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Abstract

Many advantages of supercritical fluids come from their interesting or unusual properties which liquid solvents and gas carriers do not possess. Such properties and possible applications of supercritical fluids are reviewed. As these fluids never condense at above their critical temperatures, supercritical drying is useful to prepare dry-gel. The solubility and other important parameters as a solvent can be adjusted continuously. Supercritical fluids show advantages as solvents for extraction, coating or chemical reactions thanks to these properties. Supercritical water shows a high organic matter solubility and a strong hydrolyzing ability. Supercritical water is expected to be useful in waste treatment. Although they show high solubility solutes and molecular catalyses, solvent molecules under supercritical conditions gently solvate solute molecules and have little influence on the activities of the solutes and catalysts. This property would be attributed to the local density fluctuations around each molecule due to high molecular mobility. The fluctuations in the supercritical fluids would produce heterogeneity that would provide novel chemical reactions with molecular catalyses, heterogenous solid catalyses, enzymes or solid adsorbents.

Keywords

Supercritical fluid, Supercritical water, Solubility, Solvation, Waste treatment, Coating, Organic reaction

1. Introduction

There has been rising concern in recent years over supercritical fluids for organic waste treatment and other applications. The discovery of the presence of critical point dates back to 1822.¹⁾ The temperature and pressure beyond the critical point are in the supercritical state. As indicated in **Table 1**,²⁾ critical points are often in high pressure. Therefore, a highpressure test facility (high temperature and high pressure depending on the case) is required for a systematic study of fluids in the near- or supercritical state. This might have been the main reason why studies in this field were comparatively few until recently.

Research on supercritical fluids and the

applications development reached the initial peak during the period from the second half of the 1960s to the 1970s followed by the secondary peak about 15 years later. The initial peak was for the separation and extraction technique as represented by the extraction of caffeine from coffee beans. Since the practical application in Germany in 1978, a number of practical plants have been in operation. The secondary peak concerns decomposition of organic (waste) substances, which started when the U.S. Department of Defense began studies on using supercritical water as a means for completely decomposing chemical weapons. And the tertiary peak is about to come with mounting interest in the possible development of new material program.

2. What are supercritical fluids?

Supercritical fluids are described as "fluids in the temperature and pressure state of over the critical point" as shown in **Fig. 1**. This definition, however, is not sufficient and not providing a good explanation for understanding them.

For persons handling them, they are not different from "high-pressure gas." They are not distinguishable from gas because they are in a noncondensed state, which disables handling without using a sealed container. In other words, they may be considered to be gas that does not transform to the liquid phase with discontinuous change in the density when the pressure rises under a constant temperature. Substances change their phase depending on the balance of forces between the force to form the liquid or solid phase by condensation under inter-molecular attraction and

Table 1 Children points of typical solvents	Table 1	Critical	points	of typical	l solvents
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<u>Compounds</u>	Critical Temperature <u>(°C)</u>	Critical Pressure (atm)	Critical Density (g/ml)
Carbon Dioxide	31.3	72.9	0.448
Ammonia	132.4	112.5	0.235
Water	374.15	218.3	0.315
Nitrous Oxide	36.5	71.7	0.45
Xenon	16.6	57.6	0.118
Krypton	-63.8	54.3	0.091
Methane	-82.1	45.8	0.2
Ethane	32.28	48.1	0.203
Ethylene	9.21	49.7	0.218
Propane	96.67	41.9	0.217
Pentane	196.6	33.3	0.232
Methanol	240.5	78.9	0.272
Ethanol	243.0	63.0	0.276
Isopropanol	235.3	47.0	0.273
Isobutanol	275.0	42.4	0.272
Chlorotrifluoromethane	e 28.0	38.7	0.579
Monofluoromethane	44.6	58.0	0.3
Cycrohexanol	356.0	38.0	0.273

the force to make free thermal movement. At high temperature, however, the force of particles to move about freely exceeds that of the inter-molecular force if the inter-molecular distance is minimized under pressure. The supercritical state is thus reached where no condensed phase is produced.

When the pressure rises, the gas density becomes higher, however. The inter-molecular distance then becomes shorter, making it impossible to disregard the effects of inter-molecular action. In other words, when viewed from the molecules inside or from the microscopic standpoint, they are in a state close to liquid. If the molecular movement can be directly observed, it is assumed to be as violent as in the gaseous state. When observed in a still photograph, it may resemble that of the liquid. This is the reason why "supercritical is the intermediate state between gas and liquid."

3. Characteristics of supercritical fluids

"Supercritical fluids in the intermediate state between gas and liquid have high diffusivity comparable with a gas and high solubility as a liquid." This is the popular description of supercritical fluids. This expression may mislead us to expect that supercritical fluids are wonderful



Fig. 1 Phase (Pressure-Temperature) diagram for CO₂.

solvents that make two mutually opposed properties compatible. As shown in **Fig. 2**, solubility rises as the density becomes higher under pressure, simultaneously delaying diffusion, however. In addition, it is a fact that solubility is lower than liquid in a simple system, while the diffusion is slower than gas.

Therefore, general descriptions of characteristics of supercritical fluids are limited. Their characteristics in use differ by each field of application to be stated later. They may be listed as follows:

(1) Generate no liquid (condensed phase) under pressure change or on solid surfaces.

(2) Able to control density (solubility), polarity, viscosity and other properties of the fluids continuously and over a wide range.

(3) Can change the property sharply with very little change in pressure as shown in **Fig. 3**, particularly in the vicinity of the critical temperature and pressure.³⁾ This suggests that largely different state of property can be simultaneously realized near the critical point with the addition of solutes, disturbances on the solid surfaces and fluctuations of the fluids.

(4) Molecular association by inter-molecular actions or the formation of solvation structure of solute molecules is local and short-lived, hence not inhibiting reactions.

(5) Gaseous substance under ordinary temperature and atmospheric pressure such as carbon dioxide can

be easily removed after completing the reaction by returning it to the atmospheric pressure.

In addition to these general characteristics, in the case of supercritical water, properties specific to the water expand the sphere of possible application, which will be described in detail in **Section 5**.

4. Application as extractant

4.1 Basic principle

Solubility of supercritical fluids to various solutes is not necessarily high compared with liquid. The characteristics of using the supercritical fluids for extractants are shown in Fig. 2, and their solubility can be continually changed to a large degree. Moreover, since they do not form condensed phase, they can infiltrate into very fine gaps of solids under high pressure. These properties enable them to solve a target substance efficiently from solids to be deposited outside.

Large change in the solubility is the main reason why supercritical fluids are used for extractants. To realize efficient extraction, increase of solubility itself is desirous, too. One of the effective means to do this is to add a component for increasing the solubility. This component is called an entrainer or modifier. Generally, several percent of a component that reacts strongly with the solute and which is soluble to the basic solvent is added. Such an additive not only increases solubility, it also improves the separation characteristics by controlling the solubility of the solvent. A lot of the





500°C 400°C 300°C 50 Pressure/MPa 40 30 Saturation curve 20 Critical Point 10 Tc=374°C 22 1MP 0 0 0.4 0.6 0.2 0.8

Density/g \cdot cc⁻¹

research and development done on separation and extraction concern this entrainer (additive). Still finer separation will become possible by combining the adsorptive phenomenon.⁵⁾

4.2 Applications examples

Measurement of solubility of substance to the supercritical fluids was conducted about 50 years after the discovery of the above-mentioned supercritical state. It was recognized that they have dissolving power close to that of the liquid. Research has been fully conducted since the extraction of caffeine from coffee beans was patented in 1964.⁶⁰ Since the practical application in Germany in 1978, commercial plants for extracting hop extract, perfume, tobacco nicotine, spices or medicine have been constructed.¹⁾

Operation of those plants requires high pressure $(130^{\circ}C, 35 \text{ MPa} \text{ for processing coffee beans or extracting perfume}), thus limiting the application to foods and other high-value added products. A trial conducted circa 1990 indicated that a perfume extraction plant⁷⁾ with an annual production of about 800 tons required an equipment cost of some $3 million and the processing cost of $1.10 (personnel cost of $0.43 included) per kilogram while a decaffein plant for coffee beans with an annual production of about 200,000 tons⁸⁾ required an equipment cost of $0.35 (personnel cost of $0.19 included) per kilogram. Reduction of production cost through continuous processing, etc. is yet to be developed.$

As thus far stated, research and development concerning separation and extraction have continued. In Japan, application was made for about 80 patents during the 25 years from 1970 to 1995. Most of the applications, however, state the novelty of the subject substance with only few stating development beyond the content described in the basic principle stated in the preceding subsection. These applications related to foods are characterized by the removal of grease and oil⁹⁾ from grain, cholesterol¹⁰⁾ from eggs, residual agricultural chemicals¹¹⁾ and other unnecessary or hazardous substance from foods. Also separation and extraction of neutral fat and phospholipid other fine separation¹²⁾ were attempted. In these separations, a combination was made with the above-mentioned absorbents and other separation method.⁵⁾ A method of setting the extraction condition on multiple stages was also added.¹²⁾

Around 1990, there were concentrated patent applications concerning the removal of organic components, the molding binders, from ceramic injection moldings. These applications searched for extract conditions¹³⁾ without deforming the moldings at a temperature below the softening point of the resin. Many of the applications examined extraction under high pressure of about 35 MPa at which the density of carbon dioxide, which is the dissolving power, becomes saturated, while the temperature was near the comparatively low critical temperature. However, as stated earlier, since the dissolving power of supercritical fluids is not as strong as that of organic solvent liquids, they are not suitable for removing binders having high molecular weight but for removing paraffin oil and other substance of low molecular weight.¹⁴⁾

In recent years, the number of cases directly associated with the composition of material¹⁵⁾ with the aim of improving the characteristics by removing the component of low molecular weight from the organic polymer has increased remarkably. Also there are a number of applications reflecting the rising concern of environmental problems. Reports have been made on the examination of hazardous substances (organic chlorine, organic mercury, PCB, insecticide, herbicide, etc.) from soil,¹⁶⁾ waste¹⁷⁾ or animal or plant tissues,¹⁸⁾ and their removal conditions. In most cases, these cases provide the basic extraction data using carbon dioxide as the base solvent and alcohol and/or water as the entrainer.

Separation and extraction remain the central field of application for supercritical fluids, where the basic data are most richly accumulated. Application as a cleaning solvent in semiconductor manufacturing¹⁹⁾ is as an extension of this technology.

5. Decomposition of organic using supercritical water

5.1 Specificity of supercritical water

Water is the most commonly used solvent. It is a most specific fluid having interesting properties. Because of its high critical points for temperature and pressure, attention has recently been given to its use in the supercritical state.

The outline of the characteristics of water as a reactive solvent can be understood with an ionic product and a dielectric constant. The ionic product becomes the measure for interaction with hydrolysis and the dielectric constant with solutes.²⁰⁾ As **Fig. 4** shows, water retains a comparatively high ionic product under pressure.³⁾ On the other hand, its dielectric constant decreases remarkably near the critical point³⁾ as shown in **Fig. 5**. That is, supercritical water is a non-polar solvent of low dielectric constant. It has the capability to dissolve organic compounds, simultaneously retaining active state of high hydrolysis performance.

5. 2 Application to decomposition of organic compounds

Patents applications for using water in the subcritical (under critical temperature) to supercritical state as a solvent increased in 1989 and rose sharply from 1993.

Moder, a venture company related to the chemical weapon decomposition project of the U.S. Departments of Energy and Defense applied for and received a basic patent around 1989.²¹⁾ Here, efficient oxidative degradation is realized using the properties of the oxidizing agent (oxygen), which is soluble to the critical water with ease, in addition to the above-mentioned properties of supercritical water. Furthermore, the company made it possible to separate inorganics by adroitly using the property

that water under critical temperature dissolves inorganics easily and dissolves organics when over the critical temperature where inorganic salt is extracted.

Since supercritical water requires high temperature and pressure, commercial plants could not immediately be constructed. Nippon Shokubai helped to ease this condition by using a catalyst. This company carried on systematic studies on the matter and applied for about 30 patents during the period from 1989 to 1995. They mainly examined catalysts and reported that titanium and zircon oxides,²²⁾ gold, palladium and other precious metals²³⁾ or iron or copper ion additives²⁴⁾ were effective. On the other hand, Osaka Gas applied for an almost identical number of patents in their research for possibilities under critical temperature. They searched for a method of supplementing incomplete decomposition reaction with precision filtration,²⁵⁾ biological and other processings.²⁶⁾

In recent years, organic decomposition action using supercritical water itself that contains no oxidizer has attracted attention. Nishikawa Rubber Company and Kochi University conducted joint research and development concerning the devulcanization and oil development of vulcanized rubber. They found that subcritical water with sulfuric absorbents added is effective for devulcanization and oil development²⁷⁾ and that



Fig. 4 Ion product of water.³⁾



Fig. 5 Dielectric constant of water.³⁾

supercritical water added with zinc oxide²⁸⁾ or hydrochloric acid²⁹⁾ is effective in further promoting devulcanization and oil development. In addition, Japan is the center of positive basic studies on the reactions attributable to the solubility and high ion product of supercritical water particularly from the viewpoint of reaction rate control. Using supercritical water realizes a cellulose decomposition rate of 10^2 to 10^4 compared with conventional acid catalyst-based decomposition.³⁰⁾ Based on the results of these basic studies, research has begun on the decomposition of biomass³¹⁾ and polymers³²⁾ or improvement of coal or heavy oil quality.³³⁾ Development of devices for downsizing the reaction section by a using fast reaction rate is expected along with operating cost reduction.

6. Recent studies

6. 1 Manufacture of inorganic porous bodies and use of supercritical drying

Supercritical drying is known as a method for applying supercritical fluids. This method removes solvent by using the characteristics that make it possible to change the density continuously from a density close to liquid to one close to gas without phase change. This method was used for preparing samples for observation with an electron microscope from a biosubstance with a high water content. It is possible to prevent contraction caused by the solid particles that condense when the water or other solvent dries by vaporization. Matsushita Electric Works applied this property for manufacturing inorganic oxide porous bodies.³⁴⁾ In water, alcohol and other solvents, clay mineral and inorganic particulates synthesized with sol gel reaction to form a suspension or sol where these particulates are highly dispersed. Supercritical drying is effective for drying the suspension or sol while retaining the suspended state as much as possible. By using this drying method, an inorganic porous solid is formed. Spaces where the solvent molecules existed remain as voids. They are useful as heat insulators, adsorbents or catalyst supports. In particular, a combination of sol gel reaction and supercritical drying enables transparent inorganic porous solids (aerogel)³⁵⁾ having density of under 0.01g/cc to be manufactured.

6. 2 Particulate manufacturing and coating technology - Use of extraction and crystallization growth by changing solubility

It is possible to change the solubility of supercritical fluids sharply and continuously with the pressure (density) of additives. Solubility drops sharply when the high pressure in a container in which supercritical fluids are stored is discharged rapidly. During the process, solute is extracted and inorganic or organic particulates are grown. This method is called Rapid Expansion of Supercritical Solution (RESS) by which growth of silica, alumina, zirconium and other inorganic oxides³⁶⁾ and medicines, polymers and other organic substances³⁷⁾ are verified. Particulates grown here are often noncrystal, but when made to react under supercritical water of high temperature, this method can form iron oxides, zirconia, titania (anatase), ceria and other crystal particulates.³⁸⁾ Moreover, a single spraying enables a microcapsule with the effect of the chemical content shielded with poly-lactic acid, etc.³⁹⁾ to be manufactured.

The spraying mechanism based on rapid expansion resembles coating equipment. The above-mentioned composition, however, sprays only particulates and it is not possible to expect a uniform adhesion of the particulates on the substrate. Union Carbide of the U.S. began research on a method to substitute the coating solvent and the compressed air in the air spray with supercritical carbon dioxide from the mid 1980s. The company still continues its research and applied for a number of patents concerning the basic principle,⁴⁰⁾ paints and the solvent feeding method during that period. To stably solve organic polymers, which are the basic components of paint, and realize about the same finish as ordinary coatings, the company adds ordinary organic solvents as well. It closely examines the process of solution and extraction under the ternary system.⁴¹⁾ Ideally, the polymer is solved in mixed supercritical fluids of organic solvent and carbon dioxide in a high-pressure container as Fig. 6E shows. Immediately after the spraying, the carbon dioxide first vaporizes, leaving the organic solvent and polymer behind. After attaching itself to the base material, the organic solvent vaporizes, forming the polymer film just as ordinary paints do. The principle may seem simple, but there are a number of problems, which include the sharp drop of the temperature during expansion, retention of viscosity suitable to the coating and optimal composition, processing of pigments and other additives, the spraying of high-pressure fluids of over 10 MPa, and so forth. Beside these, there is a long way to go before practical application can be achieved, including reduction of hazardous organic solvents, development of devices and operating costs. The technology is quite interesting and important.

6.3 Characteristics as synthesized organic solvents - Specific intermolecular action

In the synthesis of substances, solvents are used to accelerate or control the reaction. In this case, the solvent is first required to be able to solve the reactive material, catalyst or other additives. The characteristics when supercritical fluids are used for the reaction solvent are best described by Ikariya and Noyori, ^{4, 42)} as follows:

"To effect molecular catalytic reaction in a solution, solvents are used to form a uniform system with catalyst and reaction molecules for, and effective mass transfer. To do this, molecular catalytic reaction in the liquid phase can be



Fig. 6 Fundamentals of coating with supercritical fluids as a diluent.⁴⁾

controlled with ease for precision reaction including stereochemistry. However, the catalyst and reaction molecules in the solution are often inactive as they are always surrounded by a number of solvent molecules. Strong solvation to such solvents and reaction molecules often has a negative effect on the acceleration of reaction. The solvent least affects reaction in the gas phase when a solid catalyst is used. In this case, reaction is rapid because the catalyst and reaction molecules are in naked state. Control of reaction is difficult because of the heterogeneity of the catalytic structure, however. Furthermore, molecular catalysts cannot be applied here.

The ideal catalytic reaction is a high-speed selective reaction provided with priority given to both reactions in the gas and liquid phases. To realize this, it is necessary to have a reaction system to make molecular catalyst soluble and suppress deactivation caused by the catalyst to a minimum. This is the reason why we are paying attention to supercritical fluids having intermediate properties between liquid and gas."

Based on this point, they succeeded in accelerating the reaction by using supercritical carbon dioxide as the solvent in a reaction to form formic acid useful as a chemical material from carbon dioxide and hydrogen by using Ru-complex as the catalyst.⁴³⁾ Moreover, it is found that reaction is further accelerated by adding dimethylamine that is soluble in supercritical carbon dioxide. This extracts formic acid as amine salt insoluble in supercritical carbon dioxide. "The intermediate property between liquid and gas" mentioned here, that is, the "property that makes molecules soluble but not inactive" is attributable to the characteristics (4) of the aforementioned supercritical fluids. Section 2 stated that supercritical fluids can be handled as "gas of high density." From the viewpoint of the reaction solvent, however, it is more understandable if we think of it as liquid of intensive molecular motion.

Enzyme reaction is normally effected in an aqueous solution. Here too, supercritical fluids are being used as an interesting solvent for the very same reasons as for molecular catalysts.⁴⁴⁾ In this case, it is necessary to give consideration to the inactivation of enzymes and other restrictions caused

by reaction between enzyme protein and carbon dioxide. The characteristics of supercritical fluids are utilized for accelerating high reaction, making water-insoluble molecules react, forming organic polymers of uniform molecular weight, etc.

7. Conclusion

Supercritical fluids have a number of interesting and useful characteristics. Above all, the viewpoints of Noyori et al. in the preceding section are considered to be the most important and interesting. The characteristics of supercritical fluids are that while they form a uniform solution system as a whole, they simultaneously realize a heterogeneous state where the surrounding conditions of the molecules are in constant change with violent fluctuations. Because of such fluctuations, supercritical fluids are a solvent that can realize advantages of both liquid and gas simultaneously.

One of the interesting fields for future research and development would be to make positive studies and use of the fluctuations including solid surfaces, adsorption or heterogeneous catalytic reaction.

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