cylindrical region would accommodate any water present. Only in the XAD-4 with its smaller pores is there likely to be interaction between polar heads other than those on adjacent surface sites. Further, from this simple model it follows that the ion pairs are more tightly packed in XAD-4 than in XAD-2 from a consideration of exchange capacities and maximum mean surface areas available to each molecule (Table V).

It is interesting to compare the EPR data from the resins with those for TLMAI adsorbed on polystyrene. At low temperature (≤235 K), the label rotational barriers lie between 1 and 7 kJ/mol; these values would correspond to the energies involved in breaking very weak residual bonds or overcoming weak, rotational barriers about C–C bonds in simple molecules.[19]   At temperatures roughly in the range 235–300 K, the barriers are from 15 to 27 kJ/mol corresponding to energies required to break moderate to strong single hydrogen bonds or several weaker bonds per label ion. The evidence is that the label is held more tightly in XAD-2(CTAB) and PS-(TLMAI) than in the other coated resins below 235 K while above 235 K, PS-(TLMAI), XAD-2(CTAB), and XAD-4(CTAB) have stronger anion label to cation interactions than XAD-2(TLMAI) and XAD-4(TLMAI). This would suggest that TLMAI has greater facility in exchanging anions when in the XAD resins than does CTAB but the difference may be only of marginal practical consequence.

The data in Table III show that rotation is close to isotropic in PS-(TLMAI) at 478 K while for the others in the 373–475 K region it is anisotropic; this may be explained by breakdown of interaction between the PS and the quaternary salt while within the resins complete breakaway is restricted by the cavity walls. Alternatively, the label anion detaches from the quaternary ammonium cation as a molecular entity[20] without or with the same restraints on it as for the breakaway ion pair.

In conclusion, the anion probe is visualized as being positioned above the XAD framework with the anchorage to the framework through the hydrocarbon chains of the cations. A further study in which the probe is the cationic component is under way with the goal of consolidating the model with respect to the nature of the site of the polar head of the ion pair.

Registry No.   XAD-2, 9060-05-3; XAD-4, 37380-42-0; TLMAI, 29710-98-3; CTAB, 57-09-0; 1-oxyl-2,2,5,5-tetramethylpyrrolidine-3-carboxylate, 46147-15-3.

(19) Moore, W. J. *Physical Chemistry,* 4th ed.; Prentice Hall: Englewood Cliffs, N.J. 1972; p 766.

(20) Christofides, A.; Criddle, W. J. *Anal. Proc. (London)* **1982,** *19,* 314.

Determination of Mutual Diffusion Coefficients in Water-Rich 2-Butoxyethanol/Water Mixtures Using the Taylor Dispersion Technique

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Mutual diffusion coefficients D_{12} of 2-butoxyethanol (2BE)/water mixtures in the water-rich region were determined at 298 K by using the Taylor dispersion technique. In addition, the mutual diffusion coefficients at infinite dilution were measured at several temperatures between 293 and 323 K. At 298 K and low 2BE concentrations, the mutual diffusion coefficients display two distinct regimes: with increasing concetration of 2BE, D_{12} drops very rapidly (regime 1) to become constant at a mole fraction of 2BE of ca. 0.05 (regime 2). By use of viscosities determined at 298 K, the correlation length of the concentration fluctuations has been calculated and indicates the existence of 2BE complexes. This result supports the view, invoked in the interpretation of several bulk and surface thermodynamics properties, that 2BE molecules form aggregates or pseudomicelles in solution.

Introduction

Many amphiphilic molecules ranging from simple small organic substances to conventional surfactants have been studied through the detailed measurement of several bulk and surface properties. Among the systems studied, the mixture 2-butoxyethanol (2BE) + water (W) is particularly interesting since its bulk and surface properties undergo drastic changes with concentration and temperature. Figure 1 shows schematically the concentration dependences at 298 K of the apparent molar heat capacities[1] and expansivities,[2] the partial molar enthalpy of 2BE in the mixture,[3] the ultrasonic velocity,[4] and the surface tension and transient foam stability.[5]   These composition dependencies bear a striking resemblance to that of established micellar systems and have led to the classification of 2BE as a borderline surfactant. The formation of 2BE aggregates or pseudomicelles in the narrow concentration interval indicated in Figure 1 also receives support from spectroscopic measurements[6] as well as from other directly determined or derived thermodynamic properties.[7]

(1) Roux, G.; Perron, G.; Desnoyers, J. E. *J. Solution Chem.* **1978,** *7,* 639. Roux, G.; Perron, G.; Desnoyers, J. E. *J. Phys. Chem.* **1978,** *82,* 966. Roux, G. *Int. Data Ser. B* **1978,** 44. Roux, G. *Int. Data Ser. B* **1978,** 40.
(2) Roux, G. *Int. Data Ser. B* **1978,** 47.
(3) Andersson, B.; Olofsson, G. *J. Solution Chem.* **1988,** *17*(12), 1169.

(4) Rao, N. P.; Verrall, R. E. *Can. J. Chem.* **1987,** *65,* 810.
(5) Elizalde, F.; Gracia, J.; Costas, M. *J. Phys. Chem.* **1988,** *92,* 3565.
(6) Ito, N.; Fujiyama, T.; Udagawa, Y. *Bull. Chem. Soc. Jpn.* **1983,** *56,* 379. Ito, N.; Saito, K.; Kato, T.; Fujiyama, T. *Bull. Chem. Soc. Jpn.* **1981,** *54,* 991. Quirion, F.; Magid, L. J. *J. Phys. Chem.* **1986,** *90,* 5193.
(7) Douhéret, G.; Pal, A.; Davis, M. I. *J. Chem. Soc., Faraday Trans. 1* **1989,** *85*(9), 2723.
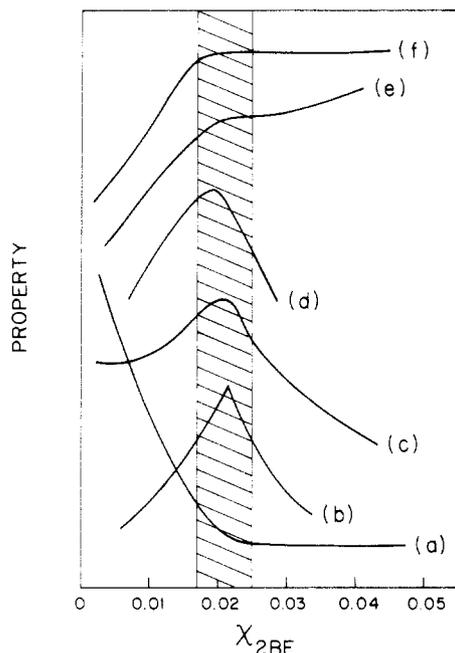
Figure 1. Concentration dependence (schematic) at 298 K for several bulk and surface properties of 2-butoxyethanol + water. Surface tension (a) and foam column height (b) from ref 5, apparent heat capacities (c) from ref 1, ultrasonic velocity (d) from ref 4, expansivities (e) from ref 2 and partial molar enthalpy (f) from ref 3.

Further insight into the formation of 2BE aggregates can be gained through the determination of transport properties such as diffusion. S. Kato et al. have performed[8] dynamic light scattering (DLS) measurements in the water-rich region of 2BE/W mixtures and found that this system exhibits an abrupt transition to diffusers of apparent hydrodynamic radius around 1000 Å. This appears to be contrary to the general impressions about the system reached by T. Kato who also performed DLS experiments.[9] These experiments were done throughout the concentration range but data at low 2BE concentrations are not as dilute as those used by S. Kato. However, a reasonable extrapolation of these results does not predict such large diffusers to exist in the system but rather concludes that they might have a hydrodynamic radii nearly equal to the molecular radius. In order to solve the contradiction between these two views about the microscopic structure in the water-rich region, Bender and Pecora determined mutual diffusion coefficients[10] at 283, 298, and 313 K. At 2BE mole fractions greater than 0.02, their results are in good agreement with the work of T. Kato. Unfortunately, below this concentration these authors were unable to obtain conclusive data since (i) the DLS technique is not appropriate at very low solute concentrations where the dispersivity is very small and (ii) the results appeared to be dependent on the source of the 2BE sample (Aldrich and Mallinckrodt). In view of the lack of reliable diffusion data at 2BE mole fractions below 0.02, we have undertaken the measurement of mutual diffusion coefficients (MDC) in such a concentration region using the Taylor dispersion technique. The present work reports these measurements and discusses the results in terms of the formation of 2BE aggregates or pseudomicelles in solution.

The Taylor Dispersion Technique

The Taylor dispersion technique is based on the dispersion, by the joint action of convection and molecular diffusion, of an injected binary-mixture pulse in a laminar flowing stream of the same mixture at slightly different composition. Under proper conditions, the pulse concentration profile will eventually become normal, and the center of gravity of the profile will move with the mean velocity of the laminar flow. The theory for the development of an ideal equipment and the criteria for the design of a practical apparatus to measure the MDC (D_{12}) have been reviewed in detail by Alizadeh et al.[11] Here, we only quote their most relevant results.

The ideal apparatus consists of a long straight tube of uniform, circular cross section of radius a_0 through which a mixture of components 1 and 2 flows, in a laminar regime, with mean velocity $\bar{u}_0$. A mixture of the same components, but with a slightly different composition, is injected in the tube as a δ-function pulse, at a distance L from the detection point. Under suitable conditions this pulse is dispersed according to a well-defined pattern, and it is possible to calculate the MDC of the binary mixture, with respect to a fixed-volume frame of reference, through a working equation relating the MDC to the first two temporal moments of the distribution of the dispersed δ-function pulse observed in the diffusion tube. For a laminar flow $(2\bar{u}_0 a_0 \rho/\eta < 2000$, where ρ is the fluid density and η is the shear viscosity), if the following conditions are fulfilled

$$D_{12}\bar{t}/a_0 > 10 \quad \text{and} \quad \bar{u}_0 > 700 D_{12}/a_0 \qquad (1)$$

the MDC can be obtained from the measurement of the first two temporal moments on an ideal diffusion apparatus. The first $(\bar{t})$ and second (σ^2) temporal moments of the distribution are given by

$$\bar{t} = \frac{L}{\bar{u}_0}(1 + 2\zeta) \qquad (2)$$

$$\sigma^2 = \left(\frac{L}{\bar{u}_0}\right)^2 (8\zeta^2 + 2\zeta) \qquad (3)$$

where

$$\zeta = \frac{\bar{u}_0 a_0^2}{48 D_{12} L} - \frac{64 k \bar{u}_0 a_0^4}{L D_{12} \bar{t}} \qquad (4)$$

Equation 4 can be written in terms of measurable quantities as

$$\zeta = \frac{2\sigma^2 - \bar{t}^2 + (\bar{t}^4 + 4\bar{t}^2 \sigma^2)^{1/2}}{8\bar{t}^2 - 4\sigma^2} - \frac{64 k \bar{u}_0^4}{L D_{12} \bar{t}} \qquad (5)$$

where $k = 2.1701 \times 10^{-5}$ and the diffusion coefficient is given by

$$D_{12} = \frac{(1 + 2\zeta)}{\zeta} \frac{a_0^2}{48\bar{t}} \qquad (6)$$

In the evaluation of the second term of eq 5 an estimate of D_{12} is needed but this correction is less than 0.6% of the measured MDC. The ideal experiment outlined above is not practicable for actual measurements. In order to perform such measurements it is necessary to make changes to the experimental method and to examine the ways in which a practical instrument differs from the ideal one. Alizadeh et al.[11] examined, with a first-order perturbation treatment, the consequences of these considerations for the design of a practical instrument and they derived a set of corrections to the ideal instrument. They found that the ideal moments have to be corrected by

$$\bar{t} = \bar{t}_{exp} + \sum \delta \bar{t}_i \qquad (7)$$

$$\sigma^2 = \sigma_{exp}^2 + \sum \delta \sigma_i^2 \qquad (8)$$

where $\bar{t}_{exp}$ and σ_{exp}^2 denote the experimentally determined moments and $\delta \bar{t}_i$ and $\delta \sigma_i^2$ are the corrections applied to them. These corrections involve the following features: the finite volume of the detector at the end of the tube, the finite volume of injection, and the change in radius in going from the diffusion tube to the detector. There is also an additional correction for the actual

(8) Kato, S.; Jobe, D.; Rao, N. P.; Ho, C. H.; Verrall, R. E. *J. Phys. Chem.* **1986**, *90*, 4167.

(9) Kato, T. *J. Phys. Chem.* **1985**, *89*, 5750.

(10) Bender, T. M.; Pecora, R. *J. Phys. Chem.* **1988**, *92*, 1675.

(11) Alizadeh, A.; Nieto de Castro, C. A.; Wakeham, W. A. *Int. J. Thermophys.* **1980**, *1*, 243.
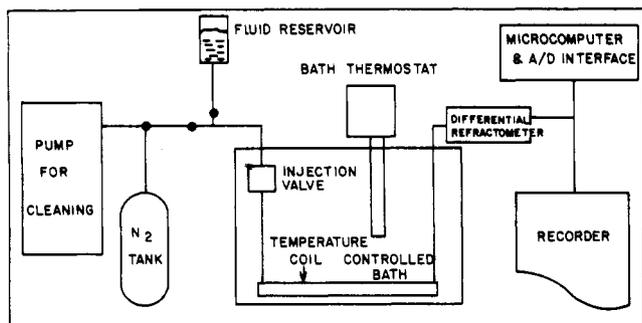
Figure 2. Schematic diagram of the experimental setup to measure mutual diffusion coefficients.

TABLE I: Parameters of the Diffusion Apparatus

diffusion-tube length, L, m	12.1256
diffusion-tube internal radius, a_0, m	3.84×10^{-4}
coil radius, m	0.41
injection volume, m^3	2×10^{-9}
detector volume, m^3	6×10^{-9}
length of connecting tube, m	0.14
internal rradius connecting tube, m	2.54×10^{-4}

concentration at which measurements are made. The reference state of the measured diffusion coefficient is defined by the experimental temperature, pressure, and composition and is given by

$$C_1 = C_{if} + \delta C_1 = C_{if} + \frac{N_1\left(\frac{5}{16} - (8\pi)^{-1/2}\right)}{\pi a_0^2 (2\zeta_0 L \bar{u}_0 \bar{t})^{1/2}} \qquad (9)$$

where N_1 is the mole number of component 1 in the injected mixture.

Instrument Design and Operation

The application of the Taylor dispersion technique according to the principles reviewed above led us to design an instrument for the measurement of the MDC. Figure 2 shows a functional diagram of this instrument and Table I reports its design parameters. The fluid reservoir, flow tubing, and fittings are of stainless steel. The sample injection system is a six-port Valco high-pressure liquid-chromatograph injection valve. The diffusion tube (1/16 m o.d.) is wound and the coil is embedded in molten lead to ensure good thermal contact and stability. This coil is placed at the bottom of an oil bath controlled with a thermostat (Cole-Parmer 125200). The temperature is kept constant within 0.1 °C and measured with a two-calibration-point thermometer. The oil bath is on a marble table, and the fluid line supports are properly isolated to avoid vibrations. The detector is a Varian Fresnel type differential refractometer (Model 02-1528-02) connected to a temperature bath (Cole-Parmer 1267-62) whose accuracy is 0.02 °C. The recorder is a Varian strip chart recorder (Model A-25).

Experimental Section

Measurements of the MDC were carried out in mixtures of 2-butoxyethanol (ethylene glycol monobutyl ether) + water at 298 K in the water-rich region. In addition, MDC at infinite dilution (2BE mole fractions between 1.1×10^{-3} and 1.5×10^{-3}) were obtained at several temperatures (293–323 K). 2-Butoxyethanol was supplied by Aldrich Chem. Co. and through gas chromatography a purity of 99.4% was determined. Water was bidistilled. The binary mixtures were prepared to an estimated error in the quoted mole fractions of less than 1×10^{-4}. It is difficult to estimate the accuracy involved in the determination of diffusion coefficients by the technique described above. Hence, we follow the common practice of employing the reproducibility of the results of a series of experiments, under nominally identical experimental conditions, as a measure of the precision of the

TABLE II: Mutual Diffusion Coefficients for 2-Butoxyethanol + Water Mixtures at 298 K

X_{2BE}	$D_{12} \times 10^{10}$, m^2/s	X_{2BE}	$D_{12} \times 10^{10}$, m^2/s
0.0019	7.45	0.0158	3.99
0.0102	5.57	0.0203	1.92

TABLE III: Mutual Diffusion Coefficient at Infinite Dilution for 2-Butoxyethanol + Water Mixtures at Several Temperatures

T, K	$D_{12}^{\infty} \times 10^{10}$, m^2/s	T, K	$D_{12}^{\infty} \times 10^{10}$, m^2/s
293	6.94	313	11.00
298	7.89	318	12.13
303	8.60	323	13.14
308	9.49		
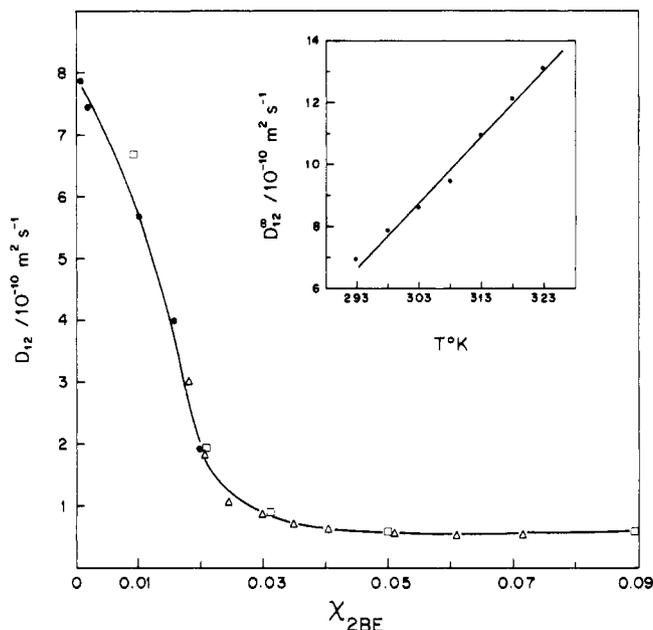
Figure 3. Mutual diffusion coefficients for 2-butoxyethanol + water mixtures from ref 9 (△), ref 10 (□), and this work (●). The most dilute point from ref 10 has an error of ±25%. Data from ref 9 are at 296 K, and those from ref 10 and this work at 298 K. Inset shows MDC at infinite dilution (D_{12}^{∞}) as a function of temperature.

determinations.[12] We determined the values of $\bar{t}$ and σ^2 graphically, and after doing the corrections discussed above, we obtained a precision of ±3%.

For a series of 2BE + water mixtures, kinematic viscosities were measured at 298 K with a Canon-Fenske viscometer. These kinematic viscosities were converted into dynamic viscosities through the measurement of densities in a vibrating tube densimeter (Sodev Inc., Canada). Dynamic viscosities were fitted to a polynomial that, in turn, allowed the calculation of the viscosities at the 2BE concentrations where there is diffusion coefficient data (this work and refs 9 and 10).

Results and Discussion

Tables II and III report the mutual diffusion coefficients for 2BE + water mixtures at 298 K and several 2BE mole fractions (X_{2BE}) and the MDC at infinite dilution (D_{12}^{∞}) for several temperatures. Both, MDC and D_{12}^{∞} are displayed in Figure 3. The present work adds data at very dilute 2BE concentrations and is in good agreement with the MDC values reported in refs 9 and 10 at somewhat higher 2BE mole fractions.

In the concentration interval displayed in Figure 3, the MDC behavior of 2BE/W mixtures is characterized by the presence of two distinctly different regimes. In the first one, the MDC decreases very rapidly from its infinite dilution value and, in the second regime, it becomes constant. The passage from one regime to another occurs smoothly over the same 2BE concentration

(12) Alizadeh, A.; Wakeham, W. A. *Int. J. Thermophys.* **1982**, *3*, 307.
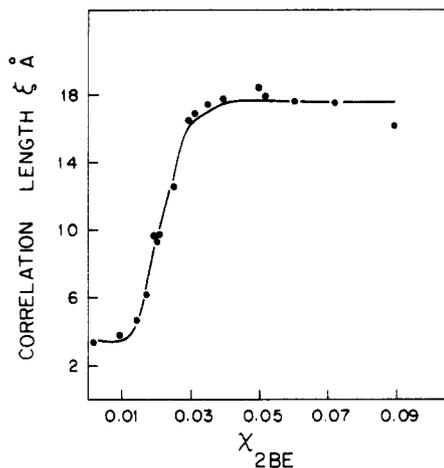
Figure 4. Correlation length of concentration fluctuations against 2BE mole fraction at 298 K. Full line is only to aid visualization.

region indicated in Figure 1 (dashed region) where bulk and surface properties display a change in their 2BE concentration dependences. In Figure 3, decreasing MDC values are a reflection of an increasing number of 2BE–water interactions in solution; however, with further increase in 2BE concentration, MDC values become constant implying that, although the concentration of 2BE is still very low, some kind of organization is present in the solution. This organization can be visualized as 2BE aggregates or pseudomicelles in solution. The MDC in Table II allows the calculation of the correlation length ξ of the concentration fluctuations in these mixtures. Assuming that velocity fluctuations are statistically

independent of the concentration fluctuations,[13] ξ is related to the MDC through

$$D = \frac{kT}{6\pi\eta\xi} \qquad (10)$$

Figure 4 displays ξ values calculated by using eq 10. At very low 2BE concentrations the magnitude of the correlation length (ca. 3.5 Å) is practically the same as the radius r of the 2BE molecule (3.7 Å) calculated by using the relation $(4\pi/3)r^3\rho = 1$, where ρ is the number density of 2BE. When the mole fraction of 2BE reaches ca. 0.015, ξ starts to increase rapidly; this increase is maintained over a 2BE concentration interval which, again, coincides with that indicated in Figure 1 (dashed region). An increase in 2BE concentration is not reflected on ξ which remains constant and equal to ca. 18 Å. The magnitude of this correlation length, when compared to the molecular radius, indicates considerable association of 2BE and water molecules. With further increase in 2BE concentration, ξ decreases, indicating that the interactions that held together the 2BE aggregates are fading away, and as a consequence the MDC increases.[9] It is important to point out that the large ξ values in Figure 4 occur at a temperature that is far from the lower critical solution temperature (LCST) which is located[5] at ca. 322 K and hence they cannot be assigned to the existence of this critical consolution point.

Registry No. 2BE, 111-76-2; W, 7732-18-5.

(13) Ferrel, R. A. *Phys. Rev. Lett.* **1970**, *24*, 1169.

Kinetics of Chemical Reactions in Condensed Media in the Framework of the Two-Dimensional Stochastic Model

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A chemical reaction proceeding in a continuum medium is modeled as a pair of stochastic equations with a δ-correlated random force. A numerical method for calculating the rate constant is elaborated in a quasi-one-dimensional approximation. Exact rate constants are found over a wide range of characteristic system parameters. The existence of a significant region with a nonequilibrium kinetic behavior, as predicted previously by Berezhkovskii and Zitserman, is confirmed. Moreover, the nonequilibrium rate constant is shown to describe not only the extreme of quasi-one-dimensional dynamics but also the case when the complete two-dimensional equation of motion operates.

1. Introduction

The theory of chemical kinetics in condensed media has been successfully developed recently in terms of stochastic equations. It is not a simple matter, however, to extract kinetic information from such a treatment. The Kramers–Grote–Hynes (KGH) method[1-3] is a conventional approximation to obtain the rate constant corresponding to a generalized Langevin equation with a double-well potential. Generalizations of the KGH theory to multidimensional stochastic systems have also been reported.[4-6]

The KGH approximation is equivalent to the transition-state (TS) theory as applied to a combined system consisting of a chemical subsystem and a continuum medium.[6-9] It follows then that important dynamical effects such as nonequilibrium solvation of a chemical subsystem for reactions proceeding in highly viscous media are lacking in the KGH treatment. Such nonequilibrium phenomena can be revealed, however, if the characteristic time scales of the components in a system "a chemical subsystem + medium" are essentially different.[10,11] Therefore, one-dimensional

(1) Kramers, H. A. *Physica (Utrecht)* **1940**, *7*, 284.
(2) Grote, R. F.; Hynes, J. T. *J. Chem. Phys.* **1980**, *73*, 2715.
(3) Hanggi, P. *J. Stat. Phys.* **1986**, *42*, 105.
(4) Langer, J. S. *Ann. Phys. (N.Y.)* **1967**, *41*, 108.
(5) Weidemuller, H. A.; Zhang, J.-S. *J. Stat. Phys.* **1984**, *34*, 191.
(6) Basilevsky, M. V.; Chudinov, G. E. *Chem. Phys.*, in press.

(7) Grabert, H.; Weiss, U. *Phys. Rev. Lett.* **1984**, *53*, 1787.
(8) Pollak, E. *J. Chem. Phys.* **1986**, *85*, 865.
(9) Dakhnovskii, Yu. I.; Ovchinnikov, A. A. *Mol. Phys.* **1986**, *58*, 237.
(10) Berezhkovskii, A. M.; Zitserman, V. Yu. *Chem. Phys. Lett.* **1989**, *158*, 369.
(11) Berezhkovskii, A. M.; Zitserman, V. Yu. *Phys. A*, in press.