Diffusion Coefficients of Quaternary Liquid System Acetone-Benzene-Carbon Tetrachloride-*n*-Hexane at 25°C

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The multicomponent diffusion coefficients, defined in a volume-fixed frame of reference, of an equimolar mixture of acetone–benzene–carbon tetrachloride–*n*-hexane are reported. The results are obtained by the diaphragm cell technique which utilizes a statistically optimum experimental design.

Precise measurement of the liquid phase diffusion coefficients of multicomponent systems is an integral part of the development of improved theories of the diffusion process in liquid systems. From the practical viewpoint, once the diffusion coefficients are known, the mass transfer coefficients can be calculated for any given physical situation. This information about the mass transfer coefficients plays a very important role in the engineering design of mass transfer equipment in which diffusion is the rate-controlling step. When multicomponent diffusion coefficients are available, a more fundamental process design approach can be adopted for such industrially important processes as adsorption, distillation, extraction, and ion exchange. From the fundamental viewpoint, a better understanding of the diffusive behavior of multicomponent liquid systems could lead to a more precise understanding of the liquid state itself.

Diffusion coefficient data for liquid systems consisting of more than two constituents are, as yet, not very plentiful. Some information is available for ternary liquid systems, but, up to the present, no data have been reported for liquid systems consisting of more than three components. In this paper, results of diaphragm cell diffusion experiments on the quaternary liquid system acetone–benzene–carbon tetrachloride–*n*-hexane are reported.

Experimental Procedure and Design

The type of diaphragm cell and the experimental procedure employed in this work are the same as those used previously *(4)*. As before, an F + M model 5750 gas chromatograph, coupled with a Hewlett Packard 3370A digital integrator, is used for the chemical analysis. The chemicals used in the cell experiments are all 99+ mol % quality reagent grade and are used as received.

The design of the experiments is based upon the analysis of Kosanovich and Cullinan *(3)*, which prescribes the optimum experimental conditions for obtaining the best estimate of the diffusion coefficients in diaphragm cell experiments. For an $n + 1$ component system the behavior of the diaphragm cell is governed by the following matrix equation *(5)*

$$d/dt\, \Delta C = -\beta\, \boldsymbol{D}\, \Delta C \qquad (1)$$

whose solution is

$$\Delta C^f = \exp(-\tau\, \boldsymbol{D})\, \Delta C^\circ \qquad (2)$$

To determine all the elements of the $n \times n$ diffusion coefficient matrix, $\boldsymbol{D}$, at least n independent cell runs must be performed at the same average concentration and at the same value of reduced run time, τ. If each vector of independent initial concentration difference, ΔC_i°, is arranged on a column of an $n \times n$ square matrix, $\Delta \boldsymbol{C}^\circ$, then

$$\Delta \boldsymbol{C}^f = \exp(-\tau\, \boldsymbol{D})\, \Delta \boldsymbol{C}^\circ \qquad (3)$$

where $\Delta \boldsymbol{C}^f$ has columns which consist of the corresponding, ΔC_i^f. Equation 3 can be directly solved (since $\Delta \boldsymbol{C}^\circ$ is nonsingular if the ΔC_i° are independent) to give

$$\exp(\tau\, \boldsymbol{D}) = \Delta \boldsymbol{C}^\circ (\Delta \boldsymbol{C}^f)^{-1} = \boldsymbol{X} \qquad (4)$$

The modal matrices of $\boldsymbol{D}$ and $\boldsymbol{X}$ are identical, and the eigenvalues of $\boldsymbol{D}$ and $\boldsymbol{X}$ are related by

$$D_i = 1/\tau \ln X_i \qquad (5)$$

so that if $\boldsymbol{P}$ is the modal matrix of $\boldsymbol{X}$, $\boldsymbol{D}$ is directly obtained from the experimental data according to

$$\boldsymbol{D} = \boldsymbol{P} \begin{bmatrix} D_1 & & \\ & D_2 & \\ & & \ddots \end{bmatrix} \boldsymbol{P}^{-1} \qquad (6)$$

Within the dual constraints that the average composition must be the same in all experiments and that the initial composition differences must not be so large as to invalidate the linearizing assumption leading to Equation 1, there are an infinite number of possible sets of initial composition differences which could be utilized in Equation 3. Kosanovich and Cullinan *(3)* have adapted the statistical methods of Box and Lucas *(1)* to the diaphragm cell method to ascertain the optimum choice of initial conditions which leads to the best estimates of the diffusion coefficients. The key result is that the best choice of initial composition differences corresponds to a maximum value for the determinant of $\Delta \boldsymbol{C}^\circ$—i.e., max $|\Delta \boldsymbol{C}^\circ|$.

Accordingly, in this work three independent experiments are first performed with initial composition differences corresponding to a maximum value of $\Delta \boldsymbol{C}^\circ$. In this work, this value corresponds to individual initial mole fraction differences of 0.10 for each component. The $\boldsymbol{D}$ matrix calculated from Equations 4 to 6 is then treated as an initial estimate in order to locate numerically the optimum value of the reduced run time, τ, again according to the methods of Kosanovich and Cullinan *(3)*.

Once the optimum run time is determined, sets of experiments, each one run at optimum time and having a maximum value of $|\Delta \boldsymbol{C}^\circ|$, are replicated a sufficient number of times to produce a precise over-all estimate of the true value of $\boldsymbol{D}$. This estimate is best in the sense of least squares as follows: If Equation 2 is rewritten by defining

$$\boldsymbol{L} = \exp(-\tau_{\text{opt}}\, \boldsymbol{D}) \qquad (7)$$

so that

$$\Delta C^f = \boldsymbol{L}\, \Delta C^\circ \qquad (8)$$

then for m replicate experiments *(2)*

$$Y = \boldsymbol{Z} L' + \epsilon \qquad (9)$$

where, for a quaternary system where $n = 3$, $L'_{i+3j-3} = L_{ij}$, Y is a $3\,m \times 1$ column constructed of the replicate

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values of ΔC^f stacked one upon the other, and $\boldsymbol{Z}$ is of the following structure:

$$\boldsymbol{Z} = \begin{bmatrix} \Delta C^\circ_{11} & \Delta C^\circ_{21} & \Delta C^\circ_{31} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \Delta C^\circ_{11} & \Delta C^\circ_{21} & \Delta C^\circ_{31} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \Delta C^\circ_{11} & \Delta C^\circ_{21} & \Delta C^\circ_{31} \\ \Delta C^\circ_{12} & \Delta C^\circ_{22} & \Delta C^\circ_{32} & 0 & \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot & 0 \\ 0 & \cdot\cdot & \cdot\cdot & \Delta C^\circ_{12} & \Delta C^\circ_{22} & \Delta C^\circ_{32} & 0 & \cdot\cdot & 0 \\ 0 & \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot & \Delta C^\circ_{12} & \Delta C^\circ_{22} & \Delta C^\circ_{32} \\ \cdot & & & & & & \cdot\cdot & \cdot\cdot & \cdot\cdot \\ \cdot & & & & & & \cdot\cdot & \cdot\cdot & \cdot\cdot \\ \cdot & & & & & & \cdot\cdot & \cdot\cdot & \cdot\cdot \\ \cdot & & & & & & \cdot\cdot & \cdot\cdot & \cdot\cdot \\ 0 & \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot & \Delta C^\circ_{1m} & \Delta C^\circ_{2m} & \Delta C^\circ_{3m} \end{bmatrix} \quad (10)$$

The first subscript refers to the component, the second to the run. The minimum likelihood estimate of $\boldsymbol{D}$ is then directly obtained from *(2)*.

$$L' = (\boldsymbol{Z}^T\boldsymbol{Z})^{-1}\boldsymbol{Z}^T Y \quad (11)$$

Thus from L', $\boldsymbol{L}$ is directly constructed, and from Equation 7 the maximum likelihood estimate of $\boldsymbol{D}$ is obtained—that is, in Equation 7 the modal matrices of $\boldsymbol{L}$ and $\boldsymbol{D}$ are identical and their eigenvalues are simply related. Thus $\boldsymbol{D}$ is directly constructed from $\boldsymbol{L}$.

Finally, confidence intervals for the estimate of each element of $\boldsymbol{D}$ can be extracted from the replicated experimental data. The replicated independent initial concentration differences and resulting final concentration differences can be used, in sets of three, in Equation 3 to produce replicate values of $\boldsymbol{D}$. From these confidence intervals can be directly obtained.

Results

After preliminary experiments had established the optimum run time, a total of 15 diaphragm cell runs were conducted, corresponding to this time and at an average mole fraction for each constituent of 0.25. The 15 experiments consisted of three sets of five replicates, each set corresponding to the desired max $|\Delta \boldsymbol{C}^\circ|$. All experiments were conducted at 25 ± 0.02°C.

The complete set of experimental data was entered into Equation 11 to obtain the maximum likelihood estimate of $\boldsymbol{D}$ in the manner described above. The results for the nine diffusion coefficients with the associated 95% confidence intervals are reported in Table I. The 95% confidence intervals for the main diffusion coefficients are all less than 3% of the best values, while the relative confidence intervals for the cross terms vary with the best values. Several cross terms are rather large,, with several values 10–20% of the corresponding main term, while several others are effectively zero at the 95% level.

Table I. Diffusion Coefficients for Equimolar Mixture of Acetone-Benzene-Carbon Tetrachloride-*n*-Hexane at 25°C

$$\boldsymbol{D} = \begin{bmatrix} D_{AA} & D_{AB} & D_{AC} \\ D_{BA} & D_{BB} & D_{BC} \\ D_{CA} & D_{CB} & D_{CC} \end{bmatrix}$$

$$\boldsymbol{D} = \begin{bmatrix} 2.321^{a} \pm 0.052^{b} & -0.494 \pm 0.043 & -0.191 \pm 0.054 \\ -0.299 \pm 0.032 & 2.962 \pm 0.042 & -0.065 \pm 0.041 \\ 0.074 \pm 0.043 & -0.026 \pm 0.033 & 2.860 \pm 0.049 \end{bmatrix}$$

[a] All D_{ij} in cm²/sec × 10^5. [b] 95% Confidence interval.

Conclusions

The diaphragm cell technique, with the utilization of an optimum design of experiments, appears capable of efficiently characterizing diffusion in systems of more than three components. The design of experiments and the analysis of the data are direct and straightforward. The main diffusion coefficients are obtainable very precisely, while the estimation of the cross diffusion coefficients improves greatly as these terms become significant in magnitude.

Nomenclature

ΔC = $n \times 1$ column of concentration differences across diaphragm
$\Delta \boldsymbol{C}$ = $n \times n$ matrix of concentration differences
$\boldsymbol{D}$ = $n \times n$ matrix of diffusion coefficients, defined in a volume fixed frame of reference
D_i = an eigenvalue of $\boldsymbol{D}$
$\boldsymbol{L}$ = matrix defined by Equation 7
L' = $3m \times 1$ column, where for $n = 3$, $L'_{i+3j-3} = L_{ij}$
m = number of replicate experiments
$n + 1$ = number of components
$\boldsymbol{P}$ = modal matrix of $\boldsymbol{D}$
t = real time
$\boldsymbol{X}$ = matrix defined by Equation 4
X_i = eigenvalue of $\boldsymbol{X}$
Y = $3m \times 1$ column of replicate values of ΔC^f
$\boldsymbol{Z}$ = matrix defined by Equation 10

Greek letters

β = diaphragm cell constant
ϵ = residual column in Equation 9
τ = reduced time, βt

Superscripts

f = final condition
° = initial condition

Operation

-1 = inverse
T = transpose
$||$ = determinant

Literature Cited

(1) Box, G. E. P., Lucas, H. L., *Biometrika*, **46**, 77 (1959).
(2) Draper, N. R., Smith, H., "Applied Regression Analysis," Wiley, New York, N.Y., 1966.
(3) Kosanovich, G., Cullinan, H. T., *Can. J. Chem. Eng.*, **49**, 753 (1971).
(4) Leffler, J., Cullinan, H. T., *Ind. Eng. Chem. Fundam.*, **9**, 84 (1970).
(5) Toor, H. L., *AIChEJ*, **10**, 448 (1964).

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