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Research Articles

Dissolution Rates of Polyphase Mixtures

By W. I. HIGUCHI, N. A. MIR, and S. J. DESAI

The theory for the dissolution rate of polyphase mixtures has been investigated and applied to several situations. Physical models involving simultaneous diffusion and rapid equilibria have led to relationships that describe experimental data rather well for the benzoic acid-salicylic acid, the benzocaine-cafféine, and the benzoic acid-trisodium phosphate mixtures.

PHYSICAL models involving the use of simultaneous diffusion and rapid equilibria have been successful (1) in describing diffusion-controlled kinetics of dissolution in reactive media. Most of these methods have been applied to single pure phases dissolving, although in a few instances the effects of surface-precipitating new phases have been examined (2).

In many practical situations one often deals with the simultaneous dissolution of more than one phase. It appeared, therefore, that it would be worthwhile to study the dissolution rate behavior of polyphase mixtures. Several situations have now been studied, and these are reported here.

Received April 1, 1965, from the College of Pharmacy, University of Michigan, Ann Arbor.

Accepted for publication July 2, 1965.

Presented to the Scientific Section, A.P.H.A., Detroit meeting, March 1965.

The authors acknowledge financial support from The Upjohn Co., Kalamazoo, Mich.

SIMPLE CASE OF TWO NONINTERACTING PHASES: BENZOIC ACID—SALICYLIC ACID

General Theory.—When a uniform, intimate, non-disintegrating mixture of two crystalline compounds, A and B , is exposed to a solvent, both phases should initially begin to dissolve at rates proportional to their solubilities and diffusion coefficients according to the Noyes-Whitney law. After a short period of time, usually one of the phases would become depleted in the solid-liquid interface region of the solid mass because N_A/N_B may not necessarily be equal to $(D_A C_A^0)/(D_B C_B^0)$, where N_A and N_B are the amounts of A and B in the mixture, D_A and D_B are the respective diffusion coefficients, and C_A^0 and C_B^0 are the solubilities. We are, of course, assuming diffusion-controlled rates. As a result of this situation, a surface layer is formed made of only one of the phases.

The three possible cases after time, t , > 0 are illustrated in Fig. 1. Most mixture ratios would lead to cases A or B . Only for the critical mixture ratio,

$$\frac{N_A}{N_B} = \frac{D_A C_A^0}{D_B C_B^0} \quad (\text{Eq. 1})$$

would the two phases always coexist at the solid-liquid interface.

Let us now consider the quantitative aspect of this problem. Assume that the situation is case A so that surface becomes pure *A* after time zero. Then let S_1 and S_2 be the coordinate value representing the phase *A*-solution boundary and the bulk mixture-phase *A* boundary, respectively. These are defined so that at time, $t = 0$, $S_2 = S_1 = 0$. At $t > 0$, $\Delta S = S_2 - S_1$ gives the thickness of the *A* phase layer.

Now since *A* is always on the surface, the dissolution rate of *A* is given by

$$G_A = \frac{D_A C_A^0}{h} \quad (\text{Eq. 2})$$

where h is the effective diffusion layer thickness. On the other hand, molecules of *B* must diffuse not only through the liquid diffusion layer but also through the *A* phase layer of thickness, $S_2 - S_1$, porosity, ϵ , and tortuosity, τ . As a result, we must write for G_B the dissolution rate of *B*

$$G_B = \frac{D_B C_B^0}{h + (\tau/\epsilon)(S_2 - S_1)} \quad (\text{Eq. 3})$$

In both Eqs. 2 and 3, we are neglecting the bulk solution build-up of *A* and *B*, and also we are considering steady-state diffusion conditions only.

We may also write

$$G_A = A_A(dS_1/dt) \quad (\text{Eq. 4})$$

and

$$G_B = A_B(dS_2/dt) \quad (\text{Eq. 5})$$

where A_A and A_B are the amounts per unit volume of *A* and *B* in the mixture. Equation 4 states that the dissolution rate of *A* must be equal to the rate of movement of boundary, S , times the *A* phase concentration in that layer. In Eq. 5, the amount of *B* that remains as solution in the pores has been neglected. For most practical situations, this is a good assumption.

Equation 4 may be combined with Eq. 2 and integrated to give

$$S_1 = (D_A C_A^0 / A_A h) t \quad (\text{Eq. 6})$$

Now Eq. 6 may be substituted into Eq. 3 and the resulting relation may be combined with Eq. 5 to give

$$A_B \frac{dS_2}{dt} = \frac{D_B C_B^0}{h + (\tau/\epsilon)[S_2 - (D_A C_A^0 / A_A h) t]} \quad (\text{Eq. 7})$$

The solution to Eq. 7 when $S_2 = S_1 = 0$ at $t = 0$ is

$$t = K_1 \left\{ S_2 - \frac{\epsilon}{\tau} \left(\frac{K_1}{K_2} - h \right) \times \left[1 - \exp \left(- \frac{K_2 \tau}{K_1 \epsilon} S_2 \right) \right] \right\} \quad (\text{Eq. 8})$$

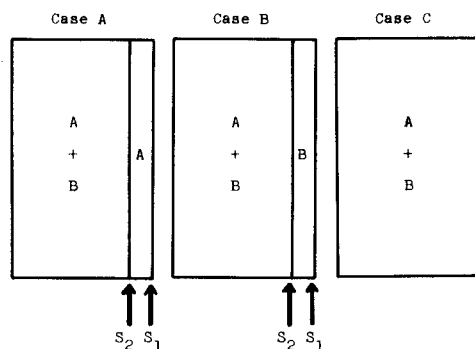
where

$$K_1 = A_A h / D_A C_A^0$$

and

$$K_2 = A_B / D_B C_B^0$$

It can be seen from Eq. 8 that when



$$\frac{N_A}{N_B} > \frac{D_A C_A^0}{D_B C_B^0} \quad \frac{N_A}{N_B} < \frac{D_A C_A^0}{D_B C_B^0} \quad \frac{N_A}{N_B} = \frac{D_A C_A^0}{D_B C_B^0}$$

Fig. 1.—Dissolution behavior of two-phase mixture of *A* and *B*. In case A, phase *B* dissolves fast enough to leave a layer of pure *A* behind; in case B, the reverse is true; while in case C, dissolution rates of *A* and *B* are proportional to their relative amounts in the mixture.

$$S_2 \gg \frac{\epsilon K_1}{\tau K_2} = \frac{\epsilon A_A h D_B C_B^0}{\tau D_A C_A^0 A_B} \quad (\text{Eq. 9})$$

Eq. 8 may be written

$$t \sim K_1 \left[S_2 - \frac{\epsilon}{\tau} \left(\frac{K_1}{K_2} - h \right) \right] \quad (\text{Eq. 10})$$

and so, from Eqs. 5 and 10 the dissolution rate of *B*, G_B , also becomes constant

$$G_B = \frac{A_B D_A C_A^0}{A_A h} = \frac{N_B}{N_A} G_A \quad (\text{Eq. 11})$$

Let us now estimate the S_2 value given by Eq. 9 for the benzoic acid-salicylic acid mixtures. Let compound *A* be benzoic acid and compound *B* = salicylic acid.

Reasonable values for the parameters for the experiments to be discussed later are $h = 2.5 \times 10^{-3}$ cm., $C_A^0 = 3.5 \times 10^{-3}$ Gm. ml.⁻¹, $C_B^0 = 2.0 \times 10^{-3}$ Gm. ml.⁻¹, $D_A \sim D_B \sim 1.2 \times 10^{-6}$ cm. sec.⁻². For the case in which the amount of entrapped air in the mixture is small, we may also write

$$(A_A / \rho_A) + (A_B / \rho_B) = 1 \quad (\text{Eq. 12})$$

where $\rho_A = 1.27$ and $\rho_B = 1.44$ are the densities for benzoic acid and salicylic acid. Then also

$$\epsilon = A_B / \rho_B \quad (\text{Eq. 13})$$

so that for the present situation, Eq. 9 becomes

$$S_2 \gg \frac{A_A h C_B^0}{\tau \rho_B C_A^0} \quad (\text{Eq. 14})$$

Now if a τ value ~ 3 is taken which is reasonable, we find that for $A_A \sim 1.0$ Gm. ml.⁻¹

$$S_2 \gg 4 \cdot 10^{-4} \text{ cm.}$$

This means that for S_2 values appreciably greater than 4×10^{-4} cm., say $\geq 10 \mu$, G_B will be well approximated by the steady-state Eq. 11 with G_A given by Eq. 2.

As most practical situations involve disks or tablets with thicknesses the order of millimeters or greater, the nonsteady-state considerations may be neglected for mixtures behaving like benzoic acid-salicylic acid mixtures. From Eq. 14 it can be seen

that the solubility ratio, C_B^0/C_A^0 , is probably the most important single factor determining whether the nonsteady-state portion of the problem may be neglected.

While the above discussion pertained to case A in Fig. 1, the same equations would be obtained for case B but with the *A* and *B* subscripts exchanged in all terms.

Comparison of Theory with Data.—Figures 2 and 3 give data on the amount dissolved of benzoic acid and salicylic acid from surfaces of compressed disks of various mixture ratios. This particular set of runs was in 0.10 *N* HCl and involved disks made from melts of the mixtures that were ground, sieved, and compressed into disks. As expected from the previous theoretical considerations, the rates appear to be constant of the entire range of composition and time.

Figure 4 presents relative rates (open circles, salicylic acid; squares, benzoic acid) calculated from the straight plots in Figs. 2 and 3. Also rate data obtained from disks made from mechanical mixtures of benzoic and salicylic acid powders are also presented (triangles, salicylic acid; closed circles, benzoic acid). The *y* axis gives the actual dissolution rate (Gm. sec.⁻¹) divided by the dissolution rate of pure benzoic acid disks.

The theoretical curves were constructed by means of Eqs. 2 and 11 in the range $N_A/N_B > (D_A/C_A^0)/(D_B C_B^0)$ and in the range $N_A/N_B < (D_A C_A^0)/(D_B C_B^0)$ by means of Eqs. 15 and 16

$$G_A = (N_A/N_B)G_B \quad (\text{Eq. 15})$$

and

$$G_B = D_B C_B^0/h \quad (\text{Eq. 16})$$

The experimental values, $C_A^0 = 3.5 \times 10^{-3}$ Gm.

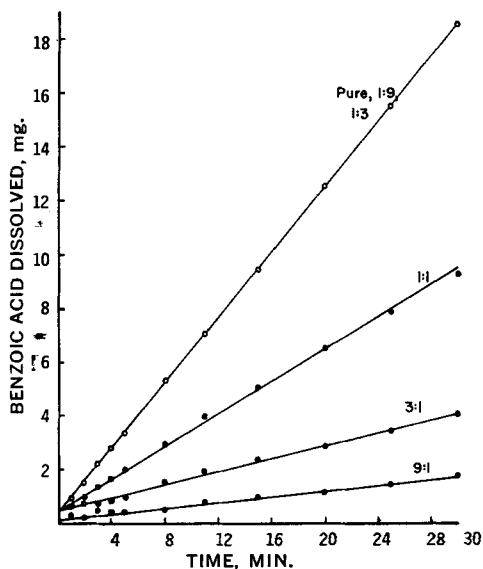


Fig. 2.—Data showing the effect of mixture ratio on the time-release behavior of benzoic acid from benzoic acid-salicylic acid mixture disks in 0.10 *N* HCl. Numbers give the salicylic acid-to-benzoic acid w/w ratio in the mixtures. Mixtures were made from melts.

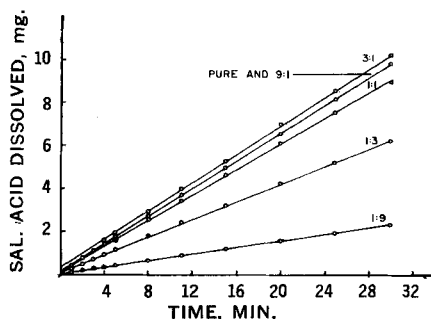


Fig. 3.—Data showing salicylic acid release in the same experiments as Fig. 2.

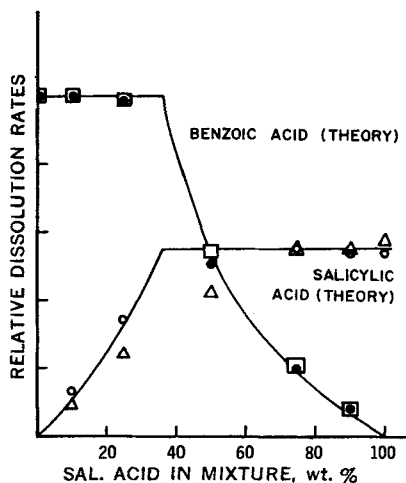


Fig. 4.—Comparison of theory with data on dissolution rate as function of the salicylic acid-benzoic acid mixture ratio. See text for more explanation.

ml.⁻¹ and $C_B^0 = 2.0 \times 10^{-3}$ Gm. ml.⁻¹, were used with $D_B = 0.96 D_A$ to give the fit as shown.

With both the melt and the mechanical mix data, the agreement of theory with data is very good. The presence of the plateaus in Fig. 4 clearly proves that the model is essentially correct for this system.

There are some deviations of theory from data near $(N_A/N_B) = (D_A C_A^0)/(D_B C_B^0)$. This is not too surprising because the dissolution rates are expected to be sensitive to small local variations in composition or to small fluctuations in the rates themselves when the mixture ratio is near the critical value. It is noteworthy that the data with the melt mixes agree better with theory in this region. This is consistent with the expected more intimate mixing of the phases in the melt preparations and the resulting better definition of the boundaries, *S*₁ and *S*₂.

A CASE INVOLVING SOLUTION INTERACTIONS: BENZOCAINE-CAFFEINE

Steady-State Theory.—Let us consider again the one-dimensional problem but only for the steady state, *i.e.*, for $S_2 - S_1 = \text{constant}$ with respect to time. As in the previous example, we expect three

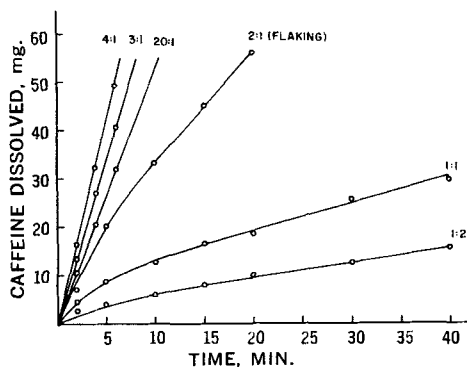


Fig. 5.—Data showing time-release behavior of caffeine from benzocaine-caffeine mixture disks in water. Numbers on plots give the caffeine-to-benzocaine w/w ratio in the mixtures. Mixtures were made from melts.

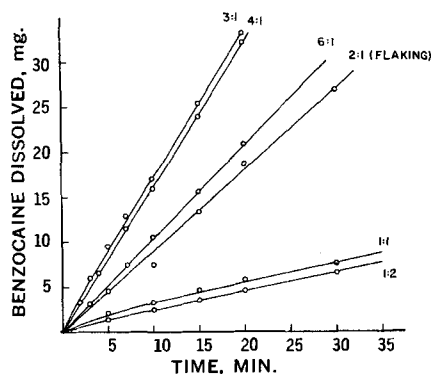


Fig. 6.—Same experiments as in Fig. 5, but plots show benzocaine release.

important cases analogous to those shown in Fig. 1. These are the situations corresponding to the caffeine surface phase, the benzocaine surface phase, and the critical mixture situation in which both phases coexist at the solid-solution boundary.

Assuming that the only interaction involves the solution reaction $B + C = B \cdot C$, we have

$$K = C_{B \cdot C} / C_B C_C \quad (\text{Eq. 17})$$

Here C_B , C_C , and $C_{B \cdot C}$ are the concentrations of benzocaine, caffeine, and the 1:1 complex. The thermodynamics of this system have been investigated by Higuchi *et al.* (3, 4) to some extent. Equation 17 is probably only approximately correct as it has been observed that caffeine self-associates considerably at the higher concentrations.

Again, the problem is symmetrical so that it suffices to consider in detail only one of the cases. Let us take, then, the situation in which caffeine is the pure phase on the surface at steady state. Then the dissolution rate of caffeine, G_C , is given by

$$G_C = D_C \frac{dC_C}{dX} + D_{B \cdot C} \frac{dC_{B \cdot C}}{dX} \quad (\text{Eq. 18})$$

where D_C and $D_{B \cdot C}$ are the diffusion coefficients for unbound caffeine and for the complex, and X is the coordinate in the direction of diffusion in the liquid

diffusion layer. For the dissolution rate of benzocaine we have

$$G_B = D_B \frac{dC_B}{dX} = +D_{B \cdot C} \frac{dC_{B \cdot C}}{dX} \quad (\text{Eq. 19})$$

where D_B is the diffusion coefficient of benzocaine. Both Eqs. 18 and 19 represent the diffusional behavior in the liquid diffusion layer, and these equations may be integrated over the limits with the boundary conditions:

at $X = 0$ (the solid-liquid interface):

$$C_C = C_C^0, C_B = C_B', \text{ and } C_{B \cdot C} = C_{B \cdot C}'$$

and at $X = h$ (the bulk solution):

$$C_C = C_B = C_{B \cdot C} = 0$$

Here C_C^0 is the caffeine solubility in the absence of benzocaine, and C_B' and $C_{B \cdot C}'$ are the concentrations of free benzocaine and the complex at the solid-solution interface. Integration then gives us the following pair of equations:

$$G_B h = D_B C_B' + D_{B \cdot C} C_{B \cdot C}' \quad (\text{Eq. 20})$$

and

$$G_C h = D_C C_C^0 + D_{B \cdot C} C_{B \cdot C}' \quad (\text{Eq. 21})$$

Because in the steady state the following relation is true,

$$G_C = \frac{N_C}{N_B} G_B \quad (\text{Eq. 22})$$

where N_C/N_B is the caffeine-to-benzocaine ratio in the bulk mixture, we may now solve Eqs. 17, 20-22, eliminating C_B' and $C_{B \cdot C}'$ and obtain the following equations for G_C and G_B ,

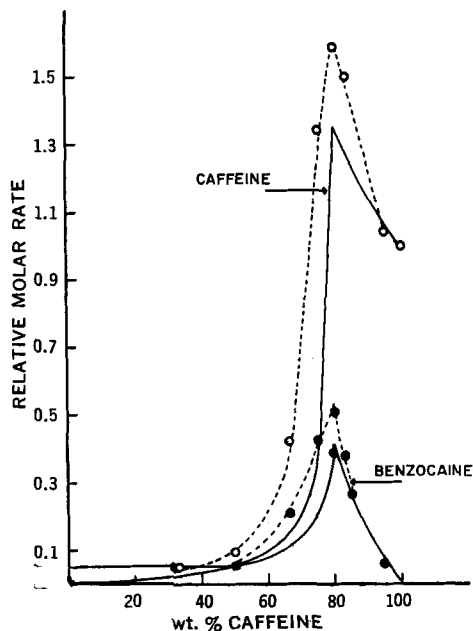


Fig. 7.—Comparison of theory with data on dissolution rate of benzocaine-caffeine mixtures as function of mixture ratio. See text for more information.

$$G_B h = \frac{D_C C_C^0}{\frac{N_C}{N_B} - \frac{D_{B.C} K C_C^0}{D_B + D_{B.C} K C_C^0}} \quad (\text{Eq. 23})$$

and

$$G_C h = \frac{D_C C_C^0}{1 - \frac{N_B D_{B.C} K C_C^0}{N_C (D_B + D_{B.C} K C_C^0)}} \quad (\text{Eq. 24})$$

By analogy it is seen that when pure benzocaine is the surface phase, the following pair of equations should result,

$$G_B h = \frac{D_B C_B^0}{1 - \frac{N_C D_{B.C} K C_B^0}{N_B (D_B + D_{B.C} K C_B^0)}} \quad (\text{Eq. 25})$$

and

$$G_C h = \frac{D_B C_B^0}{\frac{N_B}{N_C} - \frac{D_{B.C} C_B^0 K}{D_C + D_{B.C} C_B^0 K}} \quad (\text{Eq. 26})$$

For the critical mixture case, Eqs. 18 and 19 may be solved with the boundary conditions: at $X = 0$:

$$C_C = C_C^0 \text{ and } C_B = C_B^0$$

and at $X = h$:

$$C_C = C_B = 0$$

Therefore, we have in this instance

$$G_C h = D_C C_C^0 + D_{B.C} K C_B^0 C_C^0 \quad (\text{Eq. 27})$$

and

$$G_B h = D_B C_B^0 + D_{B.C} K C_B^0 C_C^0 \quad (\text{Eq. 28})$$

Comparison of Theory with Data.—Figures 5 and 6 show data on the time-dissolution behavior of disks made of benzocaine-caffeine mixtures. These were melt samples as in the one set of benzoic acid-salicylic acid experiments. It can be seen from these plots that, in some instances, the results are not linear over the entire time range. This occurs for those cases in which the mixture ratio, N_C/N_B , is relatively small. As we shall see later, in these mixtures the surface phase was benzocaine, and the curvature represents the nonsteady-state period. This follows from a consideration of Eq. 14 which is, of course, only qualitatively applicable here. From this equation, it can be seen that a relatively large S_2 will be required for steady state when C_B^0/C_A^0 is large. Thus, the curved plots, particularly the 1:1 and the 1:2 curves in Fig. 5, are consistent with this consideration when benzocaine is the surface phase.

The steady-state dissolution rates were calculated from the limiting, large-time slopes of the data in Figs. 5 and 6, and these are presented (open circles, caffeine; closed circles, benzocaine) in Fig. 7 in normalized form. The ordinate in Fig. 7 is the relative rate found by dividing the actual molar rate by the rate for pure caffeine.

The theoretically predicted behavior for this system is represented by the smooth curves in Fig. 7. The theoretical calculations were carried out with Eqs. 23-26, and the following values were used for the parameters: $C_C^0 = 0.16 M$, $C_B^0 = 5.5 \times 10^{-3} M$, $D_{B.C} = D_C = 0.70 D_B$, and $K = 59$. Some explanation is required for the choice of these values.

The C_B^0 value was determined experimentally, and this compares well with the value ($5.2 \times 10^{-3} M$) reported by Higuchi and Lach (3). The selection of the C_C^0 value was made in the following way.

The dissolution rate of disks made from pure caffeine melt was consistently greater by about 20% than the rate for disks made from nonmelt caffeine powder for which the solubility was found to be 0.136 M . Therefore, it was assumed that the solubility of the melt powder was greater by the ratio of the two dissolution rates in all of the mixtures. This problem did not exist for C_B^0 . The value for $K = 59$ was taken from the paper by Higuchi and Lach (3). The value for $D_C = 0.70 D_B$ was deduced from experiments with pure caffeine and pure benzocaine disks and assuming the usual Noyes-Whitney relation. The choice of $D_{B.C} = 0.70 D_B$, though not critical, has no basis except that it is a reasonable value. Actually both choices, $D_C = 0.70 D_B$ and $D_{B.C} = 0.70 D_B$, are consistent with the effective molecular weight of the diffusing caffeine being somewhere between that for a dimer and a trimer. This tendency for caffeine to associate forming dimers, trimers, and tetramers has been noted previously (4).

The agreement of theory with data is generally good. The experimental critical mixture ratio (80% caffeine) agrees well with theory, although the caffeine dissolution rate at this point appears to be significantly greater than theory. It is believed that this is largely due to the approximate nature of the assumption that only a 1:1 complex contributes to the increased solubility of caffeine in the presence of benzocaine. The benzocaine data for caffeine percentages greater than 80 agree extremely well with theory.

For caffeine percentages between 50 and 80, the experimental results are much larger than theory. It is believed that flaking of the disks during dissolution was responsible for this. Considerable flaking was observed in the 2:1 experiments, and the phenomenon was probably also very important for the 3:1 mixture even though it was not observable. It is reasonable to expect flaking in mixtures with caffeine percentages just less than 80, because the benzocaine residue in the surface phase would tend to have extremely high porosities and would be unable to remain as a substantial matrix. On the other hand, for caffeine percentages greater than 80 there should be ample caffeine in the surface layer giving sufficient mechanical structure.

A MORE COMPLEX SITUATION: BENZOIC ACID-TRISODIUM PHOSPHATE

One of the cases studied by Nelson (5) is the dissolution of benzoic acid-trisodium phosphate mixtures in water. Following methods similar to those for the other two examples in this paper, we may set up the appropriate equations for this problem. For benzoic acid-rich mixtures we have, in the steady state,

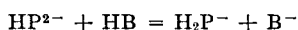
$$G_B h = D_B C_B' + D_{HB} C_{HB}^0 \quad (\text{Eq. 29})$$

$$(N_P/N_B) G_B h = D_{HP} C_{HP}' + D_{H_2P} C_{H_2P}' \quad (\text{Eq. 30})$$

$$D_B C_B' = 2 D_{H_2P} C_{H_2P}' + D_{HP} C_{HP}' \quad (\text{Eq. 31})$$

$$K = (C_{H_2P}' C_B' / C_{HP}' C_{HB}^0) \quad (\text{Eq. 32})$$

Here G_B is the dissolution rate of benzoic acid; C_B' , C_{HP}' , and C_{H_2P}' are the concentrations of the benzoate, the HPO_4^{2-} , and the $H_2PO_4^-$ ions at the disk-solution interface; C_{HB}^0 is the concentration of unionized benzoic acid in equilibrium with the solid; N_P and N_B are the amounts of total phosphate and total benzoate in the mixtures; K = the constant for the reaction



and all of the D 's are the diffusion coefficients. Since there are four equations, we may eliminate C_B' , C_{H_2P}' , and C_{HP}' , and setting all the diffusion coefficients equal we get

$$G_B h = DC_{HB}^0 \left\{ 1 + \frac{K}{2(1-k)} \left[2k + \frac{k}{K} - 1 \right] + \left(1 - 4k + \frac{k^2}{K^2} + 4k^3 - \frac{4k^2}{K} + \frac{6k}{K} \right)^{1/2} \right\} \quad (\text{Eq. 33})$$

where $k = N_P/N_B$.

For the situation in which the mixture is rich in trisodium phosphate, we may write the following equations:

$$kG_B h = D_{HP}C_{HP}' + D_{H_2P}C_{H_2P}' + D_P C_P' \quad (\text{Eq. 34})$$

$$kG_B h = \frac{1}{3} D_{Na} C_{Na}' \quad (\text{Eq. 35})$$

$$hG_B = D_B C_B' \quad (\text{Eq. 36})$$

$$D_B C_B' = 2D_{H_2P}C_{H_2P}' + D_{HP}C_{HP}' \quad (\text{Eq. 37})$$

$$K_{SP} = (C_{Na}')^2 C_P' \quad (\text{Eq. 38})$$

$$\frac{K_{3P}}{K_{2P}} = \frac{C_{H_2P}' C_P'}{(C_{H_2P}')^2} \quad (\text{Eq. 39})$$

Here C_x' is the concentration of species x at the disk-solution interface. In addition to those species entering into Eqs. 29-32, we must now include Na^+ and PO_4^{3-} . Also K_{SP} , K_{2P} , and K_{3P} are, respectively, the solubility product for trisodium phosphate, the second and third dissociation constants for phosphoric acid.

Equations 34-39 may be solved by eliminating all of the C_x' to give

$$(G_B h)^8 (2k - 1)^2 - (G_B h)^4 \left(\frac{D_{Na}}{3k} \right)^3 \times K_{SP} \left[\frac{K_{2P} D_{HP}^2 (1-k)}{K_{3P} D_{H_2P}} + 4D_P (2k - 1) \right] - \left(\frac{D_{Na}}{3k} \right)^6 K_{SP}^2 D_P \left[\frac{K_{2P} D_{HP}^2}{K_{3P} D_{H_2P}} - 4D_P \right] = 0 \quad (\text{Eq. 40})$$

In Fig. 8 theory, as represented by Eqs. 33 and 40, is compared with Nelson's data. The following values for the parameters in the theory were employed: $K_{SP} = 22$, $K_{HB} = 8 \times 10^{-6}$, $K_{2P} = 10^{-7}$, $K_{3P} = 10^{-12}$, and all D 's were taken equal to each other.

The agreement is much poorer in this instance than in the other two examples of this paper. This is perhaps not surprising for a number of reasons. The solubilities involved here become extremely high ($\sim 30 M$) near the critical mixtures. It is believed that as a result of this considerable disintegration of flaking (or incipient flaking) may

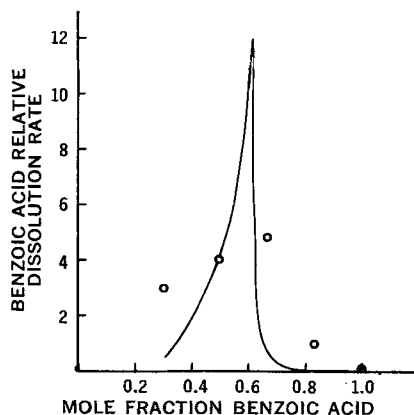


Fig. 8.—Comparison of theory with data on release of benzoic acid from benzoic acid-trisodium phosphate mixtures in water. Data taken from Nelson (5).

occur in these cases. The high solubilities also introduce considerable uncertainties in the parameters that should be used in the theoretical calculations.

Nevertheless, the theoretical maximum rate is consistent with data so that the general agreement should be considered satisfactory, at least tentatively, in view of the large uncertainties.

EXPERIMENTAL METHODS

The data presented in Figs. 2-7 were obtained in the following manner.

The mixes were compressed in a $3/8$ -in. die at 2400 lb. in a Carver press so that the disk surface was flush with the die surface. The back of the die was then wax sealed. The die was mounted directly in a Plexiglas holder in a water-jacketed beaker containing 400 ml. of solvent at 30°. Agitation was achieved by a glass stirrer attached to a Bodine synchronous motor (150 r.p.m.) mounted on the beaker cover. The Plexiglas sample holder was also mounted on the cover so that (a) the entire unit could be introduced into the solvent immediately at time zero and (b) the hydrodynamics remained constant in all experiments.

For the benzoic acid-salicylic acid runs in 0.10 N HCl, the steel dies were coated with a Plexiglas spray coating to inhibit corrosion.

Samples were pipetted out at various times for analysis by U.V. methods.

In runs with the melts, the melts were ground and only particles less than 200 mesh size were used in making the disks. These were also assayed to make certain that the compositions were correct.

The mechanical-mix disks also were made from < 200 mesh particles.

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