

Investigation of Dimethyl Ether Solubility in Liquid Hexadecane by UNIFAC Method

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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 $\text{CH}_3\text{--O--CH}_3$ 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 NO_x reduction due to the larger temperature drop of the mixture in the cylinder.
- DME's boiling point is $-24.9\text{ }^\circ\text{C}$ 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.

Symbol	Quantity	Conversion from Gaussian and
C_{exp}	Experimentl solubility	Kmol.m^{-3}
C_{cal}	Calculated solubility with Henry's law	Kmol.m^{-3}
C_{uni}	Calculated solubility with Unifac method	Kmol.m^{-3}
f	Fugacity	Pa
ϕ	Fugacity coefficient	
γ	activity coefficients	
P_f	Saturated Pressure	MPa

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:

$$f_i^l = f_i^v \quad (1)$$

Vapor phase fugacity can be expressed as:

$$f_i^v = \phi_i^v \cdot y_i \cdot P \quad (2)$$

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:

$$f_i^l = f_i^{*l} \cdot x_i \cdot \gamma_i \quad (3)$$

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

$$f_i^{*l} = p_i^{\text{sat}} \cdot \phi_i^{\text{sat}} \cdot \exp\left[\frac{v_i^l \cdot (p - p_i^{\text{sat}})}{RT}\right] \quad (4)$$

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The fugacity, f_i^{*l} , is equal to p_i^{sat} , the saturation pressure of component i at T , with two corrections. First, the fugacity coefficient ϕ_i^{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 , different from the saturation pressure, p_i^{sat} , molar volume v_i^l of solute in the liquid phase is also calculated with the equation of states [4].

If we introduce Φ_i as:

$$\Phi_i = \frac{\phi_i^v}{\phi_i^{sat}} \cdot \exp \left[-\frac{v_i^l \cdot (p - p_i^{sat})}{RT} \right] \quad (5)$$

For conditions of low pressure VLE, vapor phase approximate ideal gases, for which considered $\phi_i^v = \phi_i^{sat} = 1$, 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:

$$y_i \cdot p = x_i \cdot \gamma_i \cdot p_i^{sat} \quad (6)$$

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].

$$\ln \gamma_i = \ln \gamma_i^{\text{combinatorial}} + \ln \gamma_i^{\text{residual}} \quad (7)$$

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

$$\ln \gamma_i^c = 1 - V_i + \ln V_i - 5 \cdot q_i \cdot \left[1 - \frac{V_i}{F_i} + \ln \frac{V_i}{F_i} \right] \quad (8)$$

$$F_i = \frac{q_i}{\sum_j q_j x_j} \quad (9)$$

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,

$$r_i = \sum_k v_k^{(i)} \cdot R_k \quad (10)$$

$$q_i = \sum_k v_k^{(i)} \cdot Q_k \quad (11)$$

With $v_k^{(i)}$ 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 Γ_k ,

$$\ln \gamma_i^R = \sum v_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \quad (12)$$

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

$$\ln \Gamma_k = Q_k \cdot \left[1 - \ln \left(\sum_m \theta_m \cdot \Psi_m \right) - \sum_m \frac{\theta_m \cdot \Psi_m}{\sum_n \theta_n \cdot \Psi_n} \right] \quad (13)$$

The surface contribution θ_m and the mole fraction of the group are defined by:

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \quad (14)$$

$$X_m = \frac{\sum_j v_j^m x_j}{\sum_j \sum_n v_{n,j} x_j} \quad (15)$$

And the parameter Ψ_{nm} is defined as:

$$\Psi_{nm} = e^{\frac{-a_{nm}}{T}} \quad (16)$$

With a_{nm} as group interaction parameters between the groups n and m

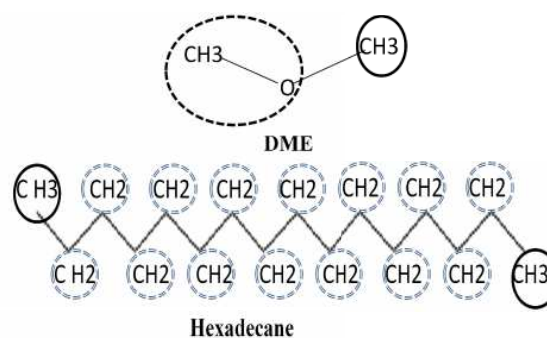


Fig. 1 group contribution technique

III. EXPERIMENTAL PART

Experimental part was done by SONG Huai-Jun [7] Experiments of dimethylether 99.99% purity bottled gas. Liquid paraffin is chemically pure reagents, molecular weight

345, boiling range greater than 573.15K, the relation between density and temperature T is temperature, K; dynamic density, g. cm³ Experiment with a mix Stainless steel mixing device FYXD05 into the autoclave Row, the top tank with the motor speed adjustment self-priming mix

Mixing paddle speed, Artificial intelligence from the AI-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.

TABLE II
EXPERIMENTAL DATA OF DIMETHYL ETHER SOLUBILITY IN LIQUID PARRAFIN

Temperature	P_f	C_{exp}	Temperature	P_f	C_{exp}
314 (K)	142000	0.9341	423 (K)	237000	0.1141
	221000	0.6133		353000	0.1768
	258000	0.7106		426000	0.2240
	316000	0.8770		479000	0.2421
	353000	0.9796		516000	0.2567
337 (K)	158000	0.2722	439 (K)	263000	0.1111
	216000	0.3820		368000	0.1484
	268000	0.4693		437000	0.1858
	311000	0.5624		495000	0.2149
	342000	0.6236		537000	0.2260
351 (K)	142000	0.1914	448 (K)	274000	0.1017
	211000	0.3035		389000	0.1460
	263000	0.3550		453000	0.1756
	316000	0.4620		511000	0.1932
	363000	0.5059		558000	0.2210
373 (K)	158000	0.1460	475(K)	321000	0.0937
	253000	0.2457		442000	0.1300
	326000	0.3128		516000	0.1540
	363000	0.3397		553000	0.1619
	426000	0.4275		589000	0.1741
396 (K)	195000	0.1369	501 (K)	279000	0.0623
	289000	0.2111		426000	0.0963
	358000	0.2496		511000	0.1197
	432000	0.3049		563000	0.1316
	489000	0.3396		595000	0.1414
411 (K)	211000	0.1191	517 (K)	311000	0.0608
	316000	0.1777		437000	0.0862
	389000	0.2317		532000	0.1108
	455000	0.2682		579000	0.1205
	489000	0.2944		621000	0.1272

IV. PUBLICATION PRINCIPLE RESULT AND DISCUSSION

Method that used for solubility prediction by authors was Henry's Law, in this method they find Henry's constant by simple adjustable relation that depends to temperature and with gas pressure they can find gas solubility in the liquid.

$$H = 0.003616 \exp \frac{2090.10}{T} \quad (17)$$

$$C_{cat} = H \cdot P_f \quad (18)$$

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 CH_3O/CH_3 , CH_3O/CH_2 , and CH_2/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 UNIFAC 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.

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TABLE III
CALCULATED DIMETHYL ETHER SOLUBILITY IN LIQUID PARAFFIN BY HENRY'S LAW AND UNIFAC

Temperature	P _f	C _{exp}	C _{cal}	C _{Uni}	Temperature	P _f	C _{exp}	C _{cal}	C _{Uni}
T=314 (K)	1.42E+05	0.3852	0.3941	0.3466	T=423 (K)	2.37E+05	0.1141	0.1197	0.0958
	2.21E+05	0.5992	0.6133	0.5093		3.53E+05	0.1768	0.1783	0.1586
	2.58E+05	0.7287	0.716	0.7301		4.26E+05	0.224	0.2151	0.2
	3.16E+05	0.8841	0.877	0.8045		4.79E+05	0.2421	0.2419	0.2227
	3.53E+05	0.9764	0.9796	0.908		5.16E+05	0.2567	0.2606	0.231
T=337 (K)	1.58E+05	0.2722	0.2829	0.2694	T=439 (K)	2.63E+05	0.1111	0.1112	0.1467
	2.16E+05	0.382	0.3868	0.3476		3.68E+05	0.1484	0.1556	0.1632
	2.68E+05	0.4693	0.4799	0.4411		4.37E+05	0.1858	0.1848	0.1672
	3.11E+05	0.5624	0.5569	0.5342		4.95E+05	0.2149	0.2093	0.2009
	3.42E+05	0.6236	0.6124	0.5425		5.37E+05	0.226	0.227	0.2133
T=351 K	1.42E+05	0.1914	0.1998	0.1799	T=448 (K)	2.74E+05	0.1017	0.1054	0.1011
	2.11E+05	0.3035	0.2969	0.2913		3.89E+05	0.146	0.1496	0.1331
	2.63E+05	0.355	0.37	0.3266		4.53E+05	0.1756	0.1743	0.1568
	3.10E+05	0.462	0.4446	0.4389		5.11E+05	0.1932	0.1966	0.1572
	3.63E+05	0.5059	0.5107	0.4603		5.58E+05	0.221	0.2147	0.1824
T=373 (K)	1.58E+05	0.146	0.1531	0.1533	T=475 (K)	3.21E+05	0.0937	0.0947	0.0823
	2.53E+05	0.2457	0.2451	0.2426		4.42E+05	0.13	0.1304	0.1482
	3.25E+05	0.3128	0.3158	0.294		5.16E+05	0.154	0.1522	0.1339
	3.63E+05	0.3397	0.3517	0.3159		5.53E+05	0.1619	0.1631	0.1402
	4.26E+05	0.4275	0.4127	0.3933		5.89E+05	0.1741	0.1738	0.1532
T=396 (K)	1.95E+05	0.1369	0.1371	0.1506	T=501 (K)	2.79E+05	0.0623	0.0651	0.0546
	2.89E+05	0.211	0.2032	0.2215		4.26E+05	0.0963	0.0993	0.0954
	3.58E+05	0.2496	0.2517	0.2491		5.11E+05	0.1197	0.1192	0.1
	4.32E+05	0.3049	0.3037	0.3097		5.63E+05	0.1316	0.1313	0.1129
	4.89E+05	0.3396	0.3438	0.326		5.95E+05	0.1414	0.1388	0.1187
T=411 (K)	2.11E+05	0.1191	0.1246	0.1107	T=517 (K)	3.11E+05	0.0608	0.0636	0.0711
	3.16E+05	0.1777	0.1865	0.1545		4.37E+05	0.0862	0.0894	0.0786
	3.89E+05	0.2317	0.2296	0.2201		5.32E+05	0.1108	0.1088	0.0935
	4.53E+05	0.2682	0.2674	0.2601		5.79E+05	0.1205	0.1185	0.1018
	4.89E+05	0.2944	0.2887	0.2708		6.21E+05	0.1272	0.1271	0.1058