Barotropic phenomena in binary mixtures

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ABSTRACT

This contribution aims to theoretically describe the most common cases of mass and molar density inversions, as they can be observed in multi-component fluid mixtures in sub-critical phase equilibrium. These phenomena – also known as barotropy – affect the relative position of phases in a gravitational field for the case of mass barotropy, while the total population of species along the interfacial length is drastically affected for the case of molar barotropy. Rigorous and analytical relationships are developed here to detect both mass and molar density inversions ending at the critical points of mixtures. These conditions, which are useful to describe the existence and persistence of density inversions, are then applied to unequivocally demonstrate that mass and molar barotropy are physically independent phenomena. Qualitative evidence pointing to that conclusion is discussed at the light of the global phase diagram of van der Waals mixtures composed by molecules of different size. Particularly, it has been established that molar density inversions appearing in feasible temperature ranges are sensitive to differences between the molecular hard core volumes of the constituents, a conclusion that is well supported by experimental results. Mass density inversions, in contrast, depend not only on the molecular size but also in the molecular weights of the constituents, in such a way that mixtures may exhibit mass barotropy without exhibiting molar inversions, and vice versa.

Analytical relationships for establishing the slope of density inversions on a $P–T$ projection have also been obtained both for mass and molar barotropy. From the comparison with the temperature slope of the three-phase line, we conclude about the possibility of observing density inversions between immiscible liquid phases or between a liquid and a gas phase.

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1. Introduction

Barotropy – also known as *density* or *volume inversions* – corresponds to a singular condition of phase equilibrium where it is observed that the densities of – at least – two phases coexisting in a heterogeneous mixture invert [1–3]. Isopycnicity, in turn, corresponds to the condition where a barotropic point or a density inversion exactly occurs [3]. In general, density inversions may be primarily classified in terms of mass or molar barotropy depending on the units in which volumes become equivalent at the specific isopycnic conditions. Particularly, from a mechanical viewpoint, mass barotropy is a phenomenon that affects the relative position of the involved phases in a gravitational field, while it has been reported that the total population of species (or total density

profiles) is affected along the interfacial length for the case of molar barotropy [4].

In a recent publication, Tardón et al. [4] developed a set of rigorous mathematical conditions for detecting ranges of molar isopycnicity. As it was established in that paper, in addition to the necessary conditions of phase equilibrium, a heterogeneous mixture exhibiting molar isopycnicity between its α-β phases is characterized by an inversion of molar volumes, $\tilde{v}$ (or molar densities ρ),

$$\tilde{v}^{\alpha} = \tilde{v}^{\beta} \;\Leftrightarrow\; \rho^{\alpha} = \rho^{\beta} \tag{1}$$

From their results systematically applied to mixtures in the vicinity of the critical point, Tardón et al. [4] were able to demonstrate that a stable critical molar density inversion point (*CMoDIP*) of a binary mixture satisfies the following relationships,

$$\tilde{A}_{2x} = \tilde{A}_{3x} = \tilde{A}_{xv} = 0 \tag{2}$$

Here, $\tilde{A}$ corresponds to the Helmholtz energy function of the mixture while $\tilde{A}_{mxnv}$ is a shorthand notation for the partial

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$\tilde{A}$	molar Helmholtz energy funcion
a	van der waals attractive/cohesive parameter
b	covolume/repulsive parameter
$\tilde{G}$	Gibbs energy function
$\overline{G}_i$	partial molar Gibbs energy function of the ith compound
k_{ij}	binary interaction parameter between the ith and jth compound
M_w^π	molecular weight of the mixture in the phase π
$M_{w,i}$	molecular weight of the ith compound
M_{nxmTkP}	partial derivative of the M function defined in Eq. (27)
N_A	Avogadro constant
P	pressure
q	molecular weight ratio defined in Eq. (7)
R	universal gas constant
T	absolute temperature
$\tilde{v}$	molar volume of the phase π
$\hat{v}$	mass volume of the phase π
x_i^π	mole fraction of the ith compound in the phase π

Subscript and superscript

c	critical state
r	reference state
i, j	refers to ith or jth compound

Greek letters

α, β, γ	fluid phases
ζ	global coordinate defined in Eq. (15)
θ_i	shorhand notations defined in Eqs. (52)–(54)
Λ	global coordinate defined in Eq. (16)
μ_i^π	chemical potential of the ith compound in the phase π
ξ	global coordinate defined in Eq. (14)
ρ	molar density
$\hat{\rho}$	mass density
σ	molecular diameter

Abbreviations

CMaDIP	critical mass density inversion point
CEP	critical end point
CLMaDI	closed loops of mass density inversion
CMoDIP	critical molar density inversion point
DCMaDIP	double critical mass density inversion point
EoS	equation of state
GPD	global phase diagram
MaDI	mass density inversion
MaDIEP	mass density inversion end point
MoDI	molar density inversion
MoDIEP	molar density inversion end point
UCEP	upper critical end point
3P	three phases

derivative $\partial^{m+n}\tilde{A}/\left(\partial x_1^m \partial \tilde{v}^n\right)$. The so-developed mechanism, appropriately constrained by the global stability condition of the equilibrium state [5,6], was then applied to the analysis of density inversion phenomena from the point of view of the global patterns of the different types of phase behavior, as them follow from the classification of van Konynenburg and Scott [7,8]. As demonstrated elsewhere [4] Eq. (2) becomes equivalent (although simpler and more direct in critical point calculation applications) to the necessary conditions previously established by Quiñones-Cisneros [9,10] who, for the first time, reported a set of rigorous theoretical

conditions able of unequivocally detecting molar barotropy ending at critical points in binary mixtures.

In close similarity to Eq. (1), besides the ordinary conditions of phase equilibrium, heterogeneous mixtures exhibiting sub-critical mass density inversions are characterized by

$$\hat{v}^\alpha = \hat{v}^\beta \;\Leftrightarrow\; \hat{\rho}^\alpha = \hat{\rho}^\beta \tag{3}$$

where $\hat{v}$ represents unit mass volume and $\hat{\rho}$ is the mass density. Considering that, for a given π-phase, the molecular weight, M_w, of the binary mixture depends on the molecular weights of pure species as

$$M_w^\pi = x_1^\pi M_{w,1} + x_2^\pi M_{w,2} \tag{4}$$

where x_i^π is the mole fraction of the ith component in phase π, mass volumes of mixtures can be calculated from molar volumes using the following transformation,

$$\hat{v}^\pi = \frac{\tilde{v}^\pi}{M_w^\pi} \tag{5}$$

Combination of Eqs. (3)–(5) allows deducing a mathematical expression for the molar volume ratio of the phases of a binary mixture at a mass density inversion point as

$$\frac{\tilde{v}^\alpha}{\tilde{v}^\beta} = \frac{x_1^\alpha (1-q) + q}{x_1^\beta (1-q) + q} \tag{6}$$

where q stands for the molecular weight ratio between pure components as

$$q = \frac{M_{w,2}}{M_{w,1}} \tag{7}$$

The limiting behavior of Eq. (6) may be clearly characterized in the following cases:

- If molecules of a given mixture have equivalent molecular weight, then $q = 1$ and $\tilde{v}^\alpha = \tilde{v}^\beta$. Consequently, we deduce that the mass density inversion point – if any – is equivalent to the molar density inversion point (see Eq. (1)) and, additionally, both density inversion phenomena present equivalent thermo-mechanical coordinates.
- In the vicinity of a critical point, where the concentration of critical phases become equivalent ($x_1^\alpha \to x_1^\beta$), Eq. 6 directly simplifies to

$$\lim_{x_1^\alpha \to x_1^\beta} \frac{\tilde{v}^\alpha}{\tilde{v}^\beta} = 1 \tag{8}$$

According to Eq. (6), the numerical values of the molar volumes of sub-critical phases involved in mass isopycnicity may be drastically different. However, if the mass density inversion condition persists up to the critical point, we can see from Eq. (8) that the pertinent molar volumes become equivalent. Although according to these results it may be tempting to establish that molar and mass density inversions coincide at the critical state, it is not possible to theoretically support such a conclusion since the condition shown in Eq. (8) holds at every – though not necessarily isopycnic – critical point. Particularly, numerical calculations in mixtures exhibiting both mass and molar density inversions have shown that these inversion points exhibit different conditions of critical temperature, pressure and phase mole fraction [11].

In concordance as it was pointed out by Flores et al. [11], the unequivocal characterization of molar and mass barotropic phenomena is far to be a solved problem yet, since the specific conditions affecting their existence should be taken into account in a mass density basis rather than in the direct observation of molar volumes. Accordingly, this work is undertaken to clarify the relation