Methanol-water solutions: A bi-percolating liquid mixture

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An extensive series of neutron diffraction experiments and molecular dynamics simulations has shown that mixtures of methanol and water exhibit extended structures in solution despite the components being fully miscible in all proportions. Of particular interest is a concentration region (methanol mole fraction between 0.27 and 0.54) where both methanol and water appear to form separate, percolating networks. This is the concentration range where many transport properties and thermodynamic excess functions reach extremal values. The observed concentration dependence of several of these material properties of the solution may therefore have a structural origin. © 2004 American Institute of Physics. [DOI: 10.1063/1.1789951]

I. INTRODUCTION AND MOTIVATION

In aqueous solutions, amphiphiles show very rich and interesting behavior governed by the tendency of the molecules to self-organize into structures where the hydrophobic regions of molecules tend to be pushed together and away from the water, enabling the hydrophilic headgroups to hydrogen bond more easily to the surrounding water molecules. This results in various supramolecular assemblies including micelles, columnar phases, and lamellar structures depending on concentration and temperature. An emerging route toward the development, testing, and refinement of detailed molecular models of the hydrophobic interaction, hydration, and the physics of aqueous macromolecules involves the use of small molecule systems (such as lower alcohols) as “prototypes.”

Despite their structural simplicity, it is well known that the thermodynamic and transport properties of alcohol-water mixtures, such as the mean molar volume, the diffusion coefficient, the compressibility, and the excess entropy, are significantly smaller, and the viscosity significantly larger, than the values that might be expected from an ideal mixture of the pure liquids. The long standing explanation of these effects in terms of an enhanced structuring of water in the presence of the alcohol does not appear to be supported by modern diffraction experiments and an alternative model is needed. Recent neutron diffraction studies of alcohol-water binary mixtures are leading to different insights into the behavior of water near molecules containing both hydrophobic and hydrophilic groups. These have established that, in the dilute alcohol limit, the alcohol molecule appears to have a mildly compressive effect on the water structure, as is seen from the slight inward movement of the second peak of the water-oxygen radial distribution function compared to the same function in pure water. This second peak, which occurs near \( r \approx 4.5 \) Å in the \( O_W-O_W \) radial distribution function of pure water, has widely been interpreted as the signature of the tetrahedral ordering in water. By contrast, in the opposite (concentrated alcohol) limit, the system segregates into what is effectively a molecular-scale microemulsion, with methyl head groups pushed towards each other, and the hydrophilic hydroxyl groups forming a boundary around small pockets of a waterlike fluid.

These simple systems have also been the subject of considerable computational investigations. The earliest of these used Monte Carlo methodologies at low or infinitely dilute concentrations of alcohol. Despite different computational models and some apparent contradictions between their results, they all found an enhanced cagelike structure of water around the methyl group, in accordance with the Frank and Evans model. Later, molecular dynamics (MD) simulations explored other mixture compositions using effective potential models. Tanaka and Gubbins were amongst the first to highlight the role of the water-water interactions in discussing aqueous solutions. More recently, Meng and Kollman have performed MD simulations of various solutes (including methanol) at infinite dilution and found that the water structure around the hydrophobic groups is preserved rather than enhanced. Laaksonen, Kusalik, and
Svishchev have explored several concentrations though there was no specific attention given to clustering. Ab initio simulations of alcohol-water mixtures have also recently been reported, however, the computational expense of these simulations is such that they are restricted to picosecond simulation on small system sizes. Nonetheless, these studies have also pointed to the lack of structural enhancement of the water surrounding the hydrophobic moiety in the alcohol. Very recently, some of us have obtained preliminary results from MD simulations of an alcohol-rich methanol-water solution that does exhibit extreme clustering and microimmiscibility.

Given the ongoing interest in these systems, the availability of experimental data only at dilute and concentrated alcohol limits, and the apparently contradictory results from computer simulation there is a strong motivation to undertake a systematic survey of extended structure (clustering) as a function of concentration in the model aqueous methanol system using both experimental and simulation techniques performed at identical state points. We are specifically interested in exploring the changes in the clustering behavior as a function of concentration, and the extent to which molecular dynamics simulations account for the experimental observations and can provide additional insight into clustering dynamics.

II. EXPERIMENTAL METHODS

A. Neutron diffraction experiments

Protiated and deuterated samples of methanol and water were obtained from Sigma-Aldrich and used without additional purification. Neutron diffraction measurements were performed on the SANDALS time-of-flight diffractometer on the ISIS pulsed neutron source at the Rutherford Appleton Laboratory, UK. Samples were placed in flat plate cells made from a Ti-Zr alloy that gives negligible coherent scattering. These were mounted on a closed cycle refrigerator, and neutron diffraction measurements were made at temperatures of 293 K (with mole fraction $x = 0.05$, $x = 0.27$, $x = 0.7$) and 298 K ($x = 0.54$), respectively. Corrections for attenuation and multiple scattering were made using the ATLAS program suite. A further correction for inelastic scattering was also made. The differential scattering crosssection for each sample was obtained by normalizing to a vanadium standard sample. A total of seven samples were measured—see Fig. 1 for $x = 0.54$. These were, respectively, (i) CD$_3$OD in D$_2$O; (ii) CD$_3$OH in H$_2$O; (iii) a 50:50 mixture of (i) and (ii); (iv) CH$_3$OD in D$_2$O; (v) a 50:50 mixture of (i) and (iv); (vi) CH$_3$OH in H$_2$O; and (vii) a 50:50 mixture of (i) and (vi). For $x = 0.05$ five samples were measured (i), (ii), (iii), (vi), and (vii). These procedures lead to a structure factor $F(Q)$ having the form $F[S_{	ext{HH}}(Q), S_{	ext{XH}}(Q), S_{XX}(Q)]$ where $S_{	ext{HH}}(Q)$ gives correlations between labeled atoms and $S_{	ext{XH}}(Q)$ and $S_{XX}(Q)$ are the two composite partial structure factors which give the remaining correlations between other types of atoms (X) and the labeled atom type (H) in the form of a weighted sum of individual site-site partial structure factors.

B. Empirical potential structure refinement

A mixture of methanol and water contains six distinct atomic components, namely C, O, M and H on the methanol molecule (here M represents the methyl hydrogen atom while H represents the hydroxyl hydrogen atom) and O$_W$ and H$_W$ on the water molecule. A full structural characterization of the system therefore requires the determination of 21 site-site radial distribution functions, which is well beyond the possibility of any existing diffraction techniques by themselves.

Therefore to build a model of the liquid structure, the experimental data are used to constrain a computer simulation of the mixture. However, unlike conventional simulations the empirical potential used here is obtained directly from the diffraction data and has the effect of driving the structure of the three-dimensional model solution toward configurations that are consistent with the measured partial structure factors. A total of 600 molecules (methanol and water) is contained in a cubic box of the appropriate dimension to give the measured density of each solution at the appropriate temperature (see Table I). Periodic boundary conditions are imposed. Reference interatomic potentials for water and methanol are taken from the literature. A comparison between the experimentally measured partial structure factors and those generated from the ensemble-averaged empirical potential structure refinement EPSR configurations are shown in Fig. 1.

In the present case a single set of site-site empirical potential coefficients was refined against the methanol-water data at each concentration, as well as for pure water and for pure methanol. The result is a set of site-site empirical potentials which are consistent with methanol-water solutions over the full range of concentrations. Comparing the results of these simulations with those where the empirical potential coefficients are refined separately for each concent-
We have performed classical molecular dynamics simulations within the NVT ensemble, utilizing previously tested intermolecular potentials for both methanol and water that have been shown to predict the structure and dynamics of the single component liquids well. Both molecules are modeled as fully flexible entities with explicit potential terms that are practically identical in all cases and conclude that our observations are not significantly dependent on the choice of system size.

In analyzing both the experimentally constrained EPSR configurations and molecular dynamics trajectories, an identical definition of a cluster is made based on bond connectivity. Specifically, water molecules are assigned to the same cluster if the number of clusters of a size \( i \) is not significantly dependent on the choice of system size.

### III. SIMULATION AND CLUSTER ANALYSIS METHODS

We have performed classical molecular dynamics simulations of methanol and water mixtures in a separate publication. We hope to present a more exhaustive study of the uncertainties involved in the EPSR analysis of molecular liquids and mixtures in a separate publication.

### IV. RESULTS AND DISCUSSION

#### A. Local structure

A comparison of radial distribution functions \( g(r) \) for CC and \( O_WO_W \) is shown in Fig. 2. A concentration of \( x = 0.27 \) and the pure solvents (water \( x = 0.0 \) and methanol \( x = 1.0 \)) are shown for both the experimentally constrained EPSR configurations and the molecular dynamics simulations. Local structure therefore appears similar in both the experimental and computational results. There are subtle differences between the experiment and simulation particularly the \( g(r) \) for CC which could be due to different potentials used in the fitting procedure and the different treatments of methyl group flexibility. However, it is clear that there is good qualitative agreement when we go on to explore extended structures in the solutions.

### TABLE I. Parameters of the methanol-water mixtures used in the empirical potential structural refinement.

<table>
<thead>
<tr>
<th>Mole fraction ( x )</th>
<th>Temp. (K)</th>
<th>Total no. molecules</th>
<th>No. of methanol molecules</th>
<th>No. of water molecules</th>
<th>No. density/atoms (Å(^2))</th>
<th>Box size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>293</td>
<td>600</td>
<td>30</td>
<td>570</td>
<td>0.0995</td>
<td>26.68</td>
</tr>
<tr>
<td>0.27</td>
<td>293</td>
<td>600</td>
<td>162</td>
<td>438</td>
<td>0.0967</td>
<td>28.69</td>
</tr>
<tr>
<td>0.54</td>
<td>298</td>
<td>600</td>
<td>324</td>
<td>276</td>
<td>0.0955</td>
<td>30.73</td>
</tr>
<tr>
<td>0.70</td>
<td>293</td>
<td>600</td>
<td>420</td>
<td>180</td>
<td>0.0930</td>
<td>32.04</td>
</tr>
</tbody>
</table>

### TABLE II. Parameters of the methanol-water mixtures used in the molecular dynamics simulations

<table>
<thead>
<tr>
<th>Mole fraction ( x )</th>
<th>Temp. (K)</th>
<th>Total no. molecules</th>
<th>No. of methanol molecules</th>
<th>No. of water molecules</th>
<th>No. density/atoms (Å(^2))</th>
<th>Box size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.27</td>
<td>298</td>
<td>600</td>
<td>162</td>
<td>438</td>
<td>0.0968</td>
<td>28.69</td>
</tr>
<tr>
<td>0.54</td>
<td>298</td>
<td>600</td>
<td>324</td>
<td>276</td>
<td>0.0953</td>
<td>30.75</td>
</tr>
<tr>
<td>0.70</td>
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<td>424</td>
<td>297</td>
<td>127</td>
<td>0.0934</td>
<td>28.50</td>
</tr>
</tbody>
</table>
B. Clustering and cluster lifetime

We consider first the results of the neutron diffraction experiments. Visual inspection of the boxes of atoms reveals significant segregation of water from methanol at all concentrations. An example is shown for \( x = 0.54 \) in Fig. 3. Visual inspection also suggests that the methanol clusters do not tend to form hydrogen-bonded chains to the same extent as in the pure alcohol. Instead the methyl headgroups tend to be in contact, with the hydroxyl headgroups bonding to water molecules forming the main boundary between methanol- and water-rich regions. This is broadly as expected for a hydrophobically-driven system and is what has been observed in earlier diffraction work.\textsuperscript{12,13} Similar snapshots are obtained from the molecular dynamics simulations (not shown).

Further evidence of the way in which the presence of water affects the structure and orientation of methanol molecules is obtained from investigation of the size of hydrogen-bonded methanol clusters from the MD simulations and radial distribution functions. Compared to the hydrogen-bonded network in the pure liquid, the cluster sizes are much smaller. For example, in the methanol-rich solution (\( x = 0.7 \)) we find that \( \sim 75\% \) of the hydrogen-bonded methanol clusters consist of only one, two, or three methanol molecules. For comparison, in pure methanol the fraction of clusters of the same size range drops to \( \sim 37\% \), with the majority of hydrogen-bonded clusters containing more than three methanol molecules.\textsuperscript{24} This indicates a substantial disruption to the methanol hydrogen-bonded network. The orientation of the methanol molecules is also affected; in the solution the methyl headgroups are pushed closer together, as evidenced by a shift to smaller \( r \) values of the first peaks in \( g_{CC} \) and \( g_{MM} \), where \( M \) denotes a methyl hydrogen, in both the EPSR procedure and MD simulations.

The persistence of clustered structures in these systems is reflected in the average lifetime of clusters and single molecules. An estimate of these lifetimes can be obtained from analysis of the molecular dynamics trajectories and are particularly interesting in the simulation performed at the \( x = 0.7 \) methanol mole fraction. Firstly, we observe that individual water molecules are short-lived and survive, on average, for only 2 ps before being absorbed into a cluster. However, in rare cases, lifetimes of 100 ps are found. A similar result is found for the other cluster sizes which show average lifetimes of about 3 ps though there are also persistent clusters surviving for up to 0.5 ns. The methanol hydrogen-bonded clusters, already noted to be much reduced in size by the presence of the water, are extremely short-lived; most persist for \( \sim 1 \) ps with no methanol hydrogen-bonded structure lasting for more than 40 ps. Thus the simulation results, in addition to being consistent with the overall structures implied by the neutron diffraction data, also suggest that the extended structures characterizing the methanol-water system are very dynamic with rapid shedding and reforming of cluster members.

C. Percolation

We now explore clustering of both species quantitatively as a function of concentration where an identical definition of a cluster is made in analyzing both the experimentally constrained EPSR configurations and molecular dynamics trajectories. For water molecules the hydrogen-bond definition was used to designate which molecules belong to a given water cluster, while for methanol clusters the C-C distance definition was used, as this criterion is more indicative of the nature of the methanol clustering than the hydrogen bond criterion.

The cluster size distributions as obtained from the EPSR ensembles (for \( x = 0.7, 0.54, 0.27, \) and 0.05) and molecular dynamics simulation (for \( x = 0.7, 0.54, \) and 0.27) are shown...
random percolation on a 3D cubic lattice.\textsuperscript{36} The experimental molar concentration range defined by 0.27
strained EPSR data and the MD simulations, in the approxi-
taneous two-component percolation occurs coincides closely
this a bipercolating liquid mixture.

they are confined to distinct, nonspanning clusters by
x
5
5
the mixture. The larger water clusters also percolate
this molar fraction, however, methanol percolates throughout
not—occurring instead only in small isolated clusters. Above
water percolates throughout the mixture while methanol does
aries determined from our simulations are insensitive to

Several “special” concentrations emerge as defined by
changes in clustering behavior. Specifically, \(x \approx 0.27\) deter-
mines the approximate alcohol concentration below which
water percolates throughout the mixture while methanol does
not—occurring instead only in small isolated clusters. Above
this molar fraction, however, methanol percolates throughout
the mixture. The larger water clusters also percolate (at \(x = 0.54\), see Fig. 4) but become increasingly isolated until
they are confined to distinct, nonspanning clusters by \(x = 0.7\). Thus, according to both the experimentally con-
strained EPSR data and the MD simulations, in the approxi-
mate concentration range defined by 0.27 < \(x < 0.54\), both
water and alcohol clusters percolate simultaneously, making
this a bipercolating liquid mixture.

Significantly, the mole fraction range over which simulta-
neous two-component percolation occurs coincides closely
with the concentration at which many thermodynamic prop-
erties show extrema.\textsuperscript{37–42} This suggests that the nature
and extent of clustering in these mixtures may offer a structural
explanation for the thermodynamic anomalies.

In earlier work on liquids, computer simulations have
identified percolation transitions in supercritical Lennard-
Jones fluids,\textsuperscript{43} supercritical water,\textsuperscript{44} water in aqueous
acetonitrile,\textsuperscript{45} and aqueous tetrahydrofuran (THF).\textsuperscript{46,47} How-
ever, to our knowledge this is the first report of simultaneous
percolation of two fully miscible fluids. Despite subtle vari-
tion in the cluster size distribution, we have obtained inde-
pendent evidence of two-component percolation from ex-
perimental and computational methods.

D. Dimensionality of clusters

A further feature of the EPSR clusters is revealed in Fig.
5 which shows the typical surface area to volume ratio (as
represented by the number of water molecules in a cluster
which form hydrogen bonds with a methanol molecule di-
vided by the number of water molecules in the cluster) for
water molecules prior to the percolation transition, together
with an exactly analogous quantity for the methanol clusters.
Clearly the ratio does not decay as \(N^{-1/3}\) as would be ex-
pected for a three-dimensional object: the clusters appear to
maximize their surface area by forming as many bonds as
possible with methanol. The observed behavior corresponds
much more closely to a two-dimensional object, suggesting
the clusters occur in the form of disordered sheets or cylin-
ders, rather than the spherelike objects that might be ex-
pected in conventional micelle formation. Only at the highest
water content, \(x = 0.05\), do the water clusters appear to have
adopted 3D characteristics.

This broad conclusion is also supported by the analysis
of the topologies of the water clusters predicted from the MD
simulations. Figure 6 shows the variation of the average ra-
dius of gyration of all the clusters of size \(i\) [\(R(i)\)] as a func-
tion of cluster size, for three different solution compositions.
The cluster topology can be characterized by a fractal dimen-
sion \(d\), determined by a power law fit to the data in Fig. 6,
such that \(R(i) \sim i^{-d}\). For solutions of methanol mole frac-
tions of \(x = 0.7\), 0.54, and 0.3, these values of \(d\) are deter-
mined to be 1.69, 1.89, and 2.03, respectively. We note that
as the mole fraction of water (and hence the proportion and
size of larger clusters) increases the characteristic dimension
increases. Interestingly, the cluster topologies of small clus-
ters determined from our simulations are insensitive to
changes in composition; all three compositions exhibit simi-
lar fractal dimension (\(d \sim 1.6\)) for clusters sizes up to \(i \sim 20\). These results indicating the 2D fractal dimension of
water clusters over a range of compositions is in agreement
with the results of a simulation study by Oleinikova \textit{et al.}\textsuperscript{46} on
the percolation of water clusters in the vicinity of a region
of immiscibility in an aqueous solution of THF. Simulta-
neous bipercolation of both THF and water was found in this
study, with THF percolating clusters having a characteristic
fractal dimension of 2.5 and those of water \(\approx 1.9\). Visual
inspection of some of our percolating clusters (of both
methanol and water) reveal that these clusters span all six
faces of the simulation box.

FIG. 4. Cluster size distributions for water (top) and methanol (below)
clusters in methanol-water mixtures. For water molecules the hydrogen-
bond definition was used to designate which molecules belong to a given
water cluster, while for methanol clusters the C-C distance definition was
used. On the left, from MD simulations with methanol mole fractions 0.27,
0.54, and 0.7 and on the right from neutron diffraction experiments for
methanol mole fractions 0.05, 0.27, 0.54 and 0.7. The dashed lines show the
predicted cluster size distribution at the percolation threshold (Ref. 36).
Percolation in the simulated box occurs when clusters of a size close to the
number of molecules in the simulation box form (vertical lines on the right
hand side of the plot).
FIG. 5. Ratio of number of water molecules at the surface of a cluster (as defined by being hydrogen-bonded to a methanol hydroxyl group) to total number of water molecules in a cluster (top). The dashed line shows the $N^{-1/3}$ behavior that would be expected for this ratio if the clusters grew equally in three-dimensions with $N$, the number of molecules in a cluster. Only for the fully percolating water cluster at $x = 0.05$ do the clusters show normal 3D behavior. Ratio of number of methanol molecules at the surface of a cluster to total number of methanol molecules in a cluster (below). Here even at $x = 0.7$ the methanol clusters do not approach full 3D behavior.

V. SUMMARY AND CONCLUSION

Isotope-labeled neutron diffraction measurements analyzed using the empirical potential structural refinement method have been combined and compared with independent molecular dynamics simulations at identical state points to explore structure in methanol-water mixtures at several concentrations. We find that local and extended structures are well described by both methods and lead to similar conclusions. We find highly heterogeneous mixing across the entire concentration range despite apparent miscibility of both components in all proportions. Extended chain, sheet, and three-dimensional structures form depending on concentration.

At a particular concentration regime near $x = 0.27$ these structures form percolating networks for both components. This concentration has long been considered special as it is near the point where many transport coefficients and thermodynamic functions have extremal values. Other alcohols also show extrema of these same material properties (at lower mole fractions) and the present work suggests a structural basis for these observations connected to the details of mixing heterogeneities.

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