INFLUENCE OF A DIELECTRIC MEDIUM ON THE PHASE STATE OF CARBON DIOXIDE

A. V. Khristoforov, F. I. Bashirov,
R. A. Dautov, and N. N. Neprimerov

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The phase state of carbon dioxide gas dissolved in liquid n-heptane is determined by experimental investigations of the temperature dependences ($180 < T < 250$°K) of the spin-lattice relaxation time of protons, the coefficient of translational self-diffusion of n-heptane molecules and the nuclear magnetic resonance (NMR) linewidth of carbon ^{13}C.

Interest in studying binary dielectric systems of the type carbon—CO_2 gas is due to the application of this latter in liquid and supercritical states as a good selective solvent [1]. At the same time, the question of what is the aggregate state of the carbon dioxide in the solution remains unclarified. Nevertheless, the set of experimental facts, the results of measuring the density [2] and viscosity of solutions and the translational self-diffusion of CO_2 molecules in solution [3], indicate in favor of the assumption that the carbon dioxide gas dissolved in liquid hydrocarbons at saturated vapor pressures below the condensation pressure of the pure carbon dioxide gas (5.75 MPa at $T = 293$°K) possesses properties inherent to the liquid state.

We performed experimental investigations of the dielectric system n-heptane—carbon dioxide gas to determine the dependence of the concentration of the carbon dioxide dissolved in the n-heptane on the saturating CO_2 gas pressure at room temperature, and to study the temperature dependences of the translational self-diffusion of n-heptane molecules, the spin-lattice relaxation time of protons, and the NMR absorption spectrum of ^{13}C nuclei of carbon dioxide in the solution $0.76CO_2 + 0.24C_7H_{16}$.

Utilized in the specimen preparation were n-heptane mark CP and alimentary carbon dioxide gas containing no less than 99% of the main substance which were additionally cleansed of other hydrocarbon, water, and oxygen impurities. The carbon dioxide gas pressure was measured with ±0.1 MPa error. The specimens were weighed on analytical balances.

The NMR experiments were performed on a laboratory pulse spectrometer in a magnetic field with constant gradient at the frequency 14 MHz for protons and on a WH-90 pulse spectrometer with Fourier transformation at the resonance frequency 22.15 MHz for the ^{13}C nuclei. The temperature band of the investigations was 180-250°K. The accuracy of maintaining and measuring this temperature was no worse than ±1°K.

Values of the limit carbon dioxide concentrations in a mixture with n-heptane are given in Fig. 1 for several carbon dioxide gas presures. Presented there are values of the carbon dioxide mass yielding a saturated solution in n-heptane, and for comparison, masses of gaseous carbon dioxide filling the same ampoule without n-heptane at corresponding pressures. It should be noted that in the presence of n-heptane under an identical pressure the CO_2 gas in the ampoule is significantly greater. For instance, the ratio of these masses is 3:1 for a 5 MPa carbon dioxide gas pressure.

It is seen from Fig. 2 that an abrupt change in the translational self-diffusion coefficient D and the time T_1 for the solution occurs in the neighborhood of the temperature 217°K, which corresponds to the melting point of solid carbon dioxide. Growth of the values of D and T_1 and diminution of the slope of the curves (Fig. 2) in the mixture as compared with their values in a pure n-heptane specimen at temperatures above the CO_2 melting point indicate an increase in the intensities of the translational and rotational motions of the n-heptane molecules when carbon dioxide gas is dissolved in it. At temperatures below the

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V. I. Ul'yanov-Lenin Kazan State University. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 52, No. 3, pp. 402-405, March, 1987. Original article submitted January 10, 1986.

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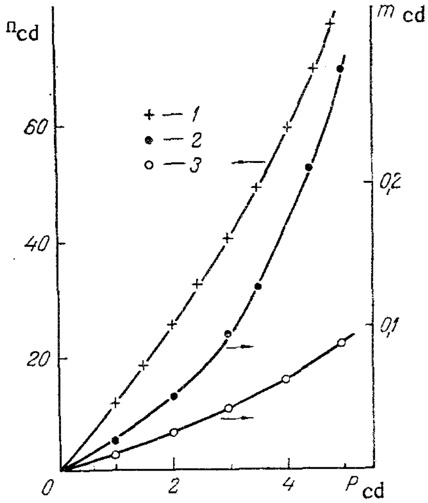

Fig. 1. Experimental dependences of the molar fraction of carbon dioxide n_{cd} dissolved in n-heptane (1) and the carbon dioxide mass m_{cd} on the saturating gas pressure P_{cd} in an ampoule of 0.71 cm^3 volume containing 0.3 cm^3 n-heptane (2) and without it (3) at the temperature 293°K. n_{cd}, %; m_{cd}, g; P_{cd}, MPa.

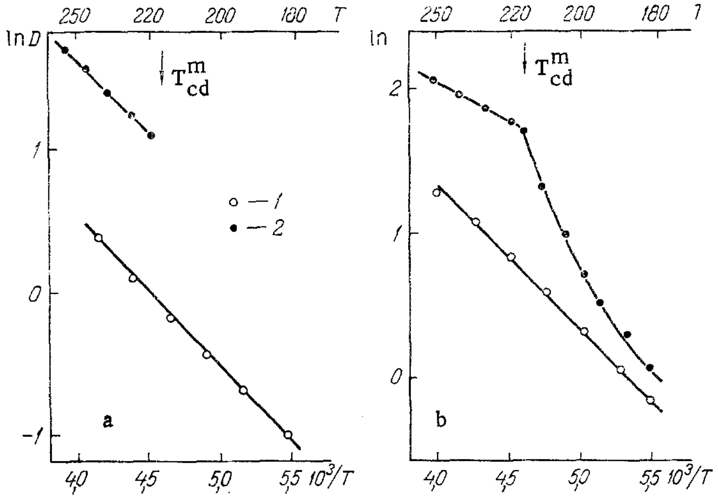

Fig. 2. Experimental temperature dependences of the translational self-diffusion coefficient of n-heptane molecules D (a) and the spin-lattice relaxation time of protons T_1 (b) for specimens containing 100% C_7H_{16} (1) and the solution 76% CO_2 + 24% C_7H_{16} (2). D, 10^{-9} m^2/sec; T_1, sec; T, °K.

CO_2 melting point the values of the coefficients D of the n-heptane molecules in the mixture diminish by several orders (they are not presented in Fig. 2a), while the times T_1 approach their values in pure n-heptane. Such behavior of the experimental curves is apparently due to blocking of the n-heptane molecule translational motion by the solid CO_2 lattice while the rotational motions of the n-heptane molecules are retarded just to the intensities of these motions in pure liquid n-heptane.

The NMR absorption spectrum of ^{13}C nuclei of carbon dioxide in the solution $0.76CO_2$ + $0.24C_7H_{16}$ consists of single lines. In the near neighborhood of the CO_2 melting point ($215 < T < 219$°K) line broadening is observed. The maximal value of the linewidth at half the height equals 9 Hz, which is approximately twice the value at other temperatures.

As a result of the experimental investigations performed on solutions of carbon dioxide in the dielectric medium n-heptane, it is established that: 1) upon the dissolution of carbon dioxide gas in liquid n-heptane at a pressure below the condensation pressure the transition of carbon dioxide from the gaseous into the liquid state occurs; 2) for carbon dioxide concentrations in the mixture that exceed 70%, a two-phase system consisting of solid carbon dioxide and liquid n-heptane, whose molecule translational motions are retarded, exists in the temperature domain below the melting point of solid CO_2.

NOTATION

T, absolute temperature; ^{13}C, carbon isotope; D, coefficient of translational self-diffusion of molecules; T_1, nuclear magnetic spin-lattice relaxation time; n_{cd}, carbon dioxide concentration in the solution; m_{cd}, P_{cd}, mass and pressure of the saturated carbon dioxide vapors.

LITERATURE CITED

1. T. P. Zhuze, Role of Compressed Gases as Solvents [in Russian], Moscow (1981).
2. V. S. Sperkach and M. I. Shakhparonov, Neftyanoe Khozyaistvo, No. 2, 43-45 (1984).
3. Hani Saad and Esin Gulari, J. Phys. Chem., 88, No. 1, 136-139 (1984).

APPROXIMATE MODEL OF THE DEPOSITION OF THIN FILMS FROM VAPOR–GAS PHASE IN A TUBULAR DIFFUSION FURNACE

G. I. Georgiev, S. G. Karbanov,
and G. A. Peev

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The analytical conditions for obtaining uniform films deposited from vapor–gas phase in a laminar–isothermal flow are determined.

The deposition of thin dielectric and semiconductor films from the gas phase as a result of heterogeneous chemical reactions is widely used in microelectronics. Cylindrical reactors with vertical substrates (silicon plates) transverse to the flow are often used for this purpose (Fig. 1). In describing the processes in such reactor, it is usually assumed [1, 2] that the longitudinal flow of the gas mixture between the bundle of plates and the reactor wall is isothermal and laminar; that the gas phase between the plates is motionless and transfer of the active component to their surface is on account of molecular diffusion; and that chemical reaction at the plate surface is of first or higher order with respect to the concentration of the active component, which remains constant around the plate over the length of the reactor.

In these conditions, the process is described [1] by the differential equation

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right)+\frac{\partial^2 C}{\partial z^2}=0 \qquad (1)$$

with the boundary conditions

$$r=R,\ C(r,\ z)=C(R,\ z)=C_0; \qquad (a)$$

$$r=0,\ \frac{\partial C}{\partial r}=0; \qquad (b)$$

$$z=0,\ z=H,\ \left|D\frac{\partial C}{\partial z}\right|=KC^{\alpha}. \qquad (c)$$

This problem is solved by the numerical methods of [1]. It was solved analytically in [2], introducing the constraint that the chemical process is of first order, i.e., α = 1. The solution is written in the form of a convergent series consisting of the products of Bessel and trigonometric functions, but is too cumbersome and inconvenient for use.

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