Cycloalkane-based Thermomorphic Electrochemical Reaction System Composed of Nitrile-solvents

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Combination of cyclohexane and nitriles in the presence of electrolytes were found to realize an effective, biphasic thermomorphic system that enable practical applications of electrochemical reactions featuring high current density followed by rapid product/electrolyte separation.

Key Words : Electrochemical Reaction, Thermomorphic, Cyclohexane, Biphasic, Nitrile Solvent

1 Introduction

In the electrochemical reaction process, electrolytes are generally essential for achieving electron transfer on electrodes, but separation of products from the electrolyte solution is always required. To reduce the unhandy process for the product isolation, novel methodologies have been extensively developed for electrochemical reactions.¹⁾ Recently, we found that cyclohexane with typical polar organic solvents play important role in the construction of thermomorphic biphasic system, that reversibly form monophasic solutions just by heating the solutions. The liquid-liquid biphasic thermomorphic process, in which a reagent or a catalyst is designed as a residue in one of the liquid phases and as a product in the other liquid phase, can be a promising approach for a commercial application of chemical reactions with high selectivity, efficiency, and ease of handling for the separation of solutes.

The thermo-sensitive liquid-liquid separation system composed of typical organic solvents of different polarity might allow for extremely efficient reactions,²⁾ for example, by the association of apolar products and polar substrates or electrolytes in a one-phase solution, which could be spatially separated after the completion of electrochemical reactions (Fig. 1).

It is well known that nitrile solvents such as acetonitrile and propionitrile play important roles in the electrochemical reactions because of their solvency of electrolytes and organic compounds, high dielectric constant and ease of solvent-removing by evaporation. Numerous applications in anodic and cathodic organic reactions have therefore been reported.³⁻⁸⁾ Herein is a report of the phase-separable electrolyte solutions constructed by cycloalkane and nitriles to realize the aimed homogeneously miscible biphasic system featuring high current density and rapid product/electrolyte separation after the completion of the electrolysis.⁹⁾

2 Experimental

2.1 Measurement of cyclic voltammograms of thermomorphic biphasic electrolyte solutions

Cyclic voltammograms were measured by using a three electrode cell. Pt wires (10 mm × 0.5 mm diameter) were used as the working electrode and the counter electrode, respectively. The electrochemical experiments were performed using an electrochemical measuring system (AC DC cyclic polarograph P-900, Yanaco). The scan rate of the cyclic voltammetry was 100 mV/sec. Potentials were recorded vs. Ag/AgCl reference electrode. Cyclic voltammograms of 3,4,5-trioctadecyloxybenzylalcohol **1** (2.0 mM) was measured in a lithium perchlorate (1000 mM) in a mixture of cyclohexane, acetonitrile and propionitrile (1:1:4 v/v/v) in a homogeneous phase and each of separated phase of biphasic solution at 40 °C, respectively.

2.2 Physical properties of compound **1**

White powder, ¹H-NMR (CDCl₃) δ 6.54 (s, 2H), 4.58 (d, *J* = 5.1 Hz, 2H), 3.96 (t, *J* = 6.6 Hz, 4H), 3.93 (t, *J* = 6.6 Hz, 2H), 1.82-1.70 (m, 6H), 1.50-1.41 (m, 6H), 1.38-1.20 (m, 84H), 0.88 (t, *J* = 6.6 Hz, 9H); ¹³C-NMR (CDCl₃) δ 153.2, 137.4, 136.0, 105.2, 73.4, 69.1, 65.7, 32.0, 30.4, 29.8, 29.7, 29.5, 26.2, 22.8, 14.2. MALDY TOF (pos) calcd. for C₆₁H₁₁₆O₄[M + Na]⁺ 935, found 935.

Fig. 1 Reaction and separation process using thermomorphic electrochemical reaction system composed of cyclohexane and electrolyte solutions.

3 Results and Discussion

Initially, the phase-separable electrolyte solution systems were constructed by combinations of cyclohexane and nitrile solvents. Figure 2 shows the phase transition temperature of the solvent mixture of cyclohexane - propionitrile in the absence and presence of typical electrolytes, lithium perchlorate or sodium *p*-trifluoromethanesulfonate.¹⁰⁾ It is noteworthy that the separation and the immixing of cyclohexane can be achieved just by a moderate thermal control in the practical range of 10 °C and 70 °C even in the presence of proper concentrations of usual electrolytes.

In the combination of acetonitrile and propionitrile as the nitrile phase, the phase transition temperature of cyclohexane - nitriles (1:1 v/v) solvent was linearly changed depending on the ratio of the nitriles even in the presence of lithium perchlorate as the electrolyte (Fig. 3). It was further revealed that diminishing the ratio of cyclohexane in the three solvent systems of

Fig. 2 Effect of concentration of electrolytes on the phase transition temperature of cyclohexane / propionitrile (1:1 v/v) biphasic thermomorphically solution.

Fig. 3 Effect of concentration of the electrolyte and polar solvent composition on the phase transition temperature of cyclohexane / nitrile solvent (1:1 v/v) thermomorphically biphasic solution.

cyclohexane / acetonitrile / propionitrile effectively assisted to construct higher concentrated electrolyte solution with the thermomorphically property (Fig. 4).

For example, by using a solvent mixture of cyclohexane / acetonitrile / propionitrile (1:1:4 v/v/v), even 1000 mM of lithium perchlorate electrolyte solution formed monophasic solution above 34 °C. After cooling back to below 34 °C, the phase - separation took place immediately. From the separated lower layer, more than 99% of lithium perchlorate was recovered. These results suggested that the thermomorphically action can be achieved in wide range of temperature, solvent composition and electrolyte concentration.

Finally, in order to show the thermomorphically characterization of the electrolyte solution, Fig. 5 shows cyclic voltammograms of 3,4,5-tris-octadecyloxy benzylalcohol **1** as a typical model compound of hydrophobic substrates.¹¹⁾ In the electrochemical process, we introduced the 1000 mM lithium perchlorate in cyclohexane / acetonitrile / propionitrile (1:1:4 v/v/v) electrolyte solution that reversibly formed biphasic and monophasic solution. In its monophasic solution at 40 °C, oxidation current of **1** was clearly observed. After cooling back to 20 °C, the solution was separated to form the biphasic solution. Each separated phase was then applied for cyclic voltammetry measurement at 40 °C, respectively. Although compound **1** was almost completely partitioned in the cyclohexane (upper) layer, no significant oxidation current was observed because of the absence of electrolyte and polar solvents. Even the lower layer (nitriles

Fig. 4 Effect of concentration of the electrolyte and polar solvent composition on the phase transition temperature of cyclohexane / nitrile solvent (1:5 v/v) thermomorphically biphasic solution.

Fig. 5 Cyclic voltammograms of 3,4,5-tris-octadecyloxybenzyl alcohol (2.0 mM) in the electrolyte solution composed of lithium perchlorate (1000 mM), cyclohexane, propionitrile and acetonitrile (1:4:1 v/v/v). Cyclic voltammograms were measured for cyclohexane layer of the biphasic solution at 40 °C, propionitrile layer of the biphasic solution at 40 °C, monophasic electrolyte solution at 40 °C, respectively.

and electrolytes) gave just a slight oxidation current because more than 99% of **1** was partitioned in the cyclohexane layer.¹²⁾ It was consistent with the absence of the electrolytic substrate in nitrile phase. This result indicated that the present thermomorphic electrolyte solution composed of cyclohexane-nitrile solution system efficiently worked reversibly in the separation and immixing of the electrolytic substrates and electrolytes.

4 Conclusion

In conclusion, a biphasic, thermomorphic liquid-liquid separation systems have been constructed for the thermomorphic biphasic system by using cyclohexane and nitrile solvents. It is noteworthy that the regulation of the separation and the immixing of solutes can be

achieved by a moderate thermal control in the practical range of 10 °C and 70 °C. Furthermore, substrates and products can be easily isolated from cyclohexane layer to complement existing electrochemical process, offering advantages with regard to compound isolation and characterization. Since those polar media, acetonitrile and propionitrile have been widely used for electro-organic reactions with varied electrolytes and reagents, the extensive electrochemical chemical applications can be also assured with the flexibly controllable temperatures and upper/lower layer ratios.

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