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# Solvent Characterization Using the Dispersion Number

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# SOLVENT CHARACTERIZATION USING THE DISPERSION NUMBER

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## ABSTRACT

When developing new solvent extraction processes, one often has to evaluate new solvents, new aqueous phases, or both for their ability to work in plant-scale equipment. To facilitate solvent characterization, a simple test is proposed based on the dimensionless dispersion number ($N_{Di}$). It allows one to characterize the ability of the solvent to separate from a two-phase dispersion and to estimate process throughput for equipment of a given size. Several ways to carry out the $N_{Di}$ test are given, including a standard test procedure. The $N_{Di}$ test was applied to the performance of solvent extraction equipment with discrete process stages, the leaching of plasticizers from plastic tubing, and the development of a new solvent for the combined extraction of strontium and transuranic elements.

## INTRODUCTION

Characterization of an organic solvent with respect to its performance when dispersed with an immiscible aqueous phase can be quite complex. It involves many variables, including the density and viscosity of organic and aqueous phases,

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interfacial tension, surface viscosity, and surface elasticity. To simplify the experimental effort, a single measurement, the dimensionless dispersion number ($N_{Di}$), can be used to characterize the solvent. The $N_{Di}$ does not identify the most-important underlying variables, but it does give an overall characterization of the dispersion that is easily applied to the operation of plant-scale solvent extraction equipment.

The importance of the dispersion number is that it lets one estimate how long it will take for a liquid-liquid dispersion to coalesce completely. It can do this for batch systems as well as continuous-flow systems and for gravity systems as well as centrifugal systems. Thus, $N_{Di}$ is an important tool in the evaluation of mixing equipment and in the design of separating zones for liquid-liquid dispersions. In particular, $N_{Di}$ allows one to calculate the separating-zone volume that is required for a given throughput. Typically, this volume determines the maximum throughput for solvent extraction equipment.

The dispersion number was originally developed to characterize dispersions created in annular centrifugal contactors during solvent extraction operations (1). A detailed evaluation of the dispersion number was published in 1981 (2). In this paper, $N_{Di}$ was used to characterize the operation of centrifugal contactors with rotor diameters ranging from 2 to 25 cm and nominal throughputs (both phases) ranging from 0.04 to 120 L/min. It was shown that, for a given continuous phase, $N_{Di}$ is essentially independent of mixing intensity as long as the mixing is turbulent. In a 1983 paper, the dispersion number concept was extended to three immiscible liquid phases (3).

After reviewing how to calculate $N_{Di,}$ this paper presents a standard dispersion number test for solvent characterization. By having a standard test, one can meaningfully compare the performance of solvents, even when their differences in composition are small. This paper also describes some alternative $N_{Di}$ tests and applies either the standard $N_{Di}$ test or one of the alternatives to several problems of importance in solvent extraction operations.

## CALCULATION OF THE DISPERSION NUMBER

The dimensionless number for characterizing dispersions is given in its most general form as

$$N_{Di} = \frac{1}{t_R}\sqrt{\frac{\Delta Z}{a}} \qquad (1)$$

where a is the acceleration on the coalescing dispersion, $t_R$ is the average residence time in the coalescing dispersion band, and $\Delta Z$ is the thickness of the dispersion band in the direction of the acceleration (2).

For a batch operation or test, Eq. (1) is rewritten as

$$N_{Di} = \frac{1}{t_B} \sqrt{\frac{\Delta Z}{a}} \tag{2}$$

where $t_B$ is the time for the dispersion to break and the $\Delta Z$ refers to the initial thickness of the dispersion band. If the batch operation or test is done using gravity settling, then acceleration becomes simply g, the gravitational acceleration (9.81 m/s$^2$), and Eq. (2) becomes

$$N_{Di} = \frac{1}{t_B} \sqrt{\frac{\Delta Z}{g}} \tag{3}$$

In a batch centrifugal settler, the acceleration used is an average acceleration given by $\bar{r}\omega^2$, where $\bar{r}$ is the average radius out from the center of rotation, and $\omega$ is the rotational velocity whose SI units are rad/s. The average radius is given by

$$\bar{r} = \frac{2\,(r_o^3 - r_i^3)}{3\,(r_o^2 - r_i^2)} \tag{4}$$

where $r_o$ is the radius to the outer edge of the dispersion band and $r_i$ is the radius to the inner edge of the dispersion band. For batch operations, $r_o$ and $r_i$ are for the initial boundaries of the dispersion band.

For continuous settler operation, Eq. (1) is rewritten as

$$N_{Di} = \frac{q}{V} \sqrt{\frac{\Delta Z}{a}} \tag{5}$$

where q is the volumetric flow rate (both phases) through the settler, and V is the volume of the dispersion band in the settling zone. As with the batch operation, the acceleration for continuous operation becomes g for a gravity mixer-settler and $\bar{r}\omega^2$ for a centrifugal mixer-settler (normally referred to as a centrifugal contactor). For a gravity mixer-settler,

$$N_{Di} = \frac{q}{V} \sqrt{\frac{\Delta Z}{g}} \tag{6}$$

and, for a centrifugal contactor, Eq. (5) becomes

$$N_{Di} = \frac{q}{V}\sqrt{\frac{\Delta Z}{\bar{r}\omega^2}} \tag{7}$$

The dispersion number is proportional to throughput for solvent extraction equipment of a given size with a given accelerational force field. As reported by Leonard et al. (2), batch tests in a gravity field and continuous operation in a centrifugal field give essentially the same $N_{Di}$ for aqueous phases containing nitric acid and an organic phase consisting of 30 vol % tri-n-butyl phosphate (TBP) in normal dodecane (nDD). Thus, at least for this case, a standard batch test for measuring $N_{Di}$ not only characterizes the solvent, but also allows one to estimate equipment throughput.

## STANDARD TEST AND VARIATIONS

In this section, we present a standard test for measuring $N_{Di}$. In addition, we have included some notes that address typical questions which a user may have on the standard test. We have also included variations on the standard test that may, in some circumstances, be appropriate and even necessary.

### Standard Test

The standard test for measuring the dispersion number is as follows.

1. Place the two immiscible phases, typically organic (O) and aqueous (A) phases, into a 100-mL graduated cylinder with a ground-glass stopper. Measure the volume of each phase to ensure that the desired O/A volume ratio (discussed later) is achieved. The total volume of the two phases should be close to 100 mL so that $\Delta Z$ is close to 200 mm. Measure $\Delta Z$ and note the position of the interface between the two phases by using the volume marks on the cylinder.

2. Seal the graduated cylinder with the glass stopper and shake vigorously *ten (10)* times. After shaking, set the cylinder down on a bench top and begin timing with a stopwatch.

3. Watch as the two phases separate. If a coalescing dispersion band appears, follow it until the last droplet in the dispersion band breaks. Then stop the stopwatch and read the time to break ($t_B$). If no dispersion band is apparent, $t_B$ is determined as follows. Note the position of the interface between the two phases as it changes with time. Use 2 to 3 min intervals if the interface is moving slowly, 0.5

to 1 min intervals if it is moving quickly. When long time intervals are used and the interface position changes slowly, e.g., about 0.25 to 0.5% of the overall liquid height (both phases) for a long time interval, use the end of this interval as the time to break. Once $t_B$ is known, use Eq. (3) to calculate $N_{Di}$. Also note the cloudiness of each phase.

4. *If the final interface position is not the same as the interface position* before the graduated cylinder is shaken for the first time, let the cylinder stand until both phases are clear, typically, 2 to 3 h or overnight. To determine $N_{Di}$, we define the interface position before the graduated cylinder was shaken for the first time as the "initial interface"; the final interface position where $t_B$ is determined, the "final I (time-to-break) interface"; the final interface position after standing until the phases are clear, the "final II (clear) interface." If the final II interface has the same position as the final I interface, then the phase that has the increased volume must have extracted some component or components from the phase with the decreased volume. If the final II interface is at a different position from the final I interface, one phase was still dispersed in the other phase at the time to break. Knowing the initial phase volumes and this volume difference, one can calculate the fraction of A in O (this is the case where the O volume for final II is less than that for final I) or O in A (this is the case where the A volume for final II is less than that for final I). In doing this calculation, assume that all of the other-phase carryover is in the swollen phase. This assumption is reasonable as long as the swollen phase is very cloudy relative to the other phase. This other-phase carryover is associated with $N_{Di}$ since it reflects conditions at the time to break. Note that $N_{Di}$ is calculated using the time ($t_B$) at which the final I interface position occurs. The calculation of other-phase carryover, if any, requires the final II interface position. Typically, the phase with significant other-phase carryover (as seen by the difference in the final I and final II interface positions) will be the more cloudy phase when $t_B$ is being measured.

## Notes on the Standard Test

While the standard test may be all that is needed to measure $N_{Di}$, the notes here address a number of questions that the user may have. The questions answered are (1) what volume ratios to use, (2) how to tell which phase is the continuous phase, (3) what sort of standard deviation to expect in the $N_{Di}$ values, (4) how to shake the graduated cylinder, (5) how to know when the time to break occurs, (6) how to read the meniscus at the interface, and (7) how to assess what $N_{Di}$ is acceptable.

1. The volume ratios used and the composition of the phases should reflect the process conditions. If only one test is to be performed, an O/A volume ratio of 1.0 should be used. If only three tests are to be completed, the same aqueous phase should be used at three different O/A volume ratios. These ratios should reflect the range of process conditions. Also, the ratios should vary enough that both organic- and aqueous-continuous conditions are realized. For example, O/A volume ratios of 1/3, 1, and 3 would be a good choice. A full test would include solvent contact with each of the different aqueous solutions at the O/A volume ratio which corresponds to the O/A flow ratio in the process.

2. A basic guideline for identifying the continuous and dispersed phases is that the continuous phase is typically the more cloudy phase. However, there are exceptions. In addition, it is not always possible to identify which phase is more cloudy. So three additional guidelines are given:

- If one phase is crystal clear and one is cloudy, the clear phase is the dispersed phase. This observation is based on the fact that as a phase is dispersed, some of the droplets created are very fine. Many of the fine droplets remain behind in the continuous phase, making it cloudy.
- If a dispersion band appears, note the location of its upper and lower bounds at a certain time (t). Use these two bounds along with the final I interface position to calculate the volume of each phase in the dispersion band at time t. The phase with the greater volume in the dispersion band at time t is the dispersed phase. This test assumes that the dispersion band consists mainly of dispersed phase droplets which are pushing out the continuous phase. For the droplets to touch, their volume must be 60 to 70% of the total volume in the dispersion band.
- If no dispersion band forms but an interface appears, note the direction in which it is moving. The interface will be moving toward that phase which is the continuous phase. This guideline assumes that the volume of the continuous phase is temporarily swollen by the droplets of the dispersed phase.

3. A dispersion number test that is repeated three or four times should have a standard deviation of 10 to 25%. If these measurements are completed without

regard to which phase is the dispersed phase, the standard deviation for $N_{Di}$ can be much higher (35 to 65% for one case where the solvent was more viscous than the aqueous phase). When this increase in the standard deviation occurs, it suggests that some tests had the organic phase as the dispersed phase while the rest had the aqueous phase as the dispersed phase.

4. As mentioned earlier, the graduated cylinder is shaken ten times quite vigorously. Shaking should be completed in about 5 s. If some liquid contains only one phase immediately after shaking, the shaking was not vigorous enough. If the one phase significantly differs in viscosity from the other phase, hold the cylinder horizontal prior to shaking so that the two liquids extend the full length of the cylinder. In some cases we have tried to control which phase would be the continuous phase by turning the sealed cylinder upside down immediately before shaking. Sometimes this made the other phase the continuous phase, the rest of the time it did not. As a general procedure, we recommend turning the sealed cylinder upside down twice in a gentle rolling motion before initiating the 10 quick shakes.

5. The time to break ($t_B$) is easy to measure if a dispersion band forms and the droplets break at a fairly constant rate until they are all gone. If one or two droplets persist at the interface long after the rest of the droplets are gone, they should be ignored in measuring $t_B$. If no dispersion band forms, $t_B$ is that time when the interface seems to have stopped moving. This final interface position determines the amount of other-phase carryover associated with $N_{Di}$. If one chooses a longer $t_B$, the value for $N_{Di}$ will be lower but the amount of other-phase carryover will be reduced.

6. One must read the interface between the two phases in a consistent manner to get the best $N_{Di}$ results. A first technique is to read the bottom of the interface meniscus. A second technique is to read a point near the middle of the meniscus that seems to appropriately divide up the volume of the two phases in this region. The second technique is recommended when the interface position is used to determine other-phase carryover. In either case, be sure your eye is perpendicular to the cylinder surface at the point where the reading is being taken. Try a number of lighting conditions and backgrounds to find which one allows you to view the meniscus most clearly.

7. As the standard test is designed to characterize a solvent, there is no right or wrong value. However, in terms of solvent acceptability for stagewise

solvent extraction equipment, an $N_{Di}$ of $2 \times 10^{-4}$ would be poor; $4 \times 10^{-4}$, fair; $8 \times 10^{-4}$, good; $\geq 16 \times 10^{-4}$, excellent. Solvents with $N_{Di}$ values much less than $2 \times 10^{-4}$ will probably be unacceptable.

### Test Variations

Because $N_{Di}$ is more consistent if $\Delta Z$ is about 200 mm or greater for gravity settlers (4), small test volumes that make $\Delta Z$ much less than 200 mm are not recommended. While a minimum diameter was never established for the $N_{Di}$ test, it should be noted that tubes or cylinders with diameters 25 mm and larger seemed to give the same value for $N_{Di}$. We have done tests in test tubes using small liquid volumes when that was all we had available. Since $\Delta Z$ was much less than 200 mm and the tube diameter was much less than 25 mm, the tests were not very accurate. They did, however, give a rough estimate of $N_{Di}$.

If larger volumes of the two phases are available, they can be used to fill a 2-L glass beaker until it is 70 to 80% full. A Teflon-coated magnetic stir bar can be used to create the dispersion. If multiple beakers are used, the speed of each stirrer is adjusted so that the shape of the free surface in each beaker is the same. As the stir bar is at the bottom of the beaker, this makes the more dense phase the continuous phase unless so little of the more dense phase is present that it becomes the dispersed phase by spontaneous phase inversion. If a paddle mixer is used, the paddle can be inserted into either the more dense or the less dense phase. The phase with the paddle in it then becomes the continuous phase unless so little of that phase is present that the dispersion undergoes a spontaneous phase inversion. Thus, with the 2-L beaker, one obtains a more consistent dispersion (in terms of energy input and, thus, drop size) and, with a paddle mixer, one gains more control over which phase will be the continuous phase.

## APPLICATIONS

The dispersion number test was applied to three areas: stagewise contactor operation, plasticizer leaching from plastic tubing, and evaluation of new solvents being developed for solvent extraction. An overview of each of these applications is presented here.

### Stagewise Contactor Operation

In the operation of a continuous-flow stagewise contactor for solvent extraction, e.g., a mixer-gravity settler (mixer settler) or a mixer-centrifugal settler (centrifugal contactor) operating at a fixed rotational speed (the typical case), the size of the two-phase dispersion band in the settling (separating) zone of each stage grows as throughput increases until it reaches the less-dense-phase weir, or the more-dense-phase underflow leading to the more-dense-phase weir, or both. At this point, the other-phase carryover in one or both of the stage effluents increases dramatically. Typically, if the other-phase carryover in a contactor is greater than 1%, its operation is considered to be unsatisfactory. If unsatisfactory other-phase carryover occurs in both effluents at the same time as the throughput increases, then the dispersion band fills the separating zone, and $N_{Di}$ can be calculated for the unit using Eq. (6) or (7). For contactors with fixed weirs (5), the point where the dispersion band will just fill the separating zone can occur at only one O/A flow ratio. For contactors with an air-controlled more-dense-phase weir (6), the dispersion band can be made to fill the separating zone at any O/A flow ratio.

When 30 vol % TBP in nDD is the organic phase and dilute nitric acid is the aqueous phase, centrifugal contactors with rotor diameters of 2, 9, and 26 cm all had a dispersion number of 8 x $10^{-4}$ for organic-continuous operation (1, 2). Essentially the same $N_{Di}$ was measured by a gravity batch test. This work with 30% TBP in nDD and dilute nitric acid has since been extended to 4- and 12-cm centrifugal contactors, and the results were found to be the same. For the centrifugal contactors with this solvent, operation is typically organic continuous at O/A flow ratios greater than 0.5. An aqueous-organic pair identified as the Key Lake system was tested in a mixer settler by Eckert and Gormely (7). Analysis of their data using our Eq. (6) yielded an $N_{Di}$ of 13.1 x $10^{-4}$ with a standard deviation of 2.7 x $10^{-4}$. In these tests, the thickness of the dispersion band varied from 3 to 34 cm. The side walls of the gravity settler were made of wire-reinforced glass so that the dispersion band could be seen. The O/A flow ratio varied from 0.67 to 3.0 with organic-continuous operation in all cases. The width of the settler was 30 cm. Its length was variable from 0 to 120 cm. Because Eckert and Gormely did not perform gravity batch tests, we could not corroborate these $N_{Di}$ results for continuous flow operation. However, the fact that a single $N_{Di}$ can characterize all the results suggests that the standard $N_{Di}$ test presented here would have been useful.

## Plasticizer Leaching

In making tests with the 2-cm annular centrifugal contactor described by Leonard et al. (1), we found that the maximum throughput for 30 vol % TBP in nDD with a dilute $HNO_3$ aqueous phase seemed to vary with time. For example, at an O/A flow ratio of 1.0, the maximum throughput (both phases) varied from 40 to 80 mL/min. Typically, initial check tests gave a value of 80 mL/min. Then, over a period of weeks of intermittent testing using the same 0.5 to 1.0 L of solvent, this check test would drop to 40 mL/min. At one point, the transparent interstage lines, which were made of flexible polyvinyl chloride (PVC) tubing, had become quite cloudy and were replaced with new PVC tubing. Shortly after that, the maximum contactor throughput increased back up to 80 mL/min.

Based on this observation as well as others with our 4-cm annular centrifugal contactor, a special $N_{Di}$ test was set up using two 2-L beakers with Teflon stirring bars. With 800 mL of fresh aqueous phase (0.5M $HNO_3$) and 800 mL of organic (30 vol % TBP in nDD) phase in each beaker, the total liquid height was 131 mm. A section of PVC tubing, 610 mm long, was cut up in pieces ranging from 4 to 6 mm in length. The inside and outside diameters of this tubing were 9.5 and 12.7 mm, respectively. The tubing pieces, which were small enough to be suspended in the dispersion without interfering with the mixing action of the stirrer, were put in the first (test) beaker. The second (control) beaker had no PVC tubing. Three tests were done to determine the effect of the PVC tubing on $N_{Di}$.

The results of the first test (test 1) are given in Fig. 1. The dispersion number, which was $(7.16 \pm 0.51) \times 10^{-4}$ prior to time zero, increased dramatically when the PVC tubing pieces were introduced at time zero and then slowly decreased to its original value. In contrast, the dispersion number in the control beaker was $(7.32 \pm 0.08) \times 10^{-4}$ prior to time zero and remained essentially constant. During these tests, the two phases were kept dispersed except when the dispersion number was being measured.

As a part of test 1, the PVC tubing pieces were removed for the four $N_{Di}$ determinations between 169 and 192 min. As shown in Fig. 1, these four data points lie about 3% below the least-squares-fit curve. Thus, the presence of the tubing pieces in the dispersion appear to retard its coalescence only slightly if at all.

The first test was repeated (test 2) with fresh solutions and tubing to verify the increase in the dispersion number caused by the PVC tubing. The results, given in Fig. 2, show the same general characteristics, a sudden increase in the dispersion

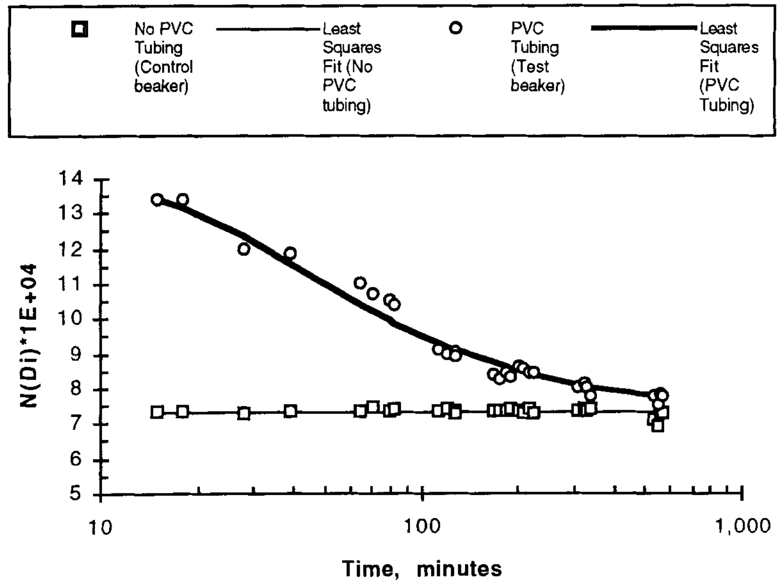

FIGURE 1. Effect of PVC tubing on the dispersion number as a function of time (Test 1).

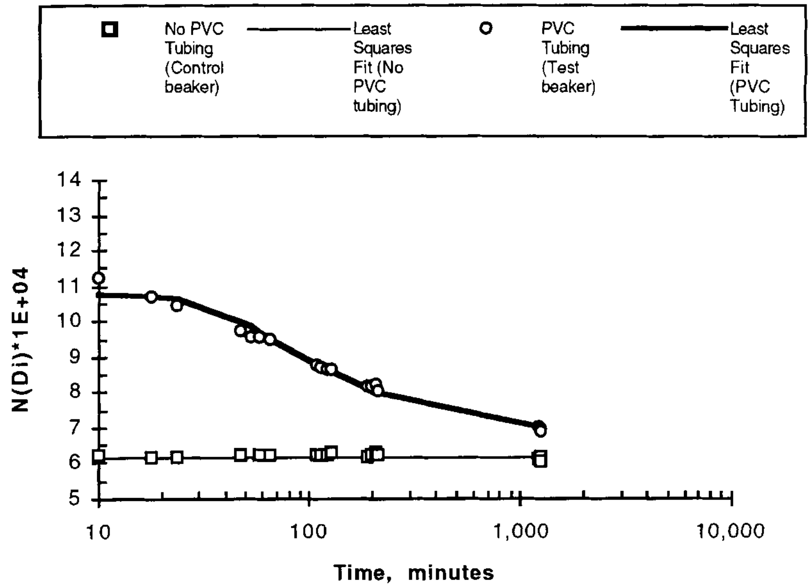

FIGURE 2. Effect of PVC tubing on the dispersion number as a function of time (Test 2).

number followed by a slow decrease with increasing time. As in test 1, the PVC tubing was added at time zero. Prior to time zero, the dispersion numbers for the test and control solution pairs were $(8.02 \pm 0.29) \times 10^{-4}$ and $(6.24 \pm 0.10) \times 10^{-4}$, respectively. The rate at which the dispersion number for the test solution decreased was slightly less than that for the initial test. After 21 h (1260 min), the dispersion number for the test beaker was $6.89 \times 10^{-4}$, 14% less than its value before the PVC tubing was added. For the control solution pair, the dispersion number was essentially unchanged.

Test 3 employed no control beaker. Its use was deemed unnecessary since $N_{Di}$ for the control beaker results remained constant in tests 1 and 2. Instead, PVC tubing was added to both beakers. Prior to time zero when the PVC tubing was added, the average dispersion numbers were $(7.16 \pm 0.16) \times 10^{-4}$ and $(7.33 \pm 0.29) \times 10^{-4}$ for test solutions 3A and 3B, respectively. One beaker (test 3A) contained the test solutions used in test 2 and fresh PVC tubing pieces. The other beaker (test 3B) contained fresh test solutions (control solutions from test 1) and the PVC tubing pieces used in test 2. For test 3B, the used PVC tubing pieces were rinsed off with distilled water before they were added to the fresh solution. As before, a rapid initial increase in the dispersion number was followed by a slow decrease, as shown in Fig. 3. However, the maximum increase in the dispersion number was much less than it was for fresh tubing (tests 1, 2, and 3A).

Overall, these tests indicate that some component of the PVC tubing, probably a plasticizer, was leached from the tubing and affected the $N_{Di}$ value for the aqueous-organic pair. The leached component increased the $N_{Di}$ value, as reflected in the increased contactor throughput when the interstage tubing was fresh.

## Solvent Development

The standard $N_{Di}$ test can be used to develop solvents for new extraction processes as well as to control solvent quality in existing processes. First, we discuss the use of $N_{Di}$ in the well-developed Purex and TRUEX processes. Second we describe the use of $N_{Di}$ in developing a solvent for the new TRUEX-SREX process.

### Purex and TRUEX Solvents

In the Purex solvent-extraction process (8), the solvent consists of an extractant, 30 vol % TBP (1.09M), in a normal paraffinic hydrocarbon (NPH)

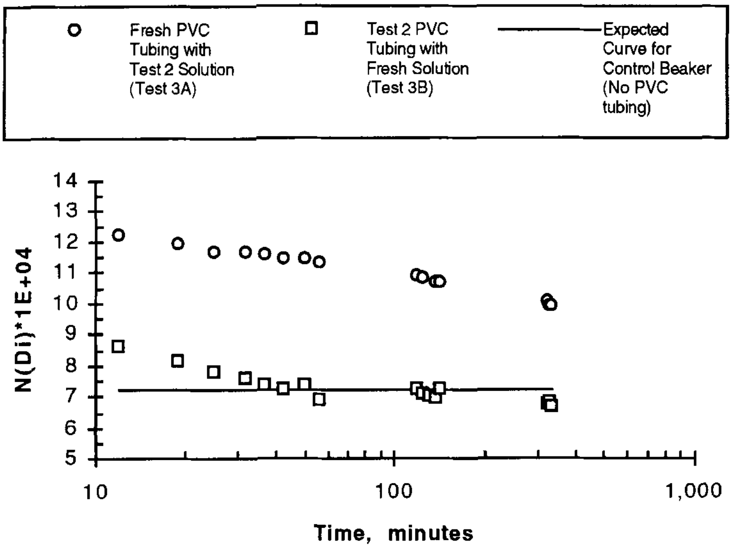

FIGURE 3. Effect of PVC tubing and solution freshness on dispersion number as a function of time (Tests 3A and 3B).

diluent such as nDD. A variety of commercial diluents, including kerosene, have been used as the Purex diluent. This Purex solvent, which we will refer to here as PUREX-NPH, has an organic-continuous $N_{Di}$ of 8 x $10^{-4}$ (2). A related solvent, which we will refer to as PUREX-$CCl_4$, consists of 1.0M TBP in carbon tetrachloride. It has an organic-continuous $N_{Di}$ of 16 x $10^{-4}$ (9).

In the TRUEX solvent extraction process, a typical solvent contains a bifunctional extractant called octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) with TBP as a modifier and a hydrocarbon or chlorocarbon diluent (10). The TRUEX solvent containing the hydrocarbon diluent consists of 0.2M CMPO and 1.4M TBP in nDD or NPH. The organic-continuous $N_{Di}$ for this solvent is about 8 x $10^{-4}$ with dilute nitric acid (11). The TRUEX solvent containing the chlorocarbon diluent consists of 0.25M CMPO and 0.75M TBP in tetrachloroethylene (TCE). While the organic-continuous $N_{Di}$ for this solvent is about 16 x $10^{-4}$, the dispersion number can be lower by a factor of two or more if the CMPO is of poor quality (12). The problem with poor-quality CMPO in the TRUEX solvent is most pronounced when the aqueous phase is 0.25M $Na_2CO_3$.

Based on these $N_{Di}$ values for Purex and TRUEX solvents, we can make three fairly general statements. First, $N_{Di}$ gives a measure of solvent quality with respect to its hydraulic performance in solvent extraction equipment. Second, the use of 0.25M $Na_2CO_3$ as the aqueous phase seems to be the most severe test of overall solvent performance. Third, the organic-continuous $N_{Di}$ values for solvents with chlorocarbon diluents are about twice those for solvents with NPH as the diluent.

### TRUEX-SREX Solvents

The TRUEX process for removing transuranic elements from nuclear waste solutions (10) is being combined with the SREX process for removing strontium (13) to create a new process, the TRUEX-SREX process (14). The combined TRUEX-SREX solvent contains the TRUEX extractant, CMPO, at a concentration of 0.2M; the SREX extractant, 4,4'(5)-di-t-butylcyclohexano-18-crown-6 (DtBuCH18C6, crown ether, or CE) at a concentration of 0.2M; and a modifier and diluent. Two modifiers considered for this solvent were 1.2M TBP and 1.2M diamyl amylphosphonate (DA[AP] or DAAP). The three diluents considered were Isopar L, Isopar M, and Norpar 12. Five of the solvent compositions evaluated are shown on Table 1 (the PS solvents), along with two TBP-in-nDD solvents (the T solvents) for comparison. The properties considered in the development of the solvent were (1) the ability of the solvent to be loaded with metal ions without the formation of a second organic phase, (2) a high flash point for process safety, and (3) the ability to work well in typical solvent extraction equipment such as a centrifugal contactor.

For a given number of carbon atoms, the normal paraffinic hydrocarbons (Norpar 12 and nDD) have higher flash points than the isoparaffinic hydrocarbons (Isopar L and Isopar M). However, even Isopar L, the solvent with the lowest flash point, 61°C, is well above the limit for a flammable liquid, 37.8°C (100°F), and is just above the limit for a Class II combustible liquid, 60°C (140°F). Once the extractants and modifiers are added to the diluent, the solvent flash point is increased with respect to that for the diluent alone (15).

TABLE 1. COMPOSITION AND SELECTED PHYSICAL PROPERTIES FOR SEVEN SOLVENTS

| Solvent Name | Solvent Composition, M |  |  |  |  | Viscosity,[a] mPa•s | Density,[b] g/L | Diluent Flash Point, °C |
|---|---|---|---|---|---|---|---|---|
|  | CMPO | CE | TBP | DAAP | Diluent |  |  |  |
| PS 6 | 0.2 | 0.2 | 1.2 | - | Isopar L | 4.5 | 871 | 61 |
| PS 9 | 0.2 | 0.2 | - | 1.2 | Isopar M | 8.4 | 875 | 81 |
| PS 10 | 0.2 | 0.2 | - | 1.2 | Norpar 12 | 4.3 | 855 | 69 |
| PS 11 | 0.2 | - | - | 1.2 | Norpar 12 | 3.0 | 827 | 69 |
| PS 12 | 0.2 | 0.2 | - | 1.2 | Isopar L | 5.4 | 865 | 61 |
| T 1[c] | - | - | 1.47 | - | nDD | 2.2 | 838 | 71 |
| T 2[d] | - | - | 2.33 | - | nDD | 2.7 | 891 | 71 |

[a] Measured at room temperature (23.5-25.0°C) using a Brookfield viscometer model LVF with an ultra-low adapter.

[b] Measured at room temperature using a 250-mL volumetric flask.

[c] T 1 is 40.3% TBP in nDD.

[d] T 2 is 63.8% TBP in nDD.

With regard to suppressing the formation of a second organic phase, the isoparaffinic hydrocarbons do a better job that the normal paraffinic hydrocarbons. In particular, the solvent with 12.0 carbon atoms (Isopar L) does a better job than the one with 13.5 carbon atoms (Isopar M). In addition, the use of DAAP as the modifier does a better job than TBP in suppressing the formation of a second organic phase (14).

In balancing these properties to choose the best TRUEX-SREX solvent, our first choice was PS 9. However, subsequent standard $N_{Di}$ measurements, given in Table 2, show this $N_{Di}$ to be much less than the design value of 8 x $10^{-4}$ for many cases. In addition, other-phase carryover is >1% in almost every case. The various aqueous phases are those that would be used in the process, including a stripping solution containing 0.2M tetrahydrofuran-2,3,4,5-tetracarboxylic acid (THFTCA). Note that the worst conditions occur with 0.25M $Na_2CO_3$ at high O/A volume ratios.

To determine a better compromise between solvent properties, we completed standard $N_{Di}$ measurements on all the solvents listed in Table 1. The results, shown in Table 2, suggest that PS 12 would be an acceptable compromise. However, $N_{Di}$ values are lower by a factor of two at the higher O/A volume ratios.

TABLE 2. DISPERSION NUMBER OVER A RANGE OF CONDITIONS FOR SEVEN SOLVENTS

| | | O/A = 0.33 | | O/A = 1.0 | | O/A = 3.0 | | |
|---|---|---|---|---|---|---|---|---|
| Solvent Name | Aqueous Phase | $N_{Di}$ x$10^4$ | Max. A in O, % | $N_{Di}$ x$10^4$ | Max. A in O, % | $N_{Di}$ x$10^4$ | Max. A in O, % | Notes |
| PS 6 | 0.25M $Na_2CO_3$ | 7.7 | 3 | 5.1 | 4 | 1.4 | 25 | |
| | 0.1M $HNO_3$ | 16.7 | 2 | 5.1 | 2 | 4.2 | 2 | |
| PS 9 | 0.25M $Na_2CO_3$ | 8.1 | 5 | 6.3 | 5 | 1.5 | 10 | |
| | 0.01M $HNO_3$ | 8.3 | 4 | 4.3 | 4 | 4.0 | 6 | |
| | 0.1M $HNO_3$ | 9.3 | 8 | 2.5 | 7 | 1.6 | 7 | a |
| | 0.1M $HNO_3$ | 7.4 | 9 | 2.7 | 3 | 2.6 | 4 | |
| | 0.1M $HNO_3$ | 12.4 | 3 | 9.2 | 1 | 3.6 | 1 | b |
| | 3.0M $HNO_3$ | 7.0 | 3 | 4.3 | 4 | 2.9 | 5 | |
| | 0.2M THFTCA | 5.0 | 1[c] | 3.5 | 4 | 4.0 | 6 | |
| PS 10 | 0.25M $Na_2CO_3$ | 7.1 | 4 | 6.5 | 4 | 4.2 | 4 | |
| | 0.1M $HNO_3$ | 13.2 | 0.4 | 5.1 | 1 | 4.6 | 2 | |
| PS 11 | 0.25M $Na_2CO_3$ | 9.9 | 2 | 7.4 | 3 | 8.7 | 3 | |
| | 0.1M $HNO_3$ | 7.9 | 1 | 7.1 | 1 | 7.1 | 1 | |
| PS 12 | 0.25M $Na_2CO_3$ | 11.6 | 4 | 8.3 | 6 | 3.7 | 3 | |
| | 0.1M $HNO_3$ | 13.4 | 2 | 4.5 | 1 | 4.1 | 4 | |
| T 1 | 0.25M $Na_2CO_3$ | 7.1 | 1 | 7.1 | 1 | 6.4 | 1 | |
| | 0.1M $HNO_3$ | 13.2 | 0 | 16.2 | 0.4 | 15 | 0.4 | |
| T 2 | 0.25M $Na_2CO_3$ | 11.6 | 1 | 6.4 | 1 | 5.8 | 1 | |
| | 0.1M $HNO_3$ | 22.9 | 0.4 | 6.8 | 0 | 6.9 | 0.8 | |

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[a] The solvent was not contacted with sodium carbonate solution before this test.

[b] These dispersion tests were done at 48 ± 5°C. All others were done at 24.3 ± 0.8°C.

[c] For this case, the maximum A in O was less than maximum O in A. Thus, the maximum A in O values are actually maximum O in A values. Aqueous phase appeared to be the continuous phase.

These results suggest that the 20-stage 2-cm contactor to be used for testing the TRUEX-SREX flowsheet might have to be operated at reduced flow rates, as much as 50% lower. The contactor has a nominal throughput of 40 mL/min (both phases) when $N_{Di} = 8 \times 10^{-4}$. After the batch $N_{Di}$ values were measured, single-stage tests were done at the specific flow rates and O/A flow ratios called for in the flowsheet with the PS 12 solvent. The contactor operated very satisfactorily at the planned operating conditions, that is, no reduction in flow rates and other-phase carryover of <0.1% in all cases. Thus, for the PS 12 solvent, $N_{Di}$ for operation of the continuous-flow centrifugal contactor appears to be higher than that predicted by the gravity-settling batch tests.

This difference in gravity-settling and centrifugal-settling $N_{Di}$ values for the PS 12 solvent is probably related to its higher viscosity. In particular, if no coalescing dispersion band forms, the interface movement is controlled by the rate at which the droplets move to the interface. This velocity, u, is given by Stokes law as

$$u = \frac{a\, D_d^2\, (\rho_d - \rho)}{18\, \mu} \tag{8}$$

where a is the accelerational force field, $D_d$ is the droplet diameter, $\rho$ is the fluid viscosity, $\rho_d$ is the density of the dispersed-phase droplet, and $\mu$ is the fluid viscosity (16). Stokes law applies as long as the Reynolds number for the spherical droplet, $N_{Re}$, is given by

$$N_{Re} = \frac{D_d\, u\, \rho}{\mu} \tag{9}$$

where $N_{Re} < 0.1$.

When Stokes law applies, droplets move as the first power of the accelerational field acting on the settling zone. When the dispersion number applies, the movement in the settling zone is proportional to the half power of the accelerational field. Thus, for more viscous solvents, separations in a centrifugal settling zone relative to those in a gravity settling zone will be even more efficient than given by the standard gravity-settling $N_{Di}$ test.

Because of the performance of solvent viscosity on equipment performance, the factors influencing viscosity are noted here. Solvent viscosity correlates with the diluent, that is, nDD solvents have viscosities in the range from 2 to 3 mPa•s; Norpar 12, 3 to 5 mPa•s; Isopar L, 4 to 6 mPa•s; and Isopar M, 8 to 9 mPa•s. Also, those PS solvents with 0.2M crown ether have viscosities that are two to four times greater than those solvents with no crown ether (PS 11, T 1, and T 2). For the results in Table 2, we found some correlation of $N_{Di}$ and other-phase carryover with solvent viscosity, that is, $N_{Di}$ decreases and other-phase carryover increases as solvent viscosity increases. In addition, since solvent viscosity decreases with temperature, doing the standard batch test at an elevated temperature should increase $N_{Di}$ and reduce other-phase carryover. Both these effects were observed for one PS 9/0.1M $HNO_3$ test (see Table 2) done at 48°C rather than 24°C.

In contrast with solvent viscosity, no correlation was found between solvent density and $N_{Di}$. In fact, when comparing Tables 1 and 2, one sees that solvent T 2, which has the highest density (that is, the smallest density difference between it and the aqueous phase), has one of the highest dispersion numbers and one of the lowest other-phase carryovers.

## CONCLUSIONS

A standard test is given for measuring the dimensionless dispersion number. This number can be used to assess how well solvents will perform in commercial solvent extraction equipment. The usefulness of this new $N_{Di}$ test was demonstrated in three areas: prediction of maximum throughput for stagewise contactors, evaluation of plasticizer leaching into a solvent, and development of a solvent for a new solvent extraction process. At higher solvent viscosities, operation of centrifugal contactors was even better than predicted by the gravity-settling standard test.

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