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EFFECT OF MOLECULAR SIZE AND SHAPE ON THE EXCESS ENTHALPY OF LIQUID HYDROCARBON MIXTURES

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ABSTRACT

Using a quasi-isothermal flow calorimeter excess enthalpies have been measured at 298.15 K and 1 bar for a series of binary mixtures of cyclohexane with hydrocarbons of different size and shape (n-alkanes, branched alkanes, non-saturated hydrocarbons). For such systems the excess enthalpy strongly depends on the number of carbon atoms, the degree of branching and the number and the location of double bonds of the hydrocarbon molecules. The results clearly indicate the existence of "Correlation of Molecular Order" (CMO) in liquids with chainlike molecules, i.e. a structural ordering effect. Upon mixing with a globular molecule the CMO is destroyed and therefore larger endothermic excess enthalpy-values are found as expected from the differences in the intermolecular forces between the different molecules. Increasing the degree of branching of a molecule with a given number of carbon atoms decreases the CMO, as the molecule itself becomes more globular. Introducing double bonds usually makes a molecule less flexible and hence the CMO is increased.

The experimental results can be described with an extended form of the Prigogine-Flory-Patterson-Theory (PFP-Theory), which takes into account the CMO. The system-specific parameters of this theory vary systematically with the size and the shape of the hydrocarbons mixed with cyclohexane.

INTRODUCTION

Liquid mixtures containing hydrocarbon molecules of different size and shape have been studied frequently. Their thermodynamic excess properties have been discussed on the basis of molecular statistics very successfully using the PFP-Theory (ref.1 - 3).

However, in addition to the known shortcomings of the PFP-Theory at low (gas-like) densities inconsistencies also have been observed for liquid systems, especially for mixtures containing n-alkanes (ref.4 - 7). For these systems that is due to special short range order (CMO) present in n-alkane liquids (ref.4) which only an extended form of the PFP-Theory takes into account (ref.8 - 10). In this work in addition to the effect of the degree of branching on the CMO the effect of the location and the number of double bonds within a hydrocarbon molecule is discussed. In particular experimental results of H^E for some binary mixtures of cyclohexane with n-alkanes, branched alkanes and non-saturated hydrocarbons are reported and the applicability of the extended PFP-Theory to describe these data is investigated.

EXPERIMENTAL

Apparatus

The quasi-isothermal flow calorimeter used in this work has already been described previously (ref.5a, ref.11) and therefore only a short summary of the experimental procedure is given here.

With constant and known flow rates the two pure components A and B are pumped continuously into a mixing coil sitting in a stirred waterbath. The energy liberated (exothermic) or absorbed (endothermic) during mixing is absorbed or delivered by the surrounding water. A Peltier cooler removes energy from the water at a constant rate. A controlled heater compensates for this energy and for the energy liberated or absorbed by the mixing process maintaining the waterbath at a constant temperature (quasi-isothermal operation). The difference in the energy supplied by the heater before and during a mixing process is a direct measure of the energy of mixing.

Knowing the volumetric flow rates delivered by precision-burettes, the molar masses and the densities of the two pure components the mole fraction of the mixture obtained in the mixing coil can be calculated. Just so the corresponding molar excess enthalpy can be calculated from these data and the change in the heating power before and during the continuous mixing process.

Materials

In this work mixtures of cyclohexane (c-C_6) with the follwing hydrocarbons have been investigated: n-decane (n-C_{10}), 2,6-dimethyloctane (i-C_{10}), 1-decene ($C_{10}^{=}$), trans-4-decene (tr-$C_{10}^{=}$), n-tetradecane (n-C_{14}), 1-tetradecene ($C_{14}^{=}$), n-hexadecane (n-C_{16}), 2,2,4,4,6,8,8 - heptamethylnonane (i-C_{16}), 2,6,10,14 - tetramethylpentadecane (pristane or i-C_{19}), 2,6,10,15,19,23 - hexamethyltetracosane (squalane or i-C_{30}), and 2,6,10,15,19,23 - hexamethyltetracosa - 2,6,10,14,18,22 - hexaene (squalene or i-$C_{30}^{6=}$). The substances were obtained from standard laboratory supply sources and the purity was in all cases >99 %. All substances were used without further purification, however, they were carefully degassed before each run.

Results and Discussion

All results obtained are shown in Figs. 1 - 4. The H^E-values are always positive (endothermic mixing). In all cases it was possible to represent the dependence of H^E on the mole fraction with the well-known Redlich-Kister-Equation. At least 4 coefficients in this equation were necessary to give such a good description of the experimental H^E-values as shown in Figs. 3 and 4. For the sake of clarity the experimental results have been omitted in Figs. 1 and 2 and only the Redlich-Kister fits are shown. The experimental results in detail and all the coefficients of the Redlich-Kister-Equation are reported elsewhere (ref.12).

Comparison of the excess enthalpies of the various mixtures investigated reveals a systematic dependence of H^E on the size, shape and degree of saturation of the molecules involved as discussed as follows.

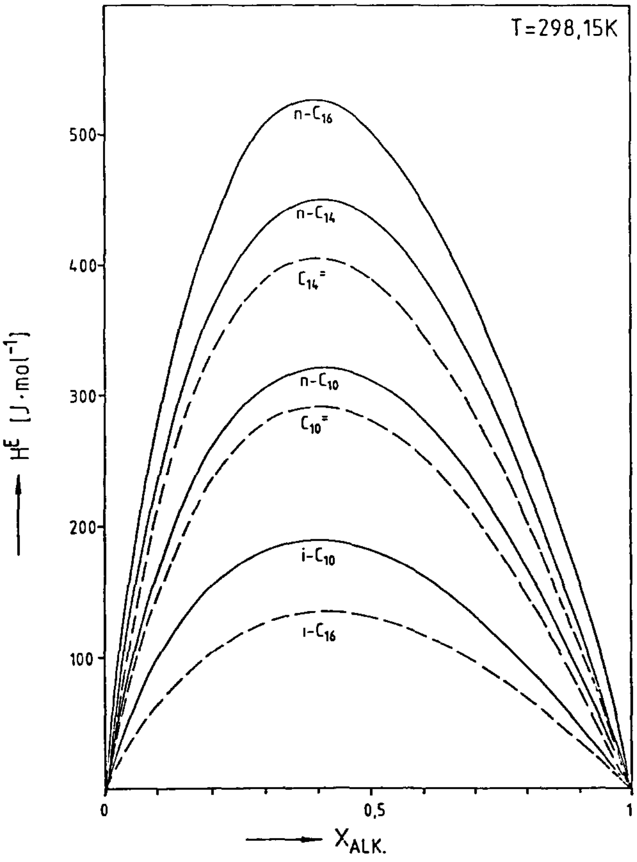

Fig. 1. Composition dependence of H^E at 1 bar for mixtures of cyclohexane with various hydrocarbons (——, - - - Redlich-Kister fit).

As shown in Fig. 1 H^E increases for the mixtures with the n-alkanes n-C_{10}, n-C_{14} and n-C_{16} with increasing number of C-atoms, i.e. with increasing chain length. Introducing a double bond in the 1-position reduces H^E with respect to the values of the corresponding n-alkane mixtures as shown for $C_{10}^{=}$ and $C_{14}^{=}$. In other words such a double bond affects H^E in the same manner as a decrease in chain length.

For mixtures with branched hydrocarbons H^E decreases the more with respect to the values of the mixtures containing the n-alkanes with the same number of C-atoms the higher the degree of branching is. This is clearly seen from the results for i-C_{10} and i-C_{16}. Again H^E is affected in the same manner as by decreasing the chain length.

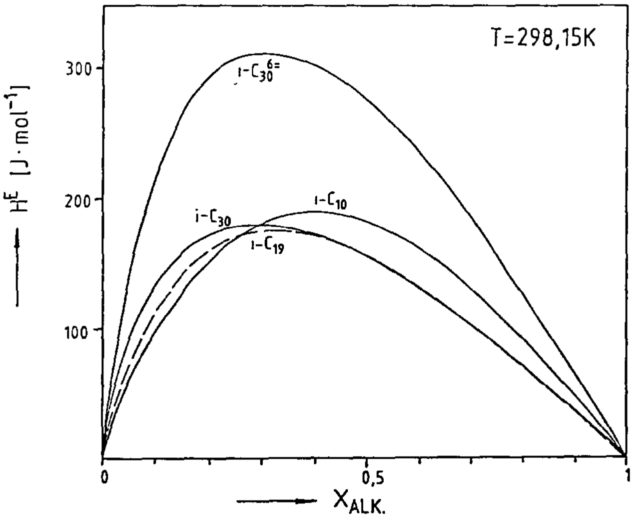

Fig. 2. Composition dependence of H^E at 1 bar for mixtures of cyclohexane with various hydrocarbons (——, - - - Redlich-Kister fit).

A simultaneous increase in chain length and degree of branching results in H^E-values remaining practically the same ones, as shown in Fig. 2 for i-C_{10}, i-C_{19} and i-C_{30}. The main chain of i-C_{19} is about two times and the one of i-C_{30} is about three times as long as that one of i-C_{10}. The number of branches (CH_3-side groups) per number of C-atoms in the main chain remains practically the same for all three hydrocarbons. In such a case the increase in H^E by increasing chain length apparently is compensated by the decrease due to branching.

The mixture with the non-saturated, branched hydrocarbon ($i\text{-}C_{30}^{6=}$) has significantly larger H^E-values as the saturated $i\text{-}C_{30}$, as shown in Fig. 2. Introducing the six double bonds in the positions 2,6,10,14,18 and 22 obviously increases H^E in contrast to the introduction of one double bond in the 1-position, which causes a decrease in H^E as already discussed. The strong effect of the location of a double bond within a molecule is most clearly indicated by the results for the mixture with trans-4-decene. As shown in Fig. 4 the double bond located nearly in the middle of the molecule $tr\text{-}C_{10}^{=}$ causes a much stronger decrease of H^E compared to $n\text{-}C_{10}$ than the double bond in the 1-position of the $C_{10}^{=}$. These results clearly show that not only the number but also the location of double bonds affect the H^E-values significantly.

THEORETICAL

Interpretation

The experimental results obtained can be explained by the existence of short range order (CMO) in liquids with chain-like molecules, i.e. especially within liquid n-alkanes (ref.4). The CMO most probably can be interpreted as a packing effect favoured between groups of segments of different n-alkane chains, being the more pronounced the longer the chain-like molecule is. Upon mixing with a compact molecule like $c\text{-}C_6$ the CMO is destroyed gradually, depending on the composition of the mixture. The energy associated leads to a larger endothermic H^E than expected from the differences in the intermolecular interactions of the different pure components. These effects are small or do not exist at all for mixtures containing branched isomeric alkanes, as these pure components show only little or no CMO due to steric hinderance (ref.9).

Introducing a double bond in the 1-position of an alkane apparently decreases somewhat the CMO in the pure component and, therefore, H^E decreases too, as observed for $C_{10}^{=}$ and $C_{14}^{=}$. The single double bond nearly in the middle of $tr\text{-}C_{10}^{=}$ obviously causes the shape of that molecule to be relatively compact. Therefore, practically no CMO is existing within pure $tr\text{-}C_{10}^{=}$ and hence the H^E-values decrease strongly (see Fig. 4). However, the six double bonds of $i\text{-}C_{30}^{6=}$ make that molecule less flexible than $i\text{-}C_{30}$ and, therefore, the CMO in the pure component $i\text{-}C_{30}^{6}$ is larger than in $i\text{-}C_{30}$. Consequently upon mixing with $c\text{-}C_6$ H^E is much larger for $i\text{-}C_{30}^{6=}$ than for $i\text{-}C_{30}$, as shown in Fig. 2. In case of the pure components $i\text{-}C_{10}$, $i\text{-}C_{19}$ and $i\text{-}C_{30}$ the CMO overall is about the same, i.e. the increase with increasing length of the main chain is compensated by the decrease caused by branching. Therefore, H^E is about the same for mixtures containing these components.

PFP-Theory

The experimental results for all mixtures investigated can be represented very well using an extended form of the PFP-Theory as developed by Heintz and Lichtenthaler (ref.8). According to this theory the molar excess enthalpy of a binary mixture is given by:

$$H^E = (V_1^* x_1 + V_2^* x_2)\ [\ (\tilde{v}_1^{-1} - \tilde{v}_M^{-1})\ \phi_1 P_1^* + (\tilde{v}_2^{-1} - \tilde{v}_M^{-1})\ \phi_2 P_2^*$$

$$+ \frac{(s_2/s_1)\ \phi_1 \phi_2}{\phi_1 + (s_2/s_1)\ \phi_2}\ X_{12}^H\ \tilde{v}_M^{-1} + P\ (\tilde{v}_M - \phi_1 \tilde{v}_1 - \phi_2 \tilde{v}_2)\ ] \qquad (1)$$

where x_1 and x_2 are the mole fractions of component 1 and 2. ϕ_1 and ϕ_2 are the hard-core-volume fractions defined as

$$\phi_1 = 1 - \phi_2 = \frac{V_1^* x_1}{V_1^* x_1 + V_2^* x_2} \qquad (2)$$

V_1^* and V_2^* are the molar hard-core-volumes which are also used to obtain the reduced volumes v_i of the pure components (index 1 and 2):

$$\tilde{v}_i = V_i / V_i^* \qquad (3)$$

where V_i is the molar volume. P is the pressure. P_1^* and P_2^* are pure component parameters to calculate the reduced pressure $\tilde{P}_i = P/P_i^*$ and T_1^* and T_2^* are the ones to calculate the reduced temperature $\tilde{T}_i = T/T_i^*$, where T is the temperature. All the pure component reducing parameters can be obtained by fitting the reduced equation of state (EOS) of the PFP-Theory to experimental P,V,T-data. Using proper mixing rules to obtain P_M^* and T_M^* characteristic for a mixture the reduced volume $\tilde{v}_M$ of the mixture can be calculated from the EOS, as this equation is valid for mixtures, too.

s_2/s_1 is the hard-core-surface to hard-core-volume ratio of component 2 divided by the one of component 1. The parameters s_i have been determined using the incremental method of Bondi (ref.13) to estimate the van der Waals-hard-core surface and volume of a molecule.

X^H_{12}, therefore, is the only parameter in Eq. (1) remaining adjustable to represent H^E properly. This parameter is related to the difference of the intermolecular interactions between different molecules.

Proper adjustment of the parameter X^H_{12} using the experimental H^E-values gives a very good representation of H^E over the whole composition range, as shown in Figs. 3 and 4 for some examples. The experimental data points, the Redlich-Kister fit of these and the curve calculated with the PFP-Theory agree very well with one another. For all the other mixtures investigated the agreement obtained is just so.

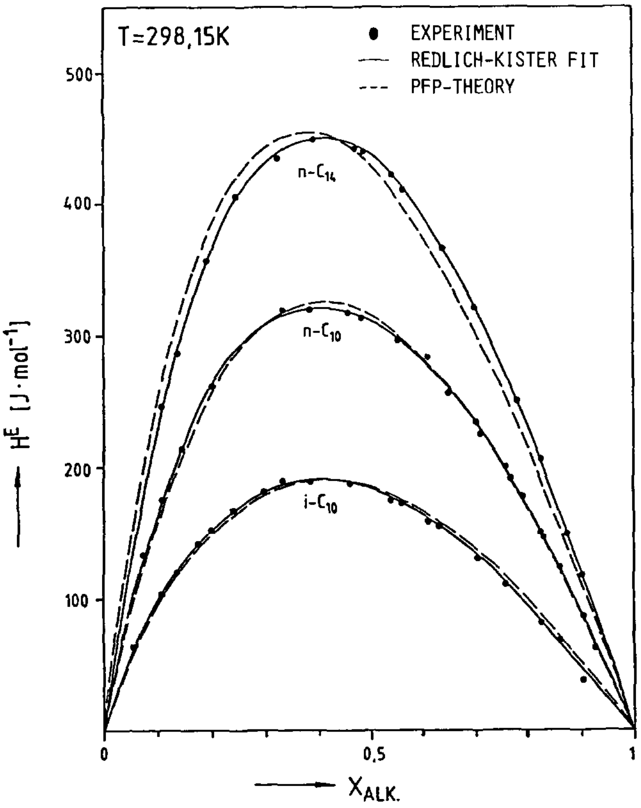

Fig. 3. Composition dependence of H^E for mixture of cyclohexane with three alkanes at 1 bar.

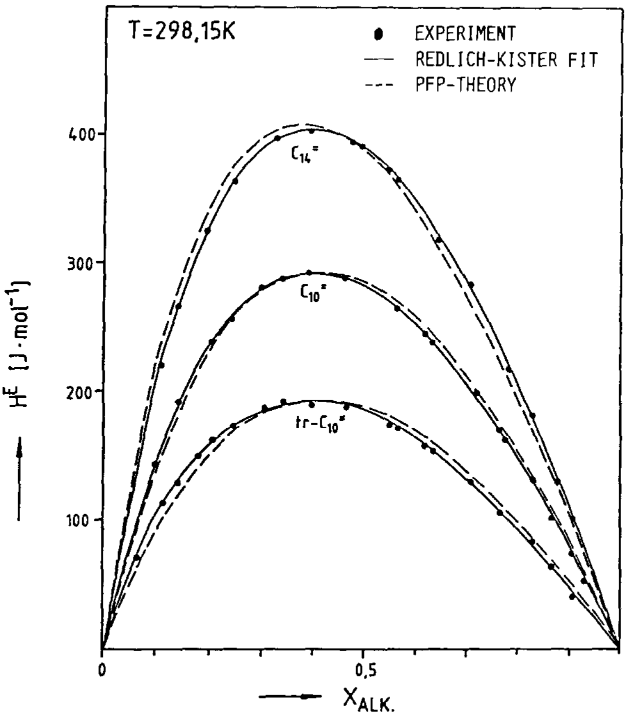

Fig. 4. Composition dependence of H^E for mixtures of cyclohexane with three alkenes at 1 bar.

The pure component reducing parameters used for the calculations with the PFP-Theory are reported elsewhere (ref.12). The parameters s_2/s_1 and X^H_{12} are specific for each mixture and are given in Tab.1. As expected the s_2/s_1 parameter is close to one and does not vary much for the different systems, as all the pure components are aliphatic hydrocarbons. For that reason the parameter X^H_{12} should be expected to be about the same for all systems, too.

However, that is not the case at all, which is due to the CMO already discussed. X^H_{12} to some extent is a measure for the CMO which has to be destroyed upon mixing. A large positive value indicates strong CMO within the pure hydrocarbon to be mixed with c-C_6. Indeed the largest values are found for the n-alkanes and the 1-alkenes, which have the CMO most pronounced as already discussed.

With increasing chain length X^H_{12} increases. The smallest values are found for the branched hydrocarbons with no or only little CMO. The small value for tr-$C_{10}^{=}$ confirms the bulkiness of this molecule caused by the double bond

TABLE 1

System-specific parameters of the PFP-Theory

Mixture (1)+(2)	s_2/s_1	X_{12}^{H} (298.15K), J cm^{-3}
c-C_6 + n-C_{10}	1.102	10.88
+ i-C_{10}	1.101	6.63
+ $C_{10}^{=}$	1.098	9.92
+ tr-C_{10}	1.098	6.60
+ n-C_{14}	1.089	14.06
+ $C_{14}^{=}$	1.086	12.77
+ n-C_{16}	1.085	15.83
+ i-C_{16}	1.112	4.81
+ i-C_{19}	1.079	5.60
+ i-C_{30}	1.071	5.91
+ i-$C_{30}^{6=}$	1.061	9.25

nearly in the middle of the molecule, i.e. only little CMO exists in that pure liquid. The values for i-C_{10}, i-C_{19} and i-C_{30} are small and not so much different from one another. This reflects the compensation of increasing and decreasing CMO due to increasing chain length and increasing degree of branching repectively. The increase of the CMO within i-$C_{30}^{6=}$ due to the six double bonds with respect to i-C_{30} is evidently indicated by the corresponding increase of X_{12}^{H}.

As the CMO depends on temperature and pressure X_{12}^{H} has to be temperature and pressure dependent, too. The extended PFP-Theory gives the following result for this dependence:

$$X_{12}^{H} = X_{12}^{\infty} \frac{T}{T - T_o(P)} \qquad (T > T_o) \qquad (4)$$

where X_{12}^{∞} is the parameter representing the differences in intermolecular interaction between the different molecules in case no CMO is present at all. That is the case at high temperatures as the CMO is already destroyed by thermal molecular motion before mixing. $T_o(P)$ is a pseudo-transition temperature for the CMO depending on pressure. Increasing pressure is expected to increase the CMO and hence $T_o(P)$, too.

In case H^E-data are available at various temperatures X_{12}^{∞} and $T_o(P)$ can be determined using Eq. (4) for the temperature dependence of X_{12}^H. For some mixtures of c-C_6 with alkanes this has been done and X_{12}^{∞} was found to have a small positive value being more or less the same for these mixtures. Furthermore X_{12}^{∞} does not depend on temperature and pressure as it should be for a molecular parameter (ref.5a). At ambient pressure T_o(1 bar) was found to be a few degrees lower than the normal melting temperature and at higher pressures the expected increase was observed (ref.8).

For most of the mixtures investigated in this work H^E was measured only at 298.15 K and 1 bar. However, for all the mixtures measurements of the total vapour pressure have been performed at 298.15 K and from those the excess Gibbs-energy G^E has been determined. Combining the H^E- and G^E-data is another possibility to evaluate X_{12}^{∞} and T_o(1 bar). That has been done (ref.12) and again nearly the same, relatively small and positive value of X_{12}^{∞} and physically reasonable values of T_o(1 bar) are obtained for all mixtures. Although the numerical values determined from H^E- and G^E-data are somewhat different from those determined from H^E-data at various temperatures, all results support the existence of CMO in liquids with chain-like molecules. As a consequence X_{12}^H has to be taken temperature and pressure dependent and Eq. (4) is at least a very good approximation to take this dependence into account quantitatively.

CONCLUSION

The excess enthalpy H^E of liquid hydrocarbon mixtures strongly depends on the number of C-atoms, the degree of branching and the number and the location of double bonds of the hydrocarbon molecules of the components forming the mixture. The existence of CMO especially in liquids with chain-like molecules is confirmed. If the CMO is destroyed upon mixing larger endothermic H^E-values are found than expected from the relatively small differences in the intermolecular interaction between the various hydrocarbons. Increasing the degree of branching of a molecule with a given number of C-atoms decreases the CMO, as the molecule itself becomes more compact.

Introducing double bonds increases the CMO if the molecule has become less flexible by this means. However, the opposite effect is possible, too. In any way the number and the location of double bonds within a molecule are affecting the CMO. An extended form of the PFP-Theory taking into account the CMO represents the experimental results very well with adjustable parameter physically reasonable.

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