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Mass Transport of Volatile Molecules in Porous Materials: Evaporation−Condensation Phenomena Described by NMR Diffusometry

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ABSTRACT: The transport mechanism of benzene in chromatographic-grade porous silica gel (10 nm pore size, 5 μm sphere diameter) was described by pulsed-field gradient (PFG) high-resolution magic-angle spinning (HRMAS) NMR by measuring the molecular mobility in a series of samples with variable filling levels of the void volume. The relevance of vapor-phase diffusion for benzene, pure or dissolved in chloroform, was established, and it implies migration of benzene between silica particles through an evaporation−condensation mechanism.

EVAPORATION−CONDENSATION TRANSPORT IN POROUS SILICA

D mobility decreases with the progressive filling of the void

f
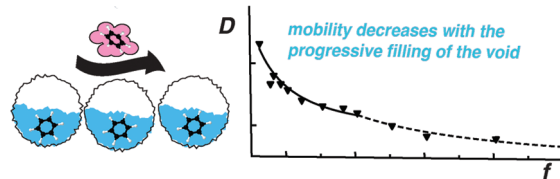
■ INTRODUCTION

The capacity of PFG-NMR for studying noninvasively transport phenomena in porous materials[1,2] has allowed the characterization of gas-phase transport in many cases, including a very accurate prediction model for zeolitic materials.[3,4] The related, but more complex, phenomenon of the contribution of vapor phase to the overall molecular displacement of confined fluids[5] has been first pointed out by PFG-NMR experiments for water by Karger et al.[6] in a zeolite and by D'Orazio et al. in a porous glass,[7−9] and it has been subsequently highlighted and investigated by several authors.[10−13] This particular diffusion mechanism is worth exploring as it can indeed play an important role in a large number of natural and industrial processes (e.g., mass transport in the environment, heterogeneous catalysis, separative techniques...),[14] which involve the processing in porous media of small-to-medium sized molecules with appreciable volatility, water, and small organic molecules being important cases. Besides the case of pure molecules, mixtures or molecules dissolved in a solvent are of special interest due to the very large selection of practical examples that falls in this category.

A characteristic signature that mass transport for molecules moving inside porous solids is occurring also in the vapor phase is an effective diffusion coefficient larger than in the bulk. This outcome may appear unexpected as confined fluids are partially constrained by the material walls, thus effectively reducing the molecular diffusivity. However, this acceleration of the average molecular mobility can be understood if the vapor-phase transport bears a sizable contribution to the overall self-diffusion process. As the amplitude of the displacements in the vapor phase can be 3−4 orders of magnitude larger than that in the bulk, this mechanism of transport is expected to be relevant if the vapor molar fraction is of the order of the reciprocal of this factor or more. A non-neglibile impact to the molecular displacement of the vapor phase is thus expected in the case of a combination

of appreciable vapor pressure and, foremost, void space in contact with the bulk phase of the molecular tracer.

A few systematic studies by PFG-NMR addressed the variation of the molecular diffusivities of volatile compounds constrained in porous materials as a function of the filling factor, the ratio between the volume of the fluid under study and the porous volume of the material. Water was the first molecule for which an effect of the vapor phase in mass transport was revealed, either in macroporous (240 nm, 95 nm,[7,9] and 1 μm[11] pore sizes) or in mesoporous silica glasses (20 nm[13]), and in a zeolite.[6] Conversely, water did not present this effect when confined in microporous glass,[9,12] or in silica gel (4 nm pore size).[15] Diffusion of cyclohexane, a molecule with a vapor pressure of about 100 mm Hg at room temperature, was also shown to have a strong contribution from the vapor−liquid equilibrium in macro- (1 μm pore size)[11] and mesoporous (4 nm pore size) silica glasses,[12] although with some deviations from the expected trend in this latter example. Many other volatile molecules have been investigated in partially filled pores, although without a systematic variation of the filling factor. Among those, the diffusion behavior of benzene has been widely probed in a selection of porous compounds, mainly linked to the interest of these systems for catalysis studies. A large spread of diffusion values has been found for this molecule. In zeolites, a low loading of benzene yields a strong reduction of the effective diffusion coefficient with respect to the bulk value.[16] Similarly, an up to 2 orders of magnitude reduction with respect to the bulk values was observed in microporous silica, where an activation energy of 11 kJ·mol^{-1} was measured for the diffusion process.[17]

In a comparative analysis in which benzene was allowed to diffuse in a family of microporous MCM41 materials of the same

pore diameter, but with different morphology, a largely varying behavior was observed. Namely, it was demonstrated that benzene may or may not show a vapor-phase diffusion contribution, along the series of microporous MCM41 samples.[18] Finally, an effective diffusion coefficient larger than the bulk values was observed for benzene in silica gel,[19] a fact that contributed to enhance the discrimination power of a pseudochromatographic NMR method for the analysis of mixtures.[20]

In this work, we investigated benzene diffusivities in the presence of a common, chromatographic-grade, mesoporous silica gel. The probe molecule was used pure and in a deuterated chloroform solution, notably to explore the possible effect played by mixing on the diffusivities in a confined environment. To enhance resolution and sensitivity, high-resolution magic-angle spinning (HRMAS) spectroscopy was applied, as this method has been shown to produce accurate diffusion measurements.[21] An aprotic solvent was chosen for dissolution of the probe molecule to simplify the NMR spectra, capitalizing on the fact that deuteration of the solvent has small effects on the molecular diffusivities of solutes even in the presence of an adsorbant.[19,22]

■ THEORY

A very common method to investigate thermally driven molecular displacements is PFG-NMR spectroscopy.[23] Most typically, the spatial position of the target molecule is labeled by a magnetic field gradient pulse, which induces a signal phase spread that is reversed by a gradient pulse of opposite sign (or by an equivalent approach) after a given time interval to allow for molecular displacement (called the diffusion time). This scheme produces a full echo only for molecules with null root-mean-square displacement, and thus the intensity of the echo can be linked to the amplitude of the molecular translational motion. Stimulated echo sequences, in which the signal intensity is affected by longitunal relaxation, are typically preferred for heterogeneous samples.[24]

For gradient pulse durations, δ, small with respect to the diffusion encoding time, Δ, the stimulated echo relative intensity varies as a function of the gradient strength, g, as[25]

$$I(g;\delta,\Delta) = S(g;\delta,\Delta)/S_{ref}(\delta,\Delta) = \exp[-Dq^2\Delta'] \qquad (1)$$

where S_{ref} is the observed amplitude of the stimulated echo obtained with a gradient pulse of zero (or very small) intensity, q is equal to the product of the gradient pulse intensity, g, its duration, δ, and the nuclear gyromagnetic ratio, γ, and, finally, Δ' is a function of the experimental setup, being $(\Delta - \delta/4 - \tau/2)$ for the half-sine-shaped gradient envelopes used in this work. The use of a relative quantity allows neglecting, to the first order, any effect due to the relaxation.

■ MODEL FOR DIFFUSION IN BIPHASIC POROUS ENVIRONMENTS

The presence of a multiphasic environment invalidates the simple premises that led to eq 1 so that a model of the contribution to the mobility from molecules in the different phases is, in principle, required.[11,26,27] However, for fast equilibration, an effective diffusion constant is observed, which is a weighed average over all states[26]

$$D_e = \Sigma_i x_i D_i \qquad (2)$$

with x_i the molar fraction for the ith state and D_i the corresponding molecular diffusion constant. Barriers to the diffusion among the phases[28,29] are not likely to provide a contribution in equilibrium conditions and were not considered. We note that, for completeness, surface diffusion should be included. However, this means of displacement for adsorbed molecules concerns likely up to the first monolayer and it is typically an order of magnitude smaller than that in the bulk. This specific contribution to the random walk will thus be non-negligible for low filling factors only,[2] the same conditions in which vapor-phase displacement becomes relevant. As a first approximation, it is thus safe to exclude the contribution from surface diffusion when the analysis concerns volatile molecules.[8,11] The effective diffusion coefficient is thus the weighed average

$$D_e = p_L D_L + p_V D_V \qquad (3)$$

with p_V and p_L mole fractions for the vapor and bulk phase, respectively.

■ MEANING OF THE D_L AND D_V COEFFICIENTS

For a pure liquid, molecular contacts are the mobility-limiting factors, resulting in the Stokes−Einstein relation

$$D = \frac{kT}{6\pi\eta r_H} \qquad (4)$$

where η is the viscosity and r_H the hydrodynamic radius, whereas k and T refer to the Boltzmann's constant and the temperature, respectively. Equation 4 has been applied for condensed phases in a confined environment,[30] where it is supposed to hold without major variations, thus allowing comparisons with bulk phase measurements.

On the other hand, self-diffusion of molecules in the vapor phase is ruled first by their mean thermal velocity, v

$$v = \sqrt{\frac{8kT}{\pi M}} \qquad (5)$$

where M is the molecular weight, and by whatever obstacle would deflect them from their inertial path, either another molecule or the wall of a porous framework.

In the case of dominant intermolecular collisions, the diffusion rate is linked to the mean free path, λ, a measure of the distance covered before an intermolecular collision, which determines the molecular term of the diffusion coefficient

$$D_M = \lambda v/3 \qquad (6)$$

For a mixture of gases, the mean free path of the tracer T, λ_T, is determined by the partial pressure, P_i, and the collision diameter, σ_i, of each component[3,31]

$$\lambda_T = \frac{RT}{\pi\sqrt{2}} \sum_i \frac{1}{P_i \left[\dfrac{\sigma_T + \sigma_i}{2}\right]^2} \qquad (7)$$

In the case studied here, the relevant molecules are, other than benzene, the air constituents and, for the benzene solution in $CDCl_3$, the solvent. In the following, we used the Lennard-Jones minimum cross-sectional diameter as an estimate for σ (with values of 0.56 nm for benzene, 0.54 nm for chloroform, 0.36 nm for oxygen, and 0.37 nm for nitrogen).

If impacts with the confining walls are the main source of deviation from a linear motion, the Knudsen regime is dominant,

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described by

$$D_K = <l_p> v/3 \qquad (8)$$

with l_p the number-averaged path length; that for regular porous materials corresponds well to the pore diameter. The general case for diffusion in the vapor phase can be described by combining eqs 7 and 8

$$1/D_v = 1/D_M + 1/D_K \qquad (9)$$

Note that such a simple representation of the porous network is just a first-order approximation.[27,32] In the present study, measurements were performed in the long-range diffusion regime, LRDR;[26] that is to say, the conditions of the experiment are such that the vapor molecules sample both the intra- and extraparticle void. In this configuration, vapor-phase mass transport for microporous materials is usually dominated by extraparticle diffusion, according to eq 8. In the following, we choose not to make any approximations, but to rather keep the explicit expression of all contributions to the apparent diffusion coefficient, including the vapor-phase molecule inside the pores, with the additional caveat that the specific design of the sample container (an NMR MAS rotor) in our experiment allowed for the presence of additional voids so that the "external" void is the sum of interparticle and residual empty space. This results in the following expression for the apparent diffusion constant

$$D_e = p_L D_L + p_{V\_int} D_{V\_int} + p_{V\_ext} D_{V\_ext} \qquad (10)$$

considering that

$$p_L = 1 - p_{V\_ext} - p_{V\_int} \qquad (11)$$

This latter expression is equivalent to neglecting any adsorption effects, which are, conversely, a known fact for aromatic molecules on silica. However, in light of the weak interaction of benzene with silica,[33] surface diffusion is likely to contribute minimally to mass transport, particularly in the presence of fast-moving vapor-phase molecules.

The molar fractions for the vapor and bulk phases can be calculated from the total number of moles introduced in the pores and those in the gas phase

$$p_V = n_V/n_{tot} \qquad (12)$$

with

$$n_{tot} = c_{0L}*f*V_0 \qquad (13)$$

where c_{0L} is the probe molecule molar concentration in the mother solution, f the filling factor, the ratio of the added volume of solution, V, and the intraparticle porous volume, V_0. The number of moles in the vapor phase, n_V, can be estimated assuming ideal gas conditions from the equilibrium vapor pressure, P^0, as

$$n_V = x_L*P^0*V(f)/RT \qquad (14)$$

with x_L the mole fraction in the mother solution and the void volume available inside or outside the pores, V_0 and V_{ext}, respectively.

For convenience, we expressed the total external volume, $V_{ext}(f = 0)$, proportionally as well to the intraparticle porous volume

$$V_{ext}(f = 0) = nV_0 \qquad (15)$$

Table 1. Characteristic Properties of the Silica Gel (LiChrosher 100Si) Used in This Study

specific area (m^2 g^{-1})	400
particle diameter (μm)	5
pore diameter (Å)	100
porous volume (mL g^{-1})	1.25

The progressive additions of a liquid or a solution to the porous silica fills the intraparticle void at first, and thus the external void remains unchanged until the intraparticle porous volume has been filled so that

$$V_{ext}(f \leq 1)/V_0 = n \qquad (16a)$$

and

$$V_{ext}(f \geq 1)/V_0 = (n - f + 1) \qquad (16b)$$

The presence of impediments to the molecular motion reduces the fraction of space accessible for mass transport, linked to the sample porosity, ε, the ratio between the porous, V_0, and the overall volume, V_{tot}. Consequently, the effective diffusion coefficient, D_e, in confined environments becomes smaller than its bulk counterpart, D_b, as[34]

$$D_e = D_b \varepsilon \qquad (17)$$

An aspect that requires discussion is that eq 14 holds for solutions if Raoult's law is respected, which may not be the case in a confined environment, for example, due to demixing[35] or interactions with the solid. Although the details of any deviation from the ideal case would require a proper thermodyamical description, we resorted to model this possible effect phenomenologically by using a polynomial correction to the concentration in the vapor phase inside the pores as

$$c_L = c_{0L}*g(f) = c_{0L}*(1 + \Sigma_i a_i f^i - \Sigma_i a_i) \qquad (18)$$
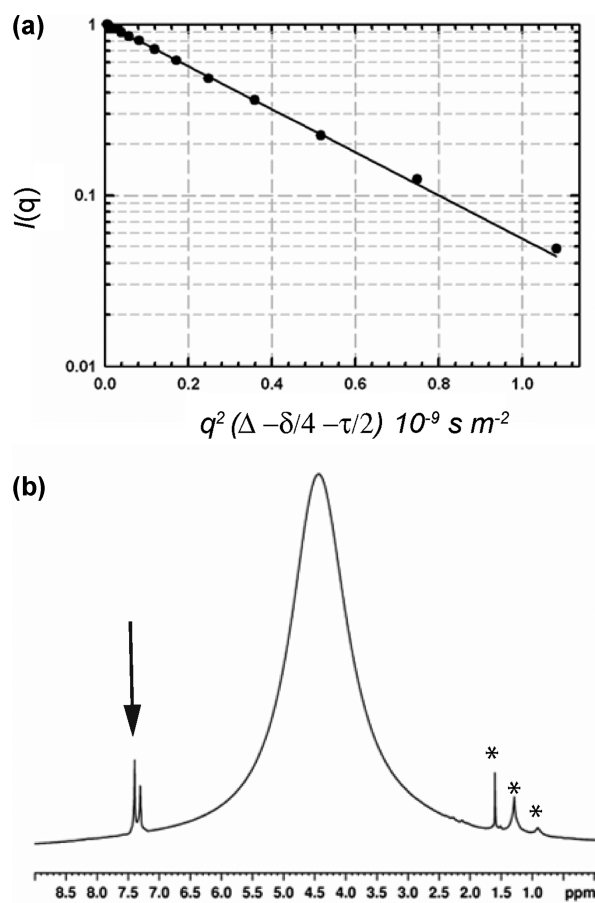
for the case of mixtures.

Finally, we note that an accurate description of mass transport in the vapor phase in partially filled pores should take into account the non-negligible liquid–vapor interphase[36] and the Gibbs–Thomson effect.[37] As both of these effects are likely to be more relevant to describe the vapor contribution to diffusion inside the pores, which is a minor component, here we neglected them as a first approximation.

■ EXPERIMENTAL SECTION

Materials. The silica gel phase used was LiChrosher 100Si, from Merck (Table 1). Benzene, purchased from Sigma-Aldrich and used as received, was analyzed pure and diluted in CDCl$_3$ (obtained from Eurisotop) at a concentration of 1 mg·mL^{-1}.

NMR. All NMR experiments were performed on a Bruker AVANCE spectrometer operating at 400 MHz and equipped with a ^{1}H HRMAS probe head producing magic-angle gradients with a maximum strength of 60 G cm^{-1}. HRMAS spectra were recorded at a spinning rate of 4000 Hz, using 4 mm o.d. zirconia rotors. Liquid diffusion measurements were performed with 12 μL volume rotors, while 50 μL volume rotors were used for the samples holding a liquid phase and silica gel. For the preparation of these latter samples, 16 mg of silica was used, with a variable volume of liquid (6–20 μL). Roughly half of the stationary phase was placed in the rotor, and then the liquid was added with a micropipet and the rotor was filled with the remaining part of the
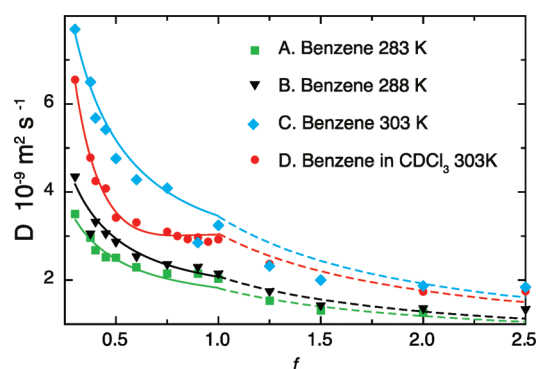
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(a)

(b)

Figure 1. BPP-LED decay of the benzene signal (a) and ^{1}H HRMAS spectrum (b) for benzene in $CDCl_3$ solution (marked by the arrow) in the presence of a porous silica gel. The large and broad peak corresponds to silanols and adsorbed water; peaks marked with a star are impurities in the rotor.

Figure 2. Evolution of the effective diffusion constant, D_e, of benzene, pure or in deuterated chloroform solution, in the presence of a porous silica gel as a function of the fraction of added liquid, expressed as the filling factor of the intraparticle void. The solid and broken lines are the outcome of the theoretical models, developed in the text, for $f \leq$ and ≥ 1, respectively, using the parameters reported in Table 2.

■ RESULTS AND DISCUSSION

All PFG experiments recorded provided monoexponential decays (Figure 1a). Thus, a fast equilibrium regime can be assumed, further confirmed by the fact that the HRMAS NMR spectrum showed line width values typical of mobile molecules (17−25 Hz, Figure 1b).

The evolution of the effective diffusion constant in the mesoporous silica gel as a function of the added volume is shown in Figure 2 for pure benzene, at 283 K (curve A), 288 K (curve B), and 303 K (curve C), and for the $CDCl_3$ solution at 303 K (curve D). When the added liquid is confined within the pores ($f < 1$), an exponential decrease of D_e is observed as f is augmented. A clear discontinuity in the exponential decay of D_e is observed for larger added volumes of solution, corresponding to the beginning of the filling of the external porosity. An exponential decrease of D_e upon progressive filling of the void space has been previously observed in porous glasses for cyclohexane,[11] which has a vapor pressure comparable to benzene, and for water in mesoporous glasses.[7] Comparison of the curves corresponding to pure benzene shows reduced mobility of the tracer with lowering the temperature along the whole range of measurements. This is consistent with the decrease in vapor pressure (e.g., 109 to 41 mm Hg in going from 303 to 283 K),[22] which dominates on the acceleration induced by the longer free mean path characteristic of less-dense vapors. The analysis of benzene in a deuterated chloroform solution shows diffusion constant values always inferior to the one of pure benzene recorded at the same temperature. The diffusion values observed for all studied cases for $f \leq 1$ exceed the bulk ones, consistently with substantial vapor phase transport. To estimate what sections of the sample are traveled by the probe molecules, it is useful to report a "cutoff" value of D, which corresponds to a mean square displacement approximately equal to half of the square of the particle diameter, d. As all measurements we performed with a diffusion encoding time, Δ, of 80 ms, the cutoff D is calculated (for $d = 5 \mu$m) to 8×10^{-11} m^2 s^{-1}. All values reported in Figure 2 exceed this threshold so that the mass transport can be qualified as being in the long range diffusion regime (LRDR). A first conclusion that can be drawn accordingly is thus that the molecules in the vapor phase travel extensively in the void space outside the particle pores. However, the classic approximation of LDLR that

silica gel. The pulse sequence used was based on the stimulated echo and incorporated bipolar gradient pulses and a longitudinal Eddy current delay (BPP-LED).[25] All gradient pulses were half-sine-shaped and the LED was held constant at 5 ms. Diffusion measurements were realized with diffusion times of 80 and 400 ms and gradient pulses of 600 and 900 μs for pure and diluted benzene, respectively. The gradient strength was logarithmically incremented in 16 steps from 2% to 95% of its maximum value, and 16 transients were recorded for each gradient strength. No significant differences were observed in the D_e values obtained with either diffusion times. After Fourier transformation and baseline correction, the Bruker XwinNMR 2.1. software package (version 3.5)[38] was used to calculate the D_e estimates through mono- or multiexponential fitting of the experimental data. To evaluate the error on the measurement, some experiments were performed in triplicate, providing an estimate of the uncertainty of the order of 10%.

Fitting Procedure. The data were fitted to eq 10, integrated with eqs 11−18, using the software ProFit (Quantum Soft). The interparticle void was estimated by measuring the maximum volume of solution that could be added to the porous silica/MAS rotor system. The tortuosity factor was set to the reciprocal of the porosity. The vapor pressure was obtained through the state equation.[25]

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Table 2. Parameters Used for Reproducing the D_e versus f Variations[a]

	T/K	c_{0L}/M	$D_{0L}/10^{-9}\ m^2 \cdot s^{-1}$
benzene	283	11.4	1.7
benzene	288	11.3	1.8
benzene	303	11.1	2.6
Benzene/CDCl$_3$[b]	303	1.3×10^{-2}	2.4

[a] Assuming a silica density of 2.2 g·cm^{-3}, $\varepsilon_{intra} = 0.73$, $\varepsilon_{ext} = 0.52$, and $V_{ext}/V_{intra} = 1.5$. [b] The parameters for the function $g(f)$ for this case were $a_1 = -7.54$, $a_2 = 9.56$, and $a_3 = -3.48$.

the displacement occurring in the vapor phase is the only relevant one is not sufficient to adequately explain the observed D_e versus f changes. Conversely, all trends in Figure 2 for pure benzene can be reproduced very satisfactorily using the model described above (eqs 9–18) without using any adjustable parameter, setting the intraparticle porosity to 0.73 and the extraparticle one to 0.52, according to the respective porous volumes. Therefore, it appers that the liquid fraction of the sample plays an important role in the diffusion process (i.e., the data cannot be reproduced withouth this contribution). The diffusion mechanism in action here is thus an evaporation–condensation one,[14] in which the tracers travel from the bulk phase confined in a first particle to the one in a second particle through a period of time in the vapor phase. Effectively, this mechanism bypasses the diffusion barriers constituted by the pores, even though capillary forces ensure confinement for $f < 1$. The fit of the case of benzene in a CDCl$_3$ solution demanded instead the use of eq 18 with three coefficients in $g(f)$ (limited to third order with values of the coefficients of -7.54, 9.56, and -3.48) to reproduce the D_e versus f trend. This is a purely phenomenological description of the observed negative deviation from Raoult's law. Although this result points qualitatively to the presence of attractive forces reducing the benzene vapor pressure, further studies are required to properly assess the origin and details of this specific issue.

CONCLUSIONS

The mobility of benzene, either pure or in a deuterated chloroform solution, in the partially filled mesopores of a chromatography-grade silica gel can be adequately described invoking a two-phase, liquid–vapor fast equilibrium, and an evaporation–condensation mechanism. The observed trends of variation of the measured effective diffusion constants of pure benzene can be modeled with purely kinetic parameters, once the specificities of the porous media are taken into account. The model presented here can be easily extended to similar cases as it uses no specific parameters. In all cases studied, no contribution to the tracer mobility from strongly adsorbed layers was discernible, possibly being obscured by the dominant phase vapor diffusion, as both these components become more influent around submonolayer coverage.

Finally, the enhanced sensitivity and resolution of HRMAS-PFG experiments allowed the application of the same protocol to a diluted solution of benzene in deuterated chloroform confined in porous silica. In this case, a trend similar to the one of pure benzene was observed, but with a negative violation of Raoult's law. This issue requires further investigations, which are underway.

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