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Semiempirical Formula for the Estimation of Organic Radical Ion Mobility in Liquid *n*-Alkanes

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The mobilities of radical ions of a series of organic compounds in *n*-alkanes with viscosities within the range of 0.2−4 cP were determined by applying the method of time-resolved electric field effect. The obtained data were used to express the correlation between the mobilities and solvent viscosity in the form of the modified Stokes−Einstein relation. The relation was parametrized in such a way that the specific molecular properties of both solvent and solute appear in the expression only as the ratio of the volumes of their molecules. A significant difference between aromatic and aliphatic compounds was found with respect to the dependence of radical ion mobility on this volume ratio, and two different parametrizations were suggested for mobility estimation in these cases.

Introduction

Organic radical ions are well-known short-lived intermediates of photo- or radiation-induced processes, and their lifetimes in solution are often determined by their recombination, which is typically controlled by diffusion.[1,2] Therefore, to analyze the kinetics of such reactions it is necessary to have information on the diffusion coefficients of these particles. However, the use of the diffusion coefficient of a molecule as estimation for that of the corresponding radical ion a priori can give a dramatic inaccuracy. In come cases, charged and open-shell species diffuse similarly to their parent molecules but sometimes their diffusion is slower by a factor of 2 or more.[3−7] When higher accuracy is required, these peculiarities of radical ions should be taken into account. Because direct measurements are not always possible, it is advisable to have a way for radical ion mobility estimation with the use of an easily obtainable characteristic of solvent and solute.

This work is aimed at obtaining a semiempirical equation for estimating mobility in the case of organic radical ions in liquid *n*-alkanes. To achieve this goal, the mobility of a series of radical ions in *n*-alkanes from hexane to docosane was measured using the technique of time-resolved electric field effect.[8,9] The data obtained were used to get a parametrization of the semiempirical equation, which was in the form of the modified Stokes−Einstein relation[10−14] as follows:

$$\mu = \frac{A_0}{\eta^{p}} \tag{1}$$

Here μ is radical ion mobility, η is solvent viscosity, p is a constant, and A_0 is the parameter related to the ratio of the molecular volumes of the species involved. By applying the well-known Nernst−Einstein relationship

$$\frac{\mu}{e} = \frac{D}{kT} \tag{2}$$

eq 1 may be immediately rearranged in the usual form as used in refs 13 and 14 where the modified Stokes−Einstein relation was employed successfully to interrelate between the solvent viscosity and diffusion coefficients of neutral molecules in alkanes.

Experimental Details

To create radical ions of interest, alkane solutions of corresponding compounds were irradiated by X-ray pulses (20 keV, 2 ns) with the use of an X-ray fluorimeter, which was described elsewhere.[15] The secondary radical ions were formed due to scavenging the primary solvent holes and excess electrons by the dissolved molecules. The irradiated solution was put between two parallel electrodes so that a uniform electric field up to 36 kV/cm could be created in the solution. The fluorescence of electronically excited states, arising as a product of radical ion pairs' recombination, under nonzero $I_E(t)$ and zero $I_0(t)$ electric field was registered to evaluate the ratio $I_E(t)/I_0(t)$. Under appropriate conditions, the ratio $I_E(t)/I_0(t)$ decayed with a time constant, which was approximately inversely proportional to the relative mobility of the recombining ions.[8,9] The mobility values were determined using the comparison of the experimental $I_E(t)/I_0(t)$ curves with the results of computer simulation of geminate recombination as was described before.[9] The typical accuracy of the mobility measurements was about 10%.

n-Hexane (99%), *n*-heptane (99%), *n*-octane (99%), *n*-nonane (98%), and *n*-decane (98%, all from "Reactive", Russia) were additionally purified by stirring with concentrated sulfuric acid, washing with water, and passing several times through a 1 m column of activated alumina. With the gas chromatography, I revealed that the main impurities in all of the cases were methyl-substituted isomers of the solvents. The presence of the isomers is believed to have no significant influence on the results obtained. Dodecane and hexadecane (99%, both from Aldrich) were passed through a 0.5 m column of activated alumina. Docosane (Aldrich, 99%) was used as received. Further, notation C*N* denotes liquid *n*-alkane solvent with *N* carbon atoms. Viscosities of *n*-alkanes were taken from the literature.[16,17]

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In this work, the mobility of radical ions of the following aromatic compounds was measured: biphenyl (99%), diphenylacethylene (DPA, 98%), *trans*,*trans*-diphenylbutadiene (98%), diphenylbutadiyne (99%), 2,5-diphenyl-1,3,4-oxadiazole (97%), 1,2,3,4-tetraphenyl-1,3-cyclopentadiene (95%), 9,10-diphenylanthracene (98%), 1,2,3,4-tetraphenylnaphthalene (TPN, 97%), 1,2-diphenylindol (94%), *N*,*N*,2,4,6-pentamethylaniline (PMA, 98%), *N*,*N*,*N*′,*N*′-tetramethyl-*para*-phenylenediamine (TMPD, 98%,), hexafluorobenzene (HFB, 99%), decafluorobiphenyl (99%, Avocado Research Chemicals Ltd.), triphenylmethane (TPM, 99%), and triptycene (TC, 9,10-*o*-benzeno-9,10-dihydroanthracene, 98%). All of them, except for decafluorobiphenyl, were received from Aldrich. PMA and TMPD were sublimed before use. Other compounds were used without additional purification.

Radical cations of some nonaromatic compounds were also studied. 2,3-Dimethylbutane (Fluka, 99%), cyclohexane (Fluka, 99%), 2,2,4-trimethylpentane (“Reactive”, 99.5%) as well as received from Aldrich *trans*-decahydronaphthalene (99%), 2,2,4,4,6,8,8-heptamethylnonane (98%), squalane (2,6,10,15,-19,23-hexamethyltetracosane, 99%) and 2,6,10,14-tetramethylpentadecane (98%) were purified by passing through a 0.5 m column of activated alumina several times. 2,4,4-Trimethyl-2-pentene (99%), adamantane (99%), norbornane (98%), and hexamethylethane (99%) were used as received from Aldrich.

The majority of the used aromatic acceptors form in *n*-alkanes both radical cations and radical anions. In these cases, the mobilities of the radical ions are considered as equal.[9,18] Molecules of PMA, TMPD, TPM, and TC were found to form no stable radical anions in alkanes, presumably due to negative electron affinity. To determine the individual mobility of radical cations of these compounds, DPA and HFB were added in the solution as electron acceptors for the former two and the latter two, respectively. HFB was also used for mobility measurements of the radical cations of olefins and aliphatic hydrocarbons in the same manner as reported in ref 9. That work also described the procedure of the determination of the mobility of HFB radical anion.

A concentration of aromatic solutes was in the range of 3−10 mM to diminish the influence of primary charge carriers and radical ion dimerization. Radical cations of all of these nonaromatic compounds were studied in C6 solutions at the solute’s concentration within 10 mM−0.1 M. The method of time-resolved magnetic field effects[19−22] was employed to make sure that the radical cation of the added alkane was formed. In addition, the mobilities of primary solvent radical cations of C10, C12, and C16 were measured at 293 and 313 K. Some of the measurements at 293 K reproduced those reported earlier,[9] and a good accordance with previous results was obtained.

The solutions under study were degassed by repeated freeze−pump−thaw cycles. The temperature was typically varied from 233 K up to 343 K (±2 K) but within the range where the solution was in liquid state.

Results and Discussion

Figure 1 shows the μ values for $\mathrm{DPA}^{+(-)\bullet}$, $\mathrm{TPN}^{+(-)\bullet}$, and $\mathrm{HFB}^{-\bullet}$ in C6 as a function of the inverse viscosity at different temperatures. Obviously, μ obeys eq 1 and A_0 and p may be obtained by accurately fitting the experimental data using this relation.

Temperature dependencies of μ for DPA in all *n*-alkanes as well as those for TPN and HFB in C6, C12, and C16 were studied. The values of parameters A_0 and p obtained with the approximations are shown in Figure 2 versus the ratio V_s/V_p of the van der Waals volumes of the solvent and solute, respectively. These volumes were calculated using data from ref 23.

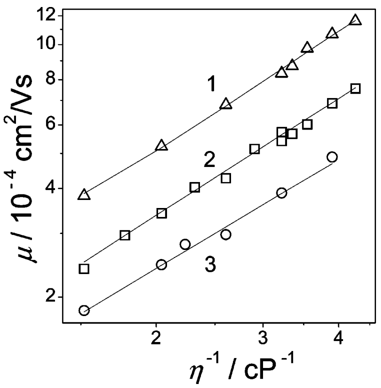

Figure 1. Mobility of radical ions of hexafluorobenzene (1), diphenyacethylene (2), and tetraphenylnaphthalene (3) in C6 vs inverse solvent viscosity η in the temperature range of 233−323 K in logarithmic scale. Straight lines show approximation of the experimental data by the power law $\mu = A_0/\eta^p$.

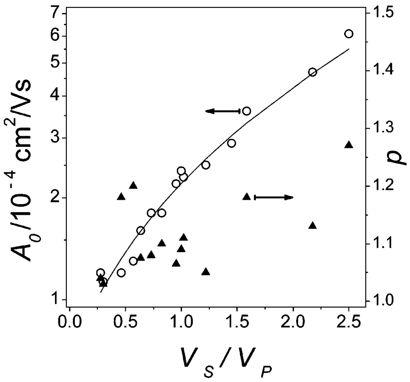

Figure 2. Dependencies of the parameters A_0 (○, semilogarithmic scale) and p (▲) vs the ratio V_s/V_p of the van der Waals volumes of solvent and solute, respectively. The solid line is the function $a[\exp(b \cdot V_s/V_p) - c]$ with $a = 4.8 \times 10^{-4}$, $b = 0.28$, and $c = 0.86$.

It is seen from Figure 2 that at $V_s/V_p > 1$ the dependence of the A_0 value versus V_s/V_p is close to an exponential one. To consider it, along with a deviation at lower V_s/V_p values, the A_0 parameter was approximated by the following formula:

$$A_0 = a\left[\exp\left(b\frac{V_s}{V_p}\right) - c\right] \qquad (3)$$

As for the value of p, the scattering of the points for p was too large to reveal the correlation with the volumes ratio, and it was assumed that p was a constant in the studied range of V_s/V_p.

Furthermore, experimental data on mobilities of DPA, TPN, and HFB radical ions in all of the solvents, except for TPN solution in C16, were used to find the values of the above parameters that provide the least-square deviation of the data points from eq 1. As a result, the parameters $p = 1.1$, $a = 4.8 \times 10^{-4}$, $b = 0.28$, $c = 0.86$ were obtained for viscosity and mobility measured in centipoises and cm^2/Vs, respectively. Interestingly, unlike the case of neutral molecules,[13,14] for the studied radical ions $p > 1$.

Figure 3 presents the values of the ratio $Q = \mu \cdot \eta^p / A_0$ as evaluated using this parametrization and the experimental μ values for radical ions of all of the aromatic compounds listed

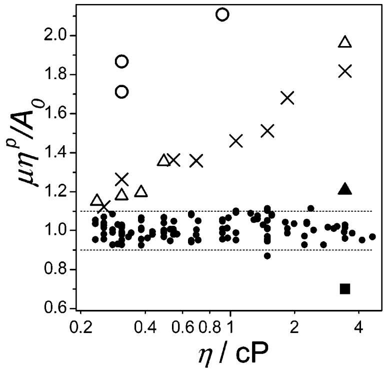

Figure 3. Values of $\mu{\cdot}\eta^p/A_0$ at $p = 1.1$, $a = 4.8 \times 10^{-4}$, $b = 0.28$, and $c = 0.86$ for radical ions of aromatic compounds listed in the Experimental section (●), except for the radical cations of triphenylmethane (△) and triptycene (×), as well as tetraphenylnaphthalene (▲) and diphenylbutadiyne (■) in C16 vs solvent viscosity. Also included are the values for radical cation of *n*-hexadecane and heptamethylnonane in C6 as well as that of squalane in C10 at 293 K (○). The units of μ are cm^2/Vs, and those of the viscosity η are cP. Dotted lines indicate the limits of 10% deviation from unity.

in the Experimental section. The highest viscosity was in C22, in which only radical ions of DPA were studied. Most of the other solutes were studied in C6, C10, and C12 solutions only. Besides, the Q values calculated for radical cations of hexadecane and heptamethylnonane in C6 determined in ref 24 as well as that of squalane in C10 from ref 9 at 293 K are included.

The majority of the Q values for aromatics fall into the range of 0.9−1.1 or very close to it (98 values as shown with solid points). About one-third of them are obtained for DPA solutions. The largest deviations from unity are observed for radical cations of TPM and TC in C16. In this solvent, noticeable deviations also appeared for radical ions of TPN and diphenylbutadiyne.

Judging from the studied collection of compounds, the semiempirical equation in the form of the modified Stokes−Einstein relation with A_0 given by eq 3 along with the suggested parametrization is suitable for estimating the mobility of radical ions of moderate in size aromatic compounds having a or similar planar structure. The equation underestimates, sometimes considerably, the radical ion mobilities for molecules, in which phenyl fragments can rotate, so these molecules become spheroid-shaped. Alternatively, the example of diphenylbutadiyne shows that the mobility of long rigid molecules in viscous *n*-alkanes may be overestimated. At the same time, the deviations decrease with the size of the solvent molecules.

The Q values have also been calculated for the literature data on radical ion mobilities measured by time-of-flight techniques in C6 at 297 K[18] as well as in C5 and C13 at various temperatures.[25] Below, the values or the range of those are given in parentheses for radical cations of TMPD (1.03−1.29), zinctetraphenylporphine (1.04), pyrene (1.18), radical anions of HFB (1.06), *para*-benzoquinone (0.8), chloranil (1.4), anthraquinone (1.45), octafluoronaphthalene (1.5), and fullerene C60 (1.5[18], 0.96−1.35[25]). The calculated Q values for these compounds, which differ very much in their properties, are scattered in the range of 0.8−1.5. This scattering is comparable with the difference in the mobility values obtained for the same radical ions in the cited works. Therefore, the suggested semiempirical equation seems to be useful for prior estimates of radical ion mobility for various classes of compounds.

At the same time, as can be seen from Figure 3, the parametrization obtained for aromatics underestimates significantly the mobility of alkane radical cations. Thus, when applying eq 1 to alkanes one should use another set of parameters a, b, c, and p.

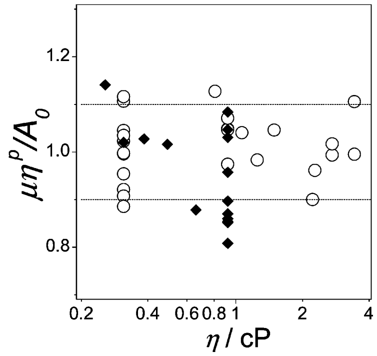

Figure 4. Values of the ratio $\mu{\cdot}\eta^p/A_0$ at $p = 0.9$, $a = 6.8 \times 10^{-4}$, $b = 0.16$, and $c = 0.68$ for radical cations of alkanes listed in the Experimental Section in C6 solutions at 293 K, for radical cations of *trans*-decalin and squalane in C10 at 293 K, and for primary radical cations of C10, C12, and C16 at various temperatures (○). Also included are the trimethylpentene radical cation in C6 and radical cations of studied olefins in C10 (◆). Dotted lines indicate the limits of 10% deviation from unity.

Figure 4 shows the Q values for alkane radical cations listed in the Experimental section at $p = 0.9$, $a = 6.8 \times 10^{-4}$, $b = 0.16$, and $c = 0.68$ (24 points). These values were obtained by the same manner as the parameters for aromatic radical ions. About half of the points were obtained in C6 solutions. The lowest Q value and the highest one for C6 solutions were observed for norbornane and hexadecane radical cations, respectively. Data on the mobility of primary solvent radical cations of C10, C12, and C16 are also included for 293 and 313 K. In comparison with the aromatic compounds, the distinctive features of the alkane radical cations are the higher value of their mobility at the same V_s/V_p, as well as the weaker dependence on both the solvent viscosity and the ratio V_s/V_p. Note that in the case of primary radical cations of *n*-alkanes, the influence of degenerate electron exchange on their mobilities can be neglected.[21]

In Figure 4, the Q values for radical cations created in solutions of 2,3-dimethyl-2-butene, 2,3-dimethyl-1,3-butadiene, 1-heptene, 1-octene, 1-decene, *c*-hexene, *cis*-cyclooctene, 2,4,4-trimethyl-2-pentene, 1,2,3,4,5,6,7,8-octahydronaphthalene, and 2,6,10,-15,19,23-hexamethyl-2,6,10,14,18,22-tetracosahexaene (squalene) that were studied in C10 solutions[9] at 293 K as well as five points for 2,4,4-trimethyl-2-pentene solution in C6 at different temperatures as obtained in the present work are also included. For alkenes studied in ref 9, it is taken into account that the corresponding molecular volume is doubled due to radical cation dimerization.[9,26] Nevertheless, the Q values obtained for radical cations of some alkenes are lower than 0.9, which may result in the formation of charged aggregates including several olefin molecules.[27,28]

It is worth noting that the large difference between aromatic and nonaromatic compounds shows that a universal model should include additional parameters accounting for the peculiarities of both intermolecular interactions and structural properties of the involved particles. For instance, the obvious cases, which are not covered by the present consideration, are aromatic molecules having relatively large aliphatic substituents. The way to take into account the divergence in interactions of the fragments of radical ions with solvent is not clear now.

In this connection, it is interesting that the exponent in eq 3, which describes satisfactorily the correlation between parameter A_0 and solvent/solute properties, includes the ratio of molecular volumes of the particles involved. Thus, neglecting a small correction, the form of eq 3 resembles that of the expression for diffusion coefficient

$$D = D_0 \exp\left(-B\frac{V^*}{V_f}\right) \quad (4)$$

as predicted by theories based on the free-volume concept.[29−31] Here $B \leq 1$, V^* is the volume that should be created adjacent to the solute to promote its diffusion, and V_f is mean free volume in the solvent. This concept gives plain terms to discuss diffusion in molecular liquids. For instance, the power-law dependence of diffusion coefficients on solvent viscosity in eq 1 can be treated as a correction to eq 4, which is needed to take into account the difference between the real solvent structure near a solute and macroscopic solvent parameters.[32]

From this point of view, the possibility that the form of eq 3 obtained by en example of aromatic solutes is not an accidental resemblance must not be ruled out, and this expression can be treated as an additional correction to account for interactions between radical ion and solvent. In other words, the correlation between the radical ion mobilities and the molecular volumes can be interpreted as an indication suggesting that the consideration of particular ion−molecular interactions within the free-volume approach would probably be reduced to a straightforward change in the volume parameters involved in an equation similar to eq 4. It is necessary, among other things, to get information about the molecular volume correlation for a larger collection of solutes than available at present in order to develop this into a real semiempirical formula for the estimation of radical ion mobility.

Concluding Remarks

In the present work, an extensive collection of radical ion mobility values for a series of organic compounds in *n*-alkanes was employed to express the correlation between the mobility and solvent viscosity in the form of the modified Stokes−Einstein relation. It was found that the parameters in this relation correlated with the ratio of the van der Waals's volumes of solvent and solute molecules. Thus, this volume ratio served as the only factor to take into account the specific molecular properties of both solvent and solute for studied solute/solvent combinations.

A significant difference between aromatic and aliphatic compounds was found in respect to the dependence of radical ion mobility on this volume ratio. Radical cations of alkanes had a higher mobility value at the same ratio of the volumes and a weaker dependence on both the solvent viscosity and the volume ratio. Two different parametrizations for these classes of organic compounds are suggested to estimate the radical ion mobility in *n*-alkane solutions with viscosity within the range of 0.2−4 cP. A control testing of the obtained formula using literature data on the radical ion mobilities gave reasonable results.

The large difference between aromatic and nonaromatic compounds shows that a universal equation describing the diffusion of radical ions in alkanes should include additional parameters allowing for the peculiarities of both intermolecular interactions and structural properties of the particles involved.

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References and Notes

(1) Mozumder, A. *Fundamentals of Radiation Chemistry*; Academic Press: San Diego, CA, 1999.

(2) Denisov, E.; Sarkisov, O.; Likhtenshtein, G. *Chemical Kinetics: Fundamentals and Recent Developments*; Elsevier: Hardbound, 2003.

(3) Terazima, M. *Acc. Chem. Res.* **2000**, *33*, 687−694.

(4) Wang, R. L.; Tam, K. Y.; Compton, R. G. *J. Electroanal. Chem.* **1997**, *434*, 105−114.

(5) Autrey, T.; Kandanarachchi, P.; Franz, J. A. *J. Phys. Chem. A* **2001**, *105*, 5948−5953.

(6) Terazima, M.; Okazaki, T.; Hirota, N. *J. Photochem. Photobiol., A* **1995**, *92*, 7−12.

(7) Schmidt, W. F.; Volychin, K. F.; Khrapak, A. G.; Illenberger, E. *J. Electrost.* **1999**, *47*, 83−95.

(8) Borovkov, V. I.; Anishchik, S. V.; Anisimov, O. A. *Chem. Phys. Lett.* **1997**, *270*, 327−332.

(9) Borovkov, V. I.; Anishchik, S. V.; Anisimov, O. A. *Rad. Phys. Chem.* **2003**, *67*, 639−650.

(10) Adamczewski, I. *Brit. J. Appl. Phys.* **1965**, *16*, 759−769.

(11) Chen, S.-H.; Davis, H. T.; Evans, D. F. *J. Chem. Phys.* **1982**, *77*, 2540−2544.

(12) Bhattacharyya, S.; Bagchi, B. *J. Chem. Phys.* **1997**, *106*, 1757−1763.

(13) Kowert, B. A.; Sobush, K. T.; Fuqua, C. F.; Mapes, C. L.; Jones, J. B.; Zahm, J. A. *J. Phys. Chem. A* **2003**, *107*, 4790−4795.

(14) Kowert, B. A.; Dang, N. C.; Sobush, K. T.; Seele, L. G., III. *J. Phys. Chem. A* **2001**, *105*, 1232−1237.

(15) Anishchik, S. V.; Grigoryants, V. M.; Shebolaev, I. V.; Chernousov, Yu. D.; Anisimov, O. A.; Molin, Yu. N. *Prib. Tekh. Eksp.* **1989**, *4*, 74−79.

(16) *Physical-Chemical Properties of Individual Hydrocarbons*; Tatevski, V. M., Ed.; Gostoptekhizdat, Moscow (in Russian), 1960.

(17) Dymond, J. H.; Øye, H. A. *J. Phys. Chem. Ref. Data* **1993**, *23*, 12−20.

(18) Lim, S. K.; Burba, M. E.; Albrecht, A. C. *J. Phys. Chem.* **1994**, *98*, 9665−9675.

(19) Brocklehurst, B. *Radiat. Phys. Chem.* **1997**, *50*, 213−225.

(20) Bagryansky, V. A.; Borovkov, V. I.; Molin, Yu. N. *Phys. Chem. Chem. Phys.* **2004**, *6*, 924−928.

(21) Borovkov, V. I.; Bagryansky, V. A.; Yeletskikh, I. V.; Molin, Yu. N. Mol. Phys. **2002**, *100*, 1379−1384.

(22) Borovkov, V. I.; Molin, Yu. N. *Phys. Chem. Chem. Phys.* **2004**, *6*, 2119−2124.

(23) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−451.

(24) Borovkov, V. I.; Velizhanin, K. A. *Chem. Phys. Lett.* **2004**, *394*, 441−445.

(25) Bakale, G.; Lacmann, K.; Schmidt, W. F. *J. Phys. Chem.* **1996**, *100*, 12477−12482.

(26) Mehnert, R. In *Radical Ionic Systems*; Lund, A., Shiotani, M., Eds.; Kluwer: Dordrecht, The Netherlands, 1991; pp 231−284.

(27) Desrosiers, M. F.; Trifunac, A. D. *J. Phys. Chem.* **1986**, *90*, 1560−1564.

(28) Mashnin, A. S.; Anishchik, S. V.; Borovkov, V. I.; Yeletskikh, I. V.; Anisimov, O. A.; Molin; Yu, N. *Appl. Magn. Reson.* **2001**, *20*, 473−482.

(29) Turnbull, D.; Cohen, M. H. *J. Chem. Phys.* **1970**, *52*, 3038−3041.

(30) Xiang, T.-X. *J. Phys. Chem.* **1998**, *109*, 7876−7884.

(31) Boned, C.; Allal, A.; Baylaucq, A.; Zeberg-Mikkelsen, C. K.; Bessieres, D.; Quinones-Cisneros, S. E. *Phys. Rev. E* **2004**, *69*, 031203.

(32) Other interpretations are also possible, of course; see, for example, ref 13.