The Structure, Dynamics and Equilibrium Properties of Colloidal Systems

The Structure, Dynamics and Equilibrium Properties of Colloidal Systems

edited by

D. M. Bloor

and

E. Wyn-Jones

Department of Chemistry and Applied Chemistry
University of Salford,
Salford, U.K.

Kluwer Academic Publishers

Dordrecht / Boston / London

Published in cooperation with NATO Scientific Affairs Division

Proceedings of the NATO Advanced Study Institute on
Properties of Colloidal Systems
Aberystwyth, Wales, U.K.
September 10–23, 1989

Library of Congress Cataloging-in-Publication Data

NATO Advanced Study Institute on the Properties of Colloidal Systems (1989 : Aberystwyth, Wales)
The structure, dynamics, and equilibrium properties of colloidal systems : proceedings of a NATO Advanced Study Institute on the Properties of Colloidal Systems, held at the University College of Wales, Aberystwyth, September 10-23, 1989 / edited by D.M. Bloor and E. Wyn-Jones.
p. cm. -- (NATO ASI series. Series C, Mathematical and physical sciences ; 324)
Includes index.
ISBN 0-7923-0993-6 (alk. paper)
1. Colloids--Congresses. 2. Surface chemistry--Congresses. I. Bloor, D. (David), 1937- . II. Wyn-Jones, E. (Evan) III. Title. IV. Series: NATO ASI series. Series C, Mathematical and physical sciences ; no. 324.
QD549.N2854 1989
541.3'45--dc20 90-48011

ISBN 0–7923–0993–6

Published by Kluwer Academic Publishers,
P.O. Box 17, 3300 AA Dordrecht, The Netherlands.

Kluwer Academic Publishers incorporates the publishing programmes of
D. Reidel, Martinus Nijhoff, Dr W. Junk and MTP Press.

Sold and distributed in the U.S.A. and Canada
by Kluwer Academic Publishers,
101 Philip Drive, Norwell, MA 02061, U.S.A.

In all other countries, sold and distributed
by Kluwer Academic Publishers Group,
P.O. Box 322, 3300 AH Dordrecht, The Netherlands.

Printed on acid-free paper

Printed in the Netherlands

The Structure, Dynamics and Equilibrium Properties of Colloidal Systems

NATO ASI Series

Advanced Science Institutes Series

A Series presenting the results of activities sponsored by the NATO Science Committee, which aims at the dissemination of advanced scientific and technological knowledge, with a view to strengthening links between scientific communities.

The Series is published by an international board of publishers in conjunction with the NATO Scientific Affairs Division

A Life Sciences **B Physics**	Plenum Publishing Corporation London and New York
C Mathematical and Physical Sciences **D Behavioural and Social Sciences** **E Applied Sciences**	Kluwer Academic Publishers Dordrecht, Boston and London
F Computer and Systems Sciences **G Ecological Sciences** **H Cell Biology**	Springer-Verlag Berlin, Heidelberg, New York, London, Paris and Tokyo

Series C: Mathematical and Physical Sciences - Vol. 324

PREFACE

The papers in this volume are as a result of contributions given at the NATO Advanced Study Institute held at Llandinam Building, University College of Wales, Aberystwyth, 10 - 23 September 1989. The Institute considered the physical and chemical properties of a variety of colloidal systems ranging from simple micellar solutions to concentrated colloidal dispersions. The purpose of the NATO Advanced Study Institute was to create a forum so that research scientists working in different areas concerned with colloid science could interact. The emphasis of the contributions were on the interpretation of the different experimental and theoretical approach to give information on the structure, dynamics and equilibrium properties of these systems. The application of several different techniques in colloid science have been described; new developments and perspectives have been covered by several authors. The present volume reviews the current state of the art in this area and it is hoped that it will be used as an incentive for further studies particularly with reference to new areas of research.

In the organisation of the scientific programme for the NATO meeting we would like to acknowledge the assistance of Professors J. Lyklema, D.G. Hall and J. Holzwarth. We wish to thank Miss Mandy Rudd for all the secretarial assistance in setting up the meeting and for the invaluable assistance in preparing the manuscripts. In connection with the proceedings we would also like to thank Miss Sandra Fahy for assistance. The help of Paul Jones and Mrs G. Wyn-Jones during the meeting is also gratefully acknowledged. We would also like to express our deepest gratitude to the NATO Science Division for the award of the grant which enabled the meeting to be held. Last but not least we are grateful for financial assistance from Unilever Ltd, B.P., I.C.I., and Harcross Chemicals.

CONTENTS

PREFACE xi

J. Lang
THE TIME-RESOLVED FLUORESCENCE QUENCHING METHOD FOR THE STUDY OF MICELLAR SYSTEMS AND MICROEMULSIONS: PRINCIPLE AND LIMITATIONS OF THE METHOD 1

H. Høiland and A.M. Blokhus
SOLUBILIZATION OF ALCOHOLS AND ALKANEDIOLS IN AQUEOUS SURFACTANT SOLUTIONS 39

Y. Moroi
THERMODYNAMICS OF SOLUBILIZATION INTO SURFACTANT MICELLES 49

M. Manabe, H. Kawamura, Y. Yamashita and S. Tokunaga
APPLICATION OF THE DIFFERENTIAL CONDUCTIVITY METHOD: THE EFFECT OF CHAIN-LENGTH OF HOMOLOGOUS SURFACTANTS ON THE PARTITION COEFFICIENT OF ALKANOLS BETWEEN BULK WATER AND MICELLES 63

J.H. Clint
MIXED MICELLE THEORY AS AN AID TO SURFACTANT FORMULATION 71

J.M. Wates
PARTITIONING OF CATIONIC SURFACTANTS BETWEEN HEPTANE AND WATER 85

H. Høiland, A.M. Blokhus, T. Lind and A. Skauge
ADSORPTION OF SODIUM DODECYL SULFATE AND 1-BUTANOL ON SOLID ALUMINIUM OXIDE 95

D. Attwood, E. Boitard, J.P. Dubès, H. Tachoire, V. Mosquera and V. Perez Villar
ASSOCIATION MODELS FOR PHENOTHIAZINE DRUGS IN AQUEOUS SOLUTION 103

B. Lindman and G. Karlström
POLYMER-SURFACTANT SYSTEMS 131

D.M. Bloor and E. Wyn-Jones
KINETIC AND EQUILIBRIUM STUDIES ASSOCIATED WITH POLYMER SURFACTANT INTERACTIONS 149

K. Shirahama, T. Watanabe and M. Harada
THE INTERACTION OF AMPHIPHILES WITH MOLECULAR ASSEMBLIES AND POLYMERS 161

J. Lyklema
STEP-WEIGHTED RANDOM WALK STATISTICS, AS APPLIED TO ASSOCIATION COLLOIDS 173

A.S. Bommarius, J.F. Holzwarth, D.I.C. Wang and T.A. Hatton
A POPULATION BALANCE MODEL FOR THE DETERMINATION OF SOLUBILIZATE EXCHANGE RATE CONSTANTS IN REVERSED MICELLAR SYSTEMS 181

E.B. Leodidis and T.A. Hatton
SELECTIVE SOLUBILISATION IN REVERSED MICELLES 201

S.E. Friberg and K. Qamheye
WHEN IS A MICROEMULSION A MICROEMULSION? 221

U. Olsson and B. Lindman
UNI- AND BICONTINUOUS MICROEMULSIONS 233

A. Malliaris
EXPERIMENTAL AND COMPUTATIONAL ASPECTS OF THE TIME-CORRELATED SINGLE PHOTON COUNTING TECHNIQUE 243

J. Lang, R. Zana and N. Lalem
DROPLET SIZE AND DYNAMICS IN WATER IN OIL MICROEMULSIONS. CORRELATIONS BETWEEN RESULTS FROM TIME-RESOLVED FLUORESCENCE QUENCHING, QUASIELASTIC LIGHT SCATTERING, ELECTRICAL CONDUCTIVITY AND WATER SOLUBILITY MEASUREMENTS 253

G.A. Van Aken
THE INFLUENCE OF THE DISTRIBUTION OF SALT ON THE PHASE BEHAVIOUR OF MICROEMULSIONS WITH IONIC SURFACTANTS 279

J. Eastoe, B.H. Robinson and D.C. Steytler
A STUDY OF MICROEMULSION STABILITY 295

P.J. Atkinson, S.J. Holland, B.H. Robinson, D.C. Clark, R.K. Heenan and A.M. Howe
STRUCTURE OF MICROEMULSION-BASED ORGANO-GELS 303

P. Lianos
LUMINESCENCE PROBE STUDY OF ORGANIZED ASSEMBLIES TREATED AS FRACTAL OBJECTS 309

E. Pelizzetti, V. Maurino, C. Minero and E. Pramauro
ORGANIZED ASSEMBLIES IN CHEMICAL SEPARATIONS 325

M.P. Pileni, J.P. Huruguen and C. Petit
STRUCTURAL CHANGES OF AOT REVERSE MICELLES BY THE PRESENCE OF PROTEINS: PERCOLATION PROCESS INDUCED BY CYTOCHROME C 355

A. Khan-Lodhi, B.H. Robinson, T. Towey, C. Herrmann, W. Knoche and U. Thesing
MICROPARTICLE FORMATION IN REVERSE MICELLES 373

H. Hoffmann and U. Krämer
ELECTRIC BIREFRINGENCE MEASUREMENTS IN MICELLAR AND COLLOIDAL SOLUTIONS 385

T.A. Bleasdale and G.J.T. Tiddy
SURFACTANT LIQUID CRYSTALS 397

H.D. Burrows
THE PHASE BEHAVIOUR OF METAL(II) SOAPS IN ONE, TWO AND THREE COMPONENT SYSTEMS 415

M. Gradzielski and H. Hoffmann
RINGING GELS: THEIR STRUCTURE AND MACROSCOPIC PROPERTIES 427

E.R. Morris
INDUSTRIAL HYDROCOLLOIDS 449

R.J. Clarke and H.J. Apell
KINETICS OF THE INTERACTION OF THE POTENTIAL-SENSITIVE DYE OXONOL V WITH LIPID VESICLES 471

A. Genz, T.Y. Tsong and J.F. Holzwarth
EQUILIBRIUM AND DYNAMIC INVESTIGATION ON THE MAIN PHASE TRANSITION OF DIPALMYTOYLPHOSPHATIDYLCHOLINE VESICLES CONTAINING POLYPEPTIDES: A DSC AND IODINE LASER T-JUMP STUDY 493

H. Suhaimi and S.E. Friberg
AN INVESTIGATION ON THE PENETRATION OF LIPIDS IN THE BILAYER OF STRATUM CORNEUM 517

S.E. Friberg and W. Mei Sun
FOAM STABILITY IN NON-AQUEOUS MULTI-PHASE SYSTEMS 529

J.B.M. Hudales and H.N. Stein
THE PROFILE OF A PLATEAU BORDER NEAR A VERTICAL FOAM FILM 541

M.S. Aston
THE ANAMOLOUS EFFECT OF ELECTROLYTES ON SURFACTANT MONOLAYER SURFACE PRESSURE-AREA ISOTHERMS 551

R. Aveyard, B.P. Binks and P.D.I. Fletcher
SURFACTANT MOLECULAR GEOMETRY WITHIN PLANAR AND CURVED MONOLAYERS IN RELATION TO MICROEMULSION PHASE BEHAVIOUR 557

V. Degiorgio
LIGHT SCATTERING EXPERIMENTS ON ANISOTROPIC LATEX PARTICLES 583

V. Degiorgio
ELECTRIC BIREFRINGENCE STUDIES OF MICELLAR AND COLLOIDAL DISPERSIONS 597

M.A. Cohen Stuart
POLYMERS AT INTERFACES: STATICS, DYNAMICS AND EFFECTS ON COLLOIDAL STABILITY 613

R. Rajagopalan and C.S. Hirtzel
EQUILIBRIUM STRUCTURE AND PROPERTIES OF COLLOIDAL DISPERSIONS 619

J.D.F. Ramsay
STRUCTURE, DYNAMICS AND EQUILIBRIUM PROPERTIES OF INORGANIC COLLOIDS 635

R. Buscall
THE RHEOLOGY OF CONCENTRATED DISPERSIONS OF AGGREGATED PARTICLES 653

J.W. Goodwin
RHEOLOGICAL PROPERTIES, INTERPARTICLE FORCES AND SUSPENSION STRUCTURE 659

J.H. Clint
INTERFACIAL RHEOLOGY AND ITS APPLICATION TO INDUSTRIAL PROCESSES 681

R. Rajagopalan
EFFECTIVE INTERACTION POTENTIALS OF COLLOIDS FROM STRUCTURAL DATA: THE INVERSE PROBLEM 695

E. Dickinson
COMPUTER SIMULATION OF THE COAGULATION AND FLOCCULATION OF COLLOIDAL PARTICLES 707

S. Toxvaerd
COMPUTER SIMULATIONS OF FLUIDS AND SOLUTIONS OF ORGANIC MOLECULES 729

D.J. Wedlock, S.D. Lubetkin, C. Edser and S. Hawksworth
THE FORM OF COLLOIDAL CRYSTALS FROM SILICA LATICES IN NON-AQUEOUS DISPERSION 741

D.J. Wedlock, A. Moman and J. Grimsey
CONSOLIDATION OF DEPLETION FLOCCULATED CONCENTRATED SUSPENSIONS: INFLUENCE OF NON ADSORBING POLYMER CONCENTRATION ON CONSOLIDATION RATE CONSTANTS 749

J.K. Thomas
COLLOIDAL SEMICONDUCTORS 759

M.A.Lopez-Quintela and J. Rivas
OBTENTION AND CHARACTERISATION OF ULTRAFINE MAGNETIC COLLOIDAL PARTICLES IN SOLUTION 773

J. Lyklema
NON-EQUILIBRIUM DOUBLE LAYERS IN CONNECTION WITH COLLOID STABILITY 789

R.D. Groot
RECENT THEORIES ON THE ELECTRIC DOUBLE LAYER 801

D.G. Hall
APPLICATION OF DOUBLE LAYER THEORY TO MODERATELY COMPLEX SYSTEMS 813

A.M. Cazabat
WETTING PHENOMENA 831

D.G. Hall
THERMODYNAMICS OF ADSORPTION FROM DILUTE SOLUTIONS 857

LIST OF PARTICIPANTS 879

INDEX OF SUBJECTS 885

THE TIME-RESOLVED FLUORESCENCE QUENCHING METHOD FOR THE STUDY OF MICELLAR SYSTEMS AND MICROEMULSIONS : PRINCIPLE AND LIMITATIONS OF THE METHOD

J. LANG
Institut Charles Sadron (CRM-EAHP), CNRS-ULP
6, rue Boussingault
67083 Strasbourg Cédex
France

ABSTRACT. The application of time-resolved fluorescence quenching method to the determination of the size of micelles and oil-in-water or water-in-oil microdroplets is described. It is also shown that this method gives information on dynamic processes occurring in micellar solutions and microemulsions. In this account the scope and limitations of the method are discussed with special emphasis placed on the assumptions used to interpret the fluorescence decay data and on the selection of appropriate probe and quencher molecules. Recent developments are also briefly presented.

1. Introduction

The time-resolved fluorescence quenching (TRFQ) method is now widely used for the determination of the size of micelles and of water-in-oil (w/o) or oil-in-water (o/w) microdroplets. This method can also be used to investigate some kinetic processes occurring in micellar solutions and in microemulsions. As a result, one of the advantages of this method is that both structural and dynamic characteristics of such systems can be investigated.

Extensive reviews of the results obtained with the TRFQ method have been reported recently [1-3]. The purpose of this article is to give a brief description of the principle and of the scope and limitations of this method so that a foundation is laid for those readers who wish to rapidly acquaint themselves with the method. Emphasis is placed on the nature of the structural and dynamic information than can be derived from these studies together with the main assumptions involved in the interpretation of the experimental data. Many original references are also quoted for the reader who wishes to pursue the technique in more detail. Finally recent developments are also mentioned.

For the sake of simplicity, the term micelle will be used to designate normal or inverse micelles and o/w or w/o microdroplets. It is only when circumstances demand that the type of aggregate will be specified. In addition the terms probe and quencher will be often referred to as reactants in the following treatment.

D. M. Bloor and E. Wyn-Jones (eds.),
The Structure, Dynamics and Equilibrium Properties of Colloidal Systems, 1–38.

2. Principle of the method

The principle of the TRFQ method is to dissoive luminescent (mostly fluorescent) probe and quencher molecules in a micelle and to measure and analyze the luminescence intensity decay of the probe. From this analysis, which assumes a given distribution of the quencher amonst the micelles, information about the size of the micelles and the dynamics of the system are obtained.

In Figure 1 the fluorescence decay curves of a fluorescent probe in the presence of quenchers in a homogeneous medium (Fig.1A) (pure solvent in which the fluorescent probe and the quencher molecules are uniformly distributed) is shown together with the fluorescence decay found in a heterogeneous medium (Fig.1B) such as micellar solutions or w/o or o/w microemulsions where appropriate probe and quencher molecules are dissolved in the micelles. It is seen that in the case of the homogeneous solutions the fluorescence decay decreases linearly

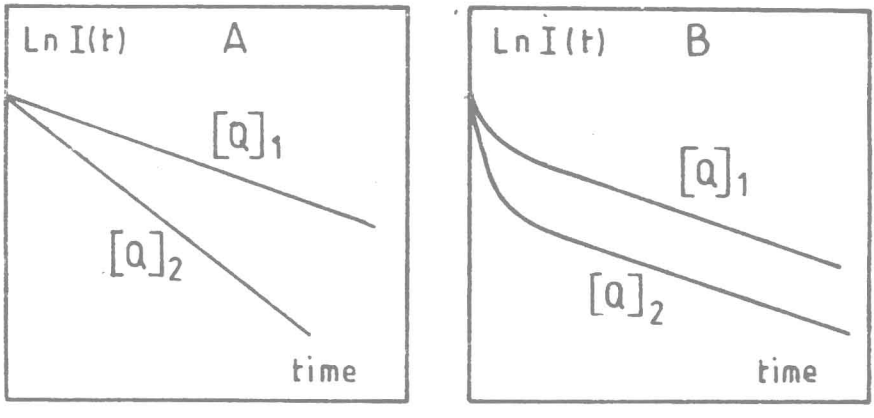

Figure 1.: Fluorescence decay curves of a fluorescent probe in the presence of a quencher in the homogeneous case (A) and in the heterogeneous case where the solution contains micelles (B). The quencher concentration increases from $[Q]_1$ to $[Q]_2$. In the heterogeneous case it is assumed that there is no intermicellar exchange of the reactants.

with time, with a slope which increases with the quencher concentration, whereas in the case of the heterogeneous solution two regimes are observed in the decay curves. A fast decay at short time followed by a linear decay at long time. The behaviour observed in the heterogeneous system, arises from the fact that the probe and quencher are compartmentalized in restricted parts of the solution, namely the micelles. Indeed the statistical distribution of the probe and quencher molecules among the micelles leads to four types of micelles which are schematically illustrated in Fig. 2A. One can distinguish : (i) empty micelles, (ii) micelles with quencher but without probe, (iii) micelles with probe but without quencher and (iv) micelles with

probe and quencher. Only the two last types of micelles will be responsible for the emitted fluorescence. In comparison to what happens in the homogeneous case where all the probe molecules have the same probability to be quenched by the quencher molecules, in the heterogeneous case only the probe molecules inside a micelle which also contains at least one quencher molecule, can be quenched. This type of micelle leads to the fast decrease observed at the beginning of the fluorescence decay curve in Fig.1B and whose amplitude increases with the quencher concentration. On the other hand the linear decrease, at long times, is due to the micelles which contain only probe molecules. The slope of this decay at long times is not affected by the increase in quencher concentration as long as the reactants are not exchanged between the micelles during the lifetime of the probe. This is the case for the examples shown in Fig.1B. The reactants are then said to be frozen or immobile in the micelles during the lifetime of the probe.

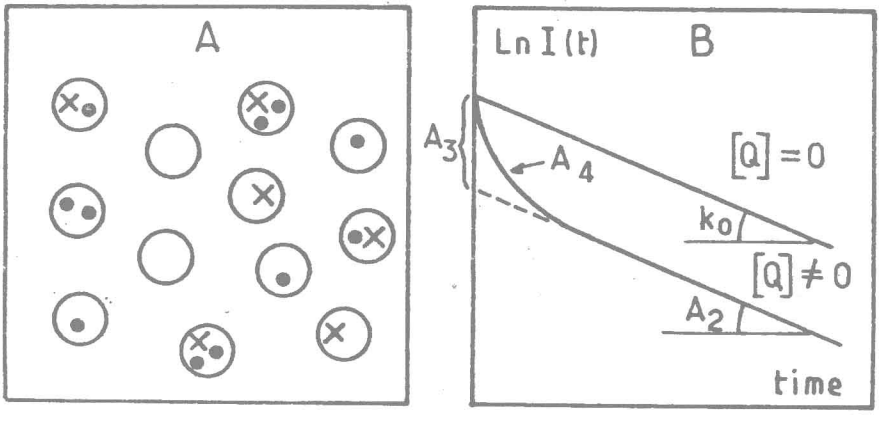

Figure 2.:(A) : Schematic representation of the distribution of probe (x) and quencher (•) molecules among micelles. (B) :Variations of the fluorescence intensity with time of probe molecules solubilized in the micelles, in the absence and presence of quencher molecules.

This argument assumes that in the heterogeneous medium there are no reactants in appreciable amount in the bulk, otherwise the situation will be that of a heterogeneous and a homogeneous medium. It will be seen that in some systems quencher molecules are partly dissolved into the bulk and this will affect the fluorescence decay curves presented in Fig.1B. However, in all the theoretical work done so far for micellar systems it has always been assumed that no quenching of the probe occurs in the bulk, although exchange of the quencher through the bulk has been considered. Quenching of the probe both in the bulk and in the micelles would lead to a situation in which an interpretation of the time resolved fluorescence decay would be extremely difficult if not impossible. Great care must therefore be taken in the choice of the reactants and especially of the probe molecule in order to have them principally solubilized into the micelles. The way these choices are made will be discussed below .

Before proceeding with the description of the TRFQ method it is worth pointing out that the first measurement of a micellar aggregation number with a fluorescence method was done by steady-state fluorescence in 1974 by Dorrance and Hunter [4]. This work has been followed by several others, for example those of Turro and Yekta [5] and Koglin et al. [6]. The steady-state fluorescence method is very easy to use but it is practically restricted to micelles of rather small aggregation number (< 70 for direct micelles) and to immobile probe and quencher [7]. For larger micelles the steady-state method underestimates the aggregation number which can be corrected if the lifetime and the intramicellar quenching rate constant of the probe are known. However this needs fluorescence decay measurements. Therefore most of the micellar size determinations are now undertaken with the TRFQ method.

3. Analysis of the fluorescence decay curves

The equation which accounts for the fluorescence decay curves in micellar systems such as those shown in Fig.1B was first given by Infelta et al. [8] and by Tachiya [9]. It was given later by others authors as for instance Rodgers and Da Silva E Wheeler [10] and Atik and Singer [11]. The variation of the fluorescence intensity with time obeys the equation:

$$I(t) = I(o) \exp \{- A_2 t - A_3 [1 - \exp(- A_4 t)]\} \qquad (1)$$

where I(t) and I(o) are the fluorescence intensities at time t and t = 0, respectively, following excitation. A_2, A_3 and A_4 are time- independent parameters which are obtained, together with I(o) by fitting eq.1 to the decay data. The relation between the parameters A_2, A_3 and A_4 and the shape of the decay curve is shown in Fig.2B. A_2 represents, in a LnI(t) versus time plot, the slope of the linear asymptotical decay at long time. A_3 is the quantity $LnI(o)-LnI_\infty(o)$ where $LnI_\infty(o)$ is the extrapolated value of the asymptote at t = 0. A_4 is a parameter which fixes the radius of curvature of the decay at short times. It will be seen that this radius increases with the size of the micelles thus causing one of the limitations of the method.

The fluorescence decay data of the excited probe are usually collected by means of a single-photon counting apparatus [12]. The fitting of eq.1 to the data is currently done with a nonlinear weighted least squares procedure which includes deconvolution of the data by the profile of the exciting pulse. It must be noticed, however, that the deconvolution is necessary only for very small micelles where intramicellar quenching of the probe is very fast and gives a decay at short time which is affected by the width of the exciting pulse.

3.1. CASE WHERE THE PROBE AND THE QUENCHER DISTRIBUTIONS ARE FROZEN ON THE PROBE FLUORESCENCE TIME SCALE

It has been shown [13] that in this case the expressions for A_2, A_3 and A_4 are :

$$A_2 = k_0, \quad A_3 = [Q]/[M], \quad A_4 = k_q \tag{2}$$

The same expressions were established to interpret the results of intramicellar photoredox reaction [14] and can be deduced from the decay equation given by Infelta et al. [8] and by Tachiya [9] assuming that the quencher molecules are exclusively solubilized into the micelles.

In eq.2, k_0 represents the fluorescence decay rate constant of the probe in the micelles without quencher ($k_0^{-1} = \tau_0$ is the probe fluorescence lifetime), k_q is the pseudo-first-order rate constant for intramicellar quenching when only one quencher is present in the micelle, [Q] is the total quencher concentration and [M] the total micelle concentration in the solution. It appears therefore that the TRFQ method gives the concentration of the micelles [M] in the solution but not a direct measurement of the size of the micelles. However, structural parameters can be deduced from [M] under fairly reasonable assumptions. For instance, the mean surfactant aggregation number, N, in a micelle is given by :

$$N = \frac{C-C_f}{[M]} = \frac{(C-C_f)A_3}{[Q]} \tag{3}$$

where C is the total surfactant concentration and C_f the free surfactant concentration i.e. the surfactant concentration in the bulk which does not participate to the formation of the micelles. In the case of direct micelles C_f is usually taken equal to the critical micelle concentration (cmc). For large values of C the error made assuming C_f = cmc is negligible. In solutions of inverse micelles or w/o microemulsions C_f is usually very low and is therefore neglected compared to C.

In Fig.2B the variation of the fluorescence intensity versus the time is shown for two identical micellar solutions, one with and one without quencher. The slopes of these two curves at long time are equal. This indicates that there is no exchange of reactants between the micelles during the lifetime of the probe. Equation 2 can then be readily used for the interpretation of the fluorescence decay data obtained with the solution containing the quencher. It will be shown that when intermicellar exchange of the reactants occurs in the solution, these two slopes are not equal. Expressions other than those given by eq.2 are then valid for A_2, A_3, and A_4.

It must be emphasized that the comparison of the values of the slopes of the decay curves obtained with and without quencher in the solution must be made for each system investigated. This is necessary in order to check if eq.2 is appropriate for the interpretation of the fluorescence decay data.

Several assumptions have been made for the determination of eqs.1 and 2, which are listed below:

a) The micelles are assumed to be monodisperse. As a consequence only one intramicellar quenching rate constant, k_q, has been considered in the kinetic equations.

b) There is no limit for probe and quencher solubility in the micelles.

c) Only one probe is excited at one time in the same micelle.

d) The number of quenchers in a micelle is independent of the presence of a probe and vice versa.

e) The kinetics of intramicellar quenching is first-order. This can be assumed for small micelles only, where diffusion process and Fick's law cannot be applied to the reactants. For large micelles, like infinite cylindrical micelles, a second-order kinetics must be considered.

f) The rate of intramicellar quenching is proportional to the number of quenchers, x, in the micelle. This assumption is sometimes referred to as a statement that the intramicellar quenching rate constant is proportional to x or that k_q must be replaced by xk_q when x quenchers are present in a micelle, k_q being the quenching rate constant when only one quencher is in the micelle.

g) The distribution of the quenchers among the micelles corresponds to a Poisson distribution.

In order to fulfil assumptions b, c and d one has to ensure that the molar concentration ratio [probes]/[micelles] is kept much below 1 (usually a ratio 0.01 is employed) and that the molar concentration ratio [quenchers]/[micelles] is close to 1. Also in order to fulfil assumption c, a small exciting pulse intensity is used.

Tachiya [15], following a treatment proposed by Hunter [16], has treated theoretically the case where there is a limit to the number of solubilized molecules in the micelles. His treatment includes also exchange of solubilizates between micelles. However, the analysis of the decay data is then much more complicated and has not yet been carried out for real systems.

3.2. DISTRIBUTION OF THE REACTANTS AMONG MICELLES

It is now generally considered that the distribution of the quenchers among the micelles corresponds to a Poisson distribution. Other distributions have also been examined as for instance the geometric distribution. The difference between these two distributions comes from the value which is taken for the exit rate constant of the quencher from the micelle. For the Poisson distribution this rate constant is assumed to be proportional to the number of quenchers in the micelle, whereas for the geometric distribution this rate constant is assumed to be independent of the number of quenchers in the micelles [17]. The association of the quencher to the micelles can be described by a series of equations of the type :

$$MQ_{x-1} + Q \underset{(x)k_{-1}}{\overset{k_1}{\rightleftharpoons}} MQ_x \qquad (4)$$

where M and Q stand for the micelles and the quencher molecules, respectively, and x is the number of quencher molecules in the micelle MQ_x. Therefore the kinetic equations at equilibrium can be written as follows:

(i) for the Poisson distribution: