Determination of viscometric and refractometric behavior of hydrophobically associating water-soluble DMAM-TBAM copolymer

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Abstract

The overlap concentration $C^*$ of DMAM-TBAM associative copolymer (the DMAM and TBAM are abbreviations of N, N-dimethylacrylamide and t-butylacrylamide) with different hydrophobic monomer ratios has been studied using viscosity and refractive index measurements at various temperatures (298.15, 303.15 and 308.15) K. The obtained overlap concentration using viscosimetry method is lower respect to what obtained from refractometry. The effect of the temperature as well as molecular weight and hydrophobic monomer ratio on the overlap concentration was investigated. The experimentally $C^*$ values compared with those calculated to the Huggins, Rao and Fuoss equations.

Keywords: Poly N,N-dimethylacrylamide-t butylacrylamide; Overlap concentration; Viscosity; Refractive index; Huggins equation; Fuoss equation; Rao equation.

Introduction

Recently some properties of the hydrophobically associating water-soluble DMAM-TBAM copolymer have been studied [1]. This copolymer contains two parts: a water-soluble hydrophilic monomer (DMAM) and a water-insoluble hydrophobic monomer (TBAM). It is interesting that the cloud point this copolymer and N-isopropylacrylamide as a smart polymer, are nearly the same, namely 288.15K [2]. For the DMAM-TBAM copolymer, as temperature increases above the cloud point, water becomes a poor solvent for the whole polymer chain and the phase-separated particles could not be stabilized in the colloidal form. In the present work, another interesting property of this copolymer, i.e. its overlap concentration is studied. The overlap concentration of aqueous solution of
DMAM-TBAM copolymer is evaluated by two methods. The first method is viscometry which is a usual dynamic method. Refractive index measurement is the second method which is applied for first time in the present paper.

Some equations for viscosity of polymer solutions

There are several equations to determine the intrinsic viscosity of polymer solution, which are given here for aqueous solutions of DMAM-TBAM copolymer.

Huggins equation:

The Huggins equation is the most common one used to determine the intrinsic viscosity with the following equation:

\[ \eta_{\text{red}} = \frac{[\eta]}{C} + K \frac{[\eta]}{C} \cdot [\eta] \]

where \( \eta_{\text{red}} \), \( [\eta] \), \( K \), and \( C \) are the reduced, the specific and the intrinsic viscosity, respectively. \( K_H \) is the Huggins constant that is an indication of polymer-solvent affinity.

Rao equation:

In the Rao equation we have,

\[ \frac{1}{2} \left( \frac{\eta}{\eta_0} - 1 \right) = \frac{1}{[\eta]} \cdot \left[ \frac{a - 1}{2.5} \right] \]

where “a” is a constant for a given polymer-solvent systems.

Fuoss equation:

\[ \frac{[\eta]}{C} = \frac{[\eta]}{C} \cdot \left( 1 + DC^{-0.5} \right) \]

where D is a constant.

Results and discussion

Viscosity behavior of the aqueous solutions of DMAM-TBAM copolymer

The viscosity behavior of aqueous solutions of copolymers A and B at various temperature (298.15, 303.15 and 308.15) K have been studied. The variation of the reduced viscosity versus the concentration of copolymers A and B in aqueous solutions have been shown in Fig.1. As this figure shows, the viscosity of solution increases with increasing the molecular weight. In the other hand, copolymers A and B are different in the amount of
hydrophobic monomer. Therefore Fig. 1 can be interpreted that by increasing the hydrophobic monomer of copolymer, the viscosity reduces. After measuring the reduce
viscosity, the viscometric data of copolymer dilute solutions with different copolymer
concentrations can be linearized by different equations. The the intrinsic viscosity of
copolymers A and B by the Huggins, Rao and Fuoss equations have been obtained. Our
calculations show that the overlap concentration corresponding to a given intrinsic viscosity
for these copolymers can be determined by the following equation: C* = \frac{2.8}{[\eta]}

The obtained C* for the Huggins, Rao and Fuoss equations were listed in Table 1. As
it can be seen from Table 1, the C* values of the Rao equation was closer to the
experimentally C* values.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>sample</th>
<th>experimental</th>
<th>Rao</th>
<th>Fuoss</th>
<th>Huggins</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.15</td>
<td>A</td>
<td>1.30</td>
<td>1.25</td>
<td>50.08</td>
<td>11.90</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>1.20</td>
<td>1.38</td>
<td>70.07</td>
<td>30.07</td>
</tr>
<tr>
<td>303.15</td>
<td>A</td>
<td>1.10</td>
<td>1.03</td>
<td>22.72</td>
<td>10.20</td>
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<tr>
<td></td>
<td>B</td>
<td>0.70</td>
<td>0.41</td>
<td>47.13</td>
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</tr>
<tr>
<td>308.15</td>
<td>A</td>
<td>0.80</td>
<td>0.81</td>
<td>23.93</td>
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<tr>
<td></td>
<td>B</td>
<td>0.65</td>
<td>0.53</td>
<td>45.25</td>
<td>18.51</td>
</tr>
</tbody>
</table>

Figure 1. Representation of reduced viscosity of aqueous solution copolymers A and B vs. concentration.

Refractive indices behavior of the aqueous solutions DMAM-TBAM copolymer

The variation of the refractive index versus the concentration for copolymers A and B
at various temperature (298.15, 303.15 and 308.15) K have been studied. Overlap
concentrations for aqueous solutions copolymers A at 298.15 K has been shown in Fig.
2. As this figure shows, there is a discontinuity when the variation of refractive index is
presented as a function of concentration for copolymer A. In Table 2 the experimental
overlap concentration C* of aqueous solution copolymers A and B which have been
obtained by viscometry and refractometry methods have been given. The experimental
overlap concentration obtained by the viscosimetry and refractometry are not the same,
because the values of the C* is sensitive to the method of measurement; however there is
good quantitative agreement between the overlap concentration obtained by viscosimetry
and refractometry.
Table 2. The experimental $C^*_{exp}$ of aqueous solution copolymers A & B obtained by viscometry and refractometry.

<table>
<thead>
<tr>
<th>$T(K)$</th>
<th>298.15</th>
<th>303.15</th>
<th>308.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>viscosimetry</td>
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<tr>
<td>A</td>
<td>0.30</td>
<td>0.50</td>
<td>0.80</td>
</tr>
<tr>
<td>B</td>
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<td>0.20</td>
<td>0.27</td>
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<tr>
<td>refractometry</td>
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<tr>
<td>A</td>
<td>1.80</td>
<td>2.20</td>
<td>2.90</td>
</tr>
<tr>
<td>B</td>
<td>2.80</td>
<td>3.40</td>
<td>3.90</td>
</tr>
</tbody>
</table>

The variation of the static and dynamic overlap concentration as a function of the temperature for copolymers A and B have been given in Fig. 3. As this figure shows an increases of the temperature causes an increases of the overlap concentration for both viscometric and refractometry studies.

Figure 3. Variation of the (a) dynamic $C^*$ and (b) static $C^*$ as a function of temperature for aqueous solution copolymers A & B.

Conclusions

The viscosity and refractive indices of DMAM-TBAM copolymer over a wide concentration range were determined. The experimental data were correlated in terms of Fuoss, Fedors, Huggins and Rao equations. The results showed that Rao equation was the best one to describe the dilute solution properties of both copolymers.

References
