Temperature dependence of the interdiffusion coefficient in a CO_2–Ne solution near the critical point for vaporization of the solvent

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The equilibration time of the concentration in a capillary is used to measure the temperature dependence of the interdiffusion coefficient near the critical point for CO_2 vaporization in a CO_2–Ne solution. It is shown that in the region of reduced temperatures $10^{-3} \lesssim \tau \lesssim 10^{-1}$ the singular part of the mobility (the Onsager coefficient) is much smaller than the regular part. The latter can be evaluated in this region by a theory of the Enskog-Chapman type. The anomalies of the diffusion coefficient in this region are governed by the derivative of the chemical potential with respect to the concentration of the solution.

A study of interdiffusion near the critical points of binary solutions is of great interest because in such a region a solution is an extremely nonideal system with substantial anomalies of its equilibrium and kinetic properties.[1–3] The first experimental studies in this field were undertaken by Krichevski and co-workers.[4,5] In 1965 Leontovich proposed a phenomenological theory[6] describing the diffusion anomalies near the critical point of the solvent. This theory was based on an equation of the van der Waals type and presupposed the absence of anomalies in the mobility of the components (Onsager coefficients). Somewhat later, experimental studies of the light-scattering spectrum near the critical point revealed the presence of an anomaly in the mobility of the components.[7,8] The special case of kinetic phenomena near the critical point for vaporization of the solvent was considered in Ref. 11.

In considering diffusion processes in nonideal solutions (such as solutions near critical points) it is necessary to take into account the fluxes arising as a result of the change in density upon mixing of the components. For this reason there is ambiguity in defining the diffusion coefficients, and it becomes necessary to describe the diffusion by a nonlinear equation.[6]

Let us define the diffusion coefficient for the mixing of the components of a solution under conditions such that one can neglect the gradients of the temperature and pressure:

$$N(v-w)=-D\partial N/\partial x. \tag{1}$$

Here D is the diffusion coefficient defined with respect to a coordinate system moving with the average velocity, with the concentration gradient expressed in terms of the gradient of the fraction N of particles of one of the components (in the present case, the solute), x is the coordinate in the laboratory system (we are considering the one-dimensional case), v is the average velocity of the solute, the flux of which with respect to the laboratory system is equal to nNv, where n is the number density of the particles, and w is the average velocity of all the particles of the solution. With allowance for the continuity equation it can be shown that this velocity is given by

$$w(x_2)-w(x_1)=-\left[D\frac{1}{n}\left(\frac{\partial n}{\partial N}\right)_{p,T}\frac{\partial N}{\partial x}\right]\Bigg|_{x_1}^{x_2} - \int_{x_1}^{x_2} nD\frac{\partial^2(1/n)}{\partial^2 N}\left(\frac{\partial N}{\partial x}\right)^2 dx. \tag{2}$$

Thus the velocity w arises as a result of the dependence of the density of the solution of the concentration when concentration gradients are present in the solution. It is also seen from equation (2) that the velocity w, like the particle fluxes, is not a local quantity relative to the laboratory coordinate system. We emphasize that the solution is in a state of mechanical equilibrium[12] and is not acted upon by external forces or fields which would set it in motion.

If the drop in concentration over a length $x_2 - x_1$ is small, one can neglect the integral in (2), and then in place of the nonlinear diffusion equation one can use the Fick equation[13]

$$\partial N/\partial t=D\partial^2 N/\partial x^2. \tag{3}$$

This is the basis of one of the experimental methods employed in this paper for determining the interdiffusion coefficient under conditions of a strong concentration dependence of the density of the solution.

According to nonequilibrium thermodynamics,[12]

$$D=Nb(\partial\mu/\partial N)_{p,T}, \tag{4}$$

where μ is the chemical potential of the component per particle, and b is its macroscopic mobility with respect to a coordinate system moving at a velocity w and is related to the corresponding Onsager coefficient. According to the fluctuation theory of second-order phase transitions[1] the mobility b and the derivative $(\partial N/\partial\mu)_{p,T}$ diverge at a critical point of a binary solution. Therefore, let us separate the quantities appearing in (4) into singular (s) and regular (r) parts[8]:

$$D=D^{(s)}+D^{(r)}, \tag{5}$$

$$D^{(s)}=\frac{Nb^{(s)}}{(\partial N/\partial\mu)^{(s)}+(\partial N/\partial\mu)^{(r)}}, \tag{6}$$

$$D^{(r)}=\frac{Nb^{(r)}}{(\partial N/\partial\mu)^{(s)}+(\partial N/\partial\mu)^{(r)}}. \tag{7}$$

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Far from the critical point the diffusion coefficient is governed by the term $D^{(r)}$, while $D^{(s)}$ becomes the governing term as one approaches close to the critical point.

According to the mode-mode interaction theory,[1,9,10] near the critical point of mixing of a binary solution, where one can neglect the regular terms, the diffusion coefficient is given by

$$D=\frac{Nb^{(s)}}{(\partial N/\partial \mu)^{(s)}}=\frac{kT}{6\pi\eta^{*}r_c}, \tag{8}$$

where k is the Boltzmann constant, η^* is the "high-frequency" viscosity (in our case for purposes of estimation one can take this to be the shear viscosity of the solution), and r_c is the correlation radius of fluctuations in the concentration. The macroscopic mobility thus diverges like τ^{-v}, where $\tau=(T-T_c)/T_c$, v is the critical exponent of the correlation radius, and T_c is the critical temperature of the solution. The phenomenological meaning of Eq. (8) is that $D^{(s)}$ is the diffusion coefficient for Brownian particles with a radius equal to the correlation radius of the fluctuations.

For states of the solution near the critical point of vaporization it becomes necessary to take into account that the concentration N is small. As was shown in Ref. 11, allowance for this fact on the basis of the isomorphism of critical phenomena yields to following expression for the mobility:

$$b^{(s)}=\frac{N}{nk^2T_k{}^3}\left(\frac{dT}{dN}\right)_k^2\lambda^{(s)}, \tag{9}$$

where $\lambda^{(S)}$ is the singular part of the thermal conductivity of the pure solvent and T_{cr} is its critical temperature of vaporization. The derivative is taken along the critical curve, near T_{cr}.

The second term on the right-hand side of (5) corresponds to the coefficient of diffusion of the molecules of the solution in a mean field of interaction which depends on the concentration of particles. One can obtain an expression for this diffusion coefficient by transforming the Bogolyubov chain of kinetic equations in the limit of weak interaction, neglecting the ternary and higher correlation functions.[14] As a result, one obtains a Boltzmann kinetic equation with an average force of interaction:

$$\left(\frac{\partial}{\partial t}+\mathbf{v}_a\frac{\partial}{\partial \mathbf{r}_a}+\mathbf{F}_a^{(c)}\frac{\partial}{\partial \mathbf{P}_a}\right)f_a(\mathbf{P}_a,\mathbf{r}_a,t)$$

$$=\sum_{b=a,b}\int d\mathbf{P}_b v_{ab}\,ds_{ab}\{f_a'f_b'-f_af_b\}, \tag{10}$$

where $\mathbf{v}_a$, $\mathbf{P}_a$, and $\mathbf{r}_a$ are the velocity, momentum, and coordinate of a particle, respectively, v_{ab} is the relative particle velocity, ds_{ab} is the differential scattering cross section, $f(\mathbf{P},\mathbf{r},t)$ and $f'(\mathbf{P},\mathbf{r},t)$ are the single-particle correlation functions before and after the collision, respectively, $F_a^{(c)}$ is the average force of interaction, which depends on the single-particle and two-particle correlation functions, and the indices a and b denote the components of the solution. Solution of equation (10) in the familiar Enskog-Chapman approximation[15] yields the following expressions for the diffusion coefficient and the mobility:

$$D^{(r)}=b^{(r)}N\frac{\partial}{\partial N}(kT\ln N+U^{(c)}), \tag{11}$$

$$b^{(r)}=\frac{0.1496}{\sigma_{12}{}^2\Omega^{(1,1)*}n}\left(\frac{m_1+m_2}{m_1m_2kT}\right)^{1/2}, \tag{12}$$

where $\Omega^{(1,1)*}$ is the reduced collision integral, σ_{12} is the effective scattering diameter, m_1 and m_2 are the particle masses, $U^{(c)}$ is the mean field of interaction associated with the average force $F^{(c)}$.

The expression for the field $U^{(c)}$ in terms of the molecular constants is rather awkward and is not amenable to evaluation for realistic models, but one can determine the field if the equation of state is known. In fact, one can see by comparing equations (7) and (11) that this field can be expressed in terms of the chemical potential:

$$\frac{\partial}{\partial N}(kT\ln N+U^{(c)})=\left(\frac{\partial \mu}{\partial N}\right)_{pT}. \tag{13}$$

Clearly, when the interaction field is zero, Eq. (11) implies

$$D^{(r)}=D_0=b^{(r)}kT. \tag{14}$$

We note that expression (12) corresponds to the result in the first approximation of Enskog-Chapman theory for a rarefied gas. By examining (10)–(14) one sees that the diffusion process governed by diffusion coefficient (7) takes place in a mean field which depends on the concentration of particles. Near the critical point the field gradient is directed along the particle-concentration gradient and inhibits equilibration of the concentration.

EXPERIMENT

In the present study experiments were carried out in a dilute solution of neon (Ne) in carbon dioxide (CO_2) in the region of reduced temperatures $10^{-3}<\tau<10^{-1}$ near the critical density of the solution at concentrations $\mathcal{N}<0.04$ mole fraction of Ne by the capillary method described previously.[16,17] The method essentially consists of determining the rate of change of the average concentration of a solution filling a capillary which is closed at one end and immersed at the open end in a solution whose density and concentration (different from the initial composition of the solution in the capillary) are held constant over the entire course of the experiment. The method ensures a constant temperature and pressure in the capillary during the diffusion and provides conditions of mechanical equilibrium of the solution.[12] In the experiments the drops in concentration were small, making it possible to use Eq. (3). The concentration measurements were made with a mass spectrometer.

The uncertainty in the measurements of the diffusion coefficients depends strongly on the proximity to the critical point and lies in the range of 2–10% of the measured quantity. There are also uncertainties in the analysis due to the necessity of taking into account the changes in the critical temperature and density of the solution and, hence, the "drift" of the reduced temperature τ. The change in the critical temperature is caused by the change in composition of the solution due to diffusive mixing of the components.

For comparison of the experimental data with the theory, Fig. 1 shows a plot of $\lg(D/D_0)$, where D is the experi-

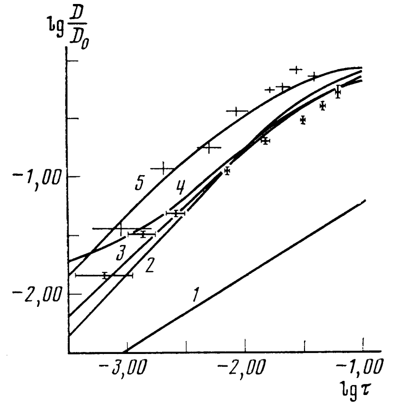

FIG. 1. Temperature dependence of the interdiffusion coefficients in CO_2–Ne and CO_2–Ar solutions near the critical point for vaporization of CO_2. CO_2–Ne: barred crosses) experimental values; 1) D/D_0, where D is described by Eq. (16) and $D_0 = 9.3 \cdot 10^{-8}$ m²/sec, 2) Eqs. (5), (16), and (22), 3) Eq. (24), 4) Eq. (29). CO_2–Ar (Ref. 17): plain crosses) experimental values; 5) Eq. (24).

mental value and D_0 is the estimate of the diffusion coefficient from Eqs. (12) and (14). The change in D_0 due to the changing density in the capillary over the course of the diffusion corresponds to the vertical hash marks in Fig. 1. The horizontal hashes correspond to the change in the reduced temperature of the solution over the same time. In calculating D_0 we used the values of the effective scattering diameter (which has units of length!) $\sigma_{12} = (\sigma_1 + \sigma_2)/2 = 3.39 \cdot 10^{-8}$ cm; $\sigma_1 = 3.996 \cdot 10^{-8}$ cm (Ref. 18); $\sigma_2 = 2.789 \cdot 10^{-8}$ cm (Ref. 19); $m_1 N_A = 44.01$ g/mole; $m_2 N_A = 20.18$ g/mole, N_A is Avogadro's number, $\varepsilon_{12} k^{-1} = k^{-1}(\varepsilon_1 \varepsilon_2)^{\frac{1}{2}} = 82.4$K; $\varepsilon_1 k^{-1} = 190$ K (Ref. 18); $\varepsilon_2 k^{-1} = 35.7$ K (Ref. 19); σ_1, ε_1, and σ_2, ε_2 are the parameters of the Lennard-Jones potential[15] for CO_2 and Ne, respectively, and $\varepsilon_{12}, \sigma_{12}$ are the parameters for their solution; $\Omega^{(1,1)*}(\varepsilon_{12}/kT)$ is the integral calculated on the basis of the Stockmayer potential and averaged over molecular orientations[15]; the critical density of the pure solvent $n_{cr} = 1.085 \cdot 10^{-2}$ mole/cm³ (Ref. 20); $(dn/dN)\mathrm{cr}|_{N \to 0} = 1.22 \cdot 10^{-2}$ mole/cm³M (Ref. 21); $N = 0.036M$ Ne (indices 1 and 2 refer to the solvent CO_2 and the solute Ne, respectively).

Let us now use (8) to estimate the temperature dependence of the singular term of Eq. (5); as we have mentioned, this term is the diffusion coefficient of Brownian particles of radius r_c. According to Ref. 1 we have

$$r_c = r_0 \tau^{-\nu}, \tag{15}$$

where r_0 is the amplitude of the temperature dependence of the correlation radius. Further, we can assume for purposes of estimation that $\eta^* \sim \eta^{(r)}$ where $\eta^{(r)}$ is the regular part of the viscosity in the temperature region of the present measurements. In fact, it is known from experiment[22] that the viscosity of CO_2 in the critical region changes by no more than 10%, and it can be assumed that the change in the viscosity of a solution will be still smaller. If it is also taken into consideration that the modern theory[23] predicts that the critical exponent of the viscosity is small, the estimate given above for the high-frequency viscosity can be considered satisfactory. In the final analysis we obtain

$$D^{(s)} = A_\nu \tau^\nu, \quad A_\nu = kT/6\pi\eta^{(r)} r_0. \tag{16}$$

Figure 1 shows a plot of D/D_0 according to (16), with $\eta^{(r)} = 3.3 \cdot 10^{-4}$ g/cm · sec (Ref. 22), $r_0 = 3 \cdot 10^{-8}$ cm (we adopted this value of r_0 on the basis of the review by Anisimov[2]), $D_0 = 9.2 \cdot 10^{-4}$ cm²/sec, and with a slope $\nu = 0.63$; it is seen that the values calculated from (16) lie significantly below the experimental data. This rough estimate implies that the experimental dependence should apparently be described mainly by the regular part of the mobility.

Let us determine the boundary temperature at which the singular part of the mobility becomes larger than the regular part. We estimate the boundary temperature at the critical density using Eq. (9), with[24]

$$\lambda^{(s)} = \frac{kT_{cr}^2}{6\pi\eta^{(r)} r_c} \left(\frac{\partial p}{\partial T}\right)_\rho^2 k_T F(\tau, \Delta n), \tag{17}$$

where

$$\Delta n = \frac{n - n_{cr}}{n_{cr}}, \quad k_T = n^{-1} \left(\frac{\partial n}{\partial p}\right)_T = A_\gamma \tau^{-\gamma},$$

γ is the critical exponent of the compressibility, and in our case $F(\tau, \Delta n) = 1$. The regular part of the mobility can either be evaluated by (12) or estimated in order of magnitude using the Stokes equation[13]:

$$b^{(r)} = [6\pi\eta(\sigma_1/2)]^{-1}. \tag{18}$$

As a result

$$\tau_0 = \left[\frac{N}{n_{cr} kT} \left(\frac{dT}{dN}\right)_{cr}^2 \left(\frac{dp}{dT}\right)_\rho^2 A \frac{\sigma_1}{2r_0}\right]^{1/\nu}. \tag{19}$$

For the investigated CO_2–Ne solution we take the average value of the concentration in the experiment as $N = 0.036$ mole fraction of Ne; $n_{cr} = 6.53 \cdot 10^{21}$ cm^{-3} (Ref.20); $T_{cr} = 304.15$K (Ref. 25); $(dT/dN)_{cr} = -24.57$ K/mole fraction (Ref. 21); $(dp/dT)_\rho = 1.71 \cdot 10^6$ dyn/cm²K (Ref. 25); $\sigma_1/2 = r_0$, $A = 7.6 \cdot 10^{-10}$ cm²/dyn (Ref. 25); $\gamma = 2\nu$, $\nu = 0.63$ (Ref. 1). We finally obtain $\tau_0 = 1.1 \cdot 10^{-6}$. If we use Eqs. (9) and (12) we get $\tau_0 = 4.2 \cdot 10^{-7}$. Consequently, in the temperature region of the present measurements the diffusion coefficient should be described by the regular part of the mobility.

For estimating the diffusion coefficient in the region we use the relation from the fluctuation theory[1]

$$(\partial N/\partial \mu)^{(s)} = A_\gamma \tau^{-\gamma} \tag{20}$$

and the approximation for a weak ideal solution

$$(\partial N/\partial \mu)^{(r)} = N/kT. \tag{21}$$

Then

$$D^{(r)} = (1 + A_\gamma' \tau^{-\gamma})^{-1}, \quad A_\gamma' = A_\gamma kT/N. \tag{22}$$

It should be noted that the applicability of estimate (23) for the mobility $b^{(r)}$ at densities clear up to the critical density is actually something more of an experimental fact, since this relation was obtained in the limit of small densities. The correctness of using Eq. (12) or the like for evaluating the regular part of the mobility at densities as high as the critical density is discussed in Ref. 14, where a review of the experimental data relevant to this question is also given. Unfortunately, at the present time the coefficients A_γ of the scaling-theory equation of state for CO_2–Ne solutions are unknown, and therefore the coefficient A'_γ here remains an adjustable parameter. The temperature dependence of the interdiffusion coefficient according to (5), (16) and (22) with $D_0 = 9.2 \cdot 10^{-4}$ cm²/sec, $A'_\gamma = 2.0 \cdot 10^{-2}$, and $A_\nu = 2.30 \cdot 10^{-4}$ cm²/sec is given by curve 2 in Fig. 1; it is seen that Eq. (22) gives satisfactory agreement with the experimental data.

Another possibility for estimating the temperature dependence arises in light of the fact that the critical exponent $\gamma = 1$ in the van der Waals–Landau theory of the critical point is not greatly different from the value $\gamma = 1.2$ from the fluctuation theory.[1] Thus one can, with a certain error, estimate $(\partial N/\partial\mu)$ using a mean-filed type theory, which in the present case of diffusion near the critical point for vaporization of the pure solvent gives[6]

$$D = D_0\left[1 + \frac{A_N{}^2 N/kT}{A_{NV}N + A_{TV}\,\Delta T + 3A_{VVV}(\Delta V)^2}\right]. \tag{23}$$

For $\Delta V = O$ we have

$$D = D_0(1 - A_1\tau^{-1})^{-1}, \quad A_1 = NA_N{}^2/kT_c{}^2A_{TV}. \tag{24}$$

In relations (23) and (24) the coefficients are given by the equation of state

$$p - p_{\mathrm{cr}} = A_N N + A_T\Delta T + A_{NV}N\Delta V + A_{TV}\Delta T\Delta V + A_{VVV}(\Delta V)^3, \tag{25}$$

where $V = 1/n$, $\Delta V = V - V_{\mathrm{cr}}$, $\Delta T = T - T_{\mathrm{cr}}$, and the subscript "cr" denotes the value of the parameter at the critical point of the pure solvent. According to Ref. 25 the coefficients of Eq. (25) are $A_T = 1.71 \cdot 10^2$ kPa/K, $A_{TV} = -1.80 \cdot 10^3$ kPa · K^{-1}kmole · m^{-3}, $A_{VVV} = -2.84 \cdot 10^{-6}$ kPa · kmole^3 · m^{-9}. For determining the remaining coefficients we use the experimental data for CO_2–Ne solutions along the critical line, which for low *Ne* concentrations is a straight line in *p-V-N-T* space, originating at the critical point of pure CO_2. From equation of state (25) we obtain the equation of the critical line as[26]

$$T_c - T_{\mathrm{cr}} = -\left(\frac{A_{NV}}{A_{TV}} + \frac{A_N{}^2}{kTA_{TV}}\right)N, \tag{26}$$

$$p_c - p_{\mathrm{cr}} = \left[A_N - A_T\left(\frac{A_{NV} + A_N{}^2/kT}{A_{TV}}\right)\right]N, \tag{27}$$

$$V_c - V_{\mathrm{cr}} = 0. \tag{28}$$

Strictly speaking, this equation for the critical line does not comply with experiment, since the data of Ref. 21 give a nonzero concentration derivative of the volume along the critical line, i.e., $(dV/dN)_{\mathrm{cr}} \neq 0$, in disagreement with (28). However, the disagreement in the case at hand is small and has no substantial affect on the interpretation of the experimental data by Eq. (25). This disagreement can be decreased further if ΔV in (25) is formally replaced by $\Delta V_c = V - V_c$ and Eq. (28) is replaced by the condition $V_c = (dV/dN)_{\mathrm{cr}}N$, where V_c is the experimental critical volume of the solution. Equations (26) and (27) can then be retained without modification in the given experimental situation. According to Ref. 21, $(dp/dN)_{\mathrm{cr}} = 4.09 \cdot 10^4$ kPa/mole fraction, yielding $A_N = 4.51 \cdot 10^4$ kPa/mole fraction and $A_{NV} = -8.49 \cdot 10^5$ kPa · kmole/m^{3}mole fraction. The temperature dependence corresponding to (24) with $A_1 = -5.3 \cdot 10^{-2}$ and with the values of the coefficients given above is shown by curve 3 in Fig. 1. It is seen that, as anticipated, this curve also agrees with experiment within the limits of error.

Using the fact that Eq. (23) applies, let us estimate the temperature dependence in the case when the density in the capillary is not equal to the critical density of the solution. Such a difference in these densities is observed in the measurement presented here. If ΔV_c is small, then Eq. (23) yields

$$D^{(r)} = D_0\left[1 - \left(\frac{1}{A_1}\tau + \frac{1}{A_2}(\delta V)^2\right)^{-1}\right]^{-1},$$
$$A_2 = \frac{NA_N{}^2}{3kT_{\mathrm{cr}}V_c{}^2A_{VVV}}, \qquad \delta V = \frac{\Delta V_c}{V_c}. \tag{29}$$

The temperature dependence from (29) is shown in Fig. 1 by curve 4, which was constructed for $A_2 = -0.403$ and $\delta V_c = -7.7 \cdot 10^{-2}$. It is seen that the correction due to the deviation from the critical density is small and can be neglected everywhere except, perhaps, in the immediate vicinity of the critical temperature, where the experimental error increases rapidly.

Figure 1 also shows values from earlier[17] diffusion experiments and the curve from (24), consistent with these values, for a CO_2–Ar solution with concentration $N = 0.043$ mole fraction of Ar ($A_1 = -2.1 \cdot 10^{-2}$). Analogous estimates for this solution give a boundary temperature of $\tau_0 = 6.0 \cdot 10^{-5}$. Thus, for this solution also the temperature dependence of the mobility in the investigated region is governed by its regular part.

Comparison of the experimental and theoretical curves shows that near the critical point for vaporization of the solvent, the diffusion coefficient can be described, to within the experimental error of less than 10%, with the aid of Eqs. (12),(14), and (23). In the interval $10^{-3} \lesssim \tau \lesssim 10^{-1}$ and for $N \lesssim 0.1$, $\rho \lesssim \rho_{\mathrm{cr}}$, the singular part of the mobility is at least an order of magnitude smaller than the regular part and can be neglected. The regular part of the mobility can be calculated using Enskog-Chapman theory in the rarefied-gas approximation (or by a similar theory; see, e.g., Ref. 27), even though the solution does not qualify as such. The anomalies of the interdiffusion coefficient for a solution in the given parameter region are governed mainly by the quantity $(\partial N/\partial\mu)_{p,T}$, which can be evaluated if the equation of state is known.

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