Engineering Journal of Qatar University, Vol. 4, 1991, p. 15 - 23.

EXPERIMENTAL MEASUREMENT OF DROP PHASE MASS TRANSFER COEFFICIENTS FOR THE CARBON TETRACHLORIDE-ACETIC ACID-WATER SYSTEM

K.H. Javed and J.F. Attiyah
Chemical Engineering Department, University of Qatar
Doha, Qatar

ABSTRACT

The overall mass transfer coefficients of single drops of carbon tetrachloride falling in a stagnant continuous phase of water containing acetic acid as solute were measured experimentally for different dispersed phase flowrates and drop falling times.

The measured mass transfer coefficients were lower than those estimated from the mass transfer models for circulating drops but were reasonably in agreement with the stagnant drop model. The observed deviation is attributed to the slow dimerization reaction which occurs in this system during the transfer of acetic acid. The agreement with the stagnant drop model indicates that even for turbulent droplet conditions the mass transfer in this system is governed by molecular diffusion.

INTRODUCTION

In liquid-liquid extraction equipment such as spray columns and perforated plate columns, the mass transfer occurs between a liquid continuous phase and a dispersed phase of liquid droplets. In the design of such columns, a knowledge of the dispersed phase mass transfer coefficient is a basic requirement. As a result, the phenomenon of mass transfer in drops has received considerable attention and a number of both theoretical and experimental investigations have been reported.

Theoretical predictions of the drop side mass transfer coefficient can be made using either of the three droplet mass transfer models listed in Table 1. A drop falling or rising in a second liquid phase may be internally stagnant (with no internal motion) or it may have either laminar or turbulent internal circulation due to its relative motion to the continuous phase. For stagnant drops the Newman (1931) model is commonly used. The models of Kronig and Brink (1950) and Handlos and Baron (1957) are applied for circulating drops with laminar and fully turbulent circulation, respectively. All three models assume that there is no mass transfer resistance in the continuous phase and the moving drops are of spherical shape.

Table 1
Models for Drop Phase Mass Transfer Coefficient

Newman (1931) Model for Stagnant/Rigid Drops

$$k_d = -\frac{d}{6t} \ln \left[\frac{6}{\pi^2} \sum_{i=1}^{\infty} \frac{1}{i^2} \exp \left[\frac{-4 D \pi^2 i^2 t}{d^2} \right] \right] \quad (1)$$

For large values of t,

$$k_d = \frac{2\pi^2 D}{3d} \quad (1.a)$$

Kronig and Brink (1950) Model for Drops with Laminar Circulation

$$k_d = -\frac{d}{6t} \ln \left[\frac{3}{8} \sum_{i=1}^{\infty} B_i^2 \exp \left[\frac{-64 \lambda_i Dt}{d^2} \right] \right] \quad (2)$$

For large values of t,

$$k_d = 17.9 \frac{D}{d} \quad (2.a)$$

Handlos and Baron (1957) Model for Fully Circulating/Oscillating Drops

$$k_d = \frac{0.00375\ U}{\left[1 + \frac{\mu_d}{\mu_c} \right]} \quad (3)$$

Experimental verification of these models has not always been very promising although on many occasions the agreement between experimental and theoretical mass transfer coefficients has been fairly good. Heertjes *et al.* (1954) investigated experimentally the transfer of water to isobutanol droplets and vice-versa. For transfer into organic drops their measurements showed agreement with the Kronig and Brink model but for the transfer in the opposite direction they observed large deviations. Handlos and Baron (1957) reported that their experimental data agreed with their model with an error of 20 percent for ternary systems comprising benzene and water as immiscible solvents and acetic acid, benzoic acid, salicylic acid, acetone and phenol as solutes.

The experimental study made by Johnson and Hamielec (1960) for transfer from the organic continuous phase to the aqueous droplet phase in the two-component systems, water-cyclohexanol, water-n-butanol and water-ethylacetate showed that at low Reynolds numbers the Kronig and Brink model was applicable whereas the

Handlos and Baron model showed good agreement for fully turbulent drops. Skelland and Wellek (1964) studied mass transfer in drops using two-component systems such as water-ethyl acetate, methyl acetoacetate-water, glycol diacetate-water and glyceryl triacetate-water. Their measurements of the mass transfer coefficient showed appreciable differences (46%, 54%, 38%) when compared with the models of Newman, Kronig and Brink and Handlos and Baron, respectively.

Mass transfer in drops was studied by many other research workers (Sherwood *et al.*, 1939; Licht and Conway, 1950; Licht and Pansing, 1953; Skelland and Minhas, 1971; Streicher and Schugerl, 1973 and 1977). Recent studies include those of Skelland and Vasti (1985), Park *et al.* (1986), Steiner (1986), Slater *et al.* (1988) and Steiner (1990). However, despite of a vast amount of research work undertaken to further our understanding of the mass transfer mechanism in drops, it is not possible to reliably predict the dispersed phase mass transfer coefficient using a purely theoretical approach and so experimental measurements of the mass transfer coefficient are often necessary for design purposes.

The objective of this study was to measure experimentally the overall mass transfer coefficients of the carbon tetrachloride-acetic acid-water system with carbon tetrachloride as the dispersed phase. This system is organic phase controlled (i.e no resistance in the continuous aqueous phase) and suitable for a comprison of the experimental mass transfer coefficients with the above theoretical drop models. Moreover, although this system was studied previously in a stirred cell (Lewis, 1954) and in a packed bed (Billet and Mackowiak, 1980), it was not used before in any single drop extraction studies.

EXPERIMENTAL WORK

Experimental Apparatus and Procedure

Single drops of carbon tetrachloride were formed using a glass nozzle immersed in the stagnant continuous aqueous phase containing acetic acid as solute. The carbon tetrachloride and acetic acid were of Analar grade while the water was laboratory distilled. The solute concentration in the continuous phase was 50 gm/l and in all the runs acetic acid was transferred from the continuous phase to the drop phase.

The glass nozzle was a capillary tube of 1.5 mm inside diameter and 8 mm outside diameter. The dispersed phase was supplied to the nozzle from a glass bottle containing the organic phase using a pre-calibrated pump. The drops formed at the nozzle fell through a glass column containing the continuous phase. Five columns of the same diameter but different heights were used. The column diameter was 3 cm and the column heights were 13.5, 23, 30.4, 38 and 48 cm. Each column was

provided with a narrow conical end to keep the interfacial area between the coalesced droplet layer and the continuous phase as small as possible to minimize the mass transfer due to the drop coalescence. The drops of carbon tetrachloride falling through the continuous phase were collected at the bottom of the column. A run was continued until the narrow tube provided at the column end was filled with the dispersed phase. The drop phase collected in the tube was drained and analyzed for acetic acid concentration using gas chromatography. Each run was repeated three times.

In each run the drop fall time was measured using a stopwatch. The volume of a drop was calculated by forming a known number of drops and measuring the total volume. The experiments were carried out at 21 $\pm 1^{0}$C. At the end of a run the apparatus was disconnected, washed with chromic acid and dried before the next run.

Two sets of measurements were made in these experiments. In the first set the dispersed phase flowrate was varied and mass transfer data were collected for only two column heights. In the second set the column heights were changed but the dispersed phase flowrate was fixed. In a typical run the data measured consisted of the dispersed phase concentration, drop fall time and the drop volume.

Data Treatment

The unsteady state mass transfer to a drop falling in a continuous phase can be described by the following equation (Skelland and Wellek, 1964):

$$\frac{C_d^{*} - C_d}{C_d^{*} - C_{do}} = \text{Exp}\ [\ -\ (K_d\ A/V)\ t_f] \qquad (4)$$

Equation (4) was used to calculate the overall dispersed phase mass transfer coefficient, K_d. The value of equilibrium concentration, C_d^*, was calculated using an equilibrium distribution constant of 0.015 (Lewis, 1954 and Billet and Mackowiak, 1980) for the solute concentration used in this work. The drop volume, V, was measured and the drop interfacial area, A, was calculated from the droplet volume assuming the drop to be a sphere.

Concentrations at the beginning and the end of the fall period were calculated from the measured data using the method suggested by Skelland and Wellek (1964) for elimination of the end effects caused by drop formation and coalescence. According to this method, when the mass transfer during drop coalescence is minimized experimentally by keeping the interfacial area between the coalescing drops and the continuous phase to a minimum (as in the present case), the mass transfer during the free fall period can be calculated by subtracting the mass

transfer in a shorter column from that in a longer column operated under the same set of experimental conditions. The concentration at the beginning of the fall period, C_{do}, is therefore considered to be the dispersed phase concentration from the shorter column and the concentration at the end of fall period, C_d, is the dispersed phase concentration in the longer column. The corresponding drop fall time, t_f, is calculated as the difference in the fall times of the two columns.

RESULTS AND DISCUSSION

The effect of the dispersed phase flowrate on the dispersed phase overall mass transfer coefficient during the fall period is shown in Figure 1. This figure indicates that the mass transfer coefficient is independent of the dispersed phase flowrate. An explanation for this behaviour may be sought by considering the factors which influence the rate of mass transfer between a droplet and the continuous phase. The rate of mass transfer, for given concentration driving force and interfacial area, depends on the droplet flow conditions which are characterized by the Reynolds number defined in terms of the droplet diamter, droplet falling velocity, and the

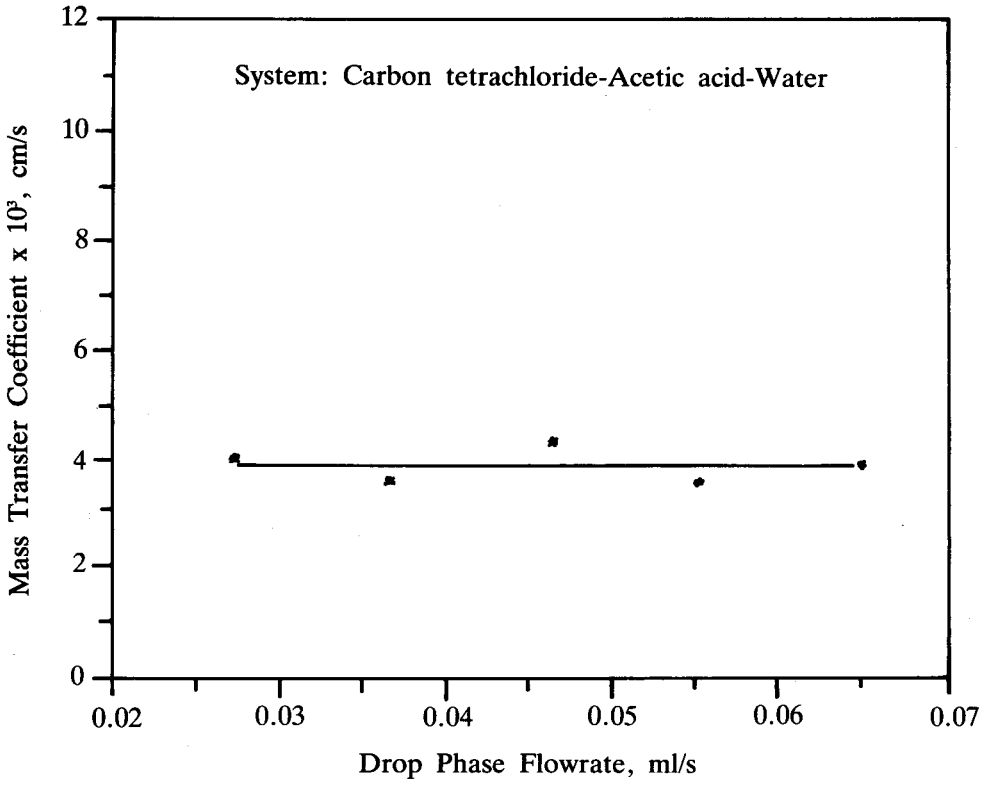

Figure 1: Effect of drop phase flowrate on the overall mass transfer coefficient for falling drops

density and viscosity of the continuous phase. In the present experiments, all of these parameters were held constant giving a value of 617 for the Reynolds number for all the runs in which the flowrate was changed. Therefore, the constant value of the mass transfer coefficient in Figure 1 is understandable.

The experimental curve between the dispersed phase overall mass transfer coefficient and the drop fall times is presented in Figure 2. This curve shows that the overall mass transfer coefficient decreases with the contact time between the two phases. This decrease in the mass transfer coefficient occurs because the mass transfer between a falling drop and the continuous phase is an unsteady state process. As the driving force for mass transfer diminishes with time the rate of mass transfer to the drop is decreased.

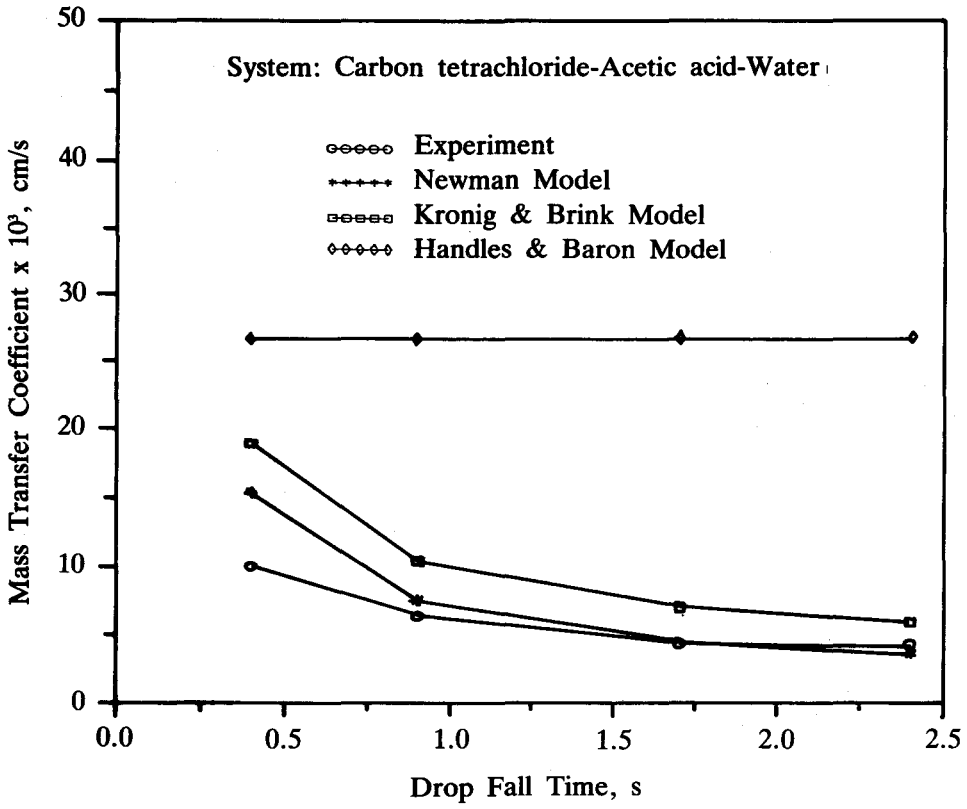

Figure 2: Comparison of experimental and theoretical overall drop phase mass transfer coefficient

To compare the experimental and theoretical overall mass transfer coefficients, the dispersed phase individual mass transfer coefficients were calculated from the Newman model (eq. 1), the Kronig and Brink model (eq. 2) and the Handlos and

Baron model (eq. 3). The dispersed phase diffusion coefficient and the dispersed phase and continuous phase viscosities were taken from Perry and Green (1984). The dispersed phase individual coefficient, k_d, calculated from these models can be combined with the individual phase transfer coefficient of the continuous phase, k_c, to calculate the overall mass transfer coefficient for the dispersed phase using the following equation (Lewis and Whitman, 1924):

$$\frac{1}{K_d} = \frac{1}{k_d} + \frac{m}{k_c} \qquad (5)$$

The individual mass transfer coefficient for the continuous phase, k_c, was assumed to be very large because in the system carbon tetrachloride-acetic acid-water the resistance to mass transfer in the organic phase is much larger than in the water phase. Therefore from equation (5) when k_c is very large the individual phase transfer coefficient, k_d, and the overall mass transfer coefficient, K_d, are equal.

The resulting comparison between the experimental and theoretical mass transfer coefficients is given in Figure 2. The comparison shows that the experimental curve is similar in trend to the theoretical curves in showing the time dependence of the overall mass transfer coefficient. However, although the drop Reynolds number was in the region of 600 indicating turbulent conditions inside the drop, the experimental values of the overall mass transfer coefficient are lower than those calculated from the circulating drop models of Kronig and Brink and Handlos and Baron but are very much comparable to those estimated from the Newman model for a stagnant drop.

In the system carbon tetrachloride-acetic acid-water, acetic acid exists as monomer in the aqueous phase but forms dimer in the organic phase (Sekine and Hasegana, 1977). Lewis (1954) reported that for the transfer of acetic acid from water to carbon tetrachloride in a stirred cell, the overall mass transfer coefficients were lower than their estimated values. This discrepancy was thought to be due to an additional interfacial resistance caused by the slow dimerization reaction. In the present study, acetic acid was transferred from water to the organic phase and it is likely that the dimerization reaction is responsible for the observed differences between the experimental mass transfer coefficients and the circulating drop models. The agreement with the Newman model shows that even for Reynolds number as high as 600, indicating fully turbulent conditions within the carbon tetrachloride drops, the mass transfer in this system takes place primarily by molecular diffusion.

CONCLUSION

For the transfer of acetic acid from the continuous aqueous phase to carbon tetrachloride drops, the overall drop phase coefficient was independent of the dispersed phase flowrate but it decreased with the droplet fall time.

The experimental mass transfer coefficients showed deviations from the circulating drop models but were reasonably in agreement with the stagnant drop model. The observed deviation from circulating drop models was attributed to the slow dimerization reaction which this system is known to exhibit for the transfer of acetic acid between the organic solvent and water. The agreement with the stagnant drop model shows that molecular diffusion may be the controlling mechanism of mass transfer in this system.

NOMENCLATURE

A	interfacial area, cm^2
C_d	dispersed phase concentration, wt%
C_{do}	initial dispersed phase concentration, wt%
D	dispersed phase diffusivity, cm^2/sec
d	drop diameter, cm
k_c	continuous phase mass transfer coefficient, cm/sec
k_d	dispersed phase mass transfer coefficient, cm/sec
K_d	overall dispersed phase coefficient, cm/sec
m	equilibrium distribution coefficient
t	time, sec
t_f	fall time, sec
U	droplet fall velocity, cm/sec
V	drop volume, cm^3
μ_c	continuous phase viscosity, Kg/m. sec
μ_d	dispersed phase viscosity, Kg/m. sec

REFERENCES

1. Billet, R. and **Mackowiak, J., 1980,** Ger. Chem. Eng., 3, 234.

2. Handlos, A.E. and **Baron, T., 1957,** AIChE J., 3, 127.

3. Heertjes, P.M., Holve, W.A., and **Talsma, H., 1954,** Chem. Eng. Sci., 3, 122.

4. Johnson, A.I. and **Hamielec, A.E., 1960,** AIChE J., 6, 145.

5. **Kronig, R.** and **Brink, J.C., 1957,** App. Sci. Res. AZ, 142.

6. **Lewis, W.K.,** and **Whitman, W.G., 1924,** Ind. Eng. Chem., 16, 1215.

7. **Lewis, J.B., 1954,** Chem. Eng. Sci., 3, 248.

8. **Licht, W.** and **Conway, J.B., 1950,** Ind Eng. Chem., 42, 1151.

9. **Licht, W.** and **Pansing, W.F., 1953,** Ind. Eng. Chem., 45, 1885.

10. **Newman, A.B., 1931,** Trans. AIChE.

11. **Park, J.S., Choi, C.K.,** and **Kim, L.H., 1986,** Int. Chem. Eng., 26, 540.

12. **Perry, R.H.** and **Green, D., 1984,** Chemical Engineers' Handbook, Sixth ed., McGraw-Hill.

13. **Sekine, T.** and **Hasegana, Y., 1977,** Solvent Extraction Chemistry, Marcel Dekker, N.Y.

14. **Sherwood, T.K., Evans, J.E.,** and **Longcor, J.V.A., 1939,** Ind. Eng. Chem., 39, 1144.

15. **Skelland, A.H.P.** and **Wellek, R.M., 1964,** AIChE J., 10, 491.

16. **Skelland, A.H.P.** and **Minhas, S.S., 1971,** AIChE J., 17, 1316.

17. **Skelland, A.H.P.** and **Vasti, N.C., 1985,** Can. J. Chem. Eng., 63, 390.

18. **Slater, M.J., Baird, M.H.I.,** and **Liang, T.B., 1988,** Chem. Eng. Sci., 43, 233.

19. **Steiner, L., 1986,** Chem. Eng. Sci., 41, 1979.

20. **Steiner, L., Oezdemir, G.,** and **Hartland, S., 1990,** Ind. Eng. Chem. Res., 29, 1313.

21. **Streicher, R.** and **Schugerl, K., 1973,** Chem. Eng. Sci., 28, 1777.

22. **Streicher, R.** and **Schugerl, K., 1977.,** Chem. Eng. Sci., 32, 23.