

HYDRODYNAMIC AND THERMODYNAMIC ASPECTS OF DIFFUSION COEFFICIENTS IN THE TERNARY SYSTEM WATER-CHLOROFORM-ACETIC ACID AT 25°C

Daniela BUZATU¹, Ana-Maria POPOVICI², Florin Dorian BUZATU³, Luigi PADUANO⁴, Roberto SARTORIO⁵

Studiul teoretic și experimental al fenomenului de separare de fază în lichide parțial miscibile este de interes pentru aplicațiile sale din domeniul farmaceutic sau biotehnologic. În această lucrare am studiat sistemul ternar acid acetic-apă-chloroform la 25 °C, în procesul de difuzie. Au fost determinați cei patru coeficienți de difuzie pentru cinci compoziții medii ale sistemului; s-a calculat determinantul acestora și s-a determinat, prin extrapolare din zona stabilă în zona instabilă, punctul de pe spinodala sistemului comparându-se ulterior cu cel teoretic obținut din echivalența modelelor Wheeler-Widom și Ising de spin ½ pentru magneți [1,2].

The theoretical and experimental investigation for phase separation in partially miscible liquids is important for their applications in pharmaceutical or biotechno-logical fields. In this paper we studied the ternary system water-chloroform-acetic acid at 25°C, in the diffusion process. We determined the four diffusion coefficients for five average compositions of this ternary system; we calculated the determinant for this experimental points and we determined, by extrapolation from homogenous to heterogeneous zone, the point of the spinodal curve; we compared this point with the theoretical one obtained from the equivalence between the Wheeler- Widom model and the spin ½ Ising model for magnets [1,2].

Keywords: ternary system, diffusion coefficients, spinodal curve

¹Reader, Physics Department, University “Politehnica” Bucharest, ROMANIA

²Lecturer, Physics Department, University “Politehnica” Bucharest, ROMANIA

³ Researcher, Horia Hulubei National Institute for Physics and Nuclear Engineering, Bucharest, ROMANIA

⁴Prof., Chemistry Department University “Federico II” of Naples Complesso Monte Sant’Angelo, Via Cinthia, ITALY

⁵ Chemistry Department University “Federico II” of Naples Complesso Monte Sant’Angelo, Via Cinthia, ITALY

1. Introduction

The complete description of an n -solute system requires an $n \times n$ matrix of diffusion coefficients relating the flux of each solute component to the gradients of all solute components [3]. In ternary systems ($n = 2$), our case, the one-dimensional flux relations could be written as:

$$-J_1 = (D_{11})_v \frac{\partial C_1}{\partial x} + (D_{12})_v \frac{\partial C_2}{\partial x} \quad (1)$$

$$-J_2 = (D_{21})_v \frac{\partial C_1}{\partial x} + (D_{22})_v \frac{\partial C_2}{\partial x} \quad (2)$$

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 [4,5]. 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 [6] defined by:

$$\sum_{i=0}^n J_i \bar{V}_i = 0 \quad (3)$$

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

The use of the Fick phenomenological law in describing the mutual diffusion phenomena is motivated by the fact that both flows and concentration gradients can be easily determined. However the concentration gradient is not the real “driving force” of the diffusion phenomena [7]. This is evident when a diffusion boundary is formed between two different phases in chemical equilibrium. In this case, in spite of the difference in the concentration of the components across the boundary diffusion does not take place. Therefore the real thermodynamic driving force of diffusion is the chemical potential gradient, and the Fick’s diffusion coefficients can then be expressed as:

$$\begin{bmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{bmatrix} = \begin{bmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{bmatrix} \times \begin{bmatrix} \mu_{11} & \mu_{12} \\ \mu_{21} & \mu_{22} \end{bmatrix} \quad (4)$$

where the L_{ij} are the thermodynamic diffusion coefficients and μ_{ij} are the derivatives of the chemical potentials:

$$\mu_{ij} = \left(\frac{\partial \mu_i}{\partial c_j} \right)_{c_i} \quad (5)$$

The L_{ij} 's account for the hydrodynamic and the μ_{ij} 's for the thermodynamic aspect of diffusion and they are not completely independent. According to equation (4), it is in principle possible to obtain, by the mutual diffusion coefficients, information of both hydrodynamic and thermodynamic of the system under investigation. This essentially means that it is possible to obtain equilibrium information by a transport technique.

The correlation between the diffusion coefficients and the thermodynamic properties of the system was used in the last seventy [8,9] to analyze the properties of the Fick D_{ij} at the plate point of the same ternary system as ours with a large solubility gap: water (W,1)-chloroform(CHCl₃,2)-acetic acid(AcH,3). Because of the thermodynamic contribution to mutual diffusion coefficients, the determinant of the matrix of the Fick D_{ij} , $\|D_{ij}\|$, must be zero at the plait point and on the spinodal curve, (the plait point is common to the binodal and spinodal curves) [9]. The theoretical condition $\|D_{ij}\|=0$ for the point belonging to the spinodal curve, can be used to experimentally determine this curve. In fact, using the diffusion coefficients experimentally determined in the homogeneous region, and their interpolation as a function of the system composition, the spinodal composition just corresponds to that for which the condition $\|D_{ij}\|=0$ is verified.

2. Experimental

The compositions used for ternary system water- chloroform-acetic acid in this paper (left line) and from the reference [8,9] 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.

This choice has the reason to simplify the solution preparation limiting the chloroform evaporation during the weights.

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} .

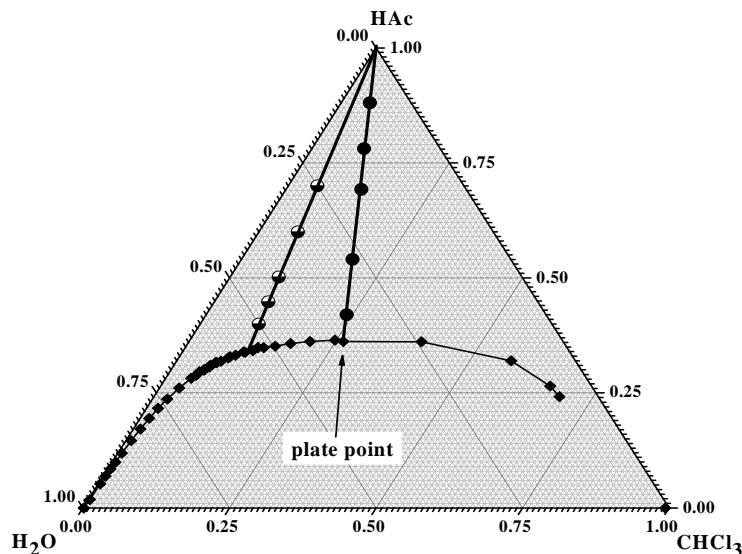


Fig.1:
Triangular diagram in molar fraction. Average compositions analyzed in the paper (the left line)

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 [10]. 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 $25.000 \pm 0.001^\circ\text{C}$. The Anton Paar densimeter model 5000 computes densities with $\pm 5 \cdot 10^{-6} \text{ g cm}^{-3}$ of error.

Diffusion experiments. The diffusion experiments were performed using the Gouy diffusimeter located at the University of Naples. A brief description of the apparatus and of the experimental procedure is reported in a recent paper [11].

3. Results and conclusions

The average compositions used in our diffusion experiments are reported in Table 1 in molar fraction and in molarity scale. The measured densities are also reported:

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

For any average composition, at least three independent Gouy experiments were performed. Each experiment requires the preparation of two solutions, top and bottom.

We calculated the four diffusion coefficients in the volume fixed reference frame using acetic acid as solvent as is shown in the Table 2.

Table 2

	$(D_{11}^0)_V$	$(D_{12}^0)_V$	$(D_{21}^0)_V$	$(D_{22}^0)_V$
	$10^9 \text{ m}^2 \text{ s}^{-1}$			
1	0.685 ± 0.069	0.394 ± 0.079	0.107 ± 0.021	0.753 ± 0.075
2	0.632 ± 0.063	0.451 ± 0.090	0.138 ± 0.028	0.811 ± 0.081
3	0.564 ± 0.056	0.403 ± 0.081	0.185 ± 0.037	0.728 ± 0.073
4	0.386 ± 0.039	0.540 ± 0.089	0.117 ± 0.023	0.699 ± 0.070
5	0.406 ± 0.041	0.461 ± 0.092	0.181 ± 0.036	0.544 ± 0.054

The choice of acetic acid as solvent is arbitrary. 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 $\|D_{ij}\|$ is an invariant. In Ref. [12] we calculated also the coefficients D_{ij} choosing as solvent the water and the chloroform; also we used another reference frame, “solvent fixed reference frame” defined by relation $J_k = 0$ where the component k is chosen as the solvent. In this way we could extract from D_{ij} all the information important for the transport process.

In Table 3 are reported the calculated values for the determinant of the matrix of the Fick D_{ij} , $\|D\|$ for each experimental point:

Table 3

Point	D
1	0.483 ± 0.076
2	0.439 ± 0.072
3	0.312 ± 0.056
4	0.222 ± 0.045
5	0.139 ± 0.035

By an extrapolation procedure, the determinant of diffusion coefficients matrix $\|D\|$ approaches to zero at the following composition point:

$$x_{\text{AcH}} = 0.33$$

$$x_{\text{H}_2\text{O}} = 0.559$$

$$x_{\text{CHCl}_3} = 0.111$$

In Fig.2 we represented this spinodal point, S. As we see from Fig.2, the spinodal point S belongs to the theoretical spinodal curve obtained by the model described in [1,2].

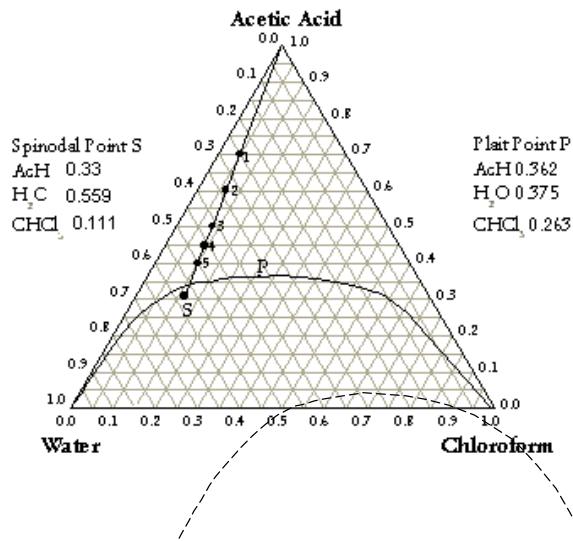


Fig.2: Triangular diagram in molar fraction; the binodal (continue) and the spinodal curve (dashed); the plait point P and the S point belonging to the spinodal

Acknowledgement

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

R E F E R E N C E S

- [1] *Huckaby, D., Pekalski, A., Buzatu, D., Buzatu, F.D.*, "Amphiphile-rich phase in a model ternary solution on the honeycomb lattice", *Journal of Chemical Physics* Vol 115 (14), pag. 6775-6779, 2001.
- [2] *Buzatu, F.D., Buzatu, D., Albright, J.G.*, "Spinodal curve of a model ternary solution", *Journal of Solution Chemistry*, Vol. 30 (11), pag. 969-983, 2001.
- [3] *Onsager, L.* Ann.N.Y.Acad.Sci, 1946, 241-265.
- [4] *Tyrrel, H.J.V.; Harris K.R.* "Diffusion in Liquids" Butterworths, London 1984.
- [5] *Miller, D.G.; Albright, J.G.* "Measurements of the Transport Properties of Fluids: Experimental Thermodynamics." Wakeham W.A., Nagashima, A., Sengers, J.V., Eds., Blackwell Scientific Publications: Oxford, 1991.
- [6] *Hooyman, G.J.; Holtan, H.; Mazur, P.; de Groot, S.R.* *Physica* 1953, 19, 1095-1108.
- [7] *Prigogine, I.* "Non-Equilibrium Thermodynamics" North-Holland, Amsterdam, 1962.

- [8] *Othmer, D.F.; Ku, P.L.* “Solubility data for ternary liquid systems-AcOH and HCO₂H distributed between CHCl₃ and H₂O.” *Journal of Chemical and Engineering Data* (1960), 5(No. 1), 42-44.
- [9] *Vitaglano, V.; Sartorio, R.; Scala, S.; Spaduzzi, D.* “Diffusion in a ternary system and the critical mixing point.”, *Journal of Solution Chemistry* (1978), 7(8), 605-621.
- [10] *McGarry, J.* “Correlation and prediction of the vapor pressures of pure liquids over large pressure ranges.”, *Industrial & Engineering Chemistry Process Design and Development* (1983), 22(2), 313-322.
- [11] *Vergara, A.; Capuano, F.; Paduano, L.; Sartorio, R.* “Lysozyme Mutual Diffusion in Solutions Crowded by Poly(ethylene glycol).”, *Macromolecules* (2006), 39(13), 4500-4506
- [12] *Buzatu, D., Buzatu, F.D., Paduano,L., Sartorio, R.*, “Diffusion coefficients in the ternary system water-chloroform-acetic acid at 25°C. Part 1, *Journal of Solution Chemistry*, to be published.