PARTIAL MOLAR VOLUMES AND DIFFUSION COEFFICIENTS FOR TERNARY SYSTEM WATER-CHLOROFORM-ACETIC ACID AT 25°C FOR DIFFERENT CHOICES OF SOLVENT

Daniela BUZATU1, Florin D. BUZATU2, Roberto SARTORIO3

The partial molar volumes and the diffusion coefficients, $D_{ij}$, for the ternary system water-chloroform-acetic acid at 25°C are reported at five compositions using different choices of solvent. The analyzed compositions have a fixed ratio between water and chloroform molar fractions and a decreasing amount of acetic acid, then approaching the binodal curve. The difficulty of interpreting the $D_{ij}$ is stressed and the use of different choices of solvent for the diffusive transport is suggested to extract from the diffusion coefficients all the possible information.

Keywords: ternary system, partial molar volume, diffusion coefficients, solvent choices

1. Introduction

The use of the Fick phenomenological law in describing the mutual diffusion phenomena [1] is motivated by the fact that both flows and concentration gradients can be easily determined:

$$-J_1 = (D_{11})_v \frac{\partial C_1}{\partial x} + (D_{12})_v \frac{\partial C_2}{\partial x}$$

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-\( J_2 = (D_{21})_v \frac{\partial C_1}{\partial x} + (D_{22})_v \frac{\partial C_2}{\partial x} \)

where \( J_1 \) and \( J_2 \) - the solute 1 (water) flux and respectively solute 2 (chloroform) flux (considering acetic acid as solvent), \((D_{11})_v\) and \((D_{22})_v\) - the main-term diffusion coefficients relating to the flux of component to its own concentration gradient, and \((D_{12})_v\) and \((D_{21})_v\) - the cross-term diffusion coefficients relating the flux of each component to the gradient of the other [2,3].

The index \( v \) from the diffusion coefficients shows that the experiment were done under the assumption the volume change on mixing and changes in concentrations across the diffusion boundary were small. Consequently, with a good approximation, the measured diffusion coefficients may be considered to be for the volume-fixed reference frame [4] defined by:

\[
\sum_{i=0}^{n} J_i \bar{V}_i = 0
\]

where \( \bar{V}_i \) is the partial molar volume of the \( i \)th species, and the subscript 0 denotes the solvent.

In performing diffusion experiments the knowledge of the density of the two solutions that will form the diffusion boundary, is necessary to be sure that, at least, the initial boundary is stable by gravitational point of view. The density of the two solution is usually measured just before the setting the diffusion experiment up. In the range of the average ternary composition, \((\bar{c}_1, \bar{c}_2)\), the solution density can be expressed as:

\[
\rho(c_1, c_2) = \rho(\bar{c}_1, \bar{c}_2) + H_1(c_1 - \bar{c}_1) + H_2(c_2 - \bar{c}_2) + \ldots
\]

and in the condition of differential diffusion as:

\[
\rho(c_1, c_2) = \rho(\bar{c}_1, \bar{c}_2) + H_1(c_1 - \bar{c}_1) + H_2(c_2 - \bar{c}_2)
\]

where:

\[
H_i = \left( \frac{\partial \rho}{\partial c_i} \right)_{c_j}
\]

From the \( \rho(\bar{c}_1, \bar{c}_2) \), \( H_1 \), \( H_2 \) values it is possible to obtain the partial molar volume of the three components of the solution just using the Gosting equation for the solutes [5]:

\[
\rho(\bar{c}_1, \bar{c}_2) = \rho(\bar{c}_1, \bar{c}_2) + H_1(c_1 - \bar{c}_1) + H_2(c_2 - \bar{c}_2)
\]
\[ \bar{V}_i = \frac{(MW)_i - 1000 \cdot d(c_1, c_2)}{d(c_1, c_2) - H_1 \cdot c_1 - H_2 \cdot c_2} \]

and for the solvent the relation:

\[ \bar{V}_0 = \frac{1000 - \bar{V}_1 \cdot c_1 - \bar{V}_2 \cdot c_2}{c_0} \]

The knowledge of the partial volume could be useful in calculating the diffusion coefficients using, in turn, all the components as the “solvent” [6].

In our system the relative amount of the three components is almost the same and it does not change very much at the different compositions and, the three components have similar hydrodynamic volumes. The choice of acetic acid as solvent is arbitrary and moreover for the last two points it can not be justified for its larger abundance respect to the other components. While in a binary system the value of the diffusion coefficients does not depend on the choice of the solvent, in a ternary system the four \( D_{ij} \) do depend on the choice of the solvent although the determinant \( \|D_{ij}\| \) is an invariant. Assuming the condition of differential diffusion, the following equations can be used to change the choice of the solvent [6].

\[
\begin{align*}
D^j_{ii} &= D^k_{ii} - (\bar{V}_i/\bar{V}) \cdot D^k_{ij} \\
D^j_{ik} &= -\left(\bar{V}_k/\bar{V}_j\right) \cdot D^k_{ij} \\
D^j_{ki} &= \left(\bar{V}_i/\bar{V}_k\right) \cdot \left[-D^k_{ii} + (\bar{V}_i/\bar{V}) \cdot D^k_{ij} - (\bar{V}_k/\bar{V}_i) \cdot D^k_{ji} + D^k_{jj}\right] \\
D^j_{kk} &= D^k_{jj} + (\bar{V}_i/\bar{V}_j) \cdot D^k_{ij}
\end{align*}
\]

We use the notation \( D^k_{ij} \) where the superscript \( k \) indicates the selected solvent.

### 2 Experimental

The compositions used for ternary system water- chloroform-acetic acid in this paper (left line) and from the reference [7,8,12] are reported in Fig.1:
From Fig 1, it follows that, for our system, the ratio between water and chloroform is constant, $K = 4.99 \pm 0.02$ (acetic acid is always in excess in respect to chloroform). That means a larger amount of water in respect to chloroform.

**Chemicals.** Acetic acid glacial (declared purity 99.8%) and Chloroform (declared purity 99.8%) have been furnished by Aldrich and used without further purification; their molecular weight were taken to be respectively 60.05 g mol$^{-1}$ and 119.38 g mol$^{-1}$. Double distilled water was always used; its molar mass was taken to be 18.015 g mol$^{-1}$.

**Solution preparation.** Each solution for the diffusion runs was prepared by weighing all components in a 100-ml flask. The double-distilled water has been weighted at first, then acetic acid, and lastly chloroform was added. This is the best way to prepare the solutions, because there is a problem about the high vapor pressure (21.2 kPa) of chloroform [9]. To minimize the chloroform evaporation, it was added as last component, so its addition forms directly the ternary system, in which the vapor pressure of chloroform is notably reduced. Flasks with very small bottleneck and glass syringes for the addition of chloroform and acetic acid were also used.

**Density measurements.** The density data were computed by Anton Paar density meter model 5000. It is an oscillating U–tube density meter which measures in wide viscosity and temperature ranges. We set the temperature at
25.000 ± 0.001°C. The Anton Paar densimeter model 5000 computes densities with ± 5 · 10⁻⁶ g cm⁻³ of error.

**Diffusion experiments.** The diffusion experiments were performed using the Gouy diffusiometer located at the University of Naples. A brief description of the apparatus and of the experimental procedure is reported in the paper [10].

3. Results and conclusions

In the Table 2 are done the values of partial molar volume for the three components used in the experiments at the five concentration points (Table 1). As can be seen from the Table 2, while the chloroform (2) partial molar volume is almost constant in the estimated error, and while the acetic acid (3) partial molar volume shows a small decrease, the water (1) partial molar volume increases notably when the acetic acid concentration in the system is decreasing. The significant variation of the water partial molar volume can be related to the variation in the water structure in hydrating hydrophilic or hydrophobic molecules. In presence of a large amount of acetic acid, the water molecules do preferentially hydrate the hydrophilic carboxylic group (both undissociated or dissociated) with the well known electrostrictional effect [11], and that produces a decrease of the water partial molar volume. At the decreasing acetic acid amount in solution, the water molecules will be less involved in hydrophilic salvation cospheres and then the partial molar volume will increase [11].

<table>
<thead>
<tr>
<th>&lt;math&gt;X_1&lt;/math&gt;</th>
<th>&lt;math&gt;X_2&lt;/math&gt;</th>
<th>&lt;math&gt;X_3&lt;/math&gt;</th>
<th>&lt;math&gt;d&lt;/math&gt;</th>
<th>&lt;math&gt;c_1&lt;/math&gt;</th>
<th>&lt;math&gt;c_2&lt;/math&gt;</th>
<th>&lt;math&gt;c_3&lt;/math&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;math&gt;X_1&lt;/math&gt;</td>
<td>0.2499</td>
<td>0.0503</td>
<td>0.7000</td>
<td>1.095000</td>
<td>5.212</td>
<td>1.049</td>
</tr>
<tr>
<td>&lt;math&gt;X_2&lt;/math&gt;</td>
<td>0.3333</td>
<td>0.0667</td>
<td>0.6000</td>
<td>1.109980</td>
<td>7.406</td>
<td>1.482</td>
</tr>
<tr>
<td>&lt;math&gt;X_3&lt;/math&gt;</td>
<td>0.4150</td>
<td>0.0830</td>
<td>0.5020</td>
<td>1.127350</td>
<td>9.844</td>
<td>1.968</td>
</tr>
<tr>
<td>&lt;math&gt;X_4&lt;/math&gt;</td>
<td>0.4597</td>
<td>0.0925</td>
<td>0.4480</td>
<td>1.138010</td>
<td>11.322</td>
<td>2.278</td>
</tr>
<tr>
<td>&lt;math&gt;X_5&lt;/math&gt;</td>
<td>0.5000</td>
<td>0.1000</td>
<td>0.4000</td>
<td>1.145760</td>
<td>12.741</td>
<td>2.548</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>&lt;math&gt;\bar{V}_1&lt;/math&gt;</th>
<th>&lt;math&gt;\bar{V}_2&lt;/math&gt;</th>
<th>&lt;math&gt;\bar{V}_3&lt;/math&gt;</th>
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<tr>
<td>&lt;math&gt;cm^3 mol^{-1}&lt;/math&gt;</td>
<td>&lt;math&gt;cm^3 mol^{-1}&lt;/math&gt;</td>
<td>&lt;math&gt;cm^3 mol^{-1}&lt;/math&gt;</td>
</tr>
<tr>
<td>1</td>
<td>13.9₄</td>
<td>82.1₅</td>
</tr>
<tr>
<td>2</td>
<td>16.0₉</td>
<td>83.4₇</td>
</tr>
<tr>
<td>3</td>
<td>16.4₉</td>
<td>83.7₂</td>
</tr>
<tr>
<td>4</td>
<td>17.9₆</td>
<td>83.2₅</td>
</tr>
<tr>
<td>5</td>
<td>18.1₇</td>
<td>84.0₈</td>
</tr>
</tbody>
</table>

Note: (1) – water; (2) – chloroform; (3) acetic acid
Diffusion coefficients. The diffusion coefficients for the three different solvents are reported in Tables 3 (acetic acid as solvent (3)) and Table 4 (water (1) and respectively chloroform (2) as solvent). We use the notation $D_{ij}^k$ where the superscript k indicates the selected solvent:

<table>
<thead>
<tr>
<th></th>
<th>$(D_{11}^3)_V$</th>
<th>$(D_{12}^3)_V$</th>
<th>$(D_{13}^3)_V$</th>
<th>$(D_{22}^3)_V$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$10^9$ m² s⁻¹</td>
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<td>$10^9$ m² s⁻¹</td>
<td>$10^9$ m² s⁻¹</td>
</tr>
<tr>
<td>1</td>
<td>0.685 ±0.069</td>
<td>0.394 0.079</td>
<td>0.107 0.021</td>
<td>0.753 0.075</td>
</tr>
<tr>
<td>2</td>
<td>0.632 0.063</td>
<td>0.451 0.090</td>
<td>0.138 0.028</td>
<td>0.811 0.081</td>
</tr>
<tr>
<td>3</td>
<td>0.564 ±0.056</td>
<td>0.403 0.081</td>
<td>0.185 0.037</td>
<td>0.728 0.073</td>
</tr>
<tr>
<td>4</td>
<td>0.386 ±0.039</td>
<td>0.540 0.089</td>
<td>0.117 0.023</td>
<td>0.699 ±0.070</td>
</tr>
<tr>
<td>5</td>
<td>0.406 ±0.041</td>
<td>0.461 ±0.092</td>
<td>0.181 ±0.036</td>
<td>0.544 ±0.054</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$(D_{22}^1)_V$</th>
<th>$(D_{23}^1)_V$</th>
<th>$(D_{32}^1)_V$</th>
<th>$(D_{33}^1)_V$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$10^9$ m² s⁻¹</td>
<td>$10^9$ m² s⁻¹</td>
<td>$10^9$ m² s⁻¹</td>
<td>$10^9$ m² s⁻¹</td>
</tr>
<tr>
<td>1</td>
<td>0.311 -0.465</td>
<td>0.456 1.362</td>
<td>0.632 -0.280</td>
<td>-0.077 1.041</td>
</tr>
<tr>
<td>2</td>
<td>0.183 -0.448</td>
<td>0.513 1.272</td>
<td>0.533 -0.289</td>
<td>-0.098 0.922</td>
</tr>
<tr>
<td>3</td>
<td>0.001 -0.479</td>
<td>0.621 1.219</td>
<td>0.420 -0.304</td>
<td>-0.122 0.799</td>
</tr>
<tr>
<td>4</td>
<td>-0.043 -0.451</td>
<td>0.581 1.124</td>
<td>0.342 -0.307</td>
<td>-0.125 0.739</td>
</tr>
<tr>
<td>5</td>
<td>-0.139 -0.463</td>
<td>0.637 1.090</td>
<td>0.274 -0.309</td>
<td>-0.137 0.678</td>
</tr>
</tbody>
</table>

As we can see all main term of diffusion coefficients are positive except the chloroform main diffusion coefficients at the compositions 4 and 5 using water as solvent, $D_{22}$. The cross diffusion coefficient are both positive using acetic acid as solvent, are both negative using chloroform as solvent, and one is positive, the $D_{32}$, and one is negative, $D_{23}$, when water is used as a solvent.

3. Conclusion

In the examined system and in the explored composition range the interpretation of the experimental diffusion coefficients is very difficult due to the comparable amounts of the three components and the large expected variation of both the hydrodynamic and thermodynamic contributions to the $D_{ij}$. In this case
the choice of different solvents in computing the diffusion coefficients can be very useful to extract from the $D_{ij}$ all the information they contain. This approach, because of its simplicity, could be extended to all the ternary systems. Another way that can help to look at the information contained in the Fick diffusion coefficients is to use a different reference frame [12].

Acknowledgement

The authors do like to thank Professor V. Vitagliano for the helpful discussion and suggestions. This research was supported by the 15th Executive Program of Scientific and Technological Cooperation between Italy and Romania 2006-2008.

REFERENCES