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Leakage and Swell in Emulsion Liquid-Membrane Systems: Batch Experiments

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ABSTRACT

Emulsion liquid-membrane systems can provide effective systems for removal of impurities in a variety of applications. In these systems, removal efficiency and the ability to concentrate impurities can be impaired because of encapsulated-phase leakage and emulsion swell. This work describes the results of a factorial experimental procedure that measured the effects of several formulation and operating variables on emulsion liquid-membrane leakage and swell. The experimental variables studied were surfactant concentration, osmotic pressure, membrane type, internal-phase volume fraction, and extraction-vessel stir rate. Encapsulated-phase leakage is influenced by all of the variables in a complex fashion. Emulsion swell results are consistent with a simple water-transport mechanism.

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Key Words: Emulsion; Emulsion liquid-membrane; Leakage; Mass transfer; Water transport.

INTRODUCTION

Emulsion liquid-membrane (ELM) separation systems are made by emulsifying a liquid internal phase in an immiscible liquid-membrane phase and dispersing this emulsion in an external liquid. Droplets of the emulsion are maintained in the external phase using agitation. Typically, the external phase is aqueous and contains a solute to be removed by mass transfer through the membrane into the internal phase. Two kinds of facilitation mechanisms have been used to enhance the effectiveness of ELM separation systems. In Type 1 facilitation, the internal phase contains a stripping agent that removes the solute from the membrane and reacts with the solute to form a species that is insoluble in the membrane phase. In Type 2 facilitation, a carrier species is incorporated into the membrane phase to augment solute mass transfer. Internal phase leakage occurs when portions of the internal phase spill into the external phase. During leakage, the stripping agent and previously extracted solute is leaked into the external phase, reducing the extraction efficiency. Emulsion swell occurs when portions of the external phase liquid enter into the internal phase. Swell reduces the concentration of the extracted solute in the internal phase and may have an effect on the stability of the emulsion. Previous experimental work dealing with the problem of ELM leakage generally falls into the category of monitoring leakage, in particular, ELM extraction systems. An important exception is a hydrodynamic study, which considered emulsion globule breakup. The following two sections give an overview of these studies.

EXTRACTION SYSTEMS

Several research groups have performed experimental studies of the stability of ELM systems. However, different ELM separation systems were used and different variables were studied to determine their effect on ELM stability. Table 1 shows a summary of previous experimental studies of ELM stability.

Hochhauser and Cussler[1] performed an early study that considered leakage from a water in oil in water (W/O/W) double-emulsion system. In their work, Span 80, a non-ionic, oil-soluble surfactant was used. Leakage rates were determined by atomic absorption measurements of tracer concentration. The observed leakage rates were initially high and then slowed considerably. The duration of the initial period of high-leakage rate depended

Table 1. Summary of previous experimental studies of ELM stability.

ELM system	Results	Reference
Oil membrane; Span 80 surfactant	Leakage by tracer measurement High initial-leakage rate followed by lower leakage rate Leakage increased with increases in surfactant concentration and internal-phase volume fraction	Hochhauser and Cussler[1]
Oil membrane; Span 80, Span 20 surfactants; LIX 64N carrier	Leakage by external-phase pH measurement Leakage linear with time Leakage decreased with decreases in internal-phase droplet size Leakage increased with increases in vessel stir rate Leakage higher for Span 20 system	Martin and Davies[2]
Kerosene membrane; Span 80 surfactant	Leakage by tracer measurement High initial-leakage rate followed by lower leakage rate Leakage decreased with decreases in internal-phase droplet size and increases in surfactant concentration Leakage increased with increases in internal-phase salt concentration and internal-phase pH values outside the range of 3–11.5	Takahashi[3]
Oil membrane; Span 80, polyamine, and a derivative of L-glutamic acid di-oleyl ester surfactants	Leakage by tracer measurement High initial-leakage rates associated with surfactant/tracer interaction Constant leakage rates for systems without surfactant/tracer interaction Leakage decreased with increased surfactant concentration	Matsumoto[4]

(continued)

Table 1. Continued.

ELM system	Results	Reference
Oil membrane; Span 80 surfactant; SME529 carrier	Leakage by tracer measurement High initial-leakage rate followed by nearly constant leakage rate	Teramoto[5]
Oil membrane; ECA4360 and ECA5025 surfactants; LIX65N carrier	Leakage by tracer measurement Constant leakage rates Leakage increased with decreases in surfactant concentration, increases in internal-phase volume fraction, and increases in carrier concentration	Bunge et al.[6]
Soltrol 220, S100N, and S500N membranes; Span 80 surfactant	Leakage by external-phase pH measurement High initial-leakage rates in some systems Leakage affected by external-vessel stir rate, emulsifying device, internal-phase volume fraction, and surfactant concentration Significant confounded two-way variable interaction effects on leakage	Shere and Cheung;[9] Pfeiffer et al.[10]

on experimental conditions, but rarely exceeded 10 min. Leakage was affected by emulsion globule viscosity, internal-phase volume fraction, and surfactant concentration. Leakage was most sensitive to surfactant concentration and internal-phase volume fraction.

Martin and Davies[2] reported stability data in their studies of Type 2 facilitation ELM copper extraction from an aqueous feed stream. LIX 64N was used as a carrier and the internal phase was sulfuric acid. Leakage results were reported for two nonionic surfactants: sorbitan monolaurate (Span 20) and sorbitan monooleate (Span 80). The internal phase plus membrane emulsion was prepared with either a high-speed axial turbine mixer or a homogenizer. Internal-phase droplet sizes were observed microscopically. Leakage was measured by observing the external-phase pH. Reported leakage was linear with time and depended upon the type of surfactant used, internal-phase droplet size, and stir rate in the extraction vessel mixer. Leakage decreased with a decrease in internal-phase droplet size. Leakage increased with an increase in extraction-vessel stir rate. Leakage was higher for the emulsions prepared with sorbitan monolaurate.

Takahashi et al.[3] used a W/O emulsion dispersed into a continuous distilled-water external phase to study internal phase leakage via a tracer technique. They used a membrane made up of kerosene and Span 80. The tracer components were NaCl, $CuSO_4$, and NaSCN. They reported that leakage rates increased as internal-phase NaCl concentration increased above 2 wt.%. Initial leakage was nonlinear and, after about 10 to 15 min, reached a constant rate. When internal-phase pH values were adjusted using sulfuric acid or sodium hydroxide, pH values outside the range of 3–11.5 were associated with increased leakage. Leakage decreased as internal-phase droplet size decreased and as surfactant concentration increased. They concluded that leakage depends on both the concentration and type of internal-phase ionic species.

Matsumoto et al.[4] also observed a decrease in leakage as surfactant concentration increased up to a point, but apparently leakage then increased with surfactant concentration for some systems. They used Span 80, polyamine, and a derivative of L-glutamic acid di-oleyl ester as surfactants and a tracer method for determining leakage. They concluded that when the membrane phase (with surfactant) interacts by dissolving tracer material, leakage determined by tracer measurements increases with increased surfactant concentration. This surfactant–tracer interaction also causes initially higher apparent leakage rates. This apparent leakage is an artifact of the interaction between surfactant and tracer material that allows transport of the tracer into the external phase by mass transfer in addition to emulsion leakage. For systems without interactions between surfactant and tracer, they observed first-order behavior for leakage with time.

Teramoto et al.[5] measured leakage rates in a batch copper-extraction system by determining lithium transfer from internal to external phase. They report an initially high rate of leakage followed by a nearly constant rate of leakage. They did not study the effects of formulation or operating parameters.

Bunge et al.[6] also studied leakage in a batch ELM copper-extraction system using lithium transfer from internal to external phase. They measured leakage for two nonionic polyamine surfactants (ECA4360 and ECA 5025) and three internal-phase volume fractions (0.6, 0.48, and 0.37). They observed that increased leakage was associated with decreased surfactant concentration, increased internal-phase volume fraction, and increased carrier species (LIX 65N) concentrations. Also, copper in the external phase reduced leakage. Leakage rates were constant throughout the observation period.

Borwankar et al.[7] describe a process of emulsion swelling due to an osmotic pressure driving force. In their proposed mechanism, the difference in electrolyte concentration between internal and external phases establishes an osmotic pressure gradient that results in water transport from the external phase into the internal phase of a W/O/W emulsion. They suggest that the resulting emulsion swelling may cause the emulsion to become unstable, leading to emulsion leakage. The effect of osmotic pressure gradient on leakage and emulsion swell has been reported. Kinugasa et al.[8] measured leakage using a nickel tracer in the internal phase and determined the amount of emulsion swell by Karl-Fisher titration for water. Their results show constant rates of leakage and emulsion swell after the first few minutes of stirring. As expected, the observed rates of leakage and emulsion swell increased as the osmotic pressure gradient increased. For aliphatic hydrocarbon membranes, emulsion stability increased with increasing number of carbons.

It is difficult to compare the results of previous leakage studies since the liquid membrane systems are usually different in each case. Table 1 shows that the range of experimental conditions used in the studies mentioned above was fairly small and did not lead to a full picture of the leakage process. The studies mentioned above showed that a number of formulation and operating variables can effect leakage. Leakage was shown to be affected by surfactant type and concentration, emulsion preparation procedure, electrolyte concentration, membrane material, and extraction-vessel stir rate. Emulsion swell was shown to be affected by the electrolyte concentration difference between the internal and external phases.

Since leakage and swell are affected by several formulation and operating variables, it is possible that variable interactions, either synergistic or antagonistic, are significant for emulsion leakage and perhaps emulsion swell. This potential variable interaction has not been well studied. A study by Shere and Cheung[9] attempted to a more systematic study of leakage. They used an unreplicated one-half fractional factorial experimental design was used to study the effects of four factors (i.e., internal-phase volume fraction, surfactant concentration, mixing speed, and emulsifying device on leakage from three different membrane types). Leakage was computed from in situ measurements of the pH in the external phase. The pH of the external phase was assumed to change due to leakage from the internal phase (a NaOH solution). They concluded that surfactant concentration and internal-phase volume fraction effects were significant. Leakage increased with increased internal-phase volume fraction and decreased with increased surfactant concentrations. They also concluded that several variable interactions were significant for leakage, depending on membrane type. Their study could not unambiguously determine two-factor interactions since their four factor one-half fractional experimental design resulted in confounded variable interactions. Unfortunately, their method of calculating leakage has an error which casts doubt on their conclusions.[10]

Pfeiffer et al.[10] provided a corrected analysis of the work of Shere and Cheung[9] which showed that all of the factors studied influence leakage either individually or in connection with the other variables that were studied. For example, for one of the less viscous membranes (S100N), leakage increased with increased extraction-vessel stir rate, leakage decreased when a blender was used to prepare the emulsion (vs. an ultrasonic dispenser), leakage increased with increased internal-phase volume fraction, and leakage decreased with increased surfactant concentration. All of the two-factor variable interactions were confounded and significant (e.g., stir rate and emulsifying device, internal phase volume fraction and surfactant concentration, etc.). Based on this result, variable interactions appear to be important for emulsion leakage.

HYDRODYNAMICS MEASUREMENTS OF EMULSION GLOBULE BREAKAGE

Stroeve and Varanasi[11] performed a hydrodynamic study of W/O emulsion globule breakup. Their investigation used a transparent cone and plate viscometer to determine emulsion breakup due to viscous shear forces. An emulsion consisting of a water and glycerin internal phase in a heavy mineral-oil membrane phase with 10 vol% Span 80 surfactant was dispersed into an aqueous external phase made of corn syrup. The internal phase was also colored with methylene blue. The cone and plate were rotated at equal speeds but opposite directions. The apparatus was mounted on an inverted microscope to allow direct observation of the W/O emulsion globules during the application of uniform shear. Observations showed that the W/O emulsion broke during shear flow, according to the B1 and B2 drop breakup categories of Rumscheidt and Mason.[12] In the B1 breakup category, the W/O emulsion globule is pulled into a long cylindrical shape that eventually forms a dumbbell shape that splits into two smaller globules. In the B2 breakup category, the W/O emulsion globule is pulled into a long cylindrical shape that eventually split into several smaller globules. In both B1 and B2 breakup categories, the stretched cylindrical shape has thinner, nodal regions that lose internal-phase material upon globule breakup.

A deformation breakup parameter was defined as the ratio of applied viscous force when the globule ruptures to the surface tension force. Their breakup parameter, a generalized Weber number[13] was correlated with the ratio of the emulsion viscosity to the viscosity of the external phase to give a globule breakup curve. Their data show that the W/O emulsion with the highest internal-phase volume fraction was the most stable with respect to emulsion breakup. If internal-phase leakage is associated with emulsion breakup, their results indicate that leakage should decrease with increasing internal-phase volume fraction. This result contradicts the data presented by other authors.[1,6] These other reports were based on leakage observed during extraction experiments and indicate that leakage increases with increasing internal-phase volume fraction.

The apparent disagreement between the hydrodynamic study of Stroeve and Varanasi and other authors may be due to differences in the emulsion preparation procedure and resulting differences in internal-phase droplet-size distribution.[14] The disagreement may also be due to the differences between the uniform shear field of a cone and plate viscometer and the conditions in a stirred extraction vessel, or the differences between emulsion formulation and preparation (e.g., surfactant type and concentration).

EXPERIMENTS

Design

The purpose of the experimental design was to determine the effects of five formulation and operating variables on internal-phase leakage and swelling in emulsion liquid-membrane systems. A series of experiments was performed to study the effects of surfactant concentration (A), osmotic pressure (B), membrane type (C), internal-phase volume fraction (D), and extraction-vessel stir rate (E) on these two response variables.

In the batch vessel experiments, the internal phase consisted of lithium hydroxide solution while the external phase was initially deionized water. No extraction was performed in these experiments. During the experiments, portions of the internal-phase solution spilled into the external aqueous phase. This internal-phase leakage was determined from measurements of lithium concentration in the external phase combined with a lithium mass balance.

$$L(t) = \left[\frac{C_{Tb} - C_{Tb}^{o}}{C_{Ti}^{o}}\right]\left[\frac{f_b}{(1 - f_b)f_i^{o}}\right] \tag{1}$$

where L is the fraction of the initial amount of internal-phase tracer (lithium) found in the external phase at time t, C_{Tb} is the external-phase lithium concentration, C_{Tj}^{o} is the initial tracer (lithium) concentration in the internal phase $(j = i)$ or external phase $(j = b)$, f_b is the volume fraction of the external phase in the vessel, and f_i^{o} is the initial volume fraction of the internal phase.

Assuming negligible volumes of mixing between internal and membrane phases and that the internal-phase density is a linear function of internal phase LiOH concentration, then emulsion swell (S), defined as the emulsion volume increase relative to the initial emulsion volume, is described by

$$S = \left(\frac{\rho_e - \rho_m}{1 - \rho_e}\right)\left(\frac{\rho_i^{o} - \rho_e^{o}}{\rho_e^{o} - \rho_m}\right) - \frac{aC_{Ti}^{o}(1 - L)}{(1 - \rho_e)} - 1 \tag{2}$$

$$\rho_i^{o} = 1 + aC_{Ti}^{o}$$

As indicated in Eq. (2), the extent of emulsion swelling was determined by measuring densities of the membrane phase (ρ_m), fresh emulsion (ρ_e^{o}), and used emulsion.

Experimental variables were studied at two levels that are listed in Table 2. A replicated half-fractional factorial design, outlined in Table 3, was used to determine the variable effects. Table 3 lists the level settings of each factor (A–E) for each experimental run. Each combination of experimental conditions was replicated, resulting in 32 experimental runs. The actual order in which experimental runs were conducted was random. In this experimental design, the main effects are confounded with four-factor interactions and the two-factor interactions are confounded with three-factor interactions. Assuming that the three-factor and four-factor interactions are negligible allows the determination of all main effects and two-factor interactions.[15]

Estimates for all experimental variable main effects and two-factor interactions along with estimates of their statistical significance were

Table 2. Factor levels used in the batch vessel experimental runs.

Variable	Low level (−)	High level (+)
A: Surfactant concentration, wt.%	1.0	3.0
B: Internal-phase lithium hydroxide concentration, Molar	1.0	2.0
C: Membrane phase	Kerosene	Mixture of kerosene (75 wt.%) and S100N (25 wt.%)
D: Internal-phase volume fraction	0.1	0.4
E: Extraction-vessel stirring rate, rpm	275	350

determined by regressing the internal phase leakage and emulsion swell results after 40 minutes. The regression models are shown below.

$$L = \beta_o + \sum_{1}^{5} \beta_j x_j + \sum_{j=1}^{5} \sum_{\substack{k=1 \\ k>j}}^{5} \beta_{jk} x_j x_k + \varepsilon_L \tag{3}$$

$$S = \delta_o + \sum_{1}^{5} \delta_j x_j + \sum_{j=1}^{5} \sum_{\substack{k=1 \\ k>j}}^{5} \delta_{jk} x_j x_k + \varepsilon_S \tag{4}$$

where β_o and δ_o are the mean values of leakage and swell, β_j and δ_j are the main effects, β_{jk} and δ_{jk} are the two-factor interactions for leakage and swell, ε_L and ε_S are the experimental error terms for leakage and swell (assumed to be distributed normally with zero mean), and x_i $(i = j \text{ or } k)$ are the experimental variables (either -1 for the low level setting or $+1$ for the high level setting). The JMP software from the SAS Institute, Inc. (Cary, NC) was used to perform the regressions.

Procedure

Internal phase was prepared with LiOH (reagent grade) and deionized water. Membrane phase was prepared using Paranox 106 (a nonionic surfactant from Exxon Chemical Co (Houston, TX, USA) with an average molecular weight of

Table 3. Level choices for the 2_V^{5-1} half-fractional factorial design.

Runs[a]	Experiment	Variables				
		A	B	C	D	E
1, 17	(1)	−	−	−	−	+
2, 18	A	+	−	−	−	−
3, 19	B	−	+	−	−	−
4, 20	Ab(e)	+	+	−	−	+
5, 21	C	−	−	+	−	−
6, 22	Ac(e)	+	−	+	−	+
7, 23	Bc(e)	−	+	+	−	+
8, 24	abc	+	+	+	−	−
9, 25	D	−	−	−	+	−
10, 26	Ad(e)	+	−	−	+	+
11, 27	Bd(e)	−	+	−	+	+
12, 28	abd	+	+	−	+	−
13, 29	Cd(e)	−	−	+	+	+
14, 30	acd	+	−	+	+	−
15, 31	bcd	−	+	+	+	−
16, 32	abcd(e)	+	+	+	+	+

[a] The experiments were executed in a randomized order.

1000) in kerosene (Fisher K10-4, Lot No. 902326) or Solvent 100 Neutral (an isoparaffinic, middle distillate from Exxon, with an average molecular weight 365–385). The external phase was deionized water. Deionized water was obtained from a Milli-Q system (Millipore, Bedford, MA, USA). To eliminate a potential source of variability, sufficient quantities of internal phase lithium hydroxide solution and membrane phase were prepared in advance to conduct each replicated set of 16 experiments. Glassware was cleaned with an Alconox wash and rinsed thoroughly with deionized water after each experiment. Before each experiment, the mixing vessel was cleaned with a chromic-acid cleaning solution and rinsed thoroughly with deionized water.

Emulsions were prepared by dispensing aqueous lithium-hydroxide solution along with previously prepared oil and surfactant membrane phase to give a total volume of 300 mL. This mixture was homogenized in a VirTis Model 23 homogenizer for 10 min at 70% power. The resulting emulsion was allowed to cool for 10 to 15 minutes to reach room temperature.

The experiments were conducted by dispensing 600 mL of external-phase aqueous solution into a baffled 1 L glass extraction vessel (Ace Glass, Vineland, NJ, USA) stirred with a Lightnin LabMaster Mixer (Rochester, NY, USA) at the appropriate rate (see Table 2) set on the Lightnin Mixer control panel. Fifty milliliters of previously prepared emulsion phase was then poured into the extraction vessel. The emulsion was added through a fixed pouring funnel to insure repeatability and took from 5 to 10 sec.

Samples of approximately 5 mL were withdrawn through a sample port at times of 2, 5, 10, 25, and 40 min. Photographs of the mixing vessel contents were taken 10 sec prior to sample withdrawal. The samples were filtered through No. 2 Whatman filter paper to separate the aqueous external phase from the emulsion phase. The aqueous portion of the sample was then poured onto a Whatman hydrophobic filter paper from which about 4 mL was withdrawn by pipette from the standing liquid. These aqueous samples were later analyzed by atomic absorption (Perkin-Elmer, Shelton, CT, USA) for lithium content.

After 40 min, mixing was stopped. The vessel contents were allowed to separate. The emulsion phase was decanted into a 500 mL separator funnel and allowed to stand for 15 to 20 minutes until further separation occurred. After phase separation, the water phase was drained and discarded. The density of the remaining emulsion phase was measured by pycnometry and used to calculate swelling according to equation (2).

RESULTS AND ANALYSIS

Internal Phase Leakage

Average values of experimental internal-phase leakage as a function of time are shown in Fig. 1. These results are for replicated runs where observed internal-phase leakage values were greater than 1%. Figure 1 consistently shows leakage values that increase with time and have a small initial leakage rate. Several, but not all of the runs show a qualitatively nonlinear leakage behavior with time.

In a similar study, Shere and Cheung observed cases in which an initially high leakage rate occurred, followed by a much smaller, but nonzero leakage rate.[9,16] None of the leakage results in this study showed this type of behavior. The initially high leakage rate observed by Shere and Cheung[9] would be consistent with an emulsion preparation procedure that incompletely emulsified the internal phase within the membrane phase. If this occurred, then the non-emulsified internal-phase liquid would mix with the external phase during the first part of the mixing process. In this study, high-speed mixing lasting for several minutes was used to prepare the emulsion. The observed initially low leakage rates shown in Fig. 1 indicate that this procedure completely emulsified the internal phase.

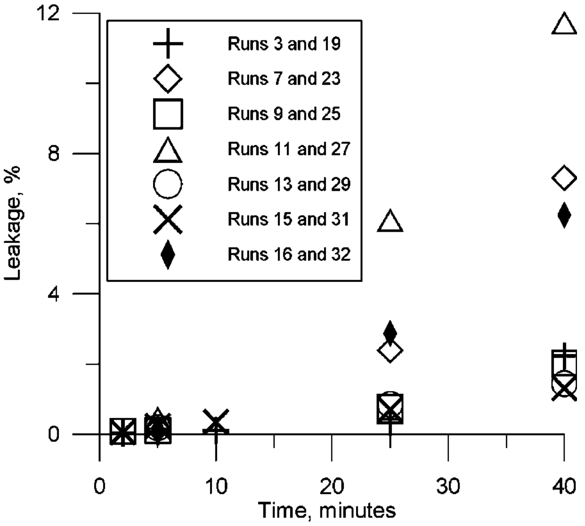

Figure 1. Average values of encapsulated-phase leakage vs. time.

To analyze the effects of the experimental variables on internal-phase leakage, leakage at the last available time ($t = 40\,\mathrm{min}$) was used as the response variable. Table 4 gives the internal-phase leakage values at $t = 40\,\mathrm{min}$ for each of the experimental runs. Each row in Table 4 gives results for two replicates of an experiment. The 16 different treatments resulted in leakage values that range from nearly zero to more than 10%. There were seven treatments (therefore, 14 experiments due to replication) that resulted in internal-phase leakage values greater than or equal to 1% at $t = 40\,\mathrm{min}$. The highest values of internal leakage were associated with the highest level of extraction-vessel stirring rate [cf. runs 11, 27, 7, and 23]. However, some of the lowest leakage rates also occurred at the highest stirring rate (runs 6 and 22). The results given in Table 4 show a complicated set of relationships between the five experimental factors and internal-phase leakage. These results can be used to estimate the effects of the experimental variables by regression analysis, or equivalently, by analysis of variance.[15] The experimental design used allows determination of the variable main effects and two-factor interactions if the confounding four-factor interactions and three-factor interactions are assumed to be negligible.

The results of a regression analysis to determine factor effects are given in Table 5 and Table 6. Table 5 gives summary statistics for regression of the batch leakage results. Table 6 gives results for the main effects and two-factor

Table 4. Encapsulated phase leakage.

Experimental run	Leakage, %[a]	Experimental run	Leakage, %[a]
1	0.56	17	0.67
2	0.17	18	0.09
3	1.92	19	2.54
4	0.13	20	0.06
5	0.54	21	0.15
6	0.06	22	0.09
7	7.45	23	7.17
8	0.09	24	0.07
9	2.54	25	1.52
10	0.70	26	0.57
11	13.17	27	10.27
12	0.77	28	0.34
13	1.00	29	1.90
14	0.47	30	0.14
15	1.56	31	1.09
16	5.52	32	6.97

[a] Encapsulated phase leakage values at $t = 40$ min.

interactions. All of the main effects except C (membrane phase) are significant at the 0.05 level or better. In addition, all but two of the two-factor interactions are significant at the 0.05 level or better. Since there is clear evidence that the two-factor interactions are important, the main effects cannot be interpreted individually.[15] All of the experimental variables influence internal-phase leakage in a complex and interrelated way. The influence of any single variable depends on the settings for other variables.

Table 5. Summary of fit for encapsulated phase leakage[a].

R-square	0.9801
R-square adjusted	0.9615
Root mean square error	0.6503
Mean response	2.1966
Observations	32

[a] Leakage values at $t = 40$ min.

Table 6. Factor analysis for encapsulated phase leakage[a].

Variable	Effect	F-ratio	Significance level
A: Surfactant concentration, wt.%	−1.1816	105.629	<0.0001
B: Internal-phase lithium hydroxide concentration, Molar	1.4984	169.882	<0.0001
C: Membrane phase	−0.0547	0.226	0.6407
D: Internal-phase volume fraction	0.8366	52.950	<0.0001
E: Extraction-vessel stirring rate, rpm	1.3216	132.144	<0.0001
AB: Surfactant concentration × Internal-phase lithium hydroxide concentration	−0.7967	44.823	<0.0001
AC: Surfactant concentration × Membrane phase	0.7159	38.781	<0.0001
AD: Surfactant concentration × Internal-phase volume fraction	0.0834	0.527	0.4785
AE: Surfactant concentration × Extraction-vessel stirring rate	−0.5741	24.934	0.0001
BC: Internal-phase lithium hydroxide concentration × Membrane phase	0.0997	0.752	0.3987
BD: Internal-phase lithium hydroxide × Internal phase volume fraction	0.4297	13.969	0.0018
BE: Internal-phase lithium hydroxide concentration × Extraction-vessel stirring rate	1.3259	133.020	<0.0001
CD: Membrane phase × Internal-phase volume fraction	−0.6472	39.691	<0.0001
CE: Membrane phase × Extraction-vessel stirring rate	0.3066	7.1106	0.0169
DE: Internal-phase volume fraction × Extraction-vessel stirring rate	0.6578	32.740	<0.0001

[a] Leakage values at $t = 40\,\text{min}$.

Emulsion Swell

Emulsion swell at $t = 40\,\text{min}$ was the response variable used to study the effects of the five experimental variables on swell. The experiments were the same experiments used to study internal-phase leakage. Experimental results for emulsion swell are given in Table 7. Each row in Table 7 gives two replicates of an experimental treatment for the variable level settings listed in

Table 7. Emulsion swell.

Experimental run	Swell, %[a]	Experimental run	Swell, %[a]
1	53	17	56
2	45	18	32
3	44	19	36
4	86	20	94
5	34	21	22
6	42	22	49
7	63	23	73
8	53	24	49
9	31	25	27
10	43	26	51
11	91	27	81
12	61	28	46
13	1	29	34
14	31	30	–
15	45	31	44
16	65	32	60

[a] Emulsion swell values at $t = 40\,\text{min}$.

Table 2. The results in Table 7 show a range of emulsion swell from about zero to nearly 90% with a mean value slightly less than 50%. Assuming that three-factor and four-factor interactions are negligible, these results can be used to determine the main effects and two-factor interactions by regression analysis.

Tables 7 and 8 give the results of the regression analysis used to analyze the emulsion-swell experimental results. Table 8 gives summary statistics for regression of the emulsion swell. Table 9 gives the main effects and two-factor interactions. All of the main effects are significant at the 0.10 level or better. Of the 10 possible two-factor interactions, three are significant at the 0.10 level or better. The three statistically significant two-factor interactions are

Table 8. Summary of fit for emulsion swell[a].

R-square	0.9165
R-square adjusted	0.8331
Root mean square error	8.4360
Mean response	49.742
Observations	31

[a] Swell values at $t = 40\,\text{min}$.

Table 9. Factor analysis for emulsion swell[a].

Variable	Effect	F-ratio	Significance level
A: Surfactant concentration, wt.%	3.2188	4.3845	0.0537
B: Internal-phase lithium hydroxide concentration, Molar	12.7813	69.1339	<0.0001
C: Membrane phase	−5.6562	13.5395	0.0022
D: Internal-phase volume fraction	−2.7812	3.2736	0.0905
E: Extraction-vessel stirring rate, rpm	9.7187	39.9729	<0.0001
AB: Surfactant concentration × Internal-phase lithium hydroxide concentration	−0.9063	0.3476	0.5643
AC: Surfactant concentration × Membrane phase	0.7813	0.2583	0.6187
AD: Surfactant concentration × Internal-phase volume fraction	−1.0937	0.5063	0.4877
AE: Surfactant concentration × Extraction-vessel stirring rate	−0.8438	0.3013	0.5912
BC: Internal-phase lithium hydroxide concentration × Membrane phase	0.2188	0.0203	0.8887
BD: Internal-phase lithium hydroxide × Internal-phase volume fraction	2.4687	2.5793	0.1291
BE: Internal-phase lithium hydroxide concentration × Extraction-vessel stirring rate	4.9688	10.4481	0.0056
CD: Membrane phase × Internal-phase volume fraction	−1.8437	1.4386	0.2490
CE: Membrane phase × Extraction-vessel stirring rate	−4.8438	9.9291	0.0066
DE: Internal-phase volume fraction × Extraction-vessel stirring rate	−2.8438	3.4224	0.0841

[a] Swell values at $t = 40\,\text{min}$.

internal-phase lithium-hydroxide concentration and extraction-vessel stir rate (BE), membrane phase and extraction-vessel stir rate (CE), and internal-phase volume fraction and extraction-vessel stir rate (DE).

The main effect of the surfactant concentration (A) is positive and none of the significant two-factor interactions involve (A). An increase in surfactant concentration results in an increase in emulsion swell over the range of level settings studied. The other variables influence emulsion swell in a more complicated way, but in all cases an increase in extraction vessel stir rate results in an increase in emulsion swell.

DISCUSSION

The emulsion swell data can be interpreted in terms of a physical mechanism for emulsion swell. There is an osmotic-pressure driving force for water transport into the emulsion from the external phase. In our experiments, variations in osmotic-pressure driving force are due to differences in internal-phase lithium hydroxide concentration (B). A higher osmotic-pressure difference is associated with the higher level setting for B. The surface area for water transport into the emulsion phase increases with the level setting for extraction-vessel stir rate (E) and decreases with the level setting for membrane type (C) (due to the lower viscosity of the low-level membrane setting). The mechanism for water transport is hypothesized as resulting from encapsulation or binding of water at the emulsion–external phase interface by surfactant in the emulsion. The water is then able to migrate toward the interior of the emulsion phase in response to the osmotic-pressure driving force. In our experiments, the amount of surfactant available to encapsulate or complex with water is directly related to the level setting of surfactant concentration (A) and the internal-phase volume fraction (D). The amount of surfactant potentially available for water transport is mitigated by the amount of surfactant already bound by the amount of water emulsified in the initial emulsification process.

The main effects and two-factor interactions for the emulsion swell data can be rationalized in terms of the water transport process outlined above. The positive main effect for surfactant concentration (A) is consistent with an increase in the amount of surfactant available to encapsulate or bind water for transport into the emulsion. The large positive main effect for internal-phase lithium hydroxide concentration (B) is consistent with an increased osmotic-pressure driving force. The negative main effect of the membrane phase (C) is consistent with a larger interfacial area available for water transport due to the lower viscosity of the low-level membrane setting. The negative main effect of internal-phase volume fraction (D) is consistent with the decrease in available surfactant for water transport purposes due to surfactant being used in the initial emulsification process. The large positive main effect for the extraction-vessel stir rate (E) is consistent with the increase in surface area available for water transport due to higher stir rates. The positive two-factor interaction involving internal-phase lithium hydroxide concentration and extraction-vessel stir rate (BE) is consistent with the proposed water transport rate being the product of a driving force and available area. The negative two-factor interaction involving membrane phase and extraction-vessel stir rate (CE) is consistent with the idea that available area for water transport increases more with an increase in stir rate for a less-viscous membrane phase. The negative two-factor interaction involving internal-phase volume fraction and extraction-vessel stir rate (DE) is consistent with the idea that an increased interfacial area for water transport associated with an increase in extraction-vessel stir rate is offset by the decrease in available surfactant associated with an increased internal-phase volume fraction.

The hypothesized water transport mechanism and experimental results are consistent. The data is also consistent with the idea that the swelling process is a rate process that has not reached equilibrium. For example, the significance of the surfactant concentration in the proposed mechanism is important in the rate of water transport, not the driving forces for water transport.

Internal Phase Leakage and Emulsion Swell

The experimental results for internal-phase leakage and emulsion swell given in Tables 3 and 6 can be used to analyze whether there is a relationship between leakage and swell. Qualitative comparison of the main effects and two-factor interactions for both leakage and swell indicates that leakage is related to the five experimental variables in a more complicated way than is swell. Figure 2 shows the emulsion swell results plotted vs. the internal-phase leakage results.

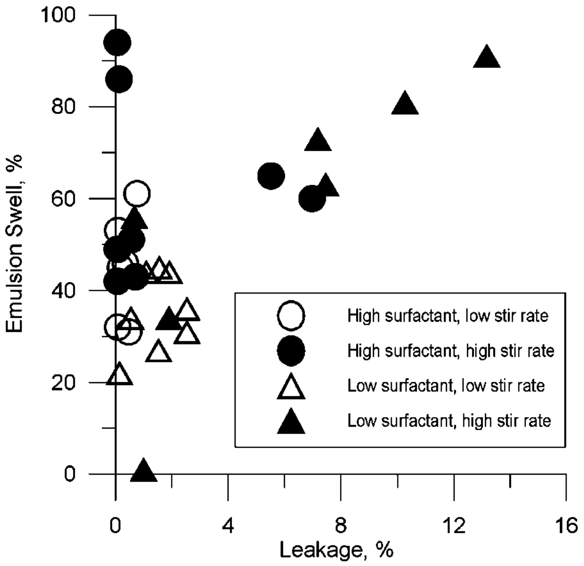

Figure 2. Emulsion swell vs. encapsulated-phase leakage.

High values of internal-phase leakage are associated with higher values of emulsion swell. However, high values of emulsion swell are not necessarily associated with high values of leakage. The simple water transport mechanism that explains the emulsion swell data results is not sufficient to explain the internal-phase leakage results. This suggests that in some cases where significant emulsion swell occurs, there is some mitigating circumstance that stabilizes the emulsion with respect to internal-phase leakage.

One possibility is surfactant concentration (A). Increasing surfactant concentration tends to stabilize the emulsion with respect to internal-phase leakage; it also tends to increase the amount of emulsion swell. However, Fig. 2 shows results with high swell and significant leakage with high surfactant concentration. Since the relationships between the five treatment variables and leakage are complex, surfactant concentration alone cannot explain the plot given in Fig. 2.

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