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An Actualized Survey of Micellar Nematic Lyophases

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An Actualized Survey of Micellar Nematic Lyophases

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A table is given for nematic solutions from amphiphilic compounds providing literature data up to 1986. The table includes the solutions reported in the summary of Forrest from 1981. The phases are classified according to their type N_C^+ , N_C^- , N_D^+ and N_D^- and grouped according to their composition.

INTRODUCTION

Since Lawson and Flautt first discovered the nematic state in lyotropic soap solutions twenty years ago,¹ there has been growing interest in this field. Such lyophases have been investigated theoretically and experimentally and they have been applied as solvents in spectroscopy as well as in chemical reactions.

The systems have been classified by Radley and coworkers^{7,9} as Type I and Type II for cylindrical and discotic aggregate symmetry axis with respectively parallel and perpendicular alignment in the magnetic field.

At the beginning of 1981, a summary of all the literature data on nematic lyophases was published by Forrest.⁷⁶ We also presented a table of the most current systems at the Sunapee Conference, the same year.

Since then, quite a number of new nematic solutions from micellar aggregates have been reported. Other properties have been discovered and a new classification has been proposed by Boden, Radley

and Holmes.⁵⁵ They have distinguished four types of aggregates with respect to shape and magnetic properties, N_C for cylindrical and N_D for discotic aggregates, + and - for parallel and perpendicular alignment in the magnetic field. This resulted in the classes N_C^+ , N_C^- , N_D^+ and N_D^- .

We have thought it useful to actualize the data at least up to 1986. The Boden classification is applied whenever possible and we have grouped the systems according to their type of composition; column [1]: soap amphiphile + water, column [2]: soap amphiphile + water + electrolyte, column [3]: soap amphiphile + water + cosurfactant and column [4]: soap amphiphile + water + electrolyte + cosurfactant (cosurfactant: long chained alcohol).

RESULTS

See table on next page.

DISCUSSION

The table shows that the nematic solutions can be obtained not only from ternary and quaternary mixtures but also from a number of binary (amphiphile + water) solutions.

In addition to the initial classes Type I (N_C^+) and Type II (N_D^-) from amphiphiles with negative magnetic anisotropy, a number of N_C^- and N_D^+ systems have now been discovered. They are partially or totally built up from amphiphiles with the opposite magnetic sign, as in the case of the first discovered fluorocarbon soaps.⁶⁴

What can be noted is that long chained N-substituted aminoacid salts are good amphiphiles for such solutions and especially interesting when applied as membrane models. Until now, these solutions have mostly been used because of the cholesteric properties when they are made from optical enantiomers.

Only recently, nonionic nematic micellar solutions have been reported. They all belong to the binary group.

The subject of nematic lyophases is certainly not closed. The literature provides frequently new information which should be attentively followed.

TABLE I
MICELLAR NEMATIC LYOPHASES

Ionic surfactant (counterion)	[1] + water	[2] + water + electrolyte	[3] + water + cosurfactant	[4] + water + electrolyte + cosurfactant
Octylsulfate (Na^+)	N_D^{-2}	$\text{N}_C^{2,3,4,5,33}$	$\text{N}_C^{+6,7,8,9}$ $\text{N}_D^{-6,7,9,10}$	N_D^{-1} $\text{N}_D^{-1,2,3,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24,25,26}$
Decylsulfate (Li^+ , Na^+ , Cs^+ , Rb^+ , NH_4^+ , CH_3NH_3^+ , $(\text{CH}_3)_2\text{NH}^+$, $(\text{CH}_3)_3\text{N}^+$, $(\text{CH}_3)_2\text{Sn}^+$, $\text{Na}^+/\text{Me}_3\text{Pb}^+$, $\text{C}_2\text{H}_5\text{NH}_3^+$, anilinium)				
Decanoate (Na^+ , K^+)		N_D^{-12}		$\text{N}_D^{-12,27}$
Dodecanoate (Na^+ , K^+ , Rb^+ , Cs^+)		$\text{N}_C^{+2,3,4,12,33,42}$	$\text{N}_C^{+28,42}$, N_D^{-28}	$\text{N}_D^{-29,30,31,32}$
Hexyloxybenzoate (K^+)			$\text{N}_C^{34,36}$	$\text{N}_D^{+34,36}$
Decanoate + Heptyloxybenzoate (K^+)				N_D^{+39}
Dodecanoate + Heptyloxybenzoate (K^+)				N_D^{+37}
Cromoglycate (Na^+)		N_C^{-35}		
Decylammonium (Br^- , Cl^- , F^- , BF_4^- , $((\text{CH}_3)_2\text{AsO}_2)^-$)	$\text{N}_C^{-40,41,42,43,70}$ $\text{N}_D^{-2,3}$	N_C^{-43} $\text{N}_D^{-3,30,44,11,45,46,14,47}$		$\text{N}_D^{-45,47,48,49,50,51}$
Tetradecyltrimethylammonium (Br^-)	$\text{N}_C^{+53,56}$			$\text{N}_D^{+53,56}$
Tetradecyltrimethylammonium benzenesulfonate	$\text{N}_C^{-53,54,55}$			N_D^{+53}
Tetradecyltrimethylammonium toluenesulfonate	N_C^{-56}			

TABLE I (continued)
MICELLAR NEMATIC LYOPHASES

Ionic surfactant (counterion)	[1] + water	[2] + water + electrolyte	[3] + water + cosurfactant	[4] + water + electrolyte + cosurfactant
{ Tetradecyltrimethylammonium (Br ⁻) + Tetradecyltrimethylammonium toluenesulfonate				N_D^{-56}
{ Hexadecyltrimethylammonium (Br ⁻ , Cl ⁻ , NO ₃ ⁻)		$N_D^{-59,60,15,58}$		$N_D^{-57,58,62}$
{ Hexadecylpyridinium (Cl ⁻)				$N_D^{-57,58,59}$
{ Hexadecylpyridinium (Cl ⁻) + Hexadecyltrimethylammonium (Br ⁻)				$N_D^{-58,62}$
{ Dodecanoate (K ⁺)				$N_D^{-61,62}$
{ Decyltrimethylammonium (Br ⁻) + Dodecanoate (K ⁺)		N_D^{-32}		$N_D^{-61,62}$
{ Hexadecyltrimethylammonium (Br ⁻) + Decylammonium (Cl ⁻)				N_D^{-62}
{ Hexadecyltrimethylammonium (Br ⁻) + Decylammonium (Cl ⁻)				N_D^{-61}
{ Decyltrimethylammonium (Br ⁻)				N_D^{-61}

$\left\{ \begin{array}{l} \text{Dodecanoate (K}^+) \\ + \\ \text{Dodecylpyridinium (Cl}^-) \\ \text{Perfluoroheptanoate (Rb}^+, \text{NH}_4^+) \\ \text{Perfluorooctanoate (Cs}^+, \text{Rb}^+, \text{NH}_4^+) \\ \text{Perfluorononanoate (Rb}^+, \text{NH}_4^+, \\ \text{N(CH}_3)_3^+) \\ \text{Dodecylsarcosinate (Na}^+) \\ \text{Dodecylsarcosinate + Heptyloxybenzoate} \\ \text{(K}^+) \\ \text{d,l},\alpha\text{-Alanine hydrochloride decylester} \\ \text{d,l},\text{N-Dodecylalaninate (K}^+) \\ \text{d,l},\text{N-Dodecylserinate (K}^+) \\ \text{d,l},\text{N-Dodecylvalinate (K}^+) \\ \text{d,l},\text{N-Dodecylaspartate (di-Na}^+) \end{array} \right\}$	N_D^{+66} $\text{N}_\text{D}^{+64,65,66}$ $\text{N}_\text{D}^{+66,67}$			N^{63} $\text{N}_\text{D}^{-34,37,38,75}$ N_D^{+37} $\text{N}_\text{D}^{70}, \text{N}_\text{D}^{-71,75}$ $\text{N}_\text{D}^{-71}, \text{N}^{-72}$ N_D^{-71} $\text{N}_\text{C}^{+73,74}, \text{N}_\text{D}^{-73,74}$
Non ionic surfactant				
$\text{Hexadiethylenecoxytriphenylene}$ Polysiloxane $\text{(ethylenecoxybiphenyl-substituted)}$ $\text{Heptylethyleneoxyacetate}$ $\text{(allyloxybiphenyloxy-substituted)}$	N_C^{-68} N_C^{-69} N_D^{77}			

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