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2002 J. Phys.: Condens. Matter 14 11453

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Transport properties of supercritical fluids and their binary mixtures

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Received 24 June 2002

Published 25 October 2002

Online at stacks.iop.org/JPhysCM/14/11453

Abstract

The molecular dynamics of the two supercritical fluids most applied in industry and some of their mixtures are characterized by their self-diffusion coefficients D_i , measured by high pressure high resolution nuclear magnetic resonance with the strengthened glass cell technique. The technical details of the apparatus will be given. The fluids studied are carbon dioxide and ammonia. For CO₂, mixtures with C₆H₆, H₂, CH₃COOH and CH₃OH were investigated. The NH₃ mixtures include C₆H₆, (CH₃)₃N, CH₃CN and CH₃OH.

1. Introduction

Supercritical fluids find various applications in modern industry. They are used in such diverse fields as inert solvents in organic and biochemical synthesis, for supercritical extraction of herbal products, textile dyeing and dry cleaning. Compared to the classical organic and haloorganic solvents, they pose less health and environmental risks. The aim of the studies presented here is to characterize the dynamic properties of the two most applied supercritical solvents, carbon dioxide and ammonia, as well as some of their mixtures by the T , p -dependence of their self-diffusion coefficients. The mixtures comprise models of nonpolar and strongly dipolar compounds, as well as compounds that may form hydrogen bonds.

2. Experimental details

The high pressure self-diffusion coefficients of the samples were determined by high resolution nuclear magnetic resonance (HRNMR) experiments using the pulsed field gradient spin echo technique [1]. Strengthened glass cells as introduced by Yamada [2] were used. Our version of this technique as well as the filling procedures used have been described in detail elsewhere [3]. Recently Yamada *et al* [4] described a very interesting new development of this technique that permits studies up to 600 MPa. Hitherto this method had been limited in routine experiments to 200 MPa. In a few cases pressures of 400 MPa had been reached.

Table 1. RHS parameter for NH₃ and CO₂ ($\sigma = \text{RHS } \emptyset$ in nm).

NH ₃			CO ₂		
$T(\text{K})$	$A(\text{NH}_3)$	$\sigma(\text{NH}_3)$	$T(\text{K})$	$A(\text{CO}_2)$	$\sigma(\text{CO}_2)$
203	0.997	0.331	223	0.762	0.366
224	1.00	0.328	243	0.917	0.368
243	0.985	0.323	273	1.09	0.369
273	0.943	0.321	298	0.957	0.361
299	1.00	0.318	333	1.05	0.362
333	1.00	0.314	373	1.12	0.362
374	0.993	0.312	424	1.09	0.360
424	1.00	0.306	450	1.39	0.372
474	1.00	0.301			

3. Results and discussion

3.1. Neat fluids

Older work on various simple fluids and liquids has shown that the self-diffusion in simple liquids is well described by the rough hard sphere (RHS) model [5, 6]. In this model $D(T, \rho)$ can be expressed in terms of the hard sphere (HS) diffusion coefficient by

$$D(T, \rho) = A D_{\text{HS}}(T, \rho, \sigma(T)) = A \left(\frac{D_0}{n} \right) P(n) \quad (1)$$

with

$$P(n) = \left(1 - \frac{n}{1.09} \right) |1 + 2n^2(0.4 - 0.83n^2)| \quad (2)$$

where D_0 is the Boltzmann diffusion coefficient for a dilute gas given by

$$D_0 = \left(\frac{3}{8} \right) \sigma \left(\frac{k_B T}{\pi m} \right)^{1/2}. \quad (3)$$

$P(n)$ is an empirical polynomial in the packing fraction ($n = \sigma^3 \rho$, $\sigma = \text{HS diameter}$) derived from the fit of all reliable results obtained from molecular dynamics simulations for the smooth HS fluid. $P(n)$ accommodates many body corrections and back-scattering effects that must occur at liquid-like densities. According to Chandler's RHS model the difference between the calculated HS self-diffusion coefficient and the experimental results for a specific liquid is due to a coupling of rotational and translational modes and is taken into account by introducing the parameter $A = D_{\text{exp}}/D_{\text{HS}} \leq 1$. By its definition this parameter should be independent of T and p . In experiments it was found that A in most substances decreases with falling temperature [7], the decrease being most pronounced for liquids in which hydrogen bonded associates can be formed. This RHS analysis is only possible if experimental p , V , T -data are available for the range of the self-diffusion data.

The older work has been reviewed in [7]. The analysis of the self-diffusion in protonated [8] and deuterated ammonia [9] showed, to our surprise, that the T , p -dependence of this fluid did not reveal any sign of hydrogen bonding. In ammonia the A -parameter of the RHS model remained $A \approx 1$ over the whole temperature range, a value typical for strictly nonpolar fluids like methane and tetrafluoromethane, while in typical hydrogen bonded liquids it decreases with falling temperature in the vicinity of the melting pressure curve to $A \approx 0.1$ and even lower. The A -parameter and the RHS diameter, σ , for NH₃ are compiled in table 1. Their inspection shows that $\sigma(\text{NH}_3)$ decreases with falling temperature, as is typical for all substances studied,

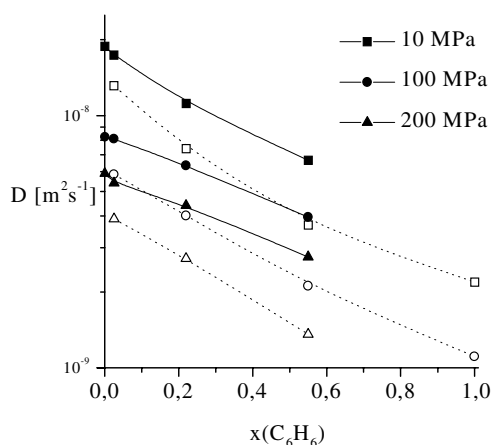


Figure 1. 298 K isobars of the concentration dependence of the intradiffusion coefficients in the carbon dioxide/benzene system (open symbols, C_6H_6 ; closed symbols, CO_2).

and ascribed to the fact that for real molecules the repulsive part of the interaction potential is not infinitely steep. In table 1 also the results of the analysis of $D_i(CO_2)$ are given. This is the first example of a simple nonpolar liquid that cannot be fitted by the RHS approach. Although the fit quality is good, the values derived for A and σ are not acceptable. Obviously this fluid has to be described as a hard dumbbell liquid.

The RHS treatment can also be applied to binary systems; however, only a few systematic MD simulations exist, and in most cases also the relevant p , V , T -data are missing. Only for a few special model cases has systematic work been done [10, 11]; a more general analysis is still required.

3.2. Binary mixtures with carbon dioxide

In figure 1 some isobars of the concentration dependence of the intradiffusion coefficients in the system carbon dioxide/benzene at 298 K are given.

They do show with almost regular solution behaviour the type of behaviour typical for most mixtures of nonpolar and polar compounds. This type of diagram allows us to characterize the whole concentration range of the mixture with experiments at a few concentrations only.

In figure 2 some isotherms for the CO_2/H_2 system are given at 100 MPa. Here we do see a very pronounced deviation from regular behaviour. Relatively small concentrations of hydrogen enhance the diffusivity of the heavier molecules. This is most probably caused by a strong decrease of the mixture density through the addition of H_2 . This effect has found some technical application in the hydrogenation of fatty oils. The rate of catalytic hydrogenation is in the physiologically unproblematic CO_2 enhanced by about an order of magnitude when compared to the neat fatty oil.

A peculiar feature visible in all diagrams of this type of mixture is the fact that the volume and mass of the two compounds in the mixture does influence the absolute value of the intradiffusion coefficient with the larger and heavier molecule being slower. However the temperature and pressure dependences for both compounds are usually very similar. This is obvious from an inspection of the spacing of the three isobars given in figure 2 and is also the most unexpected feature of the data presented for a binary mixture of carbon dioxide/palmitic acid methyl ester (PME) in figure 3.

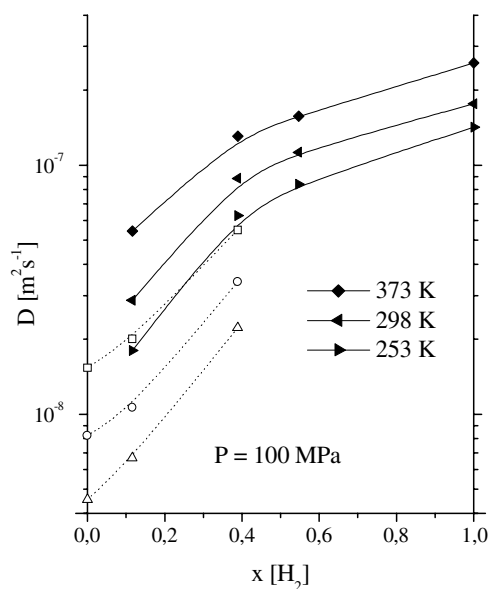


Figure 2. Isobars of the concentration dependence in the binary mixture CO_2/H_2 (full symbols, H_2 ; open symbols, CO_2).

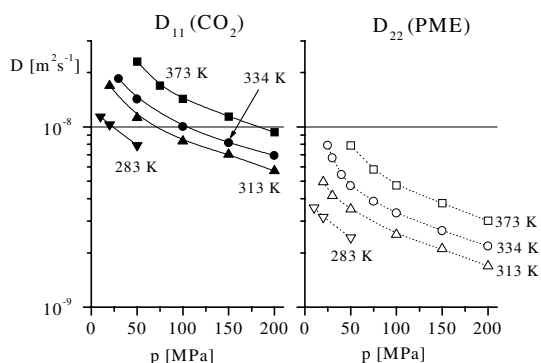


Figure 3. Pressure dependence of the intradiffusion coefficients in a binary mixture of CO_2 and PME at $x(\text{PME}) = 0.07$.

It is still a matter of controversy whether the carbon dioxide molecule does participate with its lone pair electrons at the oxygen atoms as acceptors in hydrogen bonding. A comparison of the concentration dependence of the chemical shift of the hydroxyl group of methanol in CO_2 with the behaviour observed in the acetone/methanol system [12] shows a qualitatively different behaviour. This comparison is given in figure 4. For the $\text{CO}_2/\text{CH}_3\text{OH}$ mixtures one observes a strongly curved concentration dependence, indicative of the formation of more hydrogen bonded homo-associates with increasing methanol concentration. In the acetone/methanol mixtures one sees a linear change of the chemical shift of the hydroxyl proton that is typical for a continuous exchange of methanol/methanol hydrogen bonds by methanol/acetone bonds with increasing acetone concentration.

The concentration dependence of the intradiffusion coefficients in the carbon dioxide/methanol mixture corroborates this conclusion. In figure 5 some isotherms of the

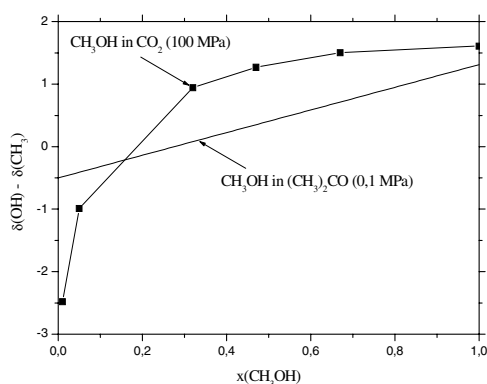


Figure 4. Comparison of the concentration dependence of the chemical shift of the hydroxyl proton in carbon dioxide/methanol mixtures at 100 MPa and in acetone/methanol mixtures at ambient pressure [12].

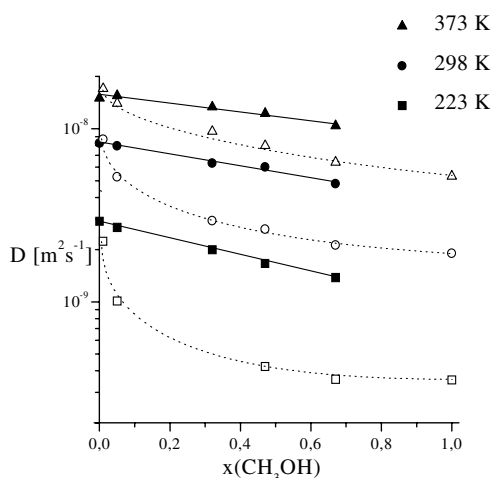


Figure 5. 100 MPa isobars of the intradiffusion coefficients in the carbon dioxide/methanol system: CH_3OH , open symbols; CO_2 , closed symbols.

D_{ii} are collected. The $D_{ii}(\text{CH}_3\text{OH})$ decrease especially at low temperatures much faster with concentration than the $D_{ii}(\text{CO}_2)$; however, they never become at a given temperature and pressure lower than the self-diffusion coefficient for neat methanol.

3.3. Binary mixtures with ammonia

In the analysis of the T , p -dependence of the self-diffusion coefficients in neat NH_3 given above, we found to our surprise no evidence for the formation of hydrogen bonds in the neat fluid. From *ab initio* structure calculations for the ammonia dimer it was deduced that a cyclic hydrogen bonded structure was the most stable form for the isolated dimer [13]. This was questioned in a later calculation, that claimed an asymmetric structure with a linear hydrogen bond to be slightly more stable [14]. Considering these results it seems feasible that rotation and with it translation in fluid ammonia is facilitated by these structures separated by low barriers, and that the observation of normal liquid behaviour typical of nonpolar liquids for the self-diffusion in NH_3 is fortuitous and does not prove the absence of hydrogen bonding.

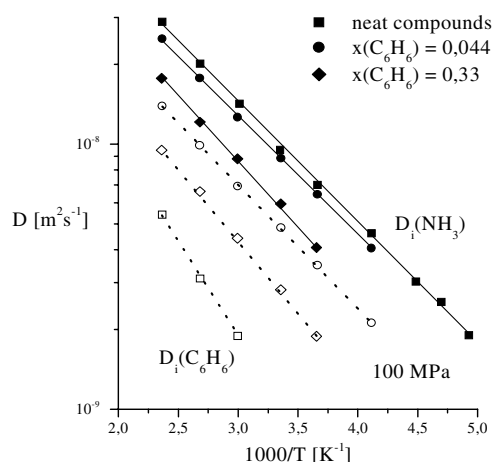


Figure 6. 100 MPa isobaric Arrhenius plot of the $D_{ii}(\text{C}_6\text{H}_6)$ and $D_{ii}(\text{NH}_3)$ at two concentrations compared to the neat compounds. $D_i(\text{C}_6\text{H}_6)$ [16, 17] and $D_{ii}(\text{NH}_3)$ [8] (full symbols, NH_3 ; open symbols, C_6H_6).

In an equimolar mixture of trimethyl amine and ammonia linear hydrogen bonds with ammonia as proton donor and trimethyl amine as acceptor should be the dominant dimer, no cyclic low energy intermediates being possible. This should result in a significant slowing down of the D_{ii} for both compounds. Experimentally however this mixture behaves like a normal fluid without any sign of hydrogen bonding [15], the $D_{ii}(\text{NH}_3)$ being slightly lower in the mixture while the $D_{ii}((\text{CH}_3)_3\text{N})$ are slightly larger. Furthermore the ratio $D_{ii}(\text{NH}_3)/D_{ii}(\text{CH}_3)_3\text{N}$ is in the whole temperature (212–425 K) and pressure range (10–200 MPa) constant around 1.8. In the case of extensive hydrogen bond formation one would expect, because of the T , p -dependence of the hydrogen bond equilibria, that this ratio should decrease with increasing pressure and decreasing temperature.

In figure 6 Arrhenius plots of the $D_{ii}(\text{C}_6\text{H}_6)$ and $D_{ii}(\text{NH}_3)$ for two binary mixtures of these compounds are given and compared to the neat compounds. They show the typical behaviour for this class of mixture, the T , p -dependence for both substances in a given mixture being the same.

Also the acetonitrile/ammonia system shows regular solution behaviour, the isotherms and isobars in $\log D$ versus mole fraction x being almost linear. The additional attractive interaction caused by the large dipole moment of CH_3CN (3.9 D) does not lead to any unusual T , p -or x -dependence of the D_{ii} .

Of all the mixtures studied hitherto ammonia/methanol showed the most interesting concentration and temperature dependence. The low temperature isotherms pass through a pronounced minimum around the mole fraction $x(\text{CH}_3\text{OH}) \approx 0.7$, this minimum becoming more pronounced with decreasing temperature and increasing pressure. Some 100 MPa isotherms are compiled in figure 7.

At most concentrations the ammonia and the hydroxyl protons of methanol exchange chemically sufficiently rapid for their proton NMR signals to coalesce into a single line. It is thus impossible to determine $D_{ii}(\text{NH}_3)$ directly by proton NMR. Therefore we attempted to measure $D_{ii}(\text{NH}_3)$ in nitrogen-15 enriched ammonia (99% N-15). However the low gyromagnetic ratio and the low NMR sensitivity resulting from it made it impossible to measure $D_{ii}(\text{NH}_3)$ in our high pressure NMR setup. Only saturation vapour pressure (SVP) data could

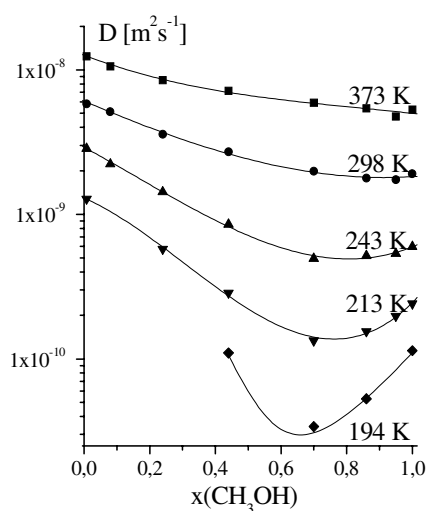


Figure 7. 100 MPa isotherms of concentration dependence of the intradiffusion coefficients of methanol in the ammonia/methanol system.

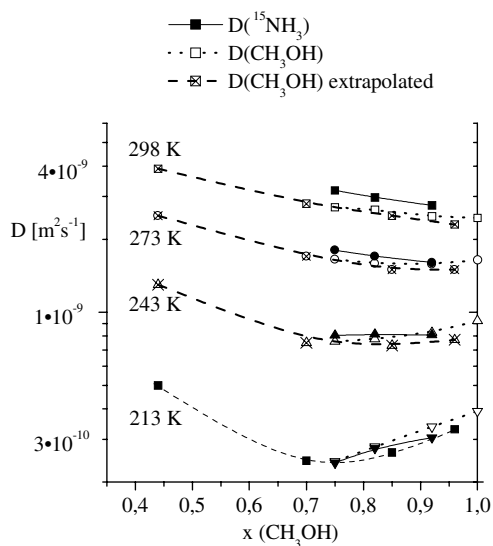


Figure 8. Intradiffusion coefficients for ammonia and methanol obtained at SVP in mixtures with N-15 (99%) enriched ammonia; the open crossed symbols were obtained by extrapolation of the data obtained at 10 MPa in the high pressure setup to SVP.

be obtained in normal 5 mm NMR tubes. These are compiled in figure 8. The data show that even at SVP both compounds have almost identical diffusion coefficients. This can only be explained by the assumption that in this mixture or more general that in alcohol/ammonia mixtures the ammonia molecule participates in the formation of hydrogen bonded networks. From molecular beam studies [18] it was derived that ammonia and amine molecules and the primary alcohols do form hydrogen bonded complexes in which the lone pair of the ammonia acts as acceptor; these hetero-dimers are more stable than the alcohol/alcohol associates.

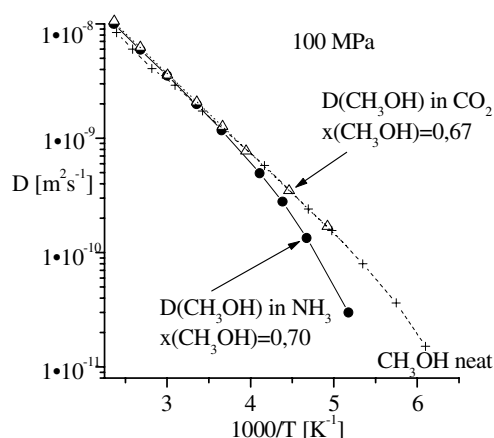


Figure 9. 100 MPa isobaric Arrhenius plots of the intradiffusion coefficients $D(\text{CH}_3\text{OH})$ in neat methanol (+), $\text{CH}_3\text{OH}/\text{CO}_2$ (Δ) and $\text{CH}_3\text{OH}/\text{NH}_3$ (\bullet) mixtures.

However this interaction does not explain all effects seen in the fluid phase. Methanol itself forms two-dimensional hydrogen bonded aggregates with its one hydroxyl proton acting as donor and the two lone pairs of the hydroxyl oxygen acting as acceptors. If ammonia acted only as another acceptor in this system, we would expect a breakdown of the two-dimensional aggregates and compared to neat methanol an increase of diffusivity. This is opposite to what is observed in the experiments and forces the conclusion that the NH_3 must participate as donor as well as acceptor in the formation of three-dimensional hydrogen bonded aggregates.

Considering the results discussed above for the neat ammonia and the ammonia/trimethyl amine mixture this is a rather surprising result. This conclusion is however supported by the comparison of the temperature dependence of the diffusion in neat methanol and in the systems methanol/carbon dioxide and methanol/ammonia. While in a carbon dioxide solution rich in methanol the temperature dependence of D is identical to the neat methanol, the decrease in the methanol/ammonia mixture is much steeper. Figure 9 gives a comparison of the 100 MPa isobars of the solutions at $x(\text{methanol}) \approx 0.7$ with neat methanol. Also the strong deviation from Arrhenian behaviour is most pronounced in the mixture with ammonia. Analysis of the data found in the $\text{CH}_3\text{OH}/\text{NH}_3$ mixtures with the Vogel–Tammann–Fulcher (VTF) or the mode coupling theory (MCT) [19] shows that the ideal glass transition temperatures T_0 of the VTF model as well as the ‘critical temperatures’ T_c of the MCT theory show pronounced maxima around $x(\text{CH}_3\text{OH}) \approx 0.7$.

4. Conclusions

It is customary to derive from the T , p -dependence of dynamic data in the fluid phase the activation energy $\Delta E_A^\#$ and the activation volume $\Delta V^\#$ defined by

$$\Delta E_A^\# = -R \left(\frac{\partial \ln D_{ii}}{\partial (1/T)} \right)_p \quad (4)$$

$$\Delta V^\# = -RT \left(\frac{\partial \ln D_{ii}}{\partial p} \right)_T \quad (5)$$

In table 2 some of these data have been compiled. They do show some very interesting general features: for a given mixture $\Delta E_A^\#$ and $\Delta V^\#$ are within the precision of the data identical

Table 2. Activation parameter for the intradiffusion coefficients.

Substance	Mole fract.	$\Delta E_A^\#$ (kJ mol ⁻¹)	$\Delta V^\#$ (cm ³ mol ⁻¹)
NH ₃	1	8.5	7.0
NH ₃	0.956	8.5	7.0
C ₆ H ₆	0.044	9.1	8.0
C ₆ H ₆	1	12.7	16.0
NH ₃	0.912	8.2	7.0
CH ₃ CN	0.088	8.1	8.0
CH ₃ CN	1	9.1	8.0
NH ₃	0.968	8.9	8.0
CH ₃ OH	0.032	10.2	9.0
CH ₃ OH	1	12.0	7.0
CO ₂	1	7.5	12.0
CO ₂	0.975	7.5	13.0
C ₆ H ₆	0.025	8.0	13.0
CO ₂	0.88	7.0	13.0
H ₂	0.12	7.2	17.0
H ₂	1	2.7	11.0
CO ₂	0.978	8.2	12.0
PME	0.022	9.6	12.0
CO ₂	0.86	8.8	12.0
CH ₃ COOH	0.14	8.9	12.0
CO ₂	0.95	8.3	13.0
CH ₃ OH	0.05	12.8	12.0

for both compounds, even if the two substances do have very different molecular masses and volumes. This is most clearly seen for the solution of PME in CO₂. Exceptions to this rule are seen for $\Delta E_A^\#$ in the CO₂/CH₃OH mixture where the temperature dependence of the hydrogen bond formation causes a higher T -dependence of the methanol mobility.

The data presented here attempt for the first time to characterize the influence of solutes upon the molecular dynamics of the common supercritical solvents. For their comprehensive in depth analysis MD simulations and p , V , T -data for these systems are needed.

Acknowledgments

Our experimental work has been supported generously over the years by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. LC gratefully received a scholarship from the China Scholarship Council for his stay in Regensburg.

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