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Self-diffusivity measurements of dimethyl, diethyl, dipropyl, dibutyl, Bis(2-ethylhexyl) adipates from (293–339) K by a PGSE–NMR spin-echo technique



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1. Introduction

ABSTRACT

The article reports self-diffusivity measurements of dimethyl (DMA), diethyl (DEA), dipropyl (DPA), dibutyl (DBA), and bis(2-ethylhexyl) (DEHA) adipates from (293–339) K by the PGSE–NMR technique. The expanded uncertainty of the results is estimated to better than $\pm 2\%$. The results are interpreted in terms of the hydrodynamic and the van der Waals radii. The former are calculated a Stokes-Einstein-Sutherland-type equation, using recently published viscosity data. Furthermore, recently published density data for those adipates are used to calculate the hard sphere radii at contact in a cubic lattice, in order to compare the radii obtained from transport properties with those obtained from equilibrium data. In this temperature range the self-diffusivities of the liquid dialkyl adipates studied have an Arrhenius-like behavior.

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The study of the diffusion process of small additive molecules is fundamental to the basic understanding of the diffusion mechanism, in many operations of polymer science, such as drug delivery, gas separation, food packaging and additive migration or in lubricant formulations. Dialkyl adipates are a very important class of esters used as plasticizers in polymers [1] and additives in fuel and synthetic oils [2]. There is a dearth of accurate data on diffusion coefficients of low molecular weight adipates in oils and polymers. As a contribution to understanding this important transport property, the self-diffusion coefficients of five dialkyl adipates were measured by the gradient spin-echo (PGSE) method in the temperature range (293-339) K. The liquids studied were dimethyl (DMA), diethyl (DEA), dipropyl (DPA), dibutyl (DBA) and bis(2ethylhexyl) (DEHA) adipates. The results are discussed with resort to an analysis of the hydrodynamic radii calculated by a Stokes-Einstein-Sutherland-type equation, and to the molecular radii

* Corresponding author. E-mail address: jose.ascenso@ist.utl.pt (J.R. Ascenso). calculated both by means of the van der Waals equation-of-state and by assuming a system of hard spheres at contact in a cubic lattice [3]. For this purpose, the viscosity and the density of the dialkyl adipates at 0.1 MPa were obtained from literature data. The van der Waals equation excluded volume was obtained with resort to estimated critical properties [4] in the absence of experimental data for all the dialkyl adipates studied. The activation energies are discussed in terms of the number of carbon atoms of the adipate side chains and the free volume into which the molecules can move [5].

2. Materials and methods

2.1. Materials

The samples of DMA, DEA and DEHA were supplied by Sigma Aldrich with a minimum purity of 99%. The samples of DPA and DBA were provided by Tokyo Chemical Industry Co., Ltd. (TCI). All the samples were supplied with a nominal minimum purity of 99%. The purity of all the samples was verified by ¹H and ¹³C nuclear magnetic resonance (NMR) spectrometry, and no contamination was detected other than water. These liquids were dried with molecular

sieves from Sigma Aldrich with 0.4 nm porosity (see Table 1).

2.2. Measurements of the self-diffusion coefficients

Self-diffusion coefficients were determined by the PGSE method in a NMR Bruker Avance III 500 MHz spectrometer with a 3 mm BBO probe with a z-gradient shielded coil. This combination gives a maximum possible gradient of 0.56 Tm⁻¹. A bipolar stimulated echo sequence (BPPLED) with sine gradients, two purge gradients and an eddy current delay of 5 ms were used [6]. The signal intensity (*I*) was monitored as a function of the square of the gradient amplitude (g) and the resulting self-diffusion coefficients (*D*) were calculated according to the echo attenuation equation for BPPLED

$$I = I_0 \exp\left[-D(\gamma \delta g)^2 \left(\Delta - \delta 3 - \tau_{g/2}\right)\right]$$
(1)

where I_0 is the intensity in the absence of gradient pulses, δ is the duration of the applied gradient, γ is the gyromagnetic ratio of the nucleus, Δ is the diffusion time and τ_g is the gradient recovery delay.

The duration of the pulse gradients and the diffusion time were adjusted in order to obtain full attenuation of the signals at 95% of maximum gradient strength. The duration of the gradient pulses (δ) and the diffusion time (Δ) were optimized in order to obtain a residual signal of 2–5% at the maximum gradient strength. Typically, the values used were (2–4) ms for the duration of the gradient pulses and (100–200) ms for the diffusion time. The gradient strength was incremented from 2% to 95% in a linear ramp with 16 steps. A delay of 7 s between echoes was used. The gradients were previously calibrated using the residual proton signal of D₂O 99.9% in deuterium atoms [7]. Sine shaped gradient pulses were used. For this shape the effective gradient is 0.636 g.

Each diffusion experiment produces a pseudo array of 16 spin echoes that were first FT processed in the t2 dimension using a LB of 0.2 Hz to generate a series of 1D spectra that were phased and baseline corrected prior to extraction of the diffusion coefficient by Gaussian fittings using the T1/T2 relaxation module of Topspin 2.1. For each adipate the areas of three single proton peaks were used in the fittings and the average D value was taken.

Pure dialkyl adipate samples (~40 μ l) were sealed in calibrated capillaries and then placed in 3 mm NMR tubes (PRECISION: Wilmad) with enough D₂O to provide for locking and thermal bath over the entire length of the adipate sample (~35 mm). To guarantee reproducibility of the results this geometry was kept in all the samples. Temperature was controlled by a BCU05 Bruker unit with an air flow of 400 lh⁻¹ and measured to within 0.1 K. For thermal equilibration of the sample a waiting time of at least 10 min between each experiment was used. The probe temperature was previously calibrated with a copper-constantan thermocouple placed inside the 3 mm NMR tube filled with a mineral oil.

3. Results

The results obtained for the self-diffusion coefficients, D, for the

Table 1

Characterization of the samples of dialkyl adipates used in this work.

| Liquid | Source | Purity ^a (Mass fraction) |
|----------------------------------|---------------|-------------------------------------|
| Dimethyl adipate (DMA) | Sigma Aldrich | 99% |
| Diethyl adipate (DEA) | Sigma Aldrich | 99% |
| Dipropyladipate (DPA) | TCI | 99% |
| Dibutyladipate (DBA) | TCI | 99% |
| Bis(2-ethylhexyl) adipate (DEHA) | Sigma Aldrich | 99% |

^a Purity reported by the supplier.

Table 2

Experimental Self-diffusion coefficients for DMA, DEA, DPA, DBA and DEHA at 0.1 MPa.

| | $10^{10} D/m^2$ | $10^{10} D/m^2 s^{-1}$ | | | | | | |
|--------|-----------------|------------------------|------|------|------|--|--|--|
| T(K) | DMA | DEA | DPA | DBA | DEHA | | | |
| 293.43 | 3.52 | 3.10 | 2.24 | 1.82 | 0.56 | | | |
| 302.44 | 4.49 | 3.98 | 2.93 | 2.38 | 0.82 | | | |
| 311.45 | 5.59 | 4.95 | 3.71 | 3.03 | 1.15 | | | |
| 320.46 | 6.82 | 6.06 | 4.56 | 3.78 | 1.52 | | | |
| 329.45 | 8.21 | 7.27 | 5.54 | 4.66 | 1.96 | | | |
| 338.47 | 9.46 | 8.51 | 6.60 | 5.62 | 2.46 | | | |

Expanded uncertainties: $U(T) = \pm 0.05$ K; $U(D) = \pm 2\%$ at a 95% confidence level.



Fig. 1. Self-diffusion coefficients of dialkyl adipates at six temperatures. Experimental data: \diamond , DMA; \times , DEA; \triangle , DPA; \bigcirc , DBA; \square , DEHA; correlation Eq. (2) with parameters given in Table 3.

dialkyl adipates studied are shown in Table 2 and in Fig. 1, for six temperatures. The expanded uncertainty of the results was estimated to be $\pm 2\%$ at a 2σ level. As expected, the increase of the self-diffusion coefficients with temperature reflects the increasing molecular mobility. The magnitude of *D* depends on the structure of the dialkyl adipates in the following order: $D_{\text{DMA}} > D_{\text{DEA}} > D_{\text{DBA}} > D_{\text{DEHA}}$. This trend was expected in terms of the molecular mass of the dialkyl adipates studied.

The diffusivity values were correlated to each fluid using the Vogel equation.

$$D = \exp\left(A_D + \frac{B_D}{C_D + T}\right)$$
(2)

The coefficients, A_D , B_D and C_D were obtained by fitting Eq. (2) to the experimental data in Table 2 and are listed in Table 3, together with the RMSD and bias of the fitting, defined as:

$$\text{RMSD} = \left[\frac{1}{N}\sum_{i}^{N} \left(\frac{D_{\text{exp},i}}{D_{\text{calc},i}} - 1\right)^{2}\right]^{\frac{1}{2}}$$
(3)

bias
$$= \frac{1}{N} \sum_{i}^{N} \left(\frac{D_{exp,i}}{D_{calc,i}} - 1 \right)$$
 (4)

4. Discussion

The diffusivity results may be interpreted by means of a Stokes–Einstein–Sutherland-type equation. In the present work the hydrodynamic radius, $R_{\rm H}$, was obtained directly from the selfDownload English Version:

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