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Isochoric heat capacity measurements for a CO_2 + *n*-decane mixture in the near-critical and supercritical regions[☆]

Nikolai G. Polikhronidi[a], Rabiyat G. Batyrova[a], Ilmutdin M. Abdulagatov[a,b,*], Joseph W. Magee[b], Genadii V. Stepanov[a]

[a] *Institute of Physics of the Dagestan Scientific Center of the Russian Academy of Sciences, Makhachkala, Russia*
[b] *Physical and Chemical Properties Division, National Institute of Standards and Technology, 325 Broadway, Boulder, CO 80305, USA*

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Abstract

The isochoric heat capacity of a (0.7367 mole fraction) $CO_2 + (0.2633$ mole fraction) *n*-decane mixture was measured in a range of temperatures from 362 to 577 K, at nine near-critical liquid and vapor densities between 298 and 521 kg m^{-3} by using a high-temperature, high-pressure, nearly constant volume adiabatic calorimeter. The measurements were performed in both one- and two-phase regions including the vapor + liquid coexistence curve. Uncertainties of the heat capacity measurements are estimated to be 2% (in this work we use a coverage factor $k = 2$). The uncertainty in temperature is 10 mK and that for density measurements is 0.15%. The liquid and vapor one- (C'_{V1}, C''_{V1}) and two-phase (C'_{V2}, C''_{V2}) isochoric heat capacities, temperatures (T_S) and densities (ρ_S) at saturation were extracted from the experimental data for each filling density. The critical temperature ($T_C = 509.71 \pm 0.2$ K), the critical density ($\rho_C = 344.7 \pm 5$ kg m^{-3}), and the critical pressure ($P_C = 15.37 \pm 0.5$ MPa) for the (0.7367 mole fraction) CO_2 + (0.2633 mole fraction) *n*-decane mixture were extracted from isochoric heat capacity measurements using the well-established method of quasi-static thermograms. The observed isochoric heat capacity along the critical isochore of the CO_2 + *n*-decane mixture exhibits a renormalization of the critical behavior of C_V unlike that of the pure components. The ranges of conditions were defined, on the *T*–*x* plane for the critical isochore and the *ρ*–*x* plane for the critical isotherm, for which we observed renormalization of the critical behavior for isochoric heat capacity. The Krichevskii parameter for this mixture was calculated by using the critical loci for the mixture and vapor pressure data for the pure solvent (CO_2), and the results are compared with published values.

Keywords: Adiabatic calorimeter; Carbon dioxide; Coexistence curve; Critical point; Equation of state; Krichevskii parameter; Isochoric heat capacity; *n*-Decane; Supercritical fluid mixture

1. Introduction

Industry continues to widely exploit the anomalous properties of supercritical fluids [1–3]. Supercritical fluids are of fundamental importance in geology and mineralogy (for hydrothermal synthesis), in chemistry, in the oil and gas industries, and for some new separation techniques, especially in supercritical fluid extraction. Supercritical fluids have also been proposed as a solvent or reaction medium for a number of technological applications including coal conversion, organic synthesis, destructive oxidation of hazardous wastes (SCWO processes), enhanced oil recovery, activated carbon regeneration, formation of inorganic films and powders, supercritical chromatography, organic reaction rate modification and precipitation polymerization [1–3]. Supercritical carbon dioxide is widely used as a solvent in supercritical fluid extractions and supercritical fluid chromatography [4–7]. A supercritical carbon dioxide solvent has been proposed for a number of separation and reaction processes [7,8].

The thermodynamic properties of CO_2 + *n*-decane mixtures are of interest to the petroleum and natural gas industry, primarily because of the growing interest in the extraction

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[*] Corresponding author. Tel.: +1 303 497 4027; fax: +1 303 497 5224.
E-mail address: ilmutdin@boulder.nist.gov (I.M. Abdulagatov).

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of viscous, low volatility compounds with supercritical CO_2 in tertiary oil recovery and new separation techniques. Near-critical and supercritical carbon dioxide has been used as a miscible flooding agent that promotes miscible displacement of hydrocarbons from underground reservoirs [9]. To improve our understanding of the mechanism of the process of miscible displacement of reservoir oils by carbon dioxide injection (oil recovery enhancement) and control those processes, a better knowledge of model systems would be helpful. Since *n*-decane is a typical component of petroleum, and is available as a high-purity ambient-temperature liquid, it makes a good choice for a model system. Precise measurements are needed to establish the behavior of the thermodynamic properties of $CO_2 + n$-decane mixtures. Although our understanding of the thermodynamic properties of CO_2 and binary (CO_2 + solute) systems at ambient conditions has improved significantly, it is far from sufficient to accurately predict the behavior of (CO_2 + solute) systems for the near-critical and supercritical conditions that are currently of great scientific and practical interest. Therefore, to use supercritical CO_2 effectively, it will be necessary to know the thermodynamic properties of CO_2 + solute mixtures at supercritical conditions.

In addition, an important theoretical question is centered upon near-critical and supercritical phenomena in systems for which one of the components is near its critical point [10–12]. For example, there is great theoretical interest in negatively or positively diverging solute partial molar properties ($\bar{V}_2^\infty$, $\bar{H}_2^\infty$, $\bar{C}_{P2}^\infty$) in the immediate vicinity of the solvent's critical point and path-dependence of the solvent properties in near-critical systems [10–12]. The critical region behavior of $CO_2 + n$-decane mixtures is also of theoretical interest, for example, to determine how *n*-decane molecules affect the critical region behavior of carbon dioxide or to examine consequences of the isomorphism principle on the critical region behavior of $CO_2 + n$-decane mixtures. The shape of the critical locus curve is of great importance for studying the real critical behavior of mixtures, since the shape of the critical locus is very sensitive to differences in molecular size and interactions of the components. Binary mixtures of CO_2 with *n*-alkanes belong to three different types in the well-known classification by van Konynenburg and Scott [13]. In this scheme, the systems $CO_2 + (C_2$ to $C_4)$ are type I, $CO_2 + n\text{-}C_8$ is type II, and $CO_2 + n\text{-}C_{16}$ is type III. This illustrates the possible complexity that can be observed experimentally for binary mixtures of this class.

Published measurements of the thermodynamic properties of $CO_2 + n$-decane are scarce. Furthermore, reports of caloric properties, in particular the isochoric heat capacity of $CO_2 + n$-decane mixtures, are unknown. Thus, the main objective of this work is to provide new reliable experimental isochoric heat capacity data for $CO_2 + n$-decane mixtures in the critical and supercritical regions. Due to a scarcity of experimental (*PVTx* and $C_V VTx$) data, it is not yet possible to understand the effect of the solvent's critical region properties on the thermodynamic behavior of a $CO_2 + n$-decane mixture or to develop an accurate scaling type equation of state. Thus, in this work we report $C_V VTx$ properties of a mixture of (0.7367 mole fraction) CO_2 + (0.2633 mole fraction) *n*-decane measured using a high-temperature, high-pressure, nearly constant-volume adiabatic calorimeter in the temperature range between 362 and 577 K and the density range from 298 to 521 kg m^{-3}. Previously, we reported the isochoric heat capacity of the pure components CO_2 [14,15] and *n*-decane [16] in the near-critical and supercritical regions. The same apparatus was used to measure C_V for the $CO_2 + n$-decane mixture. Prior to this work, thermodynamic properties of $CO_2 + n$-decane mixtures have been reported [17–23]. Table 1 shows the available thermodynamic data sets for $CO_2 + n$-decane mixtures. In this table, the first author and the year published are given together with the method employed, the uncertainty indicated by the authors, and the temperature, pressure, and concentration ranges. As expected, experimental isochoric heat capacity data for $CO_2 + n$-decane mixtures were not available in the literature. Most of the available *PVTx* and *VLE* data cover only limited ranges of temperature, pressure, and concentration. Thus, the primary objective of this work was to expand the existing thermodynamic database for the $CO_2 + n$-decane mixtures. The available experimental critical curve data sets are given in Table 2. A brief synopsis of the different data sets is given below.

Nagarajan and Robinson [18] reported experimental vapor–liquid equilibrium phase compositions and phase densities (ρ'_S, ρ''_S) for the $CO_2 + n$-decane mixtures at two temperatures of 344.3 and 377.6 K and at pressures to the critical point. The phase compositions are in excellent agreement with the data reported by Reamer and Sage [17], however, the phase densities exhibit significant differences. In this case, the values of the critical density reported by Nagarajan and Robinson [18] are substantially higher than values reported by Reamer and Sage [17].

Recently Shaver et al. [21] reported liquid and vapor equilibrium phase compositions, phase densities, and interface tensions for the $CO_2 + n$-decane mixtures at 344.3 K. By using an extrapolation technique, they derived the values of the critical parameters (T_C, P_C, and ρ_C) for the composition $x = 0.065$ mol fraction of CO_2. The phase densities measured by Shaver et al. [21] and those of Nagarajan and Robinson [18] show excellent agreement. However, fairly large disagreement exists between these two data sets and the data of Reamer and Sage [17]. The liquid densities reported by Shaver et al. [21] are lower than those of Reamer and Sage [17] with the largest differences near the critical point. The liquid compositions reported by Shaver et al. [21] agree with all of the published data sets within 0.005 mole fraction CO_2 except those of Chou et al. [22]. The vapor phase compositions reported by Shaver et al. [21] are in good agreement with those of Nagarajan and Robinson [18] at low pressures, but differences near the critical point are about 0.006 mole fraction CO_2. The critical pressure reported by Shaver et al. [21] ($P_C = 12.714$ MPa) is in good agreement with the value ($P_C = 12.741$ MPa) derived by Nagarajan and Robinson [18]