Excess energy at constant volume for *n*-alkane binary mixtures

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ABSTRACT. A comparison has been carried out between experimentally derived values of the excess energy at constant volume and calculated results from the theoretical treatment due to van Laar and Lorenz and the Solubility Parameter version of the Regular Solution Theory due to Scatchard and Hildebrand for *n*-alkane binary mixtures. The mixtures considered are *n*-hexane + *n*-hexadecane at 293.15, 303.15, 313.15, and 323.15 K, and *n*-octane + *n*-hexadecane at 303.15, 323.15, 349.15, and 379.15 K.

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1. INTRODUCTION

The systematic study of the thermodynamic properties of mixtures of fluids has contributed enormously to the development of theories which explain the experimental behaviour through the use of pure component molecular parameters or pure component thermodynamic properties. It is common to carry out experimental determinations of the thermodynamic mixing properties of liquids under conditions of constant pressure usually at 1 atmosphere (1 atmosphere = 101.325 kPa). Nonetheless, in statistical mechanics it is more convenient to keep constant the volume of a system than the pressure, so most theories of solutions yield the thermodynamic functions for a constant volume mixing process, thus, if a comparison between experiment and theory is required it is then necessary to obtain constant volume functions from the constant pressure experimental measurements. Equations relating constant pressure functions to constant volume functions were first derived by Scatchard [1]. Thus, the Gibbs free energy for the constant pressure process (ΔG^{E}) is essentially the same as the Helmholtz free energy at constant volume ($\Delta A^{\mathrm{E}}_{\mathrm{V}}$), since the second-order correction on the excess volume (ΔV^{E}) is negligible, according to

$$\Delta A^{\mathrm{E}}_{\mathrm{V}} = \Delta G^{\mathrm{E}} + \frac{(\Delta V^{\mathrm{E}})^2}{2\beta_t V}, \tag{1}$$

where β_t is the isothermal compressibility and V is the mixture volume.

The relation between the excess energy at constant volume ($\Delta U_{\mathrm{V}}^{\mathrm{E}}$) and the excess enthalpy (ΔH^{E}) is

$$\Delta U_{\mathrm{V}}^{\mathrm{E}} = \Delta H^{\mathrm{E}} - T\Delta V^{\mathrm{E}}\gamma_{\mathrm{V}}, \tag{2}$$

where T is temperature and γ_{V} is the thermal pressure coefficient $(\partial P/\partial T)_{\mathrm{V}}$ of the mixture.

It is unfortunate that the experimental data necessary to carry out the corrections in Eqs. (1) and (2) are scarce for many mixtures as to carry out a comparison between experiment and theory under constant volume conditions. Many more experimental measurements of ΔV^{E}, γ_{V} and isobaric expansivities (α_{p}) need to be done before such comparison can be made for a large number of mixtures. However, enough reliable data on the excess thermodynamic functions of some n-alkane systems are available as to carry out a comparison between experimentally and theoretically derived values of $\Delta U_{\mathrm{V}}^{\mathrm{E}}$.

We report in this work results for $\Delta U_{\mathrm{V}}^{\mathrm{E}}$ of the system n-hexane + n-hexadecane throughout the composition range at 293.15, 303.15, 313.15 and 323.15 K and also for n-octane + n-hexadecane at 303.15, 323.15, 349.15 and 379.15 K. We compare these values with results from the theoretical approaches due to van Laar and Lorenz [2] and to Scatchard and Hildebrand [3]. It will be shown that the latter treatment is in fact an elaboration of that by van Laar.

2. VAN LAAR-LORENZ THEORY

The expression derived by van Laar and Lorenz [2] for the energy change when a mole of binary mixture is formed at constant temperature and no change of volume on mixing by mixing n_1 and n_2 moles of pure components is

$$\Delta U^{\mathrm{m}} = \Delta H^{\mathrm{m}} = \frac{x_1 x_2}{x_1 v_1 + x_2 v_2} \frac{a_1 v_2^2 - 2a_{12} v_1 v_2 + a_2 v_1^2}{v_1 v_2}, \tag{3}$$

where x_i is the mole fraction, v_i is the molar volume, a_i is a constant in van der Waals' equation of state, and a_{12} is a binary interaction constant.

In Eq. (3) van Laar and Lorenz substituted actual molar volumes for the b's of van der Waals' equation as van Laar had originally used in 1906 [4].

By assuming that a_{12} satisfied the Bertherlot relation van Laar and Lorenz further simplified Eq. (3) to

$$\Delta U^{\mathrm{m}} = \Delta H^{\mathrm{m}} = \frac{x_1 x_2}{x_1 v_1 + v_1 v_2} \frac{(a_1^{1/2} v_2 - a_2^{1/2} v_1)^2}{v_1 v_2}. \tag{4}$$

The latter equation is the starting point to calculate ΔU^{m} values for mixtures of n-alkanes. In order to have Eq. (4) as a function of the number of carbon atoms n in the molecule of each of the n-alkanes studied we have considered the pure n-alkanes as composed of groups CH_3 and CH_2 thus one mole of any n-alkane contains mole fraction $x_1 = 2/n$ for CH_3 and $x_2 = (n-2)/n$ for CH_2.

According to van der Waals, the constant a, for a binary mixture is given by

$$a = a_{11}x_1^2 + 2x_1x_2(a_{11}a_{22})^{1/2} + a_{22}x_2^2, \tag{5}$$

thus, for an n-alkane containing n_1 carbon atoms and as mentioned above, considered as a mixure of molecular groups we will have

$$a_1 = n_1^2\left[a_{11}\left(\frac{2}{n_1}\right)^2 + 2(a_{11}a_{22})^{1/2}\frac{2(n_1-2)}{n_1^2} + a_{22}\left(\frac{n_1-2}{n_1}\right)^2\right],$$

which reduces to

$$a_1 = \left[2a_{11}^{1/2} + (n_1-2)a_{22}^{1/2}\right]^2. \tag{6}$$

Similarly, the value of a_2 for an n-alkane containing n_2 carbon atoms is

$$a_2 = \left[2a_{11}^{1/2} + (n_2-2)a_{22}^{1/2}\right]^2. \tag{7}$$

If the molar volumes of the pure n-alkanes are given as a function of n, for a given temperature as

$$V_i = c(n+2), \tag{8}$$

where c is a constant, and introducing Eqs. (6) and (7) in (4), then

$$\Delta U^{\mathrm{M}} = K\frac{x_1x_2}{(x_1n_1 + x_2n_2 + 2)(n_1+2)(n_2+2)}(n_2-n_1)^2. \tag{9}$$

Equation (9) allows the calculation of ΔU^{M} for mixtures of n-alkanes through the composition range using only as pure component parameters the number of carbon atoms [5].

3. SCATCHARD AND HILDEBRAND THEORY

Scatchard [6] derived the following expression for the cohesive energy of a mole of liquid mixture

$$-U = \frac{C_1V_1^2x_1^2 + 2C_{12}V_1V_2x_1x_2 + C_2V_2^2x_2^2}{x_1V_1 + x_2V_2}, \tag{10}$$

where C_i is the cohesive energy density, equal to $-U_i/V_i$, V_i is the molar volume and x_i is the mole fraction. The quantities C_i characterize the interactions between pairs of molecules of type 11, 12 and 22.

The above equation may be transformed through the use of volume fractions ϕ_i $(= x_iV_i/\sum x_iV_i)$ defined with references to the unmixed state to obtain

$$-U = (C_1\phi_1^2 + 2C_{12}\phi_1\phi_2 + C_2\phi_2^2)(x_1V_1 + x_2V_2). \tag{11}$$

The energy change upon mixing is

$$\Delta U^{\mathrm{M}} = U - x_1U_1 - x_2U_2,$$

hence, Scatchard obtained

$$\Delta U^{\mathrm{M}} = (C_1 + C_2 - 2C_{12})(x_1V_1 + x_2V_2)\phi_1\phi_2, \tag{12}$$

and by assuming that

$$C_{12} = \sqrt{C_1C_2},$$

we may write

$$\Delta U^{\mathrm{M}} = (C_1^{1/2} - C_2^{1/2})^2(x_1V_1 + x_2V_2)\phi_1\phi_2. \tag{13}$$

The square roots of C_i, renamed solubility parameters by Hildebrand [7], play such an important role in this theory of solutions that this is also widely known as "Solubility Parameter Theory".

Taking a solubility parameter as $\delta_i = C_i^{1/2}$, Eq. (13) may be written as

$$\Delta U^{\mathrm{M}} = (\delta_1 - \delta_2)^2(x_1V_1 + x_2V_2)\phi_1\phi_2, \tag{14}$$

which is identical with Eq. (4) of van Laar and Lorenz, if the van der Waals a is defined as $(V_i\delta_i)^{1/2}$.

Equation (14) was also derived by Hildebrand [8], thus it is well known as the Scatchard-Hildebrand equation. It is important to note that the mixing process considered throughout the derivation of Eq. (14) is one carried out at constant volume.

4. EXCESS ENERGY AT CONSTANT VOLUME

Equation (2) is the expression that relates the excess energy at constant volume $\Delta U_{\mathrm{V}}^{\mathrm{E}}$ to the experimentally obtained constant pressure excess enthalpy $\Delta H_{\mathrm{p}}^{\mathrm{E}}$. As in

x	$\dfrac{\Delta U_V^E}{\text{J mol}^{-1}}$	x	$\dfrac{\Delta U_V^E}{\text{J mol}^{-1}}$
293.15 K		303.15 K	
0.1	52.2	0.1	41.1
0.2	91.6	0.2	72.3
0.3	118.9	0.3	94.0
0.4	134.5	0.4	106.6
0.5	138.7	0.5	110.6
0.6	131.9	0.6	105.9
0.7	114.5	0.7	92.7
0.8	86.6	0.8	70.4
0.9	48.4	0.9	39.8
313.15 K		323.15 K	
0.1	31.6	0.1	23.7
0.2	55.7	0.2	42.1
0.3	72.8	0.3	55.3
0.4	83.1	0.4	64.0
0.5	86.9	0.5	67.8
0.6	84.1	0.6	66.7
0.7	74.5	0.7	60.0
0.8	57.2	0.8	46.4
0.9	33.1	0.9	27.6

TABLE I. Values of ΔU_V^E for the system $xn\text{-C}_6\text{H}_{14} + (1-x)n\text{-C}_{16}\text{H}_{34}$.

previous work [9] we have considered the first order correction in Eq. (2) $T\Delta V^E\gamma_V$ to be small enough so that it is sufficient to take $T\gamma_V$ as the value for the ideal mixture. In this case the thermal pressure coefficient γ_V is given by

$$\gamma_V = x_1\gamma_{V,1} + x_2\gamma_{V,2}. \tag{15}$$

For the system n-hexane + n-hexadecane the excess enthalpies were taken from the work of McGlashan and Morcom [10], the excess volumes from Díaz-Peña and Benítez [11], and the thermal pressure coefficients from Orwoll and Flory [12]. Table I contains the derived values of ΔU_V^E at 293.15, 303.15, 313.15 and 323.15 K throughout the composition range.

Considering the excellent agreement that has been obtained between experimental and calculated values with the Corresponding States Principle (CSP) for a wide range of excess thermodynamic properties of n-alkanes [13-15] we used the CSP to obtain both ΔH_p^E and ΔV^E for n-octane + n-hexadecane at 303.15, 323.15, 349.15 and 379.15 K throughout the composition range, whereas γ_V was also obtained from reference [12]. Table II shows the derived values of ΔU_V^E as a function of temperature and composition.

x	$\frac{\Delta U_V^E}{\text{J mol}^{-1}}$	x	$\frac{\Delta U_V^E}{\text{J mol}^{-1}}$
303.15 K		323.15 K	
0.1	23.5	0.1	15.8
0.2	42.6	0.2	28.7
0.3	56.6	0.3	38.1
0.4	65.1	0.4	43.7
0.5	68.4	0.5	45.8
0.6	65.9	0.6	44.2
0.7	57.8	0.7	38.6
0.8	44.0	0.8	29.4
0.9	24.7	0.9	16.4
349.15 K		379.15 K	
0.1	11.0	0.1	9.2
0.2	20.0	0.2	16.4
0.3	26.6	0.3	21.6
0.4	30.6	0.4	24.2
0.5	32.1	0.5	24.6
0.6	31.0	0.6	22.7
0.7	27.0	0.7	18.4
0.8	20.5	0.8	12.4
0.9	11.4	0.9	8.6

TABLE II. Values of ΔU_V^E for the system $xn\text{-}C_8H_{18} + (1-x)n\text{-}C_{16}H_{34}$.

5. COMPARISON BETWEEN THEORY AND EXPERIMENT

In order to compare Eq. (9) with the experimentally derived values of ΔU_V^E for the two binary systems studied here we considered the value of K to be composition independent, so that, we obtain a fitted value at each temperature by using the corresponding equimolar value of ΔU_V^E. Table III gives values of K for each binary system as a function of temperature. It may be observed that K shows a clear dependence with temperature and also with the difference in carbon atoms for each one of the two systems.

The results of the calculations of ΔU_V^E from the van Laar-Lorenz theory are shown in Figs. 1 and 2, where we have also included the experimentally derived values. In general the extent of the agreement between theory and experiment is no more than fair. The theoretical values tend to be skewed more to high mole fraction of the smaller n-alkane in each one of the two binary systems through the temperature range studied than is observed experimentally. Although the absolute magnitude of the experimental ΔU_V^E is not well reproduced, the theory does reproduce the relative magnitude since both the experimental and the calculated ΔU_V^E decrease with temperature.

T/K	10^{-4} K/J mol^{-1}	10^{-4} K/J mol^{-1}
	n-C$_6$ + n-C$_{16}$	n-C$_8$ + n-C$_{16}$
293.15	1.0383	
303.15	0.8279	1.0770
313.15	0.6508	
323.15	0.5074	0.7215
349.15		0.5059
379.15		0.3876

TABLE III. Constant K of Eq. (4) as function of temperature for each one of the binary systems studied.

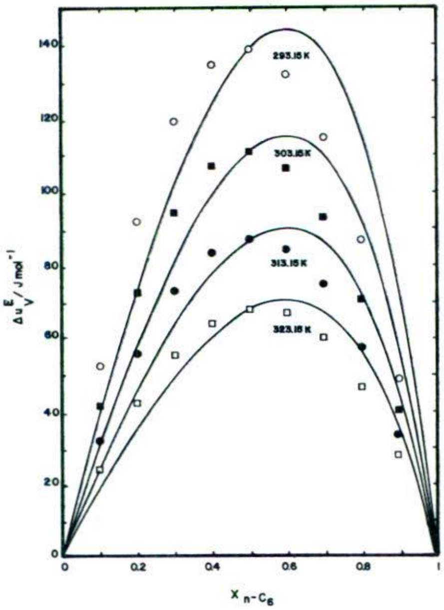

FIGURE 1. Comparison between experimentally derived and calculated excess energy at constant volume ΔU_V^E throughout the composition range at different temperatures for n-hexane + n-hexadecane. Points, experimental values at the indicated temperature; curves, calculated as indicated in the text with either the van Laar-Lorenz or the Scatchard-Hildebrand approach.

Calculated values of ΔU_V^E from the Scatchard-Hildebrand model [Eq. (14)] showed that the Berthelot relation $C_{12} = (C_1 C_2)^{1/2}$ is not valid for the present systems. Thus, we have used the following relation [16]

$$C_{12} = \ell_{12}(C_1 C_2)^{1/2}, \tag{16}$$

where ℓ_{12} has the meaning of an empirical binary coefficient, close to unity.

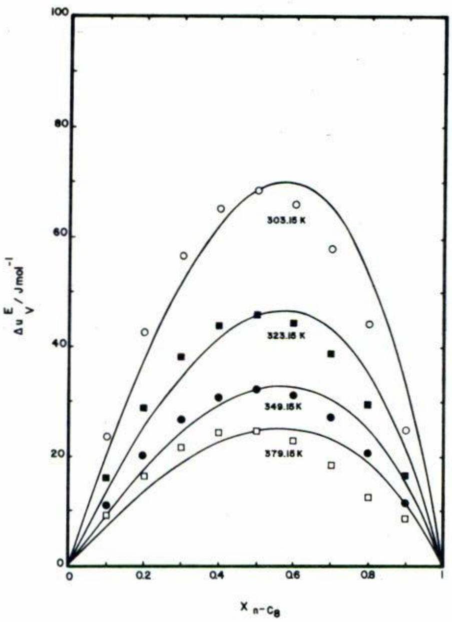

FIGURE 2. Comparison between experimentally derived and calculated excess energy at constant volume ΔU_V^E throughout the composition range and at different temperatures for n-octane + n-hexadecane. Points, experimental values at the indicated temperature; curves, calculated as indicated in the text with either the van Laar-Lorenz or the Scatchard-Hildebrand approach.

Introducing Eq. (16) in the original Scatchard-Hildebrand equation we can write

$$\Delta U^{\mathrm{M}} = \left(\delta_1^2 + \delta_2^2 - 2\ell_{12}\delta_1\delta_2\right)\left(x_1 v_1 + x_2 v_2\right)\phi_1\phi_2, \tag{17}$$

where the different symbols have their usual meaning.

The empirical constant ℓ_{12} for the two binary systems studied was chosen to fit the experimentally derived ΔU_V^E values at $x = 0.5$ for each one of the temperatures considered. The constants obtained in this way are summarized in Table IV, where it may be observed that there exists a weak temperature dependence of ℓ_{12} for each one of the systems and that the deviations with respect to unity (*i.e.*, validity of the geometric-mean assumption) are always smaller than 1%.

Pure n-alkane values of molar volumes as a function of temperature were obtained from Ref. [12] and solubility parameters from Refs. [17] and [18].

ΔU_V^E values calculated with Eq. (17) lead to the following observations: 1) a large improvement is obtained in the calculation of ΔU_V^E values by introducing the constant ℓ_{12}, which is not far from unity; 2) the dependence of ΔU_V^E with composition for both sets of systems is not exactly reproduced by the theory; 3) the change of ΔU_V^E with temperature is qualitatively given by the theory for both

T/K	ℓ_{12}	ℓ_{12}
	n-C_6 + n-C_{16}	n-C_8 + n-C_{16}
293.15	1.0097	
303.15	1.0097	1.0072
313.15	1.0095	
323.15	1.0092	1.0064
349.15		1.0049
379.15		1.0031

TABLE IV. Constant ℓ_{12} of Eq. (17) as a function of temperature for each one of the binary systems studied.

systems; and 4) the values of ΔU_V^E obtained are exactly the same as those obtained from van Laar-Lorenz equation. This is not surprising since as shown before Eqs. (4) and (14) are identical after defining the van der Waals a in terms of the solubility parameter.

6. CONCLUSION

We have carried out a comparison between experimentally derived values of ΔU_V^E and results from the theoretical treatments due to van Laar and Lorenz and to Scatchard and Hildebrand for binary mixtures of n-alkanes. The van Laar and Lorenz equation has been given specifically to treat n-alkane mixtures since apart from a constant the only input parameter required is the number of carbon atoms of the pure n-alkanes. The Solubility Parameter version of the Scatchard and Hildebrand approach embodies parameters for the pure components which are evaluated under the same conditions to those for the mixtures studied. That is, in both treatments the properties of the liquid mixtures have been related to those of their pure liquid components.

Although the derivation of the theories was performed through slightly different assumptions, both give identical results once the van Laar-Lorenz approach is divorced from the van der Waals' equation of state. The theoretical treatments had to be fitted to a value of ΔU_V^E to obtain qualitative agreement with ΔU_V^E. It appears unwise at present to attribute a physical significance to the fitted constant used in each one of the theories.

The regular solution concept embodied in both approaches used here is useful for semiquantitative work on most nonpolar binary systems.

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RESUMEN. Se derivaron valores de la energía de exceso a volumen constante a partir de resultados de la entalpía y volumen de exceso, y del coeficiente térmico de la presión para mezclas binarias de alcanos normales. Estos valores se comparan con resultados obtenidos de la teoría de van Laar y Lorentz y con la versión del parámetro de solubilidad de la teoría de soluciones regulares propuesta por Scatchard y Hildebrand. Las mezclas estudiadas son n-hexano + n-hexadecano a 293.15, 303.15, 313.15, y 323.15 K, y n-octano + n-hexadecano a 303.15, 323.15, 349.15 y 379.15 K.