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Estimation of Lennard-Jones 6–12 Pair Potential Parameters from Vapor Pressures and Thermodynamic Perturbation Theory

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Lennard-Jones 6–12 pair potential parameters were obtained for 53 liquids by fitting a thermodynamic perturbation theory developed by Chandler, Weeks, Andersen, Verlet, and Weis to experimental vapor pressure data. The values obtained for σ and ϵ/k were considerably smaller than the corresponding values obtained from other theories. A possible reason for the discrepancy is given.

Introduction

In two previous investigations cell theory and the free volume theory were used to obtain estimates for the effective Lennard-Jones 6–12 pair potential parameters for a number of liquids.[1-3] More recently, in several studies based on Pierotti's work,[4-9] the scaled particle theory was applied to gas solubility data so as to obtain estimates for the effective pair potential parameters for a large number of complex molecular liquids. It was subsequently shown[10] that the hard-sphere diameters obtained from the solubility study accounted reasonably well for the heats of vaporization and for the relative molar heat capacities of the corresponding pure liquids. These articles demonstrate that for a limited temperature range and for the above applications, the behavior of complex molecular liquids and solutions can be mimicked by spheres with effective values for σ and ϵ/k. This observation and the fact that values for these parameters are needed to predict and interpret the thermodynamic properties of solutions containing these liquids make it worthwhile to reevaluate these parameters using a more accurate theoretical framework.

The thermodynamic perturbation theories[11-16] developed over the past 10 years represent the most promising theoretical approach to the liquid state that is now available. The Chandler-Weeks-Andersen perturbation theory[13,14] as modified and expressed analytically Verlet and Weis[15,16] (hereafter the CWA-VW theory) was selected for these calculations. This theory was chosen because it provides simple and accurate analytical expressions for the thermodynamic functions of a Lennard-Jones 6–12 fluid at low temperatures and high densities.

Theory

The equilibrium vapor pressures of a large number of nonpolar liquids are accurately known in the region between their triple points and their normal boiling points. Therefore the procedure adopted here was to fit an equation derived from the CWA-VW theory to experimental vapor pressure data. Since in this temperature range the vapors are highly attenuated (i.e., $p < 1$ atm) one can, without great loss in accuracy, simplify the treatment by assuming that the vapor phase behaves ideally.

Assuming the vapor to be an ideal monatomic gas

$$\beta\mu_g = \ln p + \ln (\beta\Lambda^3) \tag{1}$$

where μ_g is the chemical potential of a molecule in the vapor,

$\beta \equiv (kT)^{-1}$, p is the equilibrium vapor pressure, and $\Lambda \equiv h/(2\pi mkT)^{1/2}$.

The chemical potential of a molecule in the liquid is given by

$$\beta\mu_l = \beta f + Z \tag{2}$$

where f is the total Helmholtz free energy per molecule in the liquid, and Z is the compressibility factor for the liquid. The Helmholtz free energy is written as the sum of a reference term, a perturbation term, and an ideal gas term. Thus

$$\beta f = \beta f_0 + \beta f_1 + \ln (\rho\Lambda^3) - 1 \tag{3}$$

In equation 3 βf_0 is the Helmholtz free energy of the reference system relative to that of an ideal gas, βf_1 is the perturbation contribution, and the remaining terms are the ideal gas contribution. From eq 1–3 and the equilibrium condition

$$\mu_g = \mu_l$$

one obtains the result

$$\ln p = \ln \left(\frac{RT}{\bar{V}}\right) + \beta(f_0 + f_1) + Z - 1 \tag{4}$$

where $\bar{V}$ represents the molar volume of the liquid. The physical significance of the terms in eq 4 with respect to the evaporation process is of some interest. The first term gives the change in standard state effect, the next term gives the excess Helmholtz free energy contribution, and $(Z - 1)$ is the compressibility change contribution. The expressions that were used to evaluate the terms in eq 4 were taken from ref 15 and 16; the details are given in the Appendix.

Calculations and Results

If both the vapor pressure and the density of a liquid are known at a particular temperature, then the sought parameters σ and ϵ/k are the only unknowns in eq 4. Therefore a numerical procedure (essentially an efficient sequence of trial calculations) was developed to obtain those pairs of values of σ and ϵ/k that resulted in a least-squares fit of eq 4 to the experimental vapor pressure data over a range of temperatures. The solutions obtained for 53 liquids are given in Table I, and the fit for benzene is demonstrated in Figure 1. The fits for the other liquids were similar to that shown in Figure 1. The vapor pressure and density data were taken from ref 17 and 18a,b respectively.

The factors that influenced the choice of liquids were: (1)

TABLE I: Lennard-Jones 6–12 Pair Potential Parameters σ (cm), ϵ/k (K), and the Temperature Range ΔT (K) for which the Experimental and Calculated Vapor Pressures Agree to within 1%

Liquid	ΔT^a	$10^8\,\sigma$	ϵ/k
A. Hydrocarbon Liquids			
Cyclopentane	260–310	4.946	398
2-Methylbutane	240–280	5.210	359
n-Pentane	240–290	5.193	368
Benzene	283–333	4.860	432
Cyclohexane	283–333	5.194	428
2,2-Dimethylbutane	260–310	5.475	380
2,3-Dimethylbutane	260–310	5.460	391
n-Hexane	270–320	5.423	399
2-Methylpentane	260–310	5.463	392
3-Methylpentane	260–310	5.446	396
Methylcyclopentane	270–310	5.242	415
Toluene	293–353	5.196	465
1,1-Dimethycyclopentane	275–315	5.498	426
cis-1,2-Dimethylcyclopentane	280–320	5.470	441
$trans$-1,2-Dimethylcyclopentane	280–320	5.505	430
cis-1,3-Dimethylcyclopentane	280–320	5.515	430
$trans$-1,3-Dimethylcyclopentane	280–320	5.518	428
Ethylcyclopentane	280–320	5.488	445
Methylcyclohexane	290–340	5.511	446
2,2-Dimethylpentane	270–320	5.696	408
2,3-Dimethylpentane	270–320	5.644	421
2,4-Dimethylpentane	260–310	5.671	407
3,3-Dimethylpentane	270–310	5.698	421
3-Ethylpentane	270–310	5.613	424
Heptane	280–330	5.612	427
2-Methylhexane	270–310	5.641	418
3-Methylhexane	270–310	5.628	420
2,2,3-Trimethylbutane	270–310	5.698	414
o-Xylene	300–380	5.417	498
m-Xylene	300–380	5.439	490
p-Xylene	300–380	4.437	488
1,1-Dimethylcyclohexane	280–330	5.748	463
cis-1,2-Dimethylcyclohexane	290–330	5.685	472
1,1,2-Trimethylcyclopentane	280–330	5.730	452
1,1,3-Trimethylcyclopentane	280–330	5.769	440
$cis,cis,trans$-1,2,4-Trimethylcyclopentane	280–330	5.746	455
$cis,trans,cis$,-1,2,4-Trimethylcyclopentane	280–330	5.765	444
Ethylbenzene	310–360	5.425	485
2-Methylheptane	280–330	5.965	434
3-Methylheptane	290–330	5.779	446
Octane	300–350	5.741	454
2,2,4-Trimethylpentane	290–330	5.911	427
2,3,4-Trimethylpentane	290–330	5.863	446
2,5-Dimethylhexane	290–340	5.836	435
2,2,3,3-Tetramethylpentane	300–340	6.048	478
2,2,3,4-Tetramethylpentane	300–340	6.071	467
2,2,4,4-Tetramethylpentane	290–330	6.097	451
2,3,3,4-Tetramethylpentane	310–350	6.061	480
2,2,5-Trimethylhexane	300–340	6.009	448
B. Miscellaneous Compounds			
Carbon tetrachloride	273–343	5.019	429
Carbon disulfide	260–310	4.364	431
1,4-Dioxane	285–325	4.832	464
Tetrachloroethylene	290–340	5.148	481

^{a} These ranges were largely determined by the availability of experimental vapor pressure and density data (see text).

the availability of vapor pressure and density data in a common range of temperatures such that the reduced temperature range corresponded (roughly) to that prescribed by the Ver-
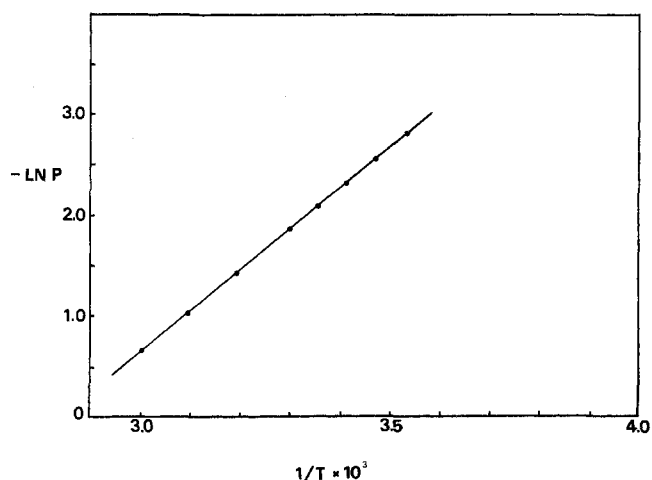
Figure 1. Vapor pressure curve for benzene: (●) experimental points; line is calculated from eq 4 with σ = 4.860, (ϵ/k) = 432.

let–Weis algorithm (see Appendix); (2) the liquids had to be nonpolar or nearly so;[19] (3) for comparisons and for further work it was desirable that there be other thermodynamic data (e.g., gas solubilities, thermodynamic excess functions of mixing) for systems involving these liquids.

It is difficult to obtain precise values for the uncertainties in σ and ϵ/k. The sources of error, apart from the assumption that the molecules are isotropic, are: (1) errors in the vapor pressure and density data (For many liquids, small extrapolations in the density and/or the vapor pressures were required in order to obtain values for these quantities in a common temperature range.); (2) a slight nonideality of the vapor phase. It was estimated by trial calculation that the upper limits for the uncertainties, due to these sources of error, were ±0.03 Å and ±5 K for σ and ϵ/k, respectively.

Discussion

In Table II our results are compared with those taken from other studies. Parameters available from second virial coefficients and gas viscosities[20] are too scattered for a meaningful comparison and are not included. It is seen from Table II that in all cases the values of both σ and ϵ/k found here are significantly smaller than the corresponding values obtained by the other approaches.

While many differences exist, it is felt that the most salient difference between this work and the other studies is that in this work, by applying the WCA–VW theory, an effective hard-sphere radial distribution function (rdf) was used in calculating the interaction energy of a molecule with its neighbors. In the other studies a uniform particle density equal to the bulk density (i.e., rdf = 1) was used either explicitly or implicitly in the calculation of this term. Since the forces involved are short range, and since the hard-sphere rdf rises rapidly at close distances (to values of $\simeq$3–4 for the reduced temperatures and densities involved here), the substantial differences displayed in Table II are hardly surprising. While the molecules we are dealing with are not spherical, it is felt that an effective hard-sphere rdf should more closely represent the structure of these dense liquids than the low-density limit of the rdf. In line with this McQuarrie and Neff,[21] in their application of the Barker–Henderson perturbation theory to gas solubilities, found that the use of the low density limit of the rdf resulted in the omission of a term that contributed significantly to the solute–solvent interaction energy.

TABLE II: Comparison of Pair Potential Parameters from This Work with Those from Other Sources
(σ in cm and ϵ/k in K)

	$10^8\sigma$				ϵ/k			
Liquid	a	b	c	d	a	b	c	d
n-Hexane	5.42	5.92		5.96	399	517		462
n-Heptane	5.61	6.25		6.24	427	573		538
n-Octane	5.74	6.54		6.50	454	611		605
3-Methylheptane	5.78	6.52			446	527		
2,2,4-Trimethylpentane	5.91	6.52			427	602		
Cyclohexane	5.19	5.63		5.62	428	573		486
Methylcyclohexane	5.51	5.99			446	599		
Benzene	4.86	5.26	5.22	5.26	432	531	501	494
Toluene	5.20	5.64			465	575		
m-Xylene	5.44	5.97			490	586		
Carbon tetrachloride	5.02	5.37	5.35	5.41	429	536	490	486

[a] Obtained in this work. [b] Parameters taken from Wilhelm and Battino[9] who obtained them from gas solubility data and the scaled particle theory. [c] Parameters were taken from Kobatake and Alder[3] who obtained them from free volume theory and vapor pressure data. [d] Parameters were taken from Salsburg and Kirkwood[2] who obtained them from the cell theory of liquids.

Of course it must be acknowledged that the treatment used here is less than exact. We have replaced very complicated anisotropic molecules by spheres, and the structure of such liquids was taken to be that of a hard-sphere fluid. Clearly, a more satisfactory model would account for angular correlations, nonadditivity of the pair potentials, restricted rotations, and the anisotropic nature of the intermolecular forces. Despite some very promising recent work on nonspherical models that mimic the angular correlations for liquids such as benzene and carbon tetrachloride,[22] a comprehensive statistical-mechanical theory that can incorporate all of the above effects still seems to be distant. In the meanwhile, the compromise taken here provides numbers that should be useful.

The WCA–VW theory has been extended to binary mixtures of simple (6–12) molecules.[23] We plan, by using the parameters obtained in this work, to apply a similar extension to the interpretation of the thermodynamic functions for mixtures of complex liquids, and to the interpretation of gas solubilities in these liquids. Hopefully this will result in semiempirical combining rules that are relevant to interactions between unlike molecules in liquid solutions.

Appendix

The molar volume of the liquid, $\tilde{V}$, required for the first term in eq 4 was calculated from the experimental density.

For the remaining terms in this equation, a value is needed for the effective hard-sphere diameter d. This was obtained from the algorithm given by Verlet and Weis.[15]

$$d = d_{\mathrm{B}}\left[1 + \left(\frac{\sigma_1}{2\sigma_0}\right)\delta\right] \quad \text{(A1)}$$

$$d_{\mathrm{B}} = (0.3837 + 1.068\beta^*)/(0.4293 + \beta^*)$$

$$\beta^* = \epsilon/kT$$

$$\delta = (210.31 + 404.6\beta^*)^{-1}$$

$$\left(\frac{\sigma_1}{2\sigma_0}\right) = \frac{1 - 4.25\eta_{\mathrm{W}} + 1.362\eta_{\mathrm{W}}^2 - 0.8751\eta_{\mathrm{W}}^3}{(1 - \eta_{\mathrm{W}})^2} \quad \text{(A2)}$$

$$\eta_{\mathrm{W}} = \eta - \frac{1}{16}\eta^2 \quad \text{(A3)}$$

$$\eta = \pi\rho^* d^3/6 \quad \text{(A4)}$$

$$\rho^* = \left(\frac{\tilde{N}D}{M}\right)\sigma^3 \quad \text{(A5)}$$

In eq A5 $\tilde{N}$, D, M, and ρ^* are Avogadro's number, the experimental density, molecular weight, and the reduced number density of the liquid, respectively. A first estimate for η is obtained from eq A4 by setting d equal to d_{B}. Subsequent iterations through eq A1–A4 provide a value for d. Convergence to seven figures is obtained after three iterations; in practice five iterations were used.

This algorithm is most accurate in the range $0.7 \leq \beta^{*-1} \leq 1.6$. The error entailed increases somewhat outside this range.[15] From Table I it is seen that the values of β^{*-1} were in the range $0.6 < \beta^{*-1} < 0.82$. For purposes of the present application, it was considered the algorithm was sufficiently accurate.

The reference system free energy was obtained from

$$\beta f_0 = \beta \hat{f}_{\mathrm{HS}}^{\mathrm{ex}} + 4\delta\beta\Delta f$$

where

$$\beta \hat{f}_{\mathrm{HS}}^{\mathrm{ex}} = \eta\frac{4 - 3\eta}{(1 - \eta)^2}$$

$$\beta\Delta f = \frac{3\eta^2(1 + 1.759\eta - 5.249\eta^3)}{(1 - \eta)^3}$$

These expressions derive from eq 6.1, 6.2, and A27 of ref 15.

Equations 46–51 of ref 16 were used to obtain the perturbation free energy βf_1. These equations are a slightly extended form of eq A26 of ref 15. Thus

$$\beta f_1 = 48\eta_{\mathrm{W}}\beta^*\left(\frac{I_1^{12} - I_2^{12}}{d_{\mathrm{W}}^{12}} - \frac{I_1^6 - I_2^6}{d_{\mathrm{W}}^6} - \frac{I_2^0}{4}\right)$$

where

$$I_1^n = \frac{1}{n - 3}\frac{1 + u_1^n\eta_{\mathrm{W}} + u_2^n\eta_{\mathrm{W}}^2 + u_3^n\eta_{\mathrm{W}}^3}{(1 - \eta_{\mathrm{W}})^2}$$

$u_1^{12} = 0$; $u_2^{12} = -0.797$; $u_3^{12} = -0.480$; $u_1^6 = -0.691$;
$$u_2^6 = -1.169; \quad u_3^6 = 0.751$$

$$I_2^n = \frac{\alpha_0}{n-2} + \frac{\alpha_1}{(n-2)(n-3)} + \frac{\alpha_2}{(n-2)(n-3)(n-4)}$$

$$+ \frac{\alpha_3}{(n-2)(n-3)(n-4)(n-5)} - \left(\frac{d_W}{r_m}\right)^n$$

$$\times \left[\frac{\alpha_0 - \alpha_1 + \frac{\alpha_2}{2} - \frac{\alpha_3}{6}}{n-2} \left(\frac{r_m}{d_W}\right)^2 + \frac{\alpha_1 - \alpha_2 + \frac{\alpha_3}{2}}{n-3} \left(\frac{r_m}{d_W}\right)^3 \right.$$

$$\left. + \frac{\frac{\alpha_2}{2} - \frac{\alpha_3}{2}}{n-4} \left(\frac{r_m}{d_W}\right)^4 + \frac{\frac{\alpha_3}{6}}{n-5} \left(\frac{r_m}{d_W}\right)^5 \right]$$

$$\alpha_0 = \left(1 + \frac{\eta_W}{2}\right)(1 - \eta_W)^{-2}$$

$$\alpha_1 = (1 - 5\eta_W - 5\eta_W^2)(1 - \eta_W)^{-3}$$

$$\alpha_2 = -3\eta_W(2 - 4\eta_W - 7\eta_W^2)(1 - \eta_W)^{-4}$$

$$\alpha_3 = 12\eta_W(1 + 3\eta_W - 4\eta_W^3)(1 - \eta_W)^{-5}$$

$$d_W = d(\eta_W/\eta)^{1/3}$$

$$r_m = 2^{1/6}$$

The expressions required to obtain the compressibility factor Z are straightforward enough but rather lengthy, so that they are not repeated here. They were obtained directly from eq A17, A33, and A34 of ref 15.

References and Notes

(1) The Lennard-Jones 6–12 pair potential has the form

$$u(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$$

$u(r)$ has a minimum equal to $-\epsilon$ at $r = 2^{1/6}\sigma$; $u(r)$ is zero when $r = \sigma$.
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A Surface Study of Cobalt–Molybdena–Alumina Catalysts Using X-Ray Photoelectron Spectroscopy

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X-ray photoelectron spectroscopy (ESCA) has been used to study the surface reactions of a commercial cobalt–molybdenum–alumina catalyst. Reduction of the catalyst in hydrogen produced a mixture of molybdenum oxidation states: Mo(VI), Mo(V), and Mo(IV). The relative amount of molybdenum in each state was determined as a function of reduction time and temperature. Exposure of fired catalysts to thiophene in an inert atmosphere showed that only thiophene adsorption occurred. In contrast fired, prereduced catalysts showed both thiophene adsorption and desulfurization capability in an inert atmosphere. The molybdenum of the catalyst was effectively sulfided in either thiophene/H_2 or H_2S/H_2. However, prereduced catalysts sulfided to a lesser extent than catalysts that had only been fired. In no case was complete sulfiding of the molybdenum observed. The cobalt of the catalyst showed little change on treatment with either hydrogen or thiophene/H_2. This was in contrast to application of H_2S/H_2 which sulfided the cobalt of the catalyst more rapidly than the cobalt in cobalt aluminate.

Introduction

Commercial hydrodesulfurization (HDS) catalysts commonly consist of molybdena (MoO_3) supported on active alumina and promoted with small amounts of cobalt or nickel. Although there are many conflicting interpretations in the literature, desulfurization activity is thought to derive from a reduced state of molybdenum on the catalyst.[1-5] ESR studies[6-8] of MoO_3 supported on alumina show that the amount of molybdenum(V) present is substantially increased upon reduction.