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Isotope effects on VLE properties of fluids and corresponding states: Critical point shifts on isotopic substitution

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Abstract

We employ an extended corresponding states theory for the description of liquid phase molar densities, ρ, and molar density isotope effects (IE's), and vapor pressures and vapor pressure IE's. In extended corresponding states, the conditions for liquid–vapor coexistence are given in terms of the critical properties of the fluid plus an additional parameter (*e.g.* the Pitzer acentric factor). Corresponding states theory is normally presented in its classical version, but thermodynamic IE's are quantum effects. We have chosen to introduce the quantization required to rationalize vapor–liquid equilibrium (VLE) isotope effects semi-empirically *via* the IE's on critical temperature, $\Delta T_C = T'_C - T_C$, critical pressure, $\Delta P_C = P'_C - P_C$, and critical density, $\Delta\rho_C = \rho'_C - \rho_C$. The primes refer to the lighter isotopomer. We limit attention to cubic or "almost cubic" equations of state (EOS), and point out useful correlations between critical temperature IE's and vapor pressure IE's in the near-critical region. When combined with EOS, such correlations allow the estimation of the other critical property IE's, and thence estimation of molar density IE's over a broad orthobaric liquidus range ($0.5 < T'_R = T/T'_C < 1$). Using a new modification of the Van der Waals EOS we find that liquid molar density IE's correlate quite well with the critical property isotope effects alone, while rationalization of vapor pressure IE's requires the addition of an isotope effect on the acentric factor.

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1. Introduction

In spite of the remarkable success of corresponding states (CS) theory for the description of the PVT properties of fluids, the approach has not been thoroughly explored so far as application to isotope effects (IE's) is concerned. In CS theories the temperature dependence of the molar volume and the conditions for liquid–vapor coexistence are expressed in terms of the critical properties of the fluid plus one or more additional parameters (*e.g.* the Pitzer acentric factor), but reliable critical property IE data are available for only a limited number of isotopomer pairs. Authors have been reluctant to apply CS to systems which show significant quantum effects (especially hydrogen and helium) because CS results from a simple idea connecting the intermolecular potential to the equation of state without explicit introduction of quantization. Even so, the successes of CS have led us to examine the application of that critical property isotope effect (CPIE) data which is available to express IE's on PVT properties far from the critical region. To do so we introduce the parametrization required to rationalize vapor–liquid equilibrium (VLE) isotope effects semi-empirically *via* the IE's on critical temperature, $\Delta T_C = T'_C - T_C$, critical pressure, $\Delta P_C = P'_C - P_C$, and critical density, $\Delta\rho_C = \rho'_C - \rho_C$ The primes refer to the lighter isotopomer. We limit attention to cubic or "almost cubic" equations of state (EOS), and point out useful correlations between critical temperature IE's and vapor pressure IE's in the near-critical region. Such correlations allow the estimation of the other critical property IE's for the first time, and estimation of molar density IE's over a broad range ($0.5 < T'_R = T/T'_C < 1$). Using a modified Van der Waals EOS we have found that liquid

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molar density IE's correlate quite well with CPIE's alone, but rationalization of vapor pressure IE's requires the addition of an isotope effect on the acentric factor.

1.1. Isotope effects (IE's)

It is now understood that isotope effects (IE's) on vapor pressure, condensed phase molar volume or molar density, vapor phase second virial coefficient, and molecular polarizability, are closely related. These effects share a common origin in quantum effects on vibrational properties. Recently we discussed the molecular origins of the virial coefficient IE [1], illustrating the close relationship between virial coefficient and vapor pressure IE's by comparing standard state free energy differences between average condensed phase molecules or average gas-phase dimers, on one hand, and the dilute gas-phase reference on the other. The approach clarified a long-standing confusion arising from the convenience of expressing virial coefficients (and their IE's) using parameter sets that define an intermolecular potential (and IE's) (ε, σ, $\Delta\varepsilon/\varepsilon$, $\Delta\sigma/\sigma$) [2–6], as compared to the use of a complete set of vibrational frequencies and their isotope dependences [7–10] to describe vapor pressure IE's. For virial coefficients the subtleties of vibrational averaging that leads from a proper isotope independent potential function to the parameter set which describes the intermolecular interaction and consequent IE's had not been clearly enough articulated. In the worst case, this resulted in interpretations which violated the Born-Oppenheimer approximation [11,12].

In this paper we explore methods of understanding isotope effects on fluids by applying corresponding states to describe molar volumes (or the equivalent molar densities, ρ) and their IE's, and vapor pressures and vapor pressure IE's in terms of isotopic differences in critical temperature, $\Delta T_C = T'_C - T_C$, critical pressure, $\Delta P_C = P'_C - P_C$, and critical density, $\Delta\rho_C = \rho'_C - \rho_C$. By this stratagem we finesse theoretically interesting problems concerning the origin of critical property IE's.

In the sections below an IE, Δ, on any property Y, is designated as $\Delta Y = Y'$ (light, primed) $- Y$ (heavy, unprimed). We limit attention to cubic or "almost cubic" equations of state, and point out useful constraints between critical temperature and critical pressure IE's, $\ln(T'_C/T_C)$ and $\ln(P'_C/P_C)$, and correlations between critical temperature and critical density IE's, $\ln(T'_C/T_C)$ and $\ln(\rho'_C/\rho_C)$, and between critical temperature and vapor pressure IE's in the near-critical region (at, for example, $T'_R = T/T'_C = 0.975$), $\ln(T'_C/T_C)$ and $\ln(P'/P_C)_{T_R=0.975}$. Combined with EOS, these relations allow the estimation of critical property IE's and liquid molar density IE's over a wide temperature range, $(0.5 < T'_R < 1)$. To that purpose we employ literature data on critical property IE's to test the application of corresponding states to molar density and vapor pressure IE's. However, from the outset we did not expect corresponding states to be as useful for rationalization of vapor pressure IE's as it is for molar density IE's. That is because the detailed molecular theory of the VPIE [7,8] shows it to depend on subtle isotopic differences in the vibrational properties of the coexisting vapor and liquid phases. The molar density IE, on the other hand, is a much simpler function of the molecular structure and the overall (external) motions in the condensed phase (albeit as perturbed by intermolecular forces in that condensed phase). We have found those expectations to hold true. Corresponding states fits to vapor pressure IE's are not as good as those to molar density IE's, even after the empirical introduction of an additional isotope dependent parameter (*vide infra*).

We are aware of several previous applications of corresponding states theory to PVT isotope effects. In the most important, DeBoer and coworkers [6] more than 50 years ago described quantum mechanical calculations, including both de Broglie diffraction and symmetry contributions, for interacting monatomic particles. That development supplemented a thorough discussion of classical corresponding states theory. Rigid sphere, square well, and Lennard Jones potentials were compared. The calculations extended to the prediction of critical property IE's, but with emphasis on application to ^{3}He/^{4}He and hydrogen/heavy hydrogen (in the rigid particle, spherical approximation). More recently Sinha and coworkers [13,14] applied an extended semi-classical theory to the calculation of the thermodynamic properties, critical points, surface tension and coexistence curves of the hydrogen isotopes H_2, HD and D_2, finding good agreement with experiment. Reed, Henderson and coworkers [15] had earlier presented quantum cell model calculations for that same series.

Closely related are theoretical studies of isotope effects on polarizability, dipole moment, and nmr shielding. Polarizability and dipole moment are straightforwardly related to the intermolecular dispersion energy (induced dipole-induced dipole interaction), and dipole-induced dipole and dipole–dipole interactions, and thence to the intermolecular potential and the equation of state. The theoretical background for such calculations was reviewed in 1975 by Buckingham and Urland [16]. Since then Adamowicz [17], and Cafiero and Adamowicz [18] have reported non-Born-Oppenheimer quantum mechanical calculations of isotope effects on polarizabilities for H_2, HD and D_2. Also, Kaila et al. [19] discussed H/D isotope effects on polarizabilities and dispersion energies of 16 organic compounds, and Van Hook and Wolfsberg [20] considered isotope effects on polarizabilities of small molecules and developed a set of bond polarizability isotope effects. Also, Schulte et al. [21] combined Feynman path integral Monte Carlo techniques with an *ab initio* Hartree–Fock Hamiltonian to study the influence of isotope substitution on the dispersion interactions between nonpolar molecules (ethane/deuteroethane, ethane-C_{12}/C_{13}, and benzene/deuterobenzene). Their prediction of the sign and magnitude of the (inverse) H/D isotope effect on dispersion is consistent with experimental data on the vapor pressure isotope effect. Unfortunately none of these results [16–21] have been combined with contributions from the repulsive part of the potential to yield an effective isotope dependent intermolecular potential and thence equations of state useful for the correlation of PVT isotope effects. However, Wolfsberg [22] has discussed the relationship between dispersion forces, and polarizabilities and polarizability isotope effects, and isotope effects on condensed phase properties like the vapor pressure.

The present emphasis is different. We are not so much interested in theoretical calculation of isotope effects on dispersion

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