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COMPARISON OF THE THERMODYNAMICS OF MIXING OF TITANIUM TETRACHLORIDE AND TIN TETRACHLORIDE WITH SUPERCRITICAL CARBON DIOXIDE

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ABSTRACT

Previous studies show that tin tetrachloride and titanium tetrachloride mix readily with supercritical CO_2. Comparison of these systems demonstrates significant differences in heats of mixing, mixture densities, and vapor-liquid equilibria. Although part of the difference may be attributable to the different densities of the pure solutes, there is some experimental and theoretical evidence that the intermolecular interactions between $SnCl_4$ and CO_2 are stronger than those between $TiCl_4$ and CO_2. These differences are consistent with the presence in tin of completed d and f orbitals which may affect interaction between $SnCl_4$ and CO_2.

INTRODUCTION

Understanding and predicting the rapid changes in fluid properties which occur near the critical point present a challenge in theoretical chemistry. The understanding of critical behavior has application both to pure compounds and to solutions. A thorough understanding of chemistry in the critical region will facilitate application of this novel chemistry to innovative separations, such as are needed in supercritical fluid chromatography (1), azeotropic mixtures (2), and the fractionation of low-vapor-pressure compounds (3).

The development of precision flow calorimeters has made possible the measurement of heats of mixing (H^E_m) on near-critical fluids (4, 5). These data have been used to explain solubilities in supercritical fluids (5,6). Wells and co-workers (7) showed that density-based correlations predict solubilities in supercritical fluids better than traditional equations of state, but noted the difficulty in obtaining experimentally measured densities of the resultant solutions. A complete description of critical phenomena requires knowledge both of the energy, derived from excess enthalpy measurements, and PVT behavior, which can be derived from density measurements. We have developed instrumentation to measure simultaneously both H^E_m and solution density values using a flow calorimeter connected to a densimeter (8). This equipment has been used to study systems containing $SnCl_4$ (9) and $TiCl_4$ (10) in supercritical CO_2. These compounds have commercial interest because they are precursors in the manufacture of metal products. The H^E_m, density, and vapor-liquid equilibrium data have been reported for the supercritical (CO_2 + $SnCl_4$) (9) and (CO_2 + $TiCl_4$) (10) systems. Molecular dynamics (MD) simulations have been reported for the supercritical (CO_2 + neopentane) (11) and (CO_2 + $SnCl_4$) (9) systems. No comparisons of these systems have been reported.

We compare here H^E_m, density, and vapor-liquid equilibrium data for the mixing of supercritical CO_2 with liquid $TiCl_4$ and $SnCl_4$. A comparison is also given of the ability of an MD model based on Lennard-Jones potentials to predict H^E_m values for the (CO_2 + $SnCl_4$) and (CO_2 + neopentane) systems.

Excess Enthalpies and Densities

Representative H^E_m and density values for (CO_2 + $SnCl_4$) are plotted in Figure 1. The H^E_m values (Figure 1a) generally were negative and the minima of the curves shifted toward the CO_2-rich

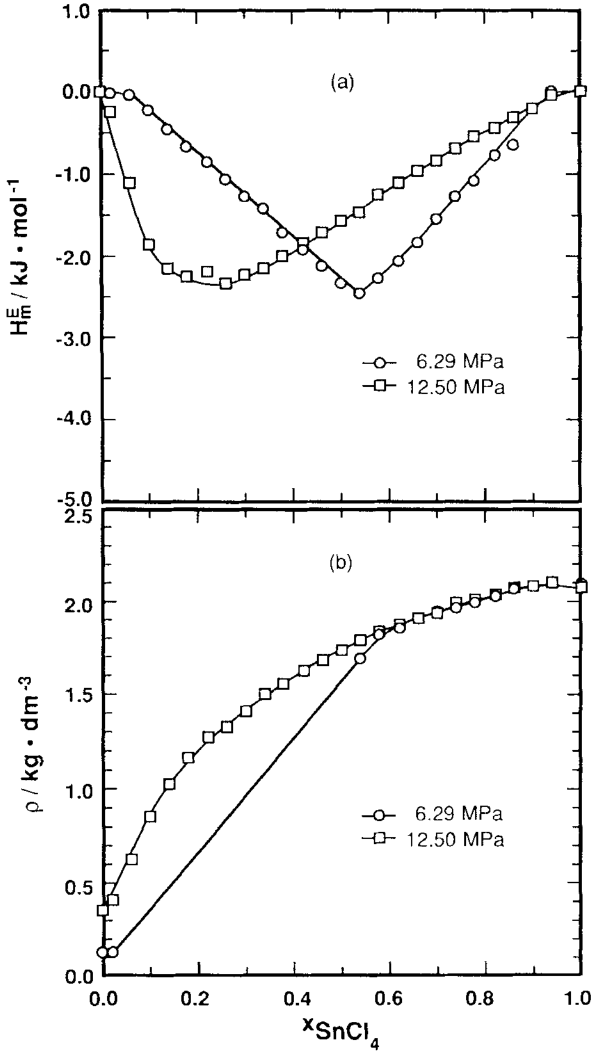

Figure 1. H^E_m (a) and densities (b) of (CO_2 + $SnCl_4$) at 348.15 K (9).

solutions with increasing pressure. A two-phase region is found for all mixtures except those at 12.50 MPa. The densities (Figure 1b) rose very rapidly with small additions of $SnCl_4$ to the CO_2. The density plots are strongly nonlinear indicating substantial interaction between the fluids.

Values of H^E_m and density for the system (CO_2 + $TiCl_4$) are plotted in Figure 2. The heats (Figure 2a) were negative except for the most CO_2-rich compositions. As with $SnCl_4$, densities (Figure 2b) rose rapidly with small additions of $TiCl_4$ to the CO_2, and continued to rise through the $TiCl_4$-rich compositions.

The large negative excess enthalpies and large positive excess densities both indicate attractive fluid-fluid interaction. In Figures 1 and 2, the results are compared at the same temperature and pressure. Because these conditions are quite removed from the solute critical points, it is assumed that a comparison of the mixing properties for the two systems at the same temperature and pressure relative to the common solvent critical point constitutes a valid comparison of intermolecular interactions. The larger negative H^E_m and V^E_m for the $SnCl_4$ mixtures may be explained in terms of two different phenomena. First, the density of $SnCl_4$ is significantly higher than that of $TiCl_4$. It is well known that mixing pure fluids of large density differences near the solvent critical point produces large negative H^E_m values (12). Therefore, the large H^E_m values in the case of $SnCl_4$ could be partially due to the higher density of $SnCl_4$. Second, the larger negative H^E_m in the case of $SnCl_4$ at 12.50 MPa, where there is no phase separation, indicates that at least part of the observed large negative H^E_m is due to stronger interactions between $SnCl_4$ and CO_2. This stronger interaction could be attributed to the presence in tin of filled d and f electron levels. Thus, $SnCl_4$ could participate in back bonding by donating these d and f electrons to empty levels on the CO_2. For this reason, the attraction between the CO_2 and $SnCl_4$ would be greater than that between CO_2 and $TiCl_4$.

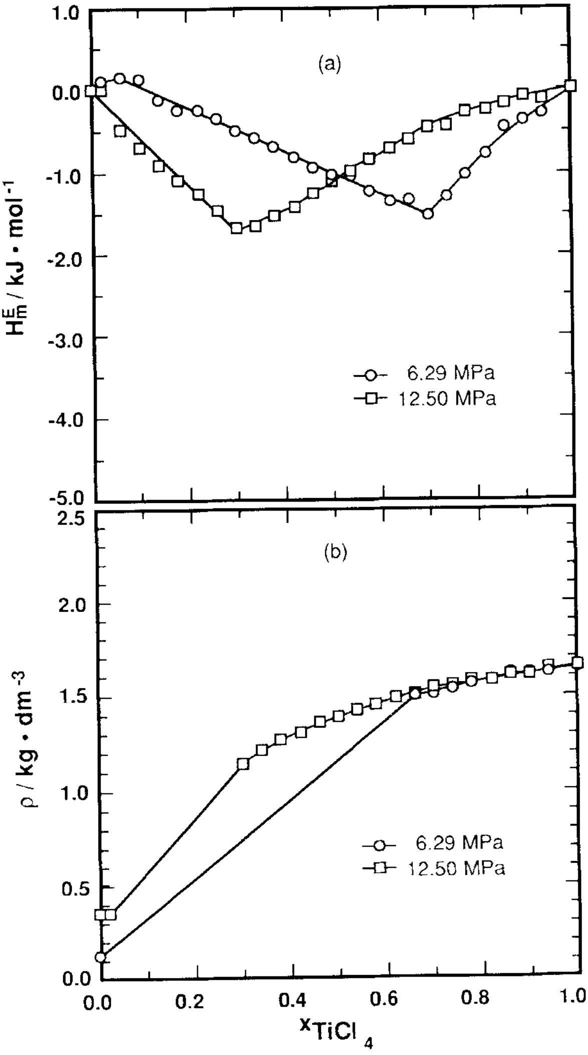

Figure 2. H^E_m (a) and densities (b) of (CO_2 + $TiCl_4$) at 348.15 K (10).

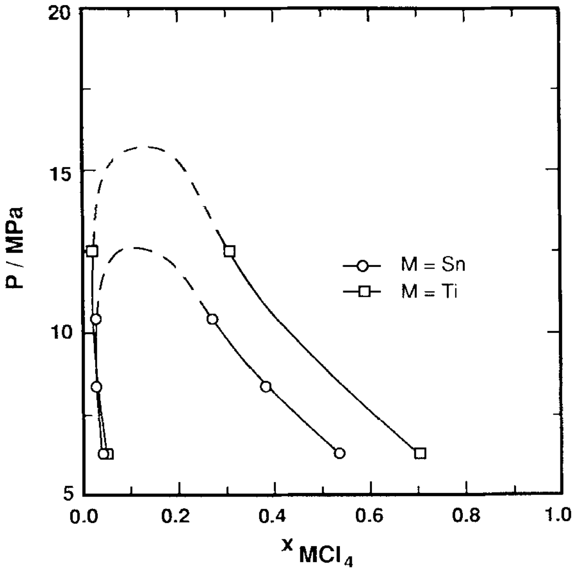

Figure 3. Vapor-liquid equilibrium data for the systems (CO_2 + $SnCl_4$) (9) and (CO_2 + $TiCl_4$) (10).

Fluid-fluid Immiscibility

A method to extract phase data from excess enthalpy curves is described by Christensen, et al. (13,14). Fluid composition boundaries for (CO_2 + $SnCl_4$) and (CO_2 + $TiCl_4$) are plotted in Figure 3. At the same temperature and pressure, the (CO_2 + $TiCl_4$) system exhibits less immiscibility than does the (CO_2 + $SnCl_4$) system. This result demonstrates that there is less attraction between CO_2 and $TiCl_4$ than between CO_2 and $SnCl_4$ In the (CO_2 + $TiCl_4$) system, the bubble points shifted to higher CO_2 contents of the fluids as the pressure increased. This is consistent with the vapor pressure of the fluid rising with increasing CO_2 content. Persistence of the fluid-fluid immiscibility to the high pressure distinguished this system from the (CO_2 + $SnCl_4$) system.

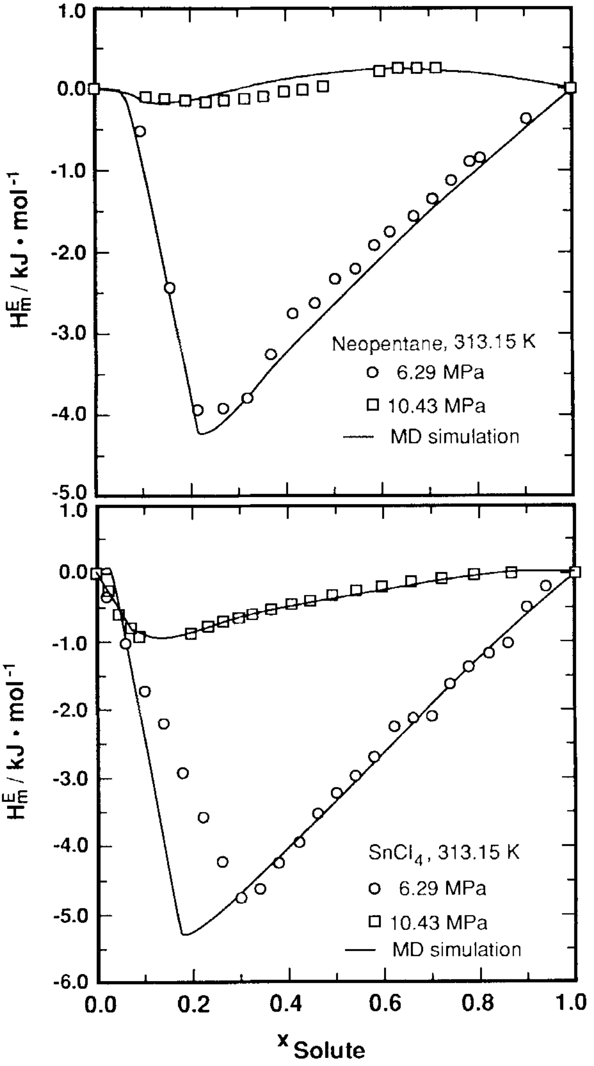

Figure 4. Comparison of experimental and modeled H^E_m values for neopentane (11), and $SnCl_4$ (9).

MOLECULAR DYNAMICS MODEL

A fundamental objective in our research was to develop a mathematical model capable of describing mixtures of supercritical CO_2 with metal tetrahalides. This model was to be based on sound physics to provide predictive capability without adjustable parameters. Molecular dynamics simulations were used to compute excess properties based on simple models for the molecular interactions. Details of our MD approach are available (9,11,15).

Results from previous MD simulations of H^E_m for (CO_2 + neopentane) (11,15) and (CO_2 + $SnCl_4$) (9) are of interest here because both solutes have similar molecular shapes, but they differ in that d orbitals are available only on the Sn. Figure 4 compares simulations for the two systems. In each case, the Lennard-Jones cross interactions were regressed at one composition, temperature, and pressure. This value was then used at all other conditions. The agreement with experiment is good except for the prediction of the phase split in the ($SnCl_4$ + CO_2) case. The MD simulations indicate that rather simple interaction models can be used to calculate mixing properties in the near-critical region. The discrepancy in the phase split compositions in Figure 4b may indicate that the influence of the d orbitals upon the intermolecular interactions is not completely accounted for by the simple models. It might also be attributable to the inadequacy of the fixed combining rule used for the cross interactions.

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