Investigation of Dimethyl Ether Solubility in Liquid Hexadecane by UNIFAC Method

F. Raouf, M. Taghizadeh

Abstract—It is shown that a modified UNIFAC model can be applied to predict solubility of hydrocarbon gases and vapors in hydrocarbon solvents. Very good agreement with experimental data has been achieved. In this work we try to find best way for predicting dimethyl ether solubility in liquid paraffin by using group contribution theory.

Keywords— UNIFAC, Henry's law, Group contribution theory, Solubility.

I. INTRODUCTION

DIMETHYL ether (DME) with the chemical formula of CH₃–O–CH₃ is the simplest ether for preparation of some chemicals such as dimethyl sulfate and high-value oxygenated compounds. In addition, it has been used as an aerosol propellant to replace chlorofluoro carbons which can destroy the ozone layer of the upper atmosphere. It is a colorless gaseous with an ethereal smell. Unlike methane, DME does not require an odorant because it has a sweet ether-like odor. Dimethyl ether is also a clean fuel alternative to liquified petroleum gas (LPG), liquified natural gas (LNG), diesel and gasoline [1].

DME can be made from natural gas, coal, or biomass. This fuel burns with a visible blue flame and is non-peroxide forming in the pure state or in aerosol formulations. DME is a volatile organic compound, but is non-carcinogenic, non-teratogenic, non-mutagenic, and non-toxic [1]. Its physical and chemical properties in comparison with diesel can be summarized as follows:

- Cetane number of DME is higher and its auto ignition temperature is lower than that of diesel.
- DME has only got C–H and C–O bonds, but no C–C bond and it contains about 34.8% oxygen, therefore the combustion products such as carbon monoxide and unburned hydrocarbon emissions are lower than those of natural gas.
- The latent heat of evaporation of DME is much higher than that of diesel, so it will be beneficial to the NOx reduction due to the larger temperature drop of the mixture in the cylinder.
- DME’s boiling point is _24.9 _°C and it must be pressurized to keep it in liquid state under ambient conditions [2].

The DME production processes are (1) an indirect synthetic method using the dehydration reaction of methanol and (2) a direct synthetic method of producing DME from natural gas, coal bed methane and synthetic gas made from coal, biomass and so on. At present, DME is usually made by the indirect method and technology development for the direct synthetic method is being implemented [3].

The solubility of gases in liquids is both practically important in the most diverse fields of technology and science and theoretically interesting, e.g. because the gas molecules can be considered as probes measuring the intermolecular force field in the solution.

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<td>P_f</td>
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II. THERMODYNAMIC MODELS

The basic equation to represent equilibrium between a vapor phase and liquid phase is equality of fugacities for any component (i) in these phases:

\[ f_i^v = f_i^l \] (1)

Vapor phase fugacity can be expressed as:

\[ f_i^v = φ_i^v \cdot y_i \cdot p \] (2)

P is the equilibrium pressure. In this work solvent considered has negligible vapor pressures, and the vapor fraction of the other component (DME) taken to equal unity. The gas phase fugacity coefficient φ_i^v is calculated with the equation of states. The liquid phase fugacity can be calculated either with an equation of state or with an activity factor-based model.

Liquid phase fugacity can be expressed as:

\[ f_i^l = f_i^{sat} \cdot x_i \cdot γ_i \] (3)

Where x_i is the liquid fraction of component i and fugacity f_i^{sat} of a pure condensed component i at T and P is obtained as:

\[ f_i^{sat} = p_i^{sat} \cdot φ_i^{sat} \cdot \exp \left[ \frac{v_i^L \cdot (p_i - p_i^{sat})}{R T} \right] \] (4)

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The fugacity, \( f_i^\gamma \), is equal to \( p_i^\text{sat} \), the saturation pressure of component \( i \) at \( T \), with two corrections. First, the fugacity coefficient \( \phi_i^\text{sat} \) corrects for deviations of the saturated vapor from ideal gas behavior. Second, the Poynting correction takes into account that the liquid is at equilibrium pressure \( p_i \), different from the saturation pressure, \( p_i^\text{sat} \), molar volume \( v_i^l \) of solute in the liquid phase is also calculated with the equation of states [4].

If we introduce \( \Phi_i \) as:

\[
\Phi_i = \frac{\phi_i^\gamma}{\phi_i^\text{sat}} \cdot \exp \left[ -\frac{v_i^l(p - p_i^\text{sat})}{RT} \right]
\]

For conditions of low pressure VLE, vapor phase approximate ideal gases, for which \( \phi_i = \phi_i^\text{sat} = 1 \), and Poynting factor differs from unity by only a few parts per thousand [5]. For this work we have low pressure VLE so we can use vapor and liquid equilibrium as:

\[
v_i^l, p = x_i, v_i^l, p_i^\text{sat}
\]

A more general method for estimating activity coefficients is provided by a group-contribution technique illustrated in Fig1 molecules are divided (somewhat arbitrarily) into functional groups. Molecule-molecule interactions are considered to be properly weighted sums of group-group interactions. Once quantitative information on the necessary group-group interactions is obtained from reduction of experimental data for binary systems, it is then possible to calculate molecule-molecule interactions (and therefore phase equilibria) for molecular pairs where no experimental data are available. The UNIFAC group contribution model has been developed to estimate the real vapor-liquid equilibrium behavior. As it say before in a group contribution model the mixture is not seen as a mixture of components but as a mixture of groups. The large advantage is that the number of structural groups is much smaller (dozens) than the number of components (millions). This means that it is possible to calculate most systems of commercial interest with very few group information. UNIFAC is based on the UNIQUAC equation. Therefore activity coefficients are calculated from two terms [6].

\[
\ln \gamma_i = \ln \gamma_i^\text{combinatorial} + \ln \gamma_i^\text{residual}
\]

The combinatorial part is calculated in the same manner as in UNIQUAC

\[
\ln \gamma_i^F = 1 - N_i + n_i \ln N_i - 5. q_F \left[ 1 - \frac{N_i}{F_i} + \ln \frac{N_i}{F_i} \right]
\]

\[
F_i = \frac{q_i}{\sum_j q_j x_j}
\]

For the calculation of the combinatorial part only the relative van der Waals volume \( r_i \) and surface \( q_i \), together with the mole fractions \( x_i \), are needed. The van der Waals volume and surface can be calculated from group volumes and surfaces,

\[
r_i = \sum_k v_k^{(i)} \cdot R_k
\]

\[
q_i = \sum_k v_k^{(i)} \cdot Q_k
\]

With \( v_i \) as the number of structural groups of type \( k \) in the molecule \( i \). The residual part has to be calculated from the group activity coefficients \( \Gamma_i \),

\[
\ln \gamma_i^R = \sum_k v_k^{(i)} \left( \ln \Gamma_k - \ln \Gamma_k^{(0)} \right)
\]

The concentration dependency of the group activity coefficients in the mixture \( \Gamma_i \) (and in the pure component \( \Gamma_i^{(0)} \)) must be calculated in analogy to the UNIQUAC equation

\[
\ln \Gamma_k = Q_k \cdot \left[ 1 - \ln (\sum m \theta_m \psi_m) - \sum m \theta_m \psi_m \right]
\]

The surface contribution \( \theta_m \) and the mole fraction of the group are defined by:

\[
\theta_m = \frac{q_m x_m}{\sum_n q_n x_n}
\]

\[
X_m = \frac{\sum_j v_{jm} x_j}{\sum_n \sum_j v_{jn} x_j}
\]

And the parameter \( \psi_{nm} \) is defined as:

\[
\psi_{nm} = e^{-a_{nm}}
\]

With \( a_{nm} \) as group interaction parameters between the groups \( n \) and \( m \).
boiling range greater than 573.15K, the relation between density and temperature \( T \) is temperature, \( K \); dynamic density, \( g. \ cm^{-3} \). Experiment with a mix Stainless steel mixing device FYXD05 into the autoclave Row, the top tank with the motor speed adjustment self-pruning mix.

Mixing paddle speed, Artificial intelligence from the Al-808P temperature control device to control the reactor temperature within \( \pm 0.5K \). Pressure transmitter used by computers on the high-pressure Pressure inside the tank to record and monitor changes. First weigh a certain amount of liquid paraffin put in high pressure Kettle, stirring conditions in the vacuum tank of liquid exclusion Body of impurities, then stop stirring, which leads to gas under test Replacement in a few times, the reactor heated to the temperature required to achieve Thermal equilibrium, the slow pressurized to the desired pressure stable. The experimental results of VLE for the binary systems hexadecane + DME are shown in Table 2.

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| 411            | 517     | Note          | Constants. | (18)

= \( 0.003616 \exp \frac{2098.10}{T} \)

The real solubility can be predicted using equation (6) and ideal solubility together with an appropriate thermodynamic model to estimate the activity coefficient. The activity coefficient is a function of many factors including molecular size, polarity, and interaction forces between solute and solvent. These depend on the physical bulk properties of the pure compound that are functions of intermolecular forces (Van der Waals forces, hydrogen bonding, and dipole-dipole forces), molar volume, and degree of polarity. There are many thermodynamic models to predict the activity coefficient, which can be categorized in predictive (theoretical) and semi-empirical models. The predictive models have no adjustable parameters and use the thermodynamic bulk properties (regular-solution theory) or group contribution (UNIFAC) of the solute and solvent, group contribution methods play an important role in the prediction of phase equilibria when experimental data are not available, experimental data have been compared with those predicted by UNIFAC. For UNIFAC, the parameters adjusted were those for the group interactions \( \text{CH}_3 \text{O/CH}_2 \text{O/CH}_2 \), and \( \text{CH}_2/\text{CH}_3 \).

The predictions of the UNIFAC model and their comparison with Henry's law are presented in Table 3. In this case, the data calculated for UINFAC model are presented with group functional that exist in the literature.

As can be seen from Table 3, at the same temperature with increasing of the pressure, dimethyl -ether solubility in liquid paraffin increased. This is because of the gas density increases and so more gas dissolved in the liquid phase. Furthermore at the same pressure, with increasing temperature DME solubility in liquid paraffin decreased.

The results show that the calculated solubility with Henry's method could better coverage for higher system temperature but the UNIFAC predicted solubility have good agreement in lower temperature.

REFERENCES


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