Separation of Liquids by Mass Diffusion

F. O. SHUCK and H. L. TOOR

Carnegie Institute of Technology, Pittsburgh, Pennsylvania

Mass diffusion studies were carried out in a diaphragm diffusion cell with the liquid system methyl alcohol, n-propyl alcohol, isobutyl alcohol. Experiments were conducted over a wide range of separating agent counterflow. The separation factor was approximately doubled and the yield decreased three orders of magnitude when the counterflow was increased one order of magnitude. Using the four ternary diffusion coefficients for the system and a diaphragm geometry based on previous calibration, the concentration and separation factors could be predicted within the range of experimental error. The theory indicates that at high counterflow considerably larger separation factors would be obtained if the diaphragm were uniform.

In the mass diffusion process a partial separation of the components of a binary gas mixture may be achieved by allowing the binary mixture to diffuse through a third gas or vapor (the separating agent). It was first noted several years ago by Maier (15) that the separation could be further enhanced by superimposing a bulk flow of the separating agent in a direction opposing the diffusional flow of the components being separated. More recent investigations (2, 5, 13) have been directed toward characterizing the mass diffusion process in terms of the diffusion behavior of the ternary gas system. The success of these attempts is in large part attributable to the fact that at present the diffusion behavior of multicomponent gaseous systems may be readily obtained from a knowledge of the diffusion behavior of the binary systems which comprise the multicomponent mixture.

Qualitatively, it might be expected that a similar sort of behavior would also occur in liquid systems. However, little consideration has been given to the application of the mass diffusion process to liquids, although it has been demonstrated that separations of binary liquid mixtures may be achieved at measurable levels of concentration (18, 19).

No attempts have been made to relate separations of liquid mixtures to the diffusion behavior of the ternary liquid systems. The lack of any such attempt may be traced to the lack of any general information regarding the diffusion behavior in complex liquid systems and to the lack of experimental measurements of diffusion coefficients for such systems. In particular, there are no relations of the generality of the Maxwell-Stefan equations for gases which describe the diffusion behavior of complex liquid systems. It is the purpose of this investigation to attempt to relate the separation achieved in mass diffusion to the diffusion coefficients for a ternary liquid system.

MULTICOMPONENT DIFFUSION

The diffusion fluxes in a multicomponent, isothermal, isobaric system with no external forces present may generally be related to the concentrations and concentration gradient by the equation (1, 11, 14)

$$\underbrace{J_{i} = -\sum_{j=1}^{n-1} D_{ij} \, \nabla \, C_{j} \, \cdot \, , \, i = 1, 2 \dots n-1}_{} \tag{1}$$

where the multicomponent diffusion coefficients are generally concentration dependent. The J_i are fluxes with respect to some average velocity of the system, and it is

F. O. Shuck is with Iowa State University, Ames, Iowa.

convenient to take this reference velocity to be the volumetric average velocity given by

$$\underline{V} = \sum_{j=1}^{n} V_{j} C_{j} \overline{v_{j}}$$
 (2)

so the fluxes with respect to a fixed coordinate are described by

$$\underline{J}_{i}' = \underline{J}_{i} + \underline{V} C_{i}, i = 1, 2 ... n - 1$$
 (3)

and it follows that $\sum_{i=1}^{n} J_i v_i = 0$; only n-1 fluxes are independent.

Equation (1) may be obtained either from the postulates of nonequilibrium thermodynamics (11, 14) or from the postulate, a generalization of Fick's law, that at a fixed composition the fluxes are linearly related to the concentration gradients. Equation (1) follows directly from the latter postulate since, by virtue of the equation

$$\sum_{j=1}^{n} \overline{v_j} C_j = 1 \tag{4}$$

there are only n-1 independent concentration gradients and, as shown, the choice of a reference frame leaves only n-1 independent fluxes. As implied above, the form of Equation (1) is unchanged if the reference velocity is changed (11, 14, 22).

Nonequilibrium thermodynamics with the assumption of microscopic reversibility leads not only to Equation (1) but also to the Onsager reciprocal relationships (17)

which yield
$$\frac{(n-1)(n-2)}{2}$$
 relationships among the D_{ij}

and the derivatives of the activity coefficients with respect to concentration (11, 14).

Equation (1) has been found to be a satisfactory description of the diffusion in all multicomponent liquid systems which have been studied (4, 6, 7, 8, 9, 11, 12, 16, 20, 21). Since the equation includes the Maxwell-Stefan equations as a special case, it also applies to ideal gases. There is no reason to expect it not to apply to non-ideal gases as well.

The diffusion coefficients in Equation (1) are sometimes referred to as the practical diffusion coefficients (14) since they are the quantities measured in the usual diffusion experiments. They are also practical in the engineering sense in that they can be directly used to describe

multicomponent mass transfer, since once the D_{ij} are measured as a function of composition Equation (1) gives a complete description of the relation between the fluxes, concentrations, and concentration gradients. (In ideal gases where the D_{ij} are known functions of composition, Equation (1) is, in special cases, more easily integrated after being inverted to the Maxwell-Stefan form.)

In liquids the D_{ij} must be measured, and since diffusion experiments yield all the D_{ij} (only ternary systems have been studied to date) thermodynamic data are needed only to check the Onsager reciprocal relationships or, if the relationships are assumed to be correct, to check the consistency of the measurements. Consequently for liquid mass transfer Equation (1) is at present more useful than the equivalent statements which introduce activities or chemical potentials as, for example, Equation 18.4-8 in reference 3.

Shuck and Toor have found that in the two non-electrolytic ternary systems which have been examined the D_{ij} may be related to the dilute binary diffusion coefficients by the following equations (21)

$$D_{ii} = \mathcal{D}^{o}_{3i} \omega_{i} + \mathcal{D}^{o}_{ij} \omega_{j} + \mathcal{D}^{o}_{i3} \omega_{3}$$
, $i, j = 1, 2$ (5)

$$D_{ij} = \omega_i \left(\mathcal{D}^o_{3i} - \mathcal{D}^o_{ji} \right) \frac{\overline{v_j}}{\overline{v_i}} \quad i, j = 1, 2$$

$$i \neq j$$

$$(6)$$

where ω is volume fraction. (The system used in this work has a constant mass density, here ω is also mass fraction.)

It follows from the limits of the D_{ii} and D_{ij} (20, 21) that, except for the trivial case in which all the dilute binary coefficients are equal, the D_{ii} and D_{ij} must always be composition dependent.

The explicit forms of Equations (5) and (6) for the system used in this study, methyl alcohol, *n*-propyl alcohol, isobutyl alcohol are given in Table 1. The measurements of these ternary coefficients were carried out in a closed diaphragm cell in which there was no volume flow (20, 21)

By virtue of the one Onsager reciprocal relationship in a ternary system there is one equation relating the four ternary diffusion coefficients (10, 11, 14). The lack of thermodynamic data does not allow a complete check of the validity of the reciprocal relationship in the present system, but if the system is treated as ideal the diffusion data are consistent with the relationship (20, 21).

MASS DIFFUSION THEORY

In the mass diffusion cell steady state diffusion and volume flow take place through a porous diaphragm. The pores are assumed to be unconnected, the cross-sectional area of any single pore is assumed to be constant, and the length-to-area ratio of every pore is assumed to be great enough so that radial concentration gradients within the pores can be neglected. Under these conditions a combination of Equations (1) and (3) and integration over the pore cross section yields

$$\bar{J}'_{1p} = -D_{11} \frac{dC_1}{dz} - D_{12} \frac{dC_2}{dz} + C_1 V_p \qquad (7a)$$

$$\overline{f}_{2p} = -D_{21} \frac{dC_1}{dz} - D_{22} \frac{dC_2}{dz} + C_2 V_p \qquad (7b)$$

If the volume change on mixing is negligible, as in this study, V_p is independent of z.

Since the system studied here has a constant mass density it is convenient to express the fluxes in terms of the mass flux and mass fractions

$$n_{1p} = -\rho D_{11} \frac{d\omega_1}{dz} - \rho D_{12} \frac{M_1}{M_2} \frac{d\omega_2}{dz} + n_p \omega_1 \quad (8a)$$

$$n_{2p} = -\rho D_{21} \frac{M_2}{M_1} \frac{d\omega_1}{dz} - \rho D_{22} \frac{d\omega_2}{dz} + n_p \omega_2$$
 (8b)

Under steady state conditions the flows are constant over the pore length. However, the D_{ij} are normally functions of concentration so that this set of equations is nonlinear and numerical methods of solution are required. Nevertheless, it is possible to formally represent the integration under steady state conditions. From Equations (8a) and (8b),

$$\rho \int_{\omega_{i}^{i}}^{\omega_{i}} \frac{d\omega_{i}}{n_{ip} - n_{p}\omega_{i}} = -$$

$$\int_{0}^{L} \frac{dz}{D_{ii}(\omega_{1}, \omega_{2}) + D_{ij}(\omega_{1}, \omega_{2})} \frac{M_{i}}{M_{j}} \frac{d\omega_{j}}{d\omega_{i}} =$$

$$- \int_{0}^{L} \frac{dz}{D_{i}}, \quad i \neq j \qquad (9)$$

where, for convenience, the denominator of the right-hand integral has been defined to be the point value of the effective diffusion coefficient (3), D_i . Although D_i is still a complex function of concentration the steady state concentrations depend on z only, so that Equation (9) may be formally represented in the form

$$\frac{\rho}{n_p} \ln \frac{n_{ip} - n_p \, \omega_i^L}{n_{ip} - n_p \, \omega_i^o} = \frac{L}{D_i}, i = 1, 2$$
 (10)

where \overline{D}_i is the space mean value of an effective diffusion coefficient for component *i*. If Equation (10) is rearranged, an expression for the flux, n_{ip} , is obtained:

$$n_{ip} = \frac{n_p(\omega_i^L - \omega_i^o e^{\lambda_{ip}})}{1 - e^{\lambda_{ip}}}, i = 1, 2$$
 (11a)

where

$$\lambda_{ip} = \frac{n_p L}{\overline{D}_{io}} \tag{11b}$$

The total flow of component i through the porous diaphragm is then

$$\sum_{p} n_{ip} A_{p}, i = 1, 2$$
 (12)

which, for a completely uniform diaphragm where n_p is the same for all pores, yields

$$n_i' = \frac{n'(\omega_i^L - \omega_i^o e^{\lambda_i})}{1 - e^{\lambda_i}}, i = 1, 2$$
 (13a)

where

$$\lambda_{i} = \frac{n'L}{\overline{D}_{i} \rho A} \tag{13b}$$

For the special case of a uniform diaphragm it is possible to carry the development further. Consider the diaphragm cell of Figure 1. Stream S in this figure consists of pure separating agent. The material balances are

$$F + S = R + P \tag{14}$$

$$F \omega_{iF} = R \omega_{iR} + P \omega_{iP}, i = 1, 2 \tag{15}$$

$$S = P - n' \tag{16}$$

$$n_i' = P_{\omega iP}, \ i = 1, 2 \tag{17}$$

By the assumption of complete mixing in the cell chambers $\omega_i^o = \omega_{iR}$ and $\omega_i^L = \omega_{iP}$. Combining these material balances with Equation (13) and rearranging, the relation

$$\frac{\omega_{iP}}{\omega_{iF}} = \frac{(1 - P/S)F/R}{(1 - P/S)P/R + e^{-\lambda_i} - P/S}, i = 1, 2$$
(18)

is obtained. A separation factor, a, may be defined by

$$\alpha = \frac{\omega_{1P}/\omega_{1F}}{\omega_{2P}/\omega_{2F}} \tag{19}$$

which, when combined with Equation (18), yields

$$\alpha = \frac{e^{-\lambda_2} - P/S + (1 - P/S) P/R}{e^{-\lambda_1} - P/S + (1 - P/S) P/R}$$
(20)

Figure 2 illustrates the behavior predicted by Equations (18) and (20) for a uniform diaphragm. The figure shows that ω_{iP}/ω_{iF} decreases sharply with increasing counterflow, -n', and α increases sharply. A comparison of these quantities illustrates the fact that increased separation is achieved only at the expense of the total amount of product obtained.

In a real situation a uniform diaphragm is rarely attainable. However, analysis of Equation (20) shows that non-uniformity will tend to decrease the separation (20) so the uniform diaphragm solution gives the upper limit of the separation factor.

EXPERIMENTAL

The diaphragm cell used in this investigation is shown in Figure 3. The cell was constructed of type 347 stainless steel. Each cell chamber was 2 in. in diam. by $\frac{1}{4}$ in. deep and was provided with a stirrer to maintain a well-mixed solution in the chamber. The diaphragm was a sintered stainless steel disk 0.02 in, thick and with a nominal pore size of $12~\mu$.

The entire experimental apparatus is shown in Figure 4. The inlet flows were controlled by maintaining constant liquid level with the constant head funnels. Stainless steel hypodermic needle tubing was employed for all flow lines; this tubing could be changed to obtain different flow resistances. The vented thistle tubes were used so that the inlet flow rates could be measured independently and the head on the outlet lines could be measured. With this technique of head control and capillary flow resistances the flow rates were maintained constant within \pm 1% for almost all cases. The cell was oriented with the diaphragm horizontal and the counterflow was upward through the diaphragm. The entire system was enclosed in an air bath at 29.0°C. \pm 0.1°C.

The concentrations of all streams were measured by vapor-liquid chromatography.

The three alcohols, methyl alcohol, n-propyl alcohol, isobutyl alcohol, were reagent grade materials and were used without further purification.

Samples were collected over short time intervals after a run had been started. These samples were weighed and analyzed, and when two successive samples of the product P were found to contain the same concentrations the steady state was assumed to have been reached. The run was continued for varying lengths of time until several successive steady state samples of the products P and R over time intervals of 4 to 10 hr. had been obtained. These samples were first weighed, then analyzed with calibration samples to determine the steady state concentrations. Samples of the inlet flow, F, were also analyzed in this manner. With the simultaneous calibration and analysis the concentrations of the unknown samples could be determined to within ± 1% of the amount of the component present for all cases except those with extremely low concentrations. For these cases the concentration could be determined to \pm 5% of the amount present. Oscillations of the concentrations at the steady state were within the precision of the analysis.

CALIBRATION

Before the system could be used for mass diffusion studies, it was necessary to determine the required stirring rate and the effective A/L of the diaphragm.

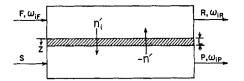


Fig. 1. Schematic diagram of cell.

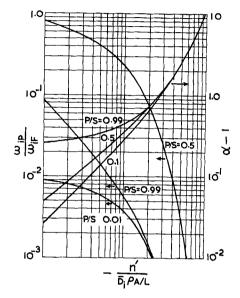
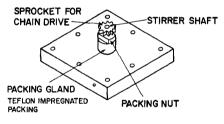


Fig. 2. Ratio of product to feed compositions and separation factor for uniform diaphragm $P/R = 0.01, \overline{D}_1 = 1.25 \overline{D}_2$.



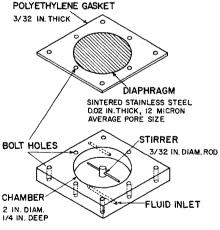


Table 1. Ternary Diffusion Coefficients

 $D_{11} = D_{MM} = 1.928 \,\omega_M + 0.557 \,\omega_B + 0.784 \,\omega_P$ $D_{22} = D_{BB} = 1.815 \,\omega_M + 0.390 \,\omega_B + 0.573 \,\omega_P$ $D_{12} = D_{MB} = 0.285 \,\omega_M$

Fig. 3. Cell.

 $D_{21} = D_{BM} = -0.072 \omega_M$

_		<u>M</u> P			M P		<u>М</u> Р			Input of mixture to be separated $F(\omega_{MF} + \omega_{BF})$	Output of separated mixture $P(\omega_{MP} + \omega_{BP})$
Run	F g./hr.	ωiF B	S° g./hr.	R g./hr.	WIR B	P g./hr.	wip B	-n' g./hr.	α	g./hr.	g./hr.
.1	21.334	0.4953 0.0000 0.5047	6.951	27.213	0.3877 0.2157 0.3948	1.072	0.0238 0.9638 0.0124	5.879	1.959	21.334	0.0388
2	15.019	0.4363 0.1144 0.4493	5.206	15.794	0.3840 0.2155 0.4005	4.431	0.1110 0.7944 0.0946	0.775	1.208	13.301	0.9110
3	12.936	0.0990 0.8007 0.1003	5.388	15.545	0.0796 0.8385 0.0819	2.779	0.01179 0.98005 0.00816	2.609	1.478	2.578	0.0554
4	19.803	0.4066 0.1740 0.4194	11.216	30.244	0.2654 0.4591 0.2755	0.775	0.00137 0.99804 0.00059	10.441	2.370	16.357	0.0015
5	18.668	0.3378 0.3092 0.3530	11.249	29.152	0.2166 0.5579 0.2255	0.765	0.00116 0.99838 0.00046	10.484	2.646	12.896	0.0012
6	16,332	0.2241 0.5407 0.2352	11.283	26.829	0.1360 0.7204 0.1436	0.787	0,00068 0.99906 0,00026	10.497	2.764	7.501	0.00074
7	14.522	0.1420 0.7083 0.1497	11.342	17.535	0.1138 0.7648 0.1214	8.329	0.00807 0.98650 0.00543	3.013	1.565	4.245	0.1124
8	14.496	0.1420 0.7083 0.1497	11.305	20,499	0.0999 0.7947 0.1054	5.302	0.00251 0.99628 0.00121	6.003	2.181	4.228	0.0197
9	12.195	0.1488 0.1502 0.7010	6.865	15.872	0.1134 0.1148 0.7718	3.188	0.00463 0.00296 0.99241	3.677	1.584	3.646†	0.0242‡

S was pure n-propanol in all cases except run 9 when it was pure isobutanol. $\dagger F(\omega_{MP} + \omega_{PP})$. $\dagger P(\omega_{MP} + \omega_{PP})$.

Equations (11a) and (11b) apply to binary as well as multicomponent systems, and in the former case \overline{D}_1 may be determined explicitly, for D₁ then is merely the binary diffusion coefficient, \mathcal{D}_{12} , which is a function of ω_1 only. If \mathcal{D}_{12} is linear in ω_1 , as is the case for the binary pairs which make up the ternary system studied here (20), then

$$\overline{D}_{1} = \mathcal{D}_{12^{o}} + (\mathcal{D}_{21^{o}} - \mathcal{D}_{12^{o}}) \left[\left(\omega_{1} - \frac{n_{1}'}{n'} \right)_{lm} + \frac{n_{1}'}{n'} \right]$$
(21)

and Equations (11) and (21) may be used to determine the diaphragm characteristics under flow conditions.

Binary flow runs were carried out with the methyl-n-propyl alcohol system. It was found that the apparent A/L of the diaphragm was independent of stirrer speed above about 40 rev./min. so all subsequent runs were carried out at 46.3 rev./min.

Two binary runs with different values of the counter-flow, -n', indicated that nonuniformity of the diaphragm could not be neglected since the apparent A/L ratio from Equations (13) and (21) was a function of the counterflow (82.3 cm. and 80.6 cm. for values of -n' of 3.758 g./hr. and 0.785 g./hr., respectively). Extrapolation to zero counterflow gave an A/L of 80 cm.

Since the diaphragm pore-size distribution is not known, it was assumed, for simplicity, that the diaphragm was composed of two uniform sections each comprising half of the open area. With that assumption two equations similar to Equation (13) (one for each half of the diaphragm) could be written for each run. These equations, with Equation (21), were solved by trial and error for the flows per unit area through the two halves of the diaphragm. The results of this calculation indicated that an effective pore-size distribution which gave a flow

through one half of the diaphragm 1.87 times greater than the flow through the other half and an A/L of 80 was consistent with the data for this range of counterflow.

EXPERIMENTAL RESULTS AND DISCUSSION

Employing the equipment and techniques discussed previously, several steady state ternary mass diffusion runs were made. These runs were designed to cover several levels of concentration and flow rates. In particular an attempt was made to cover a wide range of values of the counterflow. In all but one of these runs pure n-propyl alcohol was used as the separating agent, S, and methyl alcohol and isobutyl alcohol were used as the components to be separated. In the final run isobutyl alcohol was used as the separating agent for separation of methyl and npropyl alcohols. The data for the ternary runs are given in Table 2. The values of flow rates and concentrations reported are the averages of these values for several successive samples taken after a steady state had been attained.

The experimental results show qualitative agreement with the results that would be anticipated by the theoretical development. There is noted a significant increase in separation factor with increase in the counterflow, and the separation factor is significantly higher than the maxi-

mum value of $\frac{D_1}{\overline{D}_2}$ for the case of no counterflow (20). The

last two columns of the table point out the cost of the increased separation in terms of total throughput.

A more detailed treatment of the data requires a knowledge of the diffusion behavior of this ternary system. The ternary diffusion coefficients given in Table I may be substituted into Equation (9). The effective diffusion coefficients so defined are

$$D_{M} = 0.784 + \omega_{M} \left[1.144 - 0.285 \frac{\omega_{B}}{\omega_{M}} + 0.285 \frac{M_{M}}{M_{B}} \frac{d\omega_{B}}{d\omega_{M}} \right]$$
(22a)

$$D_{\rm B} = 0.573 + \omega_{\rm M} \left[1.242 - \right.$$

$$0.183 \frac{\omega_B}{\omega_M} - 0.072 \frac{\omega_B}{\omega_M} \frac{M_M}{M_B} \frac{d\omega_M}{d\omega_B}$$
 (22b)

It is noted that in both cases the effective diffusion coefficient is a weak function of ω_B/ω_M and $d\omega_B/d\omega_M$. Under the conditions of these experiments a suitable approximation is obtained if ω_B/ω_M and $d\omega_B/d\omega_M$ are taken as unity in Equation (22), in which case the effective diffusion coefficient for methyl alcohol becomes a function of ω_M only:

$$D_{\rm M} = 1.040 \,\omega_{\rm M} + 0.784 \tag{23}$$

With this approximation an equation like (21) is obtained for the mean effective diffusion coefficient of methyl alcohol

$$\overline{D}_{M} = 0.784 + 1.040 \left[\left(\omega_{M} - \frac{n_{M'}}{n'} \right)_{lm} + \frac{n_{M'}}{n'} \right] (24)$$

The bracketed term in Equation (24) is the mean effective concentration of methyl alcohol for the run.

With the same assumptions as above the effective diffusion coefficient for isobutyl alcohol becomes

$$D_B = 0.573 + 0.893 \,\omega_M \tag{25}$$

In this approximation the diffusion coefficient of isobutyl alcohol depends only upon the methyl alcohol concentration. It follows that \overline{D}_B is the value of D_B given by Equation (25) evaluated at the mean effective methyl alcohol concentration, the bracketed term in Equation (24)

With the preceding values of the mean effective diffusion coefficients, and Equation (11) it should be possible to predict the separation that would be achieved in a diaphragm of known characteristics. (In run 9 isobutyl alcohol was the separating agent so species 1 and 2 were taken to be methyl alcohol and normal propyl alcohol and new ternary diffusion coefficients were computed (20) for this redefined system from the values given in Table 1. This is possible because there are only four independent ternary diffusion coefficients. Approximations similar to those used above were also carried out.)

For the first attempt at such a prediction the diaphragm was assumed to be uniform with an A/L of 80 cm., so Equations (18) and (20) could be used. The calculated product concentrations and separation factors are compared to the experimental values in Figures 5 and 6. From this comparison it appears that as -n' increases the error increases. This error shows up in both the predicted concentrations and the predicted separation factor and is larger than the estimated uncertainties in the calculations and measurements.

Since the predictions based on the assumption of a uniform diaphragm differed significantly from the experimental values, a calculation based on a nonuniform diaphragm was carried out.

The diaphragm was assumed to have the simple poresize distribution considered earlier with the A/L ratio

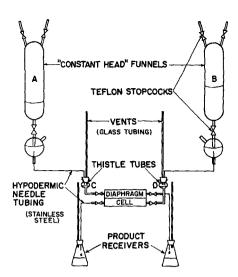


Fig. 4. Flow system.

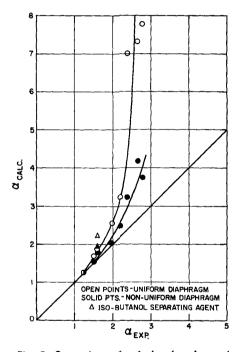


Fig. 5. Comparison of calculated and experimental separation factors.

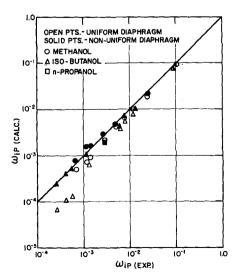


Fig. 6. Comparison of calculated and experimental product compositions.

and the relative flows through the two sections which were found to fit the binary flow data.

With this information, the mean effective diffusion coefficients, and four forms of Equation (13) (one for each of species 1 and 2 for each half of the diaphragm) the values of ωiP and α were calculated. These values are compared to the experimental values in Figures 5 and 6. It may be seen that even this extremely simple pore-size distribution yields predictions of performance which are much closer to the experimental performance than does the assumption that the diaphragm is uniform. Although the results of this second approximation still appear to differ significantly from the experimental values at high counterflow, the calculated values contain uncertainties, caused primarily by the 5% uncertainty in the diffusion coefficients, which increase as the counterflow increases.

When this uncertainty is taken into account it is found that the ranges of concentrations calculated for the nonuniform diaphragm include the experimental values while the ranges calculated for the uniform diaphragm do not include the experimental values.

CONCLUSIONS

Significant separations of the components of a miscible ternary liquid system may be achieved in the mass diffusion process. The separation may be achieved at measurable (if not in all cases reasonable) concentrations and is significantly enhanced by employing a counterflow of separating agent. The separation factors and product concentrations may be predicted with reasonable accuracy from a knowledge of the diffusion coefficients for the ternary system and a knowledge of the diaphragm geome-

ACKNOWLEDGMENT

The authors are grateful to the National Science Foundation for its financial support of this work and to the Shell Oil Company for fellowship assistance.

NOTATION

= open area of the diaphragm

= cross-sectional area of a single pore

 C_i = concentration of component i in moles per unit

= ternary diffusion coefficient D_{ij}

= point value of an effective diffusion coefficient D_i for component i

 \overline{D}_i = space mean value of the effective diffusion coefficient for component i

 \mathcal{D}_{ij} = binary diffusion coefficient

 \mathcal{D}^{o}_{ij} = binary diffusion coefficient at infinite dilution of component i

F= feed stream flow rate

= molar flux of component i with respect to some J_i average velocity of the system

= molar flux of component i with respect to a fixed $J_{i'}$

L= length of diffusion path through the diaphragm

= molecular weight of component i M_i

= number of components n= mass flux through a pore n_p

total mass flow through the diaphragm = minus the counterflow

= mass flux of component i through a pore n_{ip}

total mass flow of component i through the dia n_i'

product stream flow rate = waste stream flow rate R

= separating agent stream flow rate

volumetric average velocity

 \overline{V}_{j} = velocity of species i

= volumetric flow rate per unit area through a pore

partial molal volume of species i Vj

distance coordinate in the direction of diffusion

Greek Letters

= separation factor

 $= n_p L/D_{i\rho}$ \(\lambda_{in}\) $= n'L/\bar{D_i}\rho A$ λi

= density of the mixture ρ

mass fraction of component iωi

Subscripts

1, 2 = components 1 and 2

= component i and ji, jŔ

isobutyl alcohol

second subscript on a concentration referring to \boldsymbol{F} stream F

lm= log mean

= methyl alcohol M

= n-propyl alcohol; second subscript on a concentration referring to stream P

R second subscript on a concentration referring to stream R

Superscripts

= value at z = L

= value at z = 00

= average value

LITERATURE CITED

- 1. Baldwin, R. L., P. J. Dunlop, and L. J. Gosting, J. Am. Chem. Soc., 77, 5235 (1955).
- 2. Benedict, Manson, and Arnold Boaz, Chem. Eng. Progr., 47, 51, 111 (1951).
- 3. Bird, R. B., W. R. Stewart, and E. N. Lightfoot, "Transport Phenomena," Wiley, New York (1960).
- 4. Burchard, J. K., and H. L. Toor, J. Phys. Chem., 66, 2015
- 5. Cichelli, M. T., W. D. Weatherford, and J. R. Bowman, Chem. Eng. Progr., 47, 63, 123 (1951).
- Dunlop, P. J., and L. J. Gosting, J. Am. Chem. Soc., 77, 5238 (1955).
- 7. Dunlop, P. J., J. Phys. Chem., 61, 994 (1957).

8. *Ibid.*, p. 1619. 9. *Ibid.*, **63**, 612 (1959).

- 10. Miller, D. G., J. Phys. Chem., 63, 570 (1959).11. Fitts, D. F., "Nonequilibrium Thermodynamics," McGraw-Hill, New York (1962).
- 12. Fujita, Hiroshi, and L. J. Gosting, J. Am. Chem. Soc., 78, 1099 (1956).
- 13. Keyes, J. J., Jr., and R. L. Pigford, Chem. Eng. Sci., 6, 215 (1957).
- 14. Kirkwood, J. G., R. L. Baldwin, P. J. Dunlop, L. J. Gosting, and Gerson Kegeles, J. Chem. Phys., 33, 1505 (1960).
- 15. Maier, C. G., U.S. Bureau of Mines Bulletin, 431, (1940).
 16. O'Donnell, I. J., and L. J. Gosting, "The Structure of Electrolytic Solutions," Chapter 11, Wiley, New York (1957).
- 17. Onsager, L., Ann. New York Acad. Sci., 46, 241 (1945).
- 18. Riehl, N., and G. Wirths, Z. Physik. Chem., 6, 265 (1956).
- 19. Shuck, F. O., M.S. thesis, Carnegie Institute of Technology, Pittsburgh, Pennsylvania (1960).
- 20. Shuck, F. O., Ph.D. thesis, Carnegie Institute of Technology, Pittsburgh, Pennsylvania (1962).
- 21. Shuck, F. O., and H. L. Toor, J. Phys. Chem., 67, 540
- 22. Toor, H. L., A.I.Ch.E. Journal, 8, 561 (1962).

Manuscript received June 20, 1962; revision received December 17, 1962; paper accepted December 18, 1962.