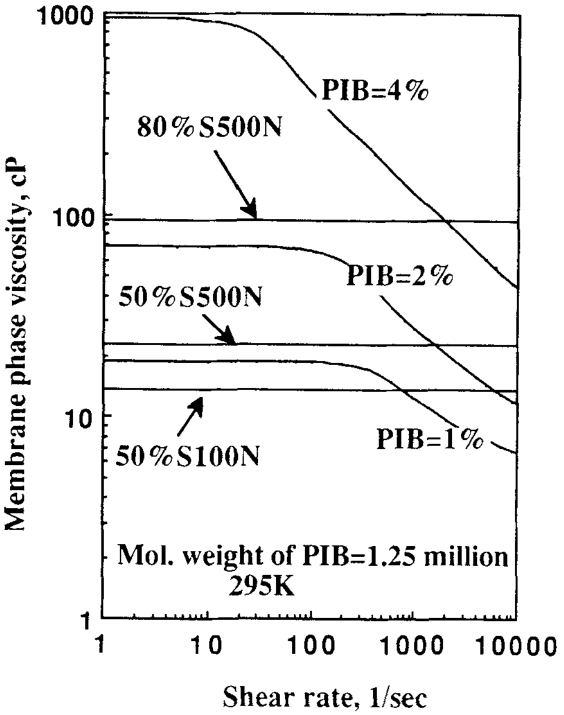

Figure 5. Effect of shear rate on viscosity of Soltrol 220 solutions containing Newtonian (S100N and S500N) and non-Newtonian (PIB) additives, obtained from Bueche's equation.

Stability enhancement and swelling reduction resulting from non-Newtonian conversion of the membranes

Takahashi et al. (1981) showed that membrane *stability* increased (that is, leakage rate decreased) with increasing concentration—up to 2%—of Span 80; Figure 6a shows a similar effect, but up to 3% of Span 80, for both the toluene and Soltrol 220 membranes in the absence of any added polymer. However, the membrane with toluene is clearly substantially weaker (that is, has a higher leakage rate) than that made with Soltrol 220 at all surfactant concentrations; furthermore, the optimum concentration of Span 80 for minimum leakage rate lies in the narrow range of 3–4%, after which leakage rates increase substantially again. This contrasts with the Soltrol 220 membrane, for which leakage rates continue to decrease slightly, up to at least 6% of surfactant. The surfactant concentration is therefore less crucial for successful operation with the Soltrol membrane. Figure 6b shows the *swelling* of the emulsion after ten minutes of continuous agitation, followed by five minutes of settling to separate the emulsion from the external phase. The ordinate represents the percentage swelling of the emulsion, corrected for leakage, as developed in the Appendix in the following expression:

$$S, \% = 100\,\frac{(\phi_{10}-\phi_0)}{(1-\phi_{10})\phi_0} + L_{10}\% \tag{2}$$

where $L_{10}\%$ is the percentage of internal phase leaked in 10 min of agitated contact. The volume fraction of internal phase in the emulsion ϕ is obtained as (Appendix):

$$\phi = \frac{\rho_e - \rho_{\text{oil}}}{\rho_{\text{aq}} - \rho_{\text{oil}}} \tag{3}$$

The quantities ϕ_0 & ϕ_{10} in Eq. 2 denote ϕ before emulsion dispersion, and after ten minutes of agitated contact plus settling, respectively. The symbols ρ_e, ρ_{aq}, and ρ_{oil} represent the densities of the emulsion, the aqueous internal phase, and the organic membrane phase; ρ_e was measured before emulsion dispersion (to obtain ϕ_0), and after five minutes of settling from the external phase following ten minutes of agitated contact (to obtain ϕ_{10}).

Figure 6b shows substantial increase in swelling for surfactant concentrations beyond 3%, presumably due to mechanisms D_2, D_3, and D_4 described earlier. With regard to the higher swelling exhibited throughout by the toluene membrane, this perhaps results from greater entrainment of external phase by the less viscous toluene membrane during dispersion, followed by reduced disengagement of entrained water from the emulsion during subsequent settling, because of the much greater toluene-emulsion viscosity at low- or zero-shear rate (Figures 3 and 4).

When one percent of polymer (polystyrene of M.W. 280,000) is dissolved in the toluene membrane, the improvements in both leakage rate and swelling are evident from Fig-

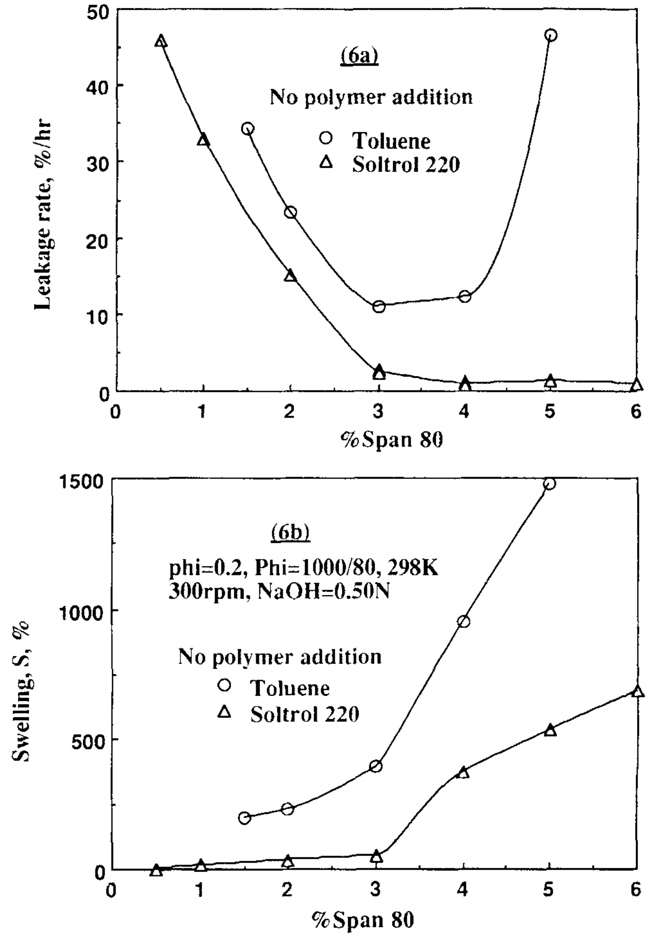

Figure 6. Comparison between leakage and swelling performances of toluene and Soltrol 220 membranes without polymer.

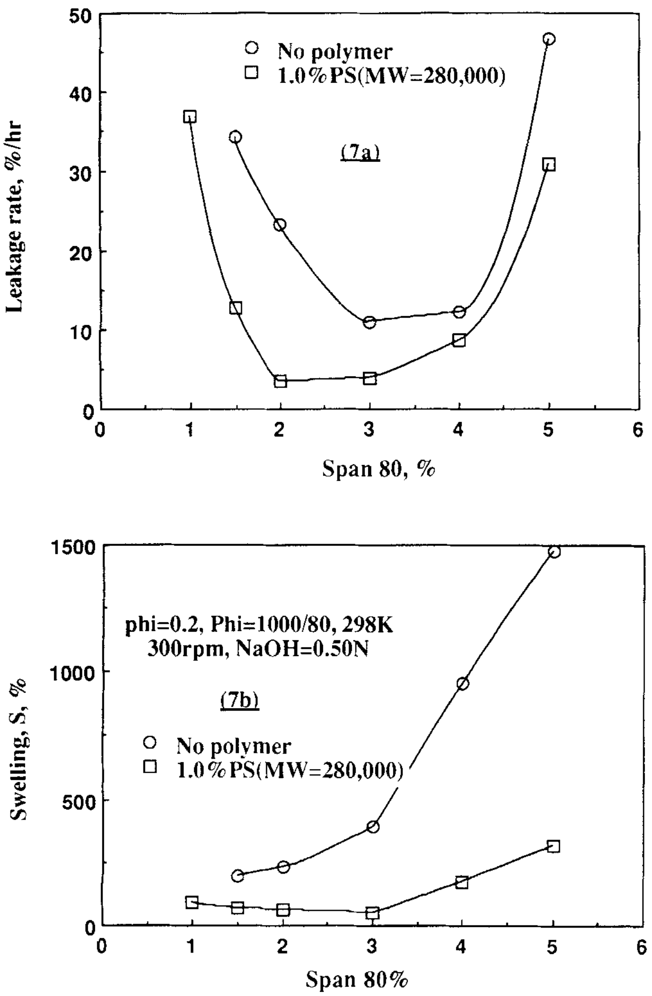

Figure 7. Effects of polymer addition on the leakage and swelling performances of toluene membranes.

ures 7a and 7b. The optimum range of surfactant concentration for minimum leakage rate is now extended *down* to 2%; the reduction in membrane stability (increased leakage rate) at surfactant concentrations above 4% is probably a consequence of the increased swelling by the mechanisms detailed earlier.

The stability (leakage rate) and swelling (after 10 min of agitated contact followed by 5 min of settling) for the toluene-based and Soltrol-based membranes, each containing 1% of their respective polymers, are compared in Figures 8a and 8b.

The corresponding plots in the absence of dissolved polymer are Figures 6a and 6b; comparison reveals substantial reductions in both leakage and swelling due to polymer addition. For the weaker (toluene) membrane, the optimum concentration range of surfactant, Span 80, for minimum leakage rate is extended *down* to 2%. Furthermore, within this optimum range (2–3.5%) the leakage performance of the toluene and Soltrol membranes become comparable.

When the swelling % is compared with the leakage rate for each membrane, first as a function of % Span 80 (Figures 6–8) and then as a function of % PBD (Figure 9), we note that a high leakage rate usually accompanies a low swelling percentage for these systems and vice versa for surfactant concentrations below about 3 or 4 %. This is consistent with the observation of Kinugasa (1989) and Tsuboi (1987) that electrolytes in the continuous phase suppress entrainment and secondary emulsification of the continuous phase solvent. Consider Figure 9ii, for example. For zero PBD and Span 80 of only 2%, the membrane has poor stability and therefore a fairly high leakage rate. This deposits NaOH (a strong electrolyte) into the continuous phase adjacent to the globules, with consequent suppression of entrainment and low swelling percentage. At higher PBD (0.5%, apparent viscosity increase from 4.2 to 7 cp), the membrane is more stable, leakage is therefore reduced, so NaOH deposition in the continuous phase is now slight. Entrainment is accordingly not suppressed, and the swelling percentage is thus greater. With continued increase in PBD the increased apparent viscosity of the membrane reduces the entrainment so that swelling decreases.

In Figure 9i the *high* Span 80 content gives a stable membrane with low leakage, despite the absence of polymer. Swelling is high (373.5%) due to both entrainment and increased permeation of the membrane by external water associated with the water-carrying Span 80 via hydration and perhaps reverse micelles. Addition of 2% PBD reduces the swelling to 139%. Next, halving the amount of Span 80 (to

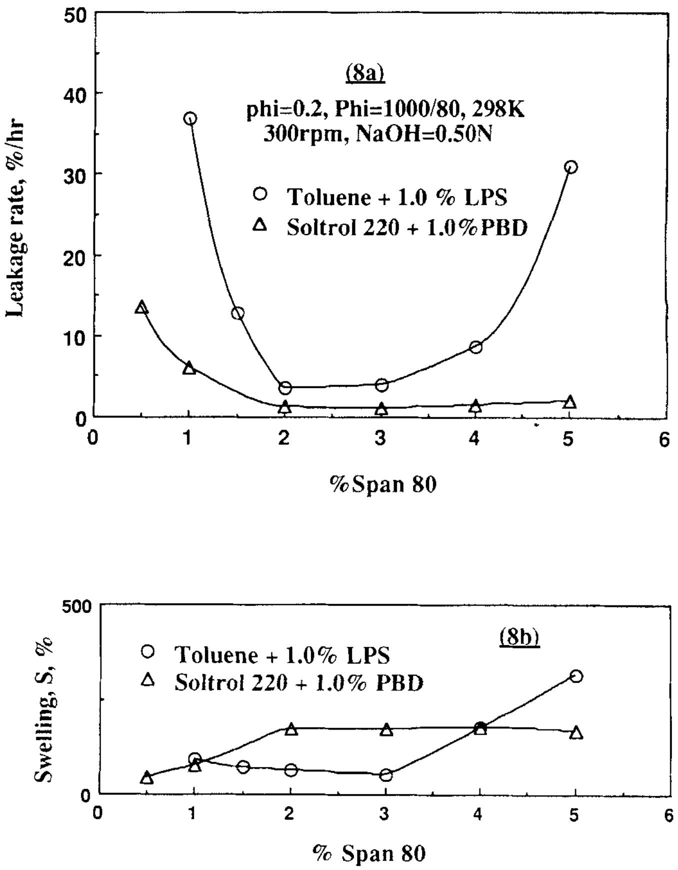

Figure 8. Comparison between leakage and swelling performances of toluene and Soltrol 220 membranes containing dissolved polymer.

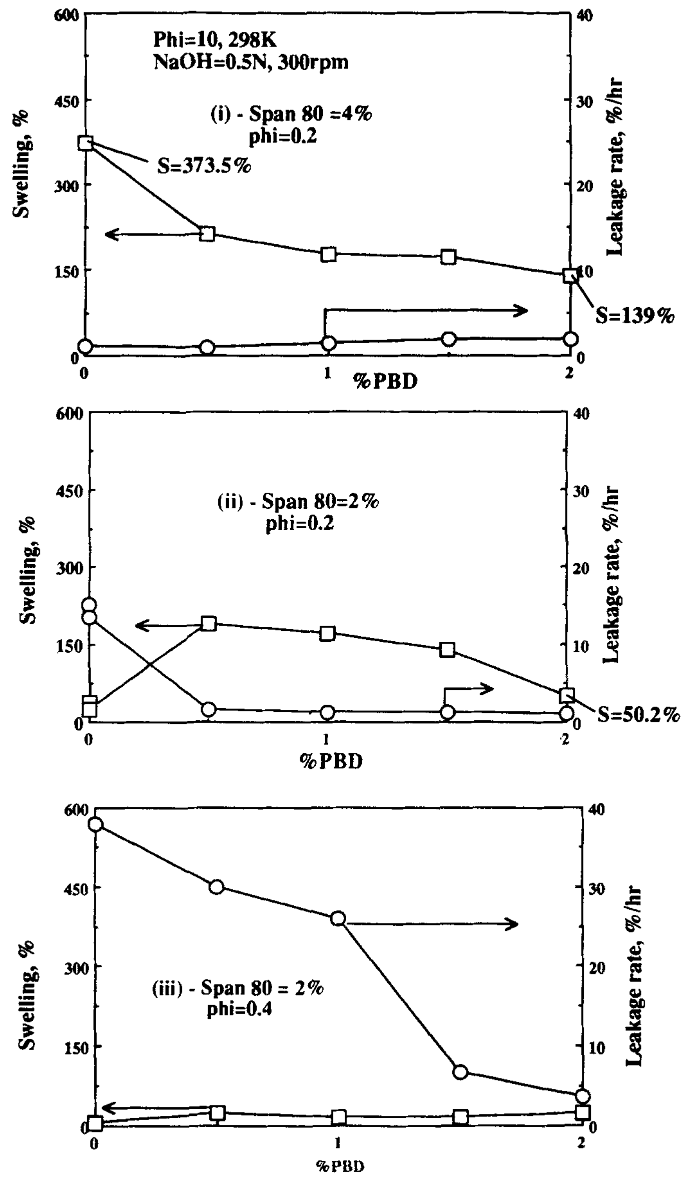

Figure 9. Interacting effects of polymer, surfactant, and volume fraction of internal phase (phi) on swelling and leakage in Soltrol 220 membranes.

2% in Figure 9ii, as permitted by the added 2% PBD) reduces the swelling further to 50.2%, for a total swelling reduction (from 373.5 to 50.2%) of about 7.4-fold. Leakage rates were less than 2% per hour throughout.

In Figure 9iii the high volume fraction of internal phase (phi = 0.4) and moderate Span 80 concentration of 2% result in a process dominated by leakage—$(V_{io} - V_{i10}) \rightarrow V_{L10}$—at the lowest PBD concentrations. Dramatic (12.7-fold) reduction in leakage rate is seen (from 38 to 3%/h) as PBD increases to 2%. Swelling does not exceed 25% throughout.

Extraction enhancement resulting from non-Newtonian conversion of the membranes

In all data presented in this section, the internal phase was 0.5N NaOH in water, and the external phase was water containing 500 ppm benzoic acid. The internal phase constituted 0.2 volume fraction (phi) of the emulsion, while the ratio of external phase to emulsion (Phi) was 1,000 mL/80 mL. Surfactant (Span 80) was 2, 4 or 5% of the membrane phase, and such concentrations including those of the polymer are expressed in percentage of weight in volume (thus, 1% signifies 1 g in 100 mL). All the extraction results are presented in graphs of C_t/C_o vs. appropriate parameters, notably time of agitated contact *t or* polymer concentration. C_t and C_o are solute (benzoic acid) concentrations in the external phase at time *t* and time zero, respectively. Better extraction corresponds to lower C_t/C_o. For purposes of comparison, the rate of solute transfer out of the external phase at a given time may be represented by the slope, $d(C_t/C_o)/d(\text{time})$, of the relevant curve. Faster extraction corresponds to a greater negative slope.

The concentration driving force causing extraction decreases with declining solute content in the external phase C_t so that the rate of extraction falls with time. Eventually, the rate of solute removal by extraction equals its rate of return (now as nonextractable salt) to the external phase by leakage, corresponding to a minimum in the plot of C_t/C_o vs. time. Beyond this point, continued decline in the concentration driving force causes the rate of return of solute to the external phase by leakage to exceed its rate of removal by extraction, so that the curve rises with increase in time. The effect has been dramatized at very low solute concentrations C_t by the use of semilogarithmic coordinates in Figures 10 and 11.

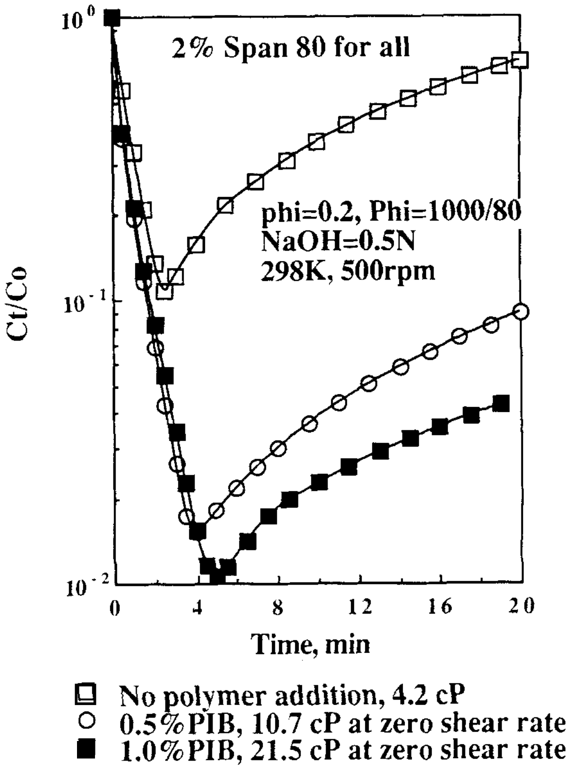

Figure 10. Enhanced benzoic acid extraction by Soltrol 220 membranes containing 2% Span 80 in which apparent viscosities are increased by PIB addition as shown.

High agitation = 500 rpm.

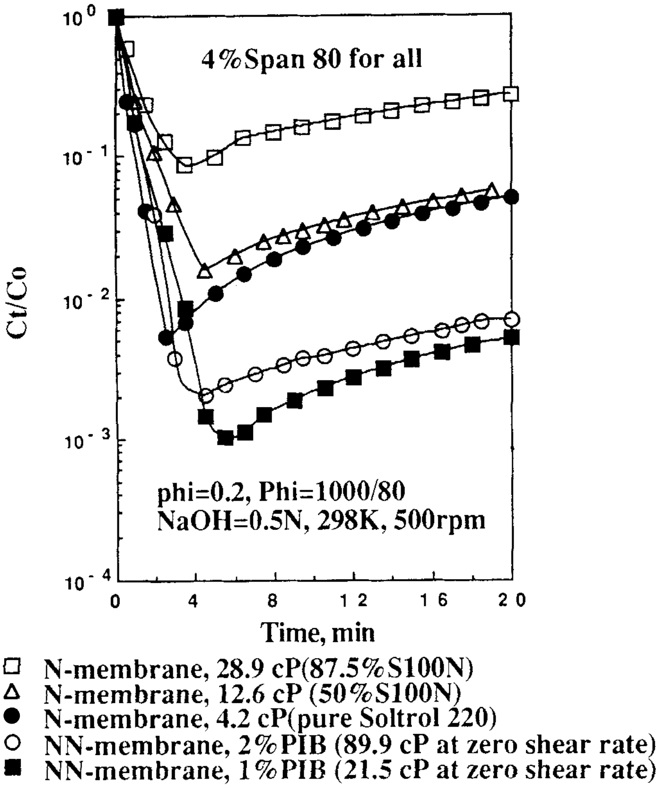

Figure 11. Benzoic acid extraction with different Soltrol 220 membranes and increased surfactant.

High agitation = 500 rpm.

With 2% Span 80 in the Soltrol 220 and under somewhat high agitation of 500 rpm, improvement of the membrane stability was achieved by non-Newtonian membranes with only a small amount of PIB, as illustrated in Figure 10. Without PIB, the traditional Newtonian membrane made of Soltrol 220 with 2% Span 80 extracts for only a few minutes and then the residual concentration of the acid in the external phase increases because of high leakage of the membrane. For example from the 3rd to the 20th min, about 60% of the initial acid in the feed phase that had been extracted leaked back into the feed phase; it had been transformed into salt which is insoluble in the membrane and so could not be extracted again. This indicates that the long-term extraction efficiency with such a traditional Newtonian membrane was low and not of industrial importance. In contrast, the non-Newtonian membranes with 0.5 or 1.0% PIB provided much better performance. The residual concentration of the solute in the external phase after 4 min of phase contact was about an order of magnitude lower than that achieved with a traditional membrane. At the same time, the mass-transfer rate in the first few minutes of extraction does not show any decrease even though the consistency of the membrane (as seen from the apparent viscosity) has increased up to 5-fold. As a matter of fact, the addition of PIB also increases the overall mass-transfer rate, as indicated by the increased negative value of $d(C_t/C_o)/d$(time).

Extractions were next carried out at 4% Span 80 under the same conditions as above, including the rather high agitation rate of 500 rpm. Comparison between the top three curves of C_t/C_o vs. time in Figure 11 for the Newtonian membranes and the bottom two curves for the non-Newtonian membranes consisting of 1 or 2% of PIB in the same Soltrol 220 shows minor or no reduction in extraction rate in the latter case, despite the much higher apparent viscosity caused by the dissolved PIB (from 4.2 to 89.9 cp, a 20-fold increase). The enhancement in membrane stability arising from the non-Newtonian conversion yields a residual acid concentration that is about an order of magnitude smaller than that for the purely Newtonian membrane at contact times beyond 4 min. This corresponds to an acid removal with such non-Newtonian membranes of the order of 99.9% after only 4–5 min of contact. The excessive use of the Newtonian additive S100N in the top two curves of Figure 11 has apparently increased the (constant) viscosities of these *Newtonian* membranes beyond the range in which stability is enhanced (Terry et al., 1982), and into the range in which the drop size of the internal phase formed during emulsification is too large (Hanna and Larson, 1985). This now results in reduced stability of the emulsion (Lissant, 1974; Hsu and Li, 1985), as evident from Figure 11. The transfer rate (dC_t/d time) is also retarded. In contrast, the enhanced dispersion of the internal phase during emulsification, resulting from dramatic reduction in apparent viscosity at high, ultrasonicating shear rates (Figure 5), yields the increased stability shown by the bottom two *non-Newtonian* curves of Figure 11. (The apparent viscosities in the latter case, of course, return to the high, stabilizing values indicated in the figure at the more gentle shearing conditions prevailing during the extraction stage, in accordance with Figure 5.)

Under the less severe agitation of 250 rpm, the effects of PIB and PBD were found to be similar as in Figures 12 and 13. The composition of the non-Newtonian membranes, however, requires a proper amount of polymer. As can be seen from Figure 12, some sort of entanglement effects become important if too much polymer is used and the diffusivity and mass-transfer rate are then significantly reduced. The effect is even clearer in Figure 13 from the curve for 1.87% PBD.

A liquid membrane containing a much higher concentration of low molecular weight copolymer in Soltrol 220 was also tried for benzoic acid extraction. (The copolymer was ethylene-vinyl acetate (EVA) of molecular weight 2,000, containing 37% by weight of vinyl acetate, supplied by Exxon.) The polar nature of one of the repeat units in this copolymer renders it surface active, so that this polymeric surfactant (Pirma, 1992) was used without Span 80. Figure 14 compares the relative ineffectiveness of this membrane with the bottom two curves for some of the formulations based on Soltrol 220 prescribed in this study, both at room temperature. The much higher concentration of low molecular weight EVA may have resulted in the formation of a significantly obstructive network within the membrane oil, so that the mass-transfer rate was substantially reduced. The results in Figure 14 demonstrate that the new formulation (bottom two curves) is different from that using this EVA, in that the formation of any obstructive polymer network (entanglements) in the membrane is slight. This is because a sufficiently dilute solution of high molecular weight polymer was used (Figures 17 and 18). The result, according to Figure 14, was improved membrane stability and mass-transfer rate. In short, Figure 14 suggests that, in the present context, "high" concentrations of low

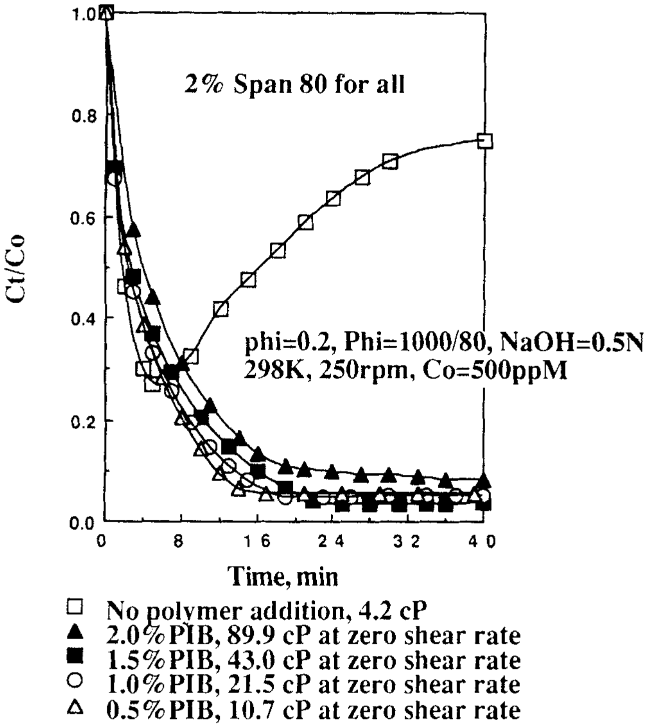

Figure 12. Effect of PIB concentration on benzoic acid extraction with Soltrol 220 membranes and 2% Span 80.

Lower agitation = 250 rpm.

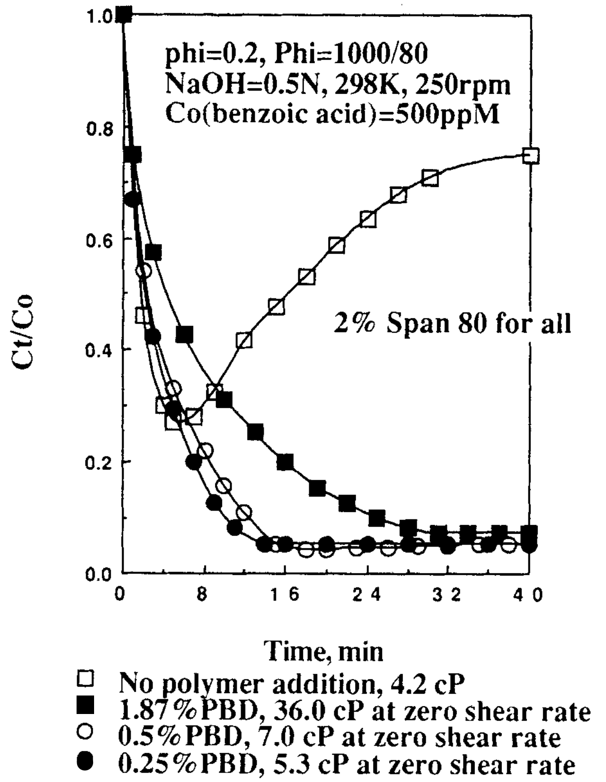

Figure 13. Effect of PBD concentration on benzoic acid extraction with Soltrol 220 membranes and 2% Span 80.

Lower agitation = 250 rpm.

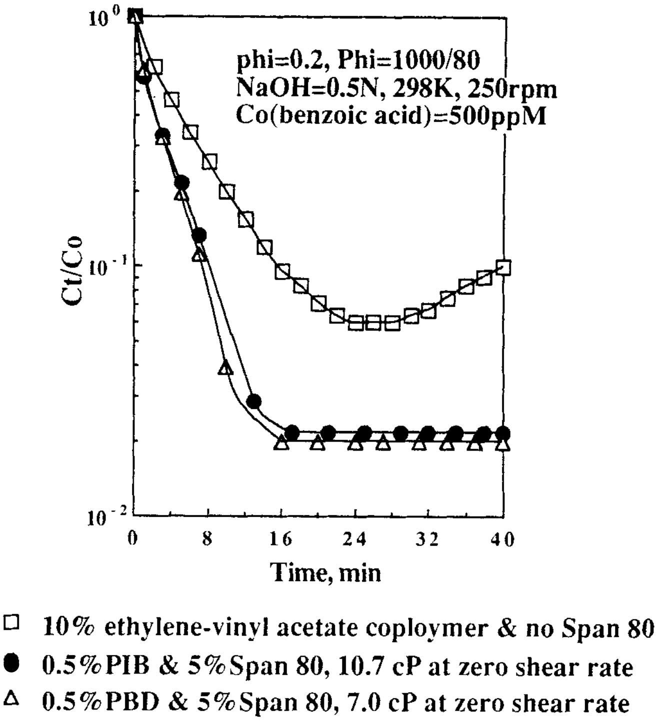

Figure 14. Comparison of a membrane containing a surface active copolymer (EVA) of low molecular weight (2,000) and high concentration (10%) with the new membrane containing nonsurface active polymers of high molecular weight and low concentration (0.5%).

molecular weight polymer are not equivalent to "low" concentrations of high molecular weight polymer.

Figure 15 compares the performance of the toluene and Soltrol-based membranes in the absence of dissolved polymer. In the early stages of the process, the rate of extraction is greater (that is, the slope is steeper) for the less viscous toluene membrane. As the duration of agitated contact increases, however, both membranes tend to leak the internal phase, thus returning the solute to the external phase. The two curves cross at t of about 15 min, so that the solute concentration in the external phase at greater times is higher for the toluene membrane.

The benefits of dissolving one percent of the appropriate polymer in each of the membranes is apparent in Figure 16. The effect on extraction rate in the earlier stages of the process is slight, as shown by the negligible change in $d(C_t/C_o)/d(\text{time})$ for the respective curves in Figures 15 and 16. The substantial increase in stability is shown after 20 min of agitated contact by the reduction in C_t/C_o from around 0.6 in the absence of polymer (Figure 15) to 0.05 for the Soltrol membrane with PIB, 0.11 for the toluene membrane with HPS, and 0.16 for the toluene membrane with LPS (Figure 16). Furthermore, the Soltrol plot remains steadily horizontal as t increases, whereas the weaker toluene membrane is showing somewhat increasing leakage with increasing t. The latter is nevertheless substantially improved by this small polymer addition, and to a greater degree by the HPS than by the LPS.

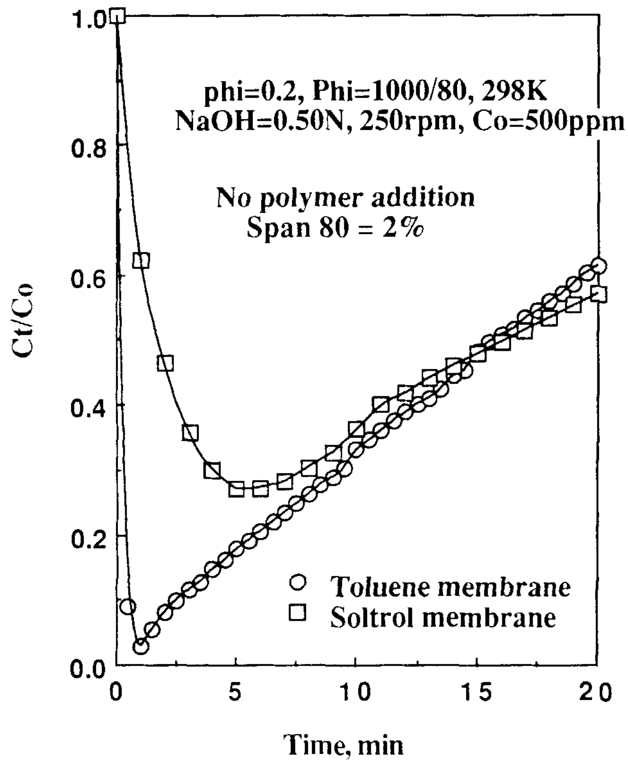

Figure 15. Comparison between benzoic acid extraction with toluene and Soltrol 220 membranes without polymer and with 2% Span 80.

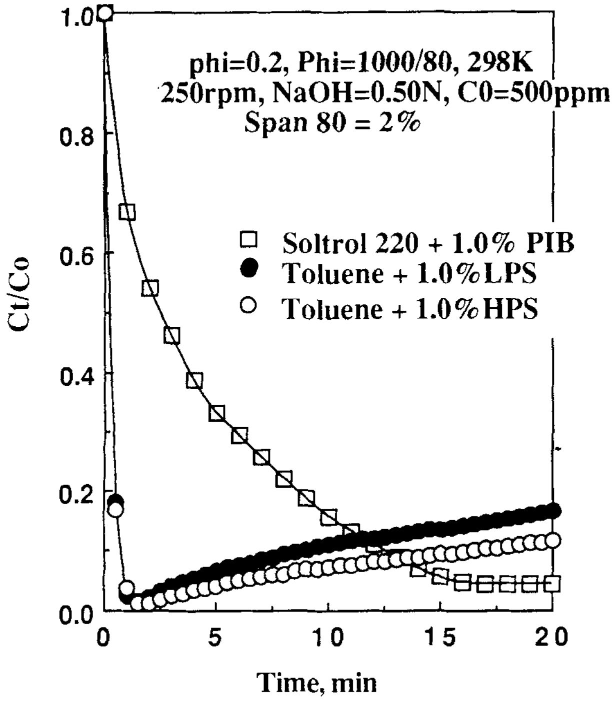

Figure 16. Comparison between benzoic acid extraction with toluene and Soltrol 220 membranes containing dissolved polymer and with 2% Span 80.

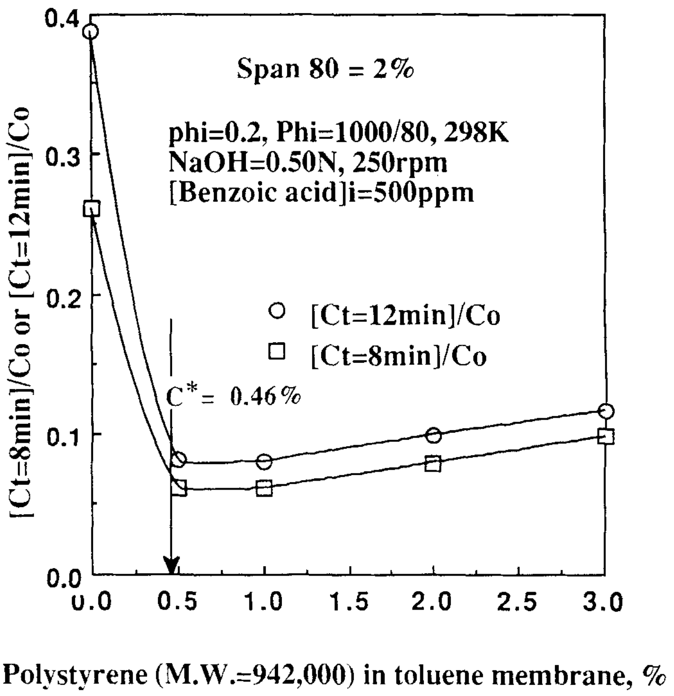

Figure 17. Optimum polymer concentration for minimum residual solute concentration in the external phase C_t at a given time t for toluene membranes.

Optimizing the non-Newtonian conversion

In view of the significance of the critical polymer concentration C^* identified earlier, further experiments were performed in which the polymer concentration was varied over the range 0–3%. The results appear in Figures 17 and 18 for the toluene and Soltrol membranes, respectively, where t was arbitrarily selected as 8 and 12 min. It is apparent that an optimum polymer concentration exists for best extraction (minimum C_t at a given t).

Skelland and Meng (1996) developed the following expression for C^* from published experimental data over the temperature range 19 to 70°C, and which included the species of polymers used here, but with different molecular weights:

$$C^*(\text{g/dL}) = 228\,\frac{(M_{\text{sru}})^{5/3}}{V_{\text{sru}} M_p^{2/3}} \qquad (4)$$

where M_{sru} and V_{sru} are the molecular weight and volume of the pure liquid single repeat unit at its normal boiling temperature (from LeBas in Perry, 1963) (see Notation for units), and M_p is the weight-average molecular weight of the polymer. Application of Eq. 4 to the three systems in Figures 17 and 18 gives the results in Table 2. Many earlier attempts estimate C^* as $B/[\eta]$, where $[\eta]$ is the intrinsic viscosity of the polymeric solution, as defined by Middleman (1968, p. 142). Although B is commonly taken to be unity, Skelland and Meng (1996) cite several substantial published exceptions. The intrinsic viscosity is related to the molecular weight of the polymer by the Mark-Houwink equation, $[\eta] = KM_p^a$, where K and a depend upon solvent, temperature, and M_p

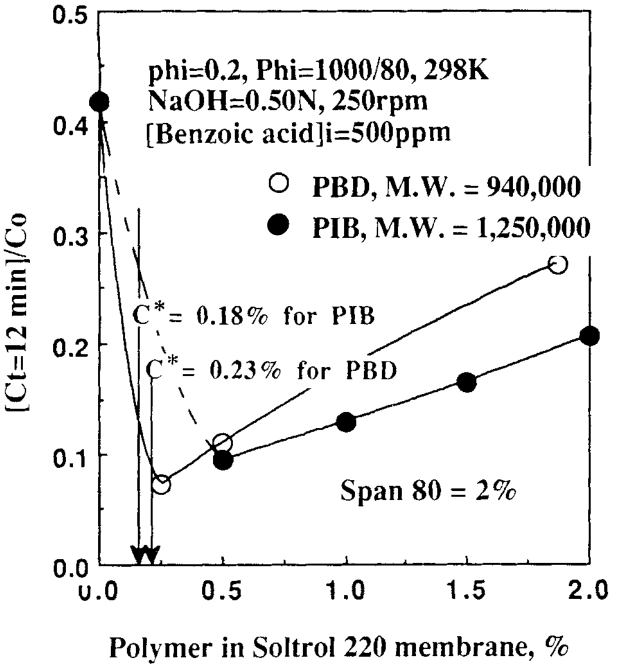

Figure 18. Optimum polymer concentration for minimum residual solute concentration in the external phase C_t at a given time t for Soltrol 220 membranes.

itself. Numerous experimental values of K and a are tabulated in Brandrup and Immergut (1989), including $K = 0.000105$ dL/g and $a = 0.73$ for polystyrene with a weight-average molecular weight of 10^6 (that is, closest to our case) dissolved in toluene at 25°C. These values, with our M_p and assuming $B = 1$, result in the estimate of $C^* = 0.415$ in Table 2. However, Simha and Zakin (1960) found $B = 1.08$ in studies applied to narrow-distribution polystyrenes in toluene, which corresponds to $C^* = 0.45$. Values of K and a at the right combination of (equivalent) solvent, temperature, and M_p could not be found for the other two polymers.

The data for PIB in Figure 18 do not permit precise location of the minimum in the curve, but its abscissa is probably less than 0.5%. With this in mind, the computed values of C^* are in good agreement with the minimal regions of the curves, as shown by the arrows in Figures 17 and 18. Any further increase in membrane stability and decrease in swelling at polymer concentrations beyond those corresponding to the minima in the curves are obtained only at the cost of decreased extraction rate.

Table 2. Estimated Critical Concentrations C^* at which Interactions between Polymer Molecules Begin in Dilute Solutions

Polymer	M_p	$C^*_{eq(4)}$ g/dL	$C^* = B/KM_p^a$, g/dL
Polyisobutylene (PIB)	1.25×10^6	0.18	—
Polybutadiene (PBD)	0.94×10^6	0.23	—
Polystyrene (HPS)	0.942×10^6	0.46	0.415 (B = 1) *or* 0.45 (B = 1.08)

Conclusions

Optimized conversion of the membrane phase in emulsion liquid membranes into suitable non-Newtonian form has been achieved by dissolution of appropriate polymers at concentrations very near C^*, the critical value at which interaction between polymer molecules begins. The following benefits have been demonstrated:

(A) Increased stability of the membrane is obtained by three (or four) separate mechanisms that are described in the text.

(B) The permeability of the membrane is retained (or enhanced) in accordance with an established characteristic that distinguishes these non-Newtonian systems from their Newtonian counterparts.

(C) Transfer enhancement occurs because of the surfactant reduction permitted by the stabilizing effects of the dissolved polymer. Two simultaneous mechanisms are identified to account for this result. Subsequent demulsification is also aided by surfactant reduction.

(D) Swelling problems are substantially reduced by a diminution in four of the five mechanisms known to produce swelling.

(E) The volume fraction of the internal phase in the emulsion may be increased because of the polymeric stabilization described, resulting in three separate contributions to improved extraction performance, plus enhancement of the subsequent demulsification process.

(F) The agitator speed during extraction may be increased, giving greater transfer rates from two sources outlined in the text.

The effect of suitable non-Newtonian conversion of the membrane phase on electrostatic demulsification has not been studied. However, its influence on key emulsion characteristics recently identified by previous workers (namely internal drop size, surfactant type and concentration, and membrane (oil) viscosity) suggests that the proposed solution may not adversely affect demulsification and might even facilitate it.

While toluene membranes are innately weaker than those made from Soltrol 220, their performance can be rendered satisfactory by appropriate combination with surfactant Span 80 and polystyrene polymers, as demonstrated here.

Acknowledgment

Financial support for this study was provided by the United States Geological Survey grant No. 14-08-0001-G2106 and by the National Science Foundation grant No. CTS-9102351.

Notation

a = Mark-Houwink exponent
B = constant
C^* = critical concentration of polymer in solution at which interaction between polymer molecules begins, g/dL
C_o, C_t = solute concentrations in the external phase at time zero and time t, respectively
et = emulsification time
HPS, LPS = polystyrene with molecular weights of 942,000 and 280,000, respectively
K = constant in the Mark-Houwink equation
L, %, L_{10}% = percentage of the internal phase that has leaked into the external phase; after 10 min of agitated contact
M_p = weight-average molecular weight of the polymer

M_{sru} = molecular weight of the single repeat unit in the polymer
N = rotational speed of the impeller, rps
PBD = polybutadiene
phi = volume ratio of internal phase to the emulsion
Phi = volume ratio of external (continuous) phase to the emulsion
PIB = polyisobutylene
PS = polystyrene
$S,\%$ = percentage swelling of the emulsion, corrected for leakage, see Eq. 2
t = time
V_c = volume of the external (continuous) phase
V_{io} = initial volume of the internal phase
V_{i10} = volume of the internal phase after 10 min of agitated dispersion
V_{L10} = volume of internal phase lost by leakage during first 10 min of agitation
V_{oil} = volume of the membrane phase
V_{S10} = volume of water gained by swelling during 10 min of agitated dispersion
V_{sru} = molal volume of the pure liquid single repeat unit in the polymer at its normal boiling temperature, calculated from LeBas, cm^3/mol
$[\eta]$ = intrinsic viscosity of the polymer solution, dL/g
$\rho_{\mathrm{aq}}, \rho_e, \rho_{\mathrm{oil}}$ = densities of the aqueous internal phase, of the emulsion, and of the oil (membrane) phase, respectively
ϕ, ϕ_0, ϕ_{10} = volume fraction of internal phase in the emulsion; before contact with the external phase ($t=0$); after 10 min of agitated contact with the external phase plus 5 min of undisturbed settling

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Appendix: Swelling Percentage, Corrected for Leakage

An expression is developed that contains correction for leakage effects from consideration of the emulsion density, as follows:

$$\rho_e = \phi\rho_{\text{aq}} + (1-\phi)\rho_{\text{oil}}$$

Then

$$\phi = \frac{\rho_e - \rho_{\text{oil}}}{\rho_{\text{aq}} - \rho_{\text{oil}}}$$

and

$$V_{i10} = V_{i0} - V_{L10} + V_{S10}$$

The swelling S of the emulsion after 10 min of continuous agitation followed by 5 min of settling is represented by:

$$S, \% = 100\,\frac{V_{S10}}{V_{i0}} = 100\,\frac{V_{i10} - V_{i0} + V_{L10}}{V_{i0}}$$

where

$$V_{i0} = V_{\text{oil}}\,\frac{\phi_0}{1-\phi_0};\quad V_{i10} = V_{\text{oil}}\,\frac{\phi_{10}}{1-\phi_{10}};\quad V_{L10} = \frac{V_{i0}(L_{10}\%)}{100}$$

Combining these expressions gives the swelling percentage corrected for leakage as:

$$S, \% = 100\,\frac{(1-\phi_0)\phi_{10}}{(1-\phi_{10})\phi_0} + L_{10}\% - 100 = 100\,\frac{(\phi_{10}-\phi_0)}{(1-\phi_{10})\phi_0} + L_{10}\%$$

Manuscript received Aug. 4, 1994, and revision received Apr. 17, 1995.