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Corrected Analysis of the Effect of Preparation Parameters on Leakage in Liquid Surfactant Membrane Systems

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Abstract

The phenomenon of encapsulated phase leakage is an important consideration in liquid surfactant membrane extraction proceses. In previous reports, values of leakage as a function of time and several formulation and operating variables were given. Unfortunately, these data analyses contain an error which significantly affects the conclusions. In this article, a reanalysis of the experimental data obtained by Shere and Cheung is performed. Much higher values of leakage are observed than reported earlier. Also, for the time duration of the leakage experiments, there is no basis for identifying a final, limiting leakage value. Further, each of the parameters studied and many of the two way interactions did influence leakage.

INTRODUCTION

Liquid surfactant membranes and their applications have been described in detail elsewhere (*1–6*). Briefly, liquid surfactant membrane systems are made by emulsifying a liquid (the internal phase) in an immiscible liquid (the liquid membrane) and then dispersing this emulsion in a third liquid phase (the external phase) under agitation. Under the influence of agitation, macrodroplets of emulsion are maintained in suspension in the ex-

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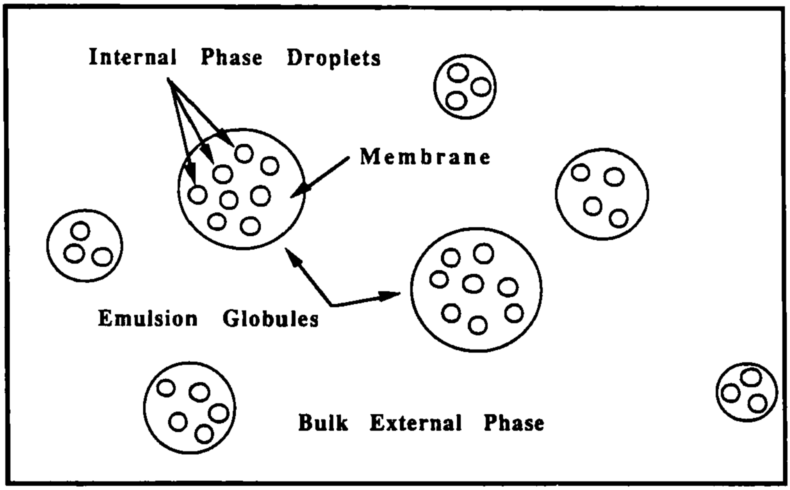

FIG. 1. Liquid membrane system.

ternal phase as shown in Fig. 1. In typical applications, the external phase is aqueous and contains a solute to be removed by partitioning into the emulsion phase and diffusing across the liquid membrane, an oil, to reach the internal aqueous phase. The internal phase contains chemical stripping reagent which removes the solute from the liquid membrane. If droplets of the internal receiving phase spill into the external phase, stripping reagent and previously extracted solute are leaked into the external phase, thereby reducing extraction efficiency.

In earlier work by Shere and Cheung (*1*) and Shere (*2*), the effects of four operating and formulation variables on internal phase leakage were studied with a one-half fractional factorial design for each of three different membrane oils. The four factors examined were percent surfactant in the membrane phase, speed of agitation in the extraction vessel, emulsifying device, and internal phase volume fraction. Sodium hydroxide was used as the internal phase stripping reagent. Internal phase leakage into the external phase was monitored by measuring the pH of the external phase as a function of time. Factor levels and level settings for the experimental runs given by Shere and Cheung (*1*) are shown in Tables 1 and 2. For details of the experimental procedure, the original paper of Shere and Cheung (*1*) should be consulted.

In the reported experiments, the external phase consisted of water initially at some known pH. If n moles of internal phase sodium hydroxide solution spill into the external phase and if we define leakage as the fraction

TABLE 1
Factor Levels Used in the Experimental Runs[a]

	Soltrol 220		S100N		S500N	
Variable	+	−	+	−	+	−
A: Agitator speed, rpm	500	275	500	370	540	370
B: Emulsifying device[b]	B	U	B	U	B	U
C: Internal phase volume fraction	0.5	0.2	0.4	0.2	0.17	0.05
D: Weight % surfactant	4	1	4	1	4	1

[a] Taken from Shere and Cheung (*1*).

[b] B = Waring blender, U = Ultrasonic dispenser.

of original internal phase solution which was spilled, we have

$$L = n/C_i^0 V_i^0 \tag{1}$$

where C_i^0 is the original concentration of sodium hydroxide in the internal phase and V_i^0 is the original internal phase volume. In the bulk external phase, conservation of mass and the water dissociation reaction require that

$$n/V_b = (C_{\mathrm{OH}} - C_{\mathrm{OH}}^0) + (C_{\mathrm{H}}^0 - C_{\mathrm{H}}) \tag{2}$$

where V_b is the bulk external phase volume and the hydroxide and hydrogen ion concentrations are bulk phase concentrations. The second term on the right side is due to the consumption of spilled hydroxide ions by hydrogen

TABLE 2
Level Choices for the Half-Fractional Factoral Design[a]

		Variables						
Run	Experiment	A	B	C	D/ABC	AB/CD	AC/BD	BC/AD
1	(1)	−	−	−	−	+	+	+
2	a(d)	+	−	−	+	−	−	+
3	b(d)	−	+	−	+	−	+	−
4	ab	+	+	−	−	+	−	−
5	c(d)	−	−	+	+	+	−	−
6	ac	+	−	+	−	−	+	−
7	bc	−	+	+	−	−	−	+
8	abc(d)	+	+	+	+	+	+	+

[a] Taken from Shere and Cheung (*1*).

ions initially present in the bulk external phase. References *1* and *2* incorrectly calculated leakage from

$$n/V_b = (C_{\mathrm{OH}} - C^0_{\mathrm{OH}}) \tag{3}$$

which is only equivalent to Eq. (2) when the bulk external solution is initially neutral.

Combining Eqs. (1) and (2) and writing in terms of pH gives the following expression for fractional leakage:

$$L = \frac{V_b}{V_i C_i^0}\left[10^{(\mathrm{pH}-\mathrm{p}K_w)} + 10^{-\mathrm{pH}(0)} - 10^{-\mathrm{pH}} - 10^{(\mathrm{pH}(0)-\mathrm{p}K_w)}\right] \tag{4}$$

Using Eq. (4), the pH data given by Shere (*2*) can be used to determine leakage as a function of time for each experimental run.

DATA ANALYSIS AND DISCUSSION

Fractional leakage values as correctly determined from pH measurements by Eq. (4) are often quite different than those reported by Shere (*2*) and Shere and Cheung (*1*) (from the same experimental data). Figures 2 and 3 show a comparison of the correct and incorrect leakage values for two different experimental runs. For the runs reported in Figs. 2 and 3, the correct leakage values are higher than previously reported. This observation is typical of runs in which the bulk external solution is not initially neutral. As shown in Fig. 4, corrected leakage values are close to those previously reported when the initial pH of the bulk external solution is nearly neutral. It should also be noted that the corrected results do not seem to support Shere and Cheung's hypothesis that at long time a constant leakage value would be reached (*1*).

The three membrane oils studied have viscosities ranging from less than 4 cP (Soltrol 220) to 198 cP (S500N). As shown in Fig. 2, leakage from an emulsion prepared with the least viscous membrane oil (Soltrol 220) occurs at a high initial rate followed by a much lower leakage but nonzero rate after the first few minutes of stirring. The transition between the two leakage rates is quite sudden. Figure 3 shows leakage from an emulsion prepared with a more viscous membrane oil (S100N, 37 cP). In this case there is no sharp transition in leakage rates with time. This qualitative difference in the shape of the leakage curves between emulsions made with the least viscous membrane oil and emulsions made with more viscous oils was observed consistently in the leakage curves.

To analyze the effects of the experimental variables, leakage at the last

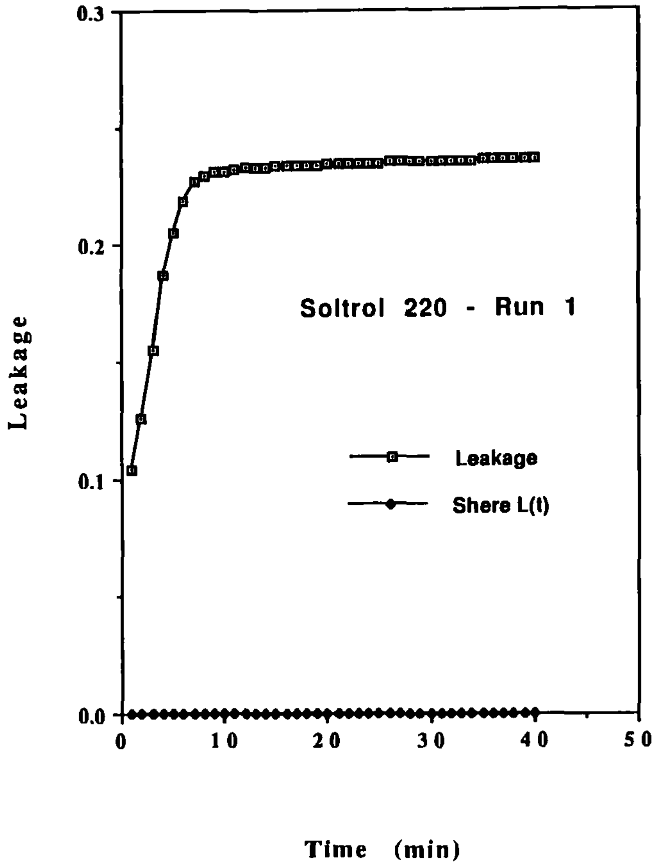

FIG. 2. Corrected leakage and previously reported leakage versus time.

available time for each of the three membrane oils was used as the response variable. Table 3 gives corrected leakage values at the longest available time for each membrane oil. Leakage values are highest for Soltrol 220 membranes and lowest for S500N membranes. This result is consistent with the observation that emulsions prepared with high viscosity oils are more stable than emulsions prepared with low viscosity oils (*1*). Using the values given in Table 3, the influence of experimental variables can be estimated by regression analysis or, equivalently, by an analysis of variance (*7*). The results of a regression analysis to determine factor effects are given in Table 4.

For Soltrol 220 membranes, the main effects A (extraction vessel stir

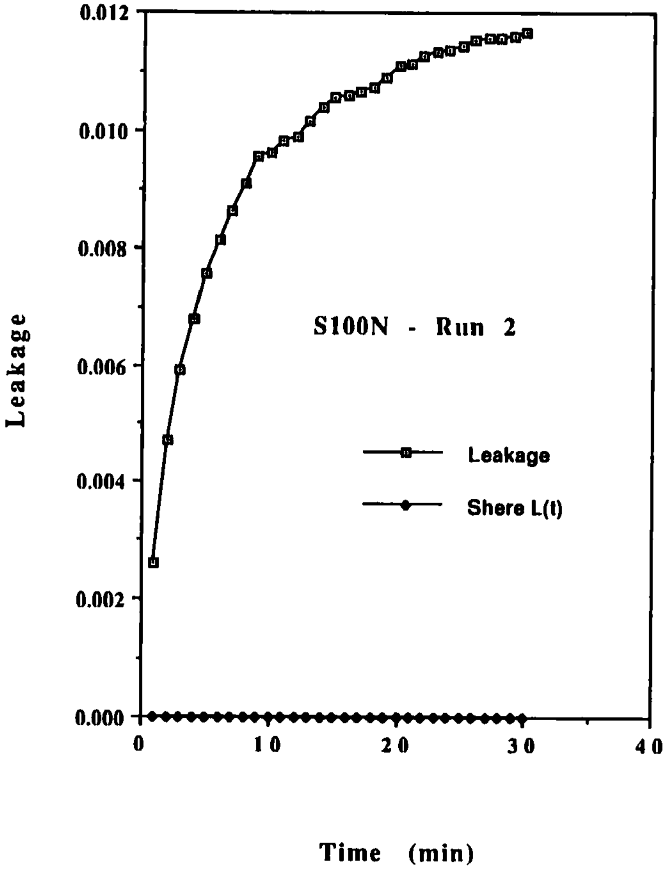

FIG. 3. Corrected leakage and previously reported leakage versus time.

rate), B (emulsifying device), and D (surfactant concentration) are significant at the 0.10 level or better. In addition, the two-way interactions AC (stirring speed–volume fraction) and BD (emulsifying device–surfactant concentration) together are also significant at the 0.10 level or better. Unfortunately, the number of experimental data points available for each membrane oil type, e.g., Soltrol 220, is not sufficient to resolve the confounded two-way interactions.

The main effects should be interpreted individually only if there is no evidence that interactions are important (7). Since the data for Soltrol 220 membranes indicates that the confounded two way interactions are significant and since the experimental data are not sufficient to resolve the two-

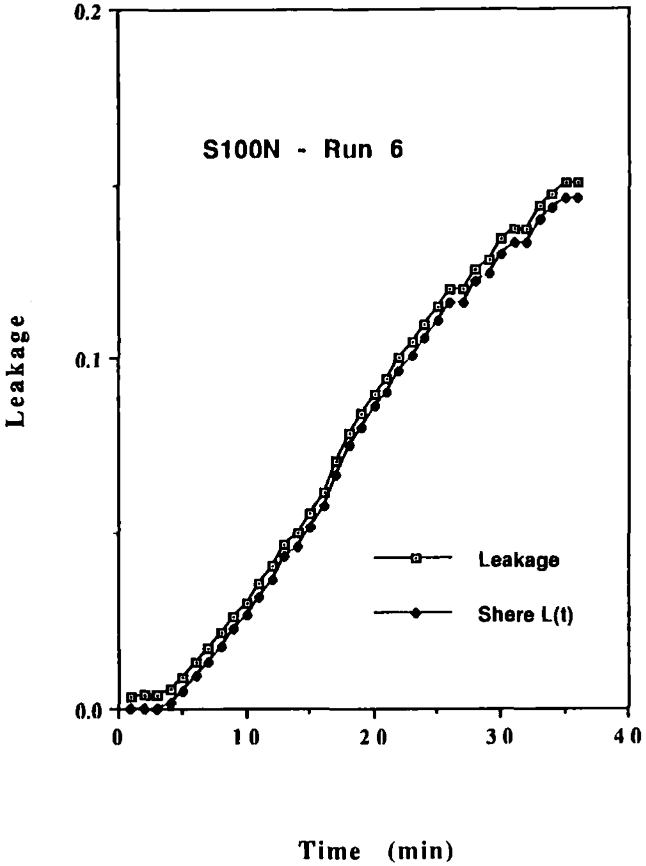

FIG. 4. Corrected leakage and previously reported leakage versus time.

way interactions, it is not possible to quantitatively interpret the effects of each variable.

For example, consider the influence of surfactant concentration (Variable D). The main effect for this variable is −0.097 and the confounded two-way interaction AC + BD (stirring rate/internal phase volume fraction + emulsifying device/surfactant concentration) is 0.053. If it is assumed that the AC interaction is unimportant, one could conclude that an increase in surfactant concentration causes a decrease in leakage. The amount of the leakage reduction would depend on emulsifying device (Variable B) with the smallest reduction occuring for emulsions made with the ultrasonic dispenser. Further, the amount of leakage reduction could be predicted from the numerical values of the effects.

TABLE 3
Corrected Encapsulated Phase Leakage

Membrane oil	Experimental run	Fractional leakage
Soltrol 220[a]	1	0.23524
	2	0.01810
	3	0.02437
	4	0.05217
	5	0.07564
	6	0.15757
	7	0.08056
	8	0.02034
S100N[b]	1	0.02107
	2	0.01166
	3	0.00373
	4	0.01141
	5	0.00432
	6	0.13422
	7	0.02726
	8	0.00311
S500N[c]	1	0.00503
	2	0.02049
	3	0.01174
	4	0.01074
	5	0.00465
	6	0.00892
	7	0.00496
	8	0.00673

[a] Leakage values at t = 28 min.
[b] Leakage values at t = 30 min.
[c] Leakage values at t = 17 min.

Now, consider the case when the AC interaction cannot be neglected. Increasing surfactant concentration could be expected to decrease leakage, but the amount of decrease could not be predicted with any useful precision. In addition, the amount of leakage decrease may or may not depend on which emulsifying device was used in the emulsion preparation. For the Soltrol 220 membranes, it appears that all four of the variables influence leakage, either individually and/or through interactions with other variables. The data do not provide a basis to quantitatively assess the extent of each variable's influence.

As shown in Table 4, leakage from liquid surfactant membranes made with S100N appears to have been influenced by all of the variables along with all of the confounded two-way interactions. Increases in stirring rate

TABLE 4
Factor Analysis for Fractional Leakage

Membrane oil	Variable	Effect	Significance level[a,b]
Soltrol 220	Mean	0.083	0.002
	A	−0.042	0.081
	B	−0.077	0.017
	C	0.001	—
	D	−0.097	0.009
	AB + CD	0.026	—
	AC + BD	0.053	0.047
	BC + AD	0.011	—
S100N	Mean	0.027	
	A	0.026	
	B	−0.031	
	C	0.030	
	D	−0.043	
	AB + CD	−0.034	
	AC + BD	0.027	
	BC + AD	−0.023	
S500N	Mean	0.0092	0.001
	A	0.005	0.036
	B	−0.001	—
	C	−0.006	0.028
	D	0.004	0.091
	AB + CD	−0.005	0.044
	AC + BD	−0.002	—
	BC + AD	0.000	—

[a] Significance levels were assigned using the insignificant effects to estimate the error variance *(7)*.

[b] Since there are no insignificant effects with which to estimate an error variance, no assignment of significance levels for S100N membranes is possible.

(A) and internal phase volume fraction (C) are associated with increased leakage values. This result differs from the Soltrol 220 oil result where internal phase volume fraction (C) was not significant. Emulsifying device (B), surfactant concentration (D), as well as each of the three pairs of two-way interactions were also influential. Unfortunately, the eight data points available for S100N oil membranes do not contain enough information to determine statistical significance levels for the effects.

For S500N membranes, three of the variables were significant at the 0.10 level or better. These three main effects, A (stirring rate), C (internal phase volume fraction), and D (surfactant concentration), are all positive.

In addition, the two-way interactions AB (stirring rate–emulsifying device) and CD (internal phase volume fraction–surfactant concentration) together are signifcant. While the above-mentioned effects are statistically significant, it should be noted that the observed leakage values for S500N oil membranes are much lower than for membranes made with S100N and especially Soltrol 220.

CONCLUSIONS

An error in previously reported calculated leakage from liquid surfactant membrane systems has been corrected. The corrected analysis shows higher values of leakage than previously reported. In addition, the data do not provide a basis for determining a final, limiting value of leakage. All of the variables studied, stirring speed, emulsifying device, internal phase volume fraction, and surfactant concentration, appear to influence leakage either individually or in connection with other variables. The available data are not sufficient to resolve the variable effects.

Leakage was highest for emulsions made with the least viscous membrane oil (Soltrol 220) and was lowest for emulsions made with the most viscous oil (S500N). Emulsions prepared with the least viscous membrane oil (Soltrol 220) showed a high initial leakage rate followed by a much lower leakage rate. The transition between the two leakage rates occurred after the first few minutes of stirring and was quite sudden. Emulsions prepared with the more viscous membrane oils (S100N and S500N) did not show a sharp transition between initial leakage rate and leakage rate at longer time.

SYMBOLS

C_H	external phase hydrogen ion concentration
C_H^0	initial external phase hydrogen ion concentration
X_i^0	initial internal phase base concentration
C_{OH}	initial external phase hydroxide concentration
L	fractional leakage
n	moles of base solution spilled into the external phase
pK_w	$-\log_{10}$ of the water dissociation constant
V_b	external phase volume
V_i^0	original internal phase volume

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