# *Diffusion of Hydrocarbon, Alcohols and Esters through the Aqueous Solutions of Cationic Detergent*

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## Introduction

There have been many reports since the Graham-age about the diffusion of solute in colloidal solutions, for example through gelatine or agar solution. In these cases, it has been shown that the velocity of diffusion is only slightly affected in the presence of gelatine if the solute molecules or ions are small and non-reacting with them, but deeply influenced if there are interactions between the solute and the gelatine[1].

Investigations have been made in this paper, as to how the diffusion of a certain substance is influenced by the presence of a detergent. In general the detergent has an amphipathic structure, which is composed by hydrophilic and oleophilic part in the molecule. According to this amphipathic property, they associate in the aqueous solution and micelle formation occurs. The association occurs between not only detergent molecules themselves but also the other substances added to the solution, for instance, non-polar compounds such as hydrocarbon occupying the non-polar loci of micelles, viz. inside the micelles, resulting in swollen micelles. On

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[1] T. Graham, *Liebig Ann.*, **121**, 1 (1862); L. Friedman and E.O. Kraemer, *J. Am. Chem. Soc.*, **52**, 1295, 1305, 1311 (1930).

the other hand the polar compounds such as alcohol take a position which is essentially similar to the detergent molecules which make up the micelles.

It will be expected in this case that the kinetic unit is different according to the absence or presence of a detergent. In the latter case the diffusion is considerably delayed. Some results have been reported by Dean and Vinograd[2] in regard to the diffusion of solubilized dyes in Aerosol OT micelles, where diffusion was measured through sintered glass and cellophane membrane. However, this porous disc method has disadvantages in many respect and the solubilizate also has a complicated chemical structure in their experiments. In this paper the diffusion of some simple compounds in detergent solution has been investigated by the free boundary method which is much more free from theoretical objection.

### Experimental Methods and Samples

The diffusion coefficient was measured in 2.37% aqueous solution of trimethyldodecylammonium chloride (TMDA). This sample was the pure grade product of Nihon Yushi Co. To obtain the concentrated aqueous solution, TMDA was dialysed[3] by cellophane membrane to remove the low molecular substances or ions supposed to be contained in this sample. Some TMDA escaped through the membrane but the portion retained was pure enough for our present purpose. The solution inside the membrane was diluted to 2.37% by weight, of which relative viscosity was 1.352 and pH was about 5.4. The diffusing substances which were recrystallized or redistillated before use were of the highest market grade.

The diffusion coefficient was measured by the method of refractive index. The diffusion-cell was Neurath-type, made of Ni-Cr stainless steel 18–8 manufactured by Kobe Steel Factory, the thickness being 30 mm. The optical system was the diagonal Schlieren type, the same as described in other papers[4]. The cell was placed in a thermostat at 25.0°C More than ten diffusion patterns (concentration-gradient curves) were photographed at almost the same time intervals in each experiment. In the case of the most rapid diffusion the time interval was about three minutes while it was about an hour for the slowest one. The diffusion coefficient was calculated from the breadth between two inflection points in diffusion pattern whose ordinate could easily be found from the maximum height of the pattern[5].

### Results and Some Considerations

**(1) Experiments with completely soluble solute in water.** — In Table I, the diffusion coefficients of some solutes in water and in the TMDA solution are listed.

TABLE I
DIFFUSION COEFFICIENTS OF SOME SOLUBLE SUBSTANCES IN TMDA-SOLUTION AND IN WATER

| Substance | $C_1$ | $C_2$ | $D_S\times10^7$ $cm^2$/sec. | $D_W\times10^7$ $cm^2$/sec. |
|---|---|---|---|---|
| Urea | 2.0% | 1.0% | 137 | 135 |
| Fructose | 0.1% | 0,0% | 76.0 | 73.4 |
| Potassium Chloride | 0.1N | 0.0N | 202 | 192 |

$C_1$ and $C_2$ show the initial concentration of the solute in lower and upper solutions on the diffusion cell respectively. $D_s$ and $D_w$ indicate the diffusion coefficient of the solute in TMDA 2.37% solution and in water respectively.

The equation of Onsager and Fuoss[6]

$$D=\frac{RT}{f}\left(1+\frac{d\ln\gamma}{d\ln c}\right)$$

was derived from a general treatment of the diffusion problem which may be used to explain the above results. In this equation, $f$ is the frictional coefficient and $\gamma$, the activity coefficient, $c$ the concentration of the solute. The hydrodynamic factor, $f$ and the thermodynamic factor, $\frac{d\ln\gamma}{d\ln c}$ also may be increased by the presence of TMDA. It is thus seen that both factors approximately may cancel one another and roughly account for the fact that $D_s$ differ only slightly from $D_w$ as seen in Table I. Similar phenomena are reported[7] in which the diffusion coefficients of certain high-polymer solutions are not sensitively dependent on concentration, since hydrodynamic and thermodynamic factors both increased with the concentration of the high polymer. Potassium chloride affects the state of micelles greatly[8], however this has no relation to the present subject.

**(2) Experiments with nonpolar substance.** —The diffusion coefficient of hexane solubilized in TMDA solution is shown in Table II.

The diffusion coefficient is far less than that of Exp. 1. At the constant concentration gradient, $D_s$ becomes somewhat greater as the concentration of hexane decreases.

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[2] R.B. Dean and J.R. Vinograd, *J. Phys. Chem.*, **46**, 1091 (1942).

[3] J.T. Yang and J.F. Foster, *J. Phys. Chem.*, **57**, 628 (1953); B.S. Harrap and I.J. O'Donnell, *J. Phys. Chem.*, **58**, 1099 (1954).

[4] N. Sata, H. Okuyama and K. Tyuzyo, *Kolloid-Z.*, **121**, 46 (1951); H. Okuyama and K. Tyuzyo, This Bulletin, **27**, 259 (1954).

[5] H. Neurath, *Chem Rev.*, **30**, 357 (1942).

[6] L. Onsager and R.M. Fuoss, *J. Phys.Chem.*, **36**, 2689 (1932).

[7] C.O. Beckmann and J. L. Rosenberg, *Ann. N. Y. Acad. Sci.*, **46** (5), 329 (1945).

[8] v.g. P. Debye and E.N. Anacker, *J. Phys. Chem.*, **53**, 1 (1949).

TABLE II

DIFFUSION COEFFICIENTS OF HEXANE SOLUBILIZED IN TMDA-SOLUTION

| $C_1$ | $C_2$ | $D_s\times10^7$ cm$^2$/sec. | $(D_1-D_2)\times10^7$ cm$^2$/sec. |
|---|---|---|---|
| 0.1%[9] | 0.6%[9] | 1.90 | 1.62 |
| 0.3 | 0.8 | 1.68 | 1.50 |
| 0.5 | 1.0 | 1.30 | 1.37 |
| 0.7 | 1.2 | 1.31 | 1.25 |
| 1.0 | 1.5 | 0.98 | 1.07 |
| 0.1 | 1.0 | 3.00 | 2.69 |
| 0.5 | 1.5 | 2.72 | 2.44 |
| 0.1 | 1.5 | 4.21 | 3.76 |

and $D_s$ considerably increases with increasing concentration gradient of hexane.

In these cases the kinetic units of diffusion must exclusively be micelles swollen by hexane molecules, because the hexane molecules exist only in solubilized micelles and the molecularly dispersed hexane is negligible. The homogenization of hexane-containing micelles must occur initially in such a manner that the more swollen micelles sink and the less swollen micelles rise. Then the observed diffusion coefficient in Table II may be considered as the difference of the diffusion coefficients of both micelles in water.

Assuming the micelle as spherical, the relation between the radius of the micelle and diffusion coefficent is shown by Einstein and Sutherland, as follows:

$$D=\frac{RT}{6\pi\eta rN} \tag{1}$$

$R$ represents gas constant, $T$, absolute temperature, $\eta$, solvent viscosity, $N$, Avogadros' number, $D$, diffusion coefficient and $r$, radius of diffusing particles. Evaluating Eq. (1), we obtain.

$$rD=2.43\times10^{-13}\ \text{C.G.S.} \tag{2}$$

The radius of the micelle can be calculated from Eq. (2) by the measurement of the difusifon coefficient alone of the TMDA solution. However the diffusion coefficient cannot be obtained owing to the influence of diffusion potential caused by the charged large micelles and small gegenions. On the other hand, in order to suppress this potential it is necessary to add sufficient amounts of electrolyte, which would change the state of micelles completely. For the same reason as mentioned above the radius of the swollen micelle cannot be obtained directly.

From the X-ray data[10] it is supposed that the diameter of the micelle of TMDA is about 35 Å and the diameter of the swollen micelle is increased linearly with the solubilized amount of solubilizate. The maximum (saturated) increment is reported to be 15 Å. In this experiment 1.5% hexane solution is nearly the saturation-value.

Assuming that the X-ray data also hold in this experiment, we can calculate the true diffusion coefficient as shown in Table III.

TABLE III

CALCULATED RADII AND DIFFUSION COEFFICIENTS OF THE SWOLLEN MICELLES BY HEXANE

| Hexane % | 0.0 | 0.1 | 0.3 | 0.5 | 0.6 | 0.7 | 0.8 | 1.0 | 1.2 | 1.5 |
|---|---|---|---|---|---|---|---|---|---|---|
| $r$(A) | 17.5 | 18.0 | 19.0 | 20.0 | 20.5 | 21.0 | 21.5 | 22·5 | 23.5 | 25.0 |
| $D\times10^7$ | 13.88 | 13.49 | 12.80 | 12.17 | 11.87 | 11.57 | 11.30 | 10.80 | 10.32 | 9.73 |

From Table III the difference between two diffusion coefficients of swollen micelles at $C_1$ and $C_2$ can be obtained, and the values $(D_1-D_2)$ are listed in the last column of Table II. Fairly good coincidence with the experimentally obtained diffusion coefficients is found.

(3) **Experiments with polar compounds.**—Table IV exhibits the diffusion coefficients of alcohols in TMDA- solution.

TABLE IV

DIFFUSION COEFFICIENTS OF VARIOUS ALCOHOLS IN TMDA-SOLUTION

| Alcohols | $C_1$ | $C_2$ | $D_s\times10^7$ cm$^2$/sec. | Solubility[11] in water |
|---|---|---|---|---|
| *n*-Amyl- | 1.0%[9] | 2.0%[9] | 15.8 | 2.20 |
| *n*-Octyl- | 1.0 | 2.0 | 6.15 | 0.059 |
| *n*-Lauryl- | 1.0 | 2.0 | 0.915 | 0.00 |
| *n*-Lauryl- | 0.1 | 1.0 | 4.87 | 0.00 |

The diffusion coefficient of iso-amylalcohol in water is $93.2\times10^{-7}$cm$^2$/sec. So *n*-amylalcohol diffuses much more slowly in the detergent solution than iso-amylalcohol in water in spite of the same molecular weight.

In Table IV, it is seen that the longer the chain length of alcohol the slower is the diffusion velocity. In these cases, however, the solubility in water has a somewhat closer relation to the diffusion velocity than the chain length of alcohols. The concentration gradient curves of diffusion obtained from *n*-amylalcohol deviate remarkably from the ideal Gaussian curves and assume the shape

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[9] volume %.

[10] W.D. Harkins, R.W. Mattoon and M.L. Corrin, *J. Colloid Sci.*, **1**, 105 (1946). W. D. Harkins, R. W. Mattoon and R. S. Stearns, *J. Chem. Phys.* **15**, 209 (1947); **16**, 646, 652 (1948).

[11] Grams of the substances in 100 g. water.

of two (at least) ideal curves superimposed, of which one is very sharp and the other very diffuse. The diffused one may be caused by simple alcohol molecules and the sharp one by complicated mixed micelles composed of alcohol and detergent molecules.

The present method of calculating the diffusion coefficient gives only the complex average value of two different diffusion coefficients of these. It is impossible to analyze the value in greater detail at the present stage.

If there were rapid equilibrium between amylalcohol in swollen micelles and that in the extra-micellar solutions, diffusion would be performed chiefly by molecularly dissolved *n*-amylalcohol; then the concentration-gradient curves would show a different patterns.

Therefore, the sorption or desorption of dissolved alcohol molecules by micelles may not occur so easily in this case as Winsor's equilibrium theory[12] of micelles suggests. The slow exchange between swollen micelles and solutes may be similar to the phenomena of surface aging which exhibit hindered diffusion to the surface by monomolecular film of surface active substances[13].

Laurylalcohol diffuses like hexane but in this case the circumstances are more complex owing to the penetration and the least diffusion coefficient value and the highest viscosity, has been obtained presumably as the result of large sandwich-micelles.

In Table V, the diffusion coefficients of esters are listed. The hydrolysis was not observed at least.

TABLE V

DIFFUSION COEFFICIENTS OF VARIOUS ESTERS IN TMDA-SOLUTION

| Esters | $C_1$ | $C_2$ | $D_s\times10^7$ cm$^2$/sec. | Solubility[11] in water |
|---|---|---|---|---|
| Ethylacetate | 1.0%[9] | 2.0%[9] | 102 | 7.56 |
| Butylacetate | 1.0 | 2.0 | 15.9 | 2.3 |
| Dimethylphthalate | 1.0 | 0.5 | 18.2 | 0.24 |
| Diethylphthalate | 1.0 | 0.5 | 8.25 | — |
| Dibutylphthalate | 1.0 | 0.5 | 4.36 | — |

Ethylacetate which is completely soluble at this concentration diffuses ordinarily, but $D_s$ of butylacetate is very small and the concentration gradient curves of diffusion of this are the composite curve of at least two parts just as in the case of *n*-amylalcohol mentioned above.

McBain found unusual behaviours in the case of solubilization of dimethylphthalate[14] in detergent solution which is insoluble both in water and in hydrocarbon and suggested that the rearrangement of micelles takes place and the solubilization of dimethylphthalate molecules is achieved by polar groups of small micelles. In such a case it will be expected that the circumstances are somewhat different in diffusion process. But the numerical value of the diffusion coefficient on Table V shows no anomaly. A parallelism is rather found between the solubility and the diffusion coefficient. McBain took up dimethylphthalate only, diethylphthalate and dibutylphthalate are also investigated in these experiments.

In Table VI the diffusion coefficients of partly water-soluble polar substances in various mean concentrations are listed.

TABLE VI

CONCENTRATION DEPENDENCE OF DIFFUSION COEFFICIENTS IN TMDA-SOLUTION

| | $C_1$ | $C_2$ | $D_s\times10^7$ cm$^2$/sec. |
|---|---|---|---|
| *n*-Amylalcohol | 1.0%[9] | 2.0%[9] | 15.8 |
| | 2.0 | 3.0 | 11.8 |
| | 3.0 | 4.0 | 6.22 |
| *n*-Butylacetate | 0.5 | 1.5 | 15.9 |
| | 1.0 | 2.0 | 15.1 |
| | 2.0 | 3.0 | 12.6 |
| | 3.0 | 4.0 | 9.75 |
| | 4.5 | 5.5 | 5.76 |
| Ethylacetate | 1.0 | 2.0 | 102 |
| | 3.0 | 4.0 | 93.8 |
| | 5.0 | 6.0 | 86.1 |
| | 7.0 | 8.0 | 63.4 |
| | 8.0 | 10.0 | 22.4 |
| | 10.0 | 13.0 | 15.7 |
| Dimethylphthalate | 1.0 | 0.5 | 18.2 |
| | 1.5 | 0.5 | 15.6 |
| | 2.7 | 1.5 | 5.16 |

These polar compounds dissolve somewhat in water but in the detergent solution much more through solubilization. The higher the concentration of these polar compounds, the smaller becomes the valueof the diffusion coefficient. This is explained by assuming that the contribution of complicated micelles to the diffusion becomes more dominant compared with the single molecules of the solute as the concentration is increased. This is also found in the diffusion curve since the diffuse part of the diffusion pattern tends to vanish as the concentration of the solute approaches saturation.

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[12] P.A. Winsor, *J. Phys. Chem.*, 56. 391 (1952).

[13] A.F.H. Ward and L. Tordai, *Rec. Trav. Chim. Pays-Bas*, 71, 396, 482, 572 (1952); A.E. Alexander and P. Johnson, "Colloid Science", Clarendon press, Oxford 1949, p. 529.

[14] J.W. Mc Bain and Mc Han, *J. Am. Chem. Soc.*, 70, 3838 (1948).

No quantitative relation between concentration and diffusion coefficient can be found, since the obtained diffusion coefficient is a complicated mean of two components.

## Summary

(1) Urea, fructose and potassium chloride which are completely soluble in water, diffuse in the TMDA solution at about the same rate as in water notwithstanding the fact that the former has higher viscosity than the later.

(2) The diffusion coefficient of hexane is in a fairly good coincidence with the difference of the calculated diffusion coefficient from X-ray data between more and less swollen micelles.

(3) The diffusion of alcohols and esters is generally governed by their solubility in water. From the concentration gradient curves of diffusion, they are considered to diffuse on two different mechanisms, one as the single molecule and the other as the complex group associated with the detergent micelles.

(4) The equilibrium between solute in micelles and in water is rather slower process when the mechanical disturbance or convection is absent in the solution.

(5) The anomalies reported on the solubilization of dimethylphthalate is not observed in these diffusion experiments.

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