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Research Article

Measurement and Modeling the Properties and Equilibrium of Fluid Systems Involving Carbon Dioxide and Hydrocarbons

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Abstract: On the basis of molecular dynamics modeling (MD modeling) and experimental data *pVTx*, a study was made of the dynamic and thermodynamic properties of a binary system based on light gases containing heavy oil (A-B). The solvent (A) used was carbon dioxide and n-alkanes (methane, ethane, and propane) in the supercritical fluid (SCF) state. Measurements of the *pVTx* properties were carried out in the temperature, density, and pressure ranges near the critical parameters of the light gas-heavy oil systems. Based on *pVTx* data and MD modeling in the A-B system, the diffusion coefficient (D) was determined near the critical parameters of the solvent. The values of D in the binary system SCF carbon dioxide or alkanes containing (methane, ethane and propane) heavy oil from the Siyazan field of Azerbaijan are calculated. The D SCF value of methane and ethane in the A-B system is higher than in a system containing SCF propane at given concentrations (c or x) of heavy oil and temperature. The value of D SCF of light gases in the A-B system increases with an increase in the concentration of heavy oil up to x = 2.5 wt. %. Diffusing molecules of SCF gases reduce the viscosity of heavy oil in the A-B system. Dependence $D = f(c)$ tends to have an asymptotic value with increasing oil concentration. In the A-B system, the dependence of D SCF gases on pressure has a non-monotonic form. To calculate mixtures of light gases, the modified Peng-Robinson equation of state (PR EOS) was used. The isothermal dependence P-x of the carbon dioxide-methane binary system is approximated. The calculated P-x curves are consistent with the experimental ones in the temperature range 277-345 K.

***Keywords*:** binary fluid systems, carbon dioxide and n-alkanes, *pVT* properties, thermodynamic parameters, MD modeling, diffusion coefficient, equilibrium

1. Introduction

The study of the nature of intermolecular interaction near supercritical fluid states (SCF) in systems with the participation of oil is a complex process. Such studies are of both fundamental and practical importance. In particular, the use of SCF technologies in the purification of oil-containing systems is a promising and environmentally friendly way of oil refining.

In SCF technologies, one of the solvents is, in particular, supercritical carbon dioxide (SCF CO_2) and SCF n-alkanes. Due to the low surface tension and high penetrating ability of SCF, solvents make it possible to intensify the processes

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of dissolution, diffusion and purification in oil systems. However, the application of SCF in the oil industry is a complex task, since different solvents and research methods are used in production and oil refining.

In mixtures, spontaneous mutual penetration of substances into each other is possible. This is due to the chaotic thermal motion of atoms and molecules. In mixtures, molecules of different types are mixed due to mutual (concentration) diffusion. The dissolution of gases in liquids reduces the viscosity of liquids. In mixtures, molecular diffusion occurs. That is, in a multiphase system, the concentration of particles spontaneously equalizes according to the occupied volume. Knowledge of the transport properties of gases in liquids makes it possible to determine the properties and rate of the mass transfer process in such systems.

Diffusion and solubility of light gases in a system with the participation of heavy oil have been studied by different authors.[1-7] For example, the diffusion coefficient of light gases in heavy oil and bitumen at 20-200 °C and 1-15 MPa ranges from 10^{-9}-10^{-10} m^2/s.[1] A similar order of the diffusion coefficient of gases is also observed in other hydrocarbon systems.[2-7]

Molecular dynamics (MD) modeling of the properties of gaseous media also makes it possible to calculate the self-diffusion coefficients of gases. For MD-modeling of gas systems, the equations of mechanics are used, the integration of which is performed using a difference scheme, for example, the Verlet scheme in velocity form. To calculate the diffusion coefficients, in particular, the Green-Kubo formulas are used. MD modeling of the properties of light gases at a pressure of 1 atm, in the temperature range of 100-900 K, shows that the calculated data of gases are in good agreement with known theoretical estimates and experimental data.

The diffusion coefficient of gases in liquids depends on various factors. These include composition, density, viscosity, nature of the solvent, structural characteristics, temperature, pressure, etc. These properties, as well as the pVT dependencies of gas-liquid systems, make it possible to correct and predict optimal compositions and properties. Such data are important, in particular, for designing the development, operation and production of oil and gas fields.

The aim of this work is MD modeling and studying the $pVTx$ properties of SCF systems light gases (carbon dioxide and n-alkanes)-heavy oil (systems A-B). The dependences of the diffusion coefficient of the SCF of components A containing oil (B) on the thermodynamic parameters of systems A-B were experimentally studied. The diffusion coefficients of the A components near the SCF states in the A-B systems were calculated by MD simulation.

2. Methodological part

It is difficult to accurately calculate the diffusion coefficient in gas-liquids using theoretical methods. Empirical relationships such as hydrodynamic, thermodynamic, and kinetic relationships for estimating the diffusion of gases in liquids also have their drawbacks. In practice, various models of diffusion of gases in mixtures are often used.

2.1 *Diffusion models*

Let us consider diffusion models in binary gas-liquid systems A-B. In such systems, mass transfer processes (for example, absorption, extraction, crystallization) are associated with the molecular diffusion of component A in substance B. In hydrocarbon systems, empirical and semi-empirical correlations are often used to determine the diffusion coefficient.

To estimate the value of D in dilute mixtures, quasicrystalline lattice models or a hydrodynamic diffusion model can be used. In the first case, diffusion in a liquid is taken similarly to transfer in a solid crystalline body. In the hydrodynamic model, diffusion in a continuous medium is associated with a force that acts on a moving flow in the form of a ball. This model is described by the Stokes-Einstein equation.[8] Both of these models can be represented in a general form:

$$D_{\mathrm{AB}}^{0}\mu = T \cdot F(V), \tag{1}$$

where D_{AB}^{0} is the diffusion coefficient of infinite dilution, m^2/s, μ is the dynamic viscosity coefficient of the continuous phase, mPa s, $F(V)$ is the function of the molar volume of the mixture V, T is the absolute temperature.

To evaluate the properties of individual components of a mixture A-B, equation (1) can be represented in the general form: $D_{\mathrm{AB}}^{0} = A/\mu^{n}$, where the parameters A and n depend only on the properties of the diffusing component.

To estimate the diffusion coefficient in liquids with low viscosity, the following equation is known:[7]

$$D_{\mathrm{AB}}^{0} = \frac{13.3 \cdot 10^{-8} T^{1.47} M_{\mathrm{B}}^{\left(\frac{10.2}{V_{\mathrm{A}}} - 0.791\right)}}{V_{\mathrm{A}}^{0.71}} \tag{2}$$

where D_{AB}^{0} is the diffusion coefficient of the gas in an infinitely dilute gas-liquid system, cm^2/s, M_{B} is the molar mass of the continuous (continuous phase), g/mol, V_{A} is the standard molar volume of gas (liquid) of diffusing particles, cm^3/mol.

In the theory of solutions, it is important to relate the properties of solutions and find ways to evaluate the properties of solutions based on the properties of pure components. The solution to this problem is related to the determination of the nature of the interaction of components in solutions and is generally difficult. Therefore, in the theory of solutions, two main types of ideal solutions are considered: infinitely dilute solutions and perfect solutions.[7]

For the case of infinite dilution, the value of D_{AB}^{0} can be estimated using the correction factor:[8]

$$D_{\mathrm{AB}} = \bar{D}_{\mathrm{AB}} \left(\frac{d \ln a_{\mathrm{A}}}{d \ln x_{\mathrm{A}}} \right) = \bar{D}_{\mathrm{AB}} \alpha \tag{3}$$

where α is the thermodynamic correction factor. This coefficient is equal to one for the pure component of the A-B system. In concentrated A-B solutions, the coefficient becomes greater than one. In equation (3), the activity coefficient of, for example, component A (a_{A}) is used to account for deviations from ideal behavior in an A-B mixture of chemicals A and B. In an ideal mixture, the microscopic interactions between each pair of chemical particles, for example, in the A-B mixture are the same or equivalent. That is, the change in enthalpy of the solution of the A-B system and the change in volume during stirring are zero. Therefore, the properties of a mixture A-B are expressed in terms of the concentrations of substances present, for example, x_{A}. Deviations from ideality are compensated by changing the concentration by the activity coefficient. Thus, an expression involving a component of the A-B system can be corrected for non-ideality by using the partial diffusion coefficients D_{AB}.

For a regular solution (a kind of real solution), it is assumed that the volume and entropy do not change during mixing: $\Delta_{mix}S = -nRT(x_1 \ln x_1 + x_2 \ln x_2)$; $\Delta_{mix}V \cong 0$; $\Delta_{mix}H \neq 0$, where R is the gas constant, x_1 and x_2 is the concentration of the 1-2 or A-B system component. That is, the change in entropy when mixing the components of a regular solution is taken as an ideal solution. For a regular solution, the following conditions are accepted: the particle sizes are the same; the interaction energies between like and unlike particles are not equal. The formation of a regular solution is accompanied by a small thermal effect. The low energy of thermal motion excludes the ordering of particles in solution.

In a regular solution, the concentration-dependent diffusion coefficient can be estimated from the equation

$$\frac{D_{\mathrm{AB}} \mu_{mix}}{(D_{\mathrm{AB}} \mu_{mix})_{x_{\mathrm{A}} \to 0}} = \left[1 + x_{\mathrm{A}} \left(\frac{V_{\mathrm{A}}}{V_{\mathrm{B}}} - 1 \right) \right] \left(\frac{d \ln a_{\mathrm{A}}}{d \ln x_{\mathrm{A}}} \right) \tag{4}$$

In contrast to the interaction energy of the components of an ideal solution, the formation of a real solution is accompanied by the contribution of the thermal effect to the total energy. Changes in the physicochemical properties of nonideal solutions make it possible to evaluate the thermal effect in mixtures. The properties of oil-containing mixtures also deviate from the properties of ideal solutions.

If the A-B system has two components, A and B, then the transfer of one component is accompanied by the transfer of the other. This is due to diffusion, that is, a process aimed at equalizing the composition of the A-B system. Therefore, in a system with two components, there will be two diffusion flows: $J_{\mathrm{A}} = -D_{\mathrm{AB}} \frac{\partial c_{\mathrm{A}}}{\partial x}$, $J_{\mathrm{B}} = -D_{\mathrm{AB}} \frac{\partial c_{\mathrm{B}}}{\partial x}$, where D_{AB} is the diffusion coefficient of component A in its mixture with B; D_{AB} is a similar coefficient for component B.

2.2 *Diffusion coefficient in a liquid*

The diffusion coefficient D allows you to determine the speed at which particles (molecules, ions, etc.) move in a liquid and the distance they cover in a certain period. Useful information is provided by the dependences of the diffusion coefficient on time and the thermodynamic parameters (composition, temperature, and pressure) of the system.

The diffusion coefficient is known to be a basic property that quantifies the speed at which particles or molecules move through a medium. A common method for determining the diffusion coefficient is to calculate it from kinetic data, such as the change in mass of a sample over time. The diffusion coefficient of a gas in the liquid (or solid) phase is determined by two methods: direct and indirect methods.

In the direct method, the concentration profile of the solute in the solvent is usually measured to calculate D. The concentration profile is measured by chemical, spectroscopic, radiographic, electron diffraction, radiometric and other methods of analysis. By analyzing the concentration profile over time, the diffusion coefficient can be determined.

In the indirect method, the calculation of D is carried out according to the distribution of the component concentration in the system. Find changes in various physical properties of a substance caused by the diffusion of an impurity.

2.2.1 *Measuring setup D*

Used laboratory setup, which contained a diffusion cell with a housing. The sample was placed in a diffusion cell and the rate at which the substance diffuses through it was measured. The light gas (CO_2 or n-alkane)-heavy oil system from the Siyazan field of Azerbaijan was used as samples. The temperature and pressure in the closed cell were controlled by a thermometer and a monometer, respectively.[9-11] The average density of the oil samples used was ~ 900 kg/m^3. In samples of the liquid-gas system, the difference in the concentrations of the components was measured during gas diffusion near the critical parameters of the gas. When measuring diffusion properties, it was assumed that the gas passes per unit time through a system of unit area (1 m^2) with a concentration gradient equal to unity. The resulting concentration profiles of the components were used to calculate the diffusion coefficient of gas in an oil-containing system. The diffusion of a gas depends on its diffusing concentration of components in the system. Therefore, the gas diffusion time was chosen to be relatively long in order to obtain a reliable shape of the concentration profile in the x coordinate.

The pressure inside the measurement cell with a light gas (CO_2 or n-alkane)- a heavy oil sample drops as the gas diffuses through the system. Taking into account the change in pressure with time, the mass of a given gas that diffused in the system was determined. The mass of the diffusing gas was calculated from the change in the mass of the initial sample. Thus, the diffusion coefficient of the gas in the system was calculated.

Changes in the diffusion coefficient in the system light gas (CO_2 or n-alkane)-heavy oil were studied depending on pressure (4-8 MPa) and temperature 298-365 K. The mass of heavy oil in the experiments was 75-95 g. The concentration of oil in the system in experiments was ≤ 2.5 wt. %.

2.2.2 *MD modeling*

Various potentials are used for MD modeling of the thermodynamic properties of light gases.[12] For example, in the elementary particle model (EPM2), the Lennard-Jones LJ 12-6 potential in combination with the Coulomb interaction is used to describe the site-to-site interaction

$$\phi_{ij} = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right] + \frac{q_i q_j}{4\pi\epsilon_r\epsilon_0 r} \tag{5}$$

where σ_{ij} and ϵ_{ij} are the parameters of length and energy, respectively, q_i is the partial charge of particles i, r is the distance between particles i and j, ϵ_0 is the vacuum permittivity, ϵ_r is the relative permittivity.

The interaction between heterogeneous molecules of light gases 1 and 2 or heterogeneous atoms (for example, in CO_2 atoms C and O) according to the EPM2 model is calculated based on the Lorentz-Berthelot unification rule.

The Large-Scale Atomic-Molecular Mass-Parallel Simulator (LAMMPS) was used for NVT MD simulation of the light gas (CO_2 or n-alkane)-heavy oil system in the range $T = 298\text{-}375$ K and $\rho = 4\text{-}8$ MPa. The initial gas configuration of $N = 1{,}024$ molecules is relaxed by energy minimization and is balanced in 4 ns. Particle trajectories are collected every 10 ps for 2 ns to calculate pair correlation functions.

The calculation of the self-diffusion coefficient based on MD simulation (D_{MD}) was carried out for 60 ps, taking into account the change in the particle trajectory every 1 fs. The self-diffusion coefficient was associated with the autocorrelation function of velocity by the Green-Kubo relation

$$D_{\mathrm{MD}} = \frac{1}{3N}\sum_{i}^{N}\int_{0}^{\infty}\langle v_i(0)\cdot v_i(t)\rangle\, dt \tag{6}$$

where v_i is the velocity vector of particle i, N is the number of molecules in the system. Calculations of the self-diffusion coefficient are repeated 10-12 times and the coefficient is averaged.

3. Results and discussion

3.1 *Critical parameters*

The experimentally obtained $pVTx$ properties of the studied liquid-gas systems, close to the critical parameters, are in good agreement with the known data (Table 1).

Table 1. Critical parameters of light gases determined by us experimentally in the liquid-gas (SCF) system

Gas	T_c	p_c, MPa	V_c, 10^{-3} m^3/kg
Carbon dioxide	304.21	7.38	2.14
Methane	190.55	4.61	6.16
Ethane	305.31	4.87	4.71
Propane	369.82	4.26	4.44

The pVT dependence calculated using the equation of state by us for light gases near critical parameters, for example, carbon dioxide, is in good agreement with the experimental data (Figure 1). The initial behavior of the critical line when heavy oil is added to the SCF CO_2 depends on the thermodynamic parameters of the system.

In the SCF CO_2 fluid system, the addition of an impurity, for example, CH_4, causes a shift in the critical parameters of the system. As can be seen from Figure 2, the shifts p_c and T_c depend asymptotically linearly on the composition.

Initial slope of the critical line (dp^c/dx) and (dT^c/dx) with a pure liquid vapor pressure limit curve $(dp_\sigma/dT)^c$ and derivative $(\partial p/\partial x)^c_{VT}$ can be determined by the Krichevsky formula

$$(\partial p / \partial x)^c_{VT} = (dp^c / dx)_{x\to 0} - (dp_\sigma / dT)^c{}_{x=0}(dT^c / dx). \tag{7}$$

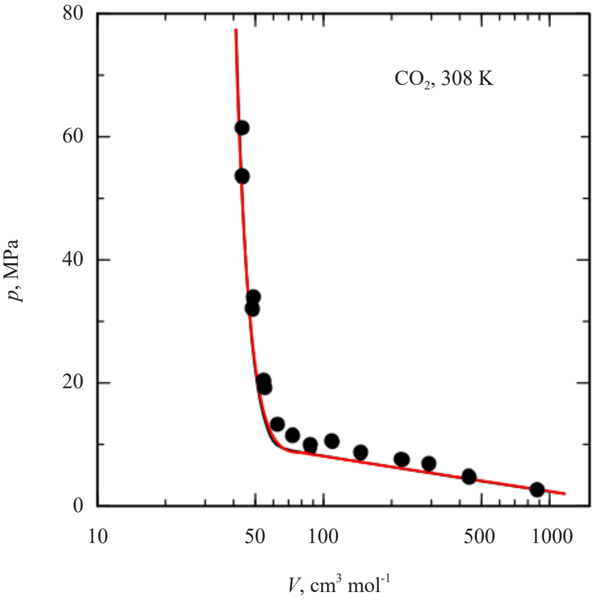

Figure 1. Calculated using the equation of state and experimental dependence of p on V of carbon dioxide at T = 308 K. The lines are the result of calculations using the equation of state, and the points are experimental data

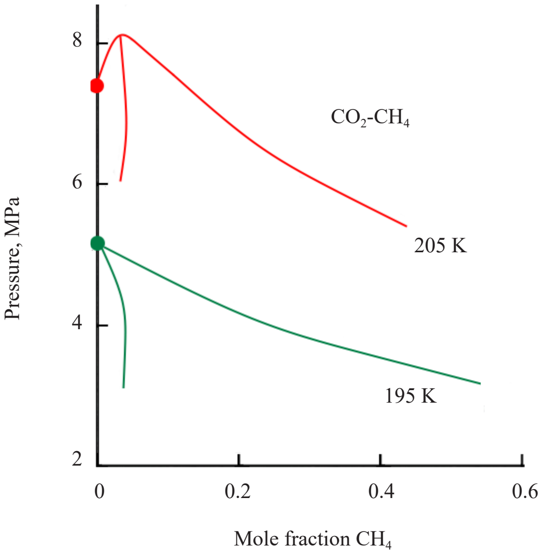

Figure 2. Calculated using the equation of state pVT line of a mixture of methane in carbon dioxide near the critical point of the SCF CO$_2$ solvent

3.2 *MD simulation of Diffusion in SCF CO$_2$*

In a multiphase system, mass transfer occurs due to the irreversible mass transfer of components in one or more phases. As a result of the chaotic movement of molecules (molar diffusion), a macroscopic movement of the entire medium occurs (convective transfer). In turbulent flows, there is also a chaotic movement of vortices of various sizes.

In convective diffusion, the transfer of matter in a moving medium is due to two mechanisms. The presence of a concentration difference in a liquid (gas) causes molecular diffusion. In addition, particles of a substance dissolved in a liquid during its movement are transferred along with the liquid. The combination of both processes characterizes convective diffusion. Convective diffusion in a laminar flow of an incompressible fluid is described by the equation:

$$\frac{\partial C_{\mathrm{A}}}{\partial \tau}+(u\cdot\nabla)C_{\mathrm{A}}=-\mathrm{div}j_{\mathrm{A}} \tag{8}$$

where C_{A} is the concentration of the diffusing component A, in mol/m^3, τ is the time, in s, u is the velocity vector of the macroscopic flow, in m/s, ∇ is the nabla (Hamilton operator), divj_{A} is the divergence, j_{A} is the vector diffusion flux density (amount of substance transferred by diffusion per unit time through the unit surface area), in mol/(m^2 s).

The final size of the system when calculating the diffusion D_{MD} by the MD simulation method gives errors. The coefficient of self-diffusion D_∞ in an infinite system can be related to the D_{MD} of a system of finite size by the relation

$$D_{\mathrm{MD}}=D_\infty\frac{k_{\mathrm{B}}T\xi}{6\pi\eta L} \tag{9}$$

where ξ is a dimensionless constant, η is the shear viscosity, L is the length of one side of the cubic system, k_{B} is the Boltzmann constant. Here D_{MD} is expressed as a function of the form:

$$D_{\mathrm{MD}}=aN^{-1/3}+b. \tag{10}$$

Taking into account that $D(N\rightarrow\infty)=b$ and selecting the values of a and b for a system N of different sizes, we can calculate the value of D_∞.

Taking into account that $D(N\rightarrow\infty)=b$ and adjusting the values of a and b to a system N of different sizes, we can calculate the value of D_∞.

The results of MD simulation with $N=256$ CO_2 molecules[12] and our calculation of D_{CO_2} are shown in Figure 3.

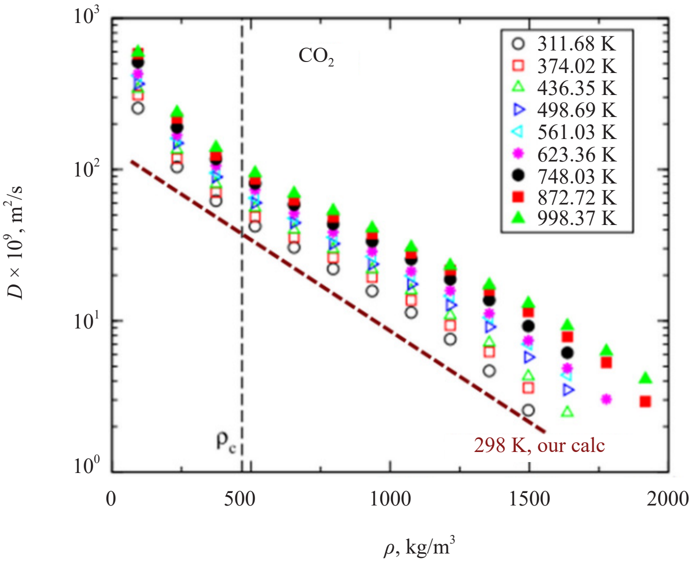

Figure 3. Self-diffusion coefficients in an infinitely dilute CO_2 system,[12] estimated by us on the basis of MD simulation. ρ_c is the experimental critical density

3.3 *MD simulation of SCF light gas-oil systems*

The concentration dependences of the diffusion coefficient in the SCF CO_2-oil system at different temperatures MD simulation is shown in Figure 4.

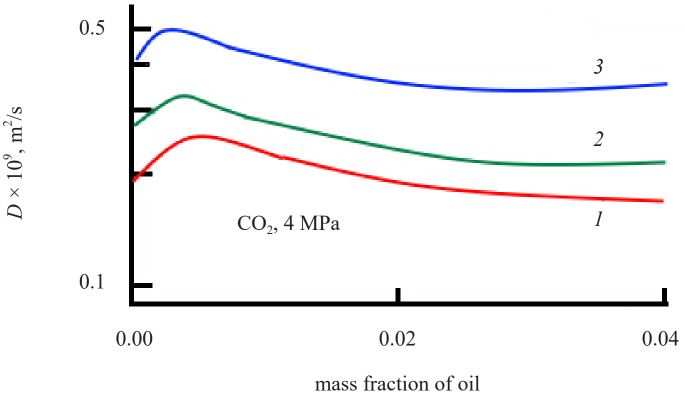

Figure 4. Dependence of the diffusion coefficient SCF CO_2 on the mass fraction of oil in the SCF CO_2-oil system obtained by MD simulation. *1* - 298, *2* - 323, *3* - 348 K, and the pressure is 4 MPa

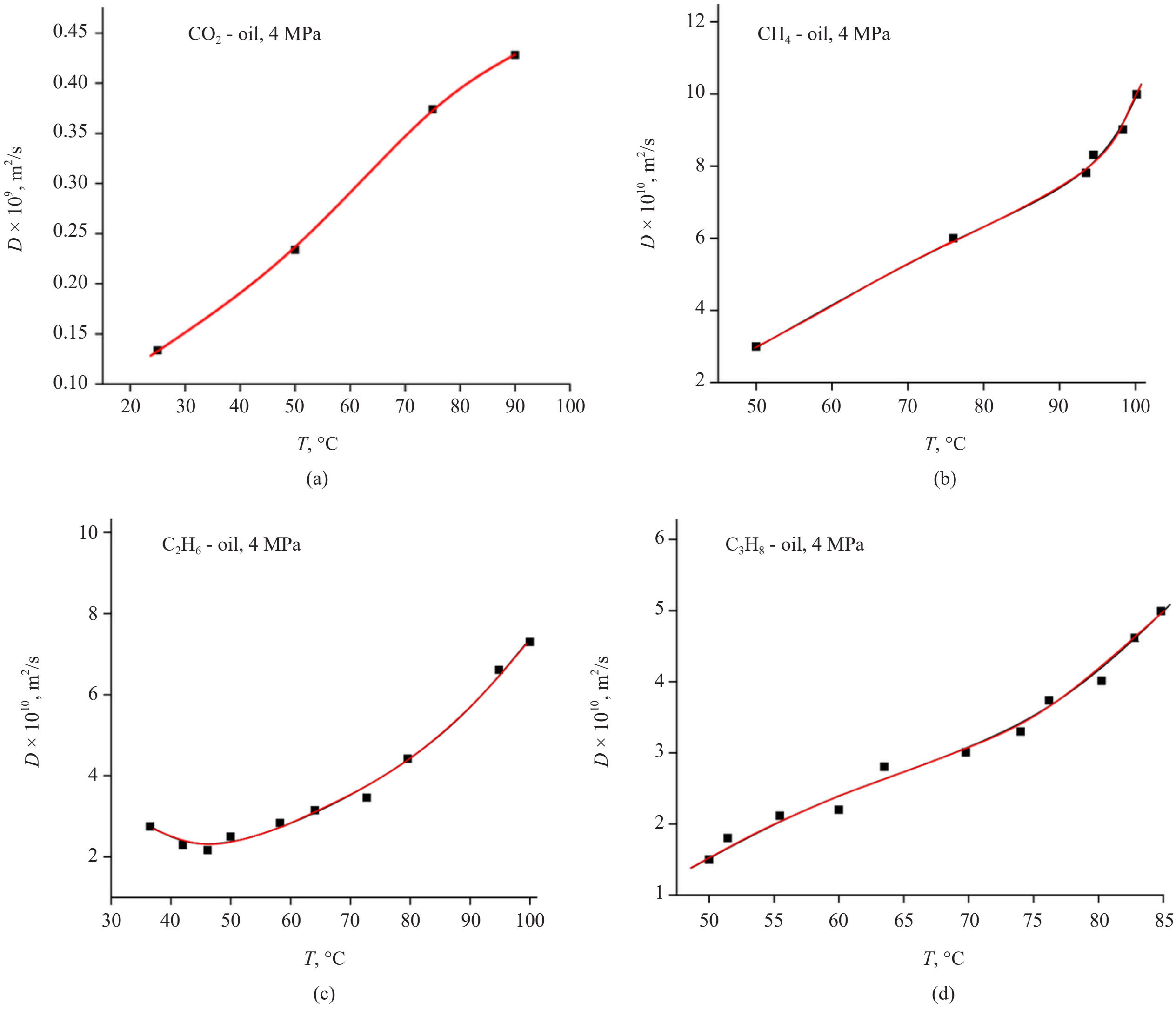

Figure 5. MD-modeled and experimental dependences of the diffusion coefficient of light gases (carbon dioxide, methane, ethane, and propane) in SCF fluid systems light gas-heavy oil (oil samples from the Siyazan field in Azerbaijan). (a) Carbon dioxide SCF-heavy oil, (b) SCF methane-heavy oil, (c) SCF ethane-heavy oil, (d) SCF propane-heavy oil. The oil concentration in the fluid systems was 3 10^{-3} wt %. share, and the pressure is 4 MPa. Lines are the result of MD calculations, points are experimental data

As can be seen from Figure 4 SCF CO_2 diffusion coefficient, calculated by us using the molecular dynamics method, is a function of oil concentration in the mixture. At a given oil concentration and pressure in the system, D_{CO_2} increases with temperature. The diffusion coefficient of SCF CO_2 also increases with increasing pressure at a given temperature and concentration of components of the SCF CO_2-oil system.

Figures 5 a, b, c, d show the dependences of the diffusion coefficient in the SCF systems of carbon dioxide and SCF of n-alkane (methane, ethane, and propane) on temperature at a fixed pressure. The MD simulation calculations of D values are in good agreement with the measurement data obtained in the experiments.

The diffusion coefficient of a gas increases with increasing pressure at a given temperature and gas concentration in a light gas-heavy oil system. The diffusion coefficient of a gas also increases with increasing temperature. An increase in the kinetic energy of gas molecules is accompanied by a decrease in the viscosity of heavy oil. The diffusion coefficient of gases in a system with heavy oil is higher than in a system containing asphaltenes. The mass transfer of the interacting components is reduced in this case. The distribution of the concentration of light gases in an oil reservoir is also determined by thermodynamic factors, in particular, solubility, diffusion, surface sorption capacity, temperature and pressure of the reservoir.

3.4 *Fick's laws in a binary mixture*

Consider diffusion in a binary mixture A-B from the point of view of Fick's laws. The mass transfer rate according to Fick's first law is determined by the molecular diffusion coefficient $D_{\text{A-B}}$ (m^2/s or cm^2/s) in the A-B system

$$m_{\text{A},x} = -D_{\text{AB}} S \frac{dc_{\text{A}}}{dx} \cdot d\tau \tag{11}$$

where $m_{\text{A},x}$ is the mass transfer rate during diffusion in the x direction, kg/s (mol/s); S - mass transfer surface area, m^2; $\frac{dc_{\text{A}}}{dx}$ is the concentration gradient of substance A in substance B, kg/m^4 (mol/m^4), $d\tau$ is the diffusion time.

In other words, molecular diffusion obeys Fick's first law in a binary A-B mixture in a bulk vessel. The diffusion flux density j_{AB} of the components is proportional to the concentration gradient ∇c_{AB}. Therefore, taking into account equation (5), we can write

$$j_{\text{A},x} = -D_{\text{AB}} S \frac{\partial c_{\text{A}}(x,\tau)}{\partial x},\ j_{\text{B},x} = -D_{\text{AB}} S \frac{\partial c_{\text{B}}(x,\tau)}{\partial x} \tag{12}$$

where $\nabla c = \partial c/\partial x$ is the relative mass flux of components in the medium at given temperature T and pressure P. The flow j_{AB} characterizes the number of particles crossing a unit area (S) per unit time (τ). In the one-dimensional case ($\rho = \rho(x)$) (when diffusion is along the x-axis) j_{AB} is equal to $\partial c/\partial x$.

The minus sign in equation (12) indicates concentration equalization during diffusion. Equilibrium ($\partial c/\partial x = 0$) is achieved by uniform distribution of the components in the volume of the vessel, where $\partial c/\partial x$ is the increase in concentration (mass, volume, mole, etc.) in the direction of the x axis. Thus, the proportionality factor D_{AB} relates the diffusion flux density (j_{AB}) of the component to the concentration gradient (∇c).

Consider a binary mixture A-B in a closed fixed vessel of finite volume. In such a system, the diffusion coefficients of the components can be reduced to unity. To do this, we accept several conditions. Suppose that in equilibrium the total concentration of components does not depend on the direction x, $c = c_{\text{A}} + c_{\text{B}} = \frac{P}{k_{\text{B}}T} = \text{const}$. The component concentration gradients are opposite: $\frac{\partial c_{\text{A}}}{\partial x} = -\frac{\partial c_{\text{B}}}{\partial x}$.

In the system, the total particle flux is constant everywhere $j = j_{\text{A}} + j_{\text{B}} = \text{const}$. At the edge of the closed vessel, the total flow is $j = 0$. These conditions are met if $D_{\text{AA}} - D_{\text{AB}} = D_{\text{BB}} - D_{\text{BA}} \equiv D$. In this case, for the mixture A-B, Fick's law takes the form

$$j_{\mathrm{A}} = -D\frac{\partial c_{\mathrm{A}}}{\partial x},\ j_{\mathrm{B}} = -D\frac{\partial c_{\mathrm{B}}}{\partial x} \tag{13}$$

Equation (13) is applicable when D_{AB} weakly depends on the concentration of the target component A in substance B. For example, in dilute solutions and in the physical absorption of gases in liquids, Fick's 1st law is valid. In this case, D_{AB} is a function of the chemical composition of the mixture A-B, temperature T and pressure P.

For binary gas-liquid systems, the molecular diffusion coefficient (m^2/s) depends on temperature by the exponential relationship $D_{\mathrm{AB}} = K \cdot \exp b \cdot T$, where K is the coefficient, b is the exponent, T is the temperature in °C.

When D_{AB} strongly depends on the concentration of component A in substance B, then the rate of mass transfer of substance A in substance B is described by Fick's second law

$$m_{\mathrm{A},x} = -D_{\mathrm{AB}} S\frac{d^2 c_{\mathrm{A}}}{dx^2} \tag{14}$$

The rate of change of the diffusion flux j_{AB} is proportional to the rate of change of concentration ∇c according to Fick's second law. Application of the law of conservation of energy, taking into account the 1st Fick's law, gives the differential equation of the 2nd Fick's law. Let us assume that the diffusion coefficient of the component does not depend on the coordinate ($D \neq D(x)$) and on the concentration ($D \neq D(c)$). Then, for $D = \mathrm{const}$, the diffusion equation for the one-dimensional case will have the form

$$\frac{\partial c(x,\tau)}{d\tau} = D\frac{\partial^2 c(x,\tau)}{\partial x^2}. \tag{15}$$

As can be seen, this equation relates the spatial distribution of concentration with its change in time.

3.5 *D in the three-dimensional case*

The scalar form of the diffusion equation in the three-dimensional case goes over into the diffusion tensor. That is, in this case, diffusion does not depend on a change in the coordinate system, but its components, when the coordinate system is changed, are transformed according to a certain mathematical law. Then only the diagonal elements D_{xx}, D_{yy}, D_{zz} of the tensor can be left in the rectangular coordinate system (reduction to the principal axes). In such a coordinate system, the diffusion equation has the following form

$$\frac{\partial c(x,y,z,\tau)}{d\tau} = D_{xx}\frac{\partial^2 c(x,\tau)}{\partial x^2} + D_{yy}\frac{\partial^2 c(y,\tau)}{\partial y^2} + D_{zz}\frac{\partial^2 c(z,\tau)}{\partial z^2}. \tag{16}$$

With $D_{xx} = D_{yy} = D_{zz} = D$ we can write

$$\frac{\partial c}{d\tau} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right) = D\Delta c \tag{17}$$

Some problems of nonlinear diffusion have not yet been fully resolved. These include the relationship between the thermodynamic activity of components in solution and the diffusion coefficient, the hyperbolic diffusion equation, and the stochastic diffusion equation (the Fokker-Planck equation). In the one-dimensional case, these three problems associated with the diffusion tensor can be represented by the equations

$$\frac{\partial c}{\partial \tau} = D\left(\frac{\ln a_i}{\ln c}\right)\frac{\partial^2 c}{\partial x^2} \tag{18}$$

$$\frac{\partial c}{\partial \tau} + \tau^2 \frac{\partial^2 c}{\partial \tau^2} = D\frac{\partial^2 c}{\partial x^2} \tag{19}$$

$$\frac{\partial W(x,\tau)}{\partial \tau} = \frac{1}{2}\frac{\partial^2 W(x,\tau)}{\partial x^2} \tag{20}$$

Here $D = 1/2$, $W(x, \tau)$ is the probability density function. It describes the states of the system when the probability of a particle has a given velocity in the interval (x, τ).

3.6 *Equilibrium in mixtures*

Mixtures and chemical solutions are non-ideal phases. At high pressures they are described by the equation of state (EOS) for liquid-liquid equilibrium (LLE). Such phases are characterized by models that include the activity coefficient of the vapor phase and the Gibbs free energy of the liquid phase. However, for supercritical phases of mixtures it is difficult to determine the standard states of the mixture components. At the same time, the description of the activity coefficient becomes more complicated.

For example, for supercritical components of mixtures, the thermodynamic parameters are strongly dependent on temperature. Therefore, the critical properties of mixtures are difficult to predict. Various models are used in calculations for the vapor and liquid phases of mixtures.

In addition, the Gibbs free energy (G is the isobaric-isothermal potential) of such mixtures is not predicted as a function of temperature and pressure: $G = U + PV - TS$, where U is the internal energy, P is the pressure of the medium, V is the volume, T is the absolute temperature of the environment, S - entropy.

Mixed EOS models including the molar excess Gibbs free energy (G^{ex}) are therefore used to calculate the equilibrium of mixtures. Such unifying EOS-G^{ex} models make it possible to evaluate the deviations of the properties of mixtures from the ideal laws of solutions.

The properties of binary non-ideal mixtures, taking into account the activity coefficient, make it possible to predict VLE equilibria. The relationship between the activity coefficient (γ_i) and EOS is written as:

$$\gamma_i = \left[\bar{\boldsymbol{\phi}}_i(\boldsymbol{T},\boldsymbol{P},\boldsymbol{x}_i)/\boldsymbol{\phi}_i(\boldsymbol{T},\boldsymbol{P})\right] \tag{21}$$

where $\bar{\boldsymbol{\phi}}_i(\boldsymbol{T}, \boldsymbol{P}, \boldsymbol{x}_i)$ is the fugacity coefficient of particles i in the mixture, $\boldsymbol{x}_i$ is the mole fraction of component i in the liquid, $\boldsymbol{\phi}_i(\boldsymbol{T}, \boldsymbol{P})$ is the fugacity coefficient of the pure component. Here, both factor values are calculated based on EOS at mixture temperature and pressure.

The molar excess of the Gibbs free energy is

$$G_m^{\text{ex}} = RT\sum\nolimits_i x_i \ln \gamma_i \tag{22}$$

Here R is the gas constant. The combination of (21) and (22) leads to the equation

$$\frac{G_{m,\text{EOS}}^{\text{ex}}(T,P,x_i)}{RT} = \ln \phi(\boldsymbol{T},\boldsymbol{P},\boldsymbol{x}_i) - \sum\nolimits_i x_i \ln \boldsymbol{\phi}_i(\boldsymbol{T},\boldsymbol{P}) \tag{23}$$

Equation (23, 24) can be represented as a two-parameter cubic equation. The transformation of the cubic equation is given by the formula

$$\frac{G^{\text{ex}}_{m,\text{EOS}}(T,P,x_i)}{RT} = Z - \sum\nolimits_i x_i Z_i - \sum\nolimits_i x_i \ln\left(\frac{Z}{Z_i}\right) - \sum\nolimits_i x_i \ln\left[\frac{\left(1-\frac{b}{V_\text{m}}\right)}{\left(1-\frac{b_i}{V_\text{m}}\right)}\right] + \left(\frac{a}{bRT}\right)C(V_\text{m}) - \sum\nolimits_i x_i\left(\frac{a_i}{b_iRT}\right)C(V_{\text{m},i}) \quad (24)$$

where $C(V_{m,i})$ is function depending on molar volume V_m, Z is compressibility factor.

Equation (23, 24) establishes a connection between the EOS parameters: coefficients a and b, mixture composition, activity coefficient and excess Gibbs free energy.

To calculate the equilibrium of the binary system carbon dioxide - methane, a combination of the EOS HVO model[13] for the liquid phase was used. According to the HVO model, the equation of state of the mixture assumes that the density of the phases is similar to the density of the liquid at zero (or low) pressure. It is accepted that at such densities, models for calculating the activity coefficient can also be applied to the mixture. To ensure this condition, the relation

$$G^{\text{ex}}_{m,\gamma}(T, P=\infty, x) = G^{\text{ex}}_{m,\text{EOS}}(T, P=\infty, x) \quad (25)$$

where $G^{\text{ex}}_{m,\gamma}(T,\ P = \infty,\ x)$ and $G^{\text{ex}}_{m,\text{EOS}}(T,\ P = \infty,\ x)$ are excess Gibbs free energies at infinite pressure (at densities similar to liquid). These energies are calculated based on the vapor phase activity coefficient model and the liquid phase EOS, respectively.

In addition, to take into account $G^{\text{ex}}_{m,\text{EOS}}$ in the HVO model it is assumed that

$$V^{\text{ex}}_m = V_m - \sum\nolimits_i x_i V_i = b - \sum\nolimits_i x_i b_i = 0 \quad (26)$$

Taking into account the above, the mixing rule of the EOS HVO model for parameter a has the form:

$$a = b\left[\sum\nolimits_i x_i\left(\frac{a_i}{b_i}\right) + \frac{G^{\text{ex}}_m}{C^*}\right] \quad (27)$$

where C^* is a molar volume dependent function specific to the selected EOS.

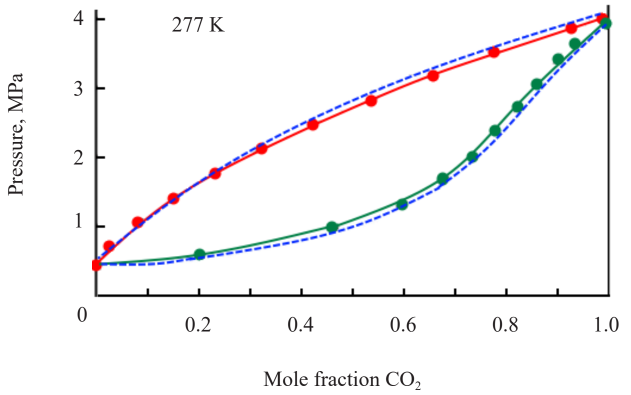

Figure 6. LLE liquid-liquid equilibrium correlation (dashed lines) for the carbon dioxide-methane binary system at 277 K. The HVO mixing rule including the excess Gibbs free energy and the PRSV equation of state were used

In other words, the isothermal dependence of pressure on the composition of CO_2 in the binary carbon dioxide-methane system was constructed using a combination of the Peng-Robinson EOS equation of state and HVO models. A typical isothermal dependence of pressure on composition in the binary carbon dioxide-methane system approximated by the EOS HVO-G^{ex} model is shown in Figure 6. The parameters of this model were adapted to the data of the liquid-liquid equilibrium of the system, taking into account the Peng-Robinson equation of state (PR EOS).[14] In this case, the temperature dependent PR EOS parameters are used. For the Peng-Robinson equation, the value of C^* at infinite pressure is $C^* = -0.62323$.

For each pure compound, an exact constant corresponding to the low-temperature saturation pressure is selected.[15] Accounting for such a modified constant in the Peng-Robinson EOS is given by the PRSV equation.

The results of isothermal calculations deteriorate as the temperature increases from 277 to 345 K. This is due to the fact that the excess Gibbs free energy of mixing is pressure dependent. For the CO_2-CH_4 system, the calculated data differ from the experimental data by 15-40% for isotherms 277-345 K.

The scientific novelty of the work is justified by the fact that measurements of the relative mass of diffusing components and calculation of the diffusion coefficient of light gases using the molecular dynamics method increase the efficiency of describing the interaction in a system involving a SCF. Liquid-heavy oil SCF systems used CO_2 and n-alkanes (gases) under thermobaric conditions at 298-365 K and 4-8 MPa. Taking into account the equations of state and models of hydrocarbon mixtures, *pVT* dependencies were approximated. New experimental data were obtained for the SCF methane-heavy oil, SCF ethane-heavy oil, and SCF propane-heavy oil systems. They differ from the diffusion coefficients calculated by molecular dynamics by less than 30%. *pVT* dependences of previously unmeasured gas-heavy oil fluid systems near critical points were constructed.

The advantages of this study and the methods of experimental and theoretical study lie in the fact that in the course of the work, models of the studied fluid mixtures and objects of study were created. This made it possible to conduct a detailed and accurate study.

The disadvantages of this study are that the fluid solution models and equation of state (PR Equ) used do not allow high-precision *pVT* calculations. For example, the calculated *P*-*x* curves of SCF CO_2-heavy oil differ by 15-40% from the experimental ones in the temperature range 277-345 K.

The obtained experimental and computational data contributes to the development of knowledge in the study of multicomponent and multiphase fluid oil mixtures.

The state of the known models for studying fluid systems is represented by gaps created by two subsystems: model binding and model checking. Model binding gaps are errors in the transformation of experimental data. For example, MD simulation data and thermodynamic *pVTx* (here *x* is the composition of the component, for example, in SCF CO_2-heavy oil) data of fluid systems based on light gases containing heavy oil have different accuracies. The model is verified after it is linked to a specific system and the reliability of the approximation is determined.

Comparison with experimental data[16] of fluid hydrocarbon systems showed that it is possible to change the research conditions and calculate the characteristics of a specific fluid composition. Thus, it is possible to approximate to which area of reality the used theoretical knowledge extends.

The new contribution in the article is related to applied research, aimed primarily at the application of new knowledge and data in binary fluid hydrocarbon systems to achieve practical goals and solve specific problems.

4. Conclusions

Studies of the diffusion of SCF CO_2 and SCF n-alkanes by molecular dynamics methods and measurements of the relative mass of diffusing components in the SCF gas-heavy oil (Siyazan field of Azerbaijan) system at 298-365 K and 4-8 MPa showed the following. The calculated *pVT* parameters and diffusion coefficients (*D*) in binary A-B systems based on the SCF of light gases are in good agreement with the experimental data. Comparing the data obtained using the experiment and MD simulation, we can conclude that the agreement between them is below 30%.

The diffusion coefficient SCF of methane and ethane in an A-B-fluid system is higher than the *D* value of propane at a given B concentration and temperature. The value of *D* in systems A-B-increases with an increase in the concentration of B up to 2.5 wt. %. A further increase in the concentration of oil in A-B-leads to a decrease in *D*, this is especially noticeable for a system involving propane SCF. Diffusing light gas molecules reduce the viscosity of heavy oil in A-B-systems. In this case, the mass transfer of gas molecules is facilitated. In a fluid mixture, the molecules of the oil components reduce the movement of the SCF gas molecules. As a result, the diffusion coefficient SCF A in the A-B system decreases. Diffusion dependences $D = f(x)$ SCF of systems A-B tend to an asymptotic value with increasing concentration B. The dependence of the gas diffusion coefficient on pressure is not monotonic for the A-B-system.

The relationship between the parameters of the Peng-Robinson equation of state (PR EOS) for mixtures of light gases is analyzed. This relationship is described by coefficients a and b, composition, activity coefficient and excess Gibbs free energy of mixing the mixture. The use of a modified PR EOS made it possible to approximate the isothermal dependence P-x of the carbon dioxide-methane binary system. It was assumed that the densities of the mixture phases are similar to the density of liquid at low pressure. The calculated P-x curves carbon dioxide-methane binary system differ from the experimental ones by 15-40% in the temperature range 277-345 K.

Conflict of interest

The authors declare that they have no conflict of interest.

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