

Comparison of the Mobilities of Negative and Positive Ions in Nonpolar Solutions

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The mobilities of organic radical ions of different molecular volumes have been determined in squalane and hexane solutions to study the influence of the ion charge sign on the ionic mobility in a weakly polar liquid. The relative mobility of geminate radical ions was measured using the method of time-resolved electric field effect in the recombination fluorescence. To determine the mobility of cations and anions separately, a trend in the value of the relative mobility was analyzed by varying the mobility of one of the geminate partners. The ratios between the mobilities of the anion and the cation of the same molecules were found to be about 1.1. It was shown that in liquid alkanes, the solvent electrostriction was the main factor determining a decrease in the mobility of an ion as compared to the parent neutral molecule. The strong dependence of the electrostrictive effect on the radius of the ionic solvation shell allows the observed difference between negative and positive charge carriers by a small but systematic difference in the effective radii of the ions to be explained.

Introduction

The mobility of negative ions μ^- in weakly polar liquids is often assumed to exceed that of positive charge carriers μ^+ .^{1–3} This assertion is based on numerous time-of-flight measurements of ionic conductivity induced by ionizing radiation in alkane solutions.^{4–6} Usually, this mobility dependence on the charge sign is explained as an effect of electronic repulsion sphere around a negatively charged ion.^{2,7} An additional free volume near anions is believed to increase the mobility of the negative charge carriers.

Quite the contrary, Schwarz⁸ has argued for the existence of a comparatively rigid glasslike molecular layer as a solvation shell around radical anions in liquid alkanes. This conclusion was drawn because the entropy change upon electron detachment from radical anions is much larger than the estimated contribution to the change due to solvent electrostriction. These mutually discordant hypotheses indicate that the above rule of thumb, concerning the role of the ion charge sign, is speculative and all of the aspects of the problem require careful consideration. Moreover, the situation also demonstrates that the up-to-date information on the ion/solvent interaction is scarce even for weakly polar solvents.

A priori, a systematic decrease in viscous friction due to the change of the ion charge to negative is questionable, since the sign itself is sure to provide a more subtle effect in the solvent/solute interaction than the uncompensated electric charge. However, ionization of a solute causes both the retardation of the solute diffusion^{9,10} and the negligible effects on it.^{11,12} There is also evidence for the accelerating diffusion of highly symmetric aromatic solutes upon ionization in viscous alkanes.¹⁰

The possible influence of the ion sign on the ion mobility should also be considered a crucial issue regarding the widely used dielectric friction theories,^{2,3,13,14} in which the solvent is described as a continuous medium. In these models, the friction coefficients depend on the square of the ion charge, thus excluding the difference between anions and cations of the same

size. If the suggested difference existed, it would be an argument supporting the necessity to use microscopic or molecular theories as the base for studying the ion/solvent interaction.¹⁵ Indeed, in the case of polar and structured liquids, like water,¹⁶ there are obvious mechanisms by which the ion/solvent interaction could depend on the ion charge sign. Particularly, for water protons, a closer approach to the anion, as compared to that to the cation, should be expected.¹⁷ Thus, the structure of the ionic solvation shell within several molecular layers can be affected to some extent by a change in charge. This is in accord with the molecular dynamic simulation reported in ref 18 where an iodine anion was found to exhibit higher mobility in liquid water as compared to that obtained for both the neutral atom and the hypothetical iodine cation. This effect was assigned to the different solvent cage structure formed by hydrogen bonds in water near diffusants.

Therefore, valuable experimental information on the ratio between the mobilities of the anions and the cations of the same molecular size is sure to be of importance for the development of theoretical models of ionic solvation and dielectric friction. At the same time, analysis of the reported experimental data has indicated that the only time-of-flight measurement by Lim et al.¹⁹ has been performed with precautions that allowed the determination of the mobilities of both the cation and the anion of the same charge acceptor. In ref 19, the mobilities of positive and negative charge carriers in pyrene solution in *n*-hexane at 297 K coincided within an experimental accuracy of about 5%. Therefore, the surprising fact is that no detailed study has been conducted to clarify the question whether the mobility of aromatic ions typically increases on going from positive to negative charge carriers.

It can be partially explained by serious experimental difficulties met in such studies. In highly polar solutions, it is not so easy to choose solutes capable of forming both stable cations and anions under the same experimental conditions. In nonre-active solvents, such as alkanes, the major experimental difficulties originate from the long time scale, typically of milliseconds, required for ion mobility measurements by the frequently used time-of-flight techniques. The conductivity signals, as measured by these techniques, are formed by the

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ions, escaping geminate recombination. Undoubtedly, any solution contains impurities with either a relatively low ionization potential (IP) or a large electron affinity (EA), and at sufficiently long time, the charge carriers in solution will be the impurity ions. For this reason, the data on anionic mobilities have been obtained mainly for the solutes with a large EA value.¹⁹ Vice versa, to neglect the influence of impurities, the cationic mobilities were usually measured using molecules with a low IP value. The IP and EA values of a particular molecule may not correlate with each other, and the charge transfer from its cation and anion to impurities within a long time range is practically unavoidable.

On the other hand, there are experimental approaches to conductivity measurements within the nanosecond time domain.²⁰ The relatively short time range studied provides more certainty in charge carrier identity. However, these methods actually determine only the relative mobility of geminate ions $\mu_s = \mu^+ + \mu^-$ because both the anions and the cations contribute equivalently to the conductivity of the irradiated solution. In this case, the simultaneous substitution $\mu^+ \rightarrow (\mu^+ - \Delta\mu)$ and $\mu^- \rightarrow (\mu^- + \Delta\mu)$ has no effect on the measured μ_s value. If $\Delta\mu$ does not depend on the solute, the measurement of μ_s fails to give reliable information on the individual mobility of geminate ions. To compare the values of cationic and anionic mobilities, the relative mobility data must be supplemented by additional assumptions.

In this work, an approach is proposed to determine both cationic and anionic mobilities using the data on the relative mobility values. It was used to ascertain the role of the ion charge sign in ion/solvent interactions and ionic motion in liquid alkanes by an example of solutions of a series of alternant aromatic solutes in squalane (viscous saturated hydrocarbon liquid) and *n*-hexane. The measurements were performed using the method of time-resolved electric field effect (TR EFE) in the radiation-induced fluorescence.^{21,22}

Concepts

Background Approximation. As noted above, if the difference in μ^+ and μ^- is independent of ion sizes, the individual mobilities cannot be determined separately by a method that gives only the relative mobility μ_s . However, such independence seems unrealistic because with very large ion radii R and, correspondingly, very low mobilities, the influence of the excess electric charge will vanish completely. More probable, this difference is in approximate proportion to the mobility value. In this case, the μ^-/μ^+ ratio is expected to be nearly constant for the different values of R , that is, for the different values of μ_s . This assumption serves as a basis for estimation of the individual mobilities of geminate ions in the present work.

An Approach To Obtain Individual Ion Mobility. The mobilities of cations and anions, formed from the same molecules, were compared using an approach similar to that described in ref 22. In that work, to determine the mobility of hexafluorobenzene (HFB) radical anion in *n*-hexane, the relative mobility of geminate radical ions was measured in two solutions. The first solution contained only an aromatic charge acceptor Ar, while the second one additionally included HFB (IP \approx 9.9 eV, and EA $>$ 0.7 eV²³). The concentration of HFB was chosen to ensure the encounter between $\text{Ar}^{\bullet-}$ and HFB in a solution within the initial part of the time range studied. For many aromatic hydrocarbons, the EA value is less than 0.5 eV,²³ and the encounter resulted in the formation of $\text{HFB}^{\bullet-}$. The lifetime of the radical anion in viscous alkane solution at room temperature exceeds at least 1 μs , because this species is readily

observable by optically detected electron spin spectroscopy (OD ESR) technique.^{24,25} In ref 19, the drift of $\text{HFB}^{\bullet-}$ in equilibrium with the dimer radical anion $(\text{HFB}_2)^{\bullet-}$ in hexane solution was studied within the millisecond time domain.

In the first solution, the primary charge carriers are scavenged by aromatic molecules with the formation of the secondary radical ion pairs $\text{Ar}^{\bullet-}/\text{Ar}^{\bullet+}$. These pairs are the precursors of fluorescing states $^1\text{Ar}^*$, which appear due to ion pair recombination. In the second solution, the precursors of $^1\text{Ar}^*$ or $^1\text{HFB}^*$ are the $\text{HFB}^{\bullet-}/\text{Ar}^{\bullet+}$ pairs. Note that in the case under consideration, the different fluorescing states are the same from the point of view of the TR EFE method.

To give the value of μ_s for geminate ions, whose recombination gives rise to the fluorescence, the TR EFE method operates with the decays of the recombination fluorescence influenced by an external electric field (see below). The measurements in the above two solutions give the two relative mobility values, respectively:

$$\mu_{s1} = \mu(\text{Ar}^{\bullet+}) + \mu(\text{Ar}^{\bullet-}) \text{ and } \mu_{s2} = \mu(\text{Ar}^{\bullet+}) + \mu(\text{HFB}^{\bullet-}) \quad (1)$$

In the previous work,²² the “observed” mobility of the HFB radical anion, μ_A , was determined as

$$\mu_A = \mu_{s2} - \frac{\mu_{s1}}{2} = \mu(\text{HFB}^{\bullet-}) - \frac{\mu(\text{Ar}^{\bullet-}) - \mu(\text{Ar}^{\bullet+})}{2} \quad (2)$$

In the case of diphenylacetylene (DPA) solution in *n*-hexane (Ar = DPA) at 297 K, the μ_A value as determined by the first equality in eq 2 coincided within a few percents with the $\text{HFB}^{\bullet-}$ mobility as measured by the time-of-flight technique.¹⁹ This coincidence supports the suggestion that the approximate equality $\mu(\text{Ar}^{\bullet+}) \approx \mu(\text{Ar}^{\bullet-})$ is valid, as seen from the second equality in eq 2 in this case. The approximate equality obtained for the *n*-hexane solutions has been used to determine radical ion mobilities in a series of normal alkanes of low and moderate viscosity.²²

In the present work, we have performed ionic mobility measurements in squalane having 2 orders of magnitude higher viscosity as compared to *n*-hexane. Because of the higher viscosity, the time domain of the geminate recombination in squalane is increased, and the effect of long fluorescence lifetimes of some luminophores used is minimized. Unfortunately, no experimental data on the mobility of organic ions in this solvent are available in the literature. Thus, we will rely upon the above assumption that the $\mu(\text{Ar}^{\bullet+})/\mu(\text{Ar}^{\bullet-})$ ratio is the same for different solutes. It implies that the $\mu(\text{Ar}^{\bullet+})$ and μ_{s1} values are in direct proportion to each other as well as the μ_{s1} and μ_{s2} ones as determined using a series of solutes. In this case, the $\mu(\text{HFB}^{\bullet-})$ value should be equal to μ_{s2} if the value of corresponding μ_{s1} is negligible.

TR EFE Method and Computer Simulation. To determine the relative mobility of geminate radical ions, we have applied the method of TR EFE in the radiation-induced recombination fluorescence. For details, see refs 21 and 22. Briefly, the TR EFE curve is determined as the $I_E(t)/I_0(t)$ ratio of the delayed fluorescence decays recorded in nonzero and zero electric fields, respectively. The time behavior of the ratio can be approximated at long times by the following relation²⁶

$$\frac{I_E(t)}{I_0(t)} \approx \exp\left(-\frac{eE^2\mu_S}{4kT}t\right) \quad (3)$$

where E is the external electric field strength, e is the electron charge, k is the Boltzmann constant, and T is the absolute temperature. It is in accord with the fact that the external electric field decreases the recombination probability for geminate ion pairs and, correspondingly, the yield of the electronically excited recombination products. Importantly, the time dependence of the TR EFE curve is determined by the relative mobility of the recombining geminate ions but not by spatial distribution of primary ion pairs in the radiation track.²²

In the present work, to improve the accuracy of the mobility measurement, particularly, to take into account the radical ion dimerization, the numerical values of μ_S were determined using computer simulation of ion pairs' recombination in a not-too-large spur in the presence of an external electric field. The simulation was performed using the computer model,^{22,27} which described both diffusion and drift of ions, formation of the secondary ions due to the scavenging of the primary charge carriers by solutes, ions' recombination, and dimerization involving neutral molecules



The model also included electronic energy transfer processes involving the excited states of both solvent and solute molecules. In the present work, these processes were of no importance within the concentration range studied in the simulation (3–5 mM).

Initially, in the computer model, four pairs of the primary charge carriers existing after the solvent ionization until their scavenging or recombination were placed within a spherical domain with the radius of 5 nm. These parameters of the typical radiation spur have been previously determined for dodecane solutions under similar experimental conditions.²⁸ In modeling, the realistic mobility values for the primary ions have been used. For the positive ions (solvent radical cations), these were of 1.6×10^{-9} and 9.6×10^{-8} m²/V s in squalane and hexane, respectively. An excess electron mobility of 5×10^{-6} m²/V s was used for both solvents. The parameters were determined by the TR EFE method as described below. Note that in the present work, the mobility values of the primary charge carriers are of no great importance because of a comparatively high solute concentration.²⁶ Variations in these mobility values by a factor of 2 did not change the modeling results.

All of the reactions except for the dimerization (eq 4) were assumed to occur on contact with the effective radius of 1 nm. As in the previous study on the ion mobility in the irradiated alkane solutions of aromatics,²² the mobility of the dimeric ions $(\text{Ar}_2)^{\bullet+}$ or $(\text{Ar}_2)^{\bullet-}$ was assumed to be by a factor of 1.4 lower than that of the monomeric ones. The effective radius of reactions 4 of 0.1 nm was used for all of the solutes except for DPA anion, for which no dimerization had been observed in the previous work.²² Note that the equality of the reaction rates for the dimerization (eq 4) of both cation and anion is an important supposition, but it is hardly to be supported by experiment (see below).

The diffusion coefficients of neutral molecules were assumed to be twice those of corresponding ions that seem to be typical for organic radical ions in viscous alkane solvents (see ref 10 and estimations given below). Note that these parameters do

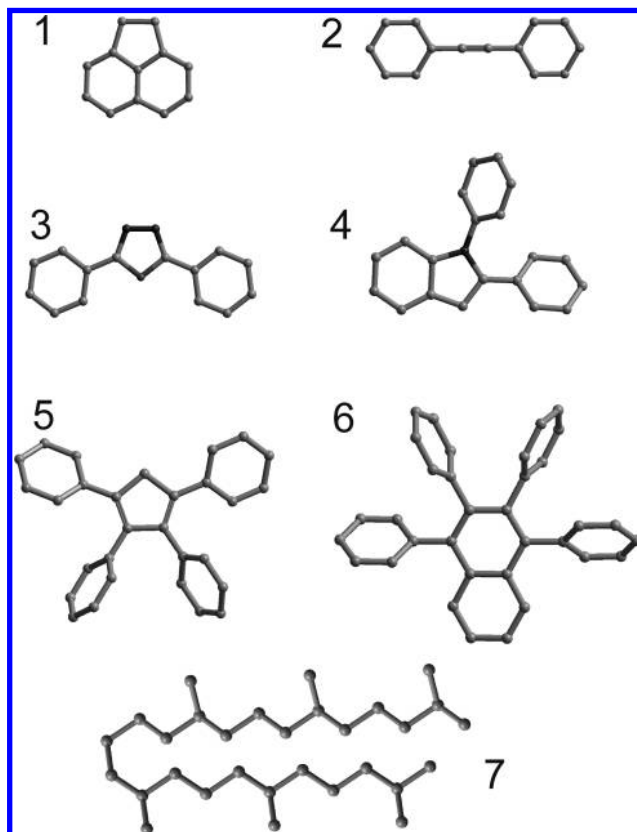


Figure 1. Molecular structures of aromatic acceptors used in the present work: ACN (1), DPA (2), PPD (3), DPI (4), TPCP (5), TPN (6), and squalane (7).

not significantly affect the modeling results at studied solute concentrations.

Experimental Section. In the experiments, the recombination fluorescence from squalane solutions of the studied aromatic compounds was excited by 3 ns X-ray pulses with a photon energy of about 20 keV and detected with single photon counting.²⁹ The sample cuvette was similar to that described elsewhere.²¹ The solution under study was poured in the gap of 1.9 mm between two flat electrodes made from titanium. One of the electrodes had a thin wall, through which the solution was irradiated. The error in the value of electric field strength in the gap was about 4%. Mostly, it has been determined by inaccuracy in the interelectrode distance, which was the same for different measurements. The experiments were carried out at 293 ± 0.5 K. The solutions under study were degassed by several freeze–pump–thaw cycles.

Both hexane (99%, Fluka) and squalane (2,6,10,15,19,23-hexamethyltetracosane, 97%, Aldrich) were additionally purified by passing twice through a column with activated alumina. Acenaphthene (ACN, 99%), DPA (97%), 2,5-diphenyloxazole (PPD, 97%), 1,2-diphenylindole (DPI, 94%), 2,3,4,5-tetraphenylcyclopentadiene (TPCP, 95%), 1,2,3,4-tetraphenyl-naphthalene (TPN, 97%), and HFB (99%) were used as received from Aldrich. The solutes have been selected since their molecular volumes are in a relatively wide range (see Figure 1), they have appropriate solubility, and their fluorescence lifetimes are very short as compared to the time domain studied, typically up to 2 μ s in squalane. An additional factor was that these acceptors were alternate aromatic molecules, whose structure favored unpaired electron delocalization over the molecule in both anionic and cationic states.

The mobility of positive ions, which existed after solvent ionization until their scavenging by aromatic solutes, was

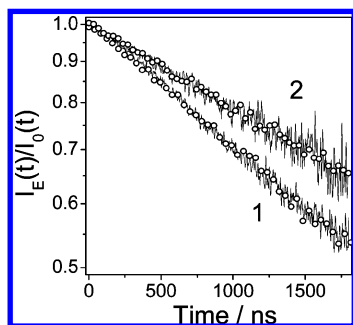


Figure 2. Experimental (noisy lines) and simulated (circles) TR EFE curves for 3 mM DPA solutions in squalane at 293 K with (1) and without (2) addition of HFB at an electric field of 36 MV/m.

estimated by the TR EFE method using the HFB solutions without another solute present because in this solvent with relatively low IP value, HFB molecules scavenged only excess electrons. The high mobile solvent hole³⁰ was not detected in the available squalane probably because of a relatively short lifetime (~ 20 ns³⁰) of this charge carrier. In the case of *n*-hexane, using gas chromatography, we have found that the solvent available contained about 0.5% of methylpentanes. Most probably, these aliphatic hydrocarbons scavenged *n*-hexane solvent holes within a few nanoseconds and did not react with HFB because of closeness of the IP values.

To determine the mobility of excess electrons, the TR EFE curves for the tetramethyl-*para*-phenylenediamine solutions in the alkanes studied were measured as previously described.²⁸ As mentioned above, approximately the same values of 5×10^{-6} m²/V s were found in both alkanes. In the case of *n*-hexane, the value is lower than the literature values.³¹ The possible reason is the presence of low amount of weak electron acceptors with negative EA values. If so, the effect of such acceptors should be negligible when organic solutes in millimolar concentration are added. *N,N,N',N'*-Tetramethyl-*para*-phenylenediamine (99%, Aldrich) was sublimed over zinc dust before experiments.

Results

Figure 2 shows the experimental and the simulated TR EFE curves for DPA solutions in squalane with and without HFB. As expected from eq 3, the curves are close to exponential dependencies on time. The slope of the TR EFE curve increases after the addition of HFB that can be assigned to the increase in the relative mobility $\mu_{S2} = \mu(\text{Ar}^{+\bullet}) + \mu(\text{HFB}^{\bullet-})$ as compared to $\mu_{S1} = \mu(\text{Ar}^{+\bullet}) + \mu(\text{Ar}^{\bullet-})$, that is, $\mu(\text{HFB}^{\bullet-}) > \mu(\text{Ar}^{\bullet-})$.²² According to the experimental curves, the charge transfer from $\text{DPA}^{\bullet-}$ to HFB molecules takes place within 200–300 ns,

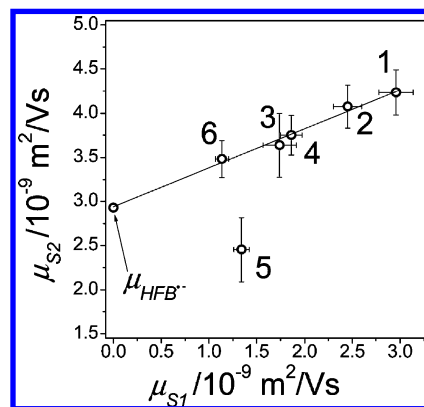


Figure 3. Dependence of the experimental values of the relative mobility μ_{S2} (circles) on μ_{S1} obtained for squalane solutions containing ACN (1), DPA (2), PPD (3), DPI (4), TPCP (5), and TPN (6). The solid line represents the linear approximation of the points except for point 5. The arrow indicates the estimated value of HFB radical anion mobility.

suggesting that the transfer rate is controlled by diffusion. Similar measurements were performed for other acceptors. The μ_{S1} values obtained for the ions studied are listed in Table 1.

In Figure 3, the μ_{S2} values are shown as a function of μ_{S1} for the same aromatic acceptor. In this plot, the straight line is a linear approximation of the experimental points except for that obtained with TPCP. The $\mu(\text{HFB}^{\bullet-})$ value was obtained from the intercept of the least-squares regression line and used to calculate the values of both $\mu(\text{Ar}^{+\bullet})$ and $\mu(\text{Ar}^{\bullet-})$ from eq 1. These values as well as the calculated ratios of $\mu(\text{Ar}^{\bullet-})$ and $\mu(\text{Ar}^{+\bullet})$ are given in Table 1. Interestingly, the relative ion mobility μ_{S1} for the studied series correlates with molecular volume, except for DPI and PPD. One of the possible explanations is that the radical cations of the latter dimerize more effectively than it was suggested in the computer model. At the same time, these ions certainly exhibit the same lower mobility, that is, the larger effective radius in solutions, containing HFB, and the use of these two compounds in the present study is not likely to lead to incorrect results.

Note that the accuracy of the data on the individual ion mobilities shown in Table 1 is not high, especially for the ions with lower mobilities, since the contribution of the cations to the μ_{S2} value is comparatively small. In the case of $\text{TPN}^{+\bullet}$, the value of the total error in the μ_{S2} measurement amounts to about 50% of the estimated contribution of this radical cation to the relative mobility, and pro forma, the $\mu(\text{TPN}^{\bullet-})/\mu(\text{TPN}^{+\bullet})$ ratio is known to within a factor of about 2. At the same time, most of the experimental points are close to the approximating line for the dependence of μ_{S2} on μ_{S1} . It implies that the linear

TABLE 1: Experimental Values^a of Relative Mobility μ_{S1} , the Evaluated Mobility of Radical Cations $\mu(\text{Ar}^{+\bullet})$, Radical Anions $\mu(\text{Ar}^{\bullet-})$, HFB Radical Anion $\mu(\text{HFB}^{\bullet-})$ ^b in Squalane, and Ratio of Anion and Cation Mobilities in Squalane and Hexane^c Solutions at 293 K

acceptor	$\mu_{S1} (\times 10^9 \text{ m}^2/\text{V s})$	$\mu(\text{Ar}^{+\bullet}) = \mu_{S2} - \mu(\text{HFB}^{\bullet-}) \times 10^9 (\text{m}^2/\text{V s})$	$\mu(\text{Ar}^{\bullet-}) = \mu_{S1} - \mu(\text{Ar}^{+\bullet}) \times 10^9 (\text{m}^2/\text{V s})$	$\mu(\text{Ar}^{\bullet-})/\mu(\text{Ar}^{+\bullet})$
HFB, $\mu(\text{HFB}^{\bullet-})$			2.94 ^b	
ACN	3.0	1.3	1.7	1.3
DPA	2.5	1.1	1.3	1.15 (1.1 \pm 0.1)
DPI	1.9	0.8	1.1	1.3
PPD	1.7	0.7	1.0	1.5 (1.7 \pm 0.4)
TPCP	1.3			
TPN	1.1	0.54	0.6	1.1 (1.1 \pm 0.2)

^a Typical errors in mobility values are $\pm 10\%$. ^b See Figure 3 and explanations in the text. ^c Values in parentheses are the ratios obtained in *n*-hexane solutions (see the text).

regression is an acceptable approximation to estimate $\mu(\text{HFB}^{\bullet-})$ and, subsequently, the $\mu(\text{Ar}^{\bullet-})/\mu(\text{Ar}^{\bullet+})$ ratios. It should also be noted that the significant contribution to the error in the measured mobility values appears from the inexactness of electric field strength, which is approximately the same for different measurements.

Interestingly, the relative ion mobility μ_{s2} is unexpectedly low in the solution containing both HFB and TPCP, which can be assigned to the aggregation involving the HFB radical anion and the TPCP molecule. A similar decrease in the charge carrier mobility has been reported in ref 19, where the aggregation of $\text{HFB}^{\bullet-}$ with one of the molecules studied in that work, *para*-benzoquinone, was observed.

The luminophores, used in the present work, do not allow one to directly verify the procedure of the $\text{HFB}^{\bullet-}$ mobility estimating as proposed for squalane in the case of *n*-hexane solutions, for which the independent measurements are available. In low viscosity solvents, the geminate recombination proceeds faster than in the viscous squalane, and the fluorescent properties of some luminophores, for example, long fluorescence lifetime in the case of ACN, make the mobility measurement inexact. We were able to determine both μ_{s1} and μ_{s2} values for DPA, PPD, and TPN in *n*-hexane solutions at 293 K. Recalculating $\mu(\text{HFB}^{\bullet-})$ reported by Lim et al.¹⁹ to 293 K, we evaluated the $\mu(\text{Ar}^{\bullet-})/\mu(\text{Ar}^{\bullet+})$ ratios for the corresponding solutes in hexane. The evaluation results agree with those obtained in squalane (see Table 1).

Discussion

Because squalane is a solvent with a high viscosity (36 cP at 293 K³²) and a comparatively long carbon chain, it is sometimes regarded as an oligomer model compound. For instance, the activation energy of methyl yellow diffusion in liquid squalane was similar to that in polyethylene.³³ At the same time, the question of whether the different ion pairs recombine in the same conditions and the solvent may be characterized using the same viscosity value can be solved positively. Indeed, the rotational diffusion study of Nile red in squalane³⁴ indicates that this fluorophore exhibits almost isotropic rotational diffusion at 298 K, while its structure is flat. Besides, the characteristic time of the α -relaxation process in squalane as extrapolated to room temperature using dielectric loss data reported in ref 35 is close to 1.5 ns. Taking into account the combination of the results of ultrasonic spectroscopy and depolarized Rayleigh scattering in long chain *n*-alkanes,³⁶ this α -relaxation time can be associated with the orientation relaxation of squalane molecules. The conformation relaxation time seems to be slightly shorter, similar to the case of long-chain normal alkanes.³⁶ The mean-square displacement of the HFB anion, which is the most diffusive particle, is 1 nm per 2 ns. The calculated³⁷ mean end-to-end distance for squalane molecules is approximately 1.8 nm. Thus, molecular dynamics in squalane is likely to be fast enough to ensure the relaxation of the solvent structure near the ion.

Components of a Friction on Moving Ion in Alkanes. The mobility of a diffusing ion in a continuous liquid is inversely proportional to the so-called friction coefficient ζ ,^{2,3}

$$\mu = \frac{e}{\zeta} \quad (5)$$

The friction coefficient may be represented as the sum of different contributions³⁸

$$\zeta = \zeta_0 + \zeta_{\text{DF}} + \zeta_{\text{EL}} \quad (6)$$

where ζ_0 is the coefficient to account for the viscous friction associated with a flow around a parent uncharged molecule, ζ_{DF} is the dielectric friction coefficient, and the third term is that associated with the electrostrictive effect in the viscous friction. Although this simple separation is questionable for polar solvents,^{39,40} it seems to be appropriate for the semiquantitative consideration in the present work.

In the framework of the Stokes model, the friction coefficient ζ_0 for the translational motion of a spherical particle of radius R is equal to $\zeta_s = f\pi\eta R$.^{2,3} Here f is the factor 4 or 6 depending on boundary conditions on the particle surface, slip or stick, respectively, and η is the liquid viscosity. The Stokes model overestimates the friction coefficient for relatively small molecules^{2,3,41} as can be illustrated by very simple considerations. In a continuous solvent, the velocity gradient near the surface of a moving spherical particle is of the same order as V/R , where V is the velocity and R is the particle radius. Thus, the estimated frictional force is approximately $4\pi R^2 \cdot \eta \cdot V/R$, which is close to the Stokes result. When describing the viscous friction in a solvent with long chain molecules, it should be taken into account that the gradient of the transversal velocity is most likely to be smoothed over a scale of the typical size R_0 of solvent molecules. The velocity gradient can be estimated to be about V/R_0 , and the viscous friction force amounts to approximately $4\pi R^2 \cdot \eta \cdot V/R_0 \sim \zeta_s \cdot R/R_0$, which is lower than the friction as predicted by the Stokes' relation.

It is of interest that this extremely crude estimation predicts the same $1/R^2$ dependence for the diffusion coefficient of a small particle, as obtained in a recent molecular dynamics simulation study.⁴² As for experimental data, this estimation gives only qualitative agreement. Particularly, at room temperature, the diffusion coefficients of dioxygen in normal hexane and squalane differ by a factor of 12,⁴¹ while the mean end-to-end distances for hexane and squalane molecules differ by a factor of 3–4 only.^{37,43}

To estimate the diffusion coefficients of neutral molecules in squalane, one can use the data available in the literature.^{41,44} In the works cited, the diffusion coefficients D in liquid alkanes were calculated using the modified Stokes–Einstein relation

$$\frac{D}{T} = \frac{A}{\eta^p} \quad (7)$$

where p and A are the parameters, which depend on the solute molecular radius, and η is the solvent viscosity measured in Poise. For squalane, we used the same p value and the by 15% higher A value as compared to those reported for normal alkanes. This choice can be substantiated using oxygen diffusivity measurements⁴¹ in these solvents. For DPA molecules, it results in $p = 0.752$, $A = 1.38 \times 10^{-9}$, and, correspondingly, in $D \approx 8.7 \times 10^{-11} \text{ m}^2/\text{s}$. It is three times higher than the diffusion coefficient of the DPA cation as calculated using the experimental value of the cation mobility (Table 1). With the parameters p and A taken from ref 10 for HFB molecule, the calculated D value is higher by a factor of 1.5 than the diffusion coefficient of HFB anion. If the empirical correlation⁴⁴ $p = 0.1347R + 0.2983$ is used with the HFB molecular radius ($R \approx 0.3 \text{ nm}$), the diffusion coefficients of the molecule and the anion differ approximately by a factor of 2.

Thus, the estimated difference in the diffusion coefficients of neutral molecules and the corresponding ions in squalane

are of the same order of magnitude as those in normal alkanes with a viscosity of about 1 cP.¹⁰ It suggests that the relative contributions of essential terms in eq 6 for different alkanes are comparable due to similarity in their dielectric and thermo-physical properties.

Dielectric Friction. The primary emphasis of studies on charge carrier movement in a continuous media^{3,13,14} was the transport of small atomic ions in strongly associated dipolar liquids. That is why the available theories are not directly applicable to alkane solutions. Nevertheless, it is instructive to estimate the value of ζ_{DF} as predicted by a conventional dielectric friction theory. A derivation by Zwanzig¹³ gave the following expression (for the slip boundary condition) for the dielectric friction contribution

$$\zeta_{\text{DF}} = \frac{3e^2}{4R^3} \left(1 - \frac{\epsilon_\infty}{\epsilon_s} \right) \frac{\tau_D}{2\epsilon_s + 1} \quad (8)$$

where τ_D , ϵ_s , and ϵ_∞ are the Debye relaxation time and the static and the high-frequency dielectric constants, respectively. In the Hubbard–Onsager theory,¹⁴ the dielectric friction coefficient is to be calculated by a more complicated relationship. However, both theories give similar results for large ions.⁴⁵

In nonpolar solvents like alkanes, eq 8, being applied directly, predicts a negligible value of ζ_{DF} because of the very small difference in the static and the high-frequency permittivity $\Delta\epsilon = \epsilon_s - \epsilon_\infty$. In normal alkanes with a viscosity of 1 cP, using eq 8 with $\Delta\epsilon = 0.023$ as determined in ref 46, one gets that $\zeta_{\text{DF}} \approx 7 \times 10^{-14}$ kg/s for the ionic radius of $R = 0.3$ nm. In this estimation, it is assumed that $\tau_D \approx 5 \times 10^{-12}$ s, which is typical of an alkane of such viscosity.³⁶ Note that the friction coefficient for the HFB molecule having similar radius is about of $\zeta \approx 3 \times 10^{-12}$, which is 2 orders of magnitude higher.

On the other hand, the solvent polarization effects also seem to be strongly underestimated when the well-developed theory of intersphere electron transfer is applied to alkanes. The electron transfer resembles the movement of ions since in both cases charge rearrangement gives rise to dynamic and relaxation processes in the polarized solvent. Within the theoretical models of electron transfer,^{47–49} these processes enter into equations via the solvent reorganization energy, λ_s , which contributes to the transfer activation energy. Being derived on the same basis of electrodynamics of continua as for dielectric friction theories, the models of electron transfer give the following expression

$$\lambda_s = \frac{e^2}{2} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_s} \right) \left(\frac{1}{R_D} + \frac{1}{R_A} - \frac{2}{R_{\text{AD}}} \right) \quad (9)$$

Experimentally, the value $\lambda_s = 0.15$ eV has been determined in liquid isooctane at $R_A \approx R_D \approx 0.33$ nm and $R \approx 1.7$ nm.⁴⁷ Thus, the “effective” value of $\Delta\epsilon$ in liquid alkanes amounts to 0.17. Nevertheless, Zwanzig’s model with this effective $\Delta\epsilon$ value gives $\zeta_{\text{DF}} \approx 5 \times 10^{-13}$, which is also insignificant as compared with the total friction force in alkanes of viscosity close to or larger than 1 cP. In alkanes of lower viscosity, the dielectric friction should be reduced because of the shortening of the Debye relaxation time.³⁶

Electrostriction Effect in Alkane Solvents. In alkanes ($\epsilon = 2$), in the approximation that the density increase ($\sim 20\%$) near an ion has no significant effect on solvent dielectric properties, the electrostrictive pressure Δp at the distance r from the singly charged ion can be estimated as follows²

$$\Delta p(r) = \frac{e^2}{32\pi^2 \epsilon_0 \epsilon^2 r^4} \quad (10)$$

The increased pressure leads to an increase in both the solvent viscosity and the friction coefficient. To characterize the relative contribution of electrostriction, the $\zeta_{\text{EL}}/\zeta_s$ ratio can be calculated as⁵⁰

$$\frac{\zeta_{\text{EL}}}{\zeta_s} = \left[R\eta(\infty) \cdot \int_R^\infty \frac{dr}{r^2 \eta(r)} \right]^{-1} - 1 \quad (11)$$

where $\eta(r)$ is the distance-dependent solvent viscosity around the ion. Using smooth approximations for the experimental dependences of viscosity on pressure for *n*-hexane,⁵¹ *n*-decane,⁵² and squalane (eq 4 in ref 32), we have found that the $\zeta_{\text{EL}}/\zeta_s$ ratios in these solvents amount to 0.3, 0.4, and 0.7, respectively, for an ion with $R = 0.3$ nm. Note that this calculation underestimates the electrostriction effect because of the neglected increase in the solvent density in eq 10.

Stiles and Hubbard have suggested³⁸ a model of friction on an ion moving in compressible polar solvents. According to that model

$$\frac{\zeta_{\text{EL}}}{\zeta_s} = \frac{1}{30} \frac{e^2}{16\pi^2 \epsilon_0 \epsilon R^4} \left(\frac{\partial \ln \epsilon}{\partial P} \right)_T \left[3\rho \left(\frac{\partial \ln \eta}{\partial \rho} \right)_T - 1 \right] \quad (12)$$

We have estimated the $\zeta_{\text{EL}}/\zeta_s$ ratio for *n*-hexane at 293 K. Taking into account the data reported in refs 53 and 54, it was assumed that $\partial \ln \epsilon / \partial P = 0.9$ GPa^{−1}. The value of $\partial \ln \eta(\rho) / \partial \rho \approx 1.3 \times 10^{-2}$ m³/kg was calculated from the isothermal viscosity–density data from NIST.⁵⁵ For an ion with $R = 0.3$ nm, eq 12 gives $\zeta_{\text{EL}}/\zeta_s \approx 0.9$.

The above consideration demonstrates that the lower mobility of most aromatic ions as compared to their parent molecules can be assigned to the solvent electrostriction effect. In contrast to solvents with high dielectric permittivity,³⁸ the contribution of the electrostrictive term in eq 6 for alkanes is comparable with that of the Stokes friction. It results in the decrease in the ion mobility by a factor of 1.5–2, as observed in the experiments.¹⁰ Note that eqs 11 and 12 predict a significant decrease of the electrostriction effect with increasing ionic radius R . Qualitatively, it is in accord with experiment,¹⁰ too.

Noting that the modified Stokes–Einstein relation (eq 7) is valid for neutral molecules at $p < 1$. It is hardly consistent with the stick boundary conditions for the molecules in viscous solvents. On the other hand, for radical ions, equation 7 is valid at $p \approx 1.1$.⁵⁶ However, according to the above estimations, the relative contribution of the electrostriction effect has a tendency to increase with increasing solvent viscosity. Thus, the results obtained demonstrate no obvious evidence that the boundary conditions, in terms of the Stokes model of viscous friction, are changed from slip to stick on going from molecules to ions in nonpolar solvents.

Influence of the Ion Charge Sign on the Ionic Mobility. Our experiments indicate that for all of the studied solutes, apart from TPCP, the $\mu(\text{Ar}^{\bullet-})/\mu(\text{Ar}^{\bullet+})$ ratio slightly exceeds unity. The observed difference, on average, is about 30% that seems to be the typical value. However, there is a factor, radical ion dimerization reaction, which is capable of decreasing the validity of the latter conclusion. In the present work, reaction 4 was

assumed to involve both cation and anion in the same extent, except for DPA. The more or less definitive conclusion about the relatively low rate of DPA radical anion dimerization was drawn in ref 22 relying on the fact that the negative charge carrier in DPA solutions had similar mobility at the DPA concentration of both 0.1 and 0.01 M. Such a high concentration range could not be studied in other cases, mainly due to the limited solubility of the compounds. We also could not apply the OD ESR method to study the complexation of the studied radical ions since a few of the polyphenyl radicals exhibit hyperfine structure in OD ESR spectra.^{24,25,57} Typically, the spectra are the unresolved singlets, and it is a complicated problem to observe the changes in the spectrum width caused by the dimerization.

Thus, in most cases, the assumption on the similarity of the dimerization rate for radical ions of a different sign is a suppositional one. If radical cations form a dimer more effectively than it is assumed in the modeling, while radical anions do it more slowly, then the comparison between the experiment and the modeling would result in the underestimation of the mobility of monomeric negative charge carriers. In some cases, like tetraphenyl-substituted compounds, the dimerization ability seems to be reduced due to the steric factor. Thus, the ratio $\mu(\text{Ar}^{\bullet-})/\mu(\text{Ar}^{\bullet+}) \approx 1.1$ observed for DPA and TPN in both *n*-hexane and squalane demonstrates the most probable scale for the effect of the ion charge changing from positive to negative. On the other hand, the larger $\mu(\text{Ar}^{\bullet-})/\mu(\text{Ar}^{\bullet+})$ ratio obtained for the different PPD ions can probably be assigned to the effect of PPD⁺⁺ dimerization. Note that the 10% increase in the anionic mobility can be explained by an approximately 10% increase in the effective solvation radius at $\zeta_{\text{EL}}/\zeta_{\text{S}} \approx 0.5$, which seems to be typical of liquid alkanes.

At the same time, several physical reasons, which could lead to significant deviations from the observed ratio, can be suggested. The most important is the difference in electronic density distributions in anions and cations, that is, the difference in highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) geometries, which can be more prominent for some molecules, as compared to the studied ones. Because the electrostrictive effect is strongly dependent on the radius of the ion solvation shell, it should be sensitive to this factor. Another probable cause is the orbital degeneracy of open-shell species, for which the influence of Jahn–Teller activity on the ionic mobility can be significant for viscous solvents, as suggested in ref 10. The strength of this effect can be different for negative and positive charge carriers due to the different degree of degeneracy of the HOMO and the LUMO levels.

Conclusions

The relative mobilities of radical ions of aromatic acceptors having different molecular volumes were measured in *n*-hexane and squalane solutions. Under reasonable assumptions, the individual mobilities of both cations and anions were evaluated for the solutes studied. It was found that the positive charge carriers were slower on average by a factor of 1.3 than the corresponding negative ions. The HFB and tetraphenylcyclopentadiene solution in squalane was the only observed exception, probably due to the complexation involving negative charge carriers in the solution. At the same time, inaccuracies in accounting for the radical ion dimerization can result in overestimating the ratio between the mobilities of monomeric ions. There is evidence that the typical magnitude of the ratio between the mobilities of anion and cation of the same aromatic molecule is about 1.1.

The analysis of the relative contributions to the friction force on moving ions has demonstrated that the dielectric friction is negligible in liquid alkanes. The main factor determining the decrease in the ionic mobility as compared to that of parent molecule in alkanes is the solvent electrostriction near the ion. Because of the strong dependence of the electrostrictive effect on the ionic radius, the observed difference between the mobilities of anions and cations can be attributed to the small but systematic increase in the ionic solvation shell in the case of negative charge carriers.

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