PHYSICAL REVIEW E VOLUME 54, NUMBER 5 NOVEMBER 1996

Mechanism of the cooperative relaxation in microemulsions near the percolation threshold

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(Received 6 June 1996)

Cooperative dynamics of three-component water-oil-surfactant microemulsions based on sodium bis(2-ethylhexyl) sulfosuccinate surfactant were investigated near the percolation threshold. The measurements were made by means of the time domain dielectric spectroscopy method in the temperature interval 12 °C–40 °C, including the percolation range. The data treatment was carried out in time domain in terms of the macroscopic dipole correlation functions (DCFs) related to the structural and kinetic properties of the system. It is shown that the DCF can be described by the Kohlrausch-Williams-Watts (KWW) expression $\exp[-(t/\tau)^{\nu}]$ (where τ is the relaxation time and ν is the stretched parameter), reflecting the peculiarities of the dipole interactions in a self-similar medium. For a physical interpretation of the phenomenological parameters τ and ν, a generalization of the known model of the cooperative relaxation was made. The model developed was adjusted for a description of the relaxation in microemulsions that have a fractal nature in the percolation region. The results obtained testify that parameters τ and ν in the KWW function are related to the structure of the system and reflect the cooperative behavior of microemulsion droplets near the percolation threshold. It was shown also that the macroscopic law of the relaxation of the KWW type is insensitive to the microscopic details of charge transport in the system and that there is a limited temporal range for the applicability of the stretched law of relaxation in time domain. In order to extend the initial temporal interval of the applicability of the relaxation function the correlation to the KWW term was found. [S1063-651X(96)09511-6]

PACS number(s): 82.70.−y, 77.22.Gm, 05.40.+j

I. INTRODUCTION

A percolation phenomenon was found in the microemulsions when the water fraction, the temperature, the pressure, or the ratio of water to the surfactant was varied [1–7]. In our recent paper [1], the dielectric relaxation properties in the sodium bis(2-ethylhexyl) sulfosuccinate (AOT) -water-decane microemulsion have been investigated in the broad temperature region near the percolation temperature threshold. It was found that the system exhibits a complex nonexponential relaxation behavior that is strongly dependent on the temperature. Below the percolation onset where the microemulsion has a structure of spherical droplets, the main contribution in the relaxation mechanism comes from the *fast relaxation processes* with characteristic relaxation times less than 1 ns. The processes are inherent to the dynamics of the single droplet components as well as to the effect of interfacial polarization. In the percolation region transient clusters of a fractal nature are formed because of attractive interactions between droplets [8,9]. In this region an interpretation of the results was done in the framework of the dynamic percolation model [10]. According to this model near the percolation threshold, in addition to the fast relaxation related to the dynamics of droplet components and interfacial polarization, there are at least two much longer characteristic time scales. The *longest process* has characteristic relaxation times greater than a few microseconds [9,11] and should be associated with the rearrangements of the typical percolation cluster [9–11]. The temporal window of the *intermediate process* is a function of temperature. The minimal time boundaries are of the order of hundreds of picoseconds, whereas the maximal time has a value of tens of nanoseconds in the beginning of the percolation region and may reach 700 ns at the percolation threshold [1]. Such an intermediate process reflects the cooperative relaxation phenomenon associated with the transfer of excitation along the percolation cluster. The excitation is caused by the transport of charge carriers that leads to a variation of the fluctuation dipole moment of droplets [12–14].

The time decay behavior of the dipole correlation function of the system was deconvoluted into normal modes and represented as a sum of two Kohlrausch-Williams-Watts (KWW) terms $\exp[-(t/\tau_M)^{\nu}]$, each with characteristic macroscopic relaxation times τ_M and stretched exponents ν, respectively [1]. Many efforts have been made to interpret the experimental results in terms of fractal and dispersion dielectric theories, in order to provide the theoretical justification of experimental results. However, the study has left no clear information about the details of possible mechanisms of cooperative relaxation, the physical meaning of the phenomenological parameters τ_M and ν, and/or knowledge with regard to the temporal range of the KWW relaxation where the stretched exponential behavior can be correctly applied. In view of this, the question arises as to the fractal nature of the relaxation and the mechanisms responsible for the aforementioned relaxation times. It is natural to suppose that near the percolation threshold the main contribution to the dynamics comes from the cooperative effect related to the transfer of charge carriers along the percolation clusters.

The purpose of this work is to further investigate the fractal dynamics of the *cooperative relaxation* process in microemulsions near the percolation threshold. In the paper we

1063-651X/96/54(5)/5420(8)/$10.00

shall review the existing models of cooperative relaxation and develop the model of cooperative relaxation in self-similar media. It will be shown that for the cooperative effect of relaxation the macroscopic law of the KWW relaxation is insensitive to the microscopic details of charge transport in the system and there is a limited temporal range for applicability of the stretched law for the cooperative process of the relaxation in time domain. From the experimental dipole correlation function we shall obtain the main parameters of the model and reveal the physical meaning of the stretched exponent ν and the characteristic relaxation time τ_M entering in the KWW decay behavior of the correlation functions. The model is shown to be capable of offering information on the fractal nature and structural changes occurring in the microemulsion near the percolation threshold.

II. THEORETICAL BACKGROUND

For a description of the mechanism of cooperative relaxation we follow the ideas developed by Klafter, Blumen, and Shlesinger [15,16]. They considered a transfer of the excitation of a donor molecule to an acceptor molecule in various condensed media. The transfer takes place through many parallel channels and gives the following relationship for this cooperative type of relaxation:

$$\psi(t)=\prod_j \{1-c+c\ \exp[-tW(R_j)]\}, \tag{1}$$

where $\psi(t)$ is the relaxation function normalized to unity, t is the current time, c is the concentration of donors in the system, R_j is the distance between the donor and acceptor, located on the jth site, and $W(R_j)$ is the microscopic relaxation rate of excitation transfer from the donor to acceptor at distance R_j. The product extends over all structure sites except for the origin.

In the Klafter-Blumen-Shlesinger (KBS) theory the $\psi(t)$ was estimated in the continuous medium approximation, i.e., when a site density function

$$\rho(R)=\sum_j \delta(R-R_j) \tag{2}$$

is taken as $\rho(R)=\text{const}$. The $W(R)$ was chosen in the form of $W(R)\sim R^{-s}$, where s is the parameter of the donor-acceptor interaction (usually $s\geqslant 6$). The case of small concentrations $c\ll 1$ was considered, i.e., when the donors do not interact with each other. In such assumptions Klafter, Blumen, and Shlesinger obtained a KWW function $\exp[-(t/\tau)^\nu]$ for the cooperative relaxation, with $\nu=D/s$, where D is the dimension of the system.

It is pertinent to note here that the continuous medium approximation of the KBS model is correct only in the case when the concentration of donors c is small and the majority of acceptors are located at distances R_j that are much longer than the minimum distance R_0 between the nearest donor and acceptor, i.e., $R_j\gg R_0$. It is relevant to bear in mind that for the model the relaxation process can be described correctly by the KWW function only in the limit of large times [15]. Meanwhile, the concentration of the droplets forming dynamic fractal clusters is high in the case of microemulsions in the percolation region. Thus the KBS theory might be modified for describing the process of the charge transfer in colliding droplets forming a cluster and giving rise to the relaxation of the entire fluctuation dipole moment.

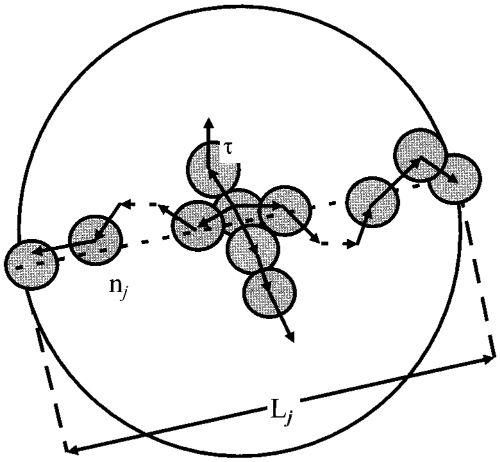

FIG. 1. Schematic picture of the excitation transfer via parallel relaxation channels in the fractal cluster of droplets in the percolating microemulsion. n_j is the number of droplets located along the segment of length L_j in the microemulsion. The time for a charge hopping between droplets is given by τ.

The normalized dipole correlation function $\psi(t)$ in the microemulsion is associated with the relaxation of the entire induced macroscopic fluctuation dipole moment $M(t)$ of the sample unit volume, which is equal to the vectorial sum of all the fluctuation dipole moments of droplets

$$\psi(t)\approx\frac{\langle \overline{M}(0)\cdot\overline{M}(t)\rangle}{\langle \overline{M}(0)\cdot\overline{M}(0)\rangle}, \tag{3}$$

where the angular brackets denote an ensemble average. The velocity and laws governing the correlation function are directly related to the structural and kinetic properties of the sample and characterize the macroscopic properties of the system studied. The relaxation of the fluctuational dipole moment of a droplet is related to the transfer of the excessive charge (excitation) within two colliding droplets from a charged droplet (donor in the KBS model) to a neutral droplet (acceptor).

Let us consider that an elementary act of the excitation transfer along the length L_j is described by the microscopic relaxation function $g(z/z_j)$, where z_j is a dimensional variable, characterizing the jth stage of the self-similarity of the considered fractal system, and z is an *intensive* variable that characterizes the system as a whole. We note that, in our case, z coincides with the dimensionless time $z=t/\tau$. The parameter τ represents the time needed for an excessive charge to hop from one droplet to its nearest neighbor within the cluster. The schematic view of the model is drawn in Fig. 1.

Let us assume that $z_j=aL_j$, where L_j is an ‘‘effective’’ length of a channel of the relaxation on the jth stage of self-similarity and a is a coefficient of proportionality. In this case, the fractal cluster relaxes as an entire indivisible unit and does not correlate with neighbor clusters. For each stage of the self-similarity j, the time of relaxation $\tau_j=\tau z_j$ is proportional to the length L_j. From fractal geometry [17,18], L_j can be expressed as

$$L_j=\lambda k^j, \tag{4a}$$

where λ is the minimal scale and k is a scaling factor ($k>1$). We assume that the total number of droplets located along the segment L_j also obeys the scaling law

$$n_j=n_0p^j, \tag{4b}$$

where p is the scaling factor ($p>1$) and n_0 is the number of the nearest neighbors near the selected droplet (i.e., $j=0$).

The relationship (1) can be generalized and expressed as

$$\psi_N(z)=\prod_{j=0}^{N}[g(z/z_j)]^{n_j}=\prod_{j=0}^{N}[g(Z\xi^j)]^{n_0p^j}, \tag{5}$$

where $Z=t/a\lambda\tau$; $\xi=1/k$ and $N=(1/\ln k)\ln(L_N/\lambda)$, where L_N is the finite size of the fractal cluster. The N refers to the last stage of the self-similarity of the fractal cluster.

The estimations of the product (5) at various values of ξ and p ($\xi<1$ and $p>1$) are given in the Appendix. The results of the calculations are

$$\psi_N(Z)/\psi_N(0)=\exp\{-\Gamma(\nu)Z^{\nu}+B(\nu)Z\}, \tag{6}$$

where the parameters $\Gamma(\nu)$ and $B(\nu)$ are given by

$$\Gamma(\nu)=\frac{n_0}{\ln(1/\xi)}\int_0^{\infty}y^{-\nu}\left|\frac{g'(y)}{g(y)}\right|dy, \tag{7}$$

$$B(\nu)=\frac{n_0a_1}{\ln(1/\xi)(1-\nu)}\,\varepsilon^{1-\nu}, \tag{8}$$

$$\nu=\ln p/\ln(1/\xi),\quad 0<\nu<1,\quad \varepsilon=\xi^{N}\ll 1. \tag{9}$$

The temporal boundaries $\tau_{\min}$ and $\tau_{\max}$ of the applicability of (6) for describing the cooperative relaxation are determined by the expression

$$\left|\frac{A_1n_0}{\bar{g}}\left(\frac{1}{2}-\frac{1}{\ln(1/\xi)(1+\nu)}\right)\right|\ll\frac{t}{a\lambda\tau}\ll\left|\left[\frac{2\ln(1/\xi)(2-\nu)}{n_0(2a_2-a_1^2)\varepsilon^{2-\nu}}\right]^{1/2}\right|. \tag{10}$$

The parameter $\Gamma(\nu)$ in (7) depends on the microscopic relaxation function g describing the elementary act of a charge transfer and affects the macroscopic relaxation time $\tau_M=\tau a\lambda[\Gamma(\nu)]^{-1/\nu}$. $B(\nu)$ is the correction for the KWW function at large times. The parameter ν in (6) characterizes the cooperative dynamics and structure of the fractal cluster. The lower temporal limit in (10) has an order of unity, i.e., $\tau_{\min}\sim a\lambda\tau$. In its turn, the upper boundary in (10) correlates to the time for the mean effective displacement of the charge carrier to be of the order of the cluster size $\tau_{\max}\sim\tau(L_N/\lambda)^{1-\nu/2}$.

It is easy to find the relationship between the exponent ν ($\nu=\ln p/\ln k$) and the fractal dimension D_f using an assumption that the fractal is isotropic and has spherical symmetry. The number of droplets that are located along the segment of length L_j on the jth step of the self-similarity is $n_j\sim p^j$. The total number of the droplets in the cluster is $S\sim n_j^{d_E}\sim(p^j)^{d_E}$, where d_E is Euclidean dimension ($d_E=3$). The similarity index η, determining by how much the linear size of the fractal is enlarged at step j, is $\eta\sim L_j\sim k^j$. In this case, we obtain the simple relationship between ν and the fractal dimension D_f [17,18], as $D_f=\ln S/\ln\eta=3j\ln p/j\ln k=3\nu$.

III. EXPERIMENT

We have studied an AOT-water-decane microemulsion with a composition of 17.5% (AOT), 21.3% water, and 61.2% decane (vol %). The molar ratio of water to surfactant has the value $W=[\text{water}]/[\text{AOT}]=26.3$. AOT and decane were purchased from Sigma and used without further purification. Deionized and bidistilled water was used throughout the experiments.

The dielectric measurements were done by means of the Dipole TDS Ltd. time domain dielectric spectroscopy (TDDS) system TDS-2 [19] in the frequency range 100 KHz–10 GHz. All samples were measured near the percolation threshold ($T_p=27$ °C) in a temperature range between 18 °C and 40 °C. The general principles of TDDS and a detailed description of the setup and a procedure of our measurements have been described elsewhere [1,19]. The data treatment was carried out in terms of the dipole correlation functions (3) directly in time domain. Because of the complexity of the theoretical correlation function (6) and a large number of the parameters that are involved in the fitting, the least-squares-fitting procedure based on the simulated annealing method was used. Details of the method are described elsewhere [20].

IV. RESULTS AND DISCUSSION

The dependence of the macroscopic dipole correlation function $\psi(t,T)$ for the AOT-water-decane microemulsion versus time and temperature is presented in Fig. 2. One can see that the decay depends essentially on the temperature and provides a complex nonexponential behavior. Given the complexity of the chemical makeup of the microemulsions, there are many various sources of polarization in the system. Depending on their nature, the dynamical processes can be classified into three types.

The first type of relaxation process reflects some characteristics inherent to the dynamics of the single droplet components. Since our system is ionic, the dielectric relaxation contributions of this type are expected to be related to the various processes connected to interfacial polarization, counterion polarization resulting from the movement of ions and/or surfactant counterions relative to the droplets and their organized clusters and interfaces. The collective motions of the anionic head groups of the surfactant molecules at the interface with the water phase can also contribute to the polarization of the system. The relaxation of the first type can also be related to various components of the system con-

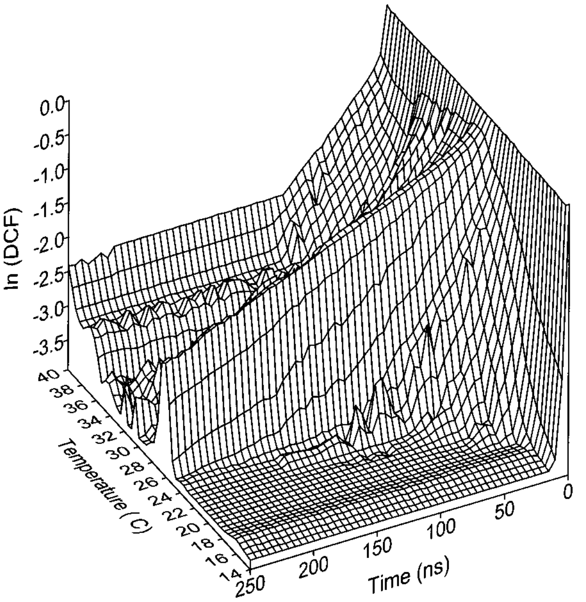

FIG. 2. Three-dimensional plot of the time and temperature dependences of the macroscopic dipole correlation function for the AOT-water-decane microemulsion.

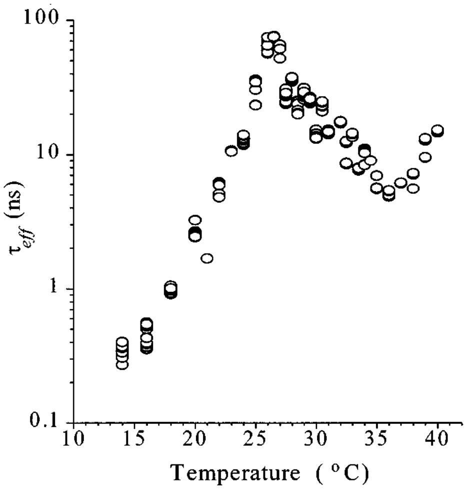

FIG. 3. Temperature dependence of the macroscopic effective relaxation time τ_{eff}.

taining active dipole groups, such as bound and free water.

The second and third types of relaxation processes characterize the collective dynamics in the system and have a *cooperative nature*. The dynamics of the second type may be associated with the transfer of an excitation caused by the transport of electrical charges within the clusters in the percolation region. The relaxation processes of the third type are caused by rearrangements of the clusters and are associated with various types of droplet and cluster motions, such as translations, rotations, collisions, fusion, and fission.

The detailed analysis and estimations of the relaxation time values [1] show the following hierarchy of the processes on the time scale: the relaxation processes of the first type, τ_1, are the fastest processes, on the order of hundreds of picoseconds when compared with the time τ_c needed to ''explore'' the cluster and with the rearrangement time τ_R. The rearrangements occur at times of hundreds or/and thousands of nanoseconds [9,11] and are considered to be the slowest process. The intermediate process ($\tau_1<\tau_c<\tau_R$), relating to the cooperative transport of charge carriers along the clusters, has the temporal window depending on temperature. The minimal time boundaries are of the order of hundreds of picoseconds, whereas the maximal time boundary has a value of tens of nanoseconds in the beginning of the percolation region and reaches 700 ns at T_p.

All these contribute to a complex behavior of the dipole correlation function (Fig. 2). Schematically, the contribution of these processes can be expressed as

$$\Psi(t)=\Psi_1(t/\tau_1)+\Psi_2(t/\tau_c)\Psi_3(t/\tau_R). \qquad (11)$$

Here the term $\Psi_1(t/\tau_1)$ is related to the *short-time* processes of the relaxation. $\Psi_2(t/\tau_c)$ and $\Psi_3(t/\tau_R)$ are the contributions of the collective processes of the second and the third type, respectively. A charge on the droplet can propagate onto a neighboring droplet only in the case of the successive event for two droplets to be fused into one cluster. Thus the contributions of the cooperative processes are presented as a product in accordance with the probability theorems [21]. We note that since the rearrangements are considered to be a slow process when compared with the time needed to explore the cluster, i.e., $\tau_R \gg \tau_c$. Therefore, within the experimental time window, the $\Psi_3(t/\tau_R)\approx$const. In addition, if there is nonexponential behavior in the first term in (11), $\psi_1(t/\tau_1)\sim\exp[-(t/\tau_1)^{\beta_1}]$; then (11) qualitatively coincides with the expression [Eq. (13) in Ref. [1]]

$$\psi(t)=A_1\ \exp[-(t/\tau_1)^{\beta_1}]+A_2\ \exp[-(t/\tau_2)^{\beta_2}], \qquad (12)$$

which we used [1] for fitting the measured correlation function (3). In turn, the first term contributes to the relaxation only at small times. Therefore, the cooperative relaxation of the second type, described by Eq. (6), is the governing relaxation process in the intermediate temporal interval.

It is relevant to note that the long-time term $\Psi_3(t/\tau_R)$ can also exhibit a stretched exponential behavior in the percolation region [22] with the characteristic relaxation time τ_R of the order of tens of milliseconds. Both the relaxation time and the corresponding stretched exponent are temperature dependent. These effects entail the existence of the anomalous (inhibited and enhanced) diffusion of charge carriers within the percolation cluster as well as the cluster rearrangements [10].

Analyzing the dynamics and structure of the microemulsion in the percolation region, we began from the decay behavior of the correlation function (3). Figure 3 shows the temperature dependence of the effective relaxation time, defined within the fractal parameters of the model as $\tau_{\mathrm{eff}}=\tau a\lambda\Gamma^{-1/\nu}$, and corresponding to the macroscopic relaxation time τ_M of the KWW model. The τ_{eff} was determined from the fitting of the model parameters a, τ, p, n_0, and N [see (4)–(9)]. The value of λ was set equal to the average diameter of the droplet of 100 Å. In the percolation threshold T_p the τ_{eff} exhibits a maximum and reflects the well-known *critical slowing down* effect [23].

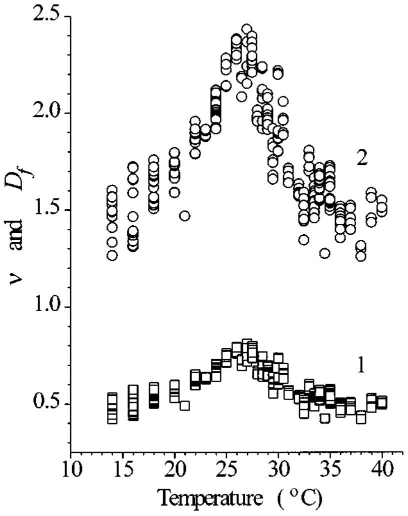

FIG. 4. Temperature dependence of the stretching parameter ν (□) and the fractal dimension D_f (○).

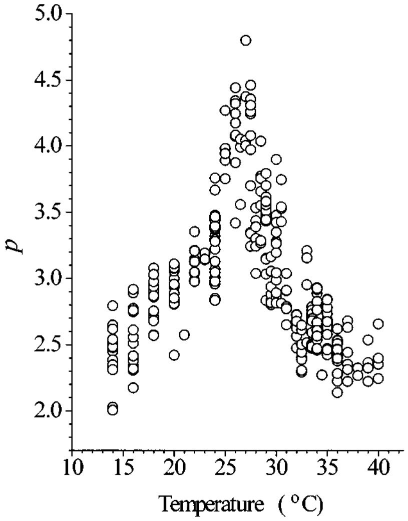

FIG. 5. Temperature dependence of the scaling parameter p.

The stretched exponent ν depends essentially on the temperature (Fig. 4). At 14 °C, the ν has a value of 0.5. However, when the temperature approaches the percolation threshold $T_p=27$ °C, the ν reaches its maximum, which is equal to 0.8, with an error margin of less than 0.1. According to the model, this rapid decay of the KWW function at the percolation threshold reflects the increase of the cooperative effect of the relaxation in the system. At temperatures above T_p, the value of the stretched exponent ν decreases and indicates that the relaxation decelerates in the interval 28 °C–34 °C. In the temperature range above 34 °C, the new increase of ν with the rise in temperature suggests that the system undergoes a structural modification. Such a change implies a transformation from L_2 phase to lamellar [2] or to bicontinuous phases [24,25].

On the other hand, in supposition that the percolation clusters have a spherical symmetry, our theoretical model yields a very simple relationship between the stretched exponent ν and the fractal dimension of the system D_f as follows: $D_f=3\nu$. The temperature behavior of the fractal dimension (Fig. 4) shows that below the percolation threshold D_f has a value of less than 2, which corresponds to a system of small clusters dispersed in space and can be described by the model of unbounded fractal sets with $D_f<2$ [17,18]. At the percolation threshold the fractal dimension is equal to 2.4, with an error margin of 0.2, satisfactorily concurring with the literature value of 2.5 [26]. Above the percolation threshold D_f decreases, which can be explained by reorganizations of the system with corresponding structural changes. A structural modification of the system in the temperature range above 34 °C and the appearance of more prolonged and/or ordered regions in the microemulsion lead to the new observable increase of D_f.

The character of the fractal structure in the microemulsion near the percolation threshold is monitored by the temperature behavior of the number of stages of self-similarity of the clusters N and the scaling parameters k and p. From the fitting it was found that the scaling parameter k is 6.7±0.9 and seems to be insensitive to the temperature. Thus the character of the ''*linear*'' fractal similarity does not change within the measured temperature region. On the other hand, when T approaches the percolation threshold T_p, Figs. 5 and 6 demonstrate a tendency of increasing values of p and N from their minimal values of 2.5 and 1 to values of 4.5 and 12 at T_p, respectively. Such behavior testifies to the changes of the type of self-similarity related to the droplet concentration and a growth of the maximal scale of the self-similarity. After the percolation threshold the values of p and N decrease to recover the tendency of forming a new structure.

The effective length of the clusters increases sharply and diverges in the percolation threshold (Fig. 7) in accordance with the percolation scaling law $L_N \sim (T-T_p)^{-\nu}$, where ν is the geometrical exponent $\nu \approx 0.88$ [23]. (We note that this symbol ν is accepted for the geometrical exponent in percolation science and it should not be confused with the stretched exponent discussed above in the KWW term.) However, a big dispersion of the data obtained from the fit-

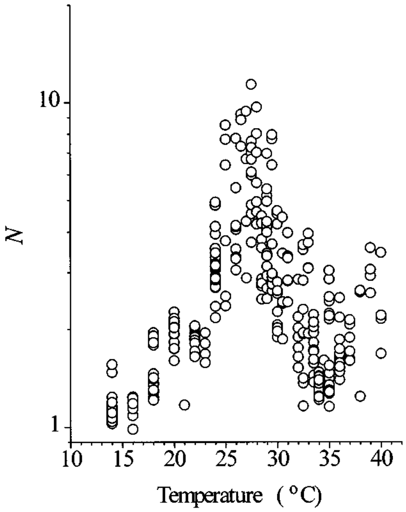

FIG. 6. Temperature dependence of the number of the maximal self-similarity stage N.

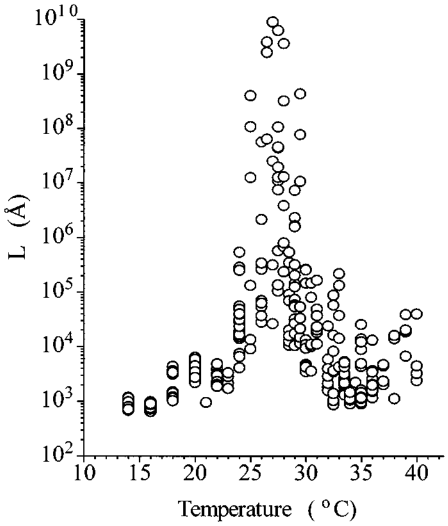

FIG. 7. Effective length of the percolation cluster L_N versus temperature.

ting does not allow a precise estimation of a critical exponent of this growth.

The typical number of droplets S in the aggregates may be estimated according to the relationship given by

$$S \sim (L_N/d_{\mathrm{drop}})^{1/D_f},$$

where d_{drop} is the diameter of the surfactant-coated water droplet, estimated to be 100 Å. The temperature dependence of the number of droplets in the typical fractal cluster S is presented in Fig. 8.

The analysis of the temperature behavior of the calculated parameters shows that at the onset of the percolation region the droplets have a tendency to form small dynamic aggregates consisting of 10 ± 5 droplets that are weakly bound one to another. The characteristic length of such aggregates changes in the interval, calculated to be $L_N \sim 600-1000$ Å. The fractal dimension at these temperatures has a value less than 2, indicating that aggregates are surrounded by empty spaces, i.e., separated from one another. We note that each of these aggregates participates in the relaxation as an independent object with no correlation between them. In the percolation threshold, these aggregates tend to form the large percolation cluster that participates in the cooperative relaxation as a whole object.

V. CONCLUSION

The above dielectric relaxation study of the AOT-water-decane microemulsion near the percolation temperature threshold leads to the following general conclusions.

(i) The macroscopic law of relaxation of the KWW type $\exp[-(t/\tau_M)^\nu]$ is insensitive to the microscopic details of the charge transport in a fractal medium for a wide class of the microscopic relaxation functions satisfying the conditions formulated in the Appendix.

(ii) The stretched relaxation behavior of the KWW type in time domain does not occur throughout the entire temporal range, rather only in the time interval given by (10). In order to extend the initial temporal interval of the applicability of the relaxation function the correction of the type $B(t/\tau)$ to the term $\Gamma(t/\tau)^\nu$ was found in (6).

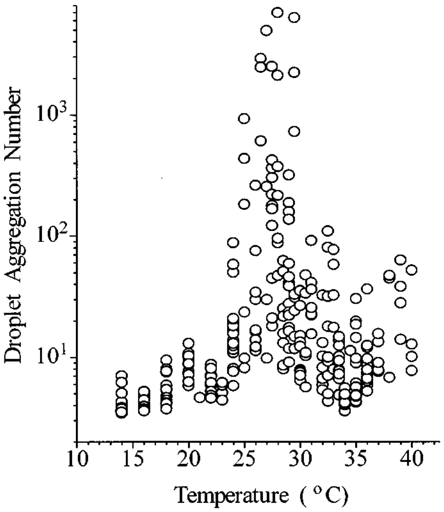

FIG. 8. Temperature dependence of the number of droplets in the typical percolation cluster.

(iii) The characteristic dependences of the stretched exponent ν, the calculated fractal dimension D_f, the scaling parameters p and k as well as the calculated length of the percolation cluster L_N, and the number of droplets in the clusters S clearly demonstrate the specific features of the system near the percolation threshold. The suggested theory satisfactorily describes the cooperative processes of the relaxation in microemulsions and can be expressed in terms of the KWW relaxation function. The stretched exponent ν, the macroscopic relaxation time τ_M entering in the stretched exponential decay behavior $\exp[-(t/\tau_M)^\nu]$ of the correlation functions, and the scaling parameters of the model k and p are related to the structural parameters of the system.

(iv) At the temperatures below the percolation threshold droplets have a tendency to form small dynamic aggregates with the characteristic length of 600–1000 Å and consisting of 5–15 droplets that are weakly bound to one another. Each of these aggregates participates in the relaxation as an independent object and there is no correlation between them. In the vicinity of the percolation threshold (around 27 °C) these aggregates tend to form the large percolation cluster that participates in the cooperative relaxation as a whole object. A continuation of this work may be the development of the proposed model of the fractal cooperative relaxation by considering a size distribution of the percolation clusters as well as taking into account the dynamics of the cluster rearrangements.

ACKNOWLEDGMENTS

The authors would like to express their appreciation to Professor Nissim Garti for helpful discussions and to Ido Nir for assistance in the measurements. Yu.F. is grateful to the Bruno Goldberg Endowment Fund for the financial support of this work. N.K. and Yu.A. acknowledge the support of the Levy Eshkol Foundation from the Israel Ministry of Science and Technology.

APPENDIX: ESTIMATION OF THE PRODUCT $I(z)=\prod_{j=0}^{N}[g(Z\xi^{j})]^{n_0p^i}$

In the case of $0<\nu<1$ [$\nu=\ln(p)/\ln(k)=\ln(p)/\ln(1/\xi)$, $\xi=1/k$], by using the corrections given by Euler-Maclaurin formula [27] we obtain

$$\begin{aligned}\ln I(z)&=n_0\sum_{j=1}^{N}p^j\ln[g(z\xi^j)]\\&\approx\left\{n_0\int_0^N p^u\ln[g(z\xi^u)]du+\frac{n_0}{2}\ln[g(z)]\right\}\\&=\frac{n_0}{2}\ln[g(z)]+\frac{n_0}{\ln(1/\xi)}z^{\nu}\int_{\varepsilon z}^{z}y^{-\nu-1}\ln[g(y)]dy\\&=\frac{n_0}{2}\ln[g(z)]+\frac{n_0}{\ln(1/\xi)}z^{\nu}\left\{\int_0^{\infty}(\cdots)dy-\int_0^{\varepsilon z}(\cdots)dy-\int_z^{\infty}(\cdots)dy\right\},\end{aligned}\tag{A1}$$

where $\varepsilon=\xi^N\ll1$ for $N\gg1$ and $\xi<1$. Let us suppose that the microscopic relaxation function $g(y)$ has the asymptotic forms

$$g(y)=\begin{cases}1-a_1y+a_2y^2+\cdots\quad\text{for } y\ll1 & \text{(A2)}\\ \overline{g}+A_1/y+A_2/y^2+\cdots\quad\text{for } y\gg1 & \text{(A3a)}\\ \text{or} & \\ \overline{g}+A_1\exp(-y)+A_2\exp(-2y)+\cdots\quad\text{for } y\gg1. & \text{(A3b)}\end{cases}$$

The function $g(y)$ satisfies the conditions as $g(0)=1$, and $dg(y)/dy<0$ and $0<\overline{g}<1$.

Let us show that if these conditions are imposed on the function $g(y)$ then the function $I(z)$ has a "universal" behavior for the certain *interval of an intermediate asymptotic* of the variable z,

$$z_m\ll z\ll z_M.\tag{A4}$$

The expansions for the $\ln[g(y)]$ that are used for calculation of the derivative $dg(y)/dy$ and the values z_m and z_M are given by

$$\ln[g(y)]=\begin{cases}-a_1y+(a_2-a_1^2/2)y^2+\cdots\quad\text{for } y\ll1 & \text{(A5)}\\ -\ln[1/\overline{g}]+\dfrac{A_1}{\overline{g}}+\left(\dfrac{A_2}{\overline{g}}-\dfrac{A_1^2}{2\overline{g}^2}\right)\dfrac{1}{y^2}+\cdots\quad\text{for } y\gg1 & \text{(A6a)}\\ \text{or} & \\ -\ln[1/\overline{g}]+\dfrac{A_1}{\overline{g}}\exp(-y)+\left(\dfrac{A_2}{\overline{g}}-\dfrac{A_1^2}{2\overline{g}^2}\right)\exp(-2y)+\cdots\quad\text{for } y\gg1. & \text{(A6b)}\end{cases}$$

The values of two last integrals in (A1) are estimated by using the expansions (A5), and (A6a) or (A6b). These terms are negligibly small in the interval of the intermediate asymptotic (A4) and the result for $I(z)$ in this case is given by

$$I(z)=\left(\frac{1}{\overline{g}}\right)^{-\theta}\{\exp\{-\Gamma(\nu)z^{\nu}+B(\nu)z\},$$

where

$$\theta=n_0(1/2+1/\delta),\quad \delta=\ln(1/\xi),$$

$$\Gamma(\nu)=\frac{n_0}{\delta}\int_0^{\infty}y^{-\nu-1}\ln[1/g(y)]dy=\frac{n_0}{\delta\nu}\int_0^{\infty}y^{-\nu}\left|\frac{g'(y)}{g(y)}\right|dy,$$

and

$$B(\nu)=-\frac{n_0a_1}{\delta(1-\nu)}\varepsilon^{1-\nu}.$$

The boundaries of the interval of the intermediate asymptotic (A4) for the microscopic correlation functions (A2) and (A3a) are given by

$$\left|\frac{A_1n_0}{\overline{g}}\left(\frac{1}{2}-\frac{1}{\delta(1+\nu)}\right)\right|\ll\frac{t}{a\lambda t}\ll\left|\left[\frac{2\delta(2-\nu)}{n_0(2a_2-a_1^2)\varepsilon^{2-\nu}}\right]^{1/2}\right|.$$

The expansion (A3b) leads to the interval of the intermediate asymptotic

$$\left|\ln\left(\frac{A_1n_0}{2\overline{g}}\right)\right|\ll\frac{t}{a\lambda\tau}\ll\left|\left[\frac{2\delta(2-\nu)}{n_0(2a_2-a_1^2)\varepsilon^{2-\nu}}\right]^{1/2}\right|,$$

which is wider from the side of the small z.

It is relevant to bear in mind that for the ν falling out the interval $[0,1)$, the integral in (A1) is divergent in the low limit ($\varepsilon z \to 0$) for $a_1 \neq 0$. We also note that if the microscopic relaxation function is exponential, i.e., $g(y) = \exp(-y)$, then the macroscopic function $I(z)$ also remains exponential, $I(z) = \exp(-Az)$, where $A = \exp[-n_0 \ln(l/\xi) \Sigma_{j=0}^{N} j p^j]$.

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