# Diffusion Coefficient of Hexamethylene Tetramine in Concentrated Aqueous Solutions

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**The diffusion coefficient of hexamethylene tetramine (HMT) in aqueous solution has been measured in concentrations ranging from 36.6 wt % up to those corresponding to saturation in the temperature interval 15–45°C (46.8 wt % to 46.0 wt %, respectively). Most of the results were obtained by following diffusion into and out of porous clay discs, but a rotating HMT disc was also used near the saturation points. Collecting together our measurements and the published values at low concentrations, we report a smooth concentration dependence of the diffusion coefficient.**

Reliable data were needed for the diffusion coefficient of hexamethylene tetramine (HMT) in concentrated aqueous solutions as a function of concentration and temperature. The solubility is 46.5% by weight HMT (ca. 10 mol %) at 25°C, and the diffusion coefficient cannot be reliable estimated from generalized correlations. Despite the extensive survey by White (*8*). no diffusion data are available in the literature except those of Costantino et al. (*1*) who reported values up to 34% by weight at 3.66°C and up to 36% by weight at 24.72°C. An experimental investigation of diffusion for the concentrated system was undertaken to provide the necessary data and further to evaluate experimental techniques.

## Theory

Wall et al. (*7*) have proposed a rapid method of determining diffusion coefficients for solutions which is simple and inexpensive compared to interferometric methods. The change in weight of a porous disc, immersed in a solution and undergoing diffusion, is accurately measured as a function of time. Although the method is probably not well suited for obtaining highly accurate data, the accuracy required for most engineering calculations can easily be attained. In spite of the above advantages, the method does not seem to have been widely employed by other investigators since its publication in 1952.

Equation 9 of Wall et al. (*7*), also given below, is the solution to the unsteady-state diffusion equation for a circular disc with parallel plane faces. Equimolal axial counterdiffusion with no convection inside the pores of the disc was assumed.

$$\log W = \frac{-Dt\pi^2}{2.303\ (2\ L)^2} + \log 2\ LAk(c_1 - c_0)(8/\pi^2) \qquad (1)$$

$W$ = (weight of disc at time $t$) − (weight of disc after infinite time)
$2\ L$ = geometrical thickness of disc
$A$ = cross-sectional area of disc
$k$ = factor which converts concentration to density
$c_1$ = initial concentration of solute at any point inside the disc
$c_0$ = constant concentration of solution at the surface of the disc and at any time
$t$ = time
$D$ = diffusion coefficient of solute

From the slopes of log $W$ vs. time plots and a knowledge of disc thickness, it was possible to determine $D$ from Equation 1.

## Experimental

The apparatus employed in this investigation was similar to that of Wall et al. (*7*). An electrical analytical balance (Mettler Model H 20 T) with readability of 0.01 mgm was employed in place of a chainomatic balance. In this work clay discs were substituted for porcelain plates. The average diameter of the discs employed was about 14 cm, with a thickness varying from 4–6 mm. Their porosities were typically 30–35%. The experiments were carried out in a thermostatic bath, whose temperature was measured, with an error of somewhat less than ±0.1°C., using a mercury in glass thermometer. All solutions were prepared by weighing HMT (recrystallized from absolute alcohol) and deionized distilled water. Each clay disc was polished with various grades of carborundum paper and its thickness was measured at a number of points along the disc surface using a deep-throat micrometer. The average and the standard deviation values for disc diameter and thickness are reported in Table I. The disc edges were sealed with nail varnish to prevent radial diffusion.

A disc was soaked in a solution of known concentration $c_1$, until it came to a constant weight. Normally a soaking period of about 24 hr was needed. The disc was then immersed in 5 liters of thermostated solution of concentration $c_2$ and attached to the balance by a thin stainless steel wire. The rate of diffusion was followed by observing the change in the weight of the disc at regular intervals of time up to about 20 hr until the disc weight was again constant.

For each experiment, the mass which diffused was determined by change in weight of the disc when solute diffused in, and the corresponding change when solute diffused out. In both cases the concentrations of the bulk solutions remained constant. When these two changes in weight differed by more than 1%, the pair of experiments was rejected.

When not in use for diffusion measurements, the clay discs were always soaked in water or an HMT solution. The measured change in weight during diffusion runs was not therefore attributed to changes in the degree of hydration of the clay, but to diffusion.

The tortuosity factor reported in Table I was defined as the ratio of the average length of the diffusion paths inside a porous

**Table I. Dimensions of Discs**

| Disc no. | Diam, cm Av | Diam, cm Std dev | Thickness, cm Av | Thickness, cm Std dev | Tortuosity factor Av | Tortuosity factor Std dev |
|---|---|---|---|---|---|---|
| 1 | 13.998 | 0.027 | 0.537 | 0.017 | 1.883 | 0.07 |
| 2 | 14.041 | 0.052 | 0.501 | 0.016 | 1.903 | 0.07 |
| 3 | 14.084 | 0.043 | 0.419 | 0.009 | 2.054 | 0.05 |

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disc to the measured, geometric thickness of that disc. The average lengths of the paths for diffusion were determined by calibration runs using a 0.479 M solution of KCl in water, for which $D = 1.848 \times 10^{-5}$ cm²/s at 25°C (*4*). The importance of such a calibration was not clear from the publication of Wall et al. (*7*).

It was also shown that the rate-determining step was indeed molecular diffusion within the pores of the disc. The viscosity of the surrounding aqueous KCl was increased by the addition of carboxymethyl cellulose to 7.6 cP while, in another set of experiments, $N_2$ bubbles scoured the disc surface. In both cases, the curves showing the change in the weight of the disc as a function of time remained the same as during the normal runs, when the fluid was not stirred.

## Results

Figure 1 shows a typical plot of the logarithm of weight change of a disc as a function of time. The initial concentration of the solution inside the disc was 41.84% and that in the outside bath was 39.585% HMT by weight. It can be seen from this figure that except for the very early time measurements, the data points lie well on a straight line. The nonlinearity of short-time measurement is due to a transient in the solution of the differential equations by Wall et al. (*7*).

The results of the experiments conducted at 25°C employing disc no. 2 and at various concentrations in the range of 36–45% HMT by weight in the solution are shown in Figure 2. Each point on this figure is the average of at least two values, namely diffusion of HMT into and out of disc no. 2.

Also shown in this figure are the results of Costantino et al. (*1*), obtained interferometrically at 24.72°C. It is clear from Figure 2 that the data taken at high concentrations in this investigation fall on a smooth curve drawn through the low concentration region data of Costantino. The concentration difference between the solution inside and outside the disc was generally about 2.5% by weight HMT. This concentration difference is about twice as large as that of Costantino, but the agreement between these two sets of data is very good.

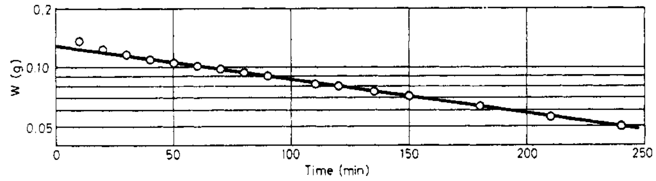

**Figure 1. Plot of log W vs. time for 40.7 (av) wt % HMT in aqueous solution at 25°C**

W = wt of disc at time *t* — wt of disc after infinite time. Disc no. 2

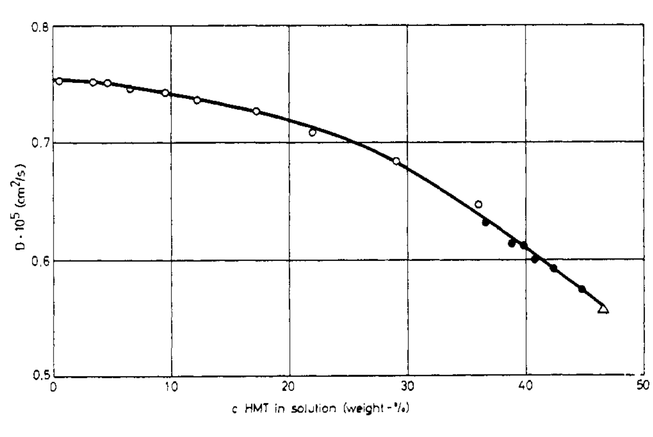

**Figure 2. Diffusion coefficient of HMT as a function of concentration at 25°C**

○ Data of Costantino et al. (*1*)
● Data of own investigation (porous disc)
△ Data of own investigation (rotating disc)

The rate of dissolution of a rotating disc of HMT was also measured in order to evaluate the diffusion coefficient at concentrations approaching saturation (*2*). This method is well known for measuring electrochemical kinetics: The simple theory was summarized in equation 9.2 of Levich (*5*) and has been extended by Spalding (*6*) and many others. Measurements in the laminar flow region with small concentration driving forces (1–3 wt %) were evaluated by Spalding's equations (Sc ≈ $10^4$) and extrapolated to the saturation concentration (46.54 wt % at 25°C). The concentration dependence at 25°C of the differential diffusivity determined by our two methods is now summarized:

| Concn, wt % | 36.6 | 38.8 | 39.8 | 40.7 | 42.3 | 44.7 | 46.5 |
|---|---|---|---|---|---|---|---|
| $D \times 10^5$ cm²/sec | 0.632 | 0.614 | 0.612 | 0.600 | 0.592 | 0.574 | 0.555 |

Most empirical correlations for the diffusivity do not correctly describe this concentration dependence. The classical equation of Wilke and Chang, for example, predicts $0.735 \times 10^{-5}$ cm²/sec at 25°C and infinite dilution (experimental $0.755 \times 10^{-5}$), but it fails badly in 40 wt % solution by predicting $0.177 \times 10^{-5}$ cm²/sec (experimental $0.610 \times 10^{-5}$ at 25°C), and the Stokes-Einstein parameter $D\eta/T$ is clearly not constant for HMT solutions.

For an average concentration of 42.34 wt % HMT in solution and with concentration difference of 2.68%, the diffusion coefficient was determined at 25°C using three different discs of varying thickness. The results obtained are shown in Table II.

The agreement between the diffusion coefficients obtained by various discs is very good. It shows that once each disc is calibrated to determine its tortuosity factor, a disc of any thick-

**Table II. Diffusion Coefficient of HMT Using Various Discs**

| Disc no. | Av thickness, cm | Tortuosity factor | Av concn of soln, wt % HMT | Diffusion coefficient, $D \times 10^5$ cm²/sec |
|---|---|---|---|---|
| 1 | 0.537 | 1.883 | 42.34 | 0.594 |
| 2 | 0.501 | 1.903 | 42.34 | 0.592 |
| 3 | 0.419 | 2.054 | 42.34 | 0.588 |

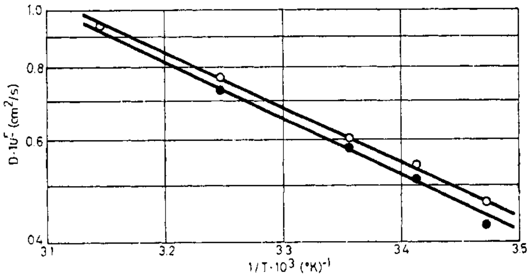

**Figure 3. Activation energy curves for HMT solutions**

Average concentration
○ 40.71 wt % HMT, concentration difference 2.255%
● 44.68 wt% HMT, concentration difference 2.0%

ness can be employed to obtain the diffusion coefficient of an unknown substance.

With average concentrations of 40.71 and 44.68 wt % HMT and employing disc no. 2, we determined the diffusion coefficients at several temperatures in the range of 15–45°C. These data are plotted in Figure 3 as logarithm of $D$ against the inverse of absolute temperature $T$. The activation energies of 4.34 and 4.44 kcal/g mol are obtained for 40.71 and 44.68 wt % HMT solutions, respectively. The activation energy calculated from the data of Costantino et al. (*1*) reported at only two temperatures, namely 3.66° and 24.72°C, is about 4.9 kcal/g mol for the various average concentrations ranging from 0.55–28.85 wt % HMT. Here again the agreement between the data of this work and that of Costantino is good. It appears that the activation energy of diffusion for HMT remains constant for the entire concentration range from 0.5 wt % to the saturation limit.

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# Furfural–Water–Formic Acid System at 25° and 35°C

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**The system furfural–water–formic acid has been studied at 25° and 35°C. The binodal curves, tie lines, and plait points have been determined. The results are compared with those of previous studies of acetic, propionic, and butyric acids distributed between furfural and water at the same temperatures.**

Although one of the major autoxidation products of furfural is formic acid (*2*), the distribution of the latter between furfural and water has not previously been reported. The effects of acids on furfural-water miscibility become increasingly significant in light of recent work on the extraction of metal ions with furfural (*6, 9*). The system furfural–water–formic acid at 25° and 35°C is described here, including binodal curves, tie lines, and plait points. Furfural–water–acetic acid, furfural–water–propionic acid, and furfural–water–butyric acid at 25° and 35°C have been reported previously (*3, 4*). This provides four homologous *n*-alkanoic acid solutes for comparison of behavior, indicating the effect on distribution equilibrium of varying the length of the hydrocarbon chain of the solutes. The present system completes those of the type where the *n*-alkanoic acid is completely miscible with water at ambient temperatures.

For brevity, in the text below, the various furfural–water–acid systems will be indicated by identifying the acid.

## MATERIALS AND EQUIPMENT

Furfural (Fisher, reagent grade) was distilled under 5-torr pressure with a Vigreux column. The middle third was recovered. After distillation, the furfural was stored in a closed container at −20°C until used. Deterioration under these conditions was previously found to be negligible (*4*). Furfural decomposition during the time required for the synthesized mixtures to reach equilibrium also has, within the stated uncertainty of the data, negligible effect on the results (*3*).

As previously (*3*), for the various batches of purified furfural, the refractive index at 25°C using the sodium-D line ranged from 1.5228 to 1.5237. The accepted value is 1.5235 (*7*). There was no measurable effect on solubility from this variation in the purity of the distilled furfural.

Formic acid (Fisher, certified ACS, mfgr. assay: wt % formic acid 90.5, acetic acid 0.2) was used without additional purification. By titration against standardized aqueous NaOH solution, 90.1 (±0.1 std dev) wt % acid was found. The equilibrium concentrations reported below have been corrected for the water in the acid.

The water was singly distilled from an ordinary laboratory still.

All analytical equipment was calibrated against certified standards. Thermostat temperature (constant to ±0.01°C) was monitored with a Beckman thermometer which had been set with another thermometer calibrated against an NBS-certified standard.

## EXPERIMENTAL PROCEDURE

The methods used in determining the equilibrium data followed established techniques.

**Binodal Curve Determination.** Homogeneous synthetic samples of known concentration were titrated in thermostated glass-stoppered bottles to the onset of turbidity. The titrant was that component, either furfural or water, the addition of which rendered the system immiscible. After the addition of each increment of titrant, the mixture was stirred vigorously with a magnetic stirrer to expedite equilibrium. To minimize errors from furfural decomposition, no more than three points on a binodal curve were established with a single sample of furfural.

**Tie-Line Determination.** Tie lines were determined by titrating the acid in each of the two immiscible phases formed from known synthetic mixtures in the two-phase region.

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