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## Microemulsion with aromatic oil as cleaner media for electropolymerisation

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**Abstract** Microemulsion polymerization is widely used as a cleaner alternative way to prepare intrinsically conductive polymers. We studied isothermal phase diagrams for microemulsions of the electropolymerizable heterocyclic aromatic oil 3,4-ethylenedioxythiophene (EDOT), aqueous  $\text{LiClO}_4$  solution and alkyl polyethoxylate. Our specific goal was to assess the effect of  $\text{LiClO}_4$  salt on the phase behaviour. The phase behaviour was characterized by stepwise titration and microscopic analyses. Here we found that the increase of the concentration of  $\text{LiClO}_4$  salt shifts the microemulsion region to lower surfactant content.

**Keywords** Microemulsion · Phase behaviour · EDOT ·  $\text{LiClO}_4$

### Introduction

Conducting polymers have a high potential for application in different technical processes and products. They are already widely used for antistatic layers (Jonas and Heywang 1994). They can also be applied in anticorrosive layers (Ferreira et al. 1996) electrochemical sensors (Contractor et al. 1994) or electroactive membranes. The classical method of polymer deposition is chemical or electrochemical synthesis in organic solvents (Roncali 1992). The microemulsions allow the organic compounds to dissolve in high concentrations in water and therefore substitute commonly used solvents such as nitrobenzene or acetonitrile. Polymerization from microemulsions is

ecologically cleaner compared with polymerization from organic solvents (nitrobenzene, acetonitrile). The anodic polymerization of oil in microemulsion with nonionic surfactant has been investigated (Haegel et al. 2001).

The rules of microemulsion formation have been extensively studied by Kahlweit (Kahlweit et al. 1988). In this paper, isothermal phase diagrams of the system ethylenedioxythiophene (EDOT) (oil)/Lutensol ON 110 (nonionic surfactant)/aqueous  $\text{LiClO}_4$  will be presented. Purpose of this study was to determine the phase diagrams and physical properties of this system because it forms colloidal solutions with a high content of thiophene derivative and is very interesting for anodic polymerization (Haegel et al. 2001). The knowledge of the phase behaviour is a decisive step for advancing the process to technical scale.

Microemulsions are thermodynamically stable dispersions of two immiscible liquids or solutions which are stabilised by at least one or more amphiphilic components (“detergents”). They exhibit no structural long-range order. The lacking long-range order distinguishes microemulsions from liquid crystals. They are therefore much less viscous and can be easily handled. There are three different types of microemulsion. Oil in water microemulsions exist at low or moderate oil content. The water in oil microemulsion is formed with a large excess of oil. Between these two types of microemulsion a third type of structure which is bicontinuous can often be found. The structure is similar to a sponge (Kahlweit et al. 1989) with water being the frame and oil being the pores. The surfactant is mainly situated at the interface of the two micro-phases.

The bicontinuous phase is found at similar content of water and oil. Sufficient amphiphile is needed for its formation. Varying the temperature the bicontinuous phase splits into two phases as well at higher as at lower temperature. For systems with nonionic surfactants the two-phase region at lower temperature exhibits a large aqueous phase which contains almost all of the surfactant and an excess oil phase. The two-phase region at higher temperature shows the reverse behaviour. The surfactant

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is now better soluble in the oil and an excess water phase is formed. The use of polar oils does not change the qualitative phase behaviour of the microemulsions. However, the phase boundaries are often shifted to unusual positions in the phase diagrams as demonstrated for microemulsions which are used for cleaning contaminated soil (Bonkhoff et al. 1997).

Adding salt to microemulsions with nonionic surfactants can have two different effects depending on whether the salt is lyotropic or hydrotropic. Lyotropic salts induce a salting-out effect of the surfactant. That means that the surfactant dissolves more readily in oil and the temperature interval in which the bicontinuous microemulsion exists shifts to lower temperatures. Hydrotropic salts enhance the mutual solubility of water and oil. Therefore the bicontinuous microemulsion is formed at higher temperature in this case.

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## Experimental

Aqueous solutions of lithium perchlorate were prepared from  $\text{LiClO}_4 \times 3\text{H}_2\text{O}$  (p.a., Acros Geel, Belgium) and Millipore water. Lutensol ON 110, a  $\text{C}_{10}$  oxoalcohol polyethoxylat with an average of 11 ethylene oxide units, is a commercial nonionic surfactant from BASF AG Ludwigshafen, Germany. It is very hydrophilic with an hydrophilic-lipophilic balance (HLB) of 15 which enables large solubility in water. 3,4-Ethylenedioxythiophene (EDOT) from Baytron M, H.C. Stark, Goslar, Germany, with chemical formula  $\text{C}_6\text{H}_6\text{O}_2\text{S}$  was redistilled at reduced pressure for purification and stored in a refrigerator in order to avoid noticeable decomposition. The influence of the molecular structure of the nonionic surfactant on the phase behaviour of microemulsion systems is important. Since ethylenedioxythiophene is a very polar substance, quite hydrophilic surfactants have to be used in order to achieve microemulsions. The surfactant used for the solubilization of ethylenedioxythiophene is Lutensol ON110.

Pseudo-ternary phase diagrams were determined at  $25^\circ\text{C}$  for the mixtures: ethylenedioxythiophene/Lutensol/water and ethylenedioxythiophene/Lutensol/aqueous  $\text{LiClO}_4$ , by stepwise titration of suitable binary or pseudo-binary solutions with the third (pseudo-) component. Concentrations of aqueous  $\text{LiClO}_4$  were  $0.25 \text{ mol l}^{-1}$  and  $1.00 \text{ mol l}^{-1}$ . The samples were shaken, weighed and stored in a water bath at  $25^\circ\text{C}$  for thermostating and equilibration after each titration step. The phase boundaries were visually detected. The presence of liquid crystals was checked by placing the sample between crossed polarizers. Two-phase regions, multiple phases I and multiple phases II, were analysed with the optical microscope Ortholux from Leitz, Germany. The samples with precisely known composition were prepared for that purpose. The water phase of the samples was marked with

the selective indicator Alizarinred S from Merck KGaA, Germany. The samples were also stored in a water bath at  $25^\circ\text{C}$  for thermostating and equilibration, before each microscopic analysis.

Phase relations of the pseudo-ternary systems were depicted by the Gibbs triangle. Each point within the triangle has a precisely defined composition at constant temperature. Each single component or pseudo-component of the system aqueous  $\text{LiClO}_4$ /Lutensol/ethylenedioxythiophene was assigned to one corner of the Gibbs triangle. The composition of the components was registered in percent. Each side of the triangle represents one binary system. The quantity of each binary system component declines towards the opposite side. Inorganic salts and water are often placed in the diagram as one component, since salt unlike surfactant, does usually not dissolve in oil. Such diagram is qualified as pseudo-ternary.

## Results and discussion

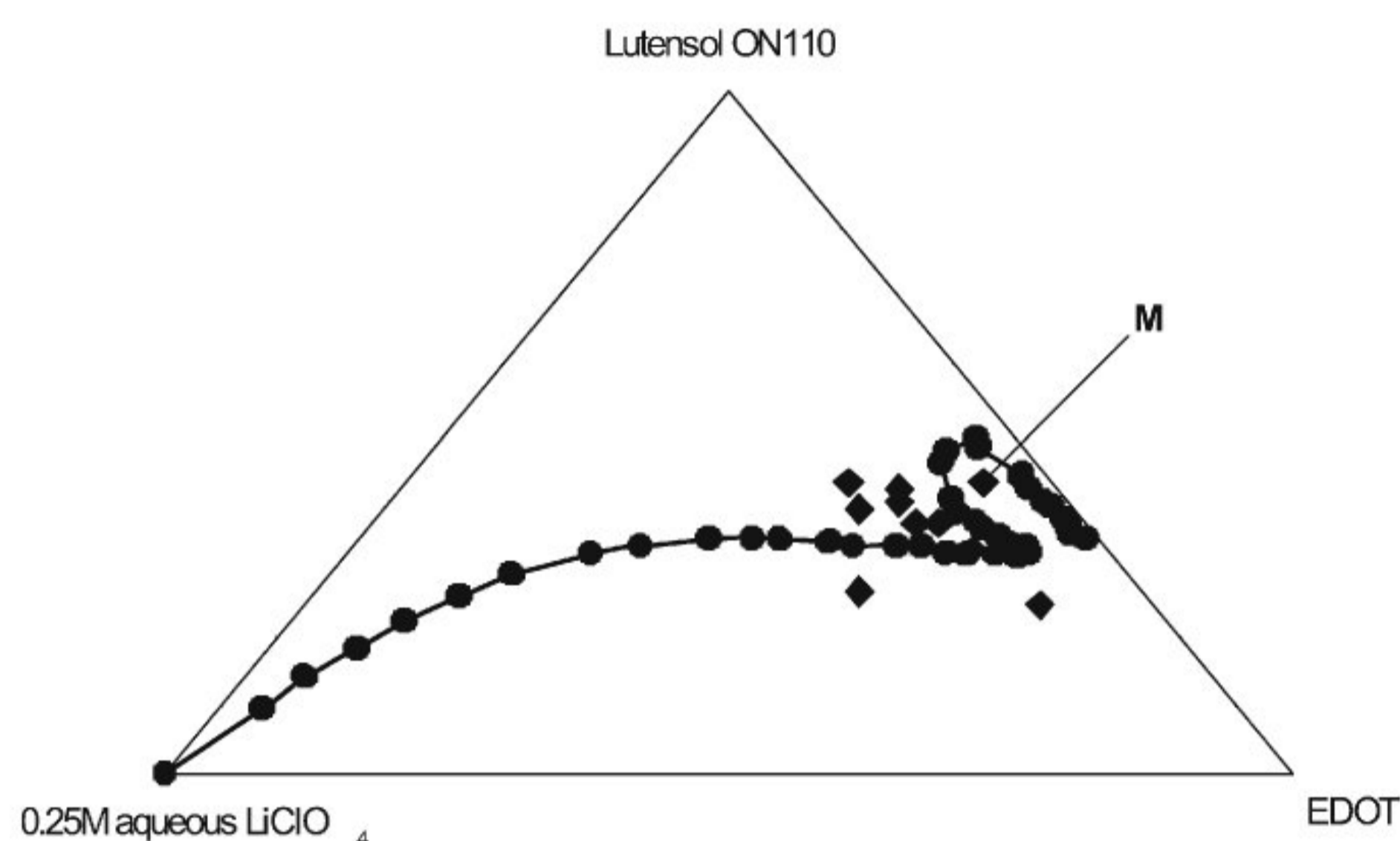
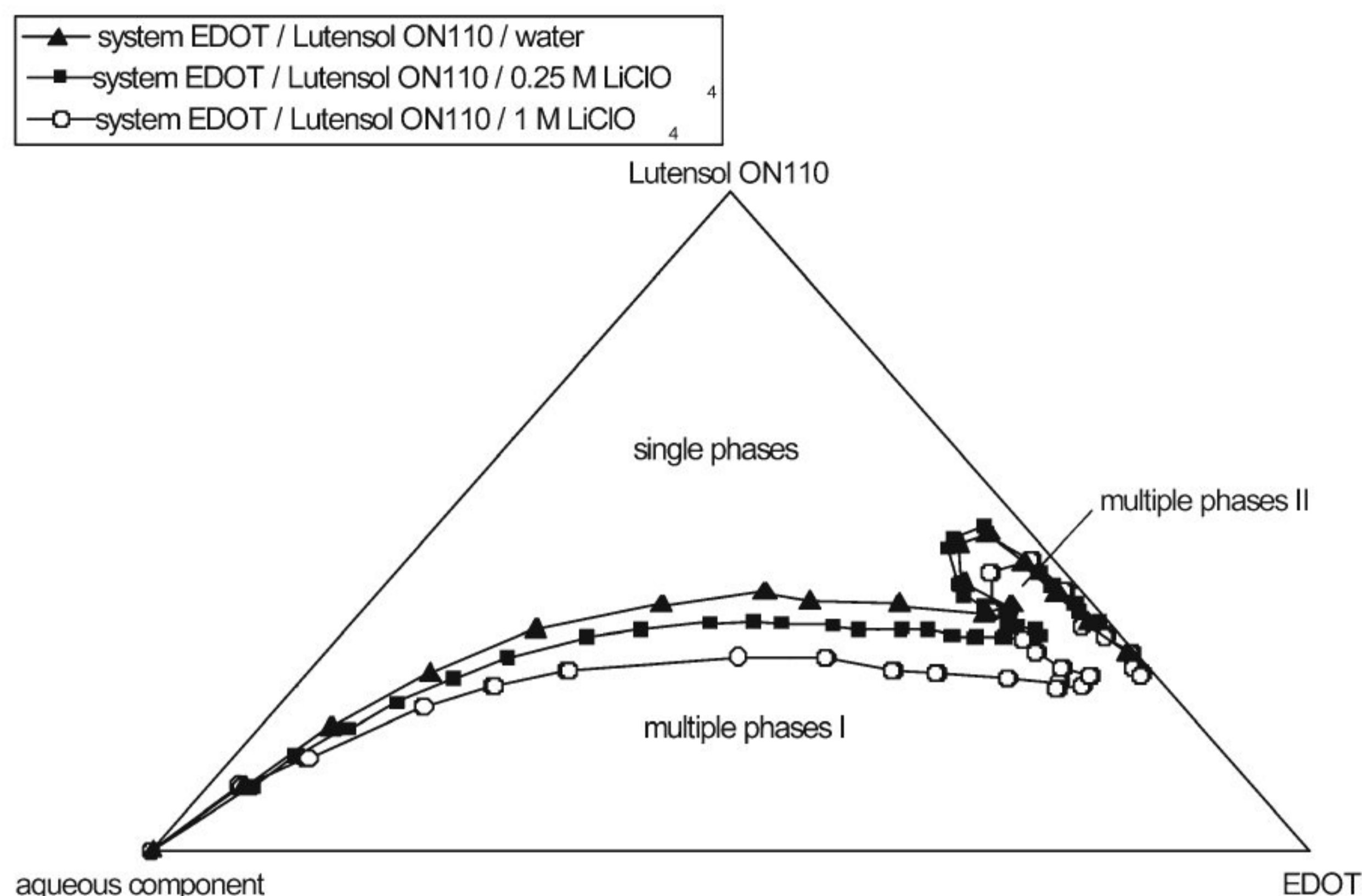
The isothermal phase behaviour of mixtures of ethylenedioxythiophene with aqueous  $\text{LiClO}_4$  and Lutensol ON 110 was studied by pseudo-ternary phase diagrams. Figure 1 shows the phase diagrams at  $25^\circ\text{C}$  of the mixtures: aqueous pseudo-component ( $0.25 \text{ M}$  and  $1.00 \text{ M LiClO}_4$ ), ethylenedioxythiophene and Lutensol. Each point within the triangle gives the composition of a pseudo-ternary mixture.

In Fig. 1 we also show the ternary system ethylenedioxythiophene/Lutensol/water.

The phase diagrams contain three different regions: an extended single phase region and two multiphase regions which have different macroscopic appearance. Multiple phases I and multiple phases II are situated at different parts of the phase diagram separated by a deep single phase channel at higher surfactant content. However a clear boundary could not be detected between them at lower surfactant content. Multiple phases I, a miscibility gap between the electrolyte solution and ethylenedioxythiophene, become narrower with increasing surfactant concentration and vanish for a mass fraction of surfactant  $x_s$  of more than 26%, at  $1.00 \text{ M}$  electrolyte solution, and 33% at  $0.25 \text{ M}$  electrolyte solution. Multiple phases II appear at very low water content of less than 10%. The mass fractions of oil  $x_o$  and surfactant are both high.  $x_o$  is in between 45–65% and  $x_s$  in between 25–50%. The surfactant used for the solubilisation of ethylenedioxythiophene is Lutensol ON 110, a very hydrophilic oxoalcohol polyethoxylat with an hydrophilic-lipophilic balance (HLB) value of 15.

The single phase region which deeply penetrates between the two different two-phase regions of the system is extremely large from the very dilute regime up to a mass fraction of the monomer oil (ethylenedioxythiophene) in the pseudo-ternary system of more than 60%. This large ethylenedioxythiophene content makes this microemulsion interesting for technical application. Figure 1 shows

**Fig. 1** Isothermal phase diagrams of the ethylenedioxythiophene/Lutensol ON 110/aqueous component systems at 25°C

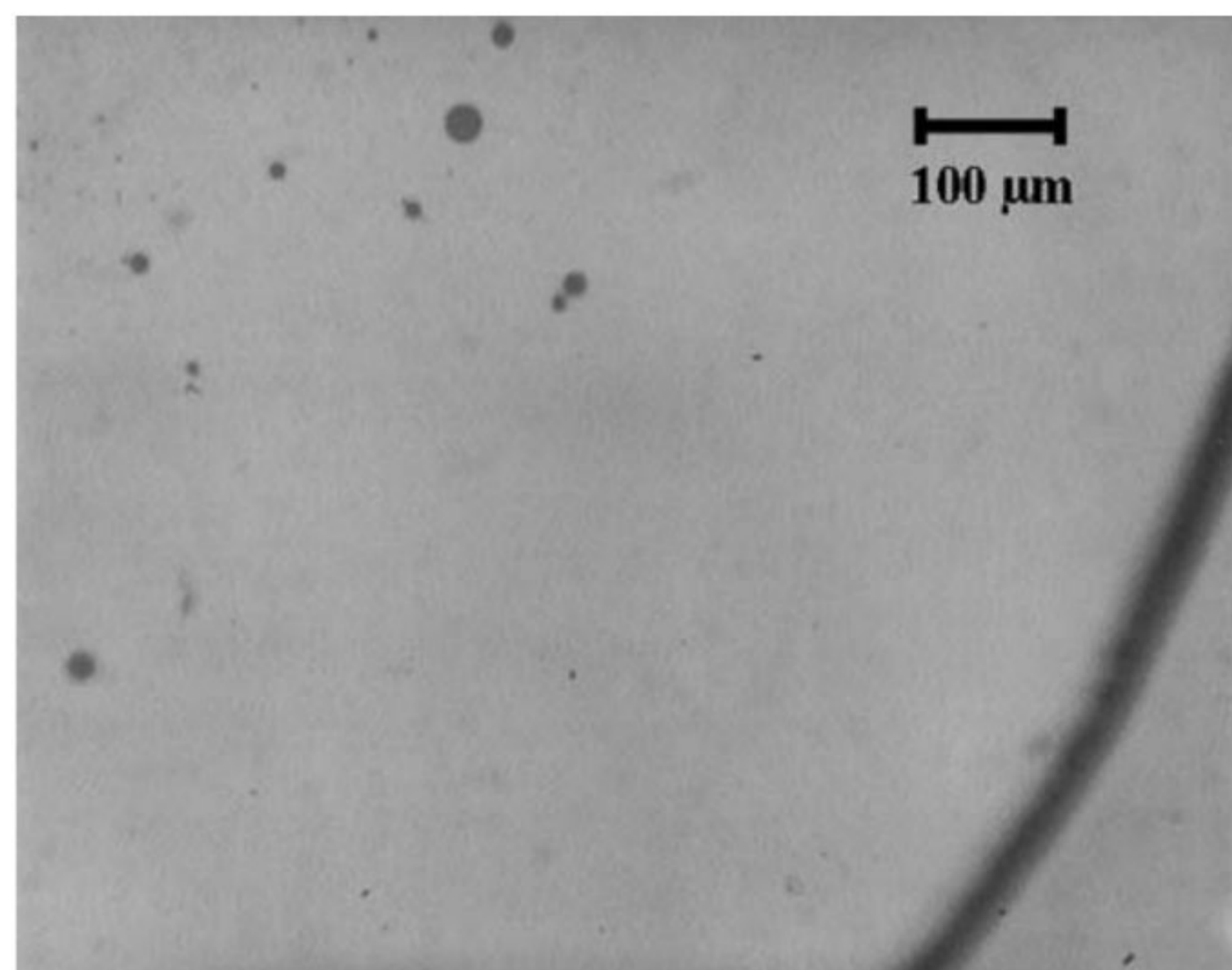


**Fig. 2** Isothermal phase diagram of the ethylenedioxythiophene/Lutensol ON 110/ $\text{LiClO}_4$  at 25°C  $\blacklozenge$  The samples stained with indicator were microscopically inspected. M denotes the sample of Fig. 3

that the form of the phase diagrams does not change with variation of salt concentration. Increase of  $\text{LiClO}_4$  concentration shifts the microemulsion region to lower surfactant content. This can be explained with enhanced mutual miscibility of water and oil in the presence of  $\text{LiClO}_4$ . Multiple phases I and multiple phases II were visually different during stepwise titration. It was observed that there was constantly more volume of one phase in multiple phases II in relation to the other one.

According to the thermodynamic rules of microemulsion formation there must be either a one-phase region or a three-phase region between these two regions (multiple phases I and multiple phases II). However, none of these two regions (one-phase or three-phase) was observed by visual detection. The properties of the different phase regions were studied microscopically for comparison with titration.

Points marked with the symbol  $\blacktriangledown$  in Fig. 2 show the composition of samples analysed under microscope.



**Figure 3** Photograph of water droplets (dark spots) in oil analysed under microscope in the sample marked as  $\blacklozenge$  M in Figure 2

Samples are situated in multiple phases I, multiple phases II and in the single phase at high oil content of ethylenedioxythiophene. Figure 3 shows the distribution of water in oil for sample M. Water droplets stained with a red indicator were registered in all samples within multiple phases I and II. Sample M shown in the micrograph is situated within multiple phases II at 12% 0.25 M  $\text{LiClO}_4$ , 55% ethylenedioxythiophene and 33% Lutensol. Micrographs of samples in multiple phases I looked similar. The size of the droplets was also less than 20  $\mu\text{m}$  and polydisperse. Due to the higher water content, however, the number of droplets per volume increases in multiple phases II. This once again confirms, as in the case of visual titration detection, that there is no sign of neither a one-phase or a three-phase region between multiple phases I and multiple phases II.

Many surfactants form lyotropic liquid crystals in aqueous solutions. In microemulsion-forming systems lamellar liquid crystals occur in most cases. The presence of oil prefers this type of liquid crystals. The structure is similar to the bicontinuous microemulsion but exhibits a long-range order with a certain periodicity. Lamellar liquid crystals are anisotropic and optically birefringent. Their viscosity is considerably higher than that of microemulsions. They are often found together with microemulsions in mixtures of water, oil and surfactant. Liquid crystals may prevent the application of certain compositions in technical processes. They can usually be suppressed by lyotropic salt. No liquid crystals were detected for the investigated systems, neither for the ternary mixture with pure water nor for the highest electrolyte concentration.

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## Conclusion

Lithium perchlorate behaves as hydrotropic salt. This knowledge opens up a new field of technical application for aqueous microemulsion systems. This type of microemulsion can be used as ecologically cleaner alternative way of making intrinsically conductive polymers instead of the classical method of polymer deposition in organic solvents. The high content of oil makes it attractive for technical application. The complexity of the system only allows a qualitative interpretation at this present time. Further investigations are necessary to understand formation and structure of the different multiphase regions in the system. The formation and nature of multiple phases II is not absolutely clear.

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