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

Daniela BUZATU[1], Florin D. BUZATU[2], Roberto SARTORIO[3]

Sunt prezentate volumele molare paţiale şi coeficieţii de difuzie D_{ij} pentru sistemul ternar apă-cloroform-acid acetic la 25°C pentru diferite alegeri ale solventului. Compoziţiile analizate au un raport fixat între fracţiile molare ale apei si cloroformului precum şi o cantitate descresătoare de acid acetic, valori ce se apropie de curba binodala. Deoarece interpretarea coeficienţilor D_{ij} este dificilă s-a recurs la schimbarea rolului de „solvent" in vederea extragerii tuturor informaţiilor posibile din valorile coeficienţiilor de difuzie.

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:

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

[1] Prof., Physics Department, University POLITEHNICA of Bucharest 77206, Romania, e-mail; buzatu@physics.pub.ro
[2] Senior Ressearcher, Institute for Atomic Physics, Atomistilor 407, Jud. Ilfov, Bucharest, Roamnia
[3] Associate Prof., Chemistry Department University "Federico II" of Naples Complesso Monte Sant'Angelo, Via Cinthia, Italy

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

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 ith 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, $\left(\bar{c}_1, \bar{c}_2\right)$, the solution density can be expressed as:

$$\rho\left(c_1, c_2\right) = \rho\left(\bar{c}_1, \bar{c}_2\right) + H_1\left(c_1 - \bar{c}_1\right) + H_2\left(c_2 - \bar{c}_2\right) + \ldots$$

and in the condition of differential diffusion as:

$$\rho\left(c_1, c_2\right) = \rho\left(\bar{c}_1, \bar{c}_2\right) + H_1\left(c_1 - \bar{c}_1\right) + H_2\left(c_2 - \bar{c}_2\right)$$

where:

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

From the $\rho\left(\bar{c}_1, \bar{c}_2\right)$, 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]:

$$\overline{V}_i = \frac{(MW)_i - 1000 \cdot d\left(\overline{c}_1, \overline{c}_2\right)}{d\left(c_1, c_2\right) - H_1 \cdot c_1 - H_2 \cdot c_2}$$

and for the solvent the relation:

$$\overline{V}_0 = \frac{1000 - \overline{V}_1 \cdot c_1 - \overline{V}_2 \cdot c_2}{c_0}$$

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 $\left\|D_{ij}\right\|$ is an invariant. Assuming the condition of differential diffusion, the following equations can be used to change the choice of the solvent [6].

$$\begin{aligned}
D_{ii}^j &= D_{ii}^k - \left(\overline{V}_i / \overline{V}_j\right) \cdot D_{ij}^k \\
D_{ik}^j &= -\left(\overline{V}_k / \overline{V}_j\right) \cdot D_{ij}^k \\
D_{ki}^j &= \left(\overline{V}_i / \overline{V}_k\right) \cdot \left[-D_{ii}^k + \left(\overline{V}_i / \overline{V}_j\right) \cdot D_{ij}^k - \left(\overline{V}_k / \overline{V}_i\right) \cdot D_{ji}^k + D_{jj}^k\right] \\
D_{kk}^j &= D_{jj}^k + \left(\overline{V}_i / \overline{V}_j\right) \cdot D_{ij}^k
\end{aligned}$$

We use the notation D_{ij}^k 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:

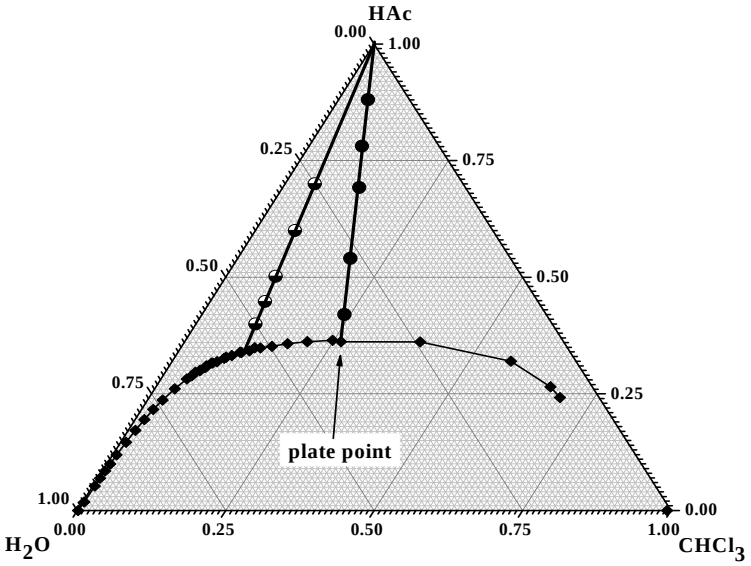

Fig.1**:** Triangular diagram in molar fraction. Average compositions analyzed in the paper (the left line)

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 $\pm 5 \cdot 10^{-6}$ 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 un-dissociated 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 1

	X_1	X_2	X_3	d	c_1	c_2	c_3
				g cm^{-3}	mol dm^{-3}	mol dm^{-3}	mol dm^{-3}
1	0.2499	0.0503	0.7000	1.095000	5.212	1.049	14.585
2	0.3333	0.0667	0.6000	1.109980	7.406	1.482	13.316
3	0.4150	0.0830	0.5020	1.127350	9.844	1.968	11.907
4	0.4597	0.0925	0.4480	1.138010	11.322	2.278	11.025
5	0.5000	0.1000	0.4000	1.145760	12.741	2.548	10.192

Table 2

	$\overline{V}_1$	$\overline{V}_2$	$\overline{V}_3$
	cm^3 mol^{-1}	cm^3 mol^{-1}	cm^3 mol^{-1}
1	13.9_4	82.1_5	57.6_7
2	16.0_1	83.4_7	56.9_0
3	16.4_8	83.7_2	56.5_2
4	17.9_6	83.2_5	55.0_6
5	18.1_1	84.0_9	54.4_6

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 3

	$(D_{11}^{3})_V$	$(D_{12}^{3})_V$	$(D_{21}^{3})_V$	$(D_{22}^{3})_V$
	10^9 m^2 s^{-1}	**10^9 m^2 s^{-1}**	**10^9 m^2 s^{-1}**	**10^9 m^2 s^{-1}**
	0.685 ±0.069	0.394 0.079	0.107 0.021	0.753 0.075
	0.632 0.063	0.451 ±0.090	0.138 0.028	0.811 0.081
	0.564 ±0.056	0.403 0.081	0.185 0.037	0.728 0.073
	0.386 ±0.039	0.540 0.089	0.117 0.023	0.699 ±0.070
	0.406 ±0.041	0.461 ±0.092	0.181 ±0.036	0.544 ±0.054

Table 4

	$\left(D_{22}^{1}\right)_V$	$\left(D_{23}^{1}\right)_V$	$\left(D_{32}^{1}\right)_V$	$\left(D_{33}^{1}\right)_V$		$\left(D_{11}^{2}\right)_V$	$\left(D_{13}^{2}\right)_V$	$\left(D_{31}^{2}\right)_V$	$\left(D_{33}^{2}\right)_V$
	10^9 m^2 s^{-1}	**10^9 m^2 s^{-1}**	**10^9 m^2 s^{-1}**	**10^9 m^2 s^{-1}**		**10^9 m^2 s^{-1}**	**10^9 m^2 s^{-1}**	**10^9 m^2 s^{-1}**	**10^9 m^2 s^{-1}**
1	0.311	-0.465	0.456	1.362		0.632	-0.280	-0.077	1.041
2	0.183	-0.448	0.513	1.272		0.533	-0.289	-0.098	0.922
3	0.001	-0.479	0.621	1.219		0.420	-0.304	-0.122	0.799
4	-0.043	-0.451	0.581	1.124		0.342	-0.307	-0.125	0.739
5	-0.139	-0.463	0.637	1.090		0.274	-0.309	-0.137	0.678

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}^{1}.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}^{1}, and one is negative, D_{23}^{1}, 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].

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