Colloids and Surfaces A: Physicochem. Eng. Aspects 324 (2008) 222–227

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Self-motion of a phenanthroline disk on divalent metal ion aqueous solutions coupled with complex formation

Satoshi Nakata[a,b,*], Yoshie Arima[b]

[a] Graduate School of Science, Hiroshima University, Kagamiyama 1-3-1, Higashi-Hiroshima 739-8526, Japan
[b] Department of Chemistry, Nara University of Education, Takabatake-cho, Nara 630 8528, Japan

ARTICLE INFO

Article history:
Received 19 November 2007
Received in revised form 5 April 2008
Accepted 10 April 2008
Available online 18 April 2008

Keywords:
Self-motion
Oscillation
Nonequilibrium
Air/water interface
Driving force

ABSTRACT

The self-motion of a 1,10-phenanthroline disk on divalent metal ion aqueous solutions was investigated as a simple autonomous motor coupled with complex formation. The characteristic features of motion (continuous and oscillatory motion) and their concentration regions differed among metal ions, and the frequency of oscillatory motion depended on the temperature of the aqueous solution. The nature of the characteristic motion is discussed in relation to the stability constant of complex formation between phenanthroline and a metal ion, and the difference in surface tension between phenanthroline and its metal complex as the driving force.

1. Introduction

Various types of autonomous motors have been investigated at immiscible interfaces [1–19] not only to develop an inorganic miniature motor but also to better understand the mechanism of motion of microscopic organisms such as bacteria. These motors can move by obtaining driving force, which is induced by spatial anisotropy of their systems or by chemical nonequilibrium, e.g., a difference in the interfacial tension around a liquid droplet [1-9], bubble generation by the decomposition of H_2O_2 [10,11], a spatial gradient in the hydrophobicity of a solid surface [12–16], application of an electronic field [17], and change in the volume of a gel [18,19].

We have been studying the vector process and mode changes in the fragments of camphor and its derivatives as a simple autonomous motor that can adapt to internal (mass, shape, and chemical structure of the mobile fragment) [20–23] and external (shape and size of the cell, and chemical property of the aqueous phase) conditions [24–26] under nonequilibrium and anisotropic environments. The essential features of this self-motion can be reproduced by a computer simulation based on the equation of motion coupled with reaction-diffusion equations and surface tension as the driving force [20–22,24,26].

We have recently reported the characteristic motion of a 1,10-phenanthroline disk on an aqueous phase with different concentrations of $FeSO_4$ as a complex-formation system [23]. However, the relationship between the kinetics of complex formation and motion has not yet been clarified. In this study, a 1,10-phenanthroline disk on divalent metal ion solutions was investigated with regard to complex formation. The concentration regions for characteristic motions (continuous and oscillatory motion) differed among these metal ions. The frequency of oscillatory motion increased with an increase in the temperature of the aqueous solution. The mechanism of these characteristic motions is discussed in relation to the surface tension on the 1,10-phenanthroline disk and the metal complex solution as the driving force, and the stability constant of the metal complex.

2. Experimental

All chemicals were of analytical grade and were used without further purification. Water was first distilled and then purified with a Millipore Milli-Q filtering system (pH of the obtained water: 6.3, resistance: >20 MΩ). $FeSO_4$, $CoSO_4$, $MnSO_4$, $ZnSO_4$, $MgSO_4$, and $CaCl_2$ aqueous solutions were used as aqueous phases with divalent metal ions (M^{2+}; M = Fe, Co, Mn, Zn, Mg, or Ca). A solid disk (diameter: 3 mm, thickness: 1 mm, mass: 7 mg) of 1,10-phenanthroline was prepared using a pellet die set. Twenty milliliters of the aqueous solution of different concentrations was poured into a glass Petri dish (inner diameter: 75 mm) as an aqueous phase (depth:

---

* Corresponding author. Tel.: +81 82 424 7409; fax: +81 82 424 7409.
E-mail address: nakatas@hiroshima-u.ac.jp (S. Nakata).

0927-7757/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.colsurfa.2008.04.021

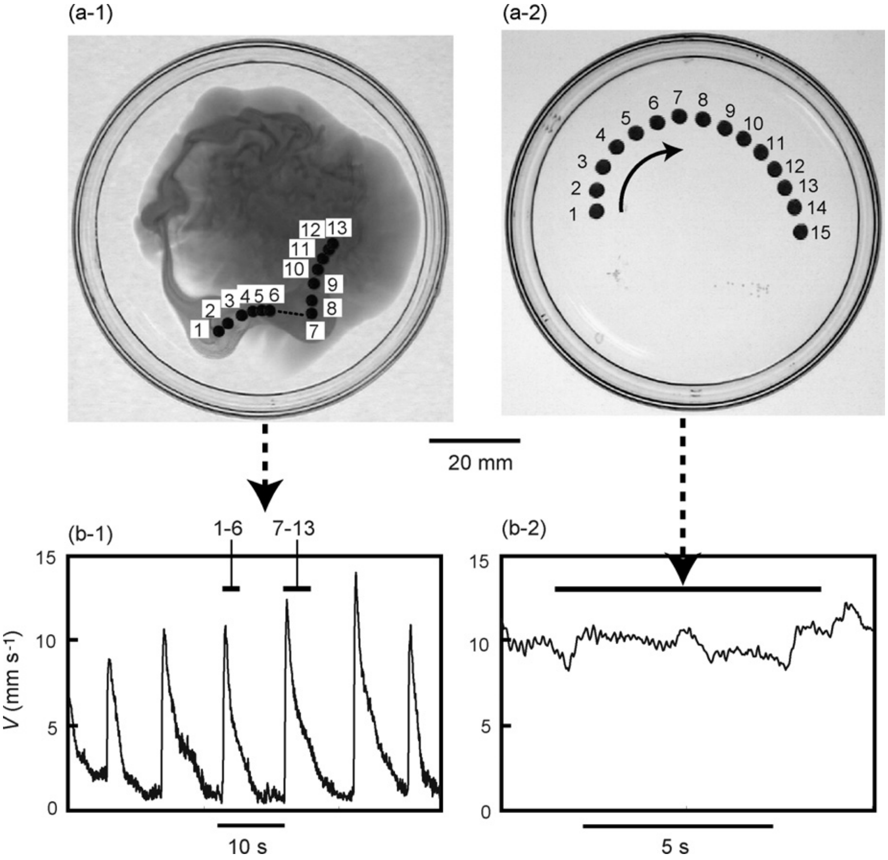

Fig. 1. (a) Snapshots of the motion (top view) and (b) time-variation of the speed of a 1,10-phenanthroline disk on (1) $FeSO_4$ and (2) $MnSO_4$ aqueous solutions at 5 mM. Time intervals in (a) were 0.5 s for 1–6, 7–13 in (1) and 1–15 in (2), and 7.1 s between 6 and 7 in (1). The horizontal bars in (b-1) and (b-2) correspond to the data in (a-1) and (a-2), respectively. The resting times for 1 and 13 in the intermittent motion in (a-1) were 3 s.

4.5 mm). The disk was carefully dropped on the aqueous phase from a few millimeter in height, and it floated from the start. Except for the experiments on temperature-dependence, the water cell was adjusted to 293 ± 1 K with a thermoplate (TP-80, AS ONE Co. Ltd., Japan). Movement of the disk was monitored with a digital video camera (SONY DCR-VX700, minimum time-resolution: 1/30 s) and then analyzed by an image-processing system (Himawari, Library Inc., Japan). The surface tension at the air–water interface was measured with a surface tensiometer (CBVP-A3, Kyowa Interface Science Co., Ltd., Saitama, Japan), and a platinum plate (length, 23.85 mm; thickness, 0.15 mm) was used as the Wilhelmy plate. The speed of the motion (V) was obtained as $\sqrt{v_x^2 + v_y^2}$, where v_x and v_y were the velocities on the x- and y-directions, and the average speed (V_{av}) was obtained as the average value of V for 1 min after the disk was dropped on the aqueous phase except for collision with the Petri dish, and the reproducibility was examined for at least 4 times.

3. Results

Fig. 1 shows (a) snapshots of the motion of a 1,10-phenanthroline disk on (1) 5 mM $FeSO_4$ and (2) 5 mM $MnSO_4$ aqueous solutions at 293 K, and (b) the time-variation of the speed in Fig. 1a. With Fe^{2+} (Fig. 1a-1), oscillatory motion, i.e., repetition among rapid acceleration → slow deceleration → rest, was maintained for ca. 5 min. The amplitude and period of this oscillatory motion were $10.2 \pm 1.7\ \mathrm{mm\,s^{-1}}$ and 8.7 ± 0.8 s, respectively. The density of a red-colored layer around the disk increased with time in the resting state, and then the disk rapidly accelerated to move to another location. With Mn^{2+}, continuous motion at $10.0 \pm 1.1\ \mathrm{mm\,s^{-1}}$ was maintained for ca. 3 min. It was actually difficult to observe the layer along the trajectory as seen in Fig.1-2, but the color of the solution became pale yellow after several trajectories. The shape of the disk was almost maintained for the duration of 3 min observation.

Fig. 2 shows a phase diagram of the mode of 1,10-phenanthroline motion that depended on the concentrations of different aqueous solutions ($FeSO_4$, $CoSO_4$, $MnSO_4$, $ZnSO_4$, $MgSO_4$, $CaCl_2$). Here, repetition between rapid acceleration and slow deceleration and a constant speed motion were categorized by oscillatory motion (O) and continuous motion (C). If the concentration region of the

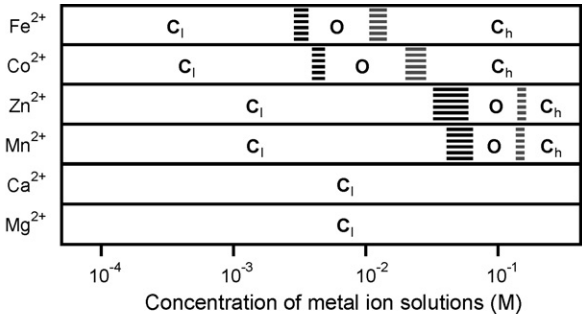

Fig. 2. Phase diagram of the mode of motion of a 1,10-phenanthroline disk depending on the concentration (C) of divalent metal ions aqueous solutions ($FeSO_4$, $CoSO_4$, $ZnSO_4$, $MnSO_4$, $CaCl_2$, and $MgSO_4$). C_l, O, and C_h denote continuous motion at the lower concentration region, oscillatory motion, and continuous motion at the higher concentration region, respectively. The thickness of the gray lines corresponds to the regions of ambiguity at the boundaries between C_l and O, and between O and C_h. For $CaCl_2$ and $MgSO_4$, the continuous motion is denoted as C since no oscillatory motion was observed.