

A METHOD FOR THE CALCULATION OF THE NONPOLAR SOLUBILITY
PARAMETER OF UNSATURATED NORMAL HYDROCARBONS

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Correlations were derived for the determination of the acentric factor and critical pressure of the homomorphs of unsaturated normal hydrocarbons from the molar liquid volume at a given temperature; with these data the solubility parameter of the homomorph - that is the nonpolar solubility parameter of the unsaturated normal hydrocarbon - can be calculated by the correlation given by LYCKMAN, ECKERT and PRAUSNITZ.

It is often necessary to describe the vapour liquid equilibrium of various systems. In most cases this cannot be done without difficult experiments. Several correlations were derived for the estimation of vapour liquid equilibria. Most of these correlations contain the solubility parameter introduced by HILDEBRAND and SCOTT. In systems that also consist of polar compounds, these correlations apply the solubility parameter split into polar and nonpolar parts. Therefore it is often necessary to calculate the polar and nonpolar solubility parameters of polar compounds.

The regular solution theory of HILDEBRAND and SCOTT has been applied to various problems of chemical engineering [1-4]. This theory contains two temperature dependent parameters for each component, the molar liquid volume (V) and the solubility parameter (δ), which is defined as the square root of the configurational energy per unit volume.

Since appropriate data for their evaluation are frequently unavailable, several generalized relationships were derived to estimate these two parameters at various temperatures. These methods are based on a three-parameter theory of corresponding state [5, 6].

The regular solution theory was applied to correlations for vapour liquid equilibria. The first of the correlations available is the equation of HILDEBRAND for the activity coefficient of component 1 at infinite dilution in solvent component 2:

$$\ln \gamma_1^\infty = \frac{V_1(\delta_1 - \delta_2)^2}{RT} \quad (1)$$

This equation is applicable to regular solutions and has wide applications in systems consisting of hydrocarbons. It is unsuitable for systems involving polar or hydrogen-bonding components.

HILDEBRAND suggested and BLANKS and PRAUSNITZ further developed the idea of splitting the solubility parameter into two parts [7, 8]:

$$\delta^2 = \lambda^2 + \tau^2 \quad (2)$$

where λ is the solubility parameter ascribed to nonpolar effects and τ is the polar solubility parameter. The value of λ for a polar component is set equal to the solubility parameter of a nonpolar molecule of the same size and shape, and at the same reduced temperature as the polar molecule. The value of τ is obtained by solving Equation (2). The nonpolar molecule used in this context is termed the homomorph of the polar molecule.

The splitting of the solubility parameter of polar compounds has proved to be useful. BLANKS and PRAUSNITZ, WEIMER and PRAUSNITZ, later HELPINSTILL and VAN WINKLE, and finally NULL and PALMER derived various equations for the estimation of the activity coefficient at infinite dilution using τ and λ [8-11]. These relationships are generally capable of predicting the vapour liquid equilibria of different systems consisting of various components.

However, these methods can be used only when the solubility parameter and its two parts can be determined. LYCKMAN, ECKERT and PRAUSNITZ correlated the solubility parameter and the acentric factor and critical pressure for nonpolar or slightly polar compounds. Their correlation is as follows [6]

$$\frac{\delta}{P_c^{1/2}} = \delta_R^{(0)} + \omega \delta_R^{(1)} + \omega^2 \delta_R^{(2)} \quad (3)$$

where P_c is the critical pressure, ω is the acentric factor, $\delta_R^{(0)}$, $\delta_R^{(1)}$ and $\delta_R^{(2)}$ are generalized functions dependent upon the reduced temperature and given by the earlier mentioned authors in tables.

The part of the solubility parameter due to polar effects is more difficult to determine. WEIMER and PRAUSNITZ, and HELPINSTILL and VAN WINKLE provided charts for the calculations of λ from where λ -s are obtained as functions of molar volume and reduced temperatures. NULL and PALMER gave an equation for this purpose which included constants determined by the regression analysis of vapour liquid equilibrium data. The published charts are limited, and so their readings can be rather inaccurate, while NULL's equation can be applied in the cases of such compounds for which the regression constants were determined.

While predicting the vapour liquid equilibria of various systems consisting of saturated and unsaturated hydrocarbons it was necessary to split the solubility parameter of the unsaturated hydrocarbons according to the polar and nonpolar effects. The earlier mentioned charts were inappropriate for the purpose, partly because of the difficulties in their reading, and partly because their limited range in reduced temperature. The constants in NULL's equation were not available either, so the derivation of a new method was necessary for the estimation of the nonpolar solubility parameter.

As mentioned earlier λ is equal by definition to the solubility parameter of a nonpolar molecule of the same size and shape, and at the same reduced temperature as the polar molecule. The new

method was derived on the basis of this definition. It uses the correlation of LYCKMAN, ECKERT and PRAUSNITZ. First the acentric factor of the hypothetic compound is determined, of which the molar liquid volume at the given reduced temperature is equal to that of the polar hydrocarbon. In possession of this acentric factor, the critical pressure of this hypothetic compound can be determined. Equation (3) can now be used to calculate the solubility parameter of the hypothetic compound, that is the nonpolar solubility parameter of the polar hydrocarbon.

The acentric factor can be calculated by Equation (4) as a function of the temperature and molar liquid volume:

$$\begin{aligned} \omega = & -0.6567970503 + 4.317033425 \times 10^{-3} T - 9.552751262 \times 10^{-6} T^2 + \\ & +(6.948576691 \times 10^{-3} - 2.366410236 \times 10^{-5} T + 5.296188633 \times 10^{-8} T^2) V + \\ & + (-7.300585551 \times 10^{-6} + 2.980456572 \times 10^{-8} T - 7.607366498 \times 10^{-11} T^2) V^2 \end{aligned}$$

The constants of Equation (4) were determined on the basis of 185 various molar liquid volumes of the C_2-C_{16} normal paraffins embracing the 25 - 105 °C temperature range by a least square fit method. The values of the molar volumes were calculated according to MEISNER [12]. His equation gives the molar volumes with a relative standard deviation (characterizing the lack of fit) of 0.22 %. Taking into account the internal precision of the molar volume measurements ($\pm 0.5 - 1.5$ % relative) this fit is quite satisfactory.

The average deviation in the case of the acentric factor was ± 2.97 %.

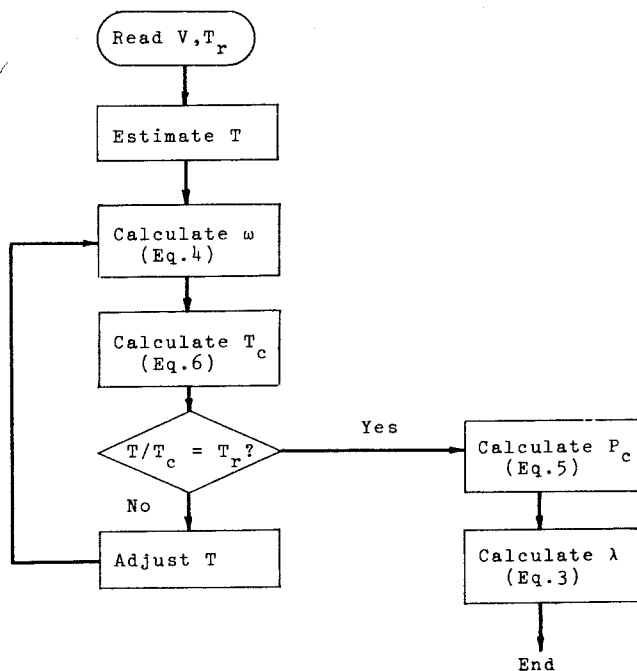
In the knowledge of the acentric factor the critical pressure and critical temperature of the hypothetic compound can be calculated by Equations (5) and (6):

$$P_c = 57.96973602 - 113.7754867 \omega + 74.25657898 \omega^2 \quad (5)$$

$$T_c = \exp(6.640208073 - 0.02744984296/\omega + 0.1289717519 \omega + 0.2985 \ln \omega) \quad (6)$$

The constants of these equations were determined from the data of the C_2 - C_{16} normal paraffins [13, 14] by a least square fit method. A comparison of the critical pressures and temperatures in literature and calculated by Equations (5) and (6) using the acentric factors determined by Equation (4) showed that the average deviation was $\pm 2.88\%$ in the case of the critical pressure and $\pm 2.80\%$ in the case of the critical temperature, taking into account the earlier mentioned 185 data.

Hence the nonpolar solubility parameter of an unsaturated normal hydrocarbon can be calculated by Equations (3)-(6) according to the scheme in the Figure.



Schematic diagram of the calculation of λ

With the knowledge of the V molar volume and T_r reduced temperature, a T temperature can be estimated, and the acentric factor of that hypothetical normal paraffin can be calculated, that has a V molar volume at the selected temperature (Equation (4)). With Equation (6) the critical temperature of this compound can be calculated. It is now possible to find out what reduced temperature corresponds to the estimated temperature in the case of the hypothetical compound. If this value does not agree with the given reduced temperature, the estimated temperature should be adjusted, and the trials should continue until the deviation is negligible. Accepting the acentric factor that corresponds to this temperature and the given molar volume, the critical pressure of the hypothetical normal paraffin can be determined by Equation (5); the solubility parameter of the hypothetical compound can then be calculated by Equation (3) - which is equal by definition to the nonpolar solubility parameter of the unsaturated normal hydrocarbon.

The method is applicable within the 25 - 105°C temperature range provided that the acentric factor of the hypothetical compound is neither less than 0.105 nor greater than 0.704. This method provides a more precise calculation of the vapour liquid equilibria of systems consisting of C_4 unsaturated hydrocarbons. The results will be published in a subsequent paper.

SYMBOLS USED

| | |
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| P | pressure atm. |
| R | gas constant |
| T | temperature ($^{\circ}K$) |
| V | liquid molar volume (cm^3/g mole) |
| v | activity coefficient |
| δ | solubility parameter (cal/cm^3) ^{1/2} |
| λ | nonpolar solubility parameter (cal/cm^3) ^{1/2} |
| τ | polar solubility parameter (cal/cm^3) ^{1/2} |
| ω | acentric factor |

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РЕЗЮМЕ

Автор составил соотношения, с помощью которых можно определить фактор ацентричности и критическое давление гомоморфа из жидкофазного молярного объема нормального углеводорода, при определенной температуре. Зная фактор ацентричности и критическое давление - с применением уравнения Лэнгмана, Энкерта и Праусница - можно определить параметр растворимости гомоморфа, т.е. часть параметра растворимости ненасыщенного нормального углеводорода, обусловленную полярными влияниями.