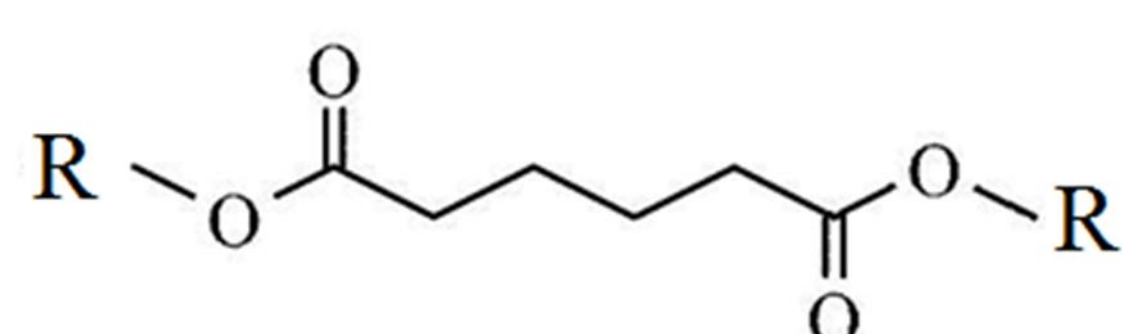


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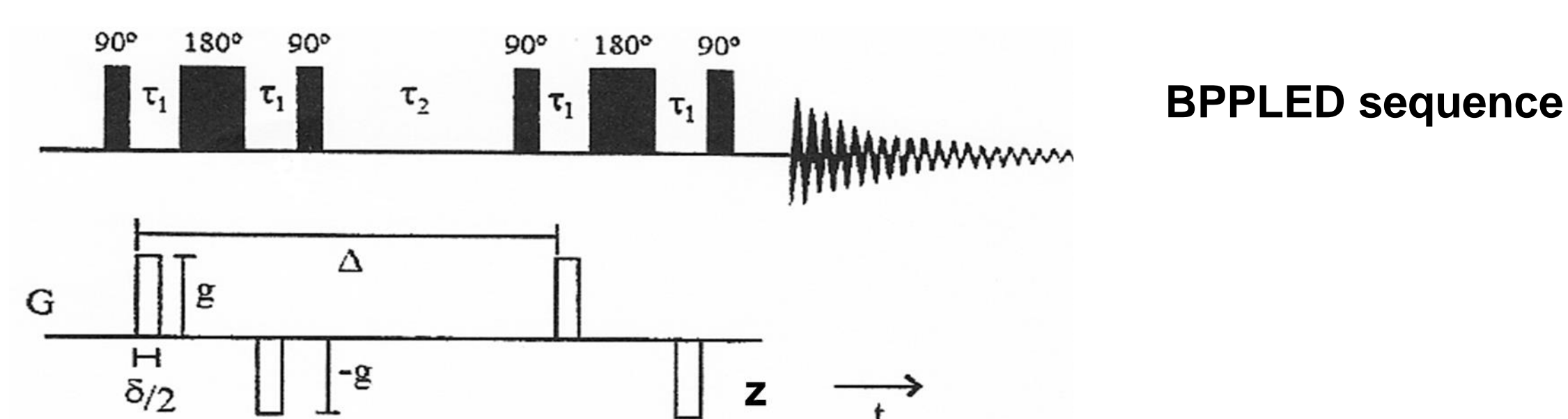
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Dialkyl adipates are a class of ester materials used as components of lubricants and plasticizers. Diffusion of plasticizers in polymers is a complex process that is difficult to study^[1]. As a contribution to understand this phenomenon, the self-diffusion coefficients of five dialkyl adipates (dimethyl, diethyl, dipropyl, dibutyl and bis(2-ethylhexyl)) were measured by the PFGSTE method in the temperature range 20 to 70°C. Simultaneous measurements of densities and viscosities of the adipates allows calculation of several types of molecular radius that provide an interpretation in terms of shape and degree of molecular association. Neat samples of pure adipates were analysed in sealed capillars placed inside of 3mm NMR tubes with a D₂O 99.9% bath to provide both for lock and temperature equilibration. The diffusivities were obtained with a 3mm BBO probe at 500MHz using the BPPLIED bipolar pulse sequence and g_{max} 56G/cm.

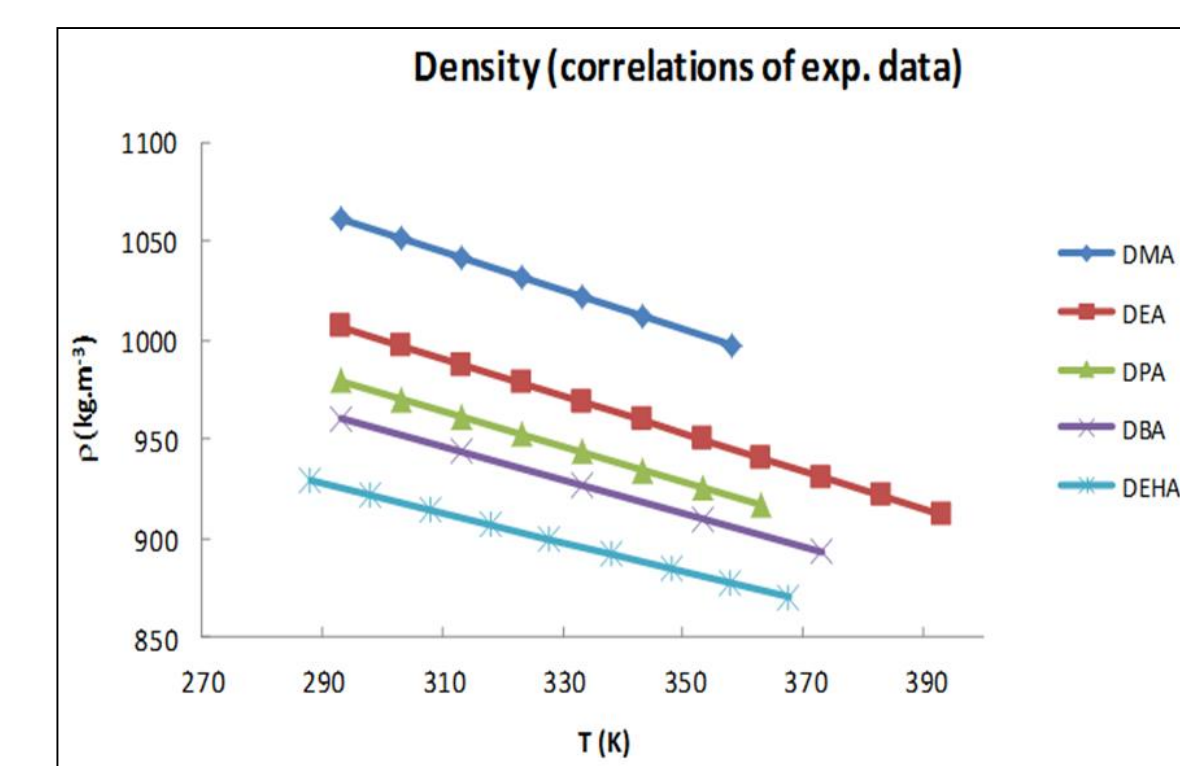
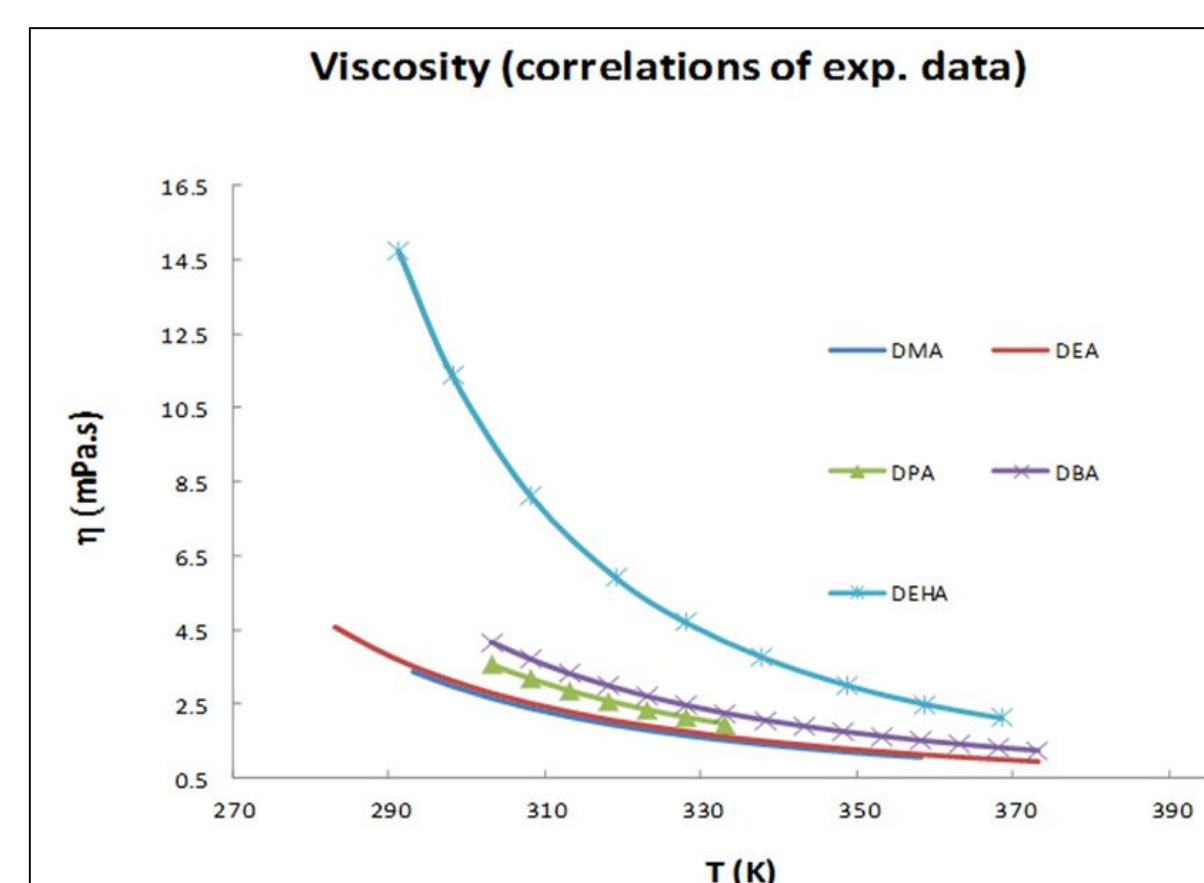
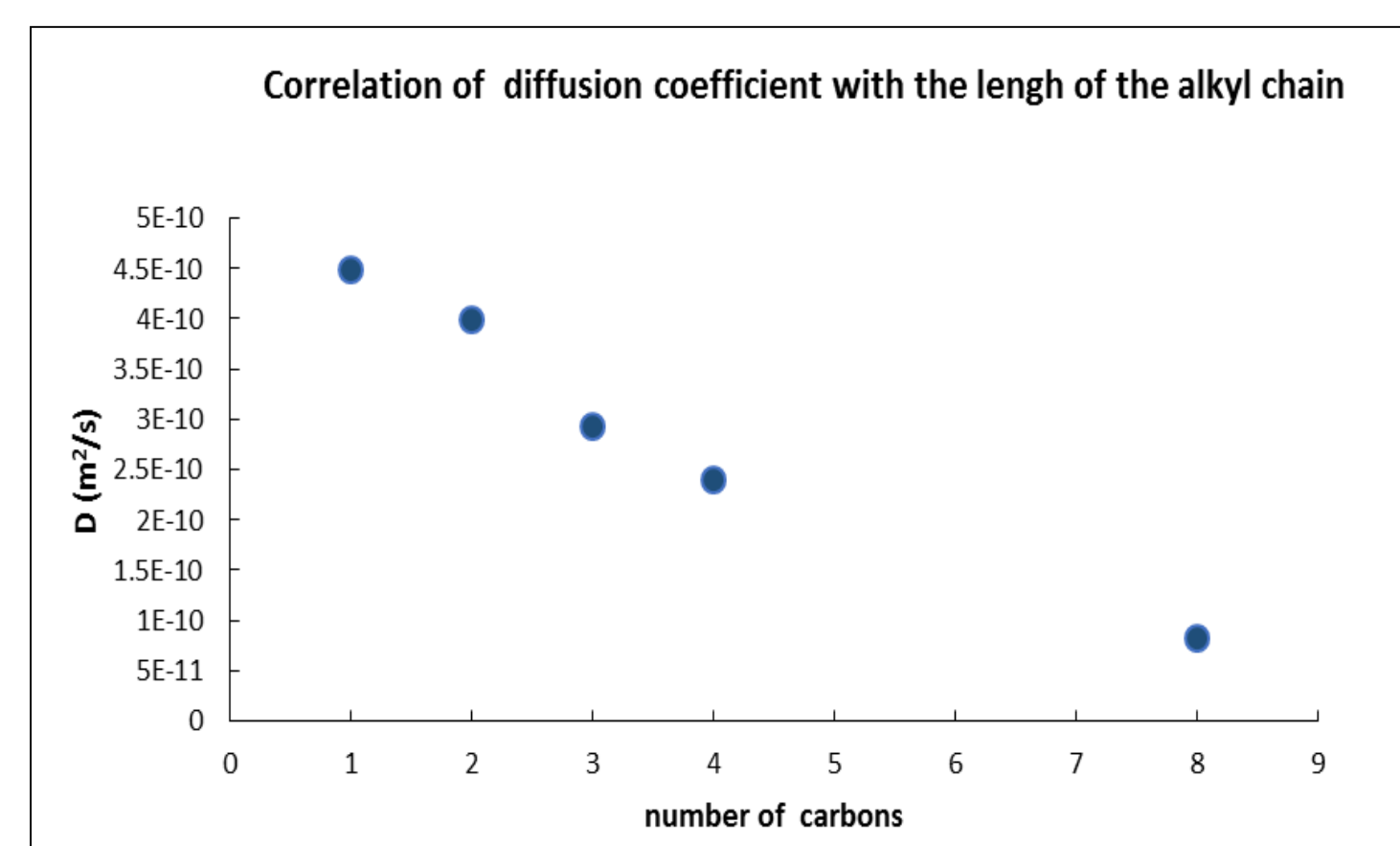
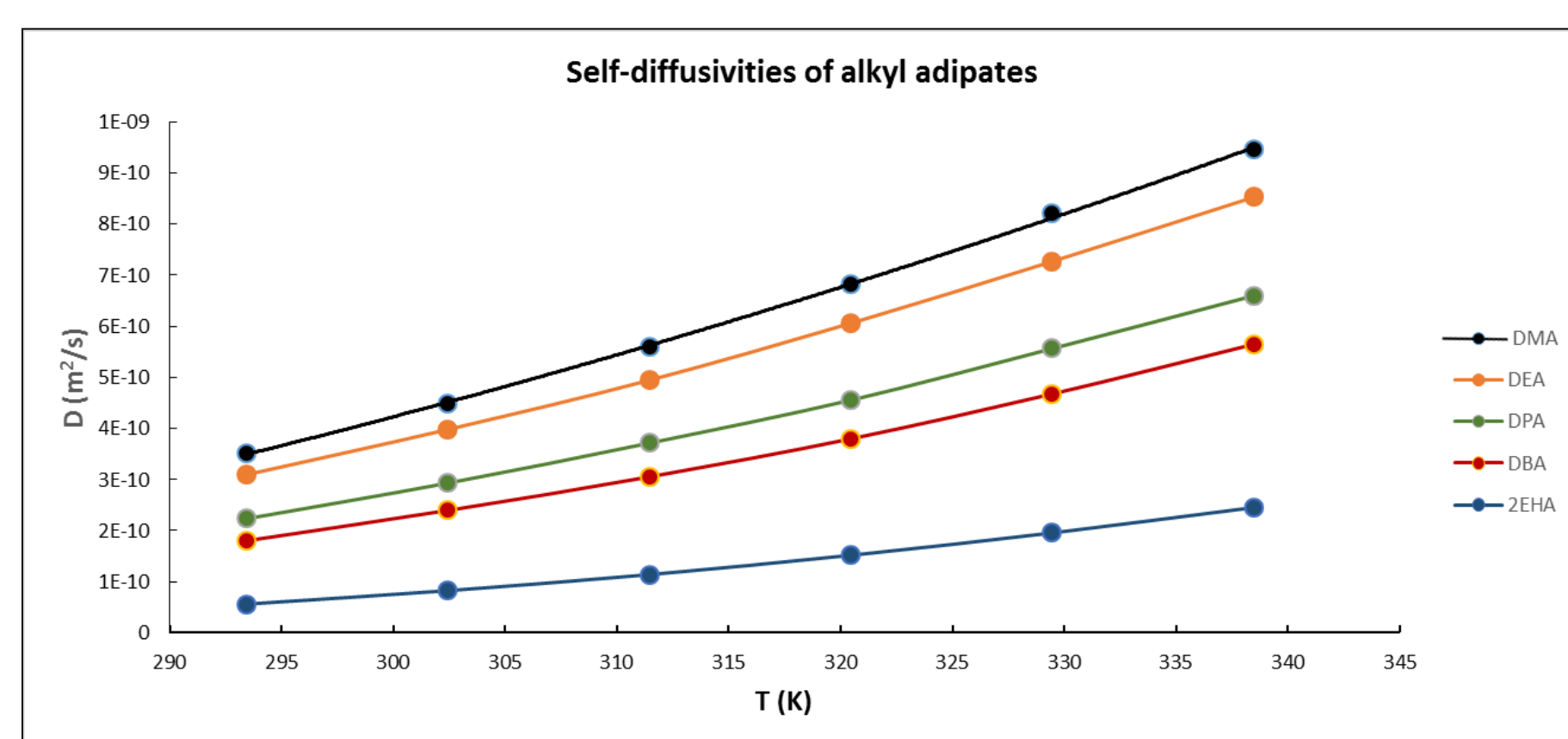


(DMA) R: -CH₃
(DEA) R: -CH₂CH₃
(DPA) R: -CH₂CH₂CH₃
(DBA) R: -CH₂CH₂CH₂CH₃
(2EHA) R: -CH₂CH(CH₂CH₃)CH₂CH₂CH₃



Self - diffusion coefficients of the adipates were measured at increasing temperatures. The diffusion time Δ was between 100 and 200ms and the gradient duration δ between 2600 and 3600 us.

Densities of DMA, DPA, DBA and DEHA were obtained in our laboratory by using a U-Tube densimeter (Anton Paar DMA HP)². Viscosities of DMA, DPA and DBA were obtained in our laboratory with a vibrating wire viscometer^{3,4}. Viscosities and density of DEA and viscosities of DEHA were obtained in literature⁵.

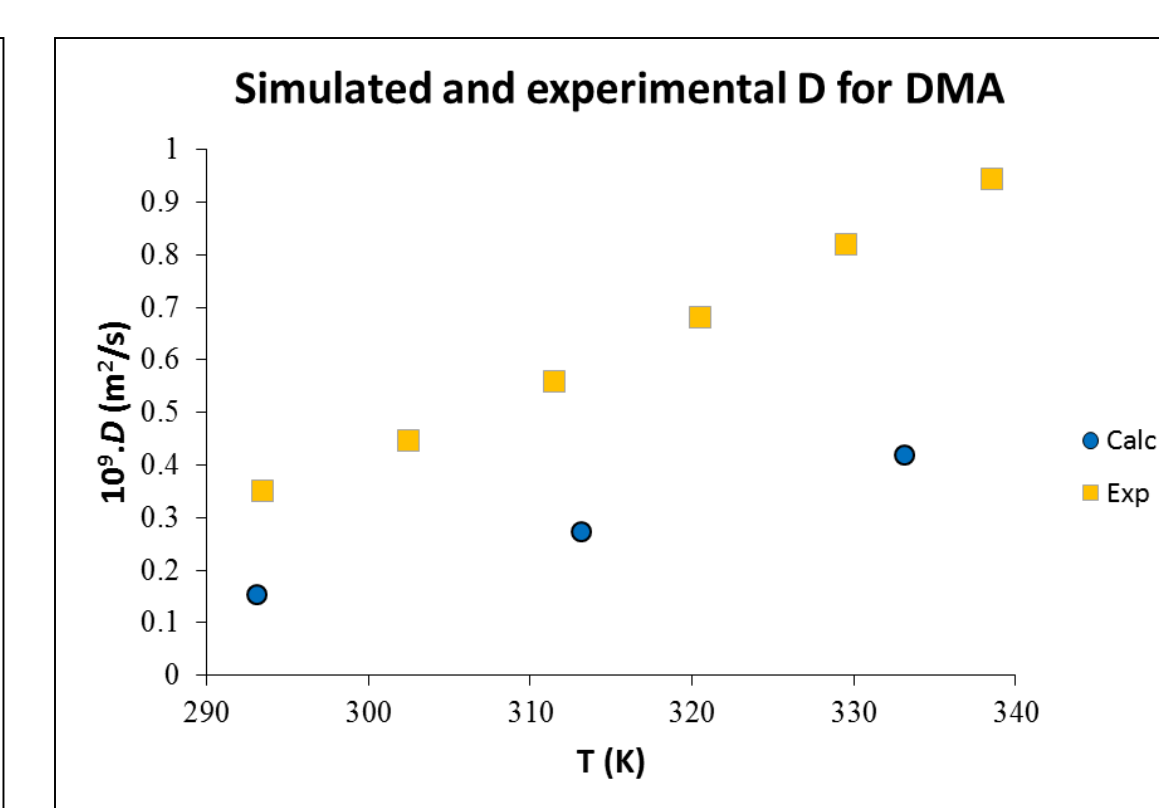
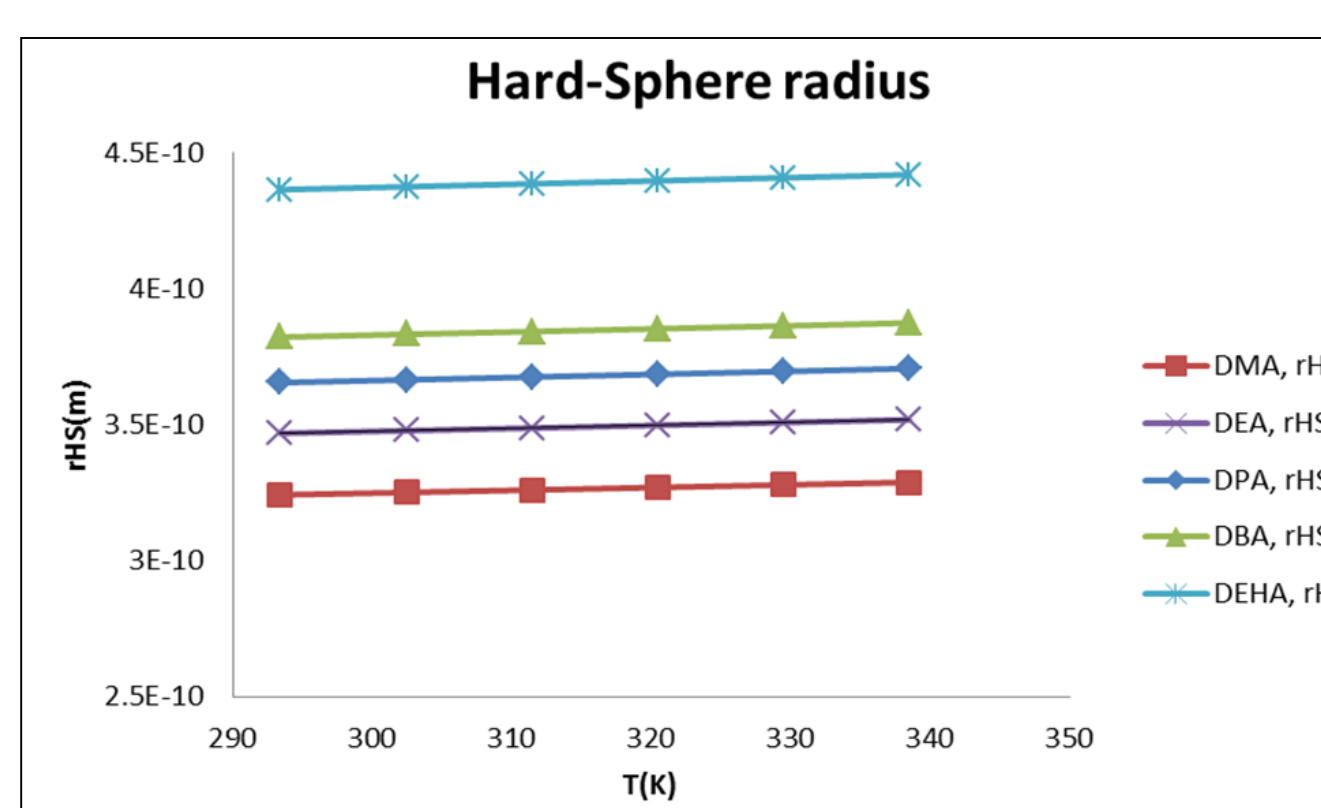
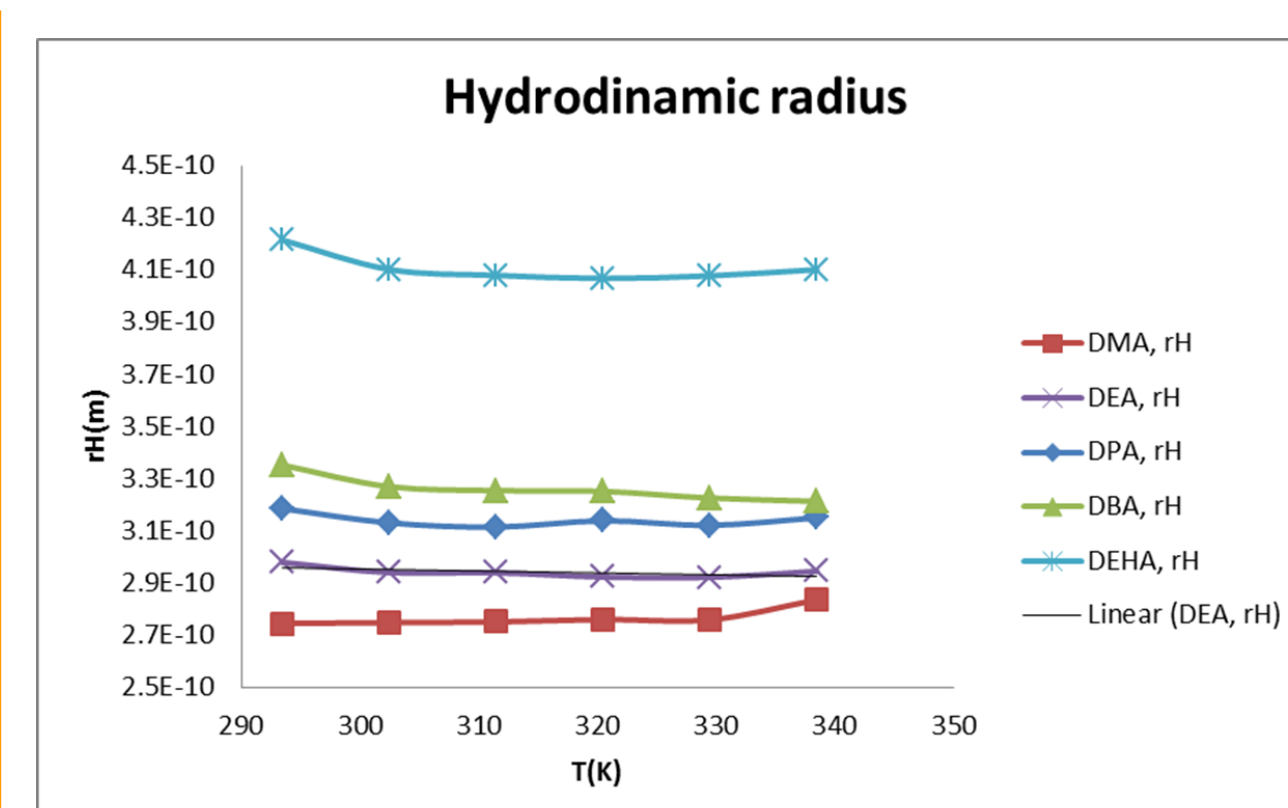


Hydrodynamic radius r_H were calculated using the Stokes-Einstein equation⁶ :

$$D = \frac{kT}{4\pi\eta r_H}$$

Hard-sphere radius r_{HS} at contact with neighbors in a cubic lattice were calculated from molar volumes V_m :

$$r_{HS} = \frac{1}{2} \left(\frac{V_m}{N_A} \right)^{1/3}$$



The hydrodynamic radius estimated from diffusivities are always smaller than the corresponding hard-sphere radius estimated from densities. The difference is around 0.5E-10m for the linear adipates, while for the branched DEHA adipate is around 0.3E-10m. This indicates that the linear adipates molecules are more strongly packed than the DEHA molecules as evidenced by the lower density of DEHA. This happens despite the higher mobility of linear adipates as indicated by comparison of the diffusivities. These differences do not change much with temperature which means that effects of self-association are not important in neat adipates.

Diffusion coefficients were estimated using molecular dynamics (MD) simulations as described elsewhere⁷. The initial results for DMA are not good as differences amount to 50%. Efforts to improve the agreement are being conducted.

CONCLUSIONS

- ✓ Diffusivities of adipates decrease almost linear with the number of carbons of the alkyl chain. Conformational effects are very subtle.
- ✓ Like in linear polymers density decreases with MW while viscosity increases.
- ✓ In liquid adipates the molecules can pack much better than spheres avoiding void volumes.
- ✓ The branched adipate DEHA is more sphere like probably due to the conformation mobility of its alkyl chains.

REFERENCES

- [1] Rahman M., Brazel C. S., *Prog. Polym. Sci.* **2004**, 29, 1223–1248.
- [2] Diogo J.C.F., Caetano F.J.P., Fareleira J.M.N.A., *Fluid Phase Equilib.* **2014**, 367, 85–94.
- [3] Diogo J.C.F., Avelino H.M.N.T., Caetano F.J.P., Fareleira J.M.N.A., *Fluid Phase Equilib.* **2014**, 374, 9–19.
- [4] Diogo J.C.F., Avelino H.M.N.T., Caetano F.J.P., Fareleira J.M.N.A., (to be submitted)
- [5] Comuñas M.J.P., Bazile J. P., Lugo L., Baylaucq A., J. Fernández J., Boned C., *J. Chem. Eng. Data* **2010**, 55, 3697–3703; Meng X., Zheng P., Wu J., Liu Z., *J. Chem. Eng. Data* **2008**, 53, 1474–1478.
- [6] Price W.S., *NMR Studies of Translation Motion*, Cambridge University Press, Cambridge, **2009**.
- [7] Pereira, L. A. M.; Martins, L. F. G.; Ascenso, J. R.; Morgado, P.; Ramalho, J. P. P.; Filipe, E. J. M., *J.Chem. Eng. Data* **2014**, accepted for publication.