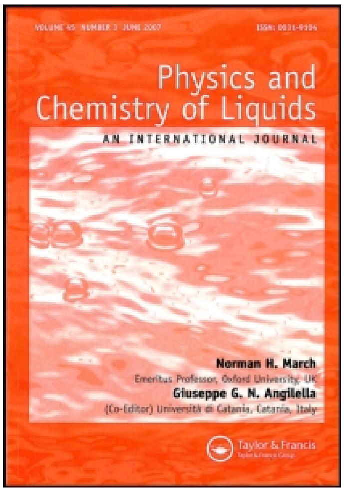

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On the Thermodynamics of Liquid Mixtures of Two *n*-Alkanes

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The excess molar volume V^E of liquid mixtures of two *n*-alkanes is predicted essentially on the basis of the van der Waals model. The important feature of the treatment is that V^E may be calculated from the respective densities, isobaric expansivities and isothermal compressibilities of the pure liquids, whereas data of solution properties need not be known. Neither any combining rules nor empirically adjusted parameters are used. Computed values are slightly less negative than the observed excess volumes, the average deviation being about 10%.

I INTRODUCTION

Numerous molecular models have been proposed to calculate the excess thermodynamic functions of liquid nonelectrolyte solutions. Much work in this field has been concerned with predicting the excess volume. Yet, even for mixtures of simple molecules such as the *n*-alkanes current sophisticated theories require an interactional parameter for species of different kind to be fixed empirically. In this situation it appears desirable to investigate the possibility of deriving a formalism that would allow to express the volume change on mixing in terms of the pure component data without using quantities which are to be adjusted to some experimentally determined solution property. The treatment presented in the following seems a possible step in this direction.

Some of the basic premises are adopted from the model designed for mixtures of chainlike molecules by Flory and coworkers[1] that is known to be one of the most successful treatments of this kind. Following Flory, we regard a chain molecule as built up of segments, which, provided the chains are sufficiently long, we may consider as being equivalent rather than to distinguish between mid-chain and terminal structural elements. Flory combined an extension of a partition function originally derived by Tonks[2] for a one-dimensional liquid of incompressible molecules with an intermolecular energy term of van der Waals (vdW) type. Another way of looking at the problem is to attribute the volume effects in a more direct form to the difference of the thermal pressure coefficients of the unmixed component liquids, while the vdW concept is introduced in a later stage. The calculation method proposed here requires no mixing rules and yields a simple expression for the excess volume as a function of the same pure component data as have been used by Flory, in a closed mathematical form.

II THEORETICAL DEVELOPMENT

We begin defining

$$\alpha_a = \sum_{i=1}^{2} \phi_i \alpha_i \qquad \beta_a = \sum_{i=1}^{2} \phi_i \beta_i \qquad \gamma_a = \sum_{i=1}^{2} \phi_i \gamma_i,$$

which are the volume fraction averages over the isobaric expansivities α_i, the isothermal compressibilities β_i and the thermal pressure coefficients γ_i $(i = 1, 2)$ of the pure liquids. The volume fractions ϕ_i refer to the molar volumes V_i of the unmixed n-alkanes

$$\phi_i = \frac{x_i V_i}{V_0} \qquad V_0 = \sum_{i=1}^{2} x_i V_i,$$

where x_i are the mole fractions. Moreover we shall use the quantities

$$\gamma_0 = \frac{\alpha_a}{\beta_a} \qquad \bar{\gamma} = \sum_{i=1}^{2} \frac{\phi_i \alpha_i \gamma_i}{\alpha_a}.$$

We approach our objective of predicting V^E by making a Taylor series expansion around V_0 and expressing the thermal pressure coefficient γ of the mixture in the form

$$\gamma - \gamma_0 = \left(\frac{\partial \gamma}{\partial V}\right)_0 V^E + \cdots = b\gamma - \bar{\gamma} \tag{1a}$$

and

$$\gamma - \gamma_0 = \left(\frac{\partial \gamma}{\partial V}\right)_0 V^E + \cdots = c\gamma_a - \bar{\gamma}, \tag{1b}$$

where b and c are parameters not far from unity. Upon dividing Eq. (1a) by b, (Eq. (1b) by c, then adding both and setting $1/b + 1/c = m$, one obtains

$$m\left(\frac{\partial \gamma}{\partial V}\right)_0 V^E = \gamma + \gamma_a - m\bar{\gamma}. \tag{2}$$

In more complicated binary liquid mixtures m may be treated as an adjustable parameter to force agreement between the left- and right-hand side of Eq. (2). As in the systems studied here no specific interactions between the constituents are to be expected, we may determine the value of m from a simple thermodynamic consideration. It has been shown by Hirschfelder *et al.*[3] for a pair of vdW type liquids and later generalized by Mauser and Kortüm[4] to any pair of substances that a necessary condition of forming an ideal liquid mixture requires agreement of the thermal pressure coefficients γ_1 and γ_2. If this requirement is satisfied then

$$\gamma_1 = \gamma_2 = \gamma = \gamma_a = \bar{\gamma}. \tag{3}$$

Introducing Eq. (3) into Eq. (2), we get in the limiting case of an ideal mixture ($V^E = 0$) the result $m = 2$. Having evaluated m, we obtain from Eq. (2)

$$V^E = \left[\frac{\gamma + \gamma_a - 2\bar{\gamma}}{2}\right]\left(\frac{\partial \gamma}{\partial V}\right)_0. \tag{4}$$

The dependence of γ on volume at $V^E = 0$, $(\partial\gamma/\partial V)_0$, must be estimated on a molecular theoretical basis. For our present purpose it seems convenient to express the thermal pressure coefficient as a function of volume on the grounds of the vdW model, because it is one of the simplest and may be derived from fundamental principles. First, we use the vdW energy-volume relation

$$E = -\frac{a}{V} \tag{5}$$

assuming that at a fixed composition a mixture behaves like a simple fluid. In Eq. (5), E denotes the configurational energy, V the volume per mole of solution and a is a parameter independent of V at constant composition. Now we conclude from Eq. (5)

$$\left(\frac{\partial E}{\partial V}\right)_{T,x} = \frac{a}{V^2}. \tag{6}$$

Comparison of the so called thermodynamic equation of state

$$\left(\frac{\partial E}{\partial V}\right)_{T,x} = \gamma T - P \tag{7}$$

with Eq. (6) at negligible pressure P results in

$$a = \gamma T V^2. \tag{8}$$

Eq. (5) and Eq. (6) imply that the coefficient a is independent of volume at a given temperature and mole fraction. Thus, an expression for $(\partial\gamma/\partial V)_0$ may be found by taking the value of the parameter a equal to that in a mixture of the same constituents, at the same composition, at zero excess volume and at the same temperature. Doing so, we derive from Eq. (8)

$$\Delta a = T\,\Delta(\gamma V^2) = 0, \tag{9}$$

where Δ symbolizes the increment of a solution property over its value in the reference mixture, in which at unchanged concentration and temperature $V^E = 0$. Utilizing Eq. (9), we may write if $\Delta\gamma$ and ΔV are small quantities

$$\Delta(\gamma V^2) = V^2\,\Delta\gamma + 2\gamma V\,\Delta V = 0. \tag{10}$$

In default of a better approximation, we equate in Eq. (10) $\Delta\gamma/\Delta V$ to $(\partial\gamma/\partial V)_0$, V to V_0 and γ to γ_0. The dependence of γ on volume at $V^E = 0$ is then

$$\left(\frac{\partial\gamma}{\partial V}\right)_0 = -\frac{2\gamma_0}{V_0}. \tag{11}$$

Upon introducing Eq. (11) into Eq. (4) and setting $\gamma = \gamma_0$, we obtain

$$\frac{V^E}{V_0} = \left[\frac{2\bar{\gamma} - (\gamma_a + \gamma_0)}{4\gamma_0}\right]. \tag{12}$$

In order to relate V^E to the mechanical properties $(\alpha_i, \beta_i, \gamma_i)$ of the pure n-alkanes, we make the following rearrangement

$$2\bar{\gamma} - (\gamma_a + \gamma_0) = 2(\bar{\gamma} - \gamma_a) + \gamma_a - \gamma_0. \tag{13}$$

It may be shown by simple algebra that

$$\bar{\gamma} - \gamma_a = \frac{\phi_1\phi_2(\alpha_1 - \alpha_2)(\gamma_1 - \gamma_2)}{\alpha_3} \tag{14a}$$

and

$$\gamma_a - \gamma_0 = -\frac{\phi_1\phi_2(\beta_1 - \beta_2)(\gamma_1 - \gamma_2)}{\beta_a}. \tag{14b}$$

Substitution of Eq. (13), (14a) and (14b) into Eq. (12) gives

$$\frac{V^E}{V_0} = \phi_1\phi_2\left[\frac{(\gamma_1 - \gamma_2)}{4\gamma_0}\right]\left[\frac{\dfrac{2(\alpha_1 - \alpha_2)}{\alpha_a} - (\beta_1 - \beta_2)}{\beta_a}\right]. \tag{15}$$

Eq. (15) is, of course, a very simple relation and in the general case some modifications have to be made to reproduce adequately the excess volume of a binary system.

III RESULTS AND DISCUSSION

As is well known, the reduced equation of state of Eyring and Hirschfelder[3,5] which is of the same form as that used by Flory for the component liquids as well as their mixtures, consists of a vdW term containing the configurational energy of the system and a modified "free volume" contribution. Extension of the equation of state for pure liquids to mixtures involves prescribing the composition dependence of its characteristic parameters by reasonable combining rules. Unfortunately, the results are in general highly sensitive to these prescriptions and, as a consequence, fitting to some mixing data is necessary, To overcome this inherent difficulty in predicting the volume effects, a departure had to be made from the usual practice by avoiding to introduce the entire equation of state explicitly into the calculations. Instead, we restricted our considerations to the energy contribution in the equation of state, choosing the particularly simple vdW approximation of Eq. (5) with one single solution parameter a that may be easily eliminated. One of the essential ideas in the treatment just described rests, as illustrated by Eq. (2), on the supposition that the difference between $(\gamma + \gamma_a)/m$ and $\bar{\gamma}$ corresponds to an equivalent volume effect. Assigning to m such a numerical value as if the mixture were ideal, seems justified in solutions of nearly identical particles interacting with each other by forces of the same nature and of about the same magnitude as those in the separated constituents.

Data of physical properties of the pure *n*-alkanes used in calculations are collected in Table I. Observed values of V^E are compared in Table II at equimolar composition with results predicted from Eq. (15) and with predictions of Orwoll and Flory[6] who computed excess volumes for a major number of binary mixtures of *n*-alkanes from Flory's theory using a parameter that has been optimized with respect to the excess enthalpies of the considered group of solutions. The results for the systems no. 5 and 9 (hexane or else octane with hexadecane) indicate that the temperature dependence of V^E is accurately predicted by Orwoll and Flory, whereas Eq. (15) yields at elevated temperatures excess volumes of less negative values than those resulting from density measurements.

Perhaps, the most important advantage of Eq. (15) is that it furnishes V^E independently of other excess functions. The volume changes on mixing for the systems investigated here are directly available from the PVT properties

TABLE I

Properties of pure liquid components

n-alkane	Temp. / °C	V / cm^{3}mol^{-1}	$10^3\alpha$ / K^{-1}	$10^3\beta$ / MPa^{-1}	Reference
C_5H_{12}	20	115	1.57	1.96^a	Flory e.a.[1]
C_6H_{14}	20	131	1.39	1.64	J. H. van der Waals[7]
	25	132	1.39	1.72	Blinowska and Brostow[8]
	50	136	1.53	2.24	” ”
C_7H_{16}	25	148	1.26	1.49	” ”
C_8H_{18}	20	163	1.15	1.24	J. H. van der Waals[7]
	50	168	1.23	1.60	Orwoll and Flory[6]
	100	180	1.42	2.53	” ”
C_9H_{20}	50	185	1.14	1.44	Blinowska and Brostow[8]
$C_{10}H_{22}$	20	195	1.04	1.07	J. H. van der Waals[7]
$C_{12}H_{26}$	25	228	0.96^b	0.98^b	Flory *et al.*[1]
$C_{16}H_{34}$	20	293	0.90	0.84	J. H. van der Waals[7]
	25	294	0.90	0.87	” ”
	50	301	0.92	1.02	Orwoll and Flory[6]
$C_{24}H_{50}$	51	434^b	0.83^b	0.86^b	Flory e.a.[1]
$C_{36}H_{74}$	100	660	0.78	1.03	Orwoll and Flory[6]

[a] Extrapolated
[b] Interpolated

TABLE II

Observed and calculated excess volumes V^E of equimolar *n*-alkane mixtures at the temperature t

No.	System	t/°C	Obs.	V^E/cm^{3}mol^{-1} Eq. (15)	Orwoll and Flory[6]
1	$C_5H_{12} + C_{10}H_{22}$	20	-0.42^a	-0.39	
2	$C_5H_{12} + C_{16}H_{34}$	20	-0.82^a	-0.77	
3	$C_6H_{14} + C_{10}H_{22}$	20	-0.20^a	-0.21	
4	$C_6H_{14} + C_{12}H_{26}$	25	-0.35	-0.36	-0.37
5	$C_6H_{14} + C_{16}H_{34}$	20	-0.49	-0.51	-0.56
		50	-0.82	-0.74	-0.89
6	$C_6H_{14} + C_{24}H_{50}$	51	-1.19	-1.06	-1.34
7	$C_7H_{16} + C_{12}H_{26}$	25	-0.17	-0.21	-0.23
8	$C_7H_{16} + C_{16}H_{34}$	25	-0.34	-0.32	-0.42
9	$C_8H_{18} + C_{16}H_{34}$	20	-0.19	-0.18	-0.24
		50	-0.33	-0.28	-0.36
10	$C_8H_{18} + C_{36}H_{74}$	96	-1.62	-1.46	-1.83
11	$C_9H_{20} + C_{24}H_{50}$	51	-0.43	-0.35	-0.42
12	$C_{10}H_{22} + C_{16}H_{34}$	20	-0.07	-0.07	-0.10

[a] McGlashan and Morcom[9]

of the pure *n*-alkanes by means of a selfconsistent formalism in which the basic physical features appear in a straightforward way.

It should be pointed out that the close connection of nonideal mixing behavior and quantitative disagreement of γ_1 and γ_2 as evident from Eq. (15), comes forward already in some earlier solution models. Assuming that the pure components are vdW type liquids and letting G^* stand for a quantity obtained on subtracting a Flory–Huggins combinatorial term from the excess molar Gibbs free energy,[10] we may write the familiar Scatchard–Hildebrand equation in the form

$$G^* = \phi_1\phi_2 V_0 T(\sqrt{\gamma_1} - \sqrt{\gamma_2})^2$$

inasmuch as in the vdW model the square of the solubility parameter of component i must be equal to the product $\gamma_i T$ as shown by Hildebrand and Scott.[11] One may note the proportionality with $\phi_1\phi_2 V_0$ in G^* as well as in Eq. (15).

In the present work we limited our attention to the excess volume. The possibility of predicting other excess functions from the PVT behavior of the pure components will be discussed in a forthcoming paper.

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