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Binary nucleation rate measurements of n-nonane/methane at high pressures

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We present homogeneous nucleation rates in the binary mixture n-nonane/methane in the supercritical regime, measured in a new pulse expansion tube at pressures up to 40 bar, at a temperature of 240 K. It is shown that both n-nonane and methane are present in the critical region. The critical supersaturation of n-nonane decreases from 30 at 10 bar, down to 6 at 40 bar total pressure. © 1995 American Institute of Physics.

I. INTRODUCTION

Homogeneous nucleation in the n-nonane/methane mixture at high pressure is of practical interest for natural gas handling. The supersaturations required for (homogeneous) droplet formation may occur during handling and transport of natural gas. Muitjens et al. observed homogeneous condensation in a Wilson cloud chamber while expanding natural gas from pressures between 5 and 50 bar. The onset of condensation, or Wilson points, were located in the coexistence region of the gas in the $pT$-plane, above the critical temperature of the main component methane. We shall refer to this region as the supercritical region. Typical about the supercritical region is the presence of real gas effects resulting in gas density dependent solubilities. The n-nonane/methane mixture, with molar fractions $n$-nonane of about $1 \cdot 10^{-4}$, exhibits gas–liquid phase behavior very similar to that of natural gas (natural gas consists of about 80 vol% methane, 16 vol% nitrogen, and numerous other species, mainly ethane and heavier hydrocarbons such as $n$-nonane).

The real gas effects in the supercritical region of the n-nonane/methane mixture affect the condensation behavior considerably. At pressures above a few bar, interactions between molecules are no longer negligible, resulting in solubilities of $n$-nonane in methane (gas phase), and methane in $n$-nonane (liquid phase) that vary with gas density. As a consequence, the equilibrium vapor density of $n$-nonane increases with total pressure, and also a considerable amount of methane dissolves in the liquid. These properties are well known for equilibrium condensation, but up to now the consequences for homogeneous condensation have not been studied experimentally.

In an earlier study we described a numerical analysis with the classical nucleation theory (CNT) of homogeneous nucleation inside the coexistence envelope of the n-nonane/methane mixture. The model predicts the critical nuclei to contain $n$-nonane as well as methane, with methane fractions in the critical cluster up to 10 mol%, at 40 bar total pressure. Therefore, methane essentially cannot be considered as an inert carrier gas, as was done so far in experimental studies on the effect of carrier gas pressure on nucleation. In this paper we present experimental nucleation rates at pressures up to 40 bar, at 240 K in the supercritical region of $n$-nonane/methane.

The experimental method to measure homogeneous nucleation rates adopted in this study is based on the nucleation pulse method. A nucleation pulse is a small period of time at which supersaturation is at a high level, such that a cloud of microscopic droplets is formed by nucleation. A small recompression then quenches the nucleation process, but because a supersaturated state is maintained, droplets grow to macroscopic sizes, large enough to be detected optically. The nucleation rate is calculated from the number of droplets formed, and the duration of the nucleation pulse. Nucleation pulses are generated in piston expansion chambers and expansion shock tubes. In the next section we describe a newly built nucleation pulse expansion tube, enabling the experimental study of nucleation and droplet growth up to a pressure of 50 bar.

II. METHOD AND MEANS

We developed a special wave tube for nucleation rate measurements, which essentially is a shock tube. The tube can be operated at initial pressures up to 100 bar, necessary for measuring nucleation rates in the supercritical region of $n$-nonane/methane.

Figure 1 shows a schematic picture of the nucleation pulse expansion tube. A nucleation pulse is realized at the endwall of the high pressure section (HPS) by means of a local widening in the low pressure section (LPS). The inner diameter of the tube is 36 mm, the widening has an inner diameter of 40 mm, this yielding a cross section ratio of 1.23. The length of the HPS is 1.2 m and the length of the LPS is over 6 m. On the left side of the HPS the observation section is situated. After the diaphragm has disrupted, the nucleation pulse is generated by the initial expansion wave, and by reflections of the shock wave at the local widening.

When the number density of nucleated droplets $n_p$, and the duration of the nucleation pulse $\Delta t$ are measured, the nucleation rate $J$ follows from $J=n_p/\Delta t$.

Detection of droplets and the subsequent droplet growth are performed by optical means. At the observation section, two optical devices are present to measure droplet size and droplet number density by utilizing the scattering of laser light by the droplets. When the droplet size (we only consider spherical droplets) is of the order of the wavelength of light, the scattering is described by Mie theory. Depending on the scattering angles $\theta$ and $\delta$ (the angle between scattering direction with laser beam axis, and with the plane of polarization, respectively), the scattering pattern exhibits maxima and minima in irradiance as a function of droplet...
size. By monitoring the irradiance scattered into a limited solid angle by the growing droplets, a typical sharply peaked pattern is observed. Then, by pattern recognition droplet size can be obtained as a function of time. Furthermore, the absolute magnitude of the irradiance scattered is proportional to the number of droplets (provided that no multiple scattering occurs).

Droplet concentration can be obtained from measurement of the attenuation of the laser beam without any calibration. According to the law of Lambert–Beer, the attenuated intensity of the beam \( I \) is given by: \( I = I_0 \exp(-\beta L) \), where \( I_0 \) is the reference value, \( L \) the path length through the cloud, and \( \beta \) the extinction coefficient. The latter also depends on droplet size and is proportional to droplet number density, so there is an exponential decay of transmitted light to the number of droplets

Through a large window in the HPS, light scattered over a \( \theta \) angle of \( 90^\circ \pm 1^\circ \) is detected with a photomultiplier PM, allowing the detection of droplets of over 0.1 \( \mu \)m in diameter. Measurement of the extinction of the laser beam by photodiode PD is used for a direct determination of droplet concentration, as well as for absolute calibration of the photomultiplier. As the signal-to-noise ratio of the light scattering method is far better than that of the light extinction method, droplet concentrations below the detection limit of the extinction setup can be measured accurately by light scattering (from \( 10^4 \) cm\(^{-3} \) up to \( 10^7 \) cm\(^{-3} \)). Intensity variations of the laser beam are monitored by means of a reference signal. Similar optical devices in combination with nucleation pulse experiments were described by Wagner and Strey\(^7\) and Peters and Paikert.\(^6\)

III. EXPERIMENTAL PROCEDURE

Prior to the preparation of the gas mixture, the HPS is evacuated by a turbomolecular vacuum pump VP (Fig. 1). Next the vapor component \( n \)-nonane is brought into the HPS. In the mixing circuit a septum is mounted through which a certain amount of liquid \( n \)-nonane (Merck > 98\%) is injected by a syringe. After the \( n \)-nonane has evaporated, the gas component methane (99.995\%) is let in until the desired pressure is reached. A mixing pump MP in the mixing circuit circulates the gas through the HPS until a homogeneous mixture is obtained.

The total pressure of the mixture is measured by a piezo resistive pressure transducer (Druck PDCR 200) with an accuracy of 0.3 bar, the initial gas temperature is considered to be in equilibrium with the wall temperature and is measured by a Pt-100 (accuracy 0.2 K). After the diaphragm (polyethylene terephthalate 100–500 \( \mu \)m) has been disrupted by a hot ribbon, a wave pattern is formed. The dynamic pressure is measured by a piezo electric pressure transducer (Kistler 603 B, accuracy \( \pm 1\%) \) mounted near the endwall. Temperature during expansion and in the nucleation pulse are calculated under the assumption of constant entropy from a real gas equation of state, described by Sychev et al.\(^5\) In this calculation the amount of \( n \)-nonane present in the mixture is not considered. This introduces a possible error less than 0.1 K. The LPS is filled with a 60\%/40\% mixture of nitrogen/hydrogen. The ratio is chosen such that the post nucleation pressure is not disturbed by reflections at the contact discontinuity. Figure 2 shows a typical pressure history for a high pressure nucleation experiment. The initial pressure was 67.3 bar. The well defined nucleation pulse with a duration of approximately 400 \( \mu \)s has a minimum pressure of 30 bar, while the temperature has decreased down to 240 K. After the nucleation pulse, a supersaturated state is maintained for about 23 ms. At \( t=5 \) ms a small bump shaped disturbance is observed, arising from the reflections of the expansion wave at the local widening. It appears that this is of no importance for the experiment.

The concentration of \( n \)-nonane in the mixture is determined by comparing the observed droplet growth rates to droplet growth predicted by a theoretical model of Gyarmathy.\(^6\) Although this is an indirect measurement, we think the accuracy to be better than \( \pm 10\% \). For the present experimental conditions droplet growth is dominated by diffusion only, so the actual error is determined by the uncertainty of the value of the available binary diffusion coefficient of \( n \)-nonane in methane. Since no direct experimental data are available for nonane/methane mixtures, we applied an empirical correlation proposed by Fuller et al.\(^7\) including a high pressure correction. Binary diffusion coefficients of several mixtures calculated with the correlation according to Fuller deviate on average 5.4\% from experimental data.
tails about this method for determining the $n$-nonane concentration will be described elsewhere.

We have performed test experiments with the pulse expansion tube with $n$-nonane and nitrogen as a carrier gas. The measured nucleation rates agreed within the experimental error with those of Wagner and Strey.\textsuperscript{7}

IV. RESULTS

In Fig. 3, measured nucleation rates are plotted as a function of $n$-nonane supersaturation $S$ ($S$ is defined as the ratio of nonane vapor density and saturated nonane vapor density at the same total pressure and temperature: $S := \rho_v / \rho_{sat}$, with the saturated vapor density calculated according to the Redlich–Kwong–Soave (RKS) equation of state\textsuperscript{15} for different pressures. The temperature in the nucleation pulse was in all cases approximately 240 K; a correction has been applied for small variations in temperature. The cause of the large scatter in the 40 bar experiments is not completely clear yet. Since these experiments correspond to very low values of $S$, small errors in the calculated equilibrium density may have a large effect.

Besides a natural increase of nucleation rate with supersaturation for each pressure, we notice that the supersaturation of $n$-nonane, required for a given nucleation rate, decreases strongly with increasing pressure. This must be considered a very important result; it clearly demonstrates a strong influence of methane on the nucleation process. Figure 3 also shows theoretical nucleation rates according to calculations based on the binary classical nucleation theory.\textsuperscript{2} A significant difference is found between experiment and theory and theory exhibit the same general behavior of decreasing supersaturation with increasing pressure. Experiment and theory point to the presence of both $n$-nonane and methane in the critical droplet; the nucleation therefore must be considered to be binary nucleation. A comparison of the present experimental results and those of a new theoretical binary nucleation model was given by Kalikmanov and van Dongen.\textsuperscript{16} For pressures of 10 and 20 bar the agreement was quite satisfactory. For the higher pressures the agreement appeared to be less.

The value of the $n$-nonane supersaturation is, of course, dependent on the saturated vapor pressure of $n$-nonane, which varies strongly with total pressure. So as an alternative representation, nucleation rate is plotted vs $n$-nonane molar density in Fig. 4. The results at 40 bar are not in the diagram because of the larger scatter. Here, all data almost overlap within the experimental uncertainty. Assuming the correctness of the droplet growth model, the explanation could be the following: with a fixed $n$-nonane density, adding methane results both into a lowering of the supersaturation, and into a dissolving of methane in the critical droplets which lowers the surface tension. Both effects have an opposing influence on nucleation rate.

Finally, we applied the method described by Oxtoby and Kashchiev\textsuperscript{17} to deduce the excess number of molecules $n_i^*$ of both species in the critical nucleus:

$$\Delta n_i^* = \left[ \frac{\partial (kT \ln J)}{\partial \mu_{0,i}} \right]_T,$$

where $\mu_{0,i}$ is the chemical potential of component $i$ in the gas mixture, and $k$ is Boltzmann’s constant.

Results are given in Table I. The numbers of methane molecules in the cluster were estimated from a linear interpolation between measurements at different pressures.

V. CONCLUSIONS

Homogeneous nucleation rates in a $n$-nonane/methane gas mixture were measured in a nucleation pulse expansion tube at different total pressures ranging up to 40 bar. The temperature in the nucleation pulse was 240±2 K in all cases. It has been demonstrated that the presence of methane drastically affects the nucleation process. With increasing total pressure the critical supersaturation of $n$-nonane necessary for homogeneous nucleation to occur decreases strongly from about 30 at 10 bar, down to 6 at 40 bar total pressure. From the relation between nucleation rate and chemical po-

![FIG. 4. Nucleation rate vs molar density for $n$-nonane/methane at 240 K.](Image)

![FIG. 3. Nucleation rate vs supersaturation for $n$-nonane/methane at 240 K. The points were measured in the pulse expansion tube, lines were calculated according to binary classical nucleation theory. The horizontal bars indicate the experimental uncertainty in supersaturation. The uncertainty in nucleation rate is of the order of the marker size.](Image)

<table>
<thead>
<tr>
<th>$p$ (bar)</th>
<th>$n$-nonane</th>
<th>methane</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>24±2</td>
<td>20</td>
</tr>
<tr>
<td>20</td>
<td>24±3</td>
<td>30</td>
</tr>
<tr>
<td>30</td>
<td>18±2</td>
<td>40</td>
</tr>
<tr>
<td>40</td>
<td>12±7</td>
<td>40</td>
</tr>
</tbody>
</table>

TABLE I. Excess number of molecules in the critical cluster at 240 K, calculated according to the relation of Oxtoby and Kashchiev. The values in the last column only give a rough indication of the number of methane molecules.
tentials the size and composition of the critical nucleus were estimated. The calculations show the number of methane molecules in the critical cluster to be of the order of 30, while the number of nonane molecules appeared to be approximately 20.

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