Excess Enthalpies of Binary Mixtures of Ethylbenzene + *n*-Alkanes

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Excess molar enthalpies of the binary mixtures ethylbenzene + *n*-octane, + *n*-dodecane, and + *n*-hexadecane have been measured at 298.15 K as a function of composition. Measurements were made in a semicontinuous dilution calorimeter. Results have been fitted to a Padé approximant by using a regression method based on the maximum likelihood principle.

Introduction

Hydrocarbon mixtures have been widely used to check liquid-state theories. *n*-Alkane systems show short-range order phenomena (*1*) which lead to important positive contributions to h^E (*2*). Molar excess enthalpies of *n*-alkane + benzene and + toluene (*3*–*5*) have been previously published. h^E values for benzene systems are much higher than those for toluene systems. The methyl substitution in the aromatic ring of benzene has shown the same effect on the excess molar volume (*6*, *7*). In order to extend our investigations to study the influence of the substitution in the aromatic ring on excess molar enthalpy we have chosen ethylbenzene + *n*-alkane systems. In this paper we report the results for mixtures with *n*-octane, *n*-dodecane, and *n*-hexadecane at 298.15 K. No h^E data have been found in the literature although excess molar volume and excess molar heat capacities have recently been published (*8*, *9*) for some ethylbenzene + *n*-alkane systems.

Experimental Section

Molar Excess Enthalpy Measurements. The excess molar enthalpy was measured in the whole concentration range by using a semicontinuous calorimeter previously described (*10*). Two overlapping dilution runs were required to cover the whole mole fraction range for each system. The accuracy of any individual measurement of molar excess enthalpy was better than 0.5 J·mol^{-1}.

Materials. Ethylbenzene (Fluka "purum") and *n*-octane (Merck "analysis") were distilled in a column with a ratio 130/1; afterward they were stored over sodium wire. *n*-Dodecane and *n*-hexadecane (Hopkin-Williams) were used without further purification and stored over sodium wire. The purity of all the substances was tested by GLC.

The experimental densities (in g·cm^{-3}) at 298.15 K were 0.862 76 (0.862 64), 0.698 64 (0.698 49), 0.745 18 (0.745 16), and 0.759 14 (0.7593) for ethylbenzene, *n*-octane, *n*-dodecane, and *n*-hexadecane, respectively. Literature values from ref *11* are given in parentheses.

Results

Experimental values of excess molar enthalpies are given in Table I; in all the binaries x is the mole fraction of ethylbenzene. Each set of results was fitted with a (n/m) Padé approximant

$$H^E/RT = x(1-x)\frac{\sum_{i=0}^{n} A_i(2x-1)^i}{1+\sum_{j=1}^{m} B_j(2x-1)^j} \tag{1}$$

The principle of maximum likelihood as described by Anderson et al. (*12*) was used in the regression method in order to obtain the parameters of eq 1. This method does not consider independent variables and provides not only the parameters A_i and B_j, but the so-called "true values" of the variables (x, h^E, T). The parameters and true values of the variables are chosen as to make the experimental observations appear to be the most likely when taken as a whole. In the formulation given by Anderson et al. (*12*) this is equivalent to minimizing

$$S = \sum_{i=1}^{N} (\mathbf{x}_i^m - \mathbf{x}_i)^T \beta_i^{-1} (\mathbf{x}_i^m - \mathbf{x}_i) \tag{2}$$

N is the number of experimental points; $\mathbf{x}_i^m$ and $\mathbf{x}_i$ are vectors which contain the experimental and true values, respectively, of all the variables for experiment i; β_i is the variance–covariance matrix of the measured variables. In our measurements it is a very good approach to suppose that the different variables are not correlated, β_i being a diagonal matrix.

It is possible to show that the weighted root mean square deviation

$$\eta = S/(N-L) \tag{3}$$

has a χ^2-type distribution with $N-L$ degrees of freedom (*13*), L being the number of adjustable parameters. The magnitude η makes possible the calculation of the variance–covariance matrix of the parameters. The diagonal elements of this matrix provide the variances of the parameters and, consequently, the value of the error ϵ_i associated with each parameter θ_i (A_i and B_j in eq 1). The ratio

$$t = \theta_i/\epsilon_i \tag{4}$$

follows a Student's distribution (*14*) and indicates the statistical significance of the parameter θ_i within a given confidence level.

The best set of parameters is chosen among all the different sets obtained by varying the n and m indices in eq 1 according to the following criteria (*15*):

(a) The deviations between experimental and true values (δ_x, $\delta_h{}^E$, δ_T) must present a random distribution with a null average. The values of the variables should be similar to those estimated from the experimental uncertainties.

(b) The eigenvalues of the variance–covariance matrix of the parameters should be positive or null (*16*).

(c) When two Padé approximants have a similar statistical significance, the one using fewer parameters is preferred. The statistical significance of the parameters should be as large as possible, and uncertainties in the thermodynamic magnitudes related to the parameters must be as small as possible.

The estimated uncertainties of the variables x, h^E, and T are 5×10^{-4}, 1 J·mol^{-1}, and 0.01 K, respectively. The values for δ_x and δ_{h^E} are given in Table I. Values for δ_T have not been represented because they are negligible ($<10^{-3}$ K). Table II shows the values of the parameters, their estimated errors, the

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Table I. Molar Excess Enthalpies, Liquid-Phase Mole Fractions of Ethylbenzene, and Their Deviations from the Smoothed Values

x	$10^4\delta_x$	h^E/ (J·mol^{-1})	δ_{h^E}/ (J·mol^{-1})
		C_8H_{10} + n-C_8H_{18}	
0.0723	−1	130	1
0.1452	−1	246	1
0.2123	1	340	−0.5
0.2706	1	410	−1
0.3228	3	464	−2
0.3700	1	502	−0.6
0.4195	−2	533	1
0.4621	−6	551	3
0.4711	−1	557	1
0.4933	−2	563	1
0.4990	−5	563	3
0.5173	0	569	−0.1
0.5331	−1	570	0.4
0.5441	2	572	−1
0.5646	2	571	−1
0.5702	2	570	−0.9
0.5924	2	566	−1
0.5983	−1	563	0.4
0.6175	2	558	−0.9
0.6295	−2	551	1
0.6391	9	553	−5
0.6591	7	541	−4
0.6639	−4	531	2
0.6981	−4	506	2
0.7354	−3	471	2
0.7728	−2	428	1
0.8142	−1	372	0.5
0.8591	1	300	−0.3
0.9077	1	209	−0.8
0.9592	1	99	−1
		C_8H_{10} + n-$C_{12}H_{26}$	
0.1090	−1	203	0.5
0.2066	−1	357	0.9
0.2894	2	472	−1
0.3639	2	555	−1
0.4271	1	610	−0.4
0.4824	−2	644	1
0.5284	−1	664	0.3
0.5314	−1	665	0.2
0.5471	−2	668	0.9
0.5667	−1	671	0.7
0.5674	−2	671	0.7
0.5890	2	673	−0.9
0.6009	0	671	0.1
0.6123	−1	669	0.3
0.6290	−1	665	0.2
0.6371	−1	662	0.4
0.6577	0	654	−0.1
0.6643	−1	650	0.4
0.6825	1	640	−0.5
0.6933	2	633	−1
0.7036	2	625	−1
0.7219	1	608	−0.6
0.7245	1	605	−0.2
0.7380	3	593	−2
0.7525	4	577	−2
0.7544	−1	571	0.5
0.7871	−4	524	2
0.8221	−3	466	2
0.8581	−1	397	0.8
0.8945	0	315	−0.3
0.9326	0	215	−0.4
0.9718	0	97	−0.6
		C_8H_{10} + n-$C_{16}H_{34}$	
0.1407	0	281	0.2
0.2520	0	471	0
0.3460	2	607	−1
0.4214	−1	692	0.4
0.4826	0	746	0
0.5329	−3	775	1
0.5748	−1	790	0.4
0.6114	−1	793	0.4
0.6426	−1	788	0.5
0.6748	1	776	−0.6
0.7029	7	760	−3
0.7075	2	754	−0.8
0.7268	2	736	−0.6
0.7297	−2	731	0.9
0.7472	1	713	−0.4
0.7568	−4	698	1
0.7647	−1	689	0.3
0.7796	1	668	−0.4
0.7863	−3	654	1
0.7931	2	647	−1
0.8048	3	627	−1
0.8146	−2	603	1
0.8450	−1	538	0.7
0.8762	−1	459	0.3
0.9101	0	357	0.2
0.9456	0	233	−0.2
0.9755	0	113	−0.4

standard deviations of the variables, $s(x)$ and $s(h^E)$, and the weighted root mean square, η. For the sake of comparison it also shows the results obtained with a (2/0) approximant for one of the systems, and also the results obtained with a (3/0) approximant for the same system using a typical unweighted least-squared method.

We can observe that the regression method used in this paper allows us to obtain for the (2/0) approximant a values of $s(h^E)$ lower than that obtained for the (3/0) one using the unweighted least-squared method, keeping $s(x)$ values within the experimental uncertainty in x. What is more important in order to compare the results is the value of η. We can observe that $s(h^E) = 1.4$ leads to $\eta = 3$; therefore, we may suppose a value $\eta > 3$ for the unweighted method ($s(h^E) = 1.8$). It has been pointed out (*17*, *18*) that a value $\eta = 1$ is reached when the smoothing equation does not introduce systematic errors

Table II. Parameters in Smoothing Eq 1, Their Estimated Uncertainties, the Standard Deviations of the Variables, and the Weighted Root Mean Squared Deviation

system	A_0	A_1	A_2	A_3	$10^4 s(x)$	$s(h^E)$	η
C_8H_{10} + n-C_8H_{18}	0.9140 ± 0.0009	0.1737 ± 0.0048	−0.0251 ± 0.0069	−0.0725 ± 0.0153	3	1.8	4.2
C_8H_{10} + n-$C_{12}H_{26}$	1.0580 ± 0.0009	0.3405 ± 0.0028	0.0585 ± 0.0064		2	1.4	3
	1.0562 ± 0.0007	0.3552 ± 0.0032	0.0660 ± 0.0046	−0.0608 ± 0.0104	2	1	1.5
a	1.0573	0.3439	0.0647	−0.0285		1.8	
C_8H_{10} + n-$C_{16}H_{34}$	1.2244 ± 0.0009	0.5193 ± 0.0022	0.1713 ± 0.0050		2	1	1.5

[a] Unweighted least-squared method.

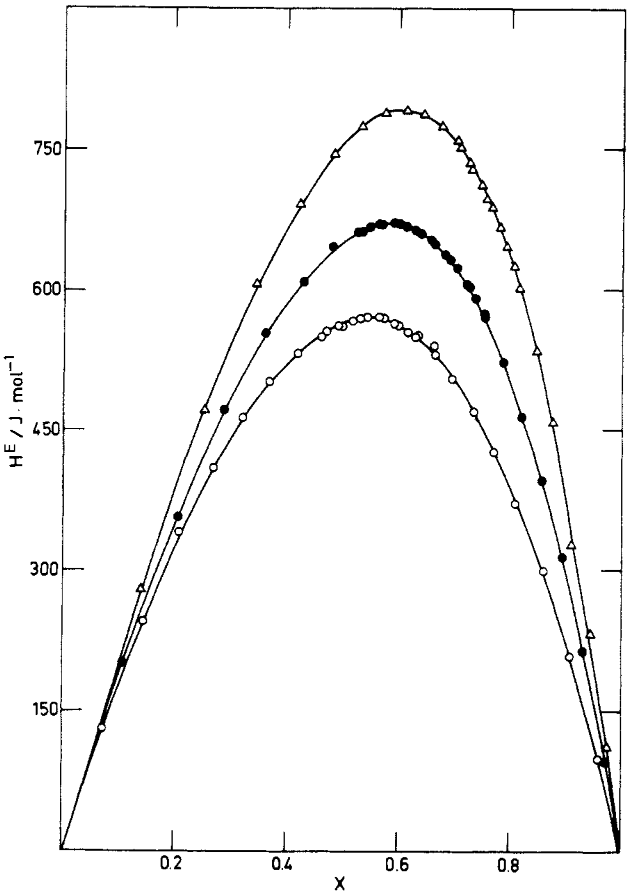

Figure 1. Excess enthalpies for ethylbenzene + n-octane (○), + n-dodecane (●), and + n-hexadecane (△) at 298.15 K. Curves have been calculated from eq 1 using the parameters in Table II.

in the regression. A value of $\eta \geq 2$ indicates that systematic errors are important. Therefore, we may conclude that the regression method based on the maximum likelihood method leads to better results than the unweighted least-squared method for this system. Similar conclusions can be reached for the other systems.

Although some of the parameters have large uncertainties, they are all statistically acceptable according to the Student's t distribution of their relative uncertainties (eq 4). A_1 and A_3 parameters have a large correlation coefficient (>0.8); consequently, it would be possible to substitute them by a linear combination of them, without an important loss of accuracy in the regression (*14*).

Figure 1 shows the experimental h^E values, and those calculated from eq 1. The results for these systems can be compared with those obtained for benzene + n-alkanes (*3*, *4*) and toluene + n-alkanes (*5*). The following behavior is observed: $h^E(C_6H_6) \gg h^E(C_8H_{10}) \simeq h^E(C_7H_8)$. The curves h^E vs. x are more skewed in the sequence $C_6H_6 > C_7H_8 > C_8H_{10}$. This behavior is probably due to the order contributions in the n-alkane + aromatic systems (*19*).

Registry No. Ethylbenzene, 100-41-4; n-octane, 111-65-9; n-dodecane, 112-40-3; n-hexadecane, 544-76-3.

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