

Determination of activity coefficients of dimethyl ether in butyl acetate and 2-propanol

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Determination of activity coefficients of dimethyl ether in butyl acetate and 2-propanol: The paper presents experimental setup, measurements data and appropriate model for determining the activity coefficients in binary mixtures dimethyl ether – butyl acetate and dimethyl ether – 2 – propanol at room temperature. Through a simple mathematical model the activity coefficients are correlated to the composition of the mixtures, and two parameter Margules equations are derived. The results could be used for prediction of vapour – liquid equilibrium in the given systems, and may bring significant support for the researchers dealing with dimethyl ether applications and especially in the aerosol industry.

Key words: Dimethyl ether, 2-propanol, butyl acetate, aerosol, activity coefficients, vapor-liquid equilibrium, Margules equation, parameter estimation

INTRODUCTION

The use of dimethyl ether (DME) in different areas of industry grows constantly within last decades. The DME is a colorless, virtual odorless and low viscosity substance, which has a boiling point ca. -25°C at 1 bar, and has a vapor pressure of 5.1 bar at 20°C . Due to its high solvency power this material is used in high amounts in aerosol industry as a valuable component in aerosol formulations which contain substances that are difficult to dissolve. The DME is an appreciated propellant (pressure making liquefied gas) in many aerosol products for pharmaceuticals (i.e. wart remover), personal care (i.e. hairsprays), home care (i.e. air fresheners), variety of technical aerosols as spray paints and polyurethane foam. In many of these products it plays dual role – (1) it creates the pressure needed for product use, sometimes together with propane-butane, and (2) acts as solvent for the incompatible components thus creating one homogenous liquid phase in the aerosol can. It has an important role in the aerosol polyurethane foam production where it ensures the good homogenization between the propane-butane which is non-polar material and more polar components as amine catalyst, polyether diols and diphenylmethane-4,4'-diisocyanate. Besides the use in the aerosol industry, the DME continually attracts more and more interest to become an alternative fuel especially for diesel engines, including DME derived by biomass conversion [1], [2]. There are many measurements in relation with vapour-liquid equilibrium of DME and other materials – water, alcohols, esters within broad range of temperatures and pressures [3]-[5]. Due to the practical interest of the aerosol industry we chose to examine the vapour-liquid equilibrium of the material systems DME + butyl acetate and DME + 2-propanol. The second of these systems has been measured at higher temperatures [4]. The methodology is quite identical with the presented in [6] – the pressure at different overall DME concentration is measured and through mass balance and equation of state for the gas phase the activity coefficients of both components in the binary mixture are determined.

EXPERIMENTAL METHOD

As container for the pressure measurement was chosen a metal vessel with full volume of 1000ml and burst pressure min 15 bar. The liquids – butyl acetate or 2-propanol were added manually in this container and after this it was sealed through a special valve, similar to this used in aerosol products. The weight of added liquid was then determined, and after this the DME was injected through the valve. The mixture was allowed to stay 24h for the full establishment of the vapor-liquid equilibrium and after this the chosen temperature was adjusted in the water bath / thermostat within 0.1K accuracy. The pressure is recorded with the digital manometer Wika DG 10, accuracy 0.5%, through direct attachment to the valve of the metal container. This procedure was repeated for each of the compositions listed below.

RESULTS AND CALCULATIONS

The experimental conditions allow that the gas phase is treated with the ideal gas law due to the relative low pressures in the system, up to 6 bar. Consequently the deviation between ideal and real gas treatment (cubic equation of state) is comparable with the experimental errors and the ideal gas law is preferred. The other important point considered during the experiments is the presence of air in the closed metal container, together with DME and 2-propanol and butyl acetate. We did a quantitative estimation of this influence, considering the binary systems air + dimethyl ether and air + butyl acetate or 2-propanol at temperatures close to our reference temperature. For such system, assuming all components are presented in both phases, and using Henry's law, the composition has been calculated using also the mass balance liquid-gas phase and ideal gas law. The Henry coefficients of nitrogen and oxygen in the solvents considered here were taken from literature [7] – [10]. The results show that the air solubility in the liquid phase during experiments could be definitely neglected. This statement is also backed-up by the fact that the butyl acetate and 2-propanol are saturated with air, so no any additional air penetration in the liquid phase is expected. Consequently, the air contributes to the overall pressure only through its partial pressure in the gas mixture.

In this work we use the following formulas in order to correlate the total measured pressure and the activity coefficients of DME and solvent.

$$p_i = n_i^G \cdot R \cdot T / V^G, i = 1 - 3$$

$$p^{\text{tot}} = \sum_{i=1}^3 p_i; \quad p_i = \gamma_i \cdot p_i^{\text{sat}}(T) \cdot x_i, i = 1, 2$$

$$n_i = n_i^G + n_i^L, i = 1, 2$$

$$V = V^G + V^L$$

$$x_i = \frac{n_i^L}{n_1^L + n_2^L}, i = 1, 2$$

In total we have 11 equations with 11 unknown variables – V^G , the two liquid molar parts x_i , the four mol amounts in both phases, the total pressure and the three partial pressures, where index 1 stands for DME, index 2 for solvent, and 3 for the air. Before applying the data regression procedure for determination of activity coefficients, we checked the above mathematical model using parameter sensitivity analysis. The purpose was to verify the influence of the activity coefficients on the thermodynamic equilibrium and particularly on the partial pressures in the system. The software used for solving the above system [11] offers a possibility to obtain the partial derivatives of the solution of the algebraic system with respect to some chosen parameters, in our case the two activity coefficients γ_i . In general the parametric sensitivity analysis may be performed together with the system solution, and having the values of Jacobi matrix one may obtain also the needed derivatives with respect to the parameters as a “by-product” of the main Newton method of solution. The table 1 and 2 present the dependency of the partial pressures of DME, butyl acetate or 2-propanol, air, and their sum from the activity coefficients in terms of their derivatives, meaning the bigger the value is, the bigger is the dependency. The values of the derivatives for each activity coefficient γ_1 (DME in mixture DME/butyl acetate) and γ_2 (butyl acetate in mixture DME/butyl acetate), respectively γ_1 (DME in mixture DME/2-propanol) and γ_2 (2-propanol in mixture DME/2-propanol) were calculated keeping both coefficients fixed at three different values – 0.5, 1.0 and 1.5, which represent a reasonable guesses for the lower and upper limit of the activity coefficients. It is clear visible tendency that the partial pressure of DME depends very strong on γ_{DME} and almost doesn't depend on the activity coefficient of butyl acetate. Similarly, the partial pressure of butyl acetate depends mostly on its own activity coefficient, but this dependency is much lower than of DME. Having in mind that the total pressure is sum of all three partial

pressures, respectively the same applies for their dependencies on the activity coefficients, we see that the total pressure depends mostly on the value of the activity coefficient of DME, and this is due to the fact that DME has very high saturated vapor pressure compared with other species. Same observation is valid for the DME/2-propanol system, but here less strong dependency is valid, because the 2-propanol has significant high vapor pressure compared to butyl acetate. In general, for all three levels of activity coefficients investigated the dependency of the total pressure in the system on the activity coefficient of DME is about 500 times higher than on activity coefficient of butyl acetate and about 60 times higher than this of 2-propanol. Fig.1 shows the simulated dependency of the total pressure as function of each of the both activity coefficient, keeping the other one fixed.

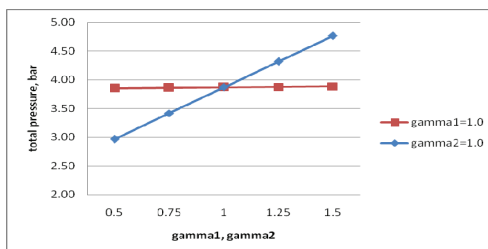


Fig. 1 Simulated pressure in system 160g DME and 411g 2-propanol at 22°C as function of the activity coefficients, index 1 = DME, 2 = 2-propanol.

Table 1. Derivatives of partial pressure with respect to γ_1 (DME, 149g) and γ_2 (Butyl acetate, 324g) at 22°C, at three different levels of γ .

	$\gamma_1 = \gamma_2 = 0.5$		$\gamma_1 = \gamma_2 = 1.0$		$\gamma_1 = \gamma_2 = 1.5$	
	$\partial p / \partial \gamma_1$	$\partial p / \partial \gamma_2$	$\partial p / \partial \gamma_1$	$\partial p / \partial \gamma_2$	$\partial p / \partial \gamma_1$	$\partial p / \partial \gamma_2$
p_{DME}	1.44E+05	1.07E+00	2.87E+05	4.30E+00	4.27E+05	9.72E+00
p_{solvent}	1.07E+00	2.86E+02	4.34E+00	5.75E+02	9.84E+00	8.65E+02
p_{air}	-6.53E+02	-4.84E-03	-1.30E+03	-1.95E-02	-1.93E+03	-4.40E-02
p_{tot}	1.44E+05	2.87E+02	2.85E+05	5.79E+02	4.25E+05	8.75E+02

Table 2. Derivatives of partial pressure with respect to γ_1 (DME, 160g) and γ_2 (2-propanol, 411g) at 22°C, at three different levels of γ .

	$\gamma_1 = \gamma_2 = 0.5$		$\gamma_1 = \gamma_2 = 1.0$		$\gamma_1 = \gamma_2 = 1.5$	
	$\partial p / \partial \gamma_1$	$\partial p / \partial \gamma_2$	$\partial p / \partial \gamma_1$	$\partial p / \partial \gamma_2$	$\partial p / \partial \gamma_1$	$\partial p / \partial \gamma_2$
p_{DME}	9.07E+04	1.34E+00	1.81E+05	5.35E+00	2.70E+05	1.20E+01
p_{solvent}	1.34E+00	1.58E+03	5.37E+00	3.17E+03	1.21E+01	4.76E+03
p_{air}	-5.24E+02	-7.71E-03	-1.04E+03	-3.09E-02	-1.56E+03	-6.95E-02
p_{tot}	9.02E+04	1.58E+03	1.80E+05	3.17E+03	2.69E+05	4.77E+03

The above discussed features of both systems justify the use of parameter estimation technique for determination of the activity coefficients, and their dependency on the composition. In the field of chemical thermodynamic exist many equations connecting the system composition and activity coefficients, and for the case studied we chose the two parameter Margules equation [12]:

$$\ln \gamma_1 = x_2^2 \cdot (A_{12} + 2(A_{21} - A_{12}) \cdot x_1), \quad \ln \gamma_2 = x_1^2 \cdot (A_{21} + 2(A_{12} - A_{21}) \cdot x_2),$$

The physical meaning of the activity coefficients is clearly visible through their connection with the excess Gibbs energy of mixing of the two components 1 and 2:

$$G^E = R \cdot T \cdot \sum_i x_i \cdot \ln \gamma_i, \text{ where } G^E \text{ is the deviation between actual and the Gibbs energy}$$

in case of ideal solution, meaning there is no interaction between the molecules. In this way the activity coefficients are measure for the deviation between the real and “ideal” state for the given system, and are very useful for prediction of vapor – liquid equilibrium in two-component non-ideal systems. The procedure for determining the coefficients A_{12} and A_{21} for DME and butyl acetate or 2-propanol as a second component is as follows: The total pressure at given temperatures in the corresponding mixtures was measured for several different compositions. In general, the pressure in the system increases when adding more DME to the mixture due to its high vapor pressure, but also because of the increased volume of the liquid phase, respectively decreased gas phase volume and corresponding compression of the air in the metal vessel. The procedure of the non-linear least squares is used with objective function constructed as the square of the difference between measured and predicted according to the above model total pressure. As a result of the solution, one may obtain the values of A_{12} and A_{21} which gives lowest deviation between calculated and measured pressure. The graphical results of this procedure are presented on Fig. 2 and Fig. 3 for the both material systems respectively. The R^2 values are 97% for both systems, and the mean deviations between calculated and measured pressures are 7.0% for DME/butyl acetate and 9.4% for DME/2-propanol. The activity coefficients for DME and solvents at temperature of 22°C and for concentrations up to 0.4 mol/mol DME may be calculated according to the above given expressions having the values $A_{12}=0.862$, $A_{21}=-2.076$ for DME/butyl acetate, and $A_{12}=1.025$, $A_{21}=-3.150$.

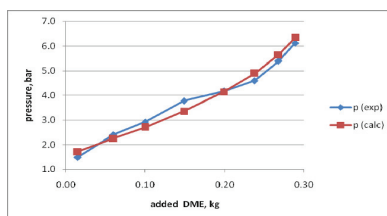


Fig. 2 Parameter estimation in system DME + 0.324kg butyl acetate, 22°C.

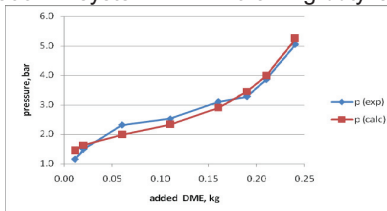


Fig. 3 Parameter Estimation in system DME + 0.411kg 2-propanol, 22°C.

CONCLUSIONS

The article presents a simplified experimental method for determination of activity coefficients in the liquid phase in two component system consisting of at least one liquefied gas – dimethyl ether. Using mass balance, known vapor pressures of the components and performing non-linear parameter estimation it is possible to estimate the concentration dependence of the activity coefficients of the both components. The results may be helpful in predicting vapor-liquid equilibrium in systems containing DME as for example in the aerosol industry.

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