THEORETICAL INVESTIGATION OF THE EXCESS FREE ENERGY OF BINARY n-ALKANE SYSTEMS

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SUMMARY

It is shown that the recent theory of Janini and Martire can be used to interpret the infinite dilution activity coefficients of 36 binary n-alkane systems at 80, 100, and 120 °C, and activity coefficients as a function of mole fraction for three n-alkane systems.

INTRODUCTION

The normal alkanes serve as reference or model systems for many applications and there is a great need for a theory of non-electrolyte solutions which can be used to interpret and/or predict thermodynamic excess properties for the n-alkanes. The partial molar excess free energy of a low-molecular-weight solute in a higher-molecular-weight solvent is easily measurable by gas chromatography; thus, the greatest emphasis has been placed on the interpretation of this function. However, any useful solution theory must also predict the other excess properties, such as volume and enthalpy. Often this is a more critical test than the ability of the theory to account for activity coefficient data.

There are presently numerous theories for predicting activity coefficients and these range from simple empirical correlations to very sophisticated and hard-to-use rigorous theories. However, they all have some points in common. One convention that is agreed upon is that the logarithm of the activity coefficient, $\ln \gamma$, is composed of a sum of two or more contributions. The earliest work was based on the concept of two contributions, *viz.*, a combinatorial or athermal portion, $\ln \gamma^{comb.}$, and an energetic or thermal contribution, $\ln \gamma^{th}$.

Ashworth and Everett[1] used a two-term expression to represent their data for several alkane systems. The combinatorial or athermal term was calculated from Guggenheim's[2] treatment of athermal solutions. The same term can also be calculated from the Flory–Huggins equation for athermal solutions[3,4], which can be obtained from Guggenheim's equations by letting the number of nearest neighbors, z, approach infinity. Ashworth and Everett[1] and Young[5] analyzed activity coefficient data using several values for z and concluded that the data could be reproduced equally well for $z = 6, 9, 12$, or ∞. Everett and Munn[6] analyzed the activity coefficient data of Mc-Glashan and Williamson[7] for n-hexane in n-hexadecane by treating the ratio of the

sizes of the solvent and solute molecules, r, as an adjustable parameter for different values of z. The "best fit" values of r varied with the choice of z and temperature; however, the "best" value of r approached the ratio of molar volumes at $z = \infty$. The authors concluded that although r varied with the choice of z, the overall fit of the data was independent of z.

The general conclusion is that the Flory–Huggins equation is as good as the more complicated theories for evaluation of the combinatorial contribution to $\ln \gamma$. The Flory–Huggins equation[3,4] is

$$\ln \gamma_1{}^{\text{comb.}} = \ln \frac{\varphi_1}{x_1} + \left(1 - \frac{r_1}{r_2}\right)\varphi_1 \tag{1}$$

$$\ln \gamma_1{}^{\text{comb.},\infty} = \ln \frac{r_2}{r_1} + 1 - \frac{r_1}{r_2} \tag{2}$$

where $\ln \gamma_1{}^{\text{comb.}}$ and $\ln \gamma_1{}^{\text{comb.},\infty}$ are the activity coefficient and infinite dilution activity coefficient, respectively, of the solute*, φ_1 and x_1 are the volume fraction and mole fraction of the solute, respectively, and r_i is some measure of the size of the ith component. The exact interpretation of the r parameter is open to discussion. The older literature generally involves an interpretation of $r = r_2/r_1$ as the ratio of the molar volumes or partial molar volumes. An alternative approach is to use the ratio of the so-called "hard-core" volumes which are proportional to the carbon numbers for n-alkanes. This latter interpretation is more theoretically sound, easier to use, and results in a combinatorial contribution which is temperature independent.

The thermal or energetic term is proportional to φ_2^2 and is generally expressed in terms of the Flory interaction parameter, χ (ref. 3).

$$\ln \gamma_1{}^{\text{th}} = \chi \varphi_2^2 \tag{3}$$

$$\ln \gamma_1{}^{\text{th},\infty} = \chi \tag{4}$$

Numerous authors[5,8–11] have interpreted χ in terms of the lattice theories of Guggenheim[12] and Barker[13]. In this treatment χ is attributed entirely to an interaction energy between segments of the molecules.

$$\chi = \left[q_1(u_1 - u_2)^2 \frac{\omega}{kT}\right]\varphi_2^2 \tag{5}$$

q_1 is the total number of contact points on the solute, u_i is the fraction of contact points of type u of molecule i and ω is the interchange energy.

Eqn. 5 has been widely used to interpret χ with ω treated as a constant independent of the solute and solvent for alkanes.

However, Orwoll and Flory[14] have shown that this treatment of χ as an enthalpy of mixing determined only by contact interactions is inadequate for the pre-

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* The subscripts 1 and 2 will be used to designate the low- and high-molecular-weight components, respectively.

diction of excess properties. This collaborated the earlier work of Prigogine[15], who discussed the excess free energy in terms of three contributions:

(a) Geometrical effect, ln $\gamma^{comb.}$, due to the different molecular volumes of the solute and solvent.

(b) Energetic effect, χ^E, due to the difference in the solute–solute, ε_{11}^{*}, solute–solvent, ε_{12}^{*}, and solvent–solvent, ε_{22}^{*}, interaction energies.

(c) Structural effect, χ^S, due to the fact that the solute and solvent may not have the same number of external degrees of freedom per segment.

Thus, the full expression for the activity coefficient would be

$$\ln \gamma = \ln \gamma^{comb.} + (\chi^E + \chi^S)\, \varphi_2^2 \tag{6}$$

Prigogine[15] presented an explicit expression for the excess free energy and recently Janini and Martire[16] have derived simplified expressions based on Prigogine's treatment, for the excess free energy, excess volumes, and excess enthalpies for n-alkane systems. The expressions derived for χ^E and χ^S are

$$\chi^E = \frac{-h_1 \delta^2}{4RT} \tag{7}$$

$$\chi^S = \frac{C_{P_1}(\lambda + \delta)^2}{2R} \tag{8}$$

where C_{P_1} and h_1 are the configurational heat capacity and enthalpy of the solute and λ and δ are defined by eqns. 9 and 10.

$$\lambda = 1 - \frac{(c/r)_2}{(c/r)_1} \tag{9}$$

$$\delta = \frac{\varepsilon_{22}^{*} - \varepsilon_{11}^{*}}{\varepsilon_{22}^{*}} \tag{10}$$

$(3c/r)_i$ is the number of external degrees of freedom per segment of molecule i and δ is a constant which is proportional to the depth of the potential well for 1–1 and 2–2 interactions. δ can be estimated from the critical temperatures and "hard-core" volumes[16]. The $(c/r)_i$ term cannot be evaluated directly and Janini and Martire[16] used this ratio as an adjustable parameter and presented an empirical equation for $(c/r)_i$ as a function of the number of segments in molecule i, r_i, from previously published activity coefficient data.

The activity coefficients of n-C_4H_{10} to n-$C_{10}H_{22}$ in n-$C_{22}H_{46}$ to n-$C_{36}H_{74}$ have recently been measured at infinite dilution[17] and three of the systems have been measured at finite concentrations[18]. This set of data will be interpreted in terms of Janini and Martire's[16] theory of non-electrolyte solutions.

INFINITE DILUTION ACTIVITY COEFFICIENTS

The detailed calculations and procedures for obtaining theoretically sound activity coefficients from elution and frontal chromatography have been presented elsewhere[17–19] and only the results will be discussed here. The Raoult's Law infinite

TABLE I

AVERAGE VALUES OF THE INFINITE DILUTION ACTIVITY COEFFICIENTS OF THE
n-ALKANES AT 80, 100, AND 120 °C

Solute	Solvents						
	$n\text{-}C_{22}H_{46}$	$n\text{-}C_{24}H_{50}$	$n\text{-}C_{28}H_{58}$	$n\text{-}C_{30}H_{62}$	$n\text{-}C_{32}H_{66}$	$n\text{-}C_{34}H_{70}$	$n\text{-}C_{36}H_{74}$
$n\text{-}C_4H_{10}$	0.805	0.739	0.693	0.681	0.639	0.619	0.594
$n\text{-}C_5H_{12}$	0.816	0.753	0.698	0.680	0.654	0.631	0.606
$n\text{-}C_6H_{14}$	0.859	0.801	0.736	0.712	0.689	0.665	0.639
$n\text{-}C_7H_{16}$	0.893	0.831	0.768	0.743	0.721	0.696	0.672
$n\text{-}C_8H_{18}$	0.927	0.854	0.796	0.772	0.753	0.728	0.701
$n\text{-}C_{10}H_{22}$	0.950	0.895	0.845	0.830	0.817	0.782	0.751

dilution activity coefficients for the n-alkane systems studied are given in Table I. The activity coefficients were independent of temperature in the range 80–120 °C with an average relative deviation of less than 1%, and the data presented in Table I are the average values for the three temperatures.

The combinatorial contribution to ln γ was calculated from eqn. 2 using r as the ratio of "hard-core" volumes. The "hard-core" volumes were calculated from the formula given by Janini and Martire[16]. The calculated values of the thermal contribution, or χ, calculated from eqn. 11 are given in Table II.

$$\chi = \ln \gamma_1^\infty - \ln \gamma_1^{\text{comb.},\infty} \tag{11}$$

TABLE II

EXPERIMENTAL VALUES OF χ CALCULATED FROM EQN. 11

Solutes	Solvents						
	$n\text{-}C_{22}H_{46}$	$n\text{-}C_{24}H_{50}$	$n\text{-}C_{28}H_{58}$	$n\text{-}C_{30}H_{62}$	$n\text{-}C_{32}H_{66}$	$n\text{-}C_{34}H_{70}$	$n\text{-}C_{36}H_{74}$
$n\text{-}C_4H_{10}$	0.553	0.535	0.593	0.632	0.622	0.641	0.648
$n\text{-}C_5H_{12}$	0.421	0.404	0.446	0.474	0.486	0.499	0.506
$n\text{-}C_6H_{14}$	0.357	0.347	0.374	0.393	0.409	0.421	0.427
$n\text{-}C_7H_{16}$	0.402	0.287	0.314	0.330	0.348	0.358	0.367
$n\text{-}C_8H_{18}$	0.263	0.234	0.264	0.280	0.301	0.311	0.315
$n\text{-}C_{10}H_{22}$	0.170	0.156	0.188	0.213	0.239	0.235	0.234

INTERPRETATION OF χ BASED ON A SINGLE (ENERGETIC) CONTRIBUTION

In this case, the combinatorial contribution to ln γ was calculated using the ratio of molar volumes so that the results could be compared with previous studies[5,8-11]. The interaction energy, ω/k, was calculated from eqn. 5, with the types u and v segments defined to be methyl and methylene groups, respectively[8,13]. The explicit expression for χ in terms of the solute and solvent carbon numbers, n_1 and n_2 is

$$\chi = 18 \, (n_1 + 1) \left(\frac{1}{n_1 + 1} - \frac{1}{n_2 + 1} \right)^2 \frac{\omega}{kT} \tag{12}$$

TABLE III

CALCULATED VALUES OF ω/k FOR *n*-ALKANES AT 80 °C BASED ON EQN. 12

Solutes	Solvents						
	$n\text{-}C_{22}H_{46}$	$n\text{-}C_{24}H_{50}$	$n\text{-}C_{28}H_{58}$	$n\text{-}C_{30}H_{62}$	$n\text{-}C_{32}H_{66}$	$n\text{-}C_{34}H_{70}$	$n\text{-}C_{36}H_{74}$
$n\text{-}C_4H_{10}$	52.6	46.1	49.5	52.9	49.6	47.8	49.9
$n\text{-}C_5H_{12}$	58.8	50.3	51.9	54.3	54.2	54.4	53.6
$n\text{-}C_6H_{14}$	71.0	61.6	59.9	60.3	61.2	61.2	59.9
$n\text{-}C_7H_{16}$	82.3	67.8	65.2	65.8	66.2	66.3	65.6
$n\text{-}C_8H_{18}$	96.4	71.5	69.6	70.2	72.7	71.7	69.2
$n\text{-}C_{10}H_{22}$	107.6	79.7	78.2	84.1	89.5	81.8	75.8
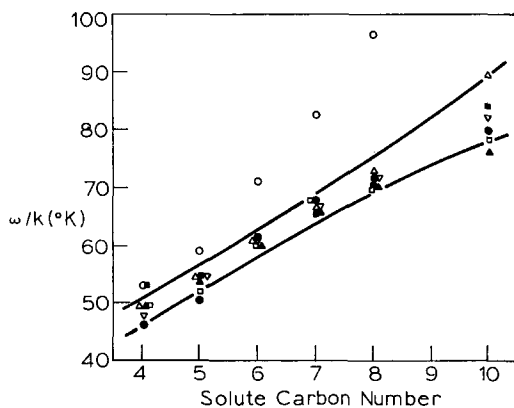
Fig. 1. Plot of ω/k calculated from eqn. 12 at 80 °C as a function of solute carbon number. $\bigcirc$, $n\text{-}C_{22}H_{46}$; ●, $n\text{-}C_{24}H_{50}$; $\square$, $n\text{-}C_{28}H_{58}$; ■, $n\text{-}C_{30}H_{62}$; $\triangle$, $n\text{-}C_{32}H_{66}$; $\triangledown$, $n\text{-}C_{34}H_{70}$; ▲, $n\text{-}C_{36}H_{74}$.

The values of ω/k calculated from the data of Table I are given in Table III and Fig. 1 for the 80 °C data set. The results for the 100 and 120 °C data were analogous to those for the 80 °C data, and the general conclusions were the same for the segment model as opposed to the contact point model. Except for the $n\text{-}C_{22}H_{46}$ column, the ω/k values are relatively independent of the solvent; however, there is a definite dependence of the interaction energy on the solute carbon number. The value of ω/k increases linearly with n_1. The causes for the discrepancy of the data for the $n\text{-}C_{22}H_{46}$ solvent are not known, although it is probably due to the liquid phase loss of this low-molecular-weight liquid during the course of the experiment. This could not be detected from the specific retention volumes, however.

It is obvious that ω/k is not a true constant and that eqn. 5 is not adequate for the interpretation of χ. It would require an interaction contribution to χ with $\omega/k \approx 25$ °K plus another contribution which increases with the molecular size of the solute for an accurate assessment of χ.

INTERPRETATION OF χ BASED ON TWO (ENERGETIC AND STRUCTURAL) CONTRIBUTIONS

Determination of the physical properties and λ *and* δ *parameters for eqns. 7 and 8*

 h_1 is the configurational enthalpy of the solute and can be obtained from the

heat of vaporization at the temperature of the experiment from eqn. 13. The heats of vaporization

$$h_1 = -\Delta h^{\mathrm{vap.}} + RT \tag{13}$$

of the solutes at 80, 100, and 120 °C were calculated from the values at the boiling point[20] using the Watson correlation (see ref. 21).

C_{P_1} is the configurational heat capacity of the solute and is best calculated[22] from the measured data for n-heptane and the theory of corresponding states using eqn. 25 of ref. 16.

The δ parameter was calculated from the equation

$$\delta = \frac{T_2^c/(V_2^*)^{\frac{1}{3}}}{T_1^c/(V_1^*)^{\frac{1}{3}}} - 1 \tag{14}$$

Where V_i^* is the "hard core" volume of component i and the T_i^c is the critical temperature of the ith component. The V_i^* values were calculated from Janini and Martire's[16] definition of r_i and the critical data were taken from the compilation of Kudchadker et al.[23].

C_{P_1}, h_1, and δ are solute parameters which, with the exception of δ, vary with temperature. The calculated values of these terms at 80, 100, and 120 °C are listed in Table IV.

TABLE IV

CALCULATED VALUES OF h_1, C_{P_1}, AND δ AT 80, 100, AND 120 °C

Solute	$-h_1$ (kcal/mole)			C_{P_1} (cal/mole·°K)			$\delta \times 10^2$
	80 °C	100 °C	120 °C	80 °C	100 °C	120 °C	
n-C$_4$H$_{10}$	3.32	2.82	2.18	10.34	10.69	11.08	11.48
n-C$_5$H$_{12}$	4.75	4.34	3.87	11.73	12.01	12.35	7.61
n-C$_6$H$_{14}$	6.01	5.63	5.21	13.08	13.25	13.52	4.94
n-C$_7$H$_{16}$	7.18	6.81	6.41	14.46	14.53	14.70	3.20
n-C$_8$H$_{18}$	8.30	7.94	7.55	15.88	15.81	15.92	2.06
n-C$_{10}$H$_{22}$	11.23	10.03	9.65	18.80	18.55	18.45	0.78

The λ term can be calculated from the $(c/r)_i$ ratios for the solute and solvent via eqn. 9; however, there is no a priori method for calculating $(c/r)_i$. Janini and Martire[16] found that the following empirical equation gave the best fit for the set of limiting activity coefficients used in their study.

$$\left(\frac{c}{r}\right)_i = 0.550 + \frac{1.817}{r_i} - \frac{1.834}{r_i^2} \tag{15}$$

However, we found that a slightly better fit was obtained for our more extensive data set by using eqn. 16.

$$\left(\frac{c}{r}\right)_i = 0.534 + \frac{1.839}{r_i} - \frac{1.813}{r_i^2} \tag{16}$$

TABLE V

CALCULATED VALUES OF λ USING EQNS. 9 AND 16

Solutes	Solvents						
	$n\text{-}C_{22}H_{46}$	$n\text{-}C_{24}H_{50}$	$n\text{-}C_{28}H_{58}$	$n\text{-}C_{30}H_{62}$	$n\text{-}C_{32}H_{66}$	$n\text{-}C_{34}H_{70}$	$n\text{-}C_{36}H_{74}$
$n\text{-}C_4H_{10}$	0.310	0.321	0.338	0.345	0.351	0.370	0.362
$n\text{-}C_5H_{12}$	0.284	0.295	0.313	0.320	0.327	0.332	0.337
$n\text{-}C_6H_{14}$	0.256	0.267	0.286	0.293	0.300	0.306	0.311
$n\text{-}C_7H_{16}$	0.229	0.240	0.260	0.267	0.274	0.281	0.286
$n\text{-}C_8H_{18}$	0.203	0.215	0.235	0.243	0.250	0.257	0.263
$n\text{-}C_{10}H_{22}$	0.158	0.171	0.192	0.201	0.208	0.215	0.221

This resulted in calculated λ values which were 0.01–0.02 units larger than the λ values quoted by Janini and Martire[16]. The calculated values of λ obtained from eqns. 9 and 16 are listed in Table V.

Comparison of calculated and experimental values of the infinite dilution activity coefficients

The average deviation for the reproduction of the infinite dilution activity coefficients, γ_1^∞, for all of the solutes in each solvent are given in Table VI. The deviation is expressed simply as

$$\frac{1}{6} \sum_{i=1}^{6} | \gamma_1^{\text{calc.}} - \gamma_1^{\text{exp.}} |_i$$

where i is used to represent the six n-alkane solutes studied. All of the values of γ_1^∞ were in the range 0.60–0.95, so this simple error expression was used rather than the more complicated measures of precision, such as the relative mean deviation or the root mean square deviation.

Again, the data for $n\text{-}C_{22}H_{46}$ do not agree with the remainder of the data set. However, for all of the other solvents, the average deviation between the calculated and experimental values was ±0.008. This is close to the 1 % relative deviation quoted for the three data sets at different temperatures and slightly larger than the value of ±0.006 given by Janini and Martire[16]. Thus, the theory adequately accounts for the data within the experimental error.

TABLE VI

AVERAGE ERROR ($\times 100$) IN THE REPRODUCTION OF γ_1^∞ FOR ALL SOLUTES

	Temperature (°C)	Solvent						
		$n\text{-}C_{22}H_{46}$	$n\text{-}C_{24}H_{50}$	$n\text{-}C_{28}H_{58}$	$n\text{-}C_{30}H_{62}$	$n\text{-}C_{32}H_{66}$	$n\text{-}C_{34}H_{70}$	$n\text{-}C_{36}H_{74}$
Ref. 16,	80	5.5	2.1	1.8	2.3	2.2	1.9	1.4
eqn. 15	100	5.2	1.8	1.5	2.0	2.0	1.7	1.1
	120	4.7	1.6	1.3	1.5	1.5	1.2	0.6
This	80	4.1	1.0	0.7	0.9	0.9	0.2	0.9
work,	100	3.9	1.0	0.7	0.9	0.8	0.3	0.8
eqn. 16	120	3.6	0.8	0.7	1.0	0.8	0.8	0.9

TABLE VII

FINITE CONCENTRATION ACTIVITY COEFFICIENTS FOR n-HEXANE IN n-TETRA-
COSANE, n-OCTACOSANE, AND n-DOTRIACONTANE

Solvent	Temperature ($^\circ C$)	x_1	$-ln\ \gamma_1$		$100\ \Delta$
			Calculated	Observed	
n-$C_{24}H_{50}$	60	0.00	0.233	0.219	−1.4
		0.07	0.190	0.180	−1.0
		0.25	0.153	0.137	−1.6
		0.27	0.141	0.164	+2.2
		0.29	0.133	0.127	−0.6
		0.34	0.098	0.120	+2.3
		0.43	0.079	0.089	+1.0
				Average	±1.4
n-$C_{24}H_{50}$	80	0.00	0.234	0.222	−1.2
		0.04	0.261	0.211	−5.0
		0.12	0.202	0.203	+0.1
		0.20	0.171	0.188	+1.7
		0.27	0.142	0.137	−0.5
		0.34	0.116	0.122	+0.6
		0.41	0.095	0.100	+0.5
		0.42	0.090	0.111	+2.1
				Average	±1.5
n-$C_{24}H_{50}$	100	0.00	0.230	0.222	−0.8
		0.03	0.177	0.228	+5.1
		0.09	0.185	0.210	+2.5
		0.10	0.183	0.192	+1.1
		0.21	0.161	0.168	+0.7
		0.32	0.120	0.149	+2.8
				Average	±2.2
n-$C_{28}H_{58}$	80	0.00	0.306	0.307	+0.1
		0.04	0.287	0.290	+0.3
		0.05	0.286	0.254	−3.2
		0.17	0.246	0.235	−1.1
		0.20	0.219	0.227	+0.8
		0.29	0.184	0.180	+0.4
		0.33	0.169	0.189	+2.0
		0.35	0.164	0.168	+0.4
		0.37	0.154	0.144	−1.0
		0.43	0.125	0.145	+2.0
				Average	±1.1
n-$C_{32}H_{66}$	80	0.00	0.375	0.373	−0.2
		0.17	0.299	0.298	−0.1
		0.18	0.280	0.318	+3.8
		0.23	0.268	0.229	−3.8
		0.26	0.247	0.255	+0.8
		0.39	0.184	0.204	+2.0
		0.41	0.179	0.234	+5.5
		0.46	0.152	0.105	−4.7
				Average	±2.6

Comparison of calculated and experimental values of the activity coefficients at finite concentrations

The activity coefficients of three of the systems studied at infinite dilution have also been measured as a function of the mole fraction of the solute, x_i, by means of frontal chromatography[18,24]. The results of this study are given in Table VII along with a comparison of the calculated values of ln γ_1. The solute mole fractions were limited to less than 0.5 by the instrumentation. In this range, however, the average deviation in ln γ_1 was ±0.018, which corresponds to a deviation of approximately ±0.015 in γ_1. This deviation was larger than the $+0.010$ quoted by Janini and Martire; however, there was no systematic deviation between the observed and calculated values. The larger deviation in the data is caused by the imprecision of the chromatographic measurements at finite concentrations rather than to any inadequacy in the theory.

Discussion of the separate contributions to χ, i.e. χ^S and χ^E

In this study, the χ^S term accounted for at least 98 % of the χ value and the deviation between the calculated and observed values of χ was larger than χ^E, so the physical significance of the energetic term is questionable. Patterson *et al.*[25] have suggested that χ can be accounted for entirely by an equation of state or structural term and that a finite value of χ^E is merely a reflection of the inaccuracy of the formulation of the χ^S term. These workers used Orwoll and Flory's[14,26] theory; however, the same conclusion could, perhaps, be drawn from this study using Janini and Martire's theory. The accuracy of the data is insufficient for a conclusive test; however, the calculations could be simplified without a significant loss of accuracy by using eqns. 6 and 8 with $\chi^E = 0$.

CONCLUSIONS

Janini and Martire[16] have previously shown that their theory gives reasonable values for the excess enthalpy and excess volume of equimolar mixtures of *n*-alkanes. This study has shown that the theory satisfactorily accounts for the partial molar excess free energy of a wide range of binary *n*-alkane mixtures at infinite dilution and up to a mole fraction of the solute in the solvent of 0.5. The method suffers the disadvantage of an empirical estimation of $(c/r)_i$; however, the equations are based on a solid theoretical foundation and the one empirical equation can be used for all of the systems and concentrations studied over a 40° range of temperatures. The ability to calculate accurate excess thermodynamic properties for a variety of systems and temperatures makes this a valuable method for the investigation of *n*-alkane solutions.

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