TABLE 1. D_w IN ORGANIC SOLVENTS

No.	Solvent	Diffusion coefficient × 10^5, 25°C. (exptl)*	N'_{Sc}	Viscosity of solvent at 25°C., centipoise	$D \times 10^5$ (4)	$D_o \times 10^5$	$D_w \times 10^5$ (present work)	Deviation, % †	††
1.	Acetone	4.56	39.5	0.32	8.50	3.70	4.30	5.7	18.8
2.	Ethyl acetate	3.26	55.4	0.45	7.52	3.27	3.06	6.1	3.1
3.	Ethyl alcohol	1.13	160.0	1.10	2.58	1.12	1.24	9.7	0.8
4.	Furfural	0.92	197.0	1.49	2.14	0.93	0.92	0.0	1.1
5.	Iso propanol	0.39	457.0	2.00	0.99	0.43	0.68	—	10.3
6.	*n*-butanol	1.22	147.5	2.60	1.43	0.62	0.53	—	—
7.	Ethylene chlorhydrin	0.46	388.0	3.43	1.20	0.52	0.40	13.0	13.0
8.	Iso-butanol	0.37	492.0	3.60	0.81	0.35	0.38	2.7	5.4
9.	Aniline	0.71	253.0	3.75	0.83	0.36	0.36	—	—
								**	
10.	Methanol	—	72.0	0.56	5.27	2.30	2.50	8.7	
11.	Diethyl ether	—	27.0	0.23	14.17	6.16	6.60	7.1	
12.	Benzene	—	79.0	0.61	5.48	2.38	2.28	4.2	

* The experimental values of diffusion coefficients were taken from (2). All the values were corrected to 25°C.

** Deviation of D_w from the D_o values.

† Deviation of D_w from the experimental values.

† † Deviation of D_o from the experimental values.

mental values in the cited cases may not be reliable.

ETHYLENE CHLORHYDRIN

The deviation for ethylene chlorhydrin is explained by the fact that the reported experimental value is for 80% water and not for infinite dilution. Hence the deviation is due to the concentration effect. If one considers the viscosity of solution (2.95) instead of viscosity of solvent, one gets $D_w = 0.46 \times 10^{-5}$ which is exactly the experimental value.

ISO PROPANOL

Applying Olander's correction to Wilke-Chang value for this case one gets $0.99/2.3 \times 10^{-5} = 0.43 \times 10^{-5}$ which differs from the value calculated from the proposed correlation by 36% (0.68×10^{-5}). The reported experimental value is 0.38×10^{-5} with 0.5% water as solute.

The calculated values from Equation (2) are given in Table 1. They agree fairly well with the experimental values except in the cases discussed above. For comparison three more systems which were not given by Olander were chosen. The values in respect of these were calculated by the present method and compared with the method of Wilke-Chang and Wilke-Chang method corrected by Olander's constant. The values calculated from present correlation are in agreement with the values obtained by the Wilke-Chang correlation with the correction factor of Olander (D_o).

NOTATION

μ = viscosity of solute (water) vapor, poise

V_m = molecular volume of solute

D_w = diffusivity of water in organic solvents

η = viscosity of solution, centipoise

D_o = diffusion coefficient of Reference 4 as corrected by Olander

D = diffusion coefficient as calculated by Wilke-Pin Chang equation

N'_{Sc} = modified Schmidt group $[= (\mu V_m)/(D)]$

LITERATURE CITED

1. Ibrahim, S. H., and N. R. Kuloor, *Brit. Chem. Eng.*, **5**, 795 (1960).
2. Olander, D. R., *A.I.Ch.E. Journal*, **7**, 175 (1961).
3. ———, Personal communication.
4. Wilke, C. R., and Pin Chang, *A.I.Ch.E. Journal*, **1**, 264 (1955).

Isothermal Diffusion with a Variable Density

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For ordinary isothermal binary diffusion with composition dependent density, the diffusion equation can be written for two-dimensional flow as (*1*)

$$\rho\left[\frac{\partial w}{\partial \theta} + u\frac{\partial w}{\partial x} + v\frac{\partial w}{\partial y}\right] = D\left[\frac{\partial}{\partial y}\left(\rho\frac{\partial w}{\partial y}\right) + \frac{\partial}{\partial x}\left(\rho\frac{\partial w}{\partial x}\right)\right] \quad (1)$$

This equation is valid for ideal solutions (that is perfect gas mixtures) for both laminar and turbulent flow, and the diffusivity D is essentially independent of composition. When one considers a perfect gas mixture, the density is given by

$$\rho = \frac{pM}{Rt} \quad (2)$$

and M is related to w by

$$\frac{1}{M} = Bw + \frac{1}{M_2} \quad (3)$$

where $B = 1/M_1 - 1/M_2$. Thus, using Equations (2) and (3), one may write

$$\rho\frac{\partial w}{\partial i} = \frac{pM}{Rt}\left(-\frac{1}{BM^2}\right)\frac{\partial M}{\partial i} = -\frac{p}{BRt}\frac{\partial \ln M}{\partial i} \quad (4)$$

By using Equation (4) with t constant, Equation (1) can be rewritten as

$$p\left[\frac{\partial \ln M}{\partial \theta} + u\frac{\partial \ln M}{\partial x} + v\frac{\partial \ln M}{\partial y}\right] = D\left[p\frac{\partial^2 \ln M}{\partial y^2} + \frac{\partial}{\partial x}\left(p\frac{\partial \ln M}{\partial x}\right)\right] \quad (5)$$

since p is independent of y. Except when the pressure gradient $\partial p/\partial x$ is a significant part of the absolute pressure in systems where longitudinal diffusion is important, Equation (5)can be reduced to

$$\frac{\partial \ln M}{\partial \theta} + \bar{u} \cdot \nabla \ln M = D\nabla^2 \ln M \quad (6)$$

This equation is valid for laminar or turbulent flow with variable density, except for the unusual case of a strong pressure gradient coupled with longitudinal diffusion. Equation (6) was first derived, although somewhat differently, by Bedingfield and Drew (2). With $\ln M = r$, Equation (6) becomes

$$\frac{\partial r}{\partial \theta} + u\frac{\partial r}{\partial x} + v\frac{\partial r}{\partial y} = D\left[\frac{\partial^2 r}{\partial y^2} + \frac{\partial^2 r}{\partial x^2}\right] \quad (7)$$

To obtain exact solutions to isothermal, variable density mass transfer problems

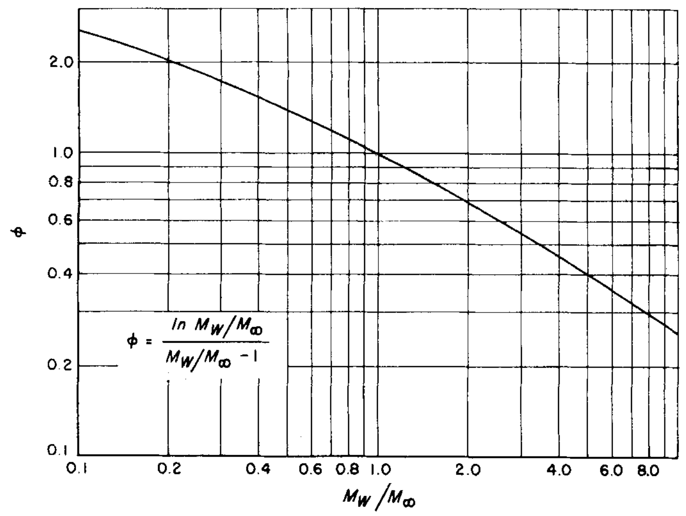

Fig. 1. Variable density correction factor vs. M_W/M_∞.

Equation (7) must be solved simultaneously with the continuity equation and the momentum equation, which is as follows:

$$\rho\left[\frac{\partial u}{\partial \theta}+u\frac{\partial u}{\partial x}+v\frac{\partial u}{\partial y}\right]=\frac{\partial}{\partial y}\left(\mu\frac{\partial u}{\partial y}\right)-\frac{\partial p}{\partial x} \tag{8}$$

Density variations cause a change in the velocity profile as is seen by Equation (8). However the wall mass flux is relatively insensitive to variations in the velocity profile, and thus the solution of Equation (7) with the constant density velocity profile would be expected to give an accurate value of the wall mass flux. With this approximation, the variable density mass flux can be easily related to the constant density mass flux for any given geometry and for turbulent or laminar flow. This is done as follows.

For a given mass transfer situation (fixed geometry, diffusivity, etc.) the constant density diffusion equation is written as

$$\frac{\partial w'}{\partial \theta}+u\frac{\partial w'}{\partial x}+v\frac{\partial w'}{\partial y}=D\left[\frac{\partial^2 w'}{\partial y^2}+\frac{\partial^2 w'}{\partial x^2}\right] \tag{9}$$

The primes here serve as a reminder that these are the mass fractions in the case of a constant density. If, as discussed above, the assumption is made that the effect of variable density on the velocity profile can be neglected in determining the wall mass flux, then u and v are the same in Equations (7) and (9). Equations (7) and (9) are clearly analogous. By substitution it can be verified that

$$r = Aw' + E \tag{10}$$

where A and E are constants to be determined from the boundary conditions $r = r_w$ for $w' = w_w$ and $r = r_\infty$ for $w' = w_\infty$. The value of A is

$$A=\frac{r_\infty - r_w}{w_\infty - w_w}=\frac{\ln\dfrac{M_\infty}{M_w}}{w_\infty - w_w} \tag{11}$$

By differentiating Equation (10) the wall mass fluxes for the constant and variable density cases can be related:

$$\left.\frac{\partial r}{\partial y}\right|_w=\left.\frac{1}{M_w}\frac{\partial M}{\partial y}\right|_w=-M_w B\left.\frac{\partial w}{\partial y}\right|_w=\left.\frac{\ln\dfrac{M_\infty}{M_w}}{w_\infty - w_w}\frac{\partial w'}{\partial y}\right|_w \tag{12}$$

But $M_w B(w_\infty - w_w)$ is equal to $(M_w/M_\infty - 1)$, so that

$$\left.\frac{\partial w}{\partial y}\right|_w=\left.\frac{\ln\dfrac{M_w}{M_\infty}}{\dfrac{M_w}{M_\infty}-1}\frac{\partial w'}{\partial y}\right|_w \tag{13}$$

Here the ratio $(\partial w/\partial y)_w/(\partial w'/\partial y)_w$ is the ratio of the mass fraction gradients at the wall in the variable density case to that in the case of constant density. Since the mass transfer coefficients are usually defined in terms of these gradients

$$\frac{k_{\mathrm{var}\,\rho}}{k_{\mathrm{const}\,\rho}}=\frac{\ln\dfrac{M_w}{M_\infty}}{\dfrac{M_w}{M_\infty}-1} \tag{14}$$

This expression will be valid for both laminar and turbulent flow for any geometry, irrespective of the value of the Schmidt number. Also, for low mass transfer rates, $k_{\mathrm{const}\,\rho}$ can be determined by means of the constant property analogy between heat and mass transfer. The magnitude of the variable density correction can be seen in Figure 1.

It must be noted that owing to the neglect of density variations on the velocity profile, this expression will become less accurate at higher values of M_w/M_∞. By using the integral method with linear profiles to calculate laminar diffusion on a flat plate with zero normal velocity at the wall and a Schmidt number of unity, it can be demonstrated that Equation (14) is accurate within 15% for $1/5 < M_w/M_\infty < 5$ and within 30% for $1/10 < M_w/M_\infty < 10$, in this situation. Equation (14) would be expected to apply with similar accuracy to other flow situations where the surface velocity is small.

The variation of viscosity with composition has been neglected here, but this effect on the mass flux is small, of the same order as the previously neglected density effect. The effect of a composition dependent viscosity on laminar constant density diffusion from a flat plate can be obtained by applying the heat-mass transfer analogy to the results of reference (3).

NOTATION

B = $1/M_1 - 1/M_2$
D = diffusion coefficient
i = any independent variable
$k_{\mathrm{var}\,\rho}$ = variable density mass transfer coefficient
$k_{\mathrm{const}\,\rho}$ = constant density mass transfer coefficient
M_i = i = 1, 2: pure component molecular weight
M = molecular weight of mixture, $1/M = B\,w + 1/M_2$
p = pressure
r = $\ln M$
R = gas constant, $\rho = pM/Rt$
t = absolute temperature
$\bar{u}$ = vector velocity
u = longitudinal velocity component
v = transverse velocity component
w = mass fraction of diffusing component
w' = mass fraction of diffusing component for constant density
x = longitudinal coordinate (measured along surface)
y = transverse coordinate (measured normal to surface)
μ = dynamic viscosity
ρ = density, $\rho = pM/Rt$
θ = time

Subscripts

w = conditions at the wall
∞ = conditions in free stream or at center line

LITERATURE CITED

1. Eckert, E. R. G., and R. M. Drake, "Heat and Mass Transfer," 2 ed., McGraw-Hill, New York (1959).
2. Bedingfield, C. H., and T. B. Drew, *Ind. Eng. Chem.*, **42**, 1164 (1950).
3. Hanna, O. T., and J. E. Myers, *A.I.Ch.E. Journal*, **7**, No. 3, p. 437 (1961).