

## Physicochemical Studies on Microemulsions. 8. The Effects of Aromatic Methoxy Hydrotropes on Droplet Clustering and Understanding of the Dynamics of Conductance Percolation in Water/Oil Microemulsion Systems

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The temperature-induced dynamic percolation of water/oil (w/o) microemulsions (water/AOT/heptane, water/AOT/octane, and water/AOT/decane) has been studied in the presence of hydrotropes (2-methoxy phenol, 4-methoxy phenol, 5-methoxy resorcinol, and 3-methoxy catechol). The results have been analyzed (1) to estimate the threshold percolation temperature, (2) to test the performance of the scaling equation, (3) to obtain the activation energy for the percolation process, and (4) to assess the thermodynamics of clustering of the dispersed nanodroplets. The influence of substitution of the methoxy group (at different positions of the phenolic moieties) on the process has been compared with their nonmethoxy analogues and analyzed in favor of “fusion—(mass transfer)—fission” mechanism of dynamic percolation. The assessment of role of the hydrophobic chain length of the hydrocarbon oil on the process of percolation has also been attempted.

### Introduction

The percolation of conductance (both volume- and temperature-induced) in water/oil (w/o) microemulsion is an interesting and fascinating phenomenon that has been fairly studied for the water/AOT/hydrocarbon oil system.<sup>1–39</sup> The droplet clustering leading to their fusion, mass transfer, and fission has been considered to be the probable mechanism of dynamic percolation.<sup>17–28</sup> For the phenomenon to occur, the surfactant-coated dispersed water droplets come in close contact augmenting fusion and effective mass (ion) transfer among the droplets in a concerted manner manifesting rapid rise in conductance. The quantification of the results of dynamic percolation has been attempted employing the “scaling equation”, together with the evaluation of activation energy for the process and energetics of droplet clustering based on pseudophase state of the clustered droplets similar to amphiphile aggregates, like micelles.<sup>24–34</sup> For establishing the mechanism of dynamic percolation, aromatic hydrotropes have been used as additives.<sup>14,15,18,20,21,24,26,27,30,38,39</sup> Their assistance to the process has been modeled as bridging of a pair of droplets by way of their adsorption at the droplet interface, whereas their resistance has been explained by way of blocking the pathway of fusion of droplets. On the basis of an elaborate dynamic percolation study of water/AOT/hydrocarbon systems in the presence of a number of aromatic hydrotropes, it has been revealed that the position of the hydroxyl groups on the aromatic ring determines their influence on the process.<sup>39</sup> It is thus anticipated that replacement of the hydroxyl group from specific centers in the molecule should then affect its influence on the process.

In view of the above, in this study, we have used methoxy hydrotropes such as 2- and 4-methoxy phenol, 5-methoxy resorcinol, and 3-methoxy catechol as additives, and have studied their influence on percolating w/o microemulsions with AOT as the surfactant and *n*-heptane, *n*-octane, and *n*-decane as the oil. The results have evidenced the determinant role of the position and number of the hydroxyl group in the hydrotrope

molecule toward the bridging and blocking phenomena leading to assistance and resistance to percolation, respectively. Understanding of the role of the chain length of hydrocarbons has been also attempted.

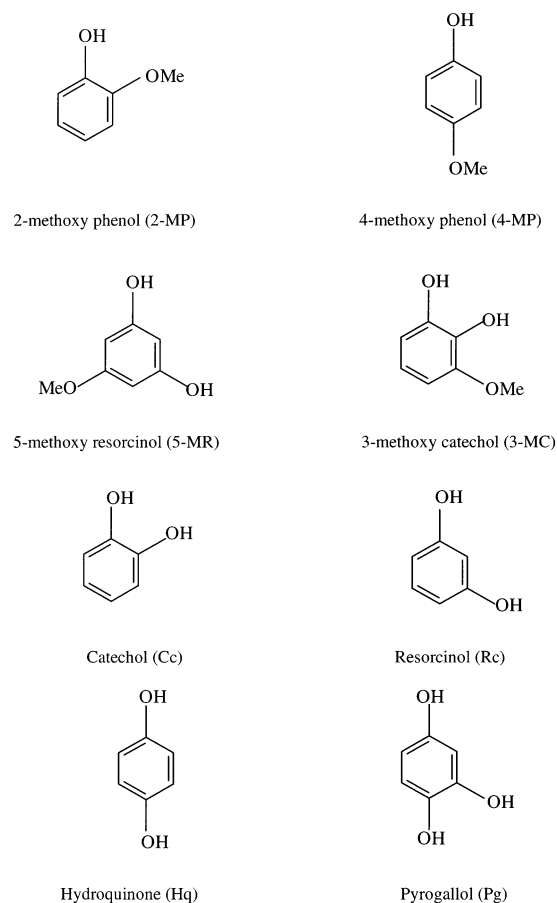
### Materials and Methods

**Materials.** The AOT (sodium bis(2-ethylhexyl) sulfosuccinate, 99% pure) was from Sigma, USA. 2-Methoxy phenol (2-MP), 4-methoxy phenol (4-MP), 5-methoxy resorcinol (5-MR), and 3-methoxy catechol (3-MC) were AR grade products of Aldrich, USA. The hydrocarbons, heptane (Hp), octane (Oc), and decane (Dc) (AR grade), were obtained from E-Merck, Germany. All of the chemicals were used as received. Triply distilled water of specific conductance, 2–4  $\mu\text{S cm}^{-1}$  at 303 K, was used to prepare all solutions. The structures of the additives with their nonmethoxy analogues are presented in Figure 1.

**Methods. Preparation of Microemulsion.** Microemulsions were prepared at water/AOT mole ratio ( $\omega$ ) = 25 at [AOT] = 0.5 mol dm<sup>-3</sup>. The requisite amount of AOT was dissolved in the oil (Hp, Oc, or Dc) and water was added to attain  $\omega$  = 25. Each system was mixed well by stirring and used. For experimenting with the hydrotropes, their aqueous solutions were used instead of pure water in the preparation of microemulsion. Their concentrations were very minor and did not affect the desired value of  $\omega$  at 25.

**Conductance Measurements.** The conductance measurements (with  $\pm 0.5\%$  accuracy) were taken at a frequency of 1 kHz using a Jenway (England) conductometer in a temperature-compensated dip-type cell of cell constant 0.92 cm<sup>-1</sup> placed in a Neslab RTE-100 temperature-controlled water bath of accuracy  $\pm 0.1$  °C. The conductance of the prepared microemulsions at  $\omega$  = 25 and at a desired droplet concentration (determined by the water/oil mole ratio) with and without additive was measured as a function of temperature until a large increase in conductance followed by a mild increase in the form of sigmoidal variation was observed.<sup>38–40</sup> The results helped to obtain the threshold stage of percolation. For the evaluation of the thermodynamic parameters of clustering of droplets, a

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**Figure 1.** Structure of the additives along with their nonmethoxy analogue.

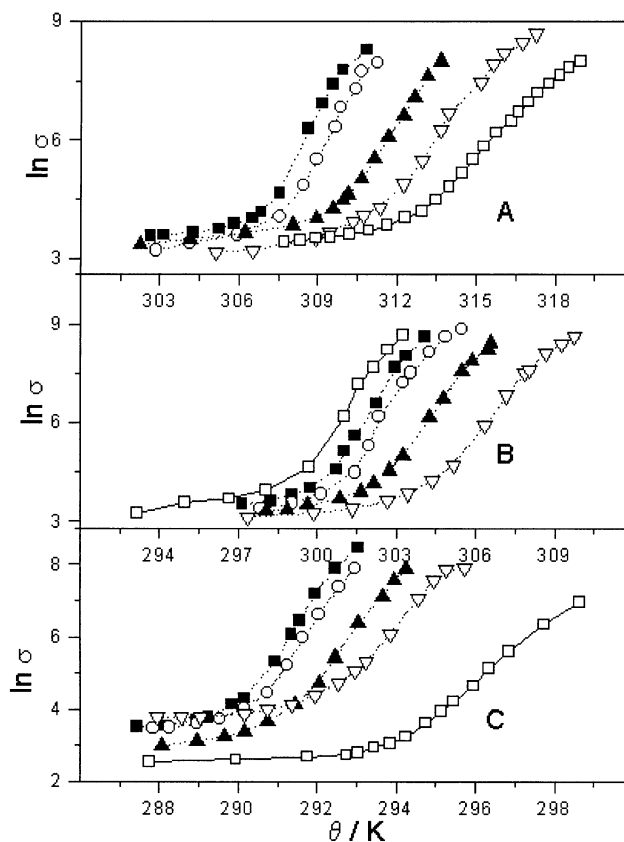
preparation (with and without additive) at  $\omega = 25$  was diluted several times with oil to vary the droplet concentration and the percolation measurements were taken at each stage of dilution following the above-mentioned procedure.<sup>23,30,38,39</sup>

## Results and Discussion

**Percolation Courses and Threshold Temperature,  $\theta_t$ .** The conductance courses of W/AOT/Hp, W/AOT/Oc, and W/AOT/Dc microemulsion systems at  $\omega = 25$  with 2-MP, 4-MP, 3-MC, and 5-MR as additives are illustrated in Figures 2, 3, 4, and 5, respectively. For a constant composition, the nature of microemulsion was considered to remain unchanged in the percolating range of temperature. Beyond the percolation range, an overall structural change by way of enhanced droplet association leading to stable conduit formation was envisaged. The influence of the additives on the percolation phenomenon was appreciable. For all of the three studied microemulsions, the additives have affected the phenomenon of percolation in different ways. The phenomenon was favored by the increasing chain length of the oils: the sigmoidal  $\ln \sigma$  vs  $\theta$  curves shifted toward lower temperature more for Dc than Oc than Hp.

The percolation transition (threshold) and the values of the asymptotes was conveniently evaluated using the sigmoidal Boltzmann equation (SBE) recently proposed and used by us.<sup>39,40</sup> The equation has the form

$$\log \sigma = \log \sigma_f \left[ 1 + \left( \frac{\log \sigma_i - \log \sigma_f}{\log \sigma_f} \right) \left\{ 1 + \exp(\theta - \theta_p)/\Delta\theta \right\}^{-1} \right] \quad (1)$$



**Figure 2.** Conductance- $\theta$  profile for the w/o microemulsion systems at  $\omega = 25$  at varied 2-MP concentration: ( $\square$ ) 0, ( $\blacksquare$ ) 5, ( $\circ$ ) 10, ( $\blacktriangle$ ) 20 and ( $\nabla$ ) 30  $\text{mol dm}^{-3}$ . Section A shows results for Hp, section B for Oc, and section C for Dc.

where  $\sigma$  and  $\theta$  represent conductance and temperature, respectively; the i, f, and p signify the values at the initial, final, and percolation stages, respectively, and  $\Delta\theta$  is the interval of temperature of measurement.

The conductance data at different temperatures were fitted to the SBE (eq 1) to yield the transition temperature ( $\theta_t$ ). The  $\theta_t$  values (evaluated using eq 1) for the studied w/o microemulsion systems at different concentrations of the additives are presented in Tables 1, 2, and 3 for the Hp, Oc, and Dc derived systems, respectively. It is seen from the tables that 2-MP has increased  $\theta_t$  at all concentrations, whereas 4-MP has a very mild effect on  $\theta_t$  in all of the systems irrespective of the oils used. The additive 5-MR has appreciably decreased  $\theta_t$  with increasing concentration in all of the systems. The 3-MC has shown oil-dependent features: in W/AOT/Hp, it has hardly affected the percolation process, whereas in both W/AOT/Oc and W/AOT/Dc systems, it has assisted the process to the same extent. Both in the absence and in the presence of the additives, increasing carbon number in the oil has assisted the process: the influence of Dc was more than that of Oc than that of Hp. The additive effect will be more intimately discussed in a subsequent section.

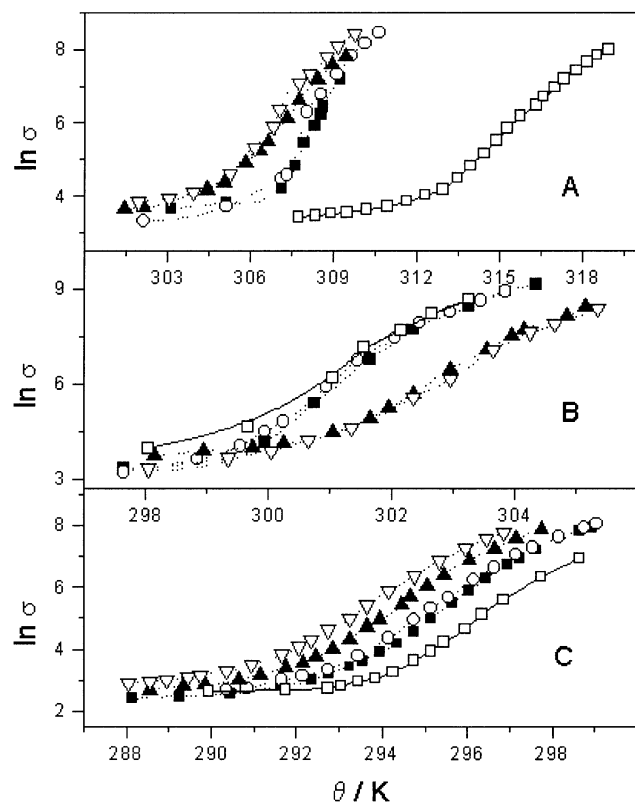
**Performance of Scaling Equation.** The temperature-dependent conductance in the percolation range obeys the scaling equation,

$$\sigma = P(\theta - \theta_t)^n \quad (2)$$

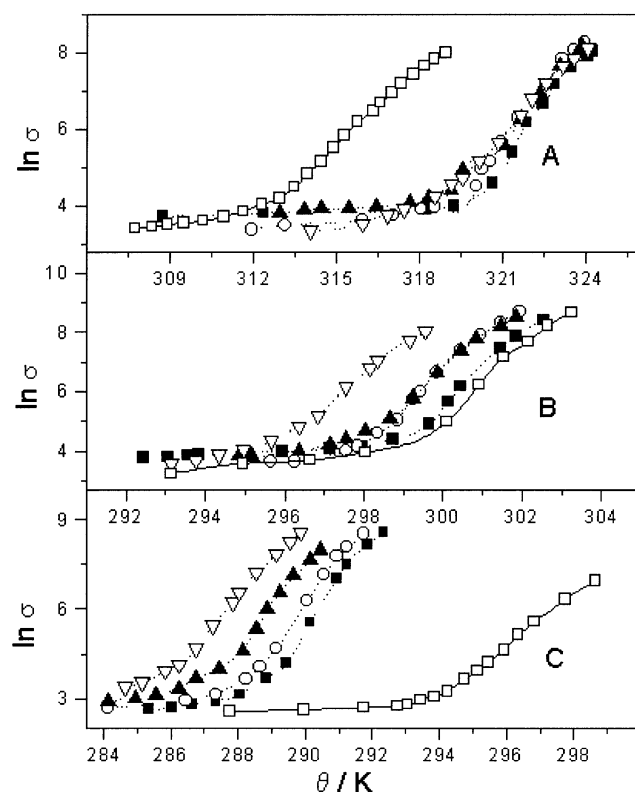
or

$$\ln \sigma = \ln P + n \ln(\theta - \theta_t) \quad (3)$$

The conductance data as a function of temperature in the

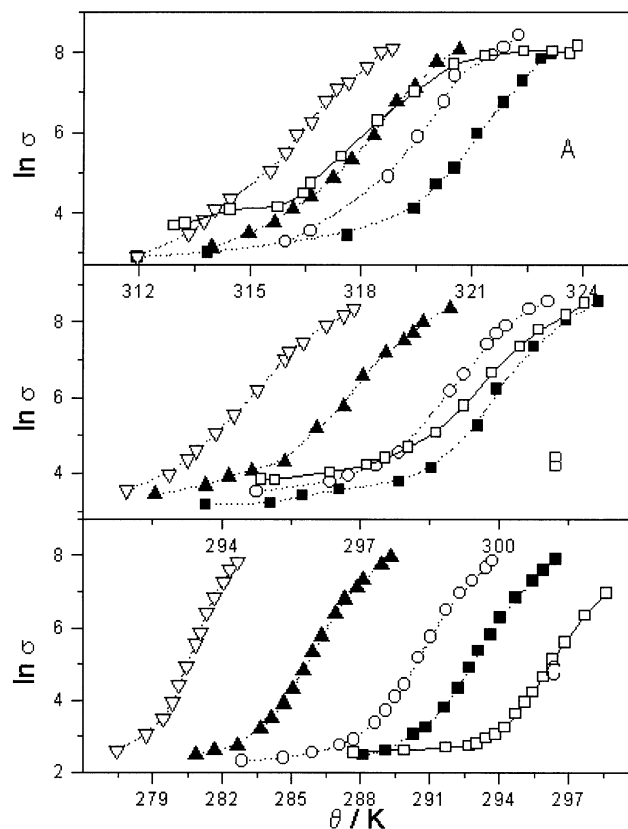


**Figure 3.** Conductance- $\theta$  profile for the w/o microemulsion systems at  $\omega = 25$  at varied 4-MP concentration: (□) 0, (■) 5, (○) 10, (▲) 20 and (▼) 30 m mol dm<sup>-3</sup>. Section A shows results for Hp, section B for Oc, and section C for Dc.



**Figure 4.** Conductance- $\theta$  profile for the w/o microemulsion systems at  $\omega = 25$  at varied 3-MC concentration: (□) 0, (■) 5, (○) 10, (▲) 20 and (▼) 30 m mol dm<sup>-3</sup>. Section A shows results for Hp, section B for Oc, and section C for Dc.

postpercolation range for the three studied microemulsion systems fairly obey the eq 3 with and without additives. The



**Figure 5.** Conductance- $\theta$  profile for the w/o microemulsion systems at  $\omega = 25$  at varied 5-MR concentration: (□) 0, (■) 5, (○) 10, (▲) 20 and (▼) 30 m mol dm<sup>-3</sup>. Section A shows results for Hp, section B for Oc, and section C for Dc.

derived results are presented in Tables 1–3. The  $n$  values were lower than the predicted value of 1.9.<sup>34,39</sup> The  $\ln P$  values varied in a wide range (6.3–7.9). The  $n$  values have a weak (not always quantitative) dependence on the oil; the magnitudes more or less follow the order  $n_{\text{Hp}} < n_{\text{Oc}} < n_{\text{Dc}}$ . The difference between the static and dynamic percolation was reflected on the deviations of  $n$  from the predicted value of 1.9.<sup>29,34,38</sup> In the first, wherein a mixture of solid conductors and insulators constitute the system, the conductance of the system remains virtually zero below the threshold condition. In the dynamic percolating system, as in w/o microemulsion, the microwater droplets are always in motion. Below  $\theta_t$ , the system conducts to some extent by way of their random rearrangement resulting in their closer approach. Near the threshold state, the droplets associate/cluster resulting in fusion causing efficient ion transport and large increase in conductance. According to a recent report, the alternative “hopping” mechanism of transfer of surfactant ion from one droplet to another makes only a minor contribution to the conductance;<sup>33</sup> it is the ion transfer by fusion, (mass exchange), and fission that makes a large contribution. The additives influenced the dynamics of the process and thus affected both  $P$  and  $n$ .

According to the scaling law, the system conductance at any temperature in the percolation stage is guided by both  $P$  and the exponent  $n$ . To attain equal levels of  $\sigma$ , the contributions of  $P$  and  $n$  are complementary; a higher  $P$  is complemented with a lower  $n$  and vice versa. On the whole, the observed  $n$  values with the percolation-resisting additives are lower and those with the percolation-assisting additives are higher although both are lower than the static percolation exponent 1.9. According to the present findings, the expected magnitude of the constant  $P$

**TABLE 1: Percolation Threshold, Scaling Law Parameters, and Energy of Activation for Temperature-Induced Percolation of Water/AOT/Heptane Microemulsion System with Varying Concentration of Additive at  $\omega = 25$** 

additive	[additive] (mM)	$\theta_i$ (K)	$S$	$\ln P$	$n$	corr. coeff.	$E_p$ (kJ mol <sup>-1</sup> )
2-MP		315.6 ± 0.07	0.21 ± 0.02	6.47 ± 0.04	1.25 ± 0.04	0.9977	508
	5	308.6 ± 0.05		7.50 ± 0.01	0.95 ± 0.02	0.9995	718
	10	309.4 ± 0.04		7.41 ± 0.08	0.82 ± 0.16	0.9643	790
	20	312.3 ± 0.06		7.77 ± 0.04	0.66 ± 0.06	0.9963	748
4-MP	30	313.6 ± 0.01	0.21 ± 0.02	6.96 ± 0.07	1.35 ± 0.07	0.9959	554
	5	308.4 ± 0.07		7.48 ± 0.06	0.82 ± 0.07	0.9896	663
	10	308.0 ± 0.09		6.97 ± 0.02	1.23 ± 0.03	0.9990	703
	20	307.7 ± 0.05		7.43 ± 0.03	0.73 ± 0.07	0.9949	555
5-MR	30	307.1 ± 0.11	-0.19 ± 0.02	7.79 ± 0.05	0.36 ± 0.07	0.9839	471
	5	321.4 ± 0.02		7.39 ± 0.05	1.12 ± 0.14	0.9925	833
	10	319.6 ± 0.05		7.20 ± 0.08	1.21 ± 0.11	0.9914	687
	20	318.3 ± 0.09		7.16 ± 0.07	1.01 ± 0.13	0.9841	737
3-MC	30	316.3 ± 0.01	0.00	7.06 ± 0.05	1.06 ± 0.08	0.9875	674
	5	321.8 ± 0.02		7.14 ± 0.01	1.00 ± 0.01	0.9997	675
	10	321.6 ± 0.07		7.37 ± 0.01	1.04 ± 0.02	0.9998	685
	20	321.9 ± 0.05		7.47 ± 0.09	0.93 ± 0.17	0.9841	680
	30	321.5 ± 0.08		7.28 ± 0.04	0.83 ± 0.06	0.9927	625

**TABLE 2: Percolation Threshold, Scaling Law Parameters, and Energy of Activation for Temperature-Induced Percolation of Water/AOT/Octane Microemulsion System with Varying Concentration of Additive at  $\omega = 25$** 

additive	[additive] (mM)	$\theta_i$ (K)	$S$	$\ln P$	$n$	corr. coeff.	$E_p$ (kJ mol <sup>-1</sup> )
2-MP		301.3 ± 0.13	0.18 ± 0.02	7.58 ± 0.04	1.39 ± 0.07	0.9999	683
	5	302.3 ± 0.05		8.06 ± 0.05	0.92 ± 0.13	0.9903	647
	10	302.5 ± 0.04		7.47 ± 0.04	1.30 ± 0.06	0.9981	590
	20	304.5 ± 0.06		7.62 ± 0.06	1.03 ± 0.12	0.9860	698
4-MP	30	306.6 ± 0.11	0.09 ± 0.03	7.21 ± 0.06	1.25 ± 0.01	0.9950	545
	5	301.3 ± 0.01		7.62 ± 0.06	1.35 ± 0.07	0.9970	668
	10	301.1 ± 0.10		7.47 ± 0.04	1.36 ± 0.06	0.9968	675
	20	303.3 ± 0.07		7.87 ± 0.04	0.81 ± 0.04	0.9888	614
5-MR	30	303.1 ± 0.04	-0.22 ± 0.01	7.44 ± 0.08	1.13 ± 0.14	0.9923	597
	5	300.0 ± 0.07		7.64 ± 0.03	1.15 ± 0.05	0.9990	648
	10	299.0 ± 0.04		7.79 ± 0.01	1.10 ± 0.02	0.9995	650
	20	296.9 ± 0.04		7.54 ± 0.05	1.07 ± 0.12	0.9830	708
3-MC	30	294.6 ± 0.02	-0.11 ± 0.03	7.34 ± 0.02	1.19 ± 0.04	0.9915	716
	5	300.7 ± 0.06		7.71 ± 0.02	1.08 ± 0.05	0.9990	644
	10	299.6 ± 0.02		7.64 ± 0.03	1.21 ± 0.06	0.9973	726
	20	299.7 ± 0.03		7.66 ± 0.03	1.06 ± 0.06	0.9967	682
	30	297.6 ± 0.02		7.37 ± 0.04	0.95 ± 0.08	0.9964	648

in the scaling equation is to be lower in the static percolation than that in the dynamic percolation. In the literature, temperature-induced static percolation results are rare restricting justification in favor of the above conclusion. One may, on the other hand, compare the concentration-induced percolation results, both static and dynamic, for assessing the similarity and dissimilarity between the two processes. Investigations in this direction are scarce in the literature.

**Activation Energy for Percolation.** The activation energy for conductance percolation ( $E_p$ ) has been estimated using an Arrhenius-type equation,

$$\sigma = A e^{-E_p/(RT)} \quad (4)$$

or

$$\ln \sigma = \ln A - \frac{E_p}{RT} \quad (5)$$

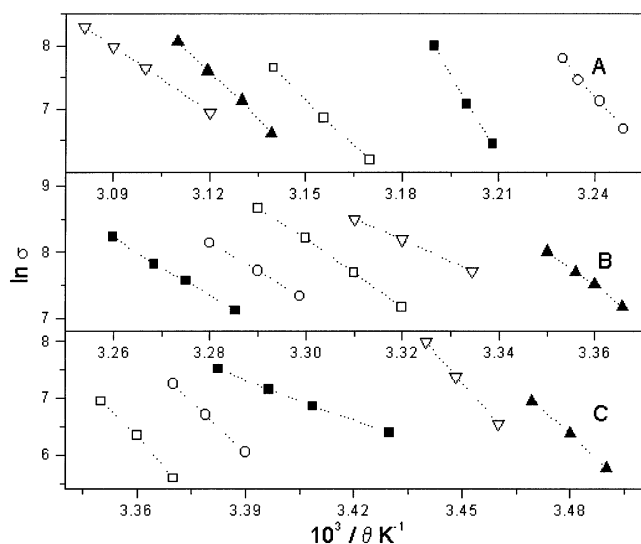
where  $A$  is a constant and  $R$  and  $T$  have their usual significance. The  $E_p$  values have been obtained from the slopes ( $-E_p/R$ ) of the  $\ln \sigma$  vs  $T^{-1}$  plots (illustrated in Figure 6) and are given in Tables 1–3. According to earlier reports,<sup>38,39</sup> the  $E_p$  may not follow a specific trend with respect to additive concentration;

the trend may show a maximum. The percolation-assisting additives may produce higher  $E_p$  than the percolation-resisting additives. These facts have led us to consider that fission of the fused droplets (scheme shown in Figure 7) is the rate-determining step for the dynamic percolation process.<sup>33,39</sup> The fission of bulky doublets into a pair of singlets with associated transfer of counterion ( $\text{Na}^+$  ion in the present system) requires higher activation energy. The bridging of droplets by an additive may reduce  $\theta_i$ , but it is the process of their separation that decides the magnitude of  $E_p$ , which can be high in the presence of an efficient bridging additive. At a fixed  $\omega$ , the  $E_p$  values do not show any specific trend with the chain length of the oil (Tables 1–3). In a system on the whole, the  $E_p$  value has a decreasing trend with increasing additive concentration. The dynamic process of conductance percolation is thus different from normal conductance. The magnitude of  $E_p$  is thus essentially controlled by the separability of the droplets from the “fused” to the “free” state. Thus, in several situations resisting additives have yielded more or less comparable  $E_p$  values. For a pragmatic correlation among the additives, the contributions of steric and interacting factors in the process of fission need to be incorporated. An elaborate and planned study in this direction is thus wanted.

**Energetics of Droplet Clustering.** The clustering of droplets

**TABLE 3: Percolation Threshold, Scaling Law Parameters, and Energy of Activation for Temperature-Induced Percolation of Water/AOT/Decane Microemulsion System with Varying Concentration of Additive at  $\omega = 25$** 

additive	[additive] (mM)	$\theta_t$ (K)	$S$	$\ln P$	$n$	corr. coeff.	$E_p$ (kJ mol <sup>-1</sup> )
2-MP		296.3 ± 0.05		6.07 ± 0.07	0.93 ± 0.12	0.8997	580
	5	291.5 ± 0.02	0.11 ± 0.01	7.95 ± 0.03	1.05 ± 0.05	0.9987	949
	10	291.8 ± 0.05		7.68 ± 0.09	0.88 ± 0.12	0.9914	1018
	20	292.8 ± 0.07		7.33 ± 0.04	1.26 ± 0.11	0.9923	759
	30	294.1 ± 0.06		7.69 ± 0.02	0.88 ± 0.06	0.9974	678
4-MP	5	295.7 ± 0.10	-0.07 ± 0.01	6.28 ± 0.04	1.39 ± 0.05	0.9988	601
	10	295.4 ± 0.01		6.29 ± 0.03	1.34 ± 0.04	0.9984	553
	20	294.6 ± 0.06		6.35 ± 0.08	1.29 ± 0.09	0.9941	545
	30	294.0 ± 0.08		6.48 ± 0.03	1.21 ± 0.04	0.9989	532
5-MR	5	293.2 ± 0.05	-0.49 ± 0.01	6.15 ± 0.05	1.43 ± 0.06	0.9982	483
	10	290.7 ± 0.02		6.25 ± 0.04	1.42 ± 0.05	0.9987	606
	20	286.0 ± 0.05		6.26 ± 0.05	1.39 ± 0.05	0.9953	624
	30	280.8 ± 0.01		7.00 ± 0.02	1.29 ± 0.05	0.9981	691
3-MC	5	290.4 ± 0.01	-0.10 ± 0.002	7.64 ± 0.04	1.35 ± 0.07	0.9986	771
	10	289.9 ± 0.07		7.71 ± 0.01	1.30 ± 0.03	0.9995	933
	20	288.9 ± 0.05		7.44 ± 0.05	1.16 ± 0.14	0.9931	819
	30	287.8 ± 0.06		7.59 ± 0.06	1.29 ± 0.12	0.9911	806
Rc <sup>a</sup>	5	293.0 ± 0.03	-0.35 ± 0.02	5.39 ± 0.07	1.57 ± 0.03	0.9946	630
	10	292.3 ± 0.01		5.03 ± 0.05	1.54 ± 0.04	0.9957	568
	20	287.9 ± 0.01		6.08 ± 0.02	1.18 ± 0.03	0.9963	583
	30	284.6 ± 0.02		6.15 ± 0.06	1.22 ± 0.02	0.9949	480
Hq <sup>a</sup>	10	289.3 ± 0.05	-0.46 ± 0.01	5.16 ± 0.04	1.51 ± 0.02	0.9942	629
	20	285.0 ± 0.7		6.03 ± 0.07	1.15 ± 0.03	0.9939	519
	30	280.1 ± 0.09		6.24 ± 0.03	1.00 ± 0.03	0.9648	520
Pg <sup>a</sup>	5	292.6 ± 0.04	-0.31 ± 0.02	5.22 ± 0.04	1.66 ± 0.03	0.9947	721
	10	291.5 ± 0.01		5.74 ± 0.03	1.47 ± 0.04	0.9995	648
	20	288.7 ± 0.05		6.37 ± 0.04	1.04 ± 0.02	0.9945	559
	30	284.8 ± 0.05		5.45 ± 0.04	1.54 ± 0.04	0.9931	578
Cc <sup>a</sup>	5	294.5 ± 0.04	-0.02 ± 0.001	4.81 ± 0.02	1.67 ± 0.04	0.9972	901
	10	295.6 ± 0.09		6.08 ± 0.06	1.07 ± 0.08	0.9913	751
	20	296.3 ± 0.08		6.33 ± 0.07	0.96 ± 0.11	0.9982	476
	30	294.5 ± 0.04		5.75 ± 0.05	1.33 ± 0.06	0.9987	595
NaC <sup>a</sup>	5	289.7 ± 0.02	-1.16 ± 0.08	5.67 ± 0.04	1.23 ± 0.07	0.9954	628
	10	283.9 ± 0.3		5.99 ± 0.04	1.09 ± 0.07	0.9949	627
NaSl <sup>a</sup>	5	298.3 ± 0.07	0.34 ± 0.02	6.20 ± 0.03	0.90 ± 0.06	0.9978	491
	10	300.0 ± 0.09		6.17 ± 0.03	0.94 ± 0.04	0.9963	499

<sup>a</sup> Taken from ref 39.**Figure 6.** The plot of  $\ln \sigma$  vs  $T^{-1}$  to evaluate  $E_p$ : (□) no additive; (■) 2-MP; (○) 4-MP; (▲) 5-MR; (▽) 3-MC. Section A shows results for Hp, section B for Oc, and section C for Dc.

is an essential requirement for conductance percolation. The process is controlled by the type of microemulsion (oil and

amphiphile), the droplet density and size (i.e.,  $\omega$ ), the type of additives, etc. It has been reported that in the AOT-derived systems, the clustered droplets on the whole retain their identity and the assembly exists in a different phase (a pseudophase, like micelles).<sup>38,39</sup> At the threshold temperature of percolation augmented by clustering, the standard Gibbs energy change for the clustering phenomenon ( $\Delta G_{cl}^o$ ) is given by the relation

$$\Delta G_{cl}^o = RT \ln X_d \quad (6)$$

The mole fraction of the droplets,  $X_d$ , is given by the relation<sup>39</sup>

$$X_d = \frac{n_d}{n_d + n_{oil}} = \frac{A_t M V_t}{(M A_t V_t + 4000 \pi r_d^2 N V d)} \quad (7)$$

where  $n_d$  and  $n_{oil}$  are number of moles of droplet and oil, respectively,  $A_t$  is the total surface area covered by the AOT headgroups,  $V_t$  is the total volume of the system,  $V$ ,  $d$ , and  $M$  are the volume, density, and molar mass of oil, respectively,  $r_d$  is the average radius of the droplet, and  $N$  is the Avogadro number.



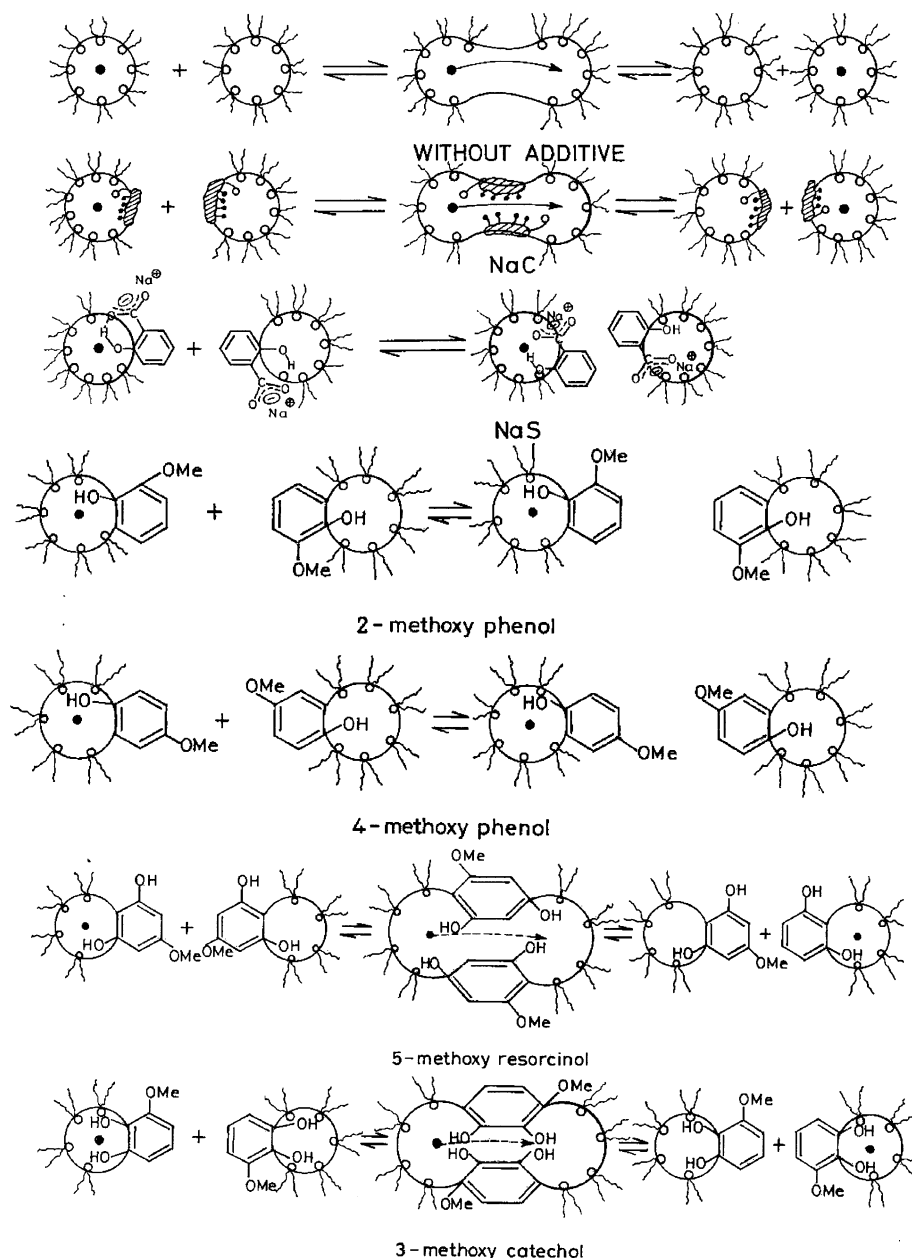


Figure 7. Additive-affected scheme for the "fusion-(mass-transfer)-fission" process.

The Gibbs–Helmholtz equation can be used to obtain the standard enthalpy change for clustering. Thus,

$$\frac{d\left(\frac{\Delta G_{cl}^{\circ}}{\theta_t}\right)}{d\left(\frac{1}{\theta_t}\right)} = \Delta H_{cl}^{\circ} \quad (8)$$

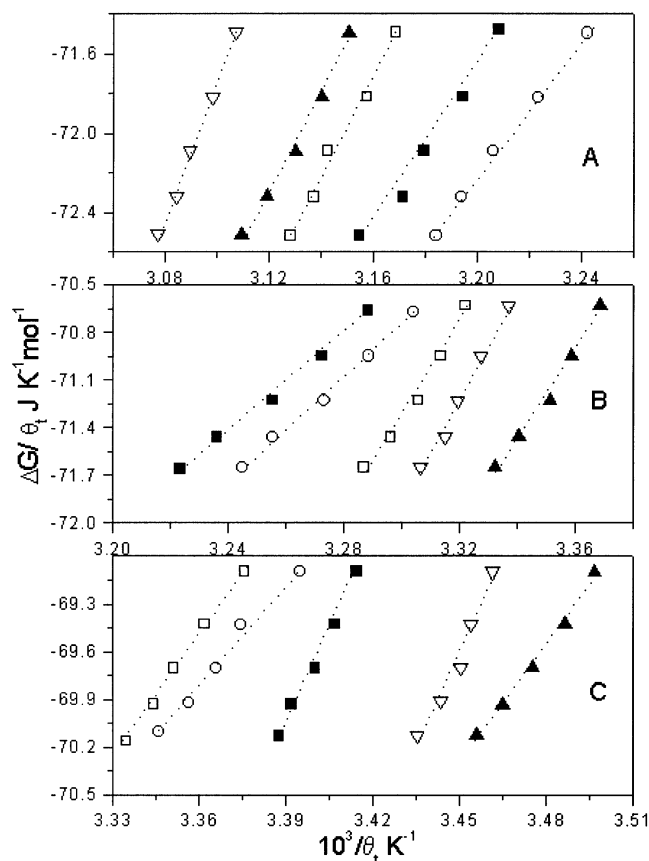
The standard entropy change for clustering then follows from the Gibbs equation,

$$\Delta S_{cl}^{\circ} = \frac{\Delta H_{cl}^{\circ} - \Delta G_{cl}^{\circ}}{\theta_t} \quad (9)$$

To derive  $\Delta H_{cl}^{\circ}$ , a microemulsion prepared at a fixed  $\omega = 25$  was diluted with several portions of oil and the  $\theta_t$  values for all of the dilutions were determined from the conductance measurements as described above.<sup>39</sup> The  $\Delta G_{cl}^{\circ}$  values were obtained from the sample compositions, and the analysis of the plots of

$\Delta G_{cl}^{\circ}/\theta_t$  as a function of  $1/\theta_t$  have yielded the values of  $\Delta H_{cl}^{\circ}$  (Figure 8). The plots are fairly linear.

The thermodynamic parameters for the droplet clustering process are presented in Table 4. The process manifested absorption of heat and positive entropy change. Prior to the droplet association, the surrounding oil barrier needed to be removed. This endothermic event was followed by the exothermic process of clustering; energetically, the first exceeded the second making the overall effect endothermic. The endothermicity of the clustering process has been reported in the literature;<sup>21,24,30,33,38,39</sup> the overall magnitudes have been found to be a complex function of the oil and the additives used. The endothermic disruption of the surrounding oil and the exothermic droplet association were thus not directly related with the oil chain length; there were other factors to influence keeping scope for further studies. The  $\Delta G_{cl}^{\circ}$  values suggested that the clustering was more spontaneous with decreasing chain length of the oil. The  $\Delta S_{cl}^{\circ}$  are all positive and have evidenced comparable magnitudes with and without additives. The entropy increase



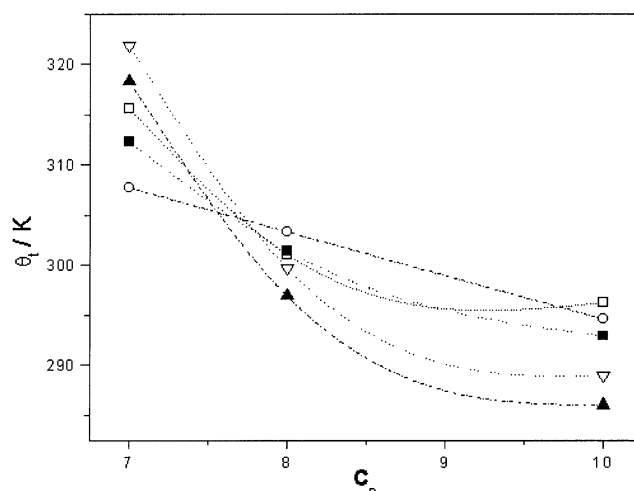
**Figure 8.**  $\Delta G_{cl}^{\circ}/\theta_t$  vs  $1/\theta_t$  plots for the water/AOT/oil systems at  $\omega = 25$  and at  $20 \text{ m mol dm}^{-3}$  of additive: (□) no additive; (■) 2-MP; (○) 4-MP; (▲) 5-MR; (▽) 3-MC. Section A shows results for Hp, section B for Oc, and section C for Dc.

**TABLE 4: Energetic Parameters for Droplet Clustering in the Water/AOT/Oil w/o Microemulsion Systems ( $\omega = 25$ ) in the Presence and Absence of Additives at 298 K**

oil	additive	$-\Delta G_{cl}^{\circ}$ <sup>b</sup> (kJ mol <sup>-1</sup> )	$\Delta H_{cl}^{\circ}$ <sup>b</sup> (kJ mol <sup>-1</sup> )	$\Delta S_{cl}^{\circ}$ <sup>b</sup> (J K <sup>-1</sup> mol <sup>-1</sup> )
heptane		22.6	25.0	151
	2-MP	22.3	21.0	139
	4-MP	22.0	15.5	122
	5-MR	22.7	25.8	152
	3-MC	23.0	24.7	148
octane		21.3	28.9	167
	2-MP	21.3	10.3	105
	4-MP	21.4	18.3	131
	5-MR	21.0	28.1	165
	3-MC	21.2	34.9	187
decane		20.5	21.8	143
	2-MP	20.2	37.3	196
	4-MP	20.4	14.3	118
	5-MR	19.8	24.8	156
	3-MC	20.0	23.2	150
	Rc <sup>a</sup>	19.9	27.0	163
	Hq <sup>a</sup>	19.7	17.4	130
	Pg <sup>a</sup>	20.0	23.3	150
	Cc <sup>a</sup>	20.5	53.9	251

<sup>a</sup> Taken from ref 39. <sup>b</sup> Standard deviations in  $\Delta G_{cl}^{\circ}$ ,  $\Delta H_{cl}^{\circ}$ , and  $\Delta S_{cl}^{\circ}$  are  $\pm 5\%$ ,  $\pm 5\%$ , and  $\pm 8\%$ , respectively.

by the disruption of the oil has surpassed the entropy decrease by the droplet association yielding overall entropy change positive for the process. This compares the disruption of hydrophobic hydration of nonpolar segment of amphiphiles prior to their micellization manifesting positive entropy change being larger than the complementary entropy decrease due to inter-



**Figure 9.** The percolation threshold ( $\theta_t$ ) vs chain length of oil ( $C_n$ ) profile for the water/AOT/oil systems at  $\omega = 25$  and at  $20 \text{ m mol dm}^{-3}$  of additive: (□) no additive; (■) 2-MP; (○) 4-MP; (▲) 5-MR; (▽) 3-MC.

facial solvation and organization. The influence of the additives on  $\Delta S_{cl}^{\circ}$  parallels that on  $\Delta H_{cl}^{\circ}$ .

The near equivalence in the magnitude of  $\Delta G_{cl}^{\circ}$  results in the compensation between  $\Delta H_{cl}^{\circ}$  and  $\Delta S_{cl}^{\circ}$ . The compensation temperatures obtained for the Hp, Oc, and Dc systems were 346, 299, and 294 K, respectively, vis-à-vis the respective average experimental temperatures of 317, 300, and 290 K. Similar plots in the absence and presence of additives were reported earlier.<sup>33,38,39</sup>

**Effect of the Hydrocarbon Oil Chain Length.** The increasing chain length of the oil assisted the percolation with a decreasing  $\theta_t$ , and the effect was exponential both in the absence and presence of the additives except for 4-MP, which exhibited a linear dependence. The results are illustrated in Figure 9. It was earlier reported<sup>8,11,13,28</sup> that a large attractive interaction between the droplets is the major factor limiting their stability as the molar volume of the oil is increased. Thus the interdroplet attractive interaction in AOT/water/oil microemulsions increased with the chain length of the oil. The increase in the molar mass of the hydrocarbon oil decreased the density of the continuous phase enabling easier approach of the interacting droplets for mass transfer. An increase in the droplet radius would also increase the overlap volume between two droplets when they come closer to form a cluster, resulting in an increase in interaction potential facilitating percolation. While droplet attraction plays an important role in percolation, the nature of the interface of the droplets has also a significant say in the process because the rupture of the droplet interface is essential for mass transfer. Although the  $\theta_t$  has shown an almost orderly trend with the oil chain length, the thermodynamic parameters  $\Delta H_{cl}^{\circ}$  and  $\Delta S_{cl}^{\circ}$  have not manifested such a pattern. The droplet clustering was thus energetically not a straightforward process.

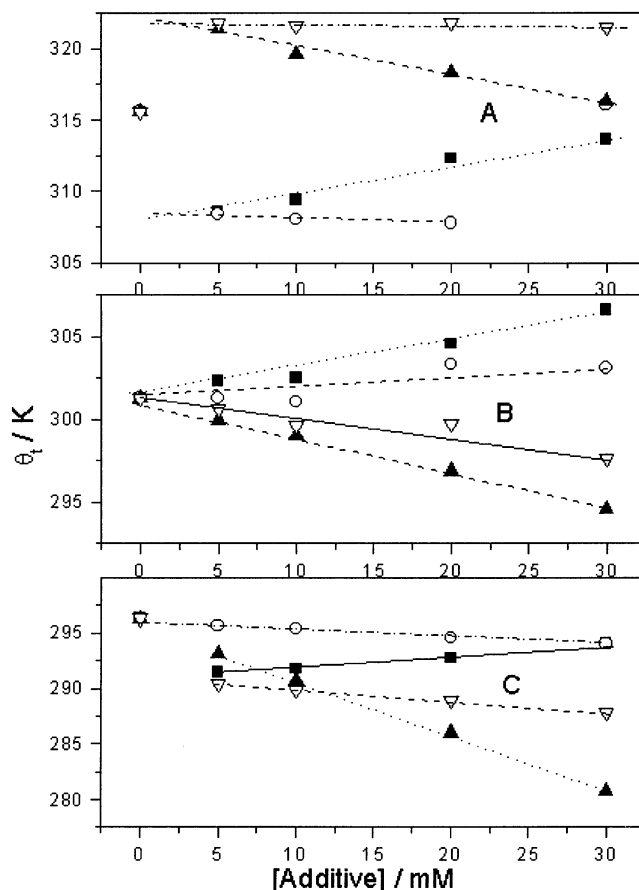
**Mechanism of Percolation in Relation to the Additive Effects.** It is considered that by the advent of thermal energy nano-water droplets in w/o microemulsion assemble manifesting large increase in conductance by way of efficient ion transport. The presence of additives may enhance the fusion of droplets and assist the dynamic percolation process; they may also hinder the fusion and resist it. The assisting additives are generally hydrotropes with two hydroxyl groups preferably at the meta and para positions; ortho-substituted compounds weakly assist the process. The bile salts, sodium cholate and sodium deoxycholate (having three and two hydroxyl groups in the molecules,

respectively), have been also observed to fairly enhance the percolation process.<sup>39</sup>

In this respect, resorcinol (Rc), catechol (Cc), pyrogallol (Pg), and hydroquinone (Hq) have been observed to be effective percolation accelerators, whereas sodium salicylate,  $\alpha$ -naphthol,  $\beta$ -naphthol, benzene, naphthalene, and anthracene have been found to be effective percolation reducers.<sup>15,18,20,26,34,38,39</sup> Among Rc, Cc, Pg, and Hq, Cc (having ortho substitution) is the weakest accelerator (such results taken from our earlier publication<sup>39</sup> are presented in Table 3). Although "hopping" of the interfacial surfactant ions from droplet to droplet at the threshold temperature causing considerable increase in conductance has been considered to be an alternative to the "fusion—(mass exchange)—fission" mechanism, experimental evidences go more in favor of the latter;<sup>32,39</sup> this also gets support from the additive effects modeled in our previous studies.<sup>38,39</sup> The functionalities of the methoxy-substituted aromatic alcohols herein studied are illustrated with sodium cholate and sodium salicylate in Figure 7. The requirement of two hydroxyl groups in the additive molecule for enhancement of percolation is readily evident. The effectivities of the hydrotropes depending on the number of hydroxyl groups, their positions, and methoxy substitution are compared in Table 3. While the di- and trihydroxy compounds can effectively bridge a pair of droplets for effective mass exchange, methoxy substitution greatly hinders the process. The requirement of hydroxyl groups in the additive molecule (as in hydrotropes and bile salts) is thus essential for the enhancement of the process. For effective fusion, a pair of water droplets has to come very close requiring higher attractive energy. By the bridging procedure, as shown in Figure 7, the amphiphilic additives at the interface can stabilize the droplets and make them to fuse and manifest the consequence. In this process, the droplets can function (mass exchange) remaining at a greater distance apart in the presence of a bridging additive compared to that in its absence. The  $\theta_t$  is thus decreased in the presence of fusion accelerators. The monohydroxy compounds (phenol, salicylate) or aromatics without hydroxyl groups (such as benzene, naphthalene, and anthracene) cannot bridge droplets and falling between resist (block) fusion and hence resist percolation. The efficacy of the additives on the process of percolation can be judged from the slopes of the linear dependence of  $\theta_t$  on additive concentration according to the relation

$$\theta_t^a = \theta_t^0 \pm SC \quad (10)$$

where  $\theta_t^0$  and  $\theta_t^a$  are the threshold percolation temperature without and with additive, respectively,  $S$  is the slope of the linear plot, and  $C$  is the experimental concentration of the additive. A representative illustration is given in Figure 10, and the slope ( $S$ ) values are presented in Tables 1–3. In Figure 10, from the Hp derived system, an initial abrupt decrease in  $\theta_t$  at the [additive] = 5 m mol dm<sup>-3</sup> has been observed both for 2-MP and 4-MP. On the other hand at the same additive concentration, both 5-MR and 3-MC have produced an abrupt increase in  $\theta_t$ . Such additive-dependent effects have not been observed for the Oc- and Dc-derived systems. In what way Hp behaves differently than Oc and Dc at very low concentration of the additives remains to be understood. The efficiencies of the additives are evident from the sign and magnitude of  $S$ . The positive slope yielding solutes are percolation retardants, whereas negative slope giving solutes are percolation assistants. The results support the efficacy trend of the additives discussed above with minor variations when slope values are small. The —OH substitution at the 1,3 positions on the phenolic moiety offers



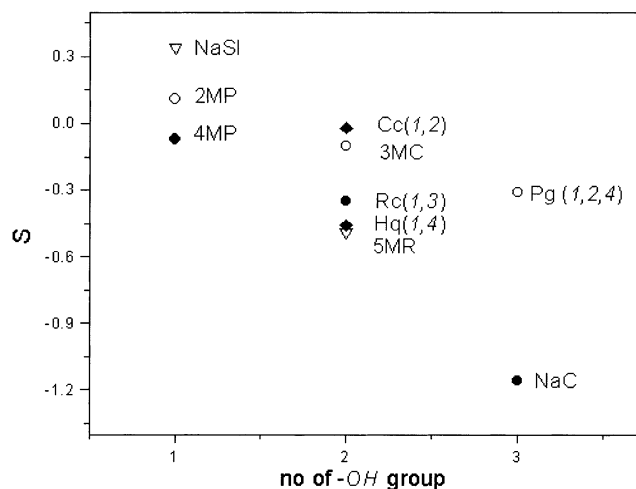
**Figure 10.** Dependence of  $\theta_t$  on hydrotrope concentration: (■) 2-MP, (○) 4-MP, (▲) 5-MR, and (▽) 3-MC. Section A shows results for Hp, section B for Oc, and section C for Dc.

maximum assistance to percolation. Replacement of a hydroxyl group by a methoxy group in a dihydroxy aromatic ring resists the percolation process compared to the nonmethoxy analogue, and such substitution in a trihydroxy aromatic moiety reduces the efficiency of bridging for favorable percolation. It may be mentioned that substitution of more than one methoxy group in the aromatic hydrotropes may effectively hinder droplet fusion by way of blocking, and as a result  $\theta_t$  should increase.

In Table 3, the slope values of NaC and NaSI (sodium salicylate) in the Dc system are presented for a comparison. The value for NaC is much higher than the maximum negative slopes offered by a hydrotrope indicating high accelerating efficiency of NaC. The percolation-accelerating activities of the additives in the Dc system are distinct; the efficiency order in terms of  $S$  is NaC  $\gg$  5-MR  $>$  Hq  $>$  Rc  $>$  Pg  $>$  3-MC  $>$  4-MP  $>$  Cc. 2-MP has shown a distinct percolation resistance in Hp, Oc, and Dc systems; such effect of 4-MP and 3-MC are only marginal in the Hp and Oc systems. The NaSI in the Dc system has shown a more distinct resistance than any of the hydrotropes falling in the resistive class.

In Figure 11, the  $S$  values are plotted against the number of hydroxyl groups in the additive molecule. The slope is found to decrease with the number of —OH groups, the magnitude being dependent on the number of —OH groups and their positions in the molecule. The effectivity of the dihydroxy compounds follows the order ortho  $<$  meta  $<$  para. Methoxy substitution in the molecule has increased their percolation-assisting efficacy. The specialty of NaC in this regard is noteworthy.





**Figure 11.** Dependence of  $S$  (slope) on the number of hydroxyl groups of the studied hydrotropes.

## Conclusions

The hydrotropes (2-MP, 4-MP, 5-MR, and 3-MC) can influence the dynamic percolation process. They can either assist the process by way of bridging a pair of droplets for efficient fusion and ion transfer or retard the process by blocking and resisting fusion of droplets to hinder mass transfer. The position of the hydroxyl groups in the phenolic hydrotrope molecule is the determining factor for its action on the dynamics of the process. The monohydroxy compounds resist percolation, whereas dihydroxy compounds assist it. The efficiency follows the order ortho < meta < para. The threshold temperature,  $\theta_t$ , linearly depends on the hydrotrope concentration.

The process of percolation has been found to be affected by the chain length of the continuous phase (or oil).

The  $E_p$  for the percolation process has been found not to have a general correlation with the type of oil and the hydrotrope.

The clustering of the microemulsion droplets is an endothermic process with associated positive entropy change parallel to the micellization of surfactants. The  $\Delta H_{cl}^\circ$  and  $\Delta S_{cl}^\circ$  nicely compensate each other.

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