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Polymers And Fluid Carbon Dioxide

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Summary: The solubility of substances in a highly critical medium at high pressure and temperature is studied, the main representatives of such media, primarily highly critical carbon dioxide, are given, their physicochemical properties, advantages and disadvantages are considered. The use of supercritical CO2 as a reaction medium, monomer, and catalyst in the synthesis of predominantly condensation-type polymers is analyzed.

Keywords. carbon dioxide, solvent, phase, fluid, supercritical state, polymer.

Under management

The dissolving ability of the supercritical , undoubtedly refers to one of the most important parameters determining the possibility of its use as a reaction medium. The solubility of substances in supercritical depends on pressure and temperature. Solubility increases in proportion to pressure. Temperature dependence is more complicated. With an increase in temperature at pressures up to 13-14 MPa, the solubility deteriorates, whereas at higher pressures it begins to increase. This dependence is associated with the superposition of two effects—a decrease in the density and, accordingly, the dissolving ability of the supercritical with an increase in temperature (at CO_2 $CO_2CO_2\rho$-*const*) and an increase in the elasticity of the vapors of the dissolved substance when heated. At lower pressures, the first effect prevails, at elevated pressures, the second.

It represents the in teres of both water andwater. While , is highly soluble in water (up to 15 wt. CO_2CO_2% at room temperature), water is very poorly soluble in it (0.0to 5% at 20°C). With an increase intemperature, the solubility increases slightly (1.5% PRand 100 ° C), while it is pressedandonly insignificantlyaffectsthis indicator. Supercritical processes of extraction of substances from aqueous solutions in the -phase, as well as the formation of nanoparticles of inorganic substances in a stabilized PAB emulsion of water in the supercritical processes of extraction of substances from aqueous solutions in the -phase, as well as the formation of nanoparticles of inorganic substances in the stabilized PAB emulsion of water in the PAB emulsion of water in the supercritical.$CO_2CO_2CO_2$

Results and their discussion. Supercritical well dissolves many non-polar and some polar organic compounds. As can be seen from Table 1, lower alcohols (methanol, ethanol, tert-amyl alcohol) are completely mixed with liquid, but with increasing length of alkyl or when switching to aromatic compounds, solubility deteriorates. Supercritical plocho dissolves phenol, while o-chloro- and o-nitrophenols are well soluble in it. Similar behavior is demonstrated by esters. Aliphatic esters

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mix well with liquid while in the transition to aromatic structures, solubility is also significantly reduced. Highly soluble in liquid lower carboxylic acids. Amines are poorly or moderately soluble in it; the exception, perhaps, is pyridine, which mixes well with liquid$CO_2 CO_2 CO_2 CO_2 CO_2 CO_2$, which has a certain value in reactions where pyridine is used as a catalyst. In a series of nitriles and amides, xoposho dissolve in liquid acetonitrile, acrylonitrile and N,N-dialkyl acetamides.CO_2

Among the organic dyes, dispersed dyes of azo- and anthraquinone series are characterized by insignificant solubility (< 1% at 35 MPa and 120 ° C). However, due to the high dye distribution coefficient between the film and the solution, staining synthetic fabrics in such an environment gives good results.

Table 1. Solubility of a number of organic compounds in liquid carbon dioxide

Compound	Solubility, wt. %	Compound	Solubility, wt. %
Methanol	Unlimited mixing	Ethyl acetate	Unlimited mixing
Ethanol	Unlimited mixing	Ethylacethoacetate	Unlimited mixing
Cinnamon alcohol	6 %	Phenylphthalate	Unlimited mixing
Furfuryl alcohol	5 %	Ethyloxalate	Unlimited mixing
Phenylmethyl alcohol	7 %	Butyloxalate	2 %
Phenylethyl alcohol	2 %	Ethyl maleinate	Unlimited mixing
Antinaya acid	Unlimited mixing	Phenyl salicylate	10 %
Acetic acid	Unlimited mixing	Amidey	2%
Lactic acid	0,6 %	Acrylonitrile	Unlimited mixing
Laurinova acid	1,3 %	Phenylacetonitrile	14 %
Oleinovaya acid	1,9 %	Formamide	0,6 %

In the late 90s, on the basis of a simple correlation between the solubility parameter and the critical pressure, they came to the erroneous idea that in terms of dissolving ability, it is close to pyridine. Calculations carried out in the early 90s using the equation of state for showed that the value is close to normal alkanes. However, the value for up to T 200 ° C is even lower than that of n-alkanes. The solubility parameter is not an optimal characteristic that allows predicting the dissolving ability of highly compressible liquids. In their opinion, it is more correct to operate with specific polarizability (polarizability / volume). In accordance with this approach, a supercritical is a very weak solvent, which is more adequately correlated with experimental results.$\delta CO_2 CO_2 \delta CO_2 \delta CO_2 \leq CO_2$

Most of the data on the solubility of polymers in supercritical media refer to . As can be seen from Table 2, some polymers, e.g., PE with M=(1-420)x10$CO_2$³, are only partially soluble in supercritical. Weakly polar polymers, e.g., PC with MM up to 10$CO_2$⁵ , partially dissolve under even harsher conditions (in temperature and pressure) than in aliphatic hydrocarbons. The first is really CO_2, CO_2-phil The polymers found by DeSimone and its co-workers are polyfluoroacrylates. Interestingly, the block copolymers of such polymers with c-phobic polymers are soluble and capable of micello formation. $CO_2 CO_2$

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Table 2. Solubility of polymers in supercriticalwithcom andCO_2 (about mixtures) with organic solvents as a solvent

Polymer	Mx10³	Solvent	T, ºS	*p*, МПа	Polymer concentration, %
Polypropylene	-	CO_2	164-207	50-90	6,3-32 %
Polyisobutylene	0,6	CO_2	25,3	20	0,45%
Polybutadiene	6	CO_2	25,2	19,5	0,3%
Поли-DL-лактид	0,85	CO_2	56	20	0,5%
Polyethylene glycol	0,5-0,7	CO_2	39,8	21	0,2-1,3%
Polyhexafluoropro-pilenoxide	13,4	CO_2	21,9	7-16	2-11%
Polyamide-6	-	CO_2	234-241	45	13,6-17%
Полидиметил-силоксан	129	CO_2	25	19	0,2-0,9%
Polystyrene	0,4-1,2	CO_2	40	25	0,02-1,1%

Polyperfluoropropylene oxide and low molecular weight polydimethylsiloxanes are partially dissolved in zh and dcom. So far, such an effect of fluorine and silicon on the solubility of polymers in does not find an adequate explanation. It is known that in terms of the parameter, fluoroalkanes and silicones are close to each other. Fluoridation of polymers can significantly increase $CO_2 CO_2 \delta CO_2 CO_2$the temperaturedue to the formation of a dipole. At the same time, fluorinated polymers have different solubility inCO_2.

Among the polymers soluble in supercritical and liquid are complex aliphatic polyesters with MM up to 10 $CO_2{}^4$ and polyamide-6. The latter dissolves in supercritical only at high temperature and pressure. Thus, only a few polymers demonstrate good solubility in supercritical media at moderate temperatures and pressures, and solubility is significantly improved at pressures above 45 MPa. CO_2

When assessing the permeability of fluorinated polymericmembres, it is assumed that the C-F and modes are both weak and do not prevent penetration through the polymer membrane$CO_2 CO_2$.

The study of this problem by computer modeling on interaction with C-C and C-F bonds also did not give a definite answer to the question of the causes of the improved solutionCO_2andbridge of fluoropolymers in CO_2.

To assess the specific interactions as a weak Lewis acid with contain$CO_2(O^{\delta-} = C^{\delta+} = O^{\delta-})$andmysia in polymers by groups C = O, C = S, a method of IR spectroscopy is proposed. By shifting the band of deformation oscillations of the group C = O, it is possible to predict solubility in polymers, and in some cases also the solubility of polymers in liquid in supercritical. The energy of such interaction withNH_2 $CO_2 CO_2 \Delta H_{CO_{2-O=C}}$cis 4.19 kzh / mol and in order of magnitude closeand close to and x the van der Waals interactions and forces of London.

CO_2 –Itcan be a polymer characterized byhigh chain flexibility (low T_c), low energy density of coges and representing a Lewis base, which provides a specificinteractionbetween the polymer andCO_2 .

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The validity of such ideas was confirmed by the example of the synthesisof a triple block copolymer with the central block of PEO (degree of sexandmeasuresandbeyondqiand 7) andco-zerofloorsipropilelen with carbonate blocks.

Since theCO_2solvent is a solvent withno dielectric potential and low energy density cogezand, it is able to dissolve polymers, has similar characteristics. For copolymers of ethylene with acrylates, it was determined that an increase in the content of the links of the latter leads to an improvement in solubility. Here the Lewis reaction can play a role. For n-alkylacrylates with an increase in the length of the alkyl radical. solubility improves, apparently, due to the growth of free volume (and thus the entropy of mixing). Polymers with low surface tensionandem at the phase interface (and therefore low density energyandcoges) are well soluble in carbon dioxide. Thus, it is clear that the phase behavior of polymers is consistent CO_2 withits low cohesion energy density and Lewis acidity.

PB is more -filen than other polymers in$CO_2$the inii, characterized by a significantly higher densityof energy and cohesion [9]. At the same time, PBA and POCO_2, , which have higher values of the energy density of coges, demonstrate better solubility in the formof imo, due to the presence of the main groups in them. Thetopology of macromolecules also plays a role: it has been shown that the branching of the side chains also leads to an improvedsolution toit.

Topology can play a very large role in determining the phase behavior of polymers in So, PBA is much better soluble in such an environment than the polymethylacrylate isomerized to it. The introduction of Lewis core gpypp into the pdms side chain significantly increases the solubility of this polymer in .CO_2.CO_2

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