PHASE SEPARATION AND SALTING OUT OF OCTYL PENTA(OXYETHYLENE GLYCOL) IN WATER AND HEAVY WATER

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Résumé – La miscibilité partielle et la précipitation par le sel sont
étudiées dans le système octyl penta (oxyéthylène glycol)/C_8E_5/-eau/eau
lourde. La séparation de phase induite par la température est due à l'ac-
croissement des interactions entre les petites micelles sphériques. On a
étudié comment les températures de séparation de phase sont modifiées en
ajoutant des sels (KCl, CsCl, NaF) et en substituant D_2O pour H_2O comme
solvant.

Abstract – Partial miscibility and salting out is studied in the system
octyl penta(oxyethylene glycol)/C_8E_5/-water/heavy water. The temperature
induced phase separation is due to increased interactions between small
spherical micelles. It is studied how the phase separation temperatures
are shifted by adding salts (KCl,CsCl,NaF) and by substituting D_2O for
H_2O as solvent.

1 – INTRODUCTION

There is currently a growing interest in various partial miscibility phenomena
in macromolecular and micellar systems. The analysis and simulation /1/ of partial
miscibility in aqueous media are substantially complicated by the peculiar proper-
ties of water as a solvent (e.g. high directionality of interactions). In macro-
molecular systems the large size difference between solute and solvent is an addi-
tional factor which must be accounted for /8/. We present here results on our
studies on the partial miscibility of a non-ionic surfactant octyl penta(oxyethylene
glycol)/C_8E_5/. The molecule consists of two parts; a hydrophobic alkyl chain and a
hydrophilic polymer part. The miscibility is obtained through a delicate water-
oxyethylene interaction, with hydrogen bond formation to the ether oxygens and,
simultaneously, a fitting of the ethylene units in water cages /2/. Since the mole-
cules have a bulky hydrocarbon chain they form (spherical) micelles above a critical
concentration (0.15 volume-%). This surfactant is interesting in being miscible with
water in all proportions at room temperature. Increasing the temperature of such a
micellar solution leads to a concentration dependent phase separation (at around
60 °C). The whole phase separation boundary is called the lower consolute boundary
(LCB).

2 – THE MECHANISM OF C_8E_5 PHASE SEPARATION IN WATER

The analysis of the phase separation of non-ionic surfactants like C_8E_5 is
complicated by the fact that the actual particles existing in solution are asso-
ciation formations of monomers. Rather elaborate NMR, light- and neutron scattering
experiments were needed /3-6/ to show that the phase separation in aqueous solutions
is a result of increased interactions between particles having approximately
constant size as a function of temperature. The apparent hydrodynamic radius (R_h')
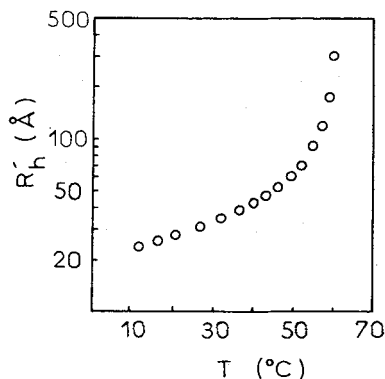
Fig.1 - The apparent hydrodynamic radius (R_h') of C_8E_5
        micelles in water as a function of temperature.

of C_8E_5 micelles (10 volume-%) as a function of temperature is shown in figure 1.
The curve is typical for non-ionic surfactants and shows a fast apparent growth of
the particles with temperature. If it is assumed that the fast growth is due to
increased interactions of particles having a constant size then a critical binary
mixture model can be applied /4/. The critical concentration fluctuations then give
rise to a power law dependence of the scattered light intensity and the apparent
hydrodynamic radius as a function of the normalized temperature difference ε
($\varepsilon = T_d-T/T_d$). This allows to extract the critical exponents γ and υ ($\gamma=1.04-0.99$
and $\upsilon = 0.565-0.538$ for C_8E_5). Thus the large apparent size of the micelles is propo-
sed to be due to the large width of the spatial interactions. Extensive neutron
scattering experiments have been conducted to show that the micelles indeed remain
essentially of constant radius as a function of temperature or concentration /6/.
The important direct evidence for only small size changes was obtained with the
technique of Quasi-elastic neutron scattering (IN11 at Institut Laue-Langevin). The
technique is unique in making it possible to determine particle displacements over
very short distances and times /7/. For a single diffusional process the characte-
ristic relaxation time τ is expected to be related to Q ($=4\pi/\lambda$ $\sin\theta/2$) by $\tau=DQ^2$.
The diffusion coefficient thus reflects Brownian motion down to distances of $2\pi/Q$.
These measurements showed that there is a single diffusional process (most probably)
due to the micelles, corresponding to a diffusion coefficient which is essentially
independent of temperature. The micelle size can now be estimated by calculating
the hydrodynamic radii using $R_h=(1-\phi)kT/(6\pi\eta(T)D_{app})$. The values of R_h increase
linearly with temperature from 25.3 Å at 25 °C to 35.3 Å at phase separation
(~60 °C) /6/. In conclusion, the observed fast increases of the static and dynamic
properties as the phase separation temperature is approached are mainly due to
increased interactions between basically constant particles(decreased interaction
of the particles with the solvent). The phase separation process can thermodynami-
cally be analyzed using the Flory-Huggins equation /8/. One important result which
emerges hereby is that observed phase separation temperatures can be transformed
to solute-solvent interaction values at a selected temperature(K.Weckström and
M.Zulauf, to be published).

3 - THE EFFECT OF ADDED INORGANIC SALTS ON THE PHASE SEPARATION

    With the microscopic and thermodynamic background outlined above it is interes-
ting to apply the system to study the salting out/in phenomena. Figure 2 thus shows
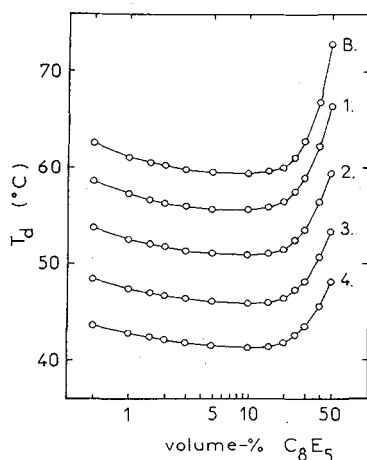the effect of added KCl on the C_8E_5 phase separation. One can see that the binary

Fig.2 - Lower consolute boundaries of C_8E_5 in B.) H_2O
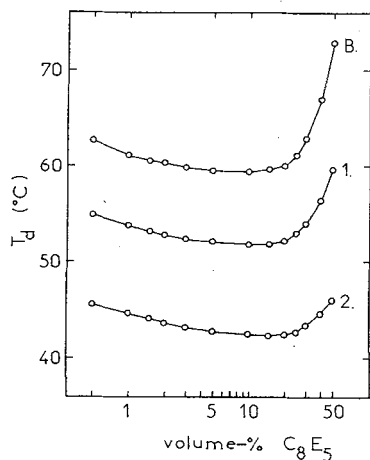1.) 0.2 m KCl 2.) 0.5 m KCl 3.) 0.9 m KCl 4.) 1.3 m KCl.

Fig.3 - Lower consolute boundaries of C_8E_5 in B.) H_2O
1.) 0.2 m NaF 2.) 0.5 m NaF.

LCB is shifted rather parallelly to lower temperatures, the critical concentrations remain at around 8 volume-% C_8E_5. Linked with the lowering of the LCB is a flattening of the LCB shape. This is most clearly seen when NaF is the salting out agent (Fig.3). The salts CsCl and KCl which are as effective in salting out also have closely the same LCB shape (Fig.4). These results thus suggest that the observed shifts of the binary LCB are closely accompanied by a change in the LCB shape.
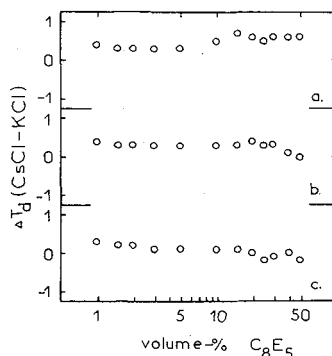
Fig.4 - Differences in phase separation temperatures
        between CsCl and KCl as a function of volume-%
        C_8E_5 at salt concentrations of a) 0.5 m
        b) 0.9 m c) 1.3 m.

4 - PHASE SEPARATION AND SALTING OUT IN HEAVY WATER

Replacing water with heavy water as solvent lowers the phase separation values of C_8E_5 (2.9 °C) without significantly affecting the LCB shape (Fig.5). This suggests that the phase separation of C_8E_5 is closely linked to the surrounding water/ heavy water structure, and to the ability of the molecules to accomodate themselves in this structure. The interaction of C_8E_5 with the surrounding network is slightly less favorable in heavy water. It is known that the temperature of the lower critical point is closely linked to the directionality of the component interactions. The more directional the interaction the more entropically disfavoured it is, and the temperature must be lowered further before interaction occur /1/. In line with a less favorable structural interplay of C_8E_5 with the heavy water network is also a more effective salting out in this solvent (Fig.6).
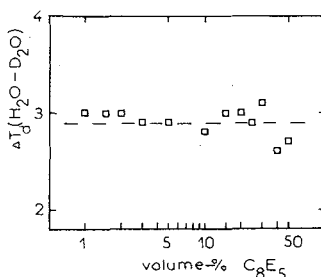
Fig.5 - Differences in phase separation temperatures
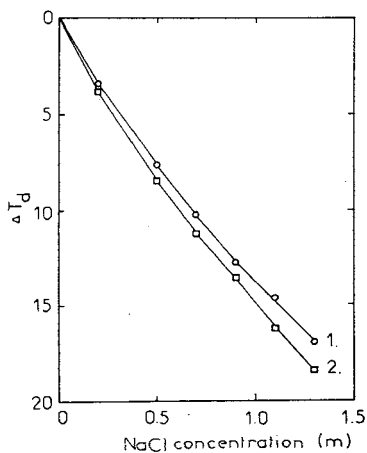   for C_8E_5 in H_2O and D_2O.

Fig.6 - Salting out of C_8E_5 (10 volume-%) in
1.) H_2O and 2.) D_2O.

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