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COMPARISON OF SOLID-LIQUID AND LIQUID-LIQUID MASS TRANSFER

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ABSTRACT

Mass transfer from solutions of m-acetotoluide, phenacetin and salicylamide into a stationary solvent, water, was studied. A sharp concentration jump was found at the leading solute front for all three liquid-liquid systmes. A comparison was made between the mass transferred in solid-liquid and liquid-liquid systems. The dissolution of m-acetotoluide, phenacetin and salicylamide was compared with mass transfer of solute from solutions with concentrations C_i, $2C_i$ and C_s into the pure solvent. In all cases, the amount dissolved from the solid was approximated by the C_i or the $2C_i$-solvent system with the amount transferred in the C_s-solvent

system approximately 100 fold greater than was dissolved from the solid. It was concluded that a concentration much less than saturation exists at the solid-liquid interface and that dissolution of the three compounds studied is controlled by the rate of solvent interaction at the solid surface.

INTRODUCTION

When two miscible liquids are in contact, as when dissolving solute molecules mix with the pure solvent, there can be no equilibrium except that of one phase distributed uniformly in the other. This process of distributing one phase (solution) into another (solvent) may be termed hydrodynamic dispersion[1]. Hydrodynamic dispersion can be considered as the result of the movement of the individual solute molecules within the medium and the physical-chemical phenomena which take place in the medium.

In a series of papers, Taylor[2-4] treated the problem of dispersion between two miscible phases and developed the concept of a dispersion coefficient to replace the diffusion coefficient. His original treatment of miscible fluid flow has been used by numerous investigators in studying fluid flow in porous media. Wooding[5], for example, expanded on Taylor's work by using a porous media as a model for flow between two miscible liquids. Von Rosenberg[6] has successfully employed Taylor's result[2] while studying the physical process of a fluid displaced from a porous medium by another fluid of the same density and viscosity under conditions of complete miscibility of these two fluids. The displacement occurred as a result of combined convective and diffusional mixing.

The descending dissolution model used previously in this laboratory[7,8] represents a physical system where two miscible liquids are in contact. These two miscible liquids are the solvated solute solution and the pure bulk solution where the solvated solution is obviously supplied by the dissolving solid. These previous studies[7,8] have indicated that a concentration, much less than saturation, may exist at the solid-liquid interface. Regardless of what concentration exists at the solid-liquid interface, it should be possible to duplicate the solid-liquid system using a liquid-liquid system with appropriate solute concentration. This work was therefore designed to study the relationship between liquid-liquid mass transfer in a vertical column and solid-liquid mass transfer from a horizontal surface in a vertical column.

EXPERIMENTAL

Materials

The materials used in this study were m-acetotoluidide (I), phenacetin NF (II) and salicylamide NF (III). The water used in this study was double distilled.

Spectrophotometric Method

The compounds I, II and III have intense spectra in the UV region. A Cary Model 17 recording spectrophotometer was used for the UV analysis. In water, I has an absorption maxima at 240 nm, II at 243 n, and III at 297 nm.

Compartmental Column

The compartmental dissolution column previously used in this lab[7,8], consisting of a series of 14 plexiglass compartments, was

employed in the liquid-liquid mass transfer studies, as was the environmental chamber for maintaining column temperature at 30 ± 0.01°. The column was rinsed by continuously adding distilled water and allowing the water to seep out of the syringe needles for 15 to 20 minutes. The column was then rinsed two additional times before being put into the environmental chamber. The column, together with the solutions and tablet preparations to be studied, were kept in the environmental chamber for at least six hours before starting the column filling procedure in order for equilibrium to be established.

Solid-Liquid Mass Transfer

Tablet preparation:

1. The solid was melted in a casserole and poured onto a highly polished stainless steel punch in a die previously warmed to 50°C and having a diameter of 1.111 cm.

2. After a thin layer of the solid has solidified on the punch surface the melt was removed from the punch and die. This procedure served to condition the punch surface.

3. The punch surface was wiped clean and the melt immediately poured again into the punch and die assembly.

4. The mass was allowed to solidify completely and the tablet removed.

The dissolution column described previously was filled with distilled water and the water was allowed to drip out of the syringe needles. This procedure avoided bubble formation and eliminated the air in the needles.

Corks were then inserted into the needles. The tablet containing slide was mounted on the top of the column and the end-cap bolted

into place. Extreme care was required to assure no air bubble anywhere inside the filled column.

The filled column was positioned on a stand, checked with a leveling bar and allowed a two-hour period to insure fluid static equilibrium inside the column. The tablet was pushed into position and the dissolution was initiated. At the end of the experimental run, the compartments were closed simultaneously by pushing the draw-rod to the closed position and the tablet was pushed out of position.

The column was then removed from its stand and the solution in each compartment was pipetted from the syringes and transferred into appropriate volumetric flasks. Following dilution, the contents were assayed spectrophotometrically.

Liquid-Liquid Mass Transfer

The same dissolution column described earlier was also employed in the liquid-liquid mass transfer studies. The lower eight compartments of the column were filled with distilled water which was allowed to drip out of the syringe needles as before, and the corks were inserted into the needles. The number six slide between the 6th and 7th compartments was pushed into the closed position to isolate the distilled water from the solution above it. In doing this, extreme care was needed to avoid bubble formation around the number six slide in the column.

The solution under study was then poured into the upper six compartments. The solution was allowed to drip out of the syringe needles as was the distilled water in the solid-liquid mass transfer studies. The corks were inserted, the top slide was mounted, an

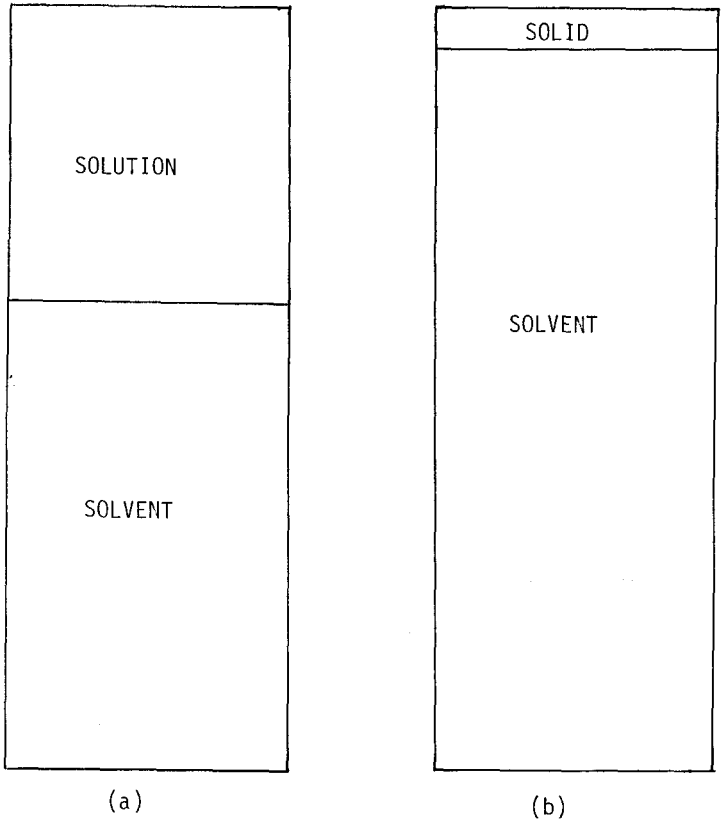

FIGURE 1

The initial configuration of the liquid-liquid system (a) as compared to the solid-liquid system (b).

end-cap was bolted into place and the column was wiped dry. Again, no bubbles were allowed anywhere inside the filled column. The configuration of the liquid-liquid system as compared to the solid-liquid system is shown in Figure 1.

The solutions used in this study were C_i, $2C_i$ and C_s for each of the three solids. The C_i values were determined by the descending

TABLE I

Concentrations of the Solutions Used in the Liquid-Liquid Mass Transfer Studies

Solution	Concentration (mg/ml)
m-Acetotoluide C_i	0.26
m-Acetotoluide $2C_i$	0.53
m-Acetotoluide C_s	6.2
Phenacetin C_i	0.058
Phenacetin $2C_i$	0.12
Phenacetin C_s	1.03
Salicylamide C_i	0.15
Salicylamide $2C_i$	0.29
Salicylamide C_s	3.1

dissolution method in previous studies[7,8]. The concentrations of these solutions are shown in Table I.

Again, the column was checked with a leveling bar and two hours were allowed in order that static equilibrium would be reached.

To initiate the experiment, the number six slide was pushed into the open position to permit liquid-liquid contact. At the end of each experimental run, the compartments were closed simultaneously, the column removed from its stand, and the solution in each compartment was withdrawn with five ml syringes. Samples from each compartment were pipetted from the syringes and transferred into

appropriate volumetric flasks. Following dilution, the contents were assayed spectrophotometrically.

RESULTS AND DISCUSSION

Liquid-liquid mass transfer studies from solutions of m-acetotoluide, phenacetin and salicylamide with concentrations of C_i, $2C_i$ and C_s into water generated concentration profiles similar to the profiles previously obtained for the solid-liquid systems[7,8]. Figure 2 is representative of the data obtained for the three compounds. The vertical dashed line at compartment 6 indicates the interface at time zero. The sharp cut-off observed during dissolution of a solid in the descending dissolution model[7,8] was again found at the leading solute front for all the liquid-liquid systems studied.

As such, the statistical model used to analyze the solid-liquid data[7,8] appears to provide a satisfactory means of describing the flow of solute in a liquid-liquid system. The similarity of the two systems is really to be expected as the concentration profile developed in the solid-liquid system should be dependent only on the concentration of solute at the interface and not on the nature of the solid. However, the nature of the model describing solute flow in the liquid-liquid and solid-liquid system does not, in itself, determine the mechanism of solid dissolution. Of particular importance is the determination of total solute transfer which, along with a comparison of dispersion coefficients determined from the model, permits a more conclusive analysis of the dissolution mechanism.

Table II shows the comparison between the amount dissolved in the solid-liquid systems and the amount of solute transferred in

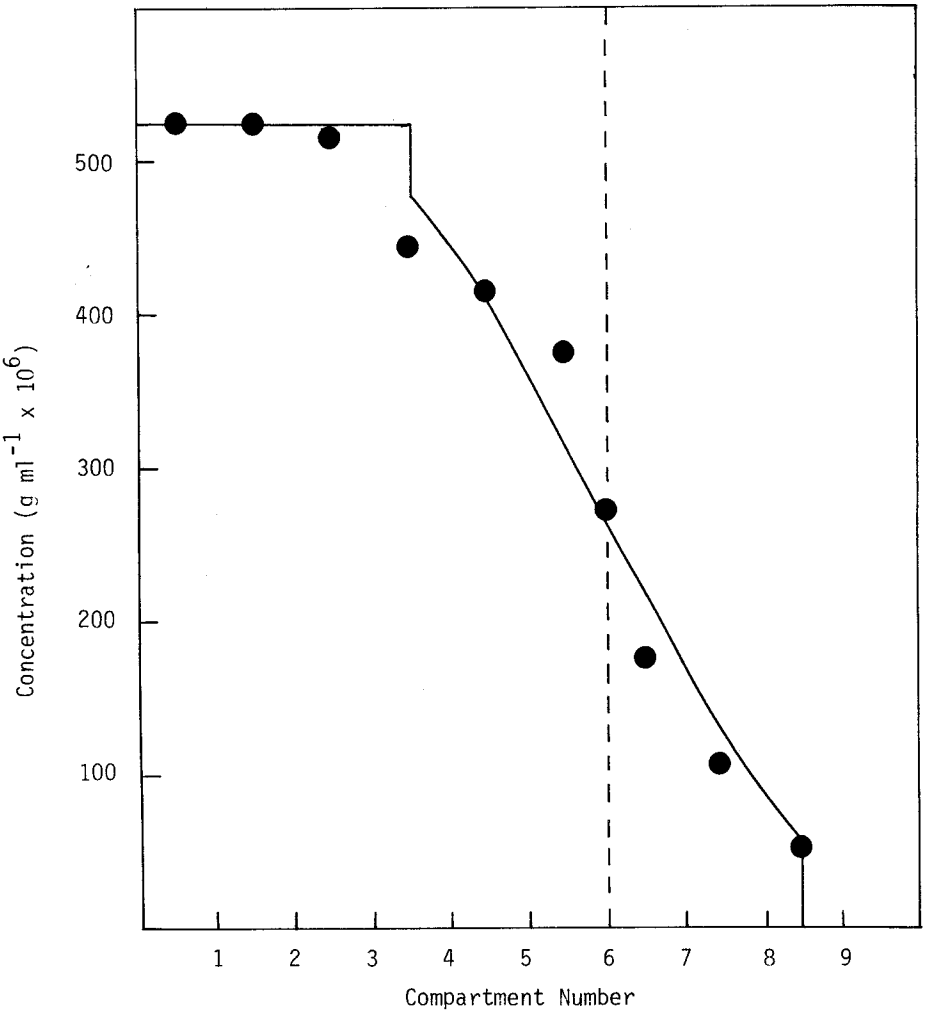

FIGURE 2

Comparison of the Theoretical (——) and Experimental (●) concentration gradients developed in the liquid-liquid mass transfer studies of m-acetotoluidide $2C_i$-H_2O system after 5 minutes.

TABLE II

Comparison of Mass Transfer in Liquid-Liquid and Solid-Liquid Systems

	Amount Transferred (mg)			
Solute	Solid-Liquid	C_i-Solvent	$2C_i$-Solvent	C_s-Solvent
Phenacetin 10 Min.	0.0923	0.0521	0.110	7.544
Salicylamide 5 Min.	0.293	0.226	0.834	27.782
m-Acetotoluidide 2 Min.	0.240	0.141	0.457	28.220
m-Acetotoluidide 5 Min.	0.516	0.354	0.984	90.225

the liquid-liquid systems. For comparison purposes, if the C_s-solvent liquid-liquid system produced solute mass transfer equivalent to the dissolving solid or solid-liquid system, it would be indicative of a saturation concentration at the solid-liquid interface with subsequent mass transfer control. If on the other hand, the solute transfer in the $2C_i$-solvent liquid-liquid system was equivalent to that in the solid-liquid system, it would indicate a concentration much less than saturation at the solid-liquid interface and interfacial control of solid dissolution.

It is obvious from Table II that a concentration much less than saturation must exist at the solid-liquid interface and that an interfacial mechanism is controlling the dissolution of the three solids. In all cases, the amount dissolved from the solid lies between the amount transferred in the C_i-solvent and $2C_i$-solvent systems with the amount transferred in the C_s-solvent systems approximately 100 fold greater than was dissolved from the solid.

Experimentally, the mass transfer of solute from solutions with concentrations of C_i, $2C_i$ and C_s into the solvent means that the effective interfacial concentrations between the solution and the solvent are $\frac{1}{2}\ C_i$, C_i and $\frac{1}{2}\ C_s$. This is a consequence of the fact that equal amounts of the solute and solvent are transferred in opposite directions across the volume-fixed interfacial sections. Solutions having effective interfacial concentrations of C_i and C_s would be ideal for elucidating which mechanism, interfacial or diffusional mass transfer, is controlling the dissolution process. Unfortunately, it is not possible to have a solution with initial concentration $2C_s$ in order to simulate an interfacial concentration

TABLE III

Dispersion Coefficients of Solid-Liquid and Liquid-Liquid Systems

Solute	System		Dispersion Coefficient, D' ($cm^2 sec^{-1}$)
m-Acetotoluidide	Liquid-Liquid	$2C_i$-H_2O	0.059
		C_s-H_2O	0.891
	Solid-Liquid		0.039
Phenacetin	Liquid-Liquid	$2C_i$-H_2O	0.011
	Solid-Liquid		0.009
Salicylamide	Liquid-Liquid	$2C_i$-H_2O	0.161
	Solid-Liquid		0.046

C_s. However, even with the lower interfacial concentration, ½ C_s, the results are very conclusive that the dissolution of a solid is probably controlled by an interfacial mechanism. The amount of solid phenacetin dissolved showed particularly good agreement with the $2C_i$-solvent system, 0.0923 mg compared to 0.110 mg, with salicylamide and m-acetotoluide-water systems showing somewhat larger differences, 0.293 mg to 0.834 mg and 0.516 mg compared to 0.984 mg. These differences are really very small compared to the amount transferred in the C_s-solvent systems and are most likely due to a small initial mixing when liquid-liquid transfer is initiated. It is worth mentioning again that the effective interfacial concentration for the C_s-solvent system is only ½ C_s so that transfer from an interfacial concentration of C_s would be even greater.

Supporting this evidence of the existence of an interfacial concentration, C_i, are the dispersion coefficient data determined in the liquid-liquid system. This data is compared with the dispersion coefficients determined for the dissolution of the same solids (Table III). The magnitude of the solid-liquid system dispersion coefficient, when compared to the liquid-liquid system of the same interfacial concentration, indicates that the driving force for solute transfer following dissolution is the effective interfacial concentration.

It would appear from the data in Tables II and III and the above analysis, that the dissolution of phenacetin, salicylamide and m-acetotoluidide, having solubilities representative of many pharmaceutical compounds, is controlled by the rate of interaction of the solvent at the solid surface and not by a diffusional mass

transfer mechanism having a saturation concentration at the solid-liquid interface. It must be remembered, however, that there is considerable evidence supporting the diffusional model and extensive data, on more than three compounds, will certainly be required before general conclusions can be reached.

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