

THERMODYNAMIC PROPERTIES OF POLAR SUBSTANCES: ENTHALPY OF HYDROCARBON-ALCOHOL SYSTEMS

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The industrial interest in petroleum compounds has generated large amounts of data for both pure components and mixtures of hydrocarbons. These data and the general similarity in molecular structure of the components have made it possible to develop reasonably precise methods for predicting thermodynamic properties of hydrocarbons over a wide range of conditions. When chemically dissimilar mixtures are encountered, much larger deviations from ideal behaviour are observed. Further, data for these systems are meagre. As a result, adequate prediction methods have not appeared for such systems. This paper presents: (1) a method of correlating data for strongly polar substances, such as alcohols in the pure state and when mixed with hydrocarbons, and (2) experimental enthalpy data for the binaries and pure components in the systems benzene-ethanol and n-pentane-ethanol.

Enthalpy data for non-polar-polar mixtures over a range of temperatures and pressure are generally not available. McCracken and Smith⁹ have reported measurements on binary mixtures of benzene-methanol over extended ranges of temperature and pressure. They proposed a correlating procedure based upon association of the methanol. Data for one composition of a ternary system, n-hexane-benzene-methanol were also reported.

SCOPE OF INVESTIGATION

Enthalpies were measured for pure ethanol, benzene and n-pentane, and binary mixtures containing 25, 50 and 75 mole per cent ethanol in benzene and n-pentane. These data covered a temperature range of 250° to 500°F at pressures from 50 to 1700 p.s.i. Additional experimental information was obtained in the critical region. In addition, the effect of pressure on the enthalpy of n-propanol was computed from the volumetric data of Ramsey and Young¹⁰.

Heat-of-mixing data of the liquids were used in order to place all mixture enthalpies on the same basis: pure liquid components at 77°F and their individual vapour pressures. The heats of mixing of Schnaible *et al.*¹¹ were used for the benzene-ethanol system. Measured values for the n-pentane-ethanol system were not available, but were estimated to be: 7.8, 9.4, and 8.7 B.t.u./lb. of mixture at 25°C for the 75, 50, and 25 mole per cent ethanol mixtures, respectively.

The experimental results covered both liquid and vapour regions. To understand more about the behaviour of polar substances, the vapour data

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only were analysed in an attempt to develop prediction procedures for the enthalpy of pure alcohols and their binary mixtures with hydrocarbons. The methods propose a means of evaluating the deviations from ideal gas behaviour.

EXPERIMENTAL

The experimental method was the same as used by McCracken and Smith⁹. This involves the measurement of the energy transferred from the mixture flowing through a calorimeter to boiling "Freon 11". The enthalpy change between the states at the inlet and the outlet to the calorimeter could be calculated from the weight of "Freon" evaporated and its latent heat of vaporization. The mixture leaving the calorimeter was always cooled to a temperature within 2°F of the boiling point of the "Freon", 74°F. The exit stream was liquid at this temperature for all of the mixtures investigated.

RESULTS

The steady-state energy balance across the calorimeter, neglecting kinetic and potential energy changes, gives the following expression for the change in enthalpy of the fluid stream,

$$\Delta H_c = \frac{-L_t W_t}{W_m} \quad (1)$$

Correction must be made to the ΔH_c values obtained from equation (1) to refer the enthalpies to the desired standard state.

Operation of the equipment was most convenient when the inlet temperature was held constant and the pressure varied as each sample was taken. Each series of runs at constant temperature establishes an isotherm on a pressure-enthalpy diagram. The intersection of the three distinct curves obtained below the critical temperature represented points on the phase envelope. A series of isotherms would then define the phase envelope for the mixture. Additional data were taken in the critical region at constant pressure at close temperature intervals. These data were used to define more accurately the critical region on the temperature-enthalpy diagrams.

PREDICTION OF ENTHALPY OF PURE COMPONENTS

The equation proposed for the enthalpy deviation of the vapour from ideal gas behaviour is as follows:

$$(H^* - H) = \Delta H_s + \Delta H_g + \Delta H_{\text{assoc}} \quad (2)$$

where ΔH_s = enthalpy deviation for a "perfect fluid" comprised of spherically symmetrical molecules;

ΔH_g = the additional contribution due to the acentricity of the molecule;

ΔH_{assoc} = the enthalpy deviation due to association, in the case of polar molecules.

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The first two terms in equation (2) can be determined by using the generalized correlation of Curl and Pitzer³, since they contain only quantities pertaining to molecular geometry. For non-polar substances such as benzene and n-pentane only these terms need be used. When applied to polar substances the third term is also significant. For such substances the first two terms are determined by using the temperature and pressure of the associating substance and the critical constants and vapour pressure of the hydrocarbon homomorph.

The third term in equation (2) is treated by supposing that association accounts for all orientational effects in the substance not accounted for by molecular geometry. A number of assumptions are made in the evaluation of ΔH_{assoc} . Since this quantity is but a relatively small contribution to the value of $(H^* - H)$ in equation (2), these assumptions are not as serious as might be expected. The association is represented by the reaction



Assuming the mole fraction of the polymers to be much less than one, the association effect is obtained from the individual heats of formation of the polymers, $\Delta H_{f,n}$, by the sum

$$\Delta H_{\text{assoc}} = \sum_{n=2}^{\infty} (-x_n \Delta H_{f,n}) \quad (4)$$

Utilizing the concept of the equilibrium constant and the van't Hoff equation, the final expression for ΔH_{assoc} is:

$$\Delta H_{\text{assoc}} = \sum_{n=2}^{\infty} -x_n^2 P^{n-1} \Delta H_{f,n} \exp \frac{\Delta S_{f,n}}{R} - \frac{\Delta H_{f,n}}{RT} \quad (5)$$

If association between pairs of alcohol molecules to form dimers can be represented by the same kind of hydrogen-bonding process, the heat of formation of the dimer should be nearly the same for each of the alcohols. This is shown in *Table 1* where the heats of dimerization for methanol and ethanol from various sources are listed.

Table 1. Heats and entropies of formation for alcohol dimerization (from the literature)

<i>Alcohol investigated</i>	ΔH_{f_2} (B.t.u./lb.-mole)	ΔS_{f_2} (e.u.)
Methanol vapour ^a	- 5800	- 16.5
Ethanol vapour ^b	- 6120	- 16.57
Methanol vapour ^c	- 5400	—
Several different alcohols ^d	- 7200	—
Liquid mixtures of ethanol and methanol in carbon tetrachloride at 45°C: ^e		
Methanol	- 6340	—
Ethanol	- 4950	—
Ethanol ^f	- 5000	- 16.04

^a Weltner and Pitzer¹²: low pressure P - V - T data, vapour heat capacity data and spectroscopic measurements.

^b Barrows²: low pressure P - V - T data, vapour heat capacity data and spectroscopic data.

^c Inskip and Kelliher⁴: spectroscopic data.

^d Kretschmer and Wiebe¹: analysis of available P - V - T data for several alcohols.

^e Barker, Brown, and Smith¹: liquid solutions of methanol and ethanol in carbon tetrachloride at 45°C.

^f Data for ΔH_{assoc} obtained from experimental data of this work.

This suggests a general procedure for calculating ΔH_{assoc} for various alcohols. The heat of dimerization would be chosen as $-5,000$ B.t.u./lb.-mole, as obtained for ethanol, and the entropy of dimerization evaluated to agree with the particular alcohol. No reliable method is available to estimate ΔS_{f_2} , but average values for methanol and n-propanol can be obtained from the enthalpy data and equations (2) and (5). The results, given in *Table 2*, indicate the magnitude for the entropy terms.

Table 2. The average entropies of formation for the dimers and trimers of methanol and n-propanol*

<i>Alcohol</i>	ΔS_{f_2} (e.u.)	ΔS_{f_3} (e.u.)
Ethanol	- 16.04	- 42.99
Methanol	- 16.11	- 44.55
n-Propanol	- 17.13	- 45.48

* Average values of entropy obtained from equations (2) and (5), using the heats of formation of the dimer and trimer for ethanol, $\Delta H_{f_2} = 5000$ B.t.u./lb.-mole and $\Delta H_{f_3} = -20,800$ B.t.u./lb.-mole.

This same procedure can be used to obtain the constants for the trimer and higher terms, taking $\Delta H_{f_3} = -20,800$ B.t.u./lb.-mole as obtained for ethanol. The average values of ΔS_{f_3} for methanol and n-propanol so determined are also listed in *Table 2*.

The parameters listed in *Table 2* were used in equations (2) and (5) to calculate the enthalpy deviation from ideality for each alcohol. The results, when compared with the experimental data, indicate an average absolute error of less than 1 B.t.u./lb. for ethanol and n-propanol and 2.7 B.t.u./lb. for methanol. In comparison, conventional, generalized correlations^{4, 7} applied to the data give average absolute errors of 5-15 B.t.u./lb.

PREDICTION OF ENTHALPY OF MIXTURES

The correlation for the enthalpy deviations of pure associating substances presented in this paper was based on isolating the effect of association from molecular geometry. An extension of this procedure to mixtures is possible, provided an adequate method is available to evaluate the geometric effect of an associating substance and hydrocarbons. The total enthalpy deviation is obtained by adding the geometric contribution and the association effect.

The geometric contribution to the mixture can be determined by combining the pure-component enthalpy deviations for the hydrocarbon and the hydrocarbon homomorph of the associating substance. The P-V-T properties of hydrocarbons are represented reliably to moderate pressures by the virial equation of state retaining only the second coefficient. Mayer⁸ has shown that the second virial coefficient for a binary mixture is related to the pure component coefficients by the expression:

$$B_m = x_1^2 B_1 + 2x_1 x_2 B_{12} + x_2^2 B_2 \quad (6)$$

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When the enthalpy deviation with pressure is calculated for the mixture, a similar expression is obtained for the relationship between the mixture and pure component enthalpy deviations.

$$\Delta H_m = x_1^2 \Delta H_1 + 2x_1 x_2 \Delta H_{12} + x_2^2 \Delta H_2 \quad (7)$$

Equation (7) can be evaluated for the mixture by calculating ΔH_1 for the hydrocarbon homomorph of the associating substance and ΔH_2 for the hydrocarbon in the mixture. The generalized correlation of Curl and Pitzer³ was used for this calculation. The geometric mean $\sqrt{\Delta H_1 \Delta H_2}$ was employed to evaluate the interaction parameter, ΔH_{12} .

Adding the association effect, ΔH_{assoc} , to the geometric contribution gives the following expression for the total deviation from ideality:

$$\Delta H_{\text{ma}} = x_1^2 \Delta H_1 + 2x_1 x_2 \Delta H_{12} + x_2^2 \Delta H_2 + \Delta H_{\text{assoc}} \quad (8)$$

In applying this equation, ΔH_{assoc} may be obtained from equation (5), and the quantity x_1 may be taken as the mole fraction of the alcohol in the mixture. As in the case of correlating the pure component data, this is equivalent to assuming that the extent of polymerization is relatively small. Equation (8) was used to calculate the enthalpy deviations for the benzene-ethanol, n-pentane-ethanol and benzene-methanol mixtures.

Comparison with the measured results indicates an average absolute error less than 3 B.t.u./lb. for all mixtures. Also, the results are generally consistent and more accurate than those obtained from the generalized correlations using pseudo or true critical constants. The advantage of equation (8) as a predicting procedure is that it does not require mixture properties. The necessary interaction parameter, ΔH_{12} , is calculated from the pure component data.

Notation

<i>B</i>	Second virial coefficient
<i>H</i>	Enthalpy at any pressure; smoothed enthalpy data
<i>L</i>	Latent heat of vaporization
<i>P</i>	Total pressure
<i>R</i>	Universal gas constant
<i>S</i>	Entropy
<i>T</i>	Absolute temperature
<i>W</i>	Weight
<i>x</i>	Mole fraction
<i>z</i>	Compressibility factor, $z = RT/PV$

Superscripts

*	Ideal gas state
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Subscripts

<i>c</i>	Critical property; calorimeter in equation (1)
<i>f</i>	Formation; "Freon 11"
<i>g</i>	Geometric contribution in addition to spherical contributions
<i>m</i>	Mixture property; mixture
<i>ma</i>	Mixture containing an associating substance
<i>n</i>	Number of monomer units in a polymer

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