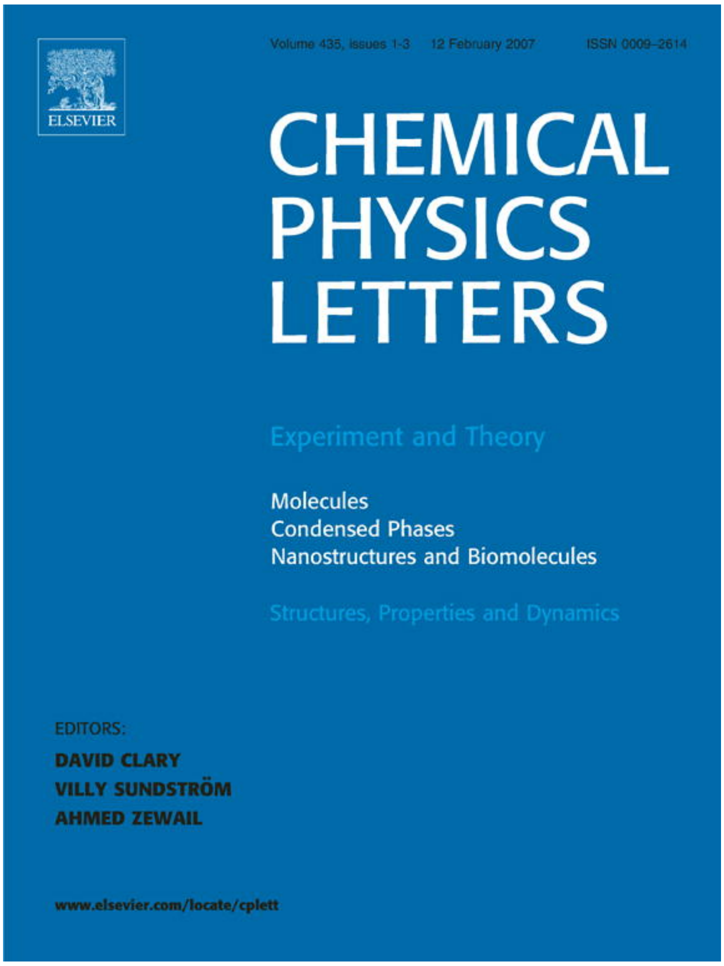

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On the question of the ratio between diffusion coefficients of radical ions and their parent molecules in solution

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Abstract

The diffusion coefficients of radical ions of hexafluorobenzene, diphenylacetylene, triptycene, and tetraphenylnaphthalene were measured in liquid *n*-hexane and *n*-hexadecane at different temperatures. These were compared with the literature values of the diffusion coefficients of the corresponding neutral molecules in these solvents. Typically, the relative change in the diffusion coefficients decreased with increasing the size of particles or the temperature of solutions. No evidence for a specific manifestation of the low solvent polarity in the relative change was observed. In the case of triptycene in hexadecane solution, the enhancement of the solute's diffusion caused by ionization was found.

1. Introduction

It is well known that both ions and radicals often diffuse in solutions more slowly as compared to stable molecules that are similar in their size and geometry [1–7]. At the same time, such slowing down does not look-like an imperative. For instance, no significant difference between the diffusion of chemically stable radicals and their closed-shell analogues was observed [1]. Besides, it was reported that some organic radicals and ions diffused similarly to their parent molecules [8,9].

Undoubtedly, the change of the diffusivity originates from that of the solvent/solute interactions upon going from molecules to charged or open-shell species. However, the actual comprehension of the nature of such interactions does not provide us with the satisfactory predictions of the molecular diffusion coefficients. The key factor, which determines the progress in this field, is sure to be the experimental investigations of the diffusion of various molecular species in liquids.

Recently [10], the mobility values for a series of organic radical ions in *n*-alkanes were determined. Particularly, it was found that radical cations of triphenylmethane and triptycene in liquid *n*-hexadecane displayed twice as high mobility as compared to other hydrocarbon radical ions with similar molecular size. It was also observed that this difference decreased approximately linearly with the decrease of solvent viscosity and in *n*-hexane solutions, the difference became insignificant.

In the present work, the literature values of the diffusion coefficients of several aromatic molecules including triptycene in liquid *n*-hexane (C6) and *n*-hexadecane (C16) were compared with the diffusion coefficient of corresponding radical ions in the same solvents. This comparison gives the opportunity to look into the above paradox and to get new information about the effect of the appearance of the excess charge and the open electronic shell on the molecular species diffusivity.

2. Experimental and calculation details

The studied solutes were hexafluorobenzene (99%, HFB), diphenylacetylene (98%, DPA), triptycene (98%,

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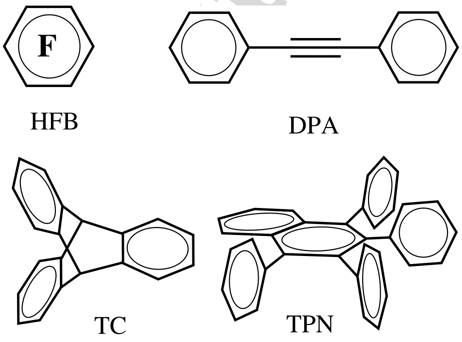
TC) and 1,2,3,4-tetraphenylnaphthalene (97%, TPN). All of these were used as received from Aldrich. The structures of the solutes are shown in Scheme 1. *n*-Hexane and *n*-hexadecane (both are from Aldrich, 99%) were purified by passing several times through 0.5 m column of activated alumina. The temperature of the solutions was typically varied from 233 K up to 348 K (±2 K) but within the range where the solvent was in liquid state.

The mobility values of the radical ions under study in alkane solutions used in the present work, except for two points for TPN in C16, were the same as reported in Ref. [10]. They were obtained using the method of time-resolved electric field effect in recombination fluorescence [11,12]. The solutions of the solutes in the concentration of 3–10 mM were irradiated by X-ray pulses (20 keV, 2 ns) with the use of X-ray fluorimeter operating in single photon counting regime [13]. The radical ions of interest were formed via the capture of primary solvent holes and excess electrons by the solutes.

The irradiated solution was between two parallel electrodes, so that uniform electric field up to 36 kV/cm could be created in the solution. Recombination fluorescence decays under nonzero $I_E(t)$ and zero $I_0(t)$ electric field were registered. The sum of the mobilities of the geminate ions could be determined with a typical accuracy of about 10% using the comparison of the calculated $I_E(t)/I_0(t)$ ratio with the results of computer simulation of geminate recombination as was described in Ref. [12].

As it was found earlier [12], in alkanes, DPA formed both radical cations and radical anions with close mobilities. The same was likely to be valid for TPN. HFB captured solely excess electrons and formed radical anions, while molecules of TC formed stable radical cations only. The radical anion of TC was found to decay via electron detachment, presumably because of rather large negative electron affinity (see, e.g., Ref. [14]). The mobility of $TC^{+\cdot}$ was determined using the solution of both HFB and TC, where excess electrons were captured by HFB molecules. The mobility of HFB radical anions was measured in the same way as reported earlier [12].

Diffusion coefficients D_I of the ions were evaluated using the Nernst–Einstein relation



Scheme 1. The structures of hexafluorobenzene (HFB), diphenylacetylene (DPA), triptycene (TC), and tetraphenylnaphthalene (TPN).

$$\frac{D_I}{kT} = \frac{\mu}{e}, \tag{1}$$

where μ is ion mobility, e is elementary charge, k is Boltzmann's factor, and T is absolute temperature. Diffusion coefficients D_M (cm^2/s) of neutral molecules were calculated using the modified Stokes–Einstein (SE) relation [15,16]:

$$\frac{D_M}{T} = \frac{A}{\eta^p}. \tag{2}$$

Here p and A are the parameters, which depends on solute molecular radius. For DPA and TC, these parameters amounted to $A = 1.2 \times 10^{-9}$, $p = 0.752$, and $A = 4.3 \times 10^{-10}$, $p = 0.873$, respectively, for solvent viscosity measured in Poises [15,16]. In the cited works, the parameters were obtained for *n*-alkane solutions at temperatures close to 293 K and these have been presumed to be the same within the temperature range studied in the present work. The viscosities η of C6 and C16 were taken from Refs. [17,18].

The diffusion coefficients of HFB molecules in both C6 and C16 solutions were estimated using the values $A = 1.5 \times 10^{-9}$ and $p = 0.77$. These values were obtained by fitting with Eq. (2) the experimental data on HFB diffusion in a series of *n*-alkanes from C6 to C16 within a temperature range of 233–353 K [19,20].

No literature values of the diffusion coefficient were found for TPN. To estimate these with Eq. (2), the simple average between A and p values for 9,10-diphenylanthracene and rubrene reported in Refs. [15,16] was used. These two compounds have structures that are similar to TPN's one, and the molecular radius of TPN falls approximately in the middle between their radii $R_{vdW} = (3V_{vdW}/4\pi)^{1/3}$, where V_{vdW} was molecular volume of the solute [21]. The average values for TPN amounted to $A = 2.4 \times 10^{-10}$ and $p = 0.92$.

3. Results and discussion

Fig. 1 shows the results of the measurements of the radical ion mobilities μ in C6 and C16 at different temperatures. In Table 1, as a reference source, the experimental values of μ at 293 K as well as the diffusion coefficients D_I of the investigated radical ions and D_M for the parent molecules calculated at this temperature are listed. The table also includes the molecular radii of the compounds and the mobility activation energy as obtained from Arrhenius approximation of the temperature dependence of μ. The values of D_M/D_I ratios at different temperatures are presented graphically in Fig. 2.

As it is demonstrated in Table 1, the calculated D_M values decrease monotonously with increasing molecular radius of the solutes. Contrary to the conventional SE relation predictions, this decrease is faster than the inverse proportion, especially in C16 solutions. However, such a deviation is in qualitative agreement with the theoretical

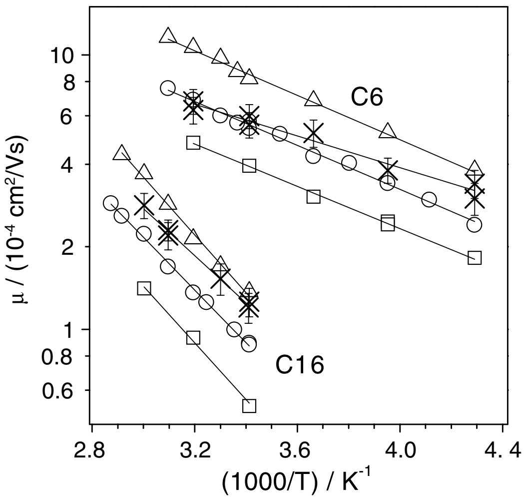


Fig. 1. The values of the radical ion mobilities of HFB (△), DPA (○), TC (×), and TPN (□) at different temperatures in C6 and C16. Solid lines are Arrhenius approximations of the experimental data.

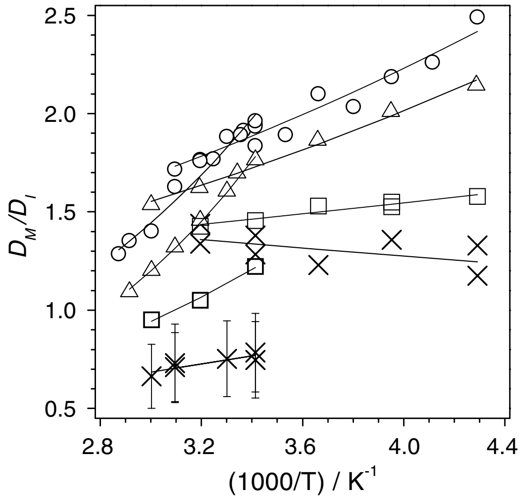


Fig. 2. The values of the ratio D_M/D_I for HFB (△), DPA (○), TPN (□), and for TC (×) in C6 (right group of curves) and C16 (left group of curves). For solutions of TC in C16 the estimated dispersion, including the errors reported for D_M, is shown. Solid lines are given as eyeguides.

calculations of the diffusion of particles that are smaller than the solvent molecules [22].

The data obtained for radical ions of HFB, DPA, and TPN do not look as something unusual. These radical ions have mobilities that relate to each other in the reverse order as their radii. Regarding the value of the D_M/D_I ratio, the neutral molecules of both DPA and HFB diffuse at 293 K approximately twice as fast as the corresponding radical ions do. Such a magnitude of the slowing down effect is similar to earlier reported observations for many small organic radicals and radical ions in polar solutions [1,7].

The lowering of the D_M/D_I ratio in the case of TPN seems to reflect an increasing importance of hydrodynamic friction as compared to other factors at the increase in molecular radius. Note that the D_M/D_I ratio calculated with the used data of Refs. [16,23] for ions of fullerene C60 in *n*-pentane gave values of about 1.3–1.4. The small difference between D_M and D_I for TPN in C16 is not quite understandable but, presumably, it can interrelate with TC results (*vide infra*).

The temperature dependence of the D_M/D_I ratio for these compounds also looks as reasonable one. In alkanes, modified SE relation is known to describe the dependence of the diffusion on viscosity for neutral molecules with $p < 1$ while in the case of radical ions this parameter is about 1.1 [2,10]. Thus, the D_M/D_I ratio should decrease with increasing temperature. For TPN, whose molecules have a larger value of p, the slope of the temperature dependence is smaller. Interestingly, from the point of view of the molecular solvation theory [2–4], the approximate equality $D_M \approx D_I$ at 350–370 K in C16 for DPA or HFB can be interpreted as the manifestation of complete destruction of the ion solvation shell.

Therefore, the examples of DPA, HFB, and TPN demonstrate that the solvent polarity is not the key factor determining the decrease in radical ion mobility. Note, although in the cases under consideration the contributions of charge and electron spin cannot be separated, the data obtained show that the simultaneous presence of these two factors does not result in a great cumulative effect.

The case of TC differs drastically from the other ones. $TC^{+\cdot}$ diffuses faster than $DPA^{+\cdot}$ and the observed value of the D_M/D_I ratio is lower than that for TPN. The D_M/D_I ratio values in C6 and C16 solutions differ more as compared to other solutes, and no significant temperature

Table 1
The values of molecular radii, R_{vdW}[a] calculated diffusion coefficient of neutral molecules D_M, diffusion coefficient of radical ions D_I as calculated using the experimental values[b] of radical ion mobility μ, and the activation energy E_a of the mobility (all parameters correspond to 293 K)

Compound	R_{vdW} (Å)	D_M (10^{-5} cm^2/s)		D_I (10^{-5} cm^2/s)		μ (10^{-4} cm^2/Vs)		E_a (kcal/mol)	
		C6	C16	C6	C16	C6	C16	C6	C16
Hexafluorobenzene (HFB)	3	3.8	0.82	2.1	0.33	8.3	1.3	1.9	5.1
Diphenylacetylene (DPA)	3.5	2.7	0.43	1.4	0.21	5.5	0.85	1.8	4.4
Triptycene (TC)	3.9	1.9	0.24	1.4	0.30	5.6	1.2	1.6	3.9
Tetraphenylnaphthalene (TPN)	4.6	1.5	0.16	1.0	0.13	4.0	0.53	1.8	4.7

[a] $R_{vdW} = (3V_{vdW}/4\pi)^{1/3}$, where V_{vdW} is molecular volume calculated with the use of data of Ref. [21].

[b] The accuracy of the values except for triptycene is ±10%, for triptycene ±15%.

dependence is observed. Moreover, according to the results obtained, in C16 $TC^{+\bullet}$ diffuses faster than the neutral molecule whilst no effect of degenerate electron transfer on the ion mobility is sure to be expected at the used solute concentrations. Therefore, these experimental data, along with the faster diffusion of $TC^{+\bullet}$ as compared to many other organic radical ions [10], can be considered as evidence that there is a factor, which manifests itself after ionization of TC and results in an enhancement of the radical cation diffusion.

As the probable cause of the enhancement of $TC^{+\bullet}$ ion diffusion, stochastic fluctuations of the internal electron charge distribution between nonconjugated *ortho*-xylene rings can be suggested. Upon ionization, the structure of $TC^{+\bullet}$, which is a Jahn–Teller active species [24], should distort in solution, so one of these rings would be strongly different from other two because of a three-minimum potential energy surface, which is typical of the TC type of symmetry [25]. On the other hand, it is known that the ESR spectrum of this radical cation in solution exhibits equivalent hyperfine interactions with protons of different rings [26]. It is sure to be result of the exchange of unpaired electron spin density and, hence, electric charge between the rings. The typical frequency of such degenerate electron exchange is probably somewhat lower than the low frequency butterfly wagging vibrations of TC molecule ($\sim$60 cm^{-1}) [27].

It is of common knowledge that the origin of the dielectric friction [2–6], which reduces the diffusion coefficients of ions in liquids, is the finite response time of the solvent polarization around the moving charge species. In the case under consideration, this implies that the TC cation with the changed internal charge distribution will be affected for a moment by the electric field created by the polarized solvent molecules whose polarization corresponds to the previous distribution of the electron density. Unlike ‘usual’ friction drags, the suggested additional force is not necessarily directed oppositely to the ion displacement. Therefore, this force should result in an enhancement of ion diffusion as it happens in the case of the enhancement due to stochastic fluctuations of dielectric friction coefficient [28,29].

As for difference between C6 and C16, note that the electronic polarization should manifest itself similarly in these solvents, following the charge redistribution and giving, probably, a small contribution to the suggested additional force. However, the local configuration of C–H bonds and the orientation of their dipole moments near the ion, follows the changes it with a time delay. This delay should correlate with the reorientation time of solvent molecules. In the case of C16, this time is two orders of magnitude longer than that for C6 [30]. At the same time, their viscosities differ by a factor of about 10 only, and this disparity can explain the more pronounced acceleration of $TC^{+\bullet}$ in C16.

Some indications supporting the above suggestion can be obtained from data on C16 solution of TPN. Molecules of TPN also have the broken conjugation between the symmetrically located phenyls and the D_M/D_I ratio in this case is lower as compared to DPA and HFB. Note that the turn of benzene rings, which leads to a weaker coupling between different fragments of the molecule, simultaneously results in the globular shape of the molecule. However, the shape of TPN and TC molecules itself is hardly to be the key factor determining the unusual diffusion because it is approximately the same for both radical ion and neutral molecule.

4. Conclusion

The diffusion coefficients of radical ions of hexafluorobenzene, diphenylacetylene, triptycene, and tetraphenylnaphthalene in liquid *n*-hexane and *n*-hexadecane were determined and compared with the literature values of those for the corresponding neutral molecules in these solvents for the first time. Except for the case of triptycene, the diffusion of the studied radical ions exhibited the expected regularities regarding solvent viscosity, solute molecular radius and temperature. No special features of the low solvent polarity were observed regarding the relative change in the diffusion coefficient of the solute caused by its ionization. The case of triptycene, for which the enhancement of the solute diffusion in hexadecane upon the ionization was found, suggests the importance of fast stochastic charge redistribution within the radical ion for its interactions with solvent and its diffusion.

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