Transition Electrolyte Concentrations for Bubble Coalescence

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Inorganic electrolytes are known to reduce the degree of bubble coalescence both in stagnant liquids (Oolman and Blanch, 1986; Lessard and Zieminski, 1971); and in gas-liquid contactors (Marrucci and Nicodemo, 1967; Prince and Blanch, 1990). In industrial gas-liquid contactors, such as aerobic fermentors or gas absorption units, the effect of electrolytes is to increase the interfacial area. Consequently, the mass transfer rate in these systems is increased. It is desirable to predict the degree to which salts affect coalescence behavior and thereby determine their influence on mass transfer rates in these applications.

The present study examines the amount of salt required to immobilize the gas-liquid interface of the film between coalescing bubbles. The analysis stems from the work of Marrucci (1969), which has been modified to account for the effects of inertia and retardation in the London attractions between surface molecules in the film.

Model Development

Salts are found to inhibit bubble coalescence by retarding the thinning of the intervening liquid film between bubble pairs. Marrucci (1969) analyzed this phenomenon by considering a constant volume element of the liquid film during the thinning process. The surface area of this element is greatly increased as film thinning proceeds. As a result, the surface excess of salt in the film is increased in relation to that on the remainder of the bubble surface. The higher salt concentration produces an increase in the surface tension of the film. Consequently, a force develops opposite to the direction of flow at the gas-liquid boundary. This results in a significant increase in the thinning time of liquid films during coalescence.

At sufficiently high salt concentrations this force will immobilize the gas-liquid interface. There is then a transition from inertial to viscous flow in the liquid film between the gas bubbles. The change in boundary conditions is significant in the overall coalescence time. Purely viscous flow results in thinning times on the order of seconds, roughly two orders of magnitude greater than that found for inertial flow with pure liquids. In the Marrucci model, allowing for transport of the salt to relieve the gradient in the surface tension which develops still leads to thinning times on the order of 100's of milliseconds (Marrucci et al., 1969).

Marrucci (1969) has developed an expression for the concentration of salt necessary to immobilize the gas-liquid interface in coalescing bubbles. The expression is based on the change in surface excess of solute which accompanies the expansion of the liquid film during coalescence. The analysis considers a constant volume element of fluid undergoing expansion to determine the degree of change in the surface excess, and utilizes a force balance on the liquid film to determine the amount of change in the surface excess necessary to immobilize the film. Marrucci assumes equilibrium between the surface and the bulk liquid in the film while neglecting transport of the solute to relieve the surface tension gradient which develops. The expression for the transition concentration takes the form:

$$c_t = 0.084 \nu R_g T (\sigma A^2 / r_b)^{1/3} (\partial \sigma / \partial c)^{-2} \qquad (1)$$

where c_t is the transition concentration, R_g is the gas constant, T is temperature, A is the Hamaker constant, r_b is the bubble radius, ν is the number of ions produced upon dissociation, and σ is the surface tension. It should be noted that both Kim and Lee (1987) and Oolman and Blanch (1986) list Eq. 1 but neglect to include the contribution of ν. An exact value for the Hamaker constant in Eq. 1 is difficult to determine with precision; however, both limited theoretical and experimental studies suggest a value of 2–3 × 10^{-13} erg (2–3 × 10^{-20} Pa) for aqueous systems (Scheludko and Exerowa, 1960; Fowkes, 1964; and Black et al. 1960). Given values for the surface tension gradi-

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ents, which may be found in the literature (*Handbook of Chemistry and Physics; International Critical Tables*), it is possible to predict the transition concentration for a wide range of aqueous salt solutions. Surface tension gradient data for the salt solutions of interest are given in Table 1. Examination of surface tension behavior of the salt solutions show that the gradient is constant over the concentration range of interest.

Experimenal data on transition concentrations of several salts are given by Lessard and Zieminski (1971) and are shown in Table 1. Additional experimental data on transition concentrations may be taken from Marrucci and Nicodemo (1967), if one assumes that the transition concentration occurs at the point where the bubble size remains stable with salt concentration, indicating that the interface has been immobilized and further addition of electrolyte no longer has a pronounced influence. Data from this source are also included in Table 1. Since these data are determined by different means, it is worthwhile to briefly examine the validity of including them in the same sample. It appears by examining the transition concentration of KCl reported by both studies, however, that the two methods are equivalent to a fair degree of accuracy. The slight difference in the transition values for KCl between the two studies is easily attributable to the small difference in bubble size and experimental error.

With this information it is possible to compare Eq. 1 to the experimental data. An illustration is given in Figure 1. It is seen that Eq. 1 consistently underpredicts the data by a factor of roughly 4 when the accepted value for the Hamaker constant is used. A best fit of the data yields a value of the Hamaker constant of 2×10^{-12} erg (2×10^{-19} Pa), an order of magnitude above both theoretical and experimental values found in the literature.

Sagert and Quinn (1978) modified Marrucci's development to include the double-layer interactions of the salt components. However, Oolman and Blanch (1986) have shown that the double-layer interactions for the salt concentrations of interest are insignificant across the range of film thickness encountered during the coalescence process in comparison with either the Hamaker forces or the capillary pressure. This is also the case for the salt concentrations examined in this study according to the criteria developed by Sagert and Quinn.

Table 1. Model and Experimental Data for the Transition Salt Concentration

Salt	$d\sigma/dc$ g · cm^3/ s^2 · mol	Bubble Radius cm	C_t from Eq. 11 Molar	Data Molar
$MgSO_4$*	3,200	0.18	0.042	0.032
$MgCl_2$*	3,400	0.18	0.056	0.055
$CaCl_2$*	3,500	0.18	0.053	0.055
Na_2SO_4*	2,700	0.18	0.089	0.061
LiCl*	1,620	0.18	0.165	0.160
NaCl*	1,700	0.18	0.150	0.175
NaBr*	1,300	0.18	0.257	0.220
KCl*	1,440	0.18	0.209	0.230
KCl**	1,440	0.205	0.196	0.210
K_2SO_4**	2,520	0.205	0.096	0.080
KOH**	1,780	0.205	0.128	0.170
$CuSO_4$**	1,850	0.205	0.12	0.07
KI**	840	0.205	0.580	0.620
KNO_3**	1,040	0.205	0.376	0.410

*From Marrucci and Nicodemo (1967).
**From Lessard and Zieminski (1971).

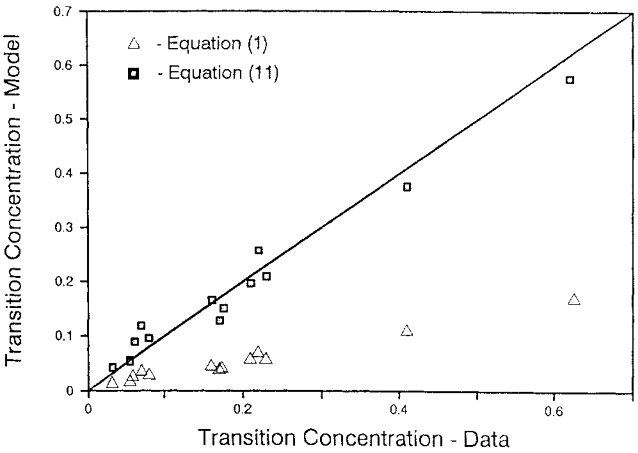

Figure 1. Model prediction and experimental data for transition salt concentrations.

Equation 1 is calculated with the Hamaker constant set equal to 2.5×10^{-13} erg.
Equation 11 is calculated with the value of B set equal to 1.5×10^{-19} erg · cm.

In view of the inadequacy of the current models, the film thinning equations developed by Marrucci are reexamined. There are two significant points of difference in relation to the Marrucci development. One is the form of the Hamaker expression used to calculate the pressure differential driving force during thinning. Marrucci chooses the force of attraction of the liquid boundaries to be:

$$F_H = \frac{A}{6\pi h^3} \tag{2}$$

Here h is the film thickness and A is the Hamaker constant. Equation 2 is appropriate for molecules that respond instantaneously to the fluctuating charge distributions on neighboring molecules. For molecules separated by a sufficient distance, Eq. 2 is no longer applicable. The appropriate distance over which Eq. 2 applies is for molecular separations less than the characteristic absorption wave length of the molecule. For distances greater than this, Casimir and Polder (1948) show that the so-called "retarded" van der Waals attractions are given by:

$$F_H = \frac{B}{h^4} \tag{3}$$

Here B is the retarded van der Waals coefficient. Tabor and Winterton (1969) found the transition from normal to retarded van der Waals interactions to occur at distances of roughly 100 angstrom (10^{-8} m). During the film thinning process, it is thought that the film thins from an initial value of approximately 10^{-4} m to a value of 10^{-8} m, where rupture occurs. Therefore, throughout the film thinning process it would appear that the appropriate expression to use for the Hamaker contribution to the pressure driving force is that given by Eq. 3.

The second deviation from Marrucci's development which will be considered here lies in the initial conservation equation. The prediction of the transition salt concentration in the

Marrucci model derives from a simple force balance, neglecting inertial terms. In the present development, we reexamine the film thinning process commencing with the Navier-Stokes equations. The development here closely follows that of Oolman and Blanch (1986). Use of an alternate expression for the Hamaker contribution results in slight differences in the final thinning equation. The liquid film between coalescing bubbles is taken to be a cylinder of radius R and height h. The equation for film thinning in cylindrical coordinates, neglecting gravity, is given by:

$$\rho\left(\frac{\partial v_r}{\partial t} + v_r\frac{\partial v_r}{\partial r} + \frac{v_\theta}{r}\frac{\partial v_r}{\partial \theta} - \frac{v_\theta^2}{r} + v_z\frac{\partial v_r}{\partial z}\right) = -\frac{\partial P}{\partial r} - \left(\frac{1}{r}\frac{\partial (r\tau_{rr})}{\partial r} + \frac{1}{r}\frac{\partial \tau_{r\theta}}{\partial \theta} - \frac{\tau_{\theta\theta}}{r} + \frac{\partial \tau_{rz}}{\partial z}\right) \quad (4)$$

The following simplifying assumptions are made. It is assumed that v_θ is zero and that the flow has no θ dependence. In addition, it is assumed that the interface is completely mobile up to the transition point. This translates to a rapid change in bubble coalescence behavior over a narrow range of salt concentrations. Data on bubble coalescence frequencies in various salt solutions given in Lessard and Zieminski (1971) show this to be a good approximation for many systems. With this assumption, $\partial v_r/\partial z$ is also equal to zero. Following Oolman and Blanch, substitution of an expression for the volume-average radial velocity, and integration over the thickness for the film yields:

$$\rho\left(\frac{\partial \bar{v}_r}{\partial t} + \bar{v}_r\frac{\partial \bar{v}_r}{\partial r}\right) = -\frac{\partial P}{\partial r} + \frac{2}{h}\frac{\partial \sigma}{\partial r} \quad (5)$$

Equation 5 may now be integrated over the radial dimension of the film. Integration and substitution of the expression for the radial velocity yield:

$$-\frac{\rho R^2}{2h}\frac{d^2h}{dt^2} + \frac{5\rho R^2}{8h^2}\left(\frac{dh}{dt}\right)^2 - \frac{2\Delta\sigma}{h} + \Delta P = 0 \quad (6)$$

This expression is identical to Marrucci's initial force balance if one sets the thinning rate (dh/dt) equal to zero. In practice, the thinning rate is never identically equal to zero, even when the gas-liquid interface is immobile. The thinning rate is merely reduced as the transition to viscous thinning occurs.

An expression for $\Delta\sigma$ may be found in Marrucci (1969), where we use Δ to refer to values at the edge of the film minus the value at the film center.

$$\Delta\sigma = -\frac{1}{\nu h}\left(\frac{2c}{R_gT}\right)\left(\frac{\partial\sigma}{\partial c}\right)^2 \quad (7)$$

Here c is the salt concentration. It should again be noted that Oolman and Blanch neglect to include ν in their development.

The pressure differential driving force for film thinning consists of a term due to capillary pressure augmented by an expression for the molecular attraction of interfacial water molecules, which becomes significant at very small film thicknesses. The appropriate form of the molecular attraction is given in Eq. 3. The resultant pressure differential is given by:

$$\Delta P = -\left(\frac{2\sigma}{r_b} + \frac{B}{h^4}\right) \quad (8)$$

Substitution of these final terms yields:

$$-\frac{\rho R^2}{2h}\frac{d^2h}{dt^2} + \frac{5\rho R^2}{8h^2}\left(\frac{dh}{dt}\right)^2 + \frac{4c}{h^2\nu R_gT}\left(\frac{\partial\sigma}{\partial c}\right)^2 - \left(\frac{2\sigma}{r_b} + \frac{B}{h^4}\right) = 0 \quad (9)$$

The development leading to Eq. 9 contains an apparent contradiction in the boundary conditions. It is assumed that the velocity profile is flat, while a term is included for the shear at the gas-liquid interface. This contradiction is explained by the assumption that there is negligible shear until the transition concentration of salt is almost reached. At that point there is a rapid transition from a mobile to an immobile interface. The transition concentration is that concentration of salt which causes the abrupt change in film thinning behavior.

The differential equation may be nondimensionalized to give:

$$\frac{\partial^2\lambda}{\partial t^{*2}} = \frac{1.25}{\lambda}\left(\frac{\partial\lambda}{\partial t^*}\right)^2 - A_1\lambda + \frac{A_2}{\lambda} - \frac{A_3}{\lambda^3} \quad (10)$$

where

$$\lambda = h/h_0 \qquad t^* = \left(\frac{\sigma}{\rho h_0^3}\right)^{1/2} t$$

$$A_1 = \frac{4h_0^3}{R^2 r_b} \qquad A_2 = \frac{8ch_0}{\nu R^2 R_g T\sigma}\left(\frac{\partial\sigma}{\partial c}\right)^2 \qquad A_3 = \frac{2B}{h_0R^2\sigma}$$

The transition concentration of salt may be calculated from the value of A_2 in Eq. 10 which causes oscillations to develop in the numerical solution (Prince, 1989). The resulting expression for the transition concentration may be rearranged utilizing the definitions A_1 and A_3 to explicitly yield the transition concentration's dependence on bubble size and the van der Waals coefficient. The result is:

$$c_t = 1.18\nu\left(\frac{B\sigma}{R_b}\right)^{1/2} R_gT\left(\frac{\partial\sigma}{\partial c}\right)^{-2} \quad (11)$$

An analytical solution to Eq. 10 has also been generously provided by Rice (1989) in Appendix 1 which matches the result obtained above. A comparison of Eq. 11 with the experimental data is shown in Table 1 and Figure 1. It is seen that the comparison is quite favorable.

Having obtained the solution of Eq. 10 which results from two modifications of the original Marrucci approach, it is interesting to now examine the individual contribution of each modification. This may be done as follows (Marrucci, 1990). If the inertial terms are neglected in Eq. 9, the following quadratic equation in

$1/h^2$ is obtained:

$$B\left(\frac{1}{h^2}\right)^2 - \frac{4c\left(\frac{d\sigma}{dc}\right)^2}{\nu R_g T}\left(\frac{1}{h^2}\right) + \frac{2\sigma}{r_b} = 0 \tag{12}$$

which admits solutions only if

$$[2c(d\sigma/dc)^2/\nu R_g T]^2 - 2\sigma B/r_b \geq 0 \tag{13}$$

Thus, the transition concentration is obtained as

$$c_t = (B\sigma/2r_b)^{1/2}\nu R_g T(d\sigma/dc)^{-2} \tag{14}$$

Equation 14 is identical to Eq. 11 with the exception of the numerical coefficient. The difference in the numerical factor shows the separate effect of inertia. Since the coefficient in Eq. 11 is greater than that in Eq. 14, it may be seen that a greater concentration of salt is required to retard coalescence when inertia is considered, i.e. inertia favors coalescence. Initially during film thinning, when the liquid must be accelerated, inertia would seem to hinder coalescence. However, when film thinning is being retarded by salts, the momentum of the outgoing liquid becomes a driving force which thins the film beyond the quasistatic result.

Notation

A = Hamaker constant, erg
A_1, A_2, A_3 = constants defined in Eq. 10, dimensionless
B = retarded Van der Waals coefficient, erg · cm
c = concentration of salt, mol/L
c_t = transition salt concentration, mol/L
F_H = force of attraction, dyne/cm^2
g = gravitational constant
h = film thickness between coalescing bubbles, cm
P = pressure, atm
R = radius of film between coalescing bubbles, cm
r_b = rubble radius, cm
R_g = gas constant
t = time, s
T = temperature
v = velocity, cm/s

Greek letters

λ = constant defined by Eq. 10, dimensionless
ρ = density, g/cm^3
σ = surface tension, g/s^2
ν = number of ions formed upon dissociation

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Appendix 1: Analytical Solution of Eq. 10 (Rice, 1989)

The equation for film thinning may be written (eq. 10):

$$\frac{d^2\lambda}{d^2t^*} = \frac{1.25}{\lambda}\left(\frac{d\lambda}{dt^*}\right)^2 - A_1\lambda + \frac{A_2}{\lambda} - \frac{A_3}{\lambda^3} \tag{A1}$$

Equation A1 may be rearranged to give:

$$\frac{d(p^2)}{d\lambda} - \frac{2.5}{\lambda}(p^2) = 2\left(-A_1\lambda + \frac{A_2}{\lambda} - \frac{A_3}{\lambda^3}\right) \tag{A2}$$

where $p = d\lambda/dt^*$. Thus we obtain the first-order inhomogeneous equation (the *I*-factor equation). The solution to Eq. A2 is given by:

$$p^2 = 4A_1\lambda^2 - \frac{2}{2.5}A_2 + \frac{2}{4.5}A_3\frac{1}{\lambda^2} + K_0\lambda^{2.5} \tag{A3}$$

where K_0 is an integration constant. At this stage, we could argue that p is finite if λ goes to ∞, so we take $K_0 = 0$. If we took $p = 0$ when $\lambda = 1$ (at $t^* = 0$), then K_0 is finite. For simplicity, since we seek the character of the solution, take $K_0 = 0$ and integrate again since $p = d\lambda/dt^*$. Note that a decision must be made regarding the roots of p. We select the negative root since for film thinning, $p < 0$. Rearrangement yields:

$$\frac{\lambda d\lambda}{\sqrt{4A_1\lambda^4 - \frac{2}{2.5}A_2\lambda^2 + \frac{2}{4.5}A_3}} = -dt^* \tag{A4}$$

Equation A4 may be solved to yield:

$$\frac{2c\lambda^2 + b}{\sqrt{4ac - b^2}} = \sinh\left(\sqrt{c}(K_1 - 2t^*)\right) \tag{A5}$$

where

$$a = \frac{2}{4.5}A_3, \quad b = -\frac{2}{2.5}A_2, \quad c = 4A_1.$$

K_1 is given by:

$$K_1 = \frac{1}{\sqrt{c}}\sinh^{-1}\frac{2c + b}{\sqrt{4ac - b^2}} \tag{A6}$$

The solution to Eq. A5 breaks down at the transition where, for increasing b (i.e., A_2):

$$b^2 = 4ac \longrightarrow b = \sqrt{4ac} \tag{A7}$$

Therefore, we can solve exactly for a limiting value A_2;

$$A_2^{\lim} = \sqrt{2.5^2 \frac{8}{4.5} A_1 A_3} \tag{A8}$$

Rearranging to solve for C_t yields

$$C_t = 1.1785(vR_gT)\left(\frac{\partial\sigma}{\partial c}\right)^{-2}\sqrt{\frac{B\sigma}{r_b}} \tag{A9}$$

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