



Form of multicomponent Fickian diffusion coefficients matrix

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ABSTRACT

The form of multicomponent Fickian diffusion coefficients matrix in thermodynamically stable mixtures is established based on the form of phenomenological coefficients and thermodynamic factors. While phenomenological coefficients form a symmetric positive definite matrix, the determinant of thermodynamic factors matrix is positive. As a result, the Fickian diffusion coefficients matrix has a positive determinant, but its elements – including diagonal elements – can be negative. Comprehensive survey of reported diffusion coefficients data for ternary and quaternary mixtures, confirms that invariably the determinant of the Fickian diffusion coefficients matrix is positive.

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1. Introduction

Multicomponent Fickian – often termed molecular – diffusion plays a critical role in a number of industrial and natural processes. However, experimental determinations of multicomponent diffusion coefficients are only available for a limited number of ternary and quaternary mixtures, although binary data is abundant. Theoretical work on multicomponent diffusion coefficients is also limited. It is known that composition variation in multicomponent mixtures may differ markedly from binary mixtures due to cross-Fickian diffusion. Therefore, there is a need for both theoretical and experimental studies on multicomponent diffusion.

In three and higher n -component mixtures, Fickian diffusion coefficients form an $(n-1) \times (n-1)$ matrix, \mathbf{D} , which is generally non-symmetric. The form of this matrix has been a subject of limited theoretical studies [1–7]. These studies use thermodynamics of irreversible processes approach of de Groot and Mazur [8] and linear algebra theorems. Furthermore, Hirschfelder *et al.* [9] show that in ideal gas mixtures, all molecular diffusion coefficients are non-negative. Standart *et al.* [10] generalize this ideal gas restriction to prove the non-negative restrictive constraints on Maxwell–Stefan diffusion coefficients.

Yao [2] argues – without proof – that main term diffusion coefficients, D_{11} and D_{22} , in ternary mixtures are always positive. He assumes that multicomponent interactions are weak, thus each component only diffuses down its own chemical potential gradient. The author proposes a model with the conditions: $D_{11} > D_{12}$, $D_{22} > D_{21}$, and $D_{11}D_{22} > D_{12}D_{21}$. These conditions are tested for six experimental data points of different compositions in two ternary

mixtures: (sodium sulfate + hydrogen sulfate + water), and (polystyrene + cyclohexane + toluene).

Cullinan [1] shows that the characteristic roots of \mathbf{D} – the eigenvalues – are invariant under transformations of reference velocity. Further, Cullinan argues that these eigenvalues are pseudo-binary diffusion coefficients; thus, they are analogous to diffusion coefficients in binary mixtures which are real positive numbers that are equivalent regardless of reference frame. Ultimately, Cullinan's work allows for decoupling of multicomponent flux equations.

Kirkaldy's [3,4] approach is specific to multicomponent diffusion coefficients based on volume-fixed frame of reference, \mathbf{D}^V (section 2.1). Using generalized Fick's laws, entropy production, and Onsager reciprocal relations, he demonstrates that \mathbf{D}^V is a product of two positive definite matrices – phenomenological coefficients matrix (\mathbf{L}) and a matrix that is a function of chemical potentials derivative – thus, \mathbf{D}^V must have all real and positive eigenvalues. Further, he states that diagonal diffusion coefficients, D_{ii}^V , need not be individually positive to satisfy thermodynamic stability requirements. Nonetheless, he points out that kinetic models invariably yield positive D_{ii}^V . Thus, he asserts that sufficient stability conditions for \mathbf{D}^V in a ternary mixture are: $D_{11}^V > 0$, $D_{22}^V > 0$, $|\mathbf{D}^V| > 0$, and $D_{12}^V D_{21}^V \geq 0$. Kirkaldy's approach and conclusions are adopted in the works by Gupta and Cooper [5] and Vrentas and Vrentas [7].

Miller *et al.* [6], discuss several aspects of multicomponent diffusion including reference frame transformations, effect of solvent (reference component) choice, and existence of negative D_{ii}^V . Using Kirkaldy's approach, the authors show that although \mathbf{D}^V is a product of two positive definite matrices, it need not be symmetric or positive definite. However, they show that \mathbf{D}^V has real and positive eigenvalues that allows it to be diagonalized to provide solutions

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to diffusion equations that are real and non-periodically decaying. Moreover, the authors state that there is no proof that all D_{ii}^V should be individually positive, and demonstrate the existence of one ternary system – chloroform (4.90 mol · L⁻¹) + acetic acid (8.57 mol · L⁻¹) + water (6.94 mol · L⁻¹) – with negative D_{ii}^V .

In general, theoretical restrictions on \mathbf{D} are based on the requirement for real and positive eigenvalues; a constraint that is based on positive definiteness of both \mathbf{L} and the matrix of the derivatives of chemical potentials. While the former is true, the latter may not be the case (sections 2.3 and 2.6). Furthermore, some of the studies argue that diagonal elements of \mathbf{D} should be individually positive. While this might be the case in ideal and slightly non-ideal mixtures, some diagonal \mathbf{D} elements may be negative in strongly non-ideal systems (sections 2.6 and 3.1). Therefore, the objective of this work is twofold:

- (i) We show that the restriction for positive determinant of \mathbf{D} can be established theoretically by application of the second law of thermodynamics and the requirement for thermodynamic stability. Further, we demonstrate the existence of negative diagonal diffusion coefficients – which are a direct result of non-ideality effect – in thermodynamically stable mixtures (section 2); and,
- (ii) We perform comprehensive examination of multicomponent diffusion coefficients reported from experimental data. We analyze these reported data to confirm that the determinant of \mathbf{D} is invariably positive (section 3).

2. Theory on form of Fickian diffusion coefficients

2.1. Diffusion flux

Diffusion coefficients quantify the proportionality constant between diffusion fluxes and composition gradients. Diffusion flux using Fick's approach can be expressed based on various reference frames for velocity [11]: molar-, mass-, and volume-average velocity. Under isothermal and isobaric conditions, molar diffusion flux of component i with respect to molar-average velocity, J_i^M , is given by,

$$J_i^M = -c_t \sum_j^{n-1} D_{ij}^M \nabla_{T,p} x_j, \quad i = 1, \dots, n-1, \quad (1)$$

where n is number of components in the mixture, c_t is total mixture's molar density, $\nabla_{T,p} x_j$ is mole fraction gradient of component j at constant temperature T and pressure p , and D_{ij}^M are Fickian diffusion coefficients based on molar-average reference frame.

Similarly, mass diffusion flux with respect to mass-average velocity, J_i^m , is given by,

$$J_i^m = -\rho_t \sum_j^{n-1} D_{ij}^m \nabla_{T,p} \omega_j, \quad i = 1, \dots, n-1, \quad (2)$$

where ρ_t is total mixture's mass density, ω_j are mass fractions, and D_{ij}^m are Fickian diffusion coefficients based on mass-average reference frame.

Lastly, molar flux with respect to volume average velocity, J_i^V , is given by,

$$J_i^V = -\sum_j^{n-1} D_{ij}^V \nabla_{T,p} c_j, \quad i = 1, \dots, n-1, \quad (3)$$

where c_j is molar concentration of component i , and D_{ij}^V are Fickian diffusion coefficients based on volume-average reference frame.

Equations (1) to (3) represent the independent diffusion fluxes since $\sum_j J_i = 0$. Generally, theoretical studies are based on either equation (1) or equation (2), while equation (3) is used in experi-

mental work. Using equation (3) eliminates complexities that may arise from systems with variable densities [1]. In this work, our focus is on mole-based diffusion coefficients matrix, \mathbf{D}^M . However, all three forms of diffusion coefficients, \mathbf{D} , – mole-based, \mathbf{D}^M , mass-based, \mathbf{D}^m , and volume-based, \mathbf{D}^V , – are necessary for our analysis of experimental data (section 3).

The mole-based diffusion coefficients matrix, \mathbf{D}^M , is an $n-1 \times n-1$ matrix:

$$\begin{bmatrix} D_{1,1}^M & D_{1,2}^M & \dots & D_{1,n-1}^M \\ D_{2,2}^M & D_{2,2}^M & \dots & D_{2,n-2}^M \\ \vdots & \vdots & \ddots & \vdots \\ D_{n-1,1}^M & D_{n-2,2}^M & \dots & D_{n-1,n-1}^M \end{bmatrix}, \quad (4)$$

where diagonal elements (D_{ii}^M) are the main-term diffusion coefficients, while off-diagonal elements (D_{ij}^M , $i \neq j$) are the cross-term diffusion coefficients of i and j .

Ghorayeb and Firoozabadi [12] use entropy production, Onsager's reciprocal relations, and Gibbs–Duhem equation to derive an expression for D_{ij}^M :

$$D_{ij}^M = \frac{R}{c_t M_n x_n} \sum_{l=1}^{n-1} \sum_{k=1}^{n-1} \frac{M_k x_k + M_n x_n \delta_{lk}}{M_k} \left. \frac{\partial \ln f_k}{\partial x_j} \right|_{T,p,\bar{x}_j} L_{li}, \quad i, j = 1, \dots, n-1, \quad (5)$$

where L_{li} are phenomenological coefficients; M_k and f_k are molecular masses and fugacities, respectively, of component k ; M_n and x_n are the molecular mass and mole fraction, respectively, of the reference component; δ_{lk} is the Kronecker delta; and R is the gas constant. Note that \bar{x}_j denotes that mole fractions, x_1, x_2, \dots, x_{n-1} , are held constant except x_j while maintaining $\sum_j x_j = 1$.

Equation (5) shows that the sign of D_{ij}^M depends on two parameters:

- (i) Phenomenological coefficients, L_{li} ; and,
- (ii) Thermodynamic factors, $F_{kj} \equiv (\partial \ln f_k / \partial x_j)_{T,p,\bar{x}_j}$.

2.2. Form of phenomenological coefficients

The restriction imposed by the second law of thermodynamics establishes the form of phenomenological coefficients as shown by de Groot and Mazur [8]. We use similar approach in this section for completeness. Irreversible thermodynamics postulates linear laws that represent generalized fluxes (J_l) as products of phenomenological coefficients (L_{li}) and thermodynamic driving forces (X_i). In an n -component isotropic mixture, these linear laws can be written as:

$$J_l = \sum_{i=1}^{n-1} L_{li} X_i, \quad l = 1, \dots, n-1. \quad (6)$$

Dot product of the fluxes and driving forces provides the expression for entropy production strength per unit volume and time, σ , which is invariant under reference frame transformation [4] and is given by,

$$\sigma = \sum_{l=1}^{n-1} J_l \cdot X_l. \quad (7)$$

The second law of thermodynamics requires that σ is always positive. Thus, σ which can be expressed in terms of phenomenological coefficients and thermodynamic driving forces using equations (6) and (7) becomes,

$$\sigma = \sum_{l=1}^{n-1} \sum_{i=1}^{n-1} L_{li} X_i \cdot X_l \geq 0. \quad (8)$$

At equilibrium, driving forces and their respective fluxes vanish, i.e. $\sigma = 0$. For conditions away from equilibrium, the quadratic form of equation (8) imposes a restriction on the phenomenological coefficients since,

$$\sigma = \sum_{l=1}^{n-1} \sum_{i=1}^{n-1} L_{li} X_i \cdot X_l \equiv \mathbf{X}^T \mathbf{L} \mathbf{X} > 0, \quad (9)$$

where \mathbf{L} is the matrix of phenomenological coefficients, and \mathbf{X}^T denotes the transpose of the column vector of thermodynamic driving forces \mathbf{X} .

The coefficients L_{li} are functions of T , p , and composition. Onsager's theorem of reciprocal relations in thermodynamics of irreversible processes, imposes symmetry of these phenomenological coefficients such that $L_{li} = L_{il}$ [8]. Thus, \mathbf{L} as shown in equation (9) is positive definite for all non-zero thermodynamic driving forces \mathbf{X} .

According to linear algebra theorems, a real symmetric matrix – such as \mathbf{L} – is positive definite if, and only if, all its eigenvalues ($\lambda_{L,i}$) are positive [13]. Algebraically, it follows that such a matrix has: positive trace and determinant, positive principal minors based on Sylvester's criterion, and can be represented as a diagonal matrix in some basis whose diagonal elements are positive [13,14]. Hence, \mathbf{L} must meet the conditions:

$$\begin{aligned} \lambda_{L,i} &> 0, \\ |\mathbf{L}| &= \prod_i \lambda_{L,i} > 0, \\ \sum_i L_{ii} &= \sum_i \lambda_{L,i} > 0, \\ L_{ii}L_{ll} - L_{il}^2 &> 0, \\ L_{ii} &> 0, \\ i, l &= 1, \dots, n-1. \end{aligned} \quad (10)$$

2.3. Form of thermodynamic factors

Thermodynamic factors, F_{kj} , quantify the mixture's non-ideality and are defined from chemical potentials, μ_k , through [15],

$$F_{kj} \equiv \left. \frac{\partial \ln f_k}{\partial X_j} \right|_{T,p,\bar{x}_j} = (RT)^{-1} \left. \frac{\partial \mu_k}{\partial X_j} \right|_{T,p,\bar{x}_j}, \quad j, k = 1, \dots, n-1. \quad (11)$$

In ideal mixtures, the fugacity coefficients, ϕ_k , are unity [11]. This implies that each component fugacity, $f_k = \phi_k X_k p$, in ideal mixtures can be expressed as $f_k = X_k p$ [15]. Thus, F_{kj} in equation (11) reduces to a function of composition:

$$\left. \frac{\partial \ln f_k}{\partial X_j} \right|_{T,p,\bar{x}_j} = \frac{1}{X_k} \delta_{kj}, \quad j, k = 1, \dots, n-1. \quad (12)$$

Equations (5) and (12) imply that the sign of D_{ij}^M in ideal mixtures depends only on L_{li} . In non-ideal mixtures, however, the F_{kj} term plays an important role. In such mixtures, fugacity (f_k) is a function of T , p , and composition and is evaluated from either activity coefficients models [11], or models based on equations of state (EOS). The sign of the derivative, $(\partial \ln f_k / \partial X_j)_{T,p,\bar{x}_j}$, cannot be predicted beforehand in three and higher component mixtures; it can be of either sign depending on the properties of the mixture under consideration (section 2.6). However, based on thermodynamic stability considerations, the determinant of $\partial \mu_k / \partial X_j$ in equation (11) is positive [15]. Therefore, imposing linear algebra determinant theorem [13] on the relation in equation (11), the determinant of F_{kj} is also positive for thermodynamically stable mixtures:

$$|\mathbf{F}| = (RT)^{-(n-1)} \left| \left(\frac{\partial \mu_k}{\partial X_j} \right)_{T,p,\bar{x}_j} \right| > 0, \quad j, k = 1, \dots, n-1. \quad (13)$$

2.4. Determinant of Fickian diffusion coefficients matrix

In compact matrix form, equation (5) can be written as,

$$\mathbf{D}^M = \mathbf{A} \cdot \mathbf{M} \cdot \mathbf{L} \cdot \mathbf{W} \cdot \mathbf{F}, \quad (14)$$

where \mathbf{L} and \mathbf{F} are matrices of phenomenological coefficients and thermodynamic factors, respectively, as previously defined; and the elements of \mathbf{A} , \mathbf{M} , and \mathbf{W} are given by,

$$A_{ij} = \frac{R L_{ij}}{c_i M_i X_i M_n X_n} \delta_{ij}, \quad i, j = 1, \dots, n-1, \quad (15)$$

$$M_{ij} = \frac{M_i X_i}{L_{ij}} \delta_{ij}, \quad i, j = 1, \dots, n-1, \quad (16)$$

$$W_{ij} = X_j + \frac{M_n X_n}{M_j} \delta_{ij}, \quad i, j = 1, \dots, n-1. \quad (17)$$

The determinant of D^M as given in equation (14) is the product of determinants of the same order $n-1 \times n-1$ contributing matrices [13]:

$$|\mathbf{D}^M| = |\mathbf{A}| \cdot |\mathbf{M}| \cdot |\mathbf{L}| \cdot |\mathbf{W}| \cdot |\mathbf{F}|. \quad (18)$$

In equation (18), $|\mathbf{L}|$ and $|\mathbf{F}|$ are positive as shown in equations (10) and (13), respectively. Moreover, \mathbf{A} and \mathbf{M} in equations (15) and (16), respectively, are positive diagonal matrices. Since the determinant of a diagonal matrix is the product of its diagonal elements [13], determinants of \mathbf{A} and \mathbf{M} are positive. Using equation (16), \mathbf{W} can be written as a product of \mathbf{M} and \mathbf{L} , thus its determinant is also positive. Therefore, the product in equation (18) is positive. Conclusively, $|\mathbf{D}^M| > 0$, – thus, the product of the eigenvalues of D^M is positive, $\prod_i \lambda_{D,i} > 0$, – for thermodynamically stable mixtures.

As the critical point is approached, the determinant of $\partial \mu_k / \partial X_j$ goes zero [15]. Thus, the determinant of thermodynamic factors, $|\mathbf{F}|$, as given in equation (13) goes to zero. This implies that the determinant of Fickian diffusion coefficients matrix, $|\mathbf{D}^M|$, as given in equation (18) also goes to zero as the mixture's critical point is approached.

2.5. Form of Maxwell–Stefan diffusion coefficients

Standart *et al.* [10] have proved the non-negative restrictive constraints on Maxwell–Stefan diffusion coefficients, $\varphi_{ij} \geq 0$. This constraint can also be shown using the generalized framework for multicomponent diffusion coefficients based on irreversible thermodynamics [11,16]. In this framework, Maxwell–Stefan diffusion coefficients are given by,

$$\varphi_{ij} = \left(D_{ij}^\infty \right)^{X_j} \left(D_{ji}^\infty \right)^{X_i} \prod_{\substack{k=1 \\ k \neq i,j}}^n \left(D_{ik}^\infty D_{jk}^\infty \right)^{X_k/2}, \quad i, j = 1, \dots, n; \quad i \neq j, \quad (19)$$

where $\varphi_{ij} = \varphi_{ji}$ are Maxwell–Stefan diffusion coefficients for each binary pair $i-j$, D_{ij}^∞ is the molecular diffusion coefficient of component i infinitely diluted in component j , and X_i is the mole fraction of component i . At infinite dilution the three forms of molecular diffusion coefficients – φ_{ij} , D_{ij}^∞ , and D_{ij} – are identical. Besides, equation (19), φ_{ij} can be related to D_{ij}^∞ using either an arithmetic mean of composition or a geometric mean that includes viscosity [11], without changing its form. Since D_{ij}^∞ and X_i are real non-negative numbers, φ_{ij} are positive.

Thermodynamic factors, F_{kj} , – which may impart negative Fickian diffusion coefficients – do not appear in the Maxwell–Stefan

formulation. Instead, thermodynamic factors are used to relate Maxwell–Stefan to Fickian diffusion coefficients:

$$\mathbf{D} = (\mathbf{B}^M)^{-1} \mathbf{\Gamma}, \quad (20)$$

where the elements of the matrices \mathbf{B}^M and $\mathbf{\Gamma}$ are given by,

$$B_{ii}^M = \frac{x_i}{\varphi_{in}} + \sum_{\substack{k=1 \\ i \neq k}}^n \frac{x_k}{\varphi_{ik}}, \quad i = 1, \dots, n-1, \quad (21)$$

$$B_{ij}^M = -x_i \left(\frac{1}{\varphi_{ij}} - \frac{1}{\varphi_{in}} \right), \quad i, j = 1, \dots, n-1; i \neq j, \quad (22)$$

and

$$\Gamma_{ij} = x_i \left. \frac{\partial \ln f_i}{\partial x_j} \right|_{T,p,x_j}, \quad i, j = 1, \dots, n-1, \quad (23)$$

respectively.

2.6. Negative diagonal elements of Fickian diffusion coefficients matrix

Sections 2.3 and 2.4 show that the form of \mathbf{D}^M is dependent on the form of \mathbf{F} ; thus, the signs of individual \mathbf{D}^M elements are unrestricted as long as $|\mathbf{D}^M| > 0$. In this section, we demonstrate that some D_{ii}^M in the gas phase of two sets of thermodynamically stable 14-component petroleum fluid mixtures – CO₂-rich and N₂-rich – are negative. Both mixtures are composed of N₂, CO₂, H₂S, the hydrocarbon series C₄ to C₁₀ which consist of pseudorized aliphatic and/or aromatic species of the same carbon number hydrocarbon, and C₁₁₊ which is the remainder of the petroleum fluid.

For each mixture, we evaluate its stability and proximity to the critical point, both of which could lead to anomalous diffusion behavior. Based on overall composition, we perform phase-split calculations at constant T and p to determine equilibrium compositions in gas and liquid phases. Proximity to the mixtures' critical point is checked based on the algorithm by Hoteit *et al.* [17]. For both mixtures, we use the algorithm to confirm that no critical point can be detected within 5% perturbations of the given compositions.

We calculate D_{ij}^M based on the generalized multicomponent diffusion coefficients framework as outlined in equations (19) to (23) of section 2.5. Infinite dilution diffusion coefficients are calculated from the correlation by Leahy-Dios and Firoozabadi [16], which is based on corresponding state theory. This correlation was extensively tested for binary and multicomponent non-polar gas, liquid, and supercritical mixtures; therefore, it is expected to provide consistent diffusion coefficients. The non-ideality in equation (23) is calculated from analytical derivatives of the Peng–Robinson EOS (PR-EOS) [15]. Fluid characterization and binary interaction parameters needed for the PR-EOS are provided in Appendix A. Also provided in Appendix A are molecular diffusion volume increments that are calculated by summing atomic diffusion volumes [18, Table 11-1] and viscosities used to calculate diffusion coefficients.

Both sets of mixtures were at $T = 394.0$ K, but the CO₂-rich mixture was at $p = 13.56$ MPa, while the N₂-rich mixture was at $p = 15.89$ MPa. Equilibrium compositions in gas and liquid phases were determined at these T and p conditions and D_{ij}^M calculated in each phase. In the liquid phase of both mixtures, all D_{ii}^M elements are non-negative; however, in the gas phase of both mixtures, some D_{ii}^M are negative. Matrices of calculated thermodynamic factors, \mathbf{F} , and the mole-based diffusion coefficients, \mathbf{D}^M , are shown in tables 1–4 for the gas phase of CO₂-rich and N₂-rich mixtures, respectively. Infinite dilution, D_{ij}^∞ , and Maxwell–Stefan, φ_{ij} , diffusion coefficients are provided in Appendix B. Gas phase composi-

tions (in mole fractions) are indicated in parenthesis in the relevant tables.

Table 2 shows that D_{22}^M , the main-term diffusion coefficient for carbon dioxide, is negative. This is because $F_{11} = -1.03$ as shown in table 1. Similarly, table 4 shows that D_{11}^M , the main-term diffusion coefficient for nitrogen, is negative, which is due to $F_{11} = -0.82$ as shown in table 3. Nonetheless, the determinant, the trace, and all the 13 eigenvalues – that characterize \mathbf{D}^M in both mixtures – are positive. Note that the absolute magnitude of some of the off-diagonal diffusion coefficients elements are greater than the diagonal elements. This implies that cross-Fickian diffusion is important in these petroleum fluid mixtures.

Diffusion coefficients influence the rate of mass transfer. In multicomponent mixtures, diffusion flux, J_i^M , quantifies the diffusion of species i relative to the flux of the mixture as a whole. Composition gradients, $\nabla_{T,p} x_j$, also affect J_i^M as shown in section 2.1. In all mixtures, $\sum_j \nabla_{T,p} x_j = 0$; thus, in binary mixtures $\nabla_{T,p} x_2 = -\nabla_{T,p} x_1$, but in multicomponent mixtures each $\nabla_{T,p} x_j$ may be different leading to diffusion interactions. In the two sets of 14-component petroleum fluid mixtures considered here, equation (1) can be used to assess the effect of the sign of D_{ii}^M on J_i^M . To that end, we assign arbitrary values to $\nabla_{T,p} x_j$ equal to equilibrium gas phase compositions in each mixture, and hold all other D_{ij}^M values constant except the signs of D_{22}^M and D_{11}^M for the CO₂-rich and N₂-rich mixtures, respectively. For each mixture, c_i is calculated from PR-EOS. Table 5 shows that $J_{CO_2}^M$ and $J_{N_2}^M$ change – in both sign and magnitude – with only change in sign of D_{22}^M and D_{11}^M for the CO₂-rich and N₂-rich mixtures, respectively.

3. Experimental data on Fickian diffusion coefficients

To establish the validity of our findings in section 2.4, we conducted extensive literature survey and analysis of multicomponent ($n \geq 3$) molecular diffusion coefficients. We also checked these data against theoretical restrictions often imposed on \mathbf{D} (section 1). The restrictions for a ternary mixture, based on the condition for real and positive eigenvalues, are outlined by Taylor and Krishna [11] and can be generalized for an n -component mixture (Appendix A) as,

- i. Positive and real eigenvalues, $\lambda_{D,i} > 0, i = 1, \dots, n-1$;
- ii. Positive trace, $\sum_{i=1}^{n-1} D_{ii} > 0$;
- iii. Positive determinant, $|\mathbf{D}| > 0$; and,
- iv. Positive diagonal elements, $D_{ii} > 0, i = 1, \dots, n-1$.

We calculated the eigenvalues ($\lambda_{D,i}$), trace ($\sum_{i=1}^{n-1} D_{ii}$), and determinant ($|\mathbf{D}|$), for all \mathbf{D} of the reported experimental data of ternary and quaternary mixtures. While all mixtures had $\sum_{i=1}^{n-1} D_{ii} > 0$ and $|\mathbf{D}| > 0$, we found a number of mixtures that do not meet the conditions outlined above, namely:

- (i) Mixtures whose \mathbf{D} have negative diagonal elements; and,
- (ii) Mixtures whose \mathbf{D} have complex eigenvalues.

A total of 888 experimental data points¹ are reported for multicomponent diffusion coefficients [19–136] for 107 different ternary and quaternary mixtures (tables 1 to 6 of the supplementary data). Of these, 881 are D_{ij}^V , 6 are D_{ij}^m and 1 is D_{ij}^M . Majority of the reported data has water as a component, but only a few data points are for mixtures with all organic components. To the best of our knowledge, no diffusion coefficients are reported based on experimental measurements for 5 or higher component mixtures. The available data

¹ A data point represents either four or nine elements of \mathbf{D} in ternary and quaternary mixtures, respectively.

TABLE 1Thermodynamic factors, F_{kj} , in the gas phase of the CO₂-rich petroleum fluid mixture.

N ₂ (0.00265), CO ₂ (0.73787), H ₂ S (0.00925), C ₁ (0.11917), C ₂ (0.03804), C ₃ (0.03287), C ₄ (0.02825), C ₅ (0.01371), C ₆ (0.00875), C ₇ (0.00362), C ₈ (0.00283), C ₉ (0.00188), C ₁₀ (0.00112), C ₁₁₊ (0.00001), T = 394.0 K, p = 13.56 MPa													
	N ₂	CO ₂	H ₂ S	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀
N ₂	370.20	-6.67	-6.38	-7.02	-6.56	-6.21	-5.87	-5.53	-5.21	-4.90	-4.58	-4.27	-3.94
CO ₂	-2.40	-1.03	-2.35	-2.34	-2.27	-2.22	-2.17	-2.12	-2.07	-2.03	-1.98	-1.94	-1.89
H ₂ S	4.41	4.18	112.24	4.34	4.20	4.10	3.99	3.88	3.78	3.68	3.58	3.48	3.38
C ₁	-2.97	-2.56	-2.40	5.48	-2.64	-2.45	-2.27	-2.09	-1.91	-1.74	-1.55	-1.38	-1.20
C ₂	5.67	5.70	5.65	5.55	31.69	5.30	5.20	5.10	4.99	4.92	4.82	4.73	4.63
C ₃	11.88	11.60	11.39	11.59	11.15	41.26	10.52	10.21	9.90	9.64	9.35	9.06	8.76
C ₄	18.07	17.50	17.13	17.62	16.90	16.37	51.24	15.32	14.81	14.37	13.87	13.39	12.89
C ₅	24.16	23.31	22.78	23.56	22.56	21.82	21.08	93.28	19.65	19.02	18.34	17.67	16.97
C ₆	30.16	29.04	28.36	29.41	28.13	27.19	26.24	25.32	138.74	23.62	22.74	21.89	21.00
C ₇	35.31	33.92	33.10	34.42	32.89	31.76	30.64	29.54	28.46	303.87	26.45	25.44	24.36
C ₈	41.04	39.38	38.41	40.02	38.21	36.88	35.56	34.26	33.00	31.86	384.30	29.44	28.18
C ₉	46.64	44.71	43.60	45.48	43.40	41.88	40.36	38.88	37.43	36.13	34.72	566.18	31.91
C ₁₀	52.55	50.35	49.08	51.25	48.89	47.17	45.45	43.77	42.12	40.65	39.06	37.51	931.45

C₁₁₊ is the reference component.**TABLE 2**Mole-based diffusion coefficients, $D_{ij}^M \times 10^9 \text{ m}^2 \cdot \text{s}^{-1}$, in the gas phase of the CO₂-rich petroleum fluid mixture.

N ₂ (0.00265), CO ₂ (0.73787), H ₂ S (0.00925), C ₁ (0.11917), C ₂ (0.03804), C ₃ (0.03287), C ₄ (0.02825), C ₅ (0.01371), C ₆ (0.00875), C ₇ (0.00362), C ₈ (0.00283), C ₉ (0.00188), C ₁₀ (0.00112), C ₁₁₊ (0.00001), T = 394.0 K, p = 13.56 MPa													
	N ₂	CO ₂	H ₂ S	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀
N ₂	113.7	-2.0	-1.9	-2.1	-2.0	-1.8	-1.7	-1.6	-1.5	-1.4	-1.3	-1.2	-1.1
CO ₂	-178.8	-68.1	-166.5	-179.2	-153.5	-140.3	-131.6	-125.0	-119.7	-115.3	-111.5	-108.1	-105.0
H ₂ S	4.1	4.0	103.9	4.0	4.0	4.0	3.9	3.8	3.7	3.7	3.6	3.5	3.4
C ₁	-40.3	-34.4	-31.3	79.7	-34.1	-30.7	-27.7	-24.9	-22.3	-19.8	-17.3	-14.9	-12.4
C ₂	19.3	20.0	19.6	18.8	110.0	18.9	18.7	18.4	18.1	17.8	17.5	17.2	16.8
C ₃	29.5	29.5	28.5	28.7	28.2	104.9	26.9	26.2	25.5	24.9	24.1	23.4	22.6
C ₄	34.4	34.0	32.8	33.5	32.6	31.8	99.8	29.9	28.9	28.1	27.2	26.2	25.3
C ₅	20.4	20.1	19.4	19.9	19.3	18.7	18.2	80.7	17.0	16.5	15.9	15.3	14.7
C ₆	15.2	14.9	14.3	14.8	14.3	13.9	13.4	13.0	71.5	12.1	11.7	11.3	10.8
C ₇	6.9	6.8	6.5	6.7	6.5	6.3	6.1	5.9	5.7	60.8	5.3	5.1	4.9
C ₈	6.0	5.8	5.6	5.8	5.6	5.4	5.2	5.1	4.9	4.7	57.1	4.4	4.2
C ₉	4.3	4.2	4.0	4.2	4.0	3.9	3.8	3.6	3.5	3.4	3.3	53.5	3.0
C ₁₀	2.8	2.7	2.6	2.7	2.6	2.5	2.4	2.4	2.3	2.2	2.1	2.0	50.4

C₁₁₊ is the reference component.**TABLE 3**Thermodynamic factors, F_{kj} , in the gas phase of the N₂-rich petroleum fluid mixture.

N ₂ (0.70796), CO ₂ (0.01713), H ₂ S (0.00583), C ₁ (0.18811), C ₂ (0.03139), C ₃ (0.01876), C ₄ (0.01531), C ₅ (0.00646), C ₆ (0.00328), C ₇ (0.00148), C ₈ (0.00148), C ₉ (0.00178), C ₁₀ (0.00103), C ₁₁₊ (0.00001), T = 394.0 K, p = 15.89 MPa													
	N ₂	CO ₂	H ₂ S	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀
N ₂	-0.82	-2.17	-2.12	-2.18	-2.09	-2.02	-1.95	-1.88	-1.81	-1.72	-1.66	-1.60	-1.53
CO ₂	2.03	60.18	1.73	2.01	1.88	1.78	1.67	1.57	1.47	1.33	1.25	1.16	1.05
H ₂ S	6.56	6.22	177.55	6.47	6.22	6.01	5.80	5.60	5.40	5.14	4.97	4.79	4.58
C ₁	1.14	1.12	1.09	6.38	1.03	0.99	0.95	0.91	0.87	0.82	0.79	0.76	0.73
C ₂	8.26	8.03	7.88	8.07	39.60	7.49	7.24	6.99	6.74	6.42	6.22	6.00	5.74
C ₃	13.52	13.12	12.86	13.22	12.68	65.58	11.86	11.45	11.04	10.51	10.17	9.82	9.39
C ₄	18.79	18.21	17.86	18.37	17.63	17.06	81.78	15.91	15.34	14.61	14.14	13.64	13.05
C ₅	24.04	23.28	22.83	23.51	22.56	21.82	21.09	175.09	19.63	18.68	18.08	17.45	16.69
C ₆	29.26	28.33	27.77	28.62	27.46	26.56	25.67	24.77	328.99	22.74	22.01	21.23	20.32
C ₇	35.99	34.84	34.16	35.22	33.79	32.68	31.58	30.48	29.39	702.28	27.08	26.12	25.00
C ₈	40.28	38.99	38.22	39.42	37.81	36.58	35.34	34.11	32.89	31.31	708.33	29.23	27.97
C ₉	44.86	43.41	42.56	43.91	42.11	40.73	39.36	37.99	36.62	34.86	33.74	594.28	31.15
C ₁₀	50.22	48.60	47.65	49.17	47.15	45.61	44.07	42.53	41.01	39.04	37.78	36.45	1004.33

C₁₁₊ is the reference component.are at $p = 0.1 \text{ MPa}$ and covers a limited temperature range $286.15 \leq T \leq 323.20 \text{ K}$.Reported D_{ij} are not unambiguous calculations, but are the best fits to experimental measurements of composition. Moreover, the accuracy of reported D_{ij} varies depending on mixture conditions and the technique used, and the uncertainty can be as high as 50%. The reported data is based on experimental measurementsmade by different techniques: Gouy and Rayleigh interferometry, laser beam deflection, Taylor dispersion, diaphragm cell, open-end capillary tube, and high performance liquid chromatography. Multicomponent data fitting of measurements of composition sometimes require imposition of constraints to determine D_{ij} . In some reported D_{ij} values [27,29], the fit of composition measurements from experiments to determine D invoked the restrictions

TABLE 4

Mole-based diffusion coefficients, $D_{ij}^M \times 10^9 \text{ m}^2 \cdot \text{s}^{-1}$, in the gas phase of the N_2 -rich petroleum fluid mixture.

N_2 (0.70796), CO_2 (0.01713), H_2S (0.00583), C_1 (0.18811), C_2 (0.03139), C_3 (0.01876), C_4 (0.01531), C_5 (0.00646), C_6 (0.00328), C_7 (0.00148), C_8 (0.00148), C_9 (0.00178), C_{10} (0.00103), C_{11+} (0.000001), $T = 394.0 \text{ K}$, $p = 15.89 \text{ MPa}$													
	N_2	CO_2	H_2S	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
N_2	-124.3	-272.2	-270.2	-296.6	-255.1	-232.5	-216.2	-202.8	-191.3	-179.4	-170.8	-162.6	-154.0
CO_2	5.0	155.5	4.2	4.7	4.7	4.7	4.5	4.3	4.0	3.7	3.5	3.3	3.0
H_2S	5.8	5.5	159.3	5.6	5.6	5.4	5.3	5.1	4.9	4.7	4.6	4.4	4.2
C_1	36.5	39.6	38.0	214.7	37.8	38.5	38.2	37.5	36.4	34.8	33.9	32.9	31.5
C_2	35.4	34.4	33.6	34.0	172.6	32.6	31.7	30.7	29.7	28.3	27.5	26.6	25.5
C_3	29.8	28.7	28.0	28.6	27.8	146.6	26.3	25.5	24.6	23.5	22.8	22.0	21.1
C_4	30.5	29.2	28.6	29.3	28.4	27.6	134.4	25.9	25.1	23.9	23.1	22.4	21.4
C_5	15.2	14.6	14.3	14.6	14.2	13.8	13.3	112.2	12.5	11.8	11.5	11.1	10.6
C_6	8.8	8.4	8.3	8.5	8.2	8.0	7.7	7.5	100.5	6.9	6.7	6.4	6.2
C_7	4.7	4.5	4.4	4.5	4.4	4.2	4.1	4.0	3.8	92.6	3.5	3.4	3.3
C_8	5.0	4.8	4.7	4.8	4.6	4.5	4.4	4.2	4.1	3.9	88.7	3.6	3.5
C_9	6.5	6.2	6.1	6.2	6.0	5.8	5.7	5.5	5.3	5.0	4.9	86.5	4.5
C_{10}	4.1	3.9	3.8	3.9	3.8	3.7	3.6	3.4	3.3	3.2	3.1	3.0	82.1

 C_{11+} is the reference component.

TABLE 5

Diffusion fluxes, J_i^M , of CO_2 and N_2 in the CO_2 -rich and N_2 -rich petroleum fluid mixtures.

CO_2 -rich mixture $T = 394.0 \text{ K}$, $p = 13.56 \text{ MPa}$ $c_t = 5.55 \times 10^3 \text{ mol} \cdot \text{m}^{-3}$, $\nabla_{T,p} x_{\text{CO}_2} = 0.738 \text{ m}^{-1}$	
$D_{\text{CO}_2}^M / (\text{m}^2 \cdot \text{s}^{-1})$	$J_{\text{CO}_2}^M / (\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1})$
-68.09×10^{-9}	5.08×10^{-4}
68.09×10^{-9}	-4.99×10^{-5}
N_2 -rich mixture $T = 394.0 \text{ K}$, $p = 15.89 \text{ MPa}$ $c_t = 4.81 \times 10^3 \text{ mol} \cdot \text{m}^{-3}$, $\nabla_{T,p} x_{\text{N}_2} = 0.708 \text{ m}^{-1}$	
$D_{\text{N}_2}^M / (\text{m}^2 \cdot \text{s}^{-1})$	$J_{\text{N}_2}^M / (\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1})$
-124.25×10^{-9}	8.11×10^{-4}
124.25×10^{-9}	-3.54×10^{-4}

TABLE 6

Volume-based diffusion coefficients, $D_{ij}^V \times 10^9 \text{ m}^2 \cdot \text{s}^{-1}$, as functions of temperature T for water(1), 2-propanol(2), and **cyclohexane**^b mixture at $p = 0.1 \text{ MPa}$ [32].

T/K	D_{11}^V	D_{12}^V	D_{21}^V	D_{22}^V
$\omega_1 = 0.1306$, $\omega_2 = 0.4623$				
310.21	-0.1071	0.1064	-0.2120	0.1984
306.64	-0.0467	0.0547	-0.0997	0.1064
304.65	-0.0309	0.0328	-0.0566	0.0571
304.15	-0.0257	0.0267	-0.0440	0.0439
303.75	-0.0347	0.0323	-0.0559	0.0510

^b Cyclohexane is the reference component.

outlined by Taylor and Krishna [11]. Inherently, such \mathbf{D} will meet all the restrictions outlined above; hence, the importance of establishing the proper restrictions on multicomponent diffusion coefficients.

3.1. Negative diagonal elements of Fickian diffusion coefficients matrix

Section 2.3 shows that for thermodynamically stable mixtures, the elements of \mathbf{F} can be of either sign, which implies that there is no restriction on the signs of the \mathbf{D} elements. Examination of the reported \mathbf{D} shows that in ternary mixtures, nine data points from two mixtures are reported with negative diagonal \mathbf{D}^V

TABLE 7

Volume-based diffusion coefficients, $D_{ij}^V \times 10^9 \text{ m}^2 \cdot \text{s}^{-1}$, as functions of composition x_i for chloroform(1), acetic acid(2), and **water**^b mixture at $T = 298.15 \text{ K}$ and $p = 0.1 \text{ MPa}$ [38,39].

x_1	x_2	D_{11}^V	D_{12}^V	D_{21}^V	D_{22}^V	Reference
0.0925	0.4480	-0.0430	-0.4510	0.5810	1.1240	[38]
0.1000	0.4000	-0.1390	-0.4630	0.6370	1.0900	[38]
0.1897	0.5405	-0.3340	-0.9390	1.0650	1.8140	[39]
0.2400	0.4199	-0.5960	-1.0950	1.1530	1.8440	[39]

^b Water is the reference component.

elements: (water + 2-propanol + **cyclohexane**) [32]; and, (acetic acid + chloroform + **water**) [38,39]. Mixture conditions and D_{ij}^V are shown in tables 6 and 7. There are no negative D_{ii} values in the reported \mathbf{D} for quaternary mixtures.

It is noteworthy that these ternary mixtures with negative D_{11}^V values have either one or two components that can form hydrogen bonds such as water and 2-propanol. Moreover, acetic acid can dissociate into ions in aqueous solution. Nonetheless, these negative D_{11}^V values are neither an artifact nor a result of the complexity of diffusion in such mixtures; they can be related to non-ideality. In spite of the negative values of D_{11}^V , $|\mathbf{D}^V|$ is positive for all nine data points.

3.2. Complex eigenvalues of Fickian diffusion coefficients matrix

Section 2.4 shows that for thermodynamically stable mixtures $|\mathbf{D}| > 0$, which implies that the product of the eigenvalues of \mathbf{D} is positive, $\prod_i \lambda_{D,i} > 0$, but provides no restriction on the individual $\lambda_{D,i}$. Our analysis of experimental data shows that it is possible to have thermodynamically stable mixtures with $|\mathbf{D}| > 0$, but with complex individual eigenvalues, $\lambda_{D,i}$. A total of 35 reported data points have \mathbf{D}^V with complex eigenvalues; of these, 34 data points are for ternary mixtures, while one data point is for a quaternary mixture. Tables 8–10 present reported mixture conditions and D_{ij}^V [19–24,31,34–36,42,64,84], and calculated $\lambda_{D,i}$ for ternary mixtures whose \mathbf{D}^V have complex eigenvalues. Similarly, reported mixture conditions and D_{ij}^V [132], and calculated $\lambda_{D,i}$ for one quaternary mixture whose \mathbf{D}^V has complex eigenvalues are shown in table 11.

It can be observed in tables 8–10 that $\lambda_{D,i}$ are complex conjugates where, on average, the imaginary part is small compared to the real part. The uncertainty – whenever reported – in D_{ij}^V does affect the eigenvalues; however, several of the data points have

² Component in bold is the reference component.

TABLE 8

Ternary mixtures with all organic components whose D have complex eigenvalues.

Mixture	x_1	x_2	T/K	D_{11}^V	D_{12}^V	D_{21}^V	D_{22}^V	$\lambda_{D,1,2}/(\text{m}^2 \cdot \text{s}^{-1})$	Ref
$p = 0.1 \text{ MPa}, D_{ij} \times 10^9 (\text{m}^2 \cdot \text{s}^{-1})$									
Toluene(1), chlorobenzene(2), bromobenzene ^b	0.7000	0.1500	302.75	2.1320	0.0510	-0.0710	2.0620	$2.0970 \pm 0.0489i$	[19]
	0.1500	0.7000	302.75	1.8530	0.0490	-0.0680	1.8410	$1.8470 \pm 0.0574i$	[19]
Acetone(1), benzene(2), carbon tetrachloride	0.1497	0.6984	298.15	1.9610	0.0130	-0.1490	1.9290	$1.9450 \pm 0.0410i$	[20]
	0.0933	0.8967	298.15	3.1105	0.5500	-0.7800	1.8600	$2.4825 \pm 0.2037i$	[20]
Acetonitrile(1), benzene(2), n-heptane	0.0628	0.2048	298.15	3.1210	-0.2910	0.8630	3.6130	$3.3670 \pm 0.4366i$	[21]
2,2-Dichloropropane(1), 1,1,1-trichloroethane(2), carbon tetrachloride	0.2854	0.3515	298.15	1.4720	-0.0280	0.0220	1.5140	$1.4930 \pm 0.0132i$	[24]
	0.1010	0.1520	308.15	1.6400	-0.0700	0.0300	1.6600	$1.6500 \pm 0.0447i$	[24]

^b Component in bold is the reference component.

TABLE 9

Ternary mixtures with at least one alcohol component whose D have complex eigenvalues.

Mixture	x_1	x_2	T/K	D_{11}^V	D_{12}^V	D_{21}^V	D_{22}^V	$\lambda_{D,1,2}/(\text{m}^2 \cdot \text{s}^{-1})$	Reference
$p = 0.1 \text{ MPa}, D_{ij} \times 10^9 \text{ m}^2 \cdot \text{s}^{-1}$									
Cyclohexane(1), toluene(2), methanol ^b	0.1001	0.0499	298.15	1.2113	0.4131	-0.3024	1.9176	$1.5645 \pm 0.0144i$	[31]
Acetone(1), benzene(2), methanol	0.7660	0.1140	298.15	4.4000	0.9210	-0.8340	2.6800	$3.5400 \pm 0.1689i$	[23]
2-Propanol(1), glycerol(2), water	0.0930	0.8140	323.15	0.3858	-0.0591	0.3513	0.5150	$0.4504 \pm 0.1288i$	[34]
	0.7387	0.1000	323.15	0.9398	0.8674	-0.0981	0.7867	$0.8633 \pm 0.2815i$	[34]
Acetone(1), water(2), 1-propanol	0.4000	0.2000	298.15	1.5662	0.0192	-0.2513	1.4278	$1.4970 \pm 0.0060i$	[35]
Methanol(1), 1-butanol(2), 1-propanol	0.0500	0.9000	298.15	0.3656	0.0102	-0.2785	0.4720	$0.4188 \pm 0.0032i$	[35]
1-Propanol(1), glycine(2), water	0.0382	0.1145	298.15	1.0530	-0.0160	0.0010	1.0570	$1.0550 \pm 0.0035i$	[36]
	0.0763	0.0763	298.15	1.0540	-0.0400	0.0010	1.0650	$1.0590 \pm 0.0020i$	[36]
	0.1145	0.0382	298.15	1.0590	-0.0170	0.0010	1.0600	$1.0595 \pm 0.0041i$	[36]
1-Propanol(1), 2-propanol(2), water	0.0382	0.1145	298.15	1.0590	-0.0220	0.0010	1.0520	$1.0525 \pm 0.0047i$	[36]
	0.0763	0.0763	298.15	1.0530	-0.0110	0.0060	1.0400	$1.0470 \pm 0.0041i$	[36]
	0.1145	0.0382	298.15	1.0540	-0.0070	0.0120	1.0320	$1.0410 \pm 0.0017i$	[36]

^b Component in bold is the reference component.

TABLE 10

Ternary mixtures with water and at least one organic component whose D have complex eigenvalues.

Mixture	x_1	x_2	T/K	D_{11}^V	D_{12}^V	D_{21}^V	D_{22}^V	$\lambda_{D,1,2}/(\text{m}^2 \cdot \text{s}^{-1})$	Reference
$p = 0.1 \text{ MPa}, D_{ij} \times 10^9/(\text{m}^2 \cdot \text{s}^{-1})$									
Glycerol(1), acetone(2), water ^b	0.0025	0.8974	298.15	2.1333	-0.1008	1.4961	2.9090	$2.5216 \pm 0.0055i$	[40]
	0.0050	0.6946	298.15	1.0903	-0.0427	0.0022	1.1095	$1.0999 \pm 0.0013i$	[40]
	0.0050	0.6946	298.15	1.0661	-0.0634	0.0102	1.1096	$1.0842 \pm 0.0012i$	[40]
	0.0030	0.5770	298.15	0.9977	-0.0077	0.2962	0.9022	$0.9499 \pm 0.0008i$	[41]
Diethanolamine(1), <i>N</i> -methyldiethanolamine(2), water	0.0420	0.0252	303.20	0.2330	-0.1420	0.0430	0.3890	$0.3110 \pm 0.0047i$	[64]
	0.0168	0.0504	313.20	0.2720	-0.0410	0.1290	0.4170	$0.3445 \pm 0.0057i$	[64]
	0.0252	0.0420	313.20	0.2890	-0.0500	0.1160	0.4410	$0.3650 \pm 0.0049i$	[64]
	0.0252	0.0420	323.20	0.4780	-0.1450	0.0150	0.5710	$0.5250 \pm 0.0036i$	[64]
Diethylene glycol(1), lithium chloride(2), water	0.0216	0.0180	303.20	0.8400	0.2560	-0.0660	0.8510	$0.8455 \pm 0.1299i$	[84]
	0.0216	0.0180	308.20	0.9130	0.3400	-0.0700	1.0280	$0.9705 \pm 0.1432i$	[84]
	0.0198	0.0495	303.20	0.6680	0.1070	-0.1860	0.9360	$0.8020 \pm 0.0441i$	[84]
	0.0301	0.0251	303.20	0.7240	0.2970	-0.0390	0.8010	$0.7625 \pm 0.1005i$	[84]
	0.0198	0.0495	308.20	0.6920	0.1270	-0.1980	0.9670	$0.8295 \pm 0.0790i$	[84]
Mannitol(1), tetraethylene glycol(2), water	0.0010	0.0030	298.15	0.6600	-0.0010	0.0110	0.6640	$0.6620 \pm 0.0026i$	[36]
	0.0030	0.0010	298.15	0.6590	-0.0010	0.0150	0.665	$0.6620 \pm 0.0024i$	[36]

^b Component in bold is the reference component.

complex $\lambda_{D,i}$ throughout the range of possible D_{ij}^V within the reported accuracy. Nonetheless, the product of these complex eigenvalues for all 35 data points is positive; thus, $|\mathbf{D}| > 0$.

4. Conclusions

We have shown that the form of multicomponent Fickian diffusion coefficients matrix, \mathbf{D} , is dictated by two contributing param-

eters: phenomenological coefficients (L_{ij}); and thermodynamic factors ($F_{kj} \equiv (\partial \ln f_k / \partial x_j)_{T,p,x_i}$). Invoking postulates of irreversible thermodynamics and using linear algebra theorems, \mathbf{L} is a symmetric matrix with all positive eigenvalues, a positive determinant, and positive diagonal elements. On the contrary, \mathbf{F} does not ascribe itself to any apparent form; its elements (including diagonal elements) can be of either sign. However, thermodynamic stability analysis requires the determinant of thermodynamic factors

TABLE A-3

Critical temperatures (T_c), critical pressures (p_c), acentric factors (ω), volume translation parameters (b), and molecular masses (M) used to calculate properties of the N₂-rich fluid from the PR-EOS; and diffusion volume increments (Σ_v), and viscosities (μ) used to calculate diffusion coefficients.

	T_c/K	p_c/MPa	ω	b	$M/(g \cdot mol^{-1})$	Σ_v	$\mu/PA \cdot s$
N ₂	126.21	3.39	0.0390	-0.2885	28.0	18.50	2.3943×10^{-5}
CO ₂	304.14	7.38	0.2390	-0.1768	44.0	26.90	2.4876×10^{-5}
H ₂ S	373.20	8.94	0.0810	-0.2388	34.1	27.52	4.6288×10^{-5}
C ₁	190.56	4.60	0.0110	-0.1540	16.0	25.14	1.6456×10^{-5}
C ₂	305.32	4.87	0.0990	-0.1002	30.1	45.66	2.3639×10^{-5}
C ₃	369.83	4.25	0.1530	-0.0850	44.1	66.18	5.4296×10^{-5}
C ₄	425.12	3.80	0.1990	-0.0641	58.1	86.70	8.9695×10^{-5}
C ₅	469.70	3.37	0.2510	-0.0418	72.2	107.22	1.3426×10^{-4}
C ₆	507.40	3.01	0.2960	-0.0148	86.2	127.74	1.8545×10^{-4}
C ₇	556.48	2.68	0.2940	0.0247	100.0	148.26	2.1856×10^{-4}
C ₈	574.76	2.52	0.4180	0.0478	114.0	168.78	2.6575×10^{-4}
C ₉	593.07	2.33	0.4910	0.0667	128.0	189.30	3.2337×10^{-4}
C ₁₀	617.07	2.16	0.5340	0.0851	142.0	209.82	3.9286×10^{-4}
C ₁₁₊	916.63	0.74	1.0490	0.4240	493.0	796.50	3.7669×10^{-2}

TABLE A-4

Binary interaction coefficients used to calculate properties of the N₂-rich fluid from the PR-EOS.

	N ₂	CO ₂	H ₂ S	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀	C ₁₁₊
N ₂	0.000	0.000	0.000	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100
CO ₂	0.000	0.000	0.000	0.150	0.150	0.150	0.150	0.150	0.150	0.150	0.150	0.150	0.150	0.239
H ₂ S	0.000	0.000	0.000	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100
C ₁	0.100	0.150	0.100	0.000	0.034	0.036	0.038	0.041	0.043	0.045	0.048	0.050	0.052	0.075
C ₂	0.100	0.150	0.100	0.034	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C ₃	0.100	0.150	0.100	0.036	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C ₄	0.100	0.150	0.100	0.038	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C ₅	0.100	0.150	0.100	0.041	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C ₆	0.100	0.150	0.100	0.043	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C ₇	0.100	0.150	0.100	0.045	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C ₈	0.100	0.150	0.100	0.048	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C ₉	0.100	0.150	0.100	0.050	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C ₁₀	0.100	0.150	0.100	0.052	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C ₁₁₊	0.100	0.239	0.100	0.075	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Appendix B. Binary diffusion coefficients

Infinite dilution, D_{ij}^∞ , and Maxwell–Stefan, φ_{ij} , diffusion coefficients for the CO₂-rich and N₂-rich petroleum fluids are provided in tables B-1 to B-4, respectively.

Appendix C. Literature restrictions on D

According to Taylor and Krishna [11], the condition for real and positive eigenvalues of D^M in a ternary mixture can be expressed in terms of the trace, the determinant, and the discriminant of the determinantal polynomial:

$$D_{11} + D_{22} > 0, \quad (C-1)$$

$$D_{11}D_{22} - D_{12}D_{21} > 0,$$

$$(D_{11} - D_{22})^2 + 4D_{12}D_{21} > 0,$$

and with recourse to kinetic theory of gases, the main term diffusion coefficients, D_{11} and D_{22} , are positive:

$$D_{11} > 0, \quad (C-2)$$

$$D_{22} > 0.$$

For an n -component mixture, equations (C-1) and (C-2) can be generalized as,

TABLE B-1

Infinite dilution diffusion coefficients, $D_{ij}^\infty \times 10^9 \text{ m}^2 \cdot \text{s}^{-1}$, for the CO₂-rich fluid.

	N ₂	CO ₂	H ₂ S	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀	C ₁₁₊
$T = 394.0 \text{ K}, p = 13.56 \text{ MPa}$														
N ₂	0.0	134.7	55.8	242.7	96.6	42.4	29.2	23.4	19.8	16.1	13.8	12.0	10.5	0.5
CO ₂	196.5	0.0	46.2	199.6	79.4	35.7	24.9	20.1	17.1	13.8	11.8	10.3	9.0	0.4
H ₂ S	202.3	110.6	0.0	200.1	81.2	37.3	26.3	21.5	18.5	15.1	13.1	11.5	10.1	0.5
C ₁	253.6	143.5	58.8	0.0	99.4	45.7	32.3	26.4	22.8	18.6	16.2	14.2	12.5	0.6
C ₂	176.8	97.9	41.8	173.3	0.0	33.1	23.4	19.1	16.5	13.5	11.7	10.2	9.0	0.5
C ₃	144.3	78.7	34.4	145.7	59.6	0.0	19.3	15.7	13.5	11.0	9.5	8.3	7.3	0.4
C ₄	125.6	67.7	30.1	129.2	52.4	24.0	0.0	13.7	11.7	9.5	8.2	7.1	6.2	0.3
C ₅	113.4	60.5	27.3	118.1	47.6	21.8	15.2	0.0	10.5	8.5	7.3	6.3	5.5	0.2
C ₆	104.6	55.4	25.4	109.9	44.2	20.2	14.1	11.3	0.0	7.7	6.6	5.7	5.0	0.2
C ₇	97.0	51.0	23.6	102.9	41.3	18.8	13.1	10.5	8.9	0.0	6.0	5.2	4.5	0.2
C ₈	91.5	47.8	22.4	97.7	39.1	17.8	12.4	9.9	8.3	6.6	0.0	4.8	4.1	0.1
C ₉	87.0	45.3	21.4	93.4	37.3	17.0	11.7	9.4	7.9	6.2	5.2	0.0	3.8	0.1
C ₁₀	83.4	43.2	20.6	89.8	35.8	16.3	11.2	8.9	7.5	5.9	4.9	4.2	0.0	0.1
C ₁₁₊	65.9	31.2	19.2	69.5	26.1	12.1	8.1	6.1	4.9	3.6	2.9	2.3	1.9	0.0

TABLE B-2

Maxwell–Stefan diffusion coefficients, $\varphi_{ij} \times 10^9 \text{ m}^2 \cdot \text{s}^{-1}$, for the CO₂-rich fluid.

N₂ (0.00265), CO₂ (0.73787), H₂S (0.00925), C₁ (0.11917), C₂ (0.03804), C₃ (0.03287), C₄ (0.02825),
C₅ (0.01371), C₆ (0.00875), C₇ (0.00362), C₈ (0.00283), C₉ (0.00188), C₁₀ (0.00112), C₁₁₊ (0.00001),
T = 394.0 K, p = 13.56 MPa

	N ₂	CO ₂	H ₂ S	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀	C ₁₁₊
N ₂	0.0	119.8	111.9	126.4	105.7	95.3	88.7	83.7	80.1	76.9	74.5	72.5	70.9	60.5
CO ₂	119.8	0.0	101.5	124.9	91.4	76.1	67.1	60.8	56.4	52.5	49.7	47.4	45.5	34.5
H ₂ S	111.9	101.5	0.0	114.0	95.9	86.6	80.6	76.1	72.8	69.9	67.7	65.9	64.4	54.9
C ₁	126.4	124.9	114.0	0.0	106.7	95.4	88.1	82.7	78.8	75.3	72.8	70.7	68.9	57.9
C ₂	105.7	91.4	95.9	106.7	0.0	81.0	75.3	71.1	68.0	65.2	63.1	61.4	60.0	50.9
C ₃	95.3	76.1	86.6	95.4	81.0	0.0	67.9	64.2	61.4	59.0	57.1	55.6	54.2	46.1
C ₄	88.7	67.1	80.6	88.1	75.3	67.9	0.0	59.8	57.3	55.0	53.3	51.8	50.6	43.0
C ₅	83.7	60.8	76.1	82.7	71.1	64.2	59.8	0.0	54.3	52.2	50.6	49.2	48.1	41.0
C ₆	80.1	56.4	72.8	78.8	68.0	61.4	57.3	54.3	0.0	50.1	48.5	47.2	46.1	39.3
C ₇	76.9	52.5	69.9	75.3	65.2	59.0	55.0	52.2	50.1	0.0	46.7	45.4	44.4	37.9
C ₈	74.5	49.7	67.7	72.8	63.1	57.1	53.3	50.6	48.5	46.7	0.0	44.0	43.0	36.7
C ₉	72.5	47.4	65.9	70.7	61.4	55.6	51.8	49.2	47.2	45.4	44.0	0.0	41.9	35.8
C ₁₀	70.9	45.5	64.4	68.9	60.0	54.2	50.6	48.1	46.1	44.4	43.0	41.9	0.0	35.0
C ₁₁₊	60.5	34.5	54.9	57.9	50.9	46.1	43.0	41.0	39.3	37.9	36.7	35.8	35.0	0.0

TABLE B-3

Infinite dilution diffusion coefficients, $D_{ij}^\infty \times 10^9 \text{ m}^2 \cdot \text{s}^{-1}$, for the N₂-rich fluid.

T = 394.0 K, p = 15.89 MPa

	N ₂	CO ₂	H ₂ S	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀	C ₁₁₊
N ₂	0.0	111.7	48.1	207.8	82.8	40.3	28.6	23.1	19.6	18.2	15.2	13.3	11.9	0.5
CO ₂	170.0	0.0	39.8	171.0	68.1	33.9	24.3	19.8	16.9	15.8	13.1	11.5	10.3	0.4
H ₂ S	175.0	91.7	0.0	171.3	69.6	35.3	25.7	21.2	18.3	17.1	14.4	12.7	11.5	0.6
C ₁	219.4	119.0	50.7	0.0	85.2	43.3	31.6	26.0	22.4	20.9	17.6	15.6	14.0	0.6
C ₂	152.9	81.2	36.0	148.4	0.0	31.4	22.9	18.9	16.3	15.2	12.8	11.3	10.2	0.5
C ₃	124.9	65.2	29.6	124.8	51.0	0.0	18.9	15.5	13.3	12.5	10.4	9.2	8.2	0.4
C ₄	108.7	56.1	26.0	110.6	44.9	22.8	0.0	13.5	11.6	10.8	9.0	7.9	7.1	0.3
C ₅	98.1	50.1	23.6	101.1	40.8	20.7	14.9	0.0	10.4	9.7	8.0	7.0	6.3	0.3
C ₆	90.5	45.9	21.9	94.1	37.9	19.1	13.8	11.2	0.0	8.9	7.3	6.4	5.7	0.2
C ₇	85.1	42.9	20.7	89.0	35.7	18.1	13.0	10.5	8.9	0.0	6.8	5.9	5.3	0.2
C ₈	80.2	40.1	19.6	84.4	33.8	17.1	12.2	9.8	8.3	7.7	0.0	5.4	4.8	0.2
C ₉	76.4	38.0	18.7	80.8	32.2	16.3	11.6	9.3	7.9	7.3	5.9	0.0	4.5	0.1
C ₁₀	73.4	36.3	18.1	77.8	31.0	15.7	11.1	8.9	7.5	6.9	5.6	4.8	0.0	0.1
C ₁₁₊	55.1	25.2	15.8	57.7	21.9	11.2	7.8	6.0	4.8	4.3	3.2	2.6	2.2	0.0

TABLE B-4

Maxwell–Stefan diffusion coefficients, $\varphi_{ij} \times 10^9 \text{ m}^2 \cdot \text{s}^{-1}$, for the N₂-rich fluid.

N₂ (0.70796), CO₂ (0.01713), H₂S (0.00583), C₁ (0.18811), C₂ (0.03139), C₃ (0.01876), C₄ (0.01531),
C₅ (0.00646), C₆ (0.00328), C₇ (0.00148), C₈ (0.00148), C₉ (0.00178), C₁₀ (0.00103), C₁₁₊ (0.000001),
T = 394.0 K, p = 15.89 MPa

	N ₂	CO ₂	H ₂ S	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀	C ₁₁₊
N ₂	0.0	151.7	155.0	187.2	138.7	116.9	104.1	95.2	88.9	84.4	80.2	77.0	74.4	57.9
CO ₂	151.7	0.0	149.1	163.7	139.5	126.3	118.0	111.9	107.4	104.2	101.1	98.7	96.7	83.1
H ₂ S	155.0	149.1	0.0	165.5	141.4	128.2	119.8	113.8	109.3	106.0	102.9	100.4	98.4	84.8
C ₁	187.2	163.7	165.5	0.0	153.3	136.7	126.3	118.8	113.4	109.4	105.7	102.8	100.4	84.1
C ₂	138.7	139.5	141.4	153.3	0.0	119.4	111.5	105.8	101.5	98.4	95.4	93.1	91.2	78.2
C ₃	116.9	126.3	128.2	136.7	119.4	0.0	101.3	96.2	92.4	89.6	87.0	84.9	83.2	71.5
C ₄	104.1	118.0	119.8	126.3	111.5	101.3	0.0	90.0	86.5	83.9	81.4	79.5	77.9	67.0
C ₅	95.2	111.9	113.8	118.8	105.8	96.2	90.0	0.0	82.3	79.9	77.6	75.7	74.2	63.9
C ₆	88.9	107.4	109.3	113.4	101.5	92.4	86.5	82.3	0.0	76.8	74.6	72.8	71.4	61.5
C ₇	84.4	104.2	106.0	109.4	98.4	89.6	83.9	79.9	76.8	0.0	72.4	70.7	69.3	59.7
C ₈	80.2	101.1	102.9	105.7	95.4	87.0	81.4	77.6	74.6	72.4	0.0	68.6	67.3	58.0
C ₉	77.0	98.7	100.4	102.8	93.1	84.9	79.5	75.7	72.8	70.7	68.6	0.0	65.7	56.6
C ₁₀	74.4	96.7	98.4	100.4	91.2	83.2	77.9	74.2	71.4	69.3	67.3	65.7	0.0	55.5
C ₁₁₊	57.9	83.1	84.8	84.1	78.2	71.5	67.0	63.9	61.5	59.7	58.0	56.6	55.5	0.0

$$\sum_i D_{ii} > 0,$$

and

$$|D| > 0,$$

$$(C-3) \quad D_{ii} > 0, \quad i = 1, \dots, n-1,$$

$$\left(\sum_i D_{ii} \right)^2 - 4|D| > 0,$$

$$(C-4)$$

$$i = 1, \dots, n-1,$$

respectively.

Appendix D. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jct.2011.03.003.

References

- [1] H.T. Cullinan Jr., *Ind. Eng. Chem. Fundam.* 4 (1965) 133–139.
- [2] Y.L. Yao, *J. Chem. Phys.* 45 (1966) 110–115.
- [3] J.S. Kirkaldy, D. Weichert, Zia-UI-Haq, *Can. J. Phys.* 41 (1963) 2166–2173.
- [4] J.S. Kirkaldy, in: H. Herman (Ed.), *Advances in Materials Research*, vol. 4, John Wiley & Sons, Inc., New York, USA, 1970, pp. 55–100.
- [5] P.K. Gupta, A.R. Cooper Jr., *Physica* 54 (1971) 39–59.
- [6] D.G. Miller, V. Vitagliano, R. Sartorio, *J. Phys. Chem.* 90 (1986) 1509–1519.
- [7] J.S. Vrentas, C.M. Vrentas, *Ind. Eng. Chem. Res.* 44 (2005) 1112–1119.
- [8] S.R. de Groot, P. Mazur, *Non-equilibrium Thermodynamics*, Dover, New York, USA, 1984.
- [9] J.O. Hirschfelder, C.F. Curtiss, R.B. Bird, *Molecular Theory of Gases and Liquids*, John Wiley & Sons, Inc., New York, USA, 1954.
- [10] G.L. Standart, R. Taylor, R. Krishna, *Chem. Eng. Commun.* 3 (1979) 277–289.
- [11] R. Taylor, R. Krishna, *Multicomponent Mass Transfer*, John Wiley & Sons, New York, USA, 1993.
- [12] K. Ghorayeb, A. Firoozabadi, *AIChE J.* 46 (2000) 883–891.
- [13] A. Horn, C.R. Johnson, *Matrix Analysis*, Cambridge University Press, Cambridge, England, 1985.
- [14] G.T. Gilbert, *Am. Math. Monthly* 9 (1991) 44–46.
- [15] A. Firoozabadi, *Thermodynamics of Hydrocarbon Reservoirs*, McGraw-Hill, New York, USA, 1999.
- [16] A. Leahy-Dios, A. Firoozabadi, *AIChE J.* 53 (2007) 2932–2939.
- [17] H. Hoteit, E. Santiso, A. Firoozabadi, *Fluid Phase Equilib.* 241 (2006) 186–195.
- [18] B.E. Poling, J.M. Prausnitz, J.P. O'Connell, *The Properties of Gases and Liquids*, 5th ed., McGraw-Hill, New York, USA, 2001.
- [19] J.K. Burchard, H.L. Toor, *J. Phys. Chem.* 66 (1962) 2015–2022.
- [20] H.T. Cullinan, H.L. Toor, *J. Phys. Chem.* 69 (1965) 3941–3949.
- [21] A. Sathy, H.T. Cullinan, *AIChE J.* 21 (1975) 571–575.
- [22] T.K. Kett, D.K. Anderson, *J. Phys. Chem.* 73 (1969) 1268–1274.
- [23] A. Alimadadian, P. Colver, *Can. J. Chem. Eng.* 54 (1976) 208–213.
- [24] R.G. Mortimer, W.R. Marlow, J.L. Shenep, *Ind. Eng. Chem. Fundam.* 14 (1975) 114–119.
- [25] R.G. Mortimer, B.C. Hicks, *J. Phys. Chem.* 80 (1976) 1376–1380.
- [26] E.L. Cussler, E.N. Lightfoot, *J. Phys. Chem.* 69 (1965) 1135–1144.
- [27] A. Leahy-Dios, M.M. Bou-Ali, J.K. Platten, A. Firoozabadi, *J. Chem. Phys.* 122 (2005) 234502.
- [28] Q. Galand, S.V. Vaerenbergh, F. Montel, *Energy Fuels* 22 (2008) 770–774.
- [29] A. Koeninger, H. Wunderlich, W. Koehler, *J. Chem. Phys.* 132 (2010) 174506.
- [30] T. Grossmann, J. Winkelmann, *J. Chem. Eng. Data* 54 (2009) 405–410.
- [31] T. Grossmann, J. Winkelmann, *J. Chem. Eng. Data* 54 (2009) 485–490.
- [32] W.M. Clark, R.L. Rowley, *Int. J. Thermophys.* 6 (1985) 631–642.
- [33] F.O. Shuck, H.L. Toor, *J. Phys. Chem.* 67 (1963) 540–545.
- [34] T.H. Riede, E.U. Schlunder, *Chem. Eng. Sci.* 46 (1991) 609–617.
- [35] S. Rehfeldt, J. Stichlmair, *Fluid Phase Equilib.* 290 (2010) 1–14.
- [36] G.B. Ray, D.G. Leaist, *J. Chem. Eng. Data* 55 (2010) 1814–1820.
- [37] R.A. Graff, T.B. Drew, *Ind. Eng. Chem. Fundam.* 7 (1968) 490–497.
- [38] D. Buzatu, F.D. Buzatu, L. Paduano, R. Sartorio, *J. Solution Chem.* 36 (2007) 1373–1384.
- [39] V. Vitagliano, R. Sartorio, S. Scala, D. Spaduzzi, *J. Solution Chem.* 7 (1978) 605–621.
- [40] T. Grossmann, J. Winkelmann, *J. Chem. Eng. Data* 52 (2007) 336–340.
- [41] T. Grossmann, J. Winkelmann, *J. Chem. Eng. Data* 50 (2005) 1396–1403.
- [42] T. Grossmann, J. Winkelmann, *J. Chem. Eng. Data* 52 (2007) 341–344.
- [43] P.W.M. Rutten, *Diffusion in Liquids*, Ph.D. Thesis, Delft University, Delft, The Netherlands, 1992.
- [44] H. Kim, R.C. Deonier, G. Reinfelds, *J. Solution Chem.* 3 (1974) 445–453.
- [45] D.G. Leaist, *J. Chem. Soc., Faraday Trans.* 87 (1991) 597–601.
- [46] D.G. Leaist, *J. Phys. Chem.* 94 (1990) 5180–5183.
- [47] H. Kim, *J. Solution Chem.* 3 (1974) 149–159.
- [48] E.L. Cussler, P.J. Dunlop, *J. Phys. Chem.* 70 (1966) 1880–1888.
- [49] M.C. Yang, J.G. Albright, J.A. Rard, D.G. Miller, *J. Solution Chem.* 27 (1998) 309–329.
- [50] D. Kirstein, E. Kahrig, J. Erpenbeck, G. Dreyer, *Z. Phys. Chemie. Leipzig* 258 (1977) 289–296.
- [51] P.N. Henrion, *Trans. Faraday Soc.* 60 (1964) 75–82.
- [52] A.C.F. Ribeiro, M.C.F. Barros, V.M.M. Lobo, G. Quintanilla, M.A. Esteso, *J. Chem. Eng. Data* 55 (2010) 897–900.
- [53] L. Paduano, R. Sartorio, V. Vitagliano, L. Costantino, *J. Solution Chem.* 24 (1995) 1143–1153.
- [54] A.C.F. Ribeiro, C.I.A.V. Santos, V.M.M. Lobo, A.M.T.D.P.V. Cabral, F.J.B. Veiga, M.A. Esteso, *J. Chem. Thermodyn.* 41 (2009) 1324–1328.
- [55] A.C.F. Ribeiro, J.J.S. Natividade, M.A. Esteso, *J. Mol. Liq.* 156 (2010) 58–64.
- [56] J.G. Albright, O. Annunziata, D.G. Miller, L. Paduano, A.J. Pearlstein, *JACS* 121 (1999) 3256–3266.
- [57] A.C.F. Ribeiro, C.I.A.V. Santos, V.M.M. Lobo, A.M.T.D.P.V. Cabral, F.J.B. Veiga, M.A. Esteso, *J. Chem. Eng. Data* 54 (2009) 115–117.
- [58] P.Y. Lo, A.S. Myerson, *AIChE J.* 35 (1989) 676–678.
- [59] H. Kim, G. Reinfelds, *J. Solution Chem.* 2 (1973) 477–488.
- [60] L. Paduano, R. Sartorio, V. Vitagliano, *J. Phys. Chem. B* 102 (1998) 5023–5028.
- [61] G. Reinfelds, L.J. Gosting, *J. Phys. Chem.* 68 (1964) 2464–2470.
- [62] W.H. Chang, M.H. Li, *J. Chem. Eng. Jpn.* 41 (2008) 336–443.
- [63] C.C. Ko, W.H. Chang, M.H. Li, *J. Chin. Inst. Chem. Eng.* 39 (2008) 645–651.
- [64] P.H. Lin, C.C. Ko, M.H. Li, *Fluid Phase Equilib.* 276 (2009) 69–74.
- [65] D.G. Leaist, S.M. Abdu, *J. Chem. Eng. Data* 46 (2001) 922–926.
- [66] H.D. Ellerton, P.J. Dunlop, *J. Phys. Chem.* 71 (1967) 1538–1540.
- [67] H. Kim, *J. Solution Chem.* 3 (1974) 271–287.
- [68] D. Ciccarelli, L. Paduano, L. Costantino, O. Ortona, V. Vitagliano, *J. Mol. Liq.* 75 (1998) 169–180.
- [69] H.M. Halvorsen, E. Wygnal, M.R. MacIver, D.G. Leaist, *J. Chem. Eng. Data* 52 (2007) 442–448.
- [70] O. Annunziata, A. Vergara, L. Paduano, R. Sartorio, D.G. Miller, J.G. Albright, *J. Phys. Chem. B* 113 (2009) 13446–13453.
- [71] D.G. Leaist, L. Hao, *J. Solution Chem.* 22 (1993) 263–277.
- [72] L.A. Woolf, *J. Phys. Chem.* 67 (1963) 273–277.
- [73] P.J. Dunlop, *J. Phys. Chem.* 69 (1965) 4276–4283.
- [74] P.J. Dunlop, L.J. Gosting, *J. Phys. Chem.* 68 (1964) 3874–3876.
- [75] P.J. Dunlop, *J. Phys. Chem.* 61 (1957) 1619–1622.
- [76] H.D. Ellerton, P.J. Dunlop, *J. Phys. Chem.* 71 (1967) 1291–1297.
- [77] L. Paduano, R. Sartorio, V. Vitagliano, J.G. Albright, D.G. Miller, J. Mitchell, *J. Phys. Chem.* 94 (1990) 6885–6888.
- [78] L.A. Woolf, D.G. Miller, L.J. Gosting, *JACS* 84 (1962).
- [79] C.N. Pepela, P.J. Dunlop, *J. Chem. Eng. Data* 17 (1972) 207–208.
- [80] E.L. Cussler, P.J. Dunlop, *Aust. J. Chem.* 19 (1966) 1661–1665.
- [81] D.A. Ivanov, T. Grossmann, J. Winkelmann, *Fluid Phase Equilib.* 228–229 (2005) 283–291.
- [82] F.J. Kelly, *Diffusion and Viscosity in Three Component Systems*, Ph.D. Thesis, University of New England, Armidale, New South Wales, 1961.
- [83] P.J. Dunlop, *J. Phys. Chem.* 61 (1957) 994–1000.
- [84] S.W. Peng, A.N. Soriano, M.H. Li, *Fluid Phase Equilib.* 297 (2010) 1–5.
- [85] V. Vitagliano, R. Sartorio, O. Ortona, L. Paduano, G. D'Errico, F. Capuano, G. Mangiapia, *J. Mol. Liq.* 195 (2010) 70–75.
- [86] A.C.F. Ribeiro, M.N. Simoes, V.M.M. Lobo, A.M.T.D.P.V. Cabral, V.F.J. B. M.A. Esteso, *J. Chem. Eng. Data* 55 (2010) 2192–2194.
- [87] A.C.F. Ribeiro, A.C.G. Santos, V.M.M. Lobo, A.J.F.N. Sobral, A.M.T.D.P.V. Cabral, M.A. Esteso, *J. Chem. Thermodyn.* 42 (2010) 886–890.
- [88] A.C.F. Ribeiro, C.I.A.V. Santos, V.M.M. Lobo, M.A. Esteso, *J. Chem. Eng. Data* 55 (2010) 2610–2612.
- [89] P.E. Gerla, A.C. Rubiolo, *J. Food Eng.* 56 (2003) 401–410.
- [90] A. Deng, D.G. Leaist, *Can. J. Chem.* 69 (1991) 1548–1553.
- [91] A. Deng, D.G. Leaist, *J. Solution Chem.* 21 (1992) 15–22.
- [92] H. Fujita, L.J. Gosting, *J. Phys. Chem.* 64 (1960) 1256–1263.
- [93] R. Mathew, J.G. Albright, D.G. Miller, J.A. Rard, *J. Phys. Chem.* 94 (1990) 6875–6878.
- [94] J.G. Albright, S.M. Gillespie, J.A. Rard, D.G. Miller, *J. Chem. Eng. Data* 43 (1998) 668–675.
- [95] J.G. Albright, R. Mathew, D.G. Miller, *J. Phys. Chem.* 91 (1987) 210–215.
- [96] O. Annunziata, J.A. Rard, J.G. Albright, L. Paduano, D.G. Miller, *J. Chem. Eng. Data* 45 (2000) 936–945.
- [97] J. Fu, L. Paduano, J.A. Rard, J.G. Albright, D.G. Miller, *J. Chem. Eng. Data* 46 (2001) 601–608.
- [98] D.G. Leaist, L. Hao, *J. Phys. Chem.* 97 (1993) 1464–1469.
- [99] D.G. Leaist, P. Anderson, J.C. Elliot, *J. Chem. Soc., Faraday Trans.* 86 (1990) 3093–3095.
- [100] D.G. Leaist, M.A. Kanakos, *Phys. Chem. Chem. Phys.* 2 (2000) 1015–1021.
- [101] H. Lu, D.G. Leaist, *J. Chem. Soc., Faraday Trans.* 87 (1991) 3667–3670.
- [102] J.P. Mitchell, J.G. Albright, *J. Solution Chem.* 36 (2007) 1457–1468.
- [103] D.G. Miller, C.M. Lee, J.A. Rard, *J. Solution Chem.* 36 (2007) 1559–1567.
- [104] D.G. Miller, J.G. Albright, R. Mathew, C.M. Lee, J.A. Rard, L.B. Eppstein, *J. Phys. Chem.* 97 (1993) 3885–3899.
- [105] D.G. Miller, A.W. Ting, J.A. Rard, L.B. Eppstein, *Geochim. Cosmochim. Acta* 50 (1986) 2397–2403.
- [106] J.A. Rard, J.G. Albright, D.G. Miller, M.E. Zeidler, *J. Chem. Soc., Faraday Trans.* 92 (1996) 4187–4197.
- [107] J.A. Rard, D.G. Miller, *J. Phys. Chem.* 91 (1987) 4614–4620.
- [108] J.A. Rard, D.G. Miller, *J. Solution Chem.* 19 (1990) 129–148.
- [109] L. Paduano, R. Mathew, J.G. Albright, D.G. Miller, J.A. Rard, *J. Phys. Chem.* 93 (1989) 4366–4370.
- [110] R. Mathew, L. Paduano, J.G. Albright, D.G. Miller, J.A. Rard, *J. Phys. Chem.* 93 (1989) 4370–4374.
- [111] J.G. Albright, R. Mathew, D.G. Miller, J.A. Rard, *J. Phys. Chem.* 93 (1989) 2176–2180.
- [112] D.G. Leaist, *Can. J. Chem.* 63 (1985) 2933–2939.
- [113] L. Hao, D.G. Leaist, *J. Solution Chem.* 24 (1995) 523–535.
- [114] D.G. Miller, R. Sartorio, L. Paduano, J.A. Rard, J.G. Albright, *J. Solution Chem.* 25 (1996) 1185–1211.
- [115] H. Kim, *J. Chem. Eng. Data* 27 (1982) 255–256.
- [116] D.G. Leaist, *Electrochim. Acta* 33 (1988) 795–799.
- [117] L. Paduano, V. Vitagliano, C.D. Volpe, L. Costantino, *J. Solution Chem.* 21 (1992) 623–634.
- [118] H. Kim, G. Reinfelds, L.J. Gosting, *J. Phys. Chem.* 77 (1973) 934–940.
- [119] J. Wu, J.G. Albright, D.G. Miller, *J. Phys. Chem.* 98 (1994) 13054–13057.
- [120] M. Tanigaki, K. Kondo, M. Harada, W. Eguchi, *J. Phys. Chem.* 87 (1983) 586–591.

- [121] A. Revzin, *J. Phys. Chem.* 76 (1972) 3419–3429.
- [122] P.J. Dunlop, *J. Phys. Chem.* 63 (1959) 612–615.
- [123] D.G. Miller, V. Vitagliano, *J. Phys. Chem.* 90 (1986) 1706–1717.
- [124] P.J. Dunlop, L.J. Gosting, *J. Phys. Chem.* 63 (1959) 86–93.
- [125] P.J. Dunlop, L.J. Gosting, *JACS* 77 (1955) 5238–5249.
- [126] H. Fujita, L.J. Gosting, *JACS* 78 (1956) 1099–1106.
- [127] I.J. O'Donnell, L.J. Gosting, in: W.J. Hamer (Ed.), *The Structure of Electrolytic Solutions*, John Wiley & Sons, Inc., New York, USA, 1959, pp. 160–182.
- [128] R.P. Wendt, *J. Phys. Chem.* 66 (1962) 1279–1288.
- [129] D.G. Miller, L.B. Eppstein, *Trans. Am. Geophys. Union* 57 (1976) 1015.
- [130] G.P. Rai, H.T. Cullinan, *J. Chem. Eng. Data* 18 (1973) 213–214.
- [131] L. Paduano, R. Sartorio, V. Vitagliano, J.G. Albright, D.G. Miller, *J. Phys. Chem.* 96 (1992) 7478–7483.
- [132] K. MacEwan, D.G. Leaist, *Phys. Chem. Chem. Phys.* 5 (2003) 3951–3958.
- [133] D.G. Leaist, *Int. J. Phys. Chem. Ber. Der Bunsen-Ges.* 95 (1991) 117–122.
- [134] O. Annunziata, D.G. Miller, J.G. Albright, *J. Mol. Liq.* 156 (2010) 33–37.
- [135] D.G. Leaist, *J. Chem. Soc., Faraday Trans. 1* (83) (1987) 829–839.
- [136] R.A. Noulty, D.G. Leaist, *J. Phys. Chem.* 91 (1987) 1655–1658.

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