Part II. Kinetic Studies

Supersaturated solutions with randomly distributed seed crystals were formed by jet mixing of saturated slurries of urea–decane adduct and decane–urea–ethanol solutions. The resulting crystal growth rates were measured quantitatively with a rapid-mixing, stopped-flow calorimeter. Nucleation of additional crystals was negligible. Times required for 90% adduction ranged between 0.375 and 25.5 sec., a 68-fold variation. A single dimensionless chronomal which adequately represented all the kinetic data was obtained. In all runs, liquid phase mass transfer appeared to control the rate of adduction, despite the fact that the rapid mixing greatly reduced mass transfer resistance. Whereas the data were consistent with several equations describing models based on diffusional rate control, the results did not support mechanisms involving surface phenomena.

Kinetic data for urea adduction are quite sparse. Reported adduction times range from less than 1 sec. to hours and even days, depending on the method of contact and the choice of solvent, if any. In all cases of slow adduction, the observed rate appeared to be influenced by a slow mass transfer process such as diffusion through a solid layer, or by slow dissolution of solid urea.

Some equilibrium investigations were carried out in nonpolar solvents with the host present as solid urea. Negligible adduction rates were observed unless an activator, commonly methanol, was added to the solution containing only guest and solvent. Even with agitation, about 1 to 8 hr. were required for essentially complete adduction (*30, 33, 39*).

McAdie and Frost (*20*) investigated the rate of adduction of gaseous *n*-octane by solid urea and found that vapor of a polar solvent was needed to initiate the process. It is unlikely that the mass transfer resistance in the adduct surface layer was negligible.

Schlenk (*29*) proposed that adduct formation proceeds by guest molecules penetrating from a pure liquid into a urea lattice. This process is quite slow and was shown by Calderbank and Nikolov (*2*) to occur only for urea particles below a small critical size. Zimmerschied et al. (*39*) considered this penetration mechanism to control even in the presence of solvents.

Lahti and Manning (*15, 16*) measured adduction rates by mixing solutions of urea and guest in a rapid-mixing, continuous-flow device. They reported apparent first-order kinetics with adduction times of well under 1 sec. It appears that plugging near the thermocouple probe influenced their measurements.

The purpose of our investigation was to study adduction in the absence of as many rate-inhibiting influences as possible. This required use of a common solvent; therefore, phase equilibria with ethanol as a solvent were also determined (*32*).

The region of interest for the present kinetic studies was *AEDA* (Figure 5, reference *32*) where a homogeneous solution is supersaturated with respect to adduct. A labile solution at point *P* would spontaneously transform to adduct, whereas a metastable solution at point *Q* would probably not transform for a very long time. The amount of each phase formed can be obtained by using the lever-arm rule. Because of the curvature of the adduct solubility isotherms, it is possible to mix very rapidly two saturated solutions of different compositions, each containing a few stable adduct crystals, and to obtain a seeded supersaturated solution which is metastable with respect to nucleation of new crystals.

THEORY

In the present work adduction proceeded at low degrees of supersaturation and hence attention will be focussed on crystal growth rather than nucleation (*7, 12, 21, 23, 34*). Attrition and coarsening (*11, 17, 25, 36*) are also neglected. The growth rate of a new phase may be governed by a number of factors, such as interfacial phenomena, mass transfer, and heat transfer. Just as the initial formation of a crystal from solution requires the formation of a three-dimensional nucleus, so can the growth of a crystal face require the existence of a two-dimensional nucleus on that face. Nielsen (*23*) has derived sets of chronomals for several limiting cases of surface mechanisms of this type when certain assumptions apply. Surface mobility, steric effects, and surface rearrangement may also be significant. The need for surface nucleation may be eliminated by the presence of self-preserving active sites such as surface dislocations or irregular lattice faces (*1, 27*). Heat transfer is unimportant, except for melts and for precipitations with large heats of crystallization or solution.

When surface phenomena control the rate of crystal growth, it is possible to simplify the problem to a consideration of individual crystals or crystal faces. When diffusion is important, however, there is interaction between crystals by means of the diffusion field, and the problem is virtually impossible to model by tractable mathematics unless very stringent assumptions are made. Some assumptions commonly made are now summarized.

In diffusion models, Fick's laws are usually assumed to be applicable. Only the simplest geometrical cases can be handled. The crystals are generally assumed to be at least ten characteristic lengths apart, a distance for which it can be argued that particle interaction is small (*8, 25, 26*). Furthermore, a quasi steady state diffusion profile is usually assumed to apply for finite time, although Nielsen (*24*) has suggested a correction to be applied when this assumption is not valid. Uniform crystal size distributions are also frequently assumed. Various attempts have been made to generate chronomals for diffusion-controlled growth. Most apply only to a portion of the precipitation process. Nielsen (*23*) presented generalized diffusion chronomals which rest upon most of the assumptions mentioned above.

Nielsen (*23, 24*) has also derived generalized chronomals for several combinations of competing mechanisms. The shape of precipitated crystals is influenced by the growth kinetics and is, in general, different from the equilibrium shape. The problem of stability has been considered (*8, 9, 13, 22, 23, 38*). Although much uncertainty exists, it appears that theoretically stable smooth shapes such as ellipsoids are unstable with respect to protrusions.

EXPERIMENTAL WORK

A detailed description of the experiments may be found elsewhere (*31*).

Selection of Stopped-Flow Calorimetry

The study of rate phenomena is facilitated if the time required to create an initially unstable state is substantially less than the relaxation time of the system. Furthermore, the means of observation should be accurate and should have a small response time in relation to the relaxation time.

One method used extensively in biological applications to introduce rapid disturbances into a liquid system involves fast mixing of two liquids to form an unstable solution. Various programmed-flow modes, especially continuous flow and stopped flow, have been used. Several reviews of these methods are available (*3, 5, 28*).

The fast-mixing technique was felt to have promise for study of urea adduction. Continuous flow was rejected because plugging occurred too readily, the importance of unknown velocity profiles could not be assessed, reactant consumption was high, and only a few discrete data points rather than a complete kinetic chronomal could be obtained. Stopped flow was selected because it relieved these problems, although it introduced the requirements of very rapid flow stoppage and rapid observation of the extent of adduction. Temperature measurement was selected from several alternatives as the method of following the rate of adduction, because the rise in temperature is proportional to the heat released by adduction, which in turn is proportional to the total adduct formed.

Equipment

Special equipment was designed to exploit the nature of the adduct solubility isotherms on the phase diagrams (*32*). Because of the concave curvature, two slurries which are at equilibrium yield a seeded supersaturated solution when mixed rapidly. Since both feed and product streams were slurries, pumping and flow measurement were best handled by positive displacement.

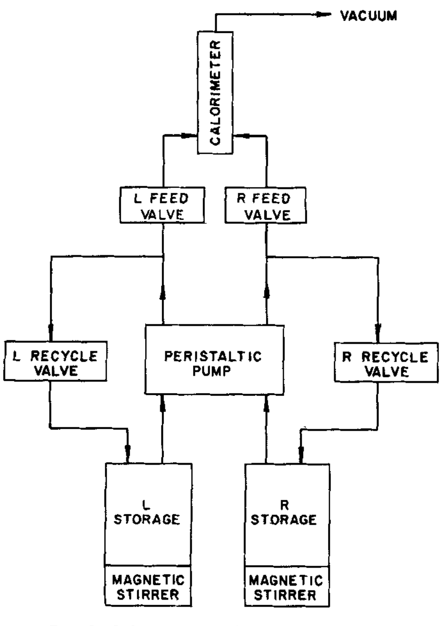

Fig. 1. Schematic of kinetic apparatus.

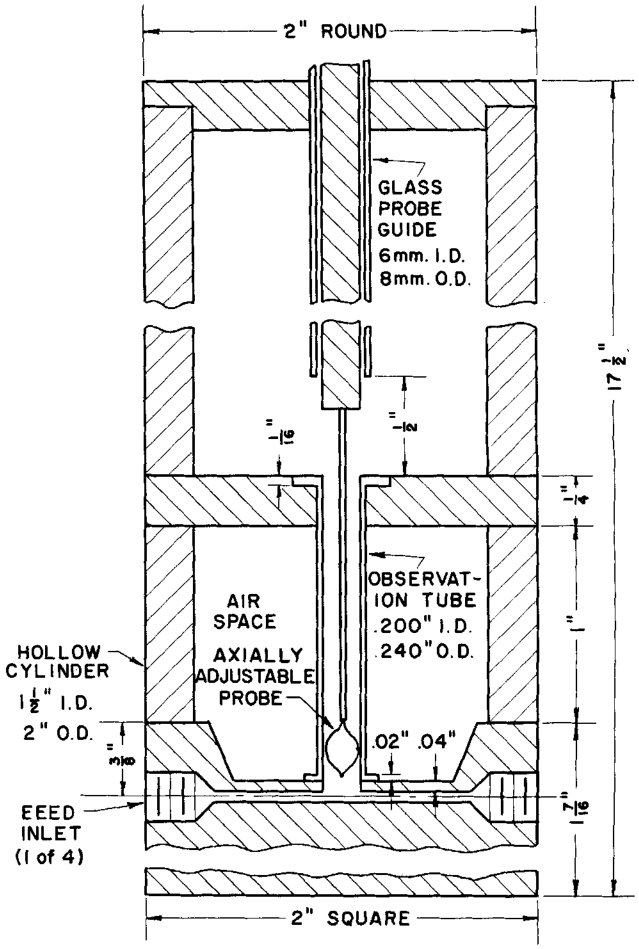

Fig. 2. Vertical cross section of Lucite calorimeter.

Figure 1 is a schematic diagram of the apparatus which gave best performance. Temperature control for the entire system was provided by air conditioning. Contents of the feed storage vessels were kept uniform by magnetic stirring. Feed streams passed from the storage vessels to a peristaltic pump, where a series of cam-operated fingers pressed flexible tubing against a flat plate. Variation of pump speed and tubing sizes allowed flow rate changes. Since both streams were pumped simultaneously, no problems of synchronization arose.

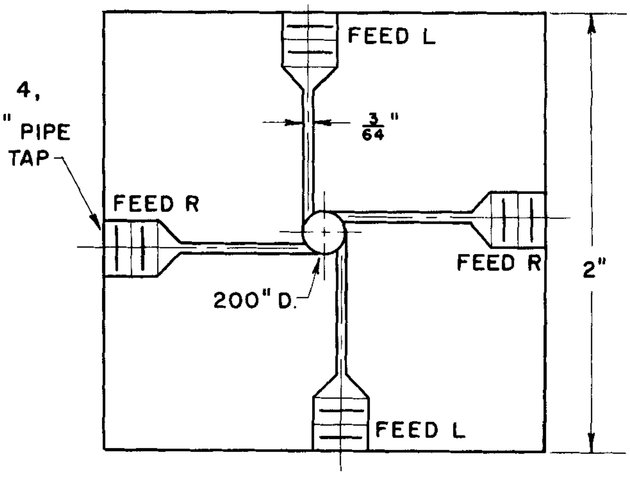

Fig. 3. Horizontal cross section of jet mixer.

After passing through the pump, each stream encountered a junction, one branch returning to the storage vessel and the other leading to the stopped flow calorimeter. The purpose of the recycle streams was to permit the pump to attain full speed before a run, during which time the recycle solenoid valves were open and the feed valves were closed. A special electrical circuit allowed all four solenoids to be reversed simultaneously (requiring only about 5 to 8 μsec.) when a switch was thrown, without causing electrical upsets in the recording circuit due to switch arcing.

The transparent calorimeter (Figure 2) consisted of a jet mixing chamber (Figure 3) followed by a thin-walled observation tube with an air jacket. Material leaving the observation tube was removed using an aspirator. Nearly all parts were made of Lucite with ethylene dichloride solvent welds.

Figure 4 shows the moveable copper-constantan thermocouple probe used to observe temperature changes. The probe, which included a loop to ensure centering in the tube, was usually positioned ¼ in. from the mixing chamber, a distance at which mixing was virtually complete. Because temperature changes of less than 1C.° were produced, the thermocouple output was amplified by more than 10,000 before being recorded with either an oscilloscope equipped with camera or with a strip-chart recorder.

The efficiency of the mixing chamber was measured by mixing unsaturated solutions with compositions close to those used in the kinetic runs, and measuring temperature profiles for steady flow. The device produced 63.2 and 90% mixing at mean residence times of about 2 and 6 μsec., respectively. For the experiments made in this equipment, the fast mixing criterion was met, even if stringent requirements such as those proposed by Vassilatos and Toor (35) for second-order reactions are used.

Both the output voltage and the response time of the combined temperature sensing and recording system were calibrated.

Heat conduction down the lead wires to the probe junction should not have been important because the probe was inserted axially. The observation tube was essentially adiabatic since unsteady state heat transfer calculations showed that negligible heat transfer to the wall occurred during a stopped flow measurement.

Since the densities of the adduct and the liquid solutions were quite similar, settling of crystals due to gravity was unimportant. Buildup of crystals against the probe tip during continuous flow was a potential source of error, and hence only a brief period of flow was used before flow stoppage.

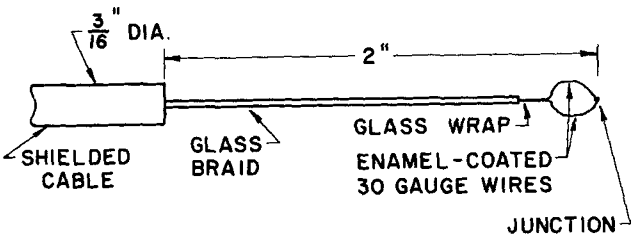

Fig. 4. Copper-constantan probe.

Visual observations revealed that a small positive axial pressure gradient existed in the core of the observation tube. This gradient produces relatively small internal recycling of fluid. The core is sustained by the angular swirling of the fluid, which creates a positive radial pressure gradient. As fluid moves down the tube, swirling decays and the center pressure increases. All of this can be easily predicted from the Bernoulli equation.

In this work, internal recycling was not a problem because adduction times far exceeded residence times. However, a quantitative analysis of the effects of flow profiles on observed rates of much faster reactions is needed to define the limitations of tangential jet mixing devices.

RESULTS AND DISCUSSION

Proper feed preparation required equilibrium solubility data (32). The overall compositions of the feed streams and the product stream had to be sufficiently close to the saturation curve at the run temperature so that crystals were not abundant enough to cause plugging. On the other hand, the solution resulting from mixing of the two slurries had to be sufficiently supersaturated to show a significant temperature rise upon adduction. The most uniform size distribution of seed crystals was obtained with vigorous stirring and addition of components in the order: ethanol, urea, decane.

Thirty runs with low electrical noise levels were made within the 22° to 27°C. temperature range. Since the original results were chart traces, it was useful to convert discrete points on each trace into digital form.

The fractional adduction α was taken to be equal to the fractional temperature rise, an assumption which was quite good for the relatively small supersaturations utilized. Not enough adduct was removed from the solution to change appreciably the heat of solution per mole of adduct.

Table 1 summarizes the kinetic data, which are given in greater detail elsewhere (31). The time required for 90% adduction ranged from 0.375 to 25.5 sec. As a check on the data temperature rises were predicted by estimating ternary heat effects from binary thermodynamic data (10, 15), giving close agreement with the observed temperature rises.

Comparison of the thirty runs led to the following conclusions:

1. By far the most important variable affecting the time required for adduction was the initial seed density (weight of seed crystals per unit weight of solution). Presumably, the size distribution of seeds would also be important, but seed size seemed to be fairly uniform in these experiments.

2. Adduction time was virtually independent of the initial supersaturation (31).

3. The kinetic traces had a common general shape, although individual runs deviated from it to some degree.

TABLE 1. SAMPLE OF KINETIC DATA

	Wt. fraction			Seconds					
Run	z_{uf}	z_{df}	ΔT_f, °C.	$t_{0.10}$	$t_{0.25}$	$t_{0.50}$	$t_{0.75}$	$t_{0.90}$	$t_{0.95}$
1	0.0415	0.0775	0.793	0.47	0.83	2.25	3.72	5.10	6.27
2	0.0415	0.0775	0.582	0.70	1.13	3.95	6.83	9.15	10.3
3	0.0415	0.0775	0.489	0.51	0.90	2.20	4.36	7.50	—
4	0.0251	0.249	0.505	0.24	1.23	7.10	13.7	25.5	30.6
5	0.0201	0.320	0.352	0.043	0.097	0.185	0.316	0.49	0.653
6	0.0201	0.320	0.336	0.080	0.121	0.150	0.321	0.600	0.758
7	0.0201	0.320	0.304	0.121	0.225	0.400	0.679	0.98	—
8	0.0251	0.249	0.675	0.19	0.78	3.87	7.40	10.9	—
9	0.0260	0.219	0.663	0.17	0.41	1.01	2.69	5.40	6.54
10	0.0260	0.219	0.595	0.18	0.50	1.24	2.01	7.80	9.00

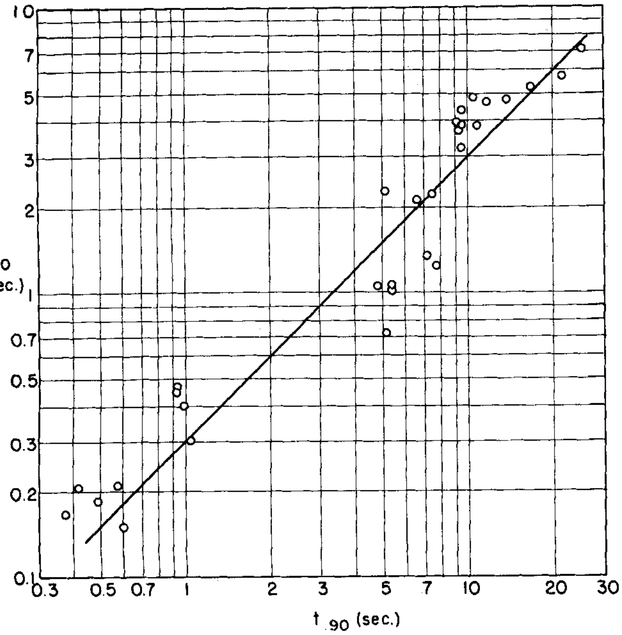

Fig. 5. Example correlation of characteristic adduction times.

Various methods were used to reduce the data to a common chronomal. The simplest was to note that the shape of an α vs. t curve was, on the average, independent of the time required for adduction, and hence the ratio of any two characteristic times would be nearly the same for all runs. Here characteristic time is defined as the time required to reach a specific fractional adduction. This hypothesis was tested by plotting the various characteristic times against each other and observing whether each resulting group of points could be correlated satisfactorily by a straight line through the origin. Because of the very large variation in adduction rates, logarithmic plots proved to be more convenient and the criterion of a straight line through the origin was replaced by the criterion of a unit slope.

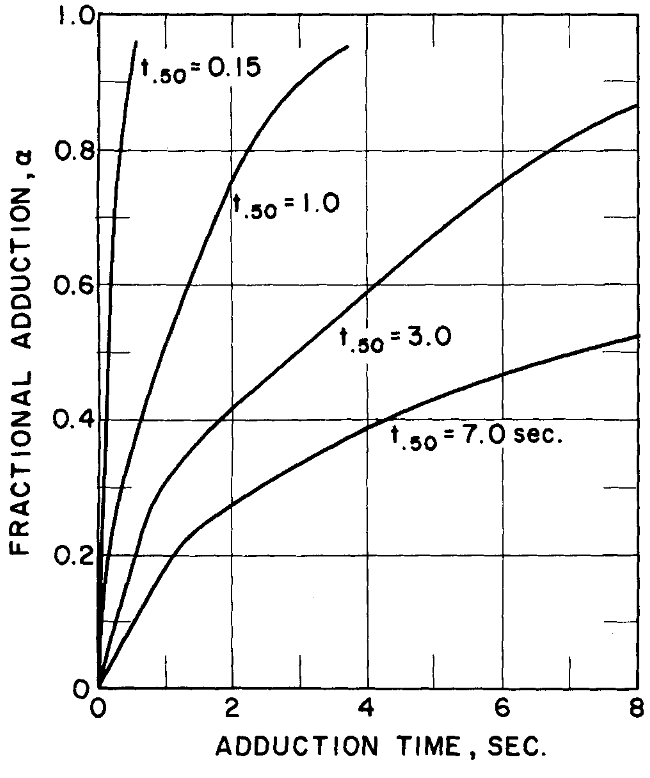

Fig. 6. Smoothed chronomals obtained from characteristic time correlations.

Such plots confirmed this hypothesis since slopes of unity were obtained for all except the most rapid runs, for which the response time of the temperature recording system was not negligible. Figure 5 presents a typical correlation. The general chronomal had the following ratios of characteristic times:

$$\begin{aligned} t_{0.10} &= 0.080 \quad (t_{0.50}) \\ t_{0.25} &= 0.234 \quad (t_{0.50}) \\ t_{0.75} &= 1.98 \quad (t_{0.50}) \\ t_{0.90} &= 3.00 \quad (t_{0.50}) \\ t_{0.95} &= 3.70 \quad (t_{0.50}) \end{aligned}$$

Smoothed chronomals for various half-times are shown in Figure 6. As stated before, individual runs did not follow the general shape exactly.

A completely satisfactory physical model cannot be obtained because of the complexity of the system. Specific difficulties are:

1. Distances between crystals were probably too small to assume noninteraction. Furthermore, the spatial distribution of crystal interfaces was unknown.
2. The crystals had the shape of long needles.
3. The system involved a quite nonideal three-component solution; hence diffusion coefficients were concentration dependent.
4. There were no unique liquid compositions which could exist at the interface during diffusion-controlled growth.

Despite these uncertainties, the experimental results presented here strongly suggest that adduction is mass transfer controlled even when rapid mixing allows closely spaced crystals to grow in an initially uniformly supersaturated liquid solution.

The observed adduction chronomal was tested against many of the customary empirical and semiempirical correlations. With the exception of those mentioned specifically below, these correlations proved to be inadequate, largely because the observed adduction rates decreased noticeably after α reached 0.3. This change in adduction rate supports the hypothesis of mass transfer control. Gross swirling of the rapidly mixed streams within the reactor was significant in the initial stages, but this swirling decayed rapidly to stagnation and this decay was augmented by the formation of precipitate. Therefore, the relatively rapid initial adduction rates are attributed to convection effects caused by the gross swirling. In the later stages, convection effects were absent and hence molecular diffusion controlled the rate. Figure 7 shows that for the major portion of the adduction chronomal, a plot of log α vs. log t was linear and had a slope of 0.50. This

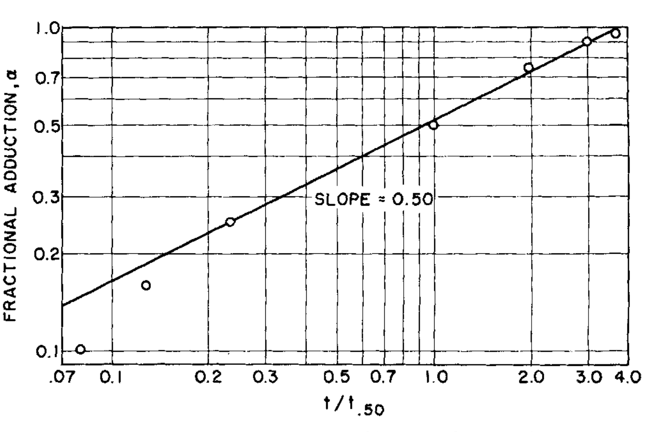

Fig. 7. Logarithmic plot of adduction chronomal.

type of square root time dependence for the total flux is characteristic of many semi-infinite diffusional processes. The deviation which occurred initially is again attributed to the early convection effects.

Some assumptions inherent in Nielsen's chronomal for diffusion from a finite medium to crystals dispersed throughout the medium (*23*, p. 34) may not apply to the present data. Nevertheless, it is interesting to compare his result with the much simpler chronomals for diffusion from finite regions to external spherical, cylindrical, and flat boundaries (*4*). Initially, there is some difference due to an appreciable moving boundary effect in Nielsen's model, but the final 40% of each chronomal (where boundary motion was unimportant) could be accurately described by an equation of the form

$$d\beta/dt = -k\beta^{0.75} \tag{1}$$

where $\beta = 1 - \alpha$.

It is significant that the adduction chronomal obtained in this work is also accurately described by Equation (1) for the last 40% of the process.

The equation

$$\alpha = 1 - \exp\left\{-\left(\frac{t}{t_{0.632}}\right)^b\right\} \tag{2}$$

has been applied to diffusion-controlled growth of precipitates, with values of b between 0.33 and 1.0 (*7*). It is theoretically valid only for $\alpha < 0.5$. This equation with $b = 1.0$ fits the data fairly well and might give a much better fit if the initial swirling had not occurred. In fact, if the first 25% of observed adduction is neglected, $b = 1.0$ gives a rather good fit.

The hypothesis of mass transfer control is supported further by the fact that the time scale of adduction did not increase with higher initial supersaturation. Crystallization controlled by surface phenomena has frequently been observed to have an exponent n in Equation (1), above the value of 0.75 observed here; a value of 2 is often cited (*6, 14, 18, 19, 37*) and a surface reaction order as high as 4 has been found (*23*, p. 60).

The fact that adduction time depends primarily upon the number of seed crystals present is also consistent with mass transfer control, since the distances between crystals are less when more crystals are present. However, this experimental observation could also be consistent with surface phenomena control, where increased surface area would be an important factor.

No model for rate control by interfacial phenomena or for combined mechanisms could be shown to be consistent with the adduction chronomal. This indicates that the process of incorporation of matter into the adduct crystals is very rapid.

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NOTATION

b = defined by Equation (2)
k defined by Equation (1)
t = elapsed time since mixing
t_α = elapsed time for fractional adduction α to occur
z_{uf} = final overall weight fraction urea
z_{df} = final overall weight fraction decane

Greek Letters

α = fractional adduction; ratio of mass of new adduct formed to final mass of new adduct
β = $1 - \alpha$
ΔT_f = final temperature rise due to adduction

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