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Pseudophase Model in Microemulsions

Antonio Cid, Aangel Acuña, Manuel Alonso-Ferrer, Gonzalo Astray, Luis García-Río, Jesus Simal-Gándara and Juan C. Mejuto

Abstract

The kinetic behaviours in microemulsions can be easily modelled using an extension of the pseudophase model previously developed for micellar catalysis. This model considers that the microheterogeneous media can be considered as the sum of different conventional reaction media, where the reagents are distributed and in which the reaction can occur simultaneously. The reaction rate observed in the microheterogeneous system will be the sum of the velocities in each one of the pseudophases. This use can be considered as an extension of the pseudophase model, which has been developed for the quantitative analysis of nitrosation reactions in AOT/isooctane/water microemulsions and has been applied successfully in the literature in a large variety of chemical reactions.

Keywords: microemulsions, reverse micelles, kinetic model, pseudophase model

1. Introduction

The use of microemulsions, in particular, colloidal self-aggregates, and in general, as reaction media [1] makes the application of kinetic models necessary for the quantitative interpretation of the observed results. In this sense, a simple thermodynamic model was developed for its application in micelles [2] and it was called the pseudophase model [3]. This model was successfully applied through extensions to different microheterogeneous systems over the last 50 years [4–10].

2. The pseudophase model

This model considers that the micellar system can be considered as the sum of two conventional reaction media, the continuous pseudophase and the micellar pseudophase, where the reagents are distributed and in which the reaction can occur simultaneously (see **Figure 1**).

In this figure, A and B are the reagents, k is the kinetic constant and the subscripts w and m denotes the reaction loci (w corresponds to the continuous pseudophase and m is the micellar pseudophase). Finally, K_A and K_B are the distribution coefficients of both reactants between different pseudophases.

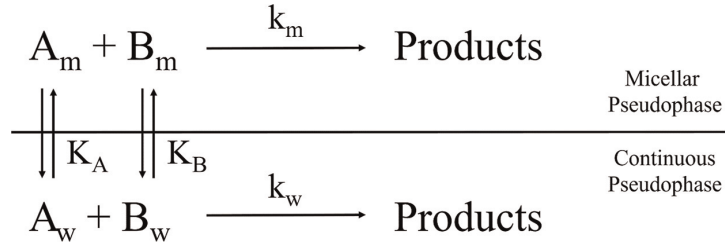


Figure 1.
Pseudophase model applied to micellar aggregates as reaction media.

The model considers that the reaction rate observed in the microheterogeneous system will be the sum of the velocities in each one of the pseudophases, and it can be expressed as shown in the following equations assuming a first-order reaction for each reactant:

$$v_T = v_w + v_m \quad (1)$$

$$v_T = k_{obs}[A_T][B_T] \quad (2)$$

$$v_w = k_w[A_w][B_w] \quad (3)$$

$$v_m = k_m[A_m][B_m] \quad (4)$$

$$k_2[A_T][B_T] = k_w[A_w][B_w] + k_m[A_m][B_m] \quad (5)$$

The mass balance on both pseudophases and the consideration of the distribution coefficients between them allow us to establish the existing relationship between the total concentrations of the reactants and the concentrations in each of the pseudophases considered.

$$[A]_T = [A]_w + [A]_m \quad (6)$$

$$[B]_T = [B]_w + [B]_m \quad (7)$$

$$K_A = \frac{[A]_m}{[A]_w[D_n]} \quad (8)$$

$$K_B = \frac{[B]_m}{[B]_w[D_n]} \quad (9)$$

In Eqs. (8) and (9), D_n denotes the concentration of surfactant micellized and $[D_n] = [D] - CMC$ (where D is the total surfactant concentration and CMC is the critical micellar concentration). Using Eqs. (8) and (9), the following equations can be written:

$$[A]_m = K_A[A]_w[D_n] \quad (10)$$

$$[B]_m = K_B[B]_w[D_n] \quad (11)$$

$$[A]_T = [A]_w + K_A[A]_w[D_n] \quad (12)$$

$$[B]_T = [B]_w + K_B[B]_w[D_n] \quad (13)$$

$$[A]_w = \frac{[A]_T}{1 + K_A[D_n]} \quad (14)$$

$$[B]_w = \frac{[B]_T}{1 + K_B[D_n]} \quad (15)$$

$$[A]_m = \frac{[A]_T K_A [D_n]}{1 + K_A [D_n]} \quad (16)$$

$$[B]_m = \frac{[B]_T K_B [D_n]}{1 + K_B [D_n]} \quad (17)$$

Using Eqs. (14)–(17) on Eq. (5), the following expressions can be deduced (Eq. (18)–(21)):

$$k_2[A_T][B_T] = k_w \frac{[A]_T}{1 + K_A[D_n]} \frac{[B]_T}{1 + K_B[D_n]} + k_m \frac{[A]_T K_A [D_n]}{1 + K_A [D_n]} \frac{[B]_T K_B [D_n]}{1 + K_B [D_n]} \quad (18)$$

$$k_2[A_T][B_T] = k_w \frac{1}{1 + K_A[D_n]} \frac{1}{1 + K_B[D_n]} [A_T][B_T] + k_m \frac{K_A [D_n]}{1 + K_A [D_n]} \frac{K_B [D_n]}{1 + K_B [D_n]} [A_T][B_T] \quad (19)$$

$$k_2 = k_w \frac{1}{1 + K_A[D_n]} \frac{1}{1 + K_B[D_n]} + k_m \frac{K_A [D_n]}{1 + K_A [D_n]} \frac{K_B [D_n]}{1 + K_B [D_n]} \quad (20)$$

$$k_2 = k_w \frac{1}{(1 + K_A[D_n])(1 + K_B[D_n])} + k_m \frac{K_A K_B [D_n]^2}{1 + K_B [D_n] + K_A [D_n]} \quad (21)$$

According to the pseudophase model, each pseudophase is evenly distributed in the total micellar dispersion volume. The value of rate constant must be corrected taking into account the molar volume of each pseudophase to compare the intrinsic reactivity in the two different domains due to the reactants distribution between both pseudophases [10].

Equation (21) can be simplified according to the distributions of A and B, and the presence of chemical reaction in one or both pseudophases. This model predicts the catalysis or inhibition processes with success due to the compartmentalising effect of these colloidal aggregates [11–28]. However, this model must be expanded to take into account possible ion exchange processes between the continuous medium and the micelle, which give rise to more complicated expressions [29]. In some cases, it is necessary to resort to Poisson-Boltzmann distribution to evaluate the concentration of the different ions in the Stern and Gouy-Chapman layers to be able to model the ion exchange process between the continuous medium and the micellar electric double layer [30].

The pseudophase model applied to micelles has also been satisfactory for the analysis of the kinetic results in more complex micellar systems such as mixed micellar-cyclodextrin systems [31–37] or pseudo-micellar humic acids aggregates [38–42].

3. The pseudophase model in microemulsions

The pseudophase model was first extended by our research group in order to quantitatively analyse the kinetic behaviour of nitrosation reactions in microemulsions based on AOT [43, 44]. Afterwards, this extended model, with minor corrections, has been satisfactorily tested on microemulsions covering all possible cases [45–55] such as: (i) different chemical reactions (ionic or non-ionic),

- (ii) reactants distributed throughout the different hydrophobic domains or (iii) with different reaction loci.

Unlike in normal micelles, where we recognised two different domains (micelles and bulk water), in a microemulsion system three domains can be found: (i) the microdroplets of the dispersed phase, (ii) the continuous phase and (iii) the surfactant film (or surfactant + cosurfactant) that stabilises the system. Due to this, in this case, three pseudophases will be considered, taking into account the same proposed considerations for the micellar model.

We will assume that the reactants can be located in each of these three pseudophases, and their distribution will be governed by the distribution coefficients defined in an analogous way to that proposed in micelles. The chemical reaction can take place in each of the three pseudophases. In this way, the model can be explained according to **Figure 2**, where A and B are the reagents, k corresponds to the kinetic constant and the subscripts d , i and c denotes the loci (c corresponds to the continuous pseudophase, d with the dispersed pseudophase and i with the surfactant film -or interphase-). $K_{A,id}$ and $K_{B,id}$ are the distribution coefficients of both reactants between the interphase and the dispersed phase. $K_{A,ic}$ and $K_{B,ic}$ correspond to distribution coefficients of both reactants between the interphase and the continuous phase.

As in the case of micelles, the reaction rate observed in the microemulsions will be the sum of the velocities in each one of the pseudophases as it shown in the following equations (as in the case of micelles *-vide supra-*, assuming a first order reaction for each reactant):

$$v_T = v_c + v_i + v_d \quad (22)$$

$$v_T = k_{obs}[A_T][B_T] \quad (23)$$

$$v_d = k_d[A_d][B_d] \quad (24)$$

$$v_i = k_i[A_i][B_i] \quad (25)$$

$$v_c = k_c[A_c][B_c] \quad (26)$$

$$k_2[A_T][B_T] = k_d[A_d][B_d] + k_i[A_i][B_i] + k_c[A_c][B_c] \quad (27)$$

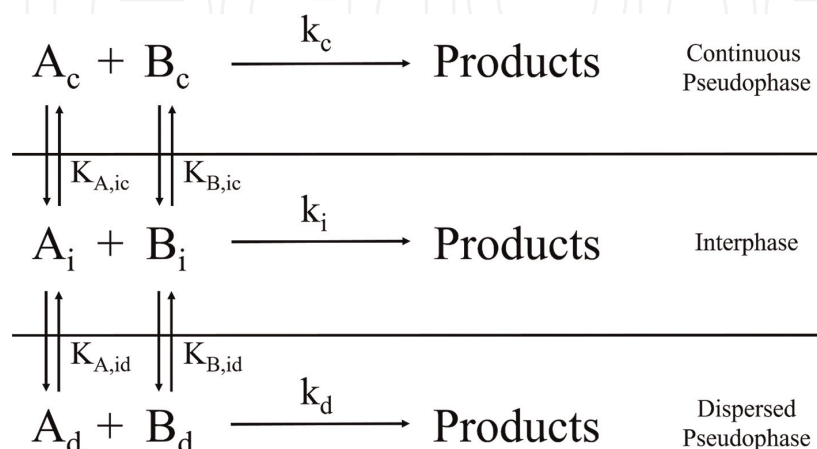


Figure 2.
Pseudophase model applied to microemulsions reaction media.

As quoted above, the mass balance on the three pseudophases and the consideration of the distribution coefficients between them allow us to establish the existing relationship between the total concentrations of the reactants and the concentrations in each of the pseudophases considered

$$[A]_T = [A]_c + [A]_i + [A]_d \quad (28)$$

$$[B]_T = [B]_c + [B]_i + [B]_d \quad (29)$$

$$K_{A,id} = \frac{[A]_i[Dis]}{[A]_d[D_n]} \quad (30)$$

$$K_{B,ic} = \frac{[B]_i[C]}{[B]_w[D_n]} \quad (31)$$

where $[C]$ is the continuous phase concentration and $[D_n]$ corresponds to the concentration of surfactant in the microemulsion. In the case of micelles, $[D_n]$ is obtained as $[D_n] = [D] - CMC$; but in the case of microemulsions, $CMC = 0$. It means that the surfactant concentration in the microemulsion is equal to the total surfactant concentration. Similar expressions can be obtained for the partition coefficients between the dispersed pseudophase and the interphase. In this case, $[Dis]$ corresponds to the dispersed phase concentration.

$$K_{A,id} = \frac{[A]_i[Dis]}{[A]_d[D_n]} \quad (32)$$

$$K_{B,id} = \frac{[B]_i[Dis]}{[B]_d[D_n]} \quad (33)$$

The previous equations (Eqs. (30)–(33)) can be rewritten using the characteristic parameters of microemulsions: z and w . Both of them are mole ratios related with the microemulsion geometry. The w ratio is the molar ratio between the disperse phase concentration and the surfactant concentration, and z is the molar ratio between continuous phase concentration and the surfactant concentration (Eqs. (34) and (35)). The w ratio is directly proportional to the droplet radius and z is inversely proportional to the number of microdroplets of the dispersed phase in the microemulsion.

$$w = \frac{[Dis]}{[D_n]} \quad (34)$$

$$z = \frac{[C]}{[D_n]} \quad (35)$$

Hence,

$$K_{A,id} = \frac{[A]_i}{[A]_d} w \quad (36)$$

$$K_{B,id} = \frac{[B]_i}{[B]_d} w \quad (37)$$

$$K_{A,ic} = \frac{[A]_i}{[A]_c} z \quad (38)$$

$$K_{B,ic} = \frac{[B]_i}{[B]_c} z \quad (39)$$

Using Eqs. (28), (29) and (36)–(39), the following equations can be written:

$$[A]_d = \frac{[A]_i w}{K_{A,id}} \quad (40)$$

$$[B]_d = \frac{[B]_i w}{K_{B,id}} \quad (41)$$

$$[A]_c = \frac{[A]_i z}{K_{A,ic}} \quad (42)$$

$$[B]_c = \frac{[B]_i z}{K_{B,ic}} \quad (43)$$

$$[A]_T = [A]_i + \frac{[A]_i w}{K_{A,id}} + \frac{[A]_i z}{K_{A,ic}} \quad (44)$$

$$[B]_T = [B]_i + \frac{[B]_i w}{K_{B,id}} + \frac{[B]_i z}{K_{B,ic}} \quad (45)$$

$$[A]_i = \frac{[A]_T}{1 + \left(\frac{w}{K_{A,id}}\right) + \left(\frac{z}{K_{A,ic}}\right)} \quad (46)$$

$$[B]_i = \frac{[B]_T}{1 + \left(\frac{w}{K_{B,id}}\right) + \left(\frac{z}{K_{B,ic}}\right)} \quad (47)$$

$$[A]_d = \left(\frac{w}{K_{A,id}}\right) \frac{[A]_T}{1 + \left(\frac{w}{K_{A,id}}\right) + \left(\frac{z}{K_{A,ic}}\right)} \quad (48)$$

$$[B]_d = \left(\frac{w}{K_{B,id}}\right) \frac{[B]_T}{1 + \left(\frac{w}{K_{B,id}}\right) + \left(\frac{z}{K_{B,ic}}\right)} \quad (49)$$

$$[A]_c = \left(\frac{z}{K_{A,ic}}\right) \frac{[A]_T}{1 + \left(\frac{w}{K_{A,id}}\right) + \left(\frac{z}{K_{A,ic}}\right)} \quad (50)$$

$$[B]_c = \left(\frac{z}{K_{B,ic}}\right) \frac{[B]_T}{1 + \left(\frac{w}{K_{B,id}}\right) + \left(\frac{z}{K_{B,ic}}\right)} \quad (51)$$

Then, using Eqs. (46)–(51), the following expressions are obtained:

$$\begin{aligned} k_2[A_T][B_T] &= k_d \left(\frac{w}{K_{A,id}}\right) \frac{[A]_T}{1 + \left(\frac{w}{K_{A,id}}\right) + \left(\frac{z}{K_{A,ic}}\right)} \left(\frac{w}{K_{B,id}}\right) \frac{[B]_T}{1 + \left(\frac{w}{K_{B,id}}\right) + \left(\frac{z}{K_{B,ic}}\right)} + \\ &+ k_i \frac{[A]_T}{1 + \left(\frac{w}{K_{A,id}}\right) + \left(\frac{z}{K_{A,ic}}\right)} \frac{[B]_T}{1 + \left(\frac{w}{K_{B,id}}\right) + \left(\frac{z}{K_{B,ic}}\right)} + \\ &+ k_c \left(\frac{z}{K_{A,ic}}\right) \frac{[A]_T}{1 + \left(\frac{w}{K_{A,id}}\right) + \left(\frac{z}{K_{A,ic}}\right)} \left(\frac{z}{K_{B,ic}}\right) \frac{[B]_T}{1 + \left(\frac{w}{K_{B,id}}\right) + \left(\frac{z}{K_{B,ic}}\right)} \quad (52) \end{aligned}$$

$$\begin{aligned}
 k_2 = & k_d \left(\frac{w}{K_{A,id}} \right) \frac{1}{1 + \left(\frac{w}{K_{A,id}} \right) + \left(\frac{z}{K_{A,ic}} \right)} \left(\frac{w}{K_{B,id}} \right) \frac{1}{1 + \left(\frac{w}{K_{B,id}} \right) + \left(\frac{z}{K_{B,ic}} \right)} + \\
 & + k_i \frac{1}{1 + \left(\frac{w}{K_{A,id}} \right) + \left(\frac{z}{K_{A,ic}} \right)} \frac{1}{1 + \left(\frac{w}{K_{B,id}} \right) + \left(\frac{z}{K_{B,ic}} \right)} + \\
 & + k_c \left(\frac{z}{K_{A,ic}} \right) \frac{1}{1 + \left(\frac{w}{K_{A,id}} \right) + \left(\frac{z}{K_{A,ic}} \right)} \left(\frac{z}{K_{B,ic}} \right) \frac{1}{1 + \left(\frac{w}{K_{B,id}} \right) + \left(\frac{z}{K_{B,ic}} \right)} \quad (53)
 \end{aligned}$$

$$\begin{aligned}
 k_2 = & k_d \left(\frac{w^2}{K_{A,id}K_{B,id}} \right) \frac{1}{1 + \left(\frac{w}{K_{A,id}} \right) + \left(\frac{z}{K_{A,ic}} \right)} \frac{1}{1 + \left(\frac{w}{K_{B,id}} \right) + \left(\frac{z}{K_{B,ic}} \right)} + \\
 & + k_i \frac{1}{1 + \left(\frac{w}{K_{A,id}} \right) + \left(\frac{z}{K_{A,ic}} \right)} \frac{1}{1 + \left(\frac{w}{K_{B,id}} \right) + \left(\frac{z}{K_{B,ic}} \right)} + \\
 & + k_c \left(\frac{z^2}{K_{A,ic}K_{B,ic}} \right) \frac{1}{1 + \left(\frac{w}{K_{A,id}} \right) + \left(\frac{z}{K_{A,ic}} \right)} \frac{1}{1 + \left(\frac{w}{K_{B,id}} \right) + \left(\frac{z}{K_{B,ic}} \right)} \quad (54)
 \end{aligned}$$

$$\begin{aligned}
 k_2 = & \frac{K_{A,ic}K_{B,ic}w^2k_d}{(K_{A,id}K_{A,ic} + K_{A,ic}w + K_{A,id}z)(K_{B,id}K_{B,ic} + K_{B,ic}w + K_{B,id}z)} + \\
 & + \frac{K_{A,id}K_{A,ic}K_{B,id}K_{B,ic}k_i}{(K_{A,id}K_{A,ic} + K_{A,ic}w + K_{A,id}z)(K_{B,id}K_{B,ic} + K_{B,ic}w + K_{B,id}z)} + \\
 & + \frac{K_{A,id}K_{B,id}z^2k_c}{(K_{A,id}K_{A,ic} + K_{A,ic}w + K_{A,id}z)(K_{B,id}K_{B,ic} + K_{B,ic}w + K_{B,id}z)} \quad (55)
 \end{aligned}$$

$$k_2 = \frac{K_{A,ic}K_{B,ic}w^2k_d + K_{A,id}K_{A,ic}K_{B,id}K_{B,ic}k_i + K_{A,id}K_{B,id}z^2k_c}{(K_{A,id}K_{A,ic} + K_{A,ic}w + K_{A,id}z)(K_{B,id}K_{B,ic} + K_{B,ic}w + K_{B,id}z)} \quad (56)$$

This expression (Eq. (56)) can be simplified considering pseudo-first order conditions, and, of course, taking into account the reagents partitions and the loci of reaction (see **Table 1**).

Finally, to compare the obtained results, as quoted above for micelles model - *vide supra* -, the rate constant values must be corrected taking into account each pseudophase molar volume because the pseudophase model considers that each pseudophase is evenly distributed in the total microemulsion volume [47].

4. Conclusions

The presented model is capable of modelling, as shown in **Table 1**, all the possible circumstances that can occur when the microemulsion is used as a chemical nanoreactor. In all the cases, the adjustment of the experimental data to the model is satisfactory, which shows us that despite its simplicity it presents a great versatility.

We must also indicate that it has not only been applied to micellar systems and microemulsions but also, with satisfactory results, to kinetic processes in other colloidal aggregates such as vesicles [61, 62].

Reaction		A			B			Reaction Loci			Ref.
		Partition			Partition			Loci			
		D	I	C	D	I	C	D	I	C	
Hydrolysis	Nitrophenyl Acetate (A) + OH ⁻ (B)										[56]
	Cristal Violet (A) + OH ⁻ (B)										[57]
	Malachite Green (A) + OH ⁻ (B)										[57]
	Sodium nitroprusside (A) + OH ⁻ (B)										[58]
	Carbofuran (A) + OH ⁻ (B)										[46]
	3-hydroxy-carbofuran (A) + OH ⁻ (B)										[46]
	3-keto-carbofuran (A) + OH ⁻ (B)										[46]
Nitrosation	Piperazine (A) + N-Methyl-N-nitroso-p-toluene sulfonamide (B)										[43]
	N-Methyl-benzyl amine (A) + N-Methyl-N-nitroso-p-toluene sulfonamide (B)										[43]
	Methyl-ethyl amine (A) + N-Methyl-N-nitroso-p-toluene sulfonamide (B)										[48]
	Methyl-butyl amine (A) + N-Methyl-N-nitroso-p-toluene sulfonamide (B)										[48]
	Methyl-hexyl amine (A) + N-Methyl-N-nitroso-p-toluene sulfonamide (B)										[48]
	Methyl-octyl amine (A) + N-Methyl-N-nitroso-p-toluene sulfonamide (B)										[48]
	Methyl-dodecyl amine (A) + N-Methyl-N-nitroso-p-toluene sulfonamide (B)										[48]
	N-Methyl-benzyl amine (A) + Ethoxy-ethyl nitrite (B)										[44]
	N-Methyl-benzyl amine (A) + Bromo-ethyl nitrite (B)										[44]
	Piperidine (A) + N-Methyl-N-nitroso-p-toluene sulfonamide (B)										[43]
Nitrosation	Dimethylamine (A) + N-Methyl-N-nitroso-p-toluene sulfonamide (B)										[43]
	Morphonile (A) + N-Methyl-N-nitroso-p-toluene sulfonamide (B)										[43]
	Pyrrolidine (A) + N-Methyl-N-nitroso-p-toluene sulfonamide (B)										[43]
	Piperazine (A) + Ethoxy-ethyl nitrite (B)										[44]
	Piperazine (A) + Bromo-ethyl nitrite (B)										[44]
	Morpholine (A) + Ethoxy-ethyl nitrite (B)										[44]
	Morpholine (A) + Bromo-ethyl nitrite (B)										[44]
Aminolysis	Sarcosine (A) + Nitrophenyl Acetate (B)										[49]
	Piperazine (A) + Nitrophenyl Acetate (B)										[49]
	Glycine (A) + Nitrophenyl Acetate (B)										[50]
	N-decyl amine (A) + + Nitrophenyl Acetate (B)										[49]
	N-methyl-benzyl amine (A) + Nitrophenyl Acetate (B)										[51]

Reaction		A			B			Reaction Loci			Ref.
		Partition			Partition						
		D	I	C	D	I	C	D	I	C	
	Morpholine (A) + Nitrophenyl Acetate (B)										[59]
	N-butylamine (A) + Nitrophenyl caprate (B)										[60]
Michael addition	Piperazine (A) + N-ethylmaleimide (B)										[51]
Solvólisis	Benzoyl chloride (A) + H ₂ O (B)										[53]
	4-Methoxy-benzoyl chloride (A) + H ₂ O (B)										[53]
	Diphenylmethyl chloride (A) + H ₂ O (B)										[53]

D and C correspond to the dispersed or the continuous phase, respectively, I denotes the surfactant film. Reactions in w/o microemulsions of AOT/isooctane/water.

Table 1.
 Examples of reactions in microemulsions satisfactorily modelled with the pseudophase model.

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This chapter is dedicated to Professor Julio Casado Linarejos (*sit tibi terra levis*) who taught us chemistry and, what really matters, to be better people.

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