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Temperature Dependence of the Heat Capacity and Vapor Pressure of Pure Self-Associated Liquids. A New Correlation Based on a Two-State Association Model

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A recently reported [*J. Chem. Phys.* **2004**, *120*, 6648] two-state association model (TSAM) is reformulated to obtain an expression for the residual Gibbs free energy of pure self-associating liquids. From the proposed partition function, where association is considered a perturbation, a vapor pressure correlation was obtained, with a clear and separable nonspecific contribution. The new formulation does not change the reported three- or four-parameter equation for calculating residual heat capacities, their values being determined solely from experimental heat capacity data. Two new parameters are necessary to describe the nonspecific reference fluid Gibbs free energy. The resulting vapor pressure equation was fitted to experimental data for pure 1-alcohols, 1-thiols, 1-amines, and carboxylic acids with very good agreement, up to the critical point.

Introduction

Efforts to explain the thermophysical properties of self-associating substances have concentrated on three main approaches:¹ (i) chemical theories, such as the Extended Real Associated Solution (ERAS) and Lattice Fluid Association (LFAS) models,² where the association is regarded as a chemical reaction between two or more monomers (dissociated molecules) to form new associated species in the system; (ii) quasi-chemical or local composition theories, where the nonidealities are originated by nonrandom mixing at molecular level; examples of theories based on this approach are the extensively used Non Random Two Liquids (NRTL), the Universal Quasi-Chemical (UNIQUAC), the group contribution theories UNIFAC and ASOG, among others;² and (iii) Hamiltonian-based statistical models, where association is the consequence of an explicit expression for the intermolecular potential energy. Using techniques of statistical mechanics, such as integral equations, perturbation theories, and molecular simulations, the thermodynamic properties of self-associated fluids can be determined. The main examples of this approach are the Statistical Association Fluid Theory (SAFT) related equations of state (EOS).^{1–4} The SAFT approach, based on the Wertheim perturbation theory, has been used to produce many EOS with an explicit term due to association. The characteristics of the above-mentioned models and of SAFT equations of state have been summarized and discussed in Gubbins and Müller¹ and in Prausnitz et al.²

Recently, a simple statistical model, the so-called two-state association model (TSAM),^{5,6} has been proposed to describe

association in liquids. The major goal of TSAM was to explain the general behavior of the temperature dependence of the heat capacity (C_p) for self-associating pure compounds. The main idea in the TSAM is that a molecule can reside in only two energy states, that where molecules are associated (state A_i) with other molecules of its kind and that where they are not associated and hence in monomer form (state A). Each state is defined by its enthalpy (h_{A_i} and h_A) and degeneracy number (ω_{A_i} and ω_A). Hence, the residual isothermal–isobaric partition function per particle due to association (Δ_r^{as}) is given by

$$\Delta_r^{as} = \omega_A e^{-h_A/kT} + \omega_{A_i} e^{-h_{A_i}/kT} \quad (1)$$

where k is the Boltzmann constant and T is the temperature. Using thermodynamic connections and assuming temperature-independent enthalpies and degeneracy numbers, the contribution to the heat capacity due to association (C_p^{as}) was obtained as⁵

$$\frac{C_p^{as}}{R} = \left(\frac{\Delta h}{RT}\right)^2 \frac{r e^{\Delta h/RT}}{(r + e^{\Delta h/RT})^2} \quad (2)$$

where Δh is the association enthalpy ($\Delta h = h_A - h_{A_i}$) and r is the ratio of degeneracies ($r = \omega_A/\omega_{A_i}$). In ref 5, to obtain the desired residual heat capacity (C_p^r), the contribution to the heat capacity arising from nonspecific interactions (C_p^{ns}) was added to C_p^{as} , that is,

$$\frac{C_p^r}{R} = \frac{C_p^{ns}}{R} + \left(\frac{\Delta h}{RT}\right)^2 \frac{r e^{\Delta h/RT}}{(r + e^{\Delta h/RT})^2} \quad (3)$$

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with C_p^{ns} being considered either temperature independent or a weak function of temperature, based on the experimental behavior of the heat capacity of nonassociating compounds and on the Flory theory.⁷ The fitting of eq 3 to liquid state heat capacity data for the series of 1-alcohols and 1-thiols was very successful, finding that a single value for the enthalpy of association of each of the series of compounds suffices to reach a good description of the experimental data. In ref 5, the TSAM was shown to be able to provide a unified description of the several different temperature dependences experimentally found for the heat capacity of pure liquids. Furthermore, based on the physical meaning and on the trend of the fitted parameters (Δh , r , and C_p^{ns}), the TSAM predicted that highly sterically hindered alcohols such as 3-methyl-3-pentanol and 3-ethyl-3-pentanol should display a maximum in their C_p versus temperature curve, a fact that was confirmed by accurate C_p measurements.

To understand the molecular foundations of the association effects on the heat capacity at constant pressure, Medeiros⁸ presented a Monte Carlo simulation study of methanol. In that work, it was shown that heat capacity is the result of a delicate balance among several fluctuations of the intermolecular energy contributions and that there is a strong correlation between these fluctuations. In particular, it was found that the maximum in the $C_p(T)$ curve reported in ref 5 for highly branched alcohols must likely arise from the correlation between the electrostatic energy fluctuations and the short-range Lennard-Jones energy fluctuations. Because of this correlation, it is not possible to relate univocally each force field term to each heat capacity contribution. This implies that C_p^{ns} in eq 3 does not include the effect of association over the average nonspecific forces and hence it is not only the heat capacity due to nonspecific forces.

In this work, the TSAM is reformulated by rewriting the partition function in such a way that C_p^{ns} appears naturally and does not have to be empirically added to C_p^{as} to obtain C_p^r . In other words, we show that not only C_p^{as} in eq 2 but also C_p^r in eq 3 can be obtained from statistical mechanics considerations. From the proposed partition function, where association is considered a perturbation, an expression for the residual Gibbs free energy and a vapor pressure correlation for pure self-associating liquids were obtained, both with clear and separated association and nonspecific contributions. This reformulation involves two new parameters that were fitted to experimental vapor pressures for several series of compounds, the values of the three original TSAM parameters being kept equal to those obtained solely from heat capacity data. As a consequence, the reformulated TSAM presented here is able to correlate simultaneously heat capacity and vapor pressure data.

TSAM Reformulation

The Monte Carlo simulations for methanol reported in ref 8 are a useful guide for reformulating the TSAM. In this work, using the simulations reported in ref 8, the temperature dependence of the average configurational enthalpies of associated and dissociated molecules ($h_{as} = h_{ns} + h_{Ai}$ and $h_{dis} = h_{ns} + h_A$) has been estimated, and the resulting values are displayed in Table 1. To estimate h_{as} and h_{dis} , the relations $h_r = x_A h_{dis} + (1 - x_A) h_{as}$ and $\Delta h = h_{dis} - h_{as}$ were used with the residual enthalpy h_r being that determined directly from the NPT ensemble averages of intermolecular potential energy and residual volumes.⁸ To determine x_A (the fraction of non-associated molecules) and Δh , a molecule was considered nonassociated if the geometrical hydrogen-bonding criterion of Soper⁹ failed. If associated, the potential energy between the pair of associated molecules was calculated. The average value

Table 1. Monte Carlo Simulation⁸ Results for Methanol at 50 MPa^a

T/K	x_A	h_r	Δh	h_{dis}	h_{as}
300	0.021	-36.5	-21.1	-57.2	-36.1
350	0.047	-33.9	-20.2	-53.2	-33.0
400	0.091	-31.0	-19.5	-48.7	-29.2
450	0.157	-27.9	-18.9	-43.8	-24.9
500	0.243	-24.6	-18.4	-38.5	-20.1
550	0.344	-21.2	-17.9	-33.0	-15.1
600	0.454	-17.9	-17.5	-27.4	-9.9
650	0.561	-14.7	-17.1	-22.2	-5.1

^a Symbols and units: x_A , average fraction of nonassociated molecules; h_r , average residual enthalpy (kJ/mol); Δh , average enthalpy of association (kJ/mol); h_{as} and h_{dis} , average enthalpies of associated and nonassociated molecules, respectively. See ref 8 for the simulation details.

of this energy was assumed a good approximation to Δh . Table 1 shows that h_{dis} and h_{as} are strong functions of temperature. In contrast, their differences, that is, Δh , do not exhibit a substantial change with temperature. Furthermore, the calculated Δh 's in Table 1 are close to the values determined from the TSAM in ref 5, fitting to experimental 1-alcohols $C_p(T)$ data (23.1 kJ/mol). This suggests that it is reasonable to assume a temperature-independent Δh . Unfortunately, the degeneracies ω_A and ω_{Ai} and their ratio r cannot be estimated directly from the Monte Carlo simulations of ref 8 due to their entropic nature. However, an immediate consequence of assuming a temperature-independent Δh is that the change in heat capacity due to association is null and hence the entropy of association Δs does not depend on temperature. Because r is directly related to Δs through $\Delta s = R \ln r$, the simulation results suggest that, for a good first approximation, the ratio of degeneracies can also be considered temperature independent.

To consider both the association and the nonspecific contributions, the following one particle isothermal–isobaric partition function is written as

$$\Delta_r = \omega_A(T) e^{-h_A(T)/kT} + \omega_{Ai}(T) e^{-h_{Ai}(T)/kT} \quad (4)$$

where h_{Ai} , h_A , ω_A , and ω_{Ai} are temperature dependent, but, based on the above-described results from the Monte Carlo simulations, the association enthalpy Δh and the degeneracy ratio r are assumed as constants. In other words, even though the available energy levels change as the temperature varies, the molecules in the system are still capable of being in only two states. Now, a hypothetical fluid where all of the molecules are in the nonassociated or monomeric state is defined as the reference state. This reference fluid, referred to as the non-specific fluid, has a residual one particle partition function given by

$$\Delta_{ns} = \omega_A e^{-h_A/kT} \quad (5)$$

and hence eq 4 can be rewritten as

$$\Delta_r = \Delta_{ns} + \omega_{Ai} e^{-h_{Ai}/kT} = \Delta_{ns} \left(1 + \frac{e^{\Delta h/kT}}{r} \right) \quad (6)$$

In eq 6, the term in parentheses represents the perturbation to the reference fluid caused by association. Using the thermodynamic connection between the residual Gibbs free energy and the partition function Δ_r , the residual molar heat capacity at constant pressure can be promptly determined as

$$\frac{C_p^r}{R} = \frac{C_p^{ns}(T)}{R} + \left(\frac{\Delta h}{RT} \right)^2 \frac{r e^{\Delta h/RT}}{(r + e^{\Delta h/RT})^2} \quad (7)$$

where

$$C_p^{ns}(T) = \left(\frac{\partial h_A}{\partial T} \right)_p = T \left(\frac{\partial s_A}{\partial T} \right)_p = RT \left(\frac{\partial}{\partial T} \ln \omega_A \right)_p \quad (8)$$

with s_A being the entropy of the nonspecific fluid ($s_A = \ln \omega_A$). Equation 7 has exactly the same form as eq 3, obtained in the original formulation of TSAM.⁵ The main difference introduced by the present formulation is the existence of an explicit partition function Δ_{ns} for the reference fluid, which, in turn, cancels the need of introducing heuristically the nonspecific contribution to the residual heat capacity C_p^r as done in ref 5. Now, the contribution C_p^{ns} appears naturally and the physical meaning of the two contributions to C_p^r is clearer: C_p^{ns} is the heat capacity of the reference nonspecific fluid and C_p^{as} is the perturbation or deviation to this reference state caused by association. Note that in the present formulation, the presence of association affects the nonspecific forces, and that the separation of these two contributions does not correspond to a Hamiltonian split into nonspecific and association intermolecular potential energies. These energy fluctuations, and their contributions to the heat capacity of self-associating compounds, can be highly correlated as shown by the simulations in ref 8. Another advantage of the present formulation of the TSAM is that the ratio of degeneracies r directly provides the entropy of association $\Delta s = R \ln r$, that is, the entropy difference between a fluid in which all molecules are in the associated state and the nonspecific fluid.

At constant pressure, the residual Gibbs free energy of the reference fluid is given by

$$g_A = \int C_p^{ns}(T) dT - T \int \frac{C_p^{ns}(T)}{T} dT \quad (9)$$

and hence the evaluation of g_A requires knowledge of $C_p^{ns}(T)$. Based on the Flory theory,⁷ in ref 5 it was assumed that for strong association C_p^{ns} is a weak function of temperature and hence it was taken as constant in the temperature interval where heat capacity data are available. On the other hand, for weak association, as that in thiols, a linear function to represent $C_p^{ns}(T)$ was used. In this context, it is worthwhile noting that in the present TSAM formulation C_p^{ns} is also the temperature derivative of h_A , the enthalpy of a fully associated fluid. This is a consequence of the assumption of temperature-independent Δh . Microscopically, this means that a molecule, associated or not, experiences the same forces produced by the set of molecules that surrounds it; that is, in response to temperature changes, the environment around a given molecule will be altered in a similar average way irrespective of the state (associated or nonassociated) in which that molecule is. This mean field approximation can be useful for future elucidation of the temperature dependence of C_p^{ns} . Here, for simplicity, C_p^{ns} will be considered a linear function of temperature:

$$C_p^{ns}(T) = C_p^{ns(0)} + C_p^{ns(1)}T \quad (10)$$

and eq 9 transforms into

$$g_A = C_p^{ns(0)}T(1 - \ln T) - \frac{C_p^{ns(1)}}{2}T^2 + h_0 - Ts_0 \quad (11)$$

where h_0 and s_0 are integration constants. Hence, the residual molar free energy can be expressed as

$$g_r = -RT \ln \left(1 + \frac{e^{\Delta h/RT}}{r} \right) + C_p^{ns(0)}T(1 - \ln T) - \frac{C_p^{ns(1)}}{2}T^2 + h_0 - Ts_0 \quad (12)$$

from which the thermodynamic properties of associated compounds can be determined. Below, as in the original TSAM, the temperature-dependent coefficient $C_p^{ns(1)}$ will be neglected when dealing with strong association. It should be noted that in eq 12 there is no explicit pressure dependence. It will be assumed here that no parameter is pressure dependent and that the product $p\Delta v$ (where Δv is the change of volume due to association) is very small as compared to the energy difference between the two states. This last assumption restricts the use of the TSAM model to the liquid phase, far from the critical point.

Vapor Pressure Equation

Using eq 12, it is possible to derive an expression for calculating vapor pressures. Assuming that at low vapor pressures, where the vapor phase is ideal, the Clausius–Clayperon equation is adequate to represent the self-associating system,

$$\frac{d}{dT} \ln(p_{\text{sat}}) = -\frac{h_r}{RT^2} \quad (13)$$

where p_{sat} is the saturation vapor pressure and h_r is the residual enthalpy of the liquid phase. Applying the Gibbs–Helmholtz equality $d \ln p_{\text{sat}}/dT = d(g_r/RT)/dT$,

$$\ln(p_{\text{sat}}) = \frac{C_p^{ns(0)}}{R}(1 - \ln T) - \frac{C_p^{ns(1)}}{2R}T + \frac{h_0}{RT} + \ln(p_0) + \ln\left(\frac{r}{r + e^{\Delta h/RT}}\right) \quad (14)$$

where $\ln(p_0)$ is another integration constant. The last term in eq 14 corresponds to the contribution to the vapor pressure due to association, because the parameters involved arise uniquely from the perturbation term in eq 6. The effect of association is to decrease the fluid vapor pressure, because r is a positive number. In eq 14, the new parameters h_0 and $\ln(p_0)$ are related to reference states properties and reference temperatures, and they will be used here as adjustable parameters when fitting the model to experimental p_{sat} data. In the foregoing discussion, we will use $\ln(p_{\text{sat}}^{ns})$ and $\ln(p_{\text{sat}}^{as})$ to refer to the nonspecific and association contributions to vapor pressure, respectively:

$$\ln(p_{\text{sat}}^{ns}) = \frac{C_p^{ns(0)}}{R}(1 - \ln T) - \frac{C_p^{ns(1)}}{2R}T + \frac{h_0}{RT} + \ln(p_0) \quad (15)$$

$$\ln(p_{\text{sat}}^{as}) = \ln\left(\frac{r}{r + e^{\Delta h/RT}}\right) \quad (16)$$

Parameter Regression and Discussion

Tables 2 and 3 and Figures 1–4 show the results of adjusting eq 14 to vapor pressure experimental data for several members of four series of compounds. The experimental data were obtained from CDATA.¹⁰ The parameters were adjusted separately to fit liquid heat capacity ($C_p^{ns(0)}$, $C_p^{ns(1)}$, Δh , and r) and vapor pressure (h_0 and p_0). The heat capacity parameters of 1-alcohols and 1-thiols were taken directly from ref 5, while

Table 2. TSAM Parameters for Heat Capacity Correlation

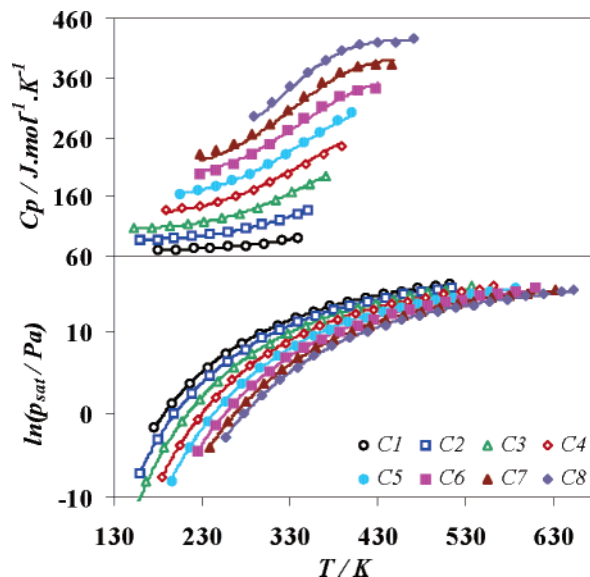
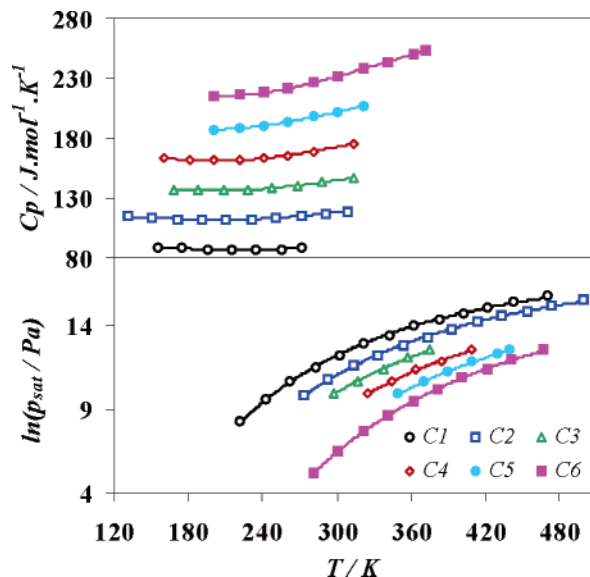
chain length	r	$C_p^{ns(0)}$ $J\ mol^{-1}\ K^{-1}$	$C_p^{ns(1)}$ $J\ mol^{-1}\ K^{-2}$	AAD ^b %	min K	max K
1-Alcohols ^a $\Delta h = 23\ 124\ J\ mol^{-1}$						
1	89.0	31.26		0.05	180	337
2	158.3	37.49		0.10	159	350
3	242.1	43.88		0.21	153	370
4	264.4	54.35		0.92	188	390
5	333.4	55.31		0.29	205	400
6	315.0	67.18		1.61	227	430
7	423.0	65.84		1.84	275	448
8	558.6	65.72		0.65	290	468
1-Thiols ^a $\Delta h = 3756\ J\ mol^{-1}$						
1	8.6	23.98	0.03947	0.05	155	271
2	7.2	39.18	0.00501	0.16	131	308
3	6.5	50.16	-0.01702	0.03	168	314
4	9.3	59.45	-0.03226	0.03	161	314
5	6.3	69.95	-0.04818	0.02	201	321
6	16.6	83.86	-0.06799	0.09	201	371
Acids $\Delta h = 22\ 147\ J\ mol^{-1}$						
2	26.3	57.52		0.07	293	400
3	41.1	58.61		0.26	255	447
4	30.5	60.23		0.42	273	373
1-Amines $\Delta h = 6876\ J\ mol^{-1}$						
1	5.7	58.89	-0.07367	0.00	186	258
3	16.9	64.38	-0.02953	0.05	190	334
4	16.0	46.96	0.04239	0.01	233	343

^a Parameters from ref 5. ^b Absolute average deviation.**Table 3. TSAM Parameters for Vapor Pressure Correlation**

chain length	$\ln(p_0)^a$	h_0 $J\ mol^{-1}$	AAD ^b %	min K	max K
1-Alcohols					
1	42.38	24 970	0.64	176	512
2	46.93	30 872	0.97	159	513
3	51.95	37 983	1.07	147	536
4	60.56	47 767	0.82	185	562
5	62.05	53 594	1.29	196	587
6	71.19	62 394	1.48	226	610
7	70.92	67 207	1.61	240	632
8	71.37	71 872	1.29	258	652
1-Thiols					
1	40.66	34 327	0.35	222	469
2	50.42	41 509	0.26	273	498
3	56.81	45 421	0.03	297	375
4	63.29	52 533	0.03	324	409
5	70.64	59 412	0.03	349	439
6	80.06	67 760	0.07	281	467
Acids					
2	62.40	41 630	0.89	302	592
3	64.20	49 633	0.49	344	603
4	66.28	55 199	0.30	363	623
1-Amines					
1	60.71	36 622	0.21	200	429
3	67.03	49 861	0.32	235	496
4	58.43	52 985	0.48	255	531

^a p_0 has units compatible with pressures in Pa and temperatures in K when using eq 14. ^b Absolute average deviation.

those for acids and 1-amines were evaluated here. The maximum average absolute deviation (AAD) on $\ln(p_{\text{sat}})$ and on liquid C_p was only 1.48% and 1.84%, respectively. Despite the assumption of ideal gas when developing the vapor pressure equation, excellent correlations of the experimental data were found, up to the critical point. The nonideality of the vapor phase must be included in h_0 and p_0 , because the other parameters were obtained from liquid C_p fitting exclusively, where there was no need to make any assumption regarding vapor phase. It is important to emphasize that adjusting all of the parameters to vapor pressure only, that is, not including liquid C_p data, did not produce reasonable parameters. Clearly, it is very easy to

**Figure 1.** Low-pressure heat capacities and vapor pressures of 1-alcohols. Continuous lines, TSAM correlation; dots, experimental.¹⁰**Figure 2.** Low-pressure heat capacities and vapor pressures of 1-thiols. Continuous lines, TSAM correlation; dots, experimental.¹⁰

represent vapor pressure curves with a five-parameter equation, and the fittings are good. However, this strategy produces parameters whose values are devoid of physical meaning. Thus, it is necessary to use reliable liquid C_p data to obtain meaningful parameters. This is the reason for ethanamine not being included in Tables 2 and 3. For this substance, the reported error¹⁰ on liquid C_p is large (10%) and, in addition, the data do not follow the trend observed for the other three amines. A different approach for parameter regression is to simultaneously fit together C_p and p_{sat} data with a single objective function. Using this fitting strategy produced good correlations, but no significant improvement was obtained when Δh was kept common for an entire family of compounds. Clearly, fitting a value of Δh (an additional parameter) for each substance would have resulted in better fitting to the experimental data, but for consistency with the original TSAM formulation it was preferred to keep a single Δh value for each family of compounds. For long chain alcohols ($n > 10$), in ref 5 it was suggested that their self-association has two components, H-bonding and the association due to correlation of molecular orientations (cmo)

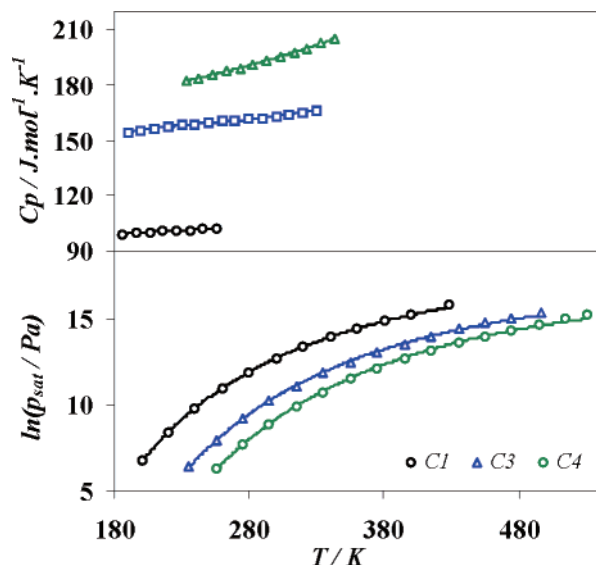


Figure 3. Low-pressure heat capacities and vapor pressures of 1-amines. Continuous lines, TSAM correlation; dots, experimental.¹⁰

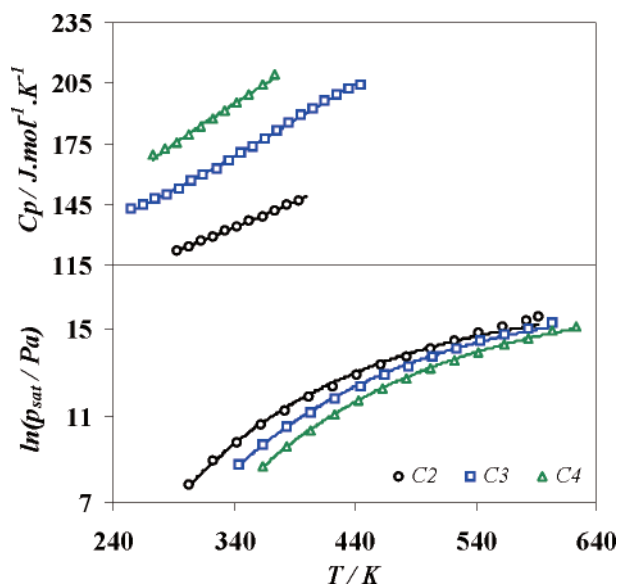


Figure 4. Low-pressure heat capacities and vapor pressures of acids. Continuous lines, TSAM correlation; dots, experimental.¹⁰

between the alkyl chains. This cmo association was evaluated using the C_p data of the n -alkane with same chain length, allowing for the isolation of the association due to hydrogen bonding. Such long chain 1-alcohols were not included in this work because the cmo contribution should arise naturally with a better description of C_p^{ns} . This could be accomplished, for example, using some EOS for the evaluation of C_p^{ns} . The simple linear function of temperature cannot capture this feature, because it is known that the cmo decrease nonlinearly with temperature.¹¹

It is quite common to use the six-parameter (four polynomial constants and two critical properties) Wagner^{12,13} equation to correlate saturation pressures in broad temperature ranges. The equation proposed here has also six (or five) parameters, and it is also able to correlate p_{sat} from the triple point to the critical point. Furthermore, only two parameters are specifically used for p_{sat} correlation, the three remaining ones being fixed to the values obtained from correlating C_p data. The main advantage of TSAM with respect to Wagner's equation rests on its ability to simultaneously correlate of p_{sat} and C_p . If no C_p data are

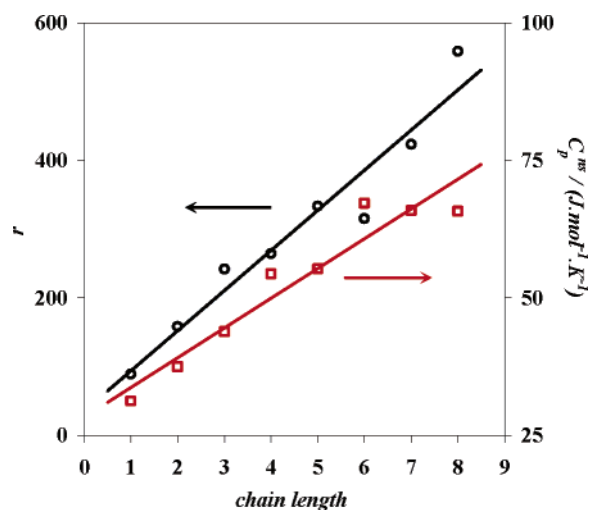


Figure 5. 1-Alcohols degeneracy ratio r (O) and nonspecific heat capacity C_p^{ns} (□) as a function of the chain length. The continuous lines are the linear trends.

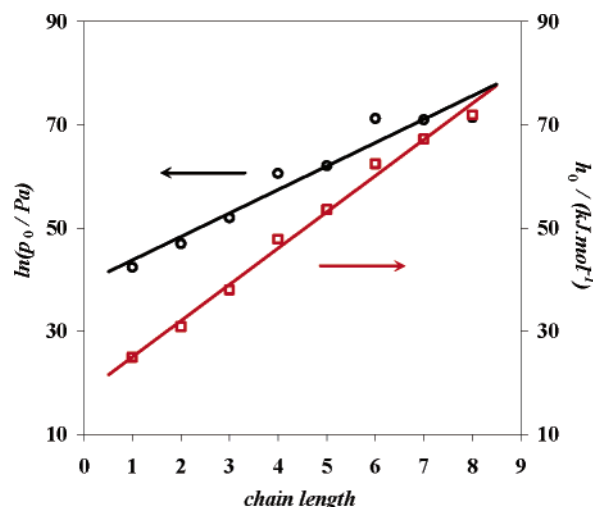


Figure 6. Parameters of eq 14 for 1-alcohols: $\ln(p_0)$ (O) and h_0 (□) as a function of the chain length. The continuous lines are the linear trends.

available, all five or six TSAM parameters can be adjusted to p_{sat} , producing results equivalent to those of the Wagner equation, with no need to know the critical properties. Note that when dealing with a family of substances the present model can be used in a predictive form, provided a minimum amount of experimental information is available for some members of that family. For example, if the parameters in Tables 2 and 3 would have been fitted to the odd carbon number 1-alcohols, the value of the interpolated parameters for the even carbon number ones produces predictions for their vapor pressures that are quite good, particularly for industrial applications.

For 1-alcohols, the TSAM parameters h_0 and p_0 in Table 3 are correlated with the chain length, as shown in Figures 5 and 6. Following the linear trends, the corresponding 1-nonanol and 1-decanol parameters were estimated ($r = 560.4$ and 618.7 , $C_p^{ns} = 76.94$ and 82.34 J mol⁻¹ K⁻¹, $h_0 = 81$ 139 and 88 151 J mol⁻¹, and $\ln(p_0) = 80.14$ and 84.68 , respectively). Figure 7 displays the TSAM predicted vapor pressures for 1-nonanol and 1-decanol as compared against the experimental data,¹⁰ up to the critical point. The very good agreement between them suggests that the model has predictive nature. For 1-thiols, the parameters h_0 and p_0 in Table 3 also show a linear dependence with chain length, but there are no vapor pressure data available for longer 1-thiols to compare against a TSAM prediction. For

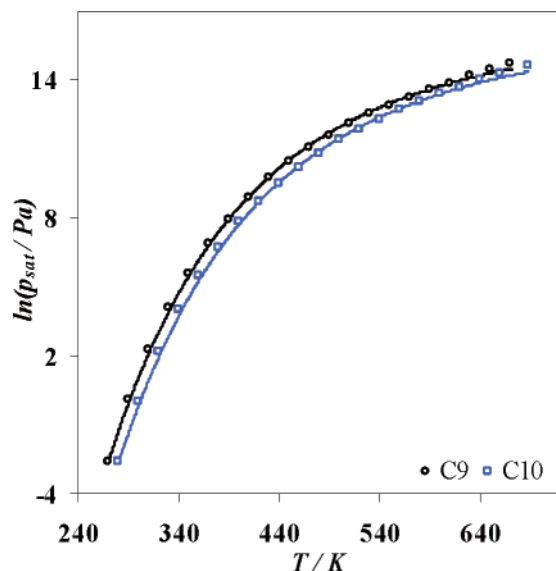


Figure 7. Vapor pressures of 1-nonanol and 1-decanol. Continuous lines, TSAM prediction; dots, experimental.¹⁰ The TSAM parameters were extrapolated from their linear trend with the chain length. See Figures 5 and 6.

acids and 1-amines, the number of compounds where data are available is too small to allow the evaluation of a correlation between h_0 and p_0 and chain length.

To investigate the nature of the nonspecific contribution to vapor pressure, we compared this contribution [eq 15] for several 1-alcohols against the experimental vapor pressure of the corresponding similar chain length n -alkane (for instance, 1-pentanol was compared to n -hexane). It seems logical that the difference between the $\ln(p_{\text{sat}}^{\text{ns}})$ versus T curves for the 1-alcohol and the n -alkane must be equal to the multipolar long-range contributions. Because for long chains the dispersion forces dominate the total interaction, the longer the chain length is, the closer to each other these curves should be. Figure 8 shows that this is the observed behavior. The vapor pressures of n -alkanes are systematically slightly higher than the corresponding $p_{\text{sat}}^{\text{ns}}$ curves of 1-alcohols. The differences between the curves can be mainly attributed to dipole–dipole interactions, which are not present in n -alkanes. Confident that association effects are properly isolated by eq 16, the results in Figure 8 allow for an estimation of the dipole–dipole contribution to vapor pressure.

Concluding Remarks

We have presented a simple model that is able to correlate simultaneously low-pressure liquid heat capacities and vapor pressures of self-associating pure substances. This was possible through a reformulation of the original TSAM.⁵ The obtained good correlations of the experimental data and the clear physical meaning of the parameters improve our understanding of the microscopic origin of those thermophysical properties. The association contribution to these two properties can be easily isolated and quantified from the resulting equations. The model can be further improved with the employment of a better reference fluid partition function. The assumption of constant C_p^{ns} works well for highly associated systems, but it is necessary to include a temperature-dependent term when association is weak and hence its magnitude is comparable to the other

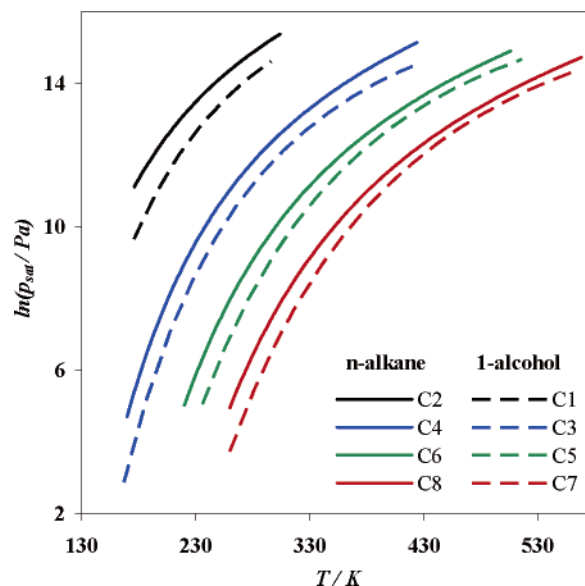


Figure 8. Comparison between vapor pressures of n -alkanes with the nonspecific contribution to the vapor pressures of 1-alcohols. Continuous lines, CDATA¹⁰ equation for n -alkanes; dashed lines, TSAM prediction for $\ln(p_{\text{sat}}^{\text{ns}})$ of 1-alcohols, as defined in eq 15.

interactions. This upgrade, however, is not directly related to association, but to a general theory of liquid heat capacities and vapor pressures of nonassociating substances. Presently, we are already considering the use of an EOS for this purpose. Modifying the model to be able to describe data at high pressures and developing mixing rules that would allow an extension to associating mixtures constitute other future important TSAM improvements.

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