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Effect of bivalent cation inorganic salts on isobaric vapor–liquid equilibrium of methyl acetate–methanol system

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ABSTRACT

The salt effect of four inorganic salts, namely; zinc nitrate, calcium nitrate, magnesium nitrate and magnesium chloride on the vapor liquid equilibria of the binary methyl acetate–methanol system was investigated using a modified Othmer still at 1 atm. The salting out effect of methyl acetate was studied at different salt concentrations. For a salt concentration of 5 wt%, it was found that zinc nitrate gives better salting out effect than calcium and magnesium nitrate. Magnesium chloride also shows a salting out effect, but could not eliminate the azeotrope completely, even at higher salt concentrations. It is observed that the bivalent cation salts ($ZnNO_3$, $CaNO_3$, $MgNO_3$ and $MgCl_2$) had greater salting out effect than univalent cation salts ($LiNO_3$,LiCl) reported earlier. Further, salting out coefficients were calculated using the scaled particle theory. The experimental vapor–liquid equilibrium data with the salts was compared with that calculated using the scaled particle theory, but only qualitative agreement was observed.

1. Introduction

Methyl acetate and methanol mixture is used in many processes including poly vinyl alcohol manufacture and in esterification [1]. This binary mixture forms a minimum boiling azeotrope at 0.64 mole fraction of methyl acetate at 327.2 K and 1 atm [2]. The separation of binary liquid mixtures is generally accomplished by distillation. Conventional distillation is not possible for the separation of azeotropic mixtures. Thus, special distillation techniques such as extractive distillation are used to separate azeotropic or close boiling mixtures beyond their azeotropic compositions as their liquid and vapor compositions are the same at the azeotropic composition [3–5]. In extractive distillation, a salt is added as an entrainer in order to increase the relative volatility of the components in the mixture and is usually referred to as the salting out effect [6,7]. Therefore, the azeotropic composition shifts or breaks towards higher concentration of the more volatile compound in the mixture and the elimination of the azeotrope is accomplished. Hence, the phase equilibria of the mixed-solvent systems are of practical interest in designing of distillation columns.

Many investigators have reported a salt effect on the ternary vapor–liquid equilibrium of methyl acetate–methanol systems [8–12]. The salting out effect was observed for sodium thiocyanate at saturation [9], calcium chloride [10] and potassium acetate [11] but could not eliminate the azeotropic composition of the methyl acetate–methanol system completely. It has been reported that even at low salt concentrations, zinc chloride [11] had a strong salting out effect compared to lithium nitrate [12] and complete elimination of the azeotrope was possible. However, the vapor–liquid equilibrium data of methyl acetate–methanol with salts are still limited and it is essential to develop salt effect theories for the design of extractive distillation processes, which requires vapor–liquid equilibrium data over the whole concentration range for comparison between theory and experiment.

It is most important to choose the “best” entrainer from different salts for the specific application of separation of azeotropic mixtures. Also, the selection of the solvent plays a major role in extractive distillation [3]. The different salts influence salting out or salting in effect on the phase behavior of azeotropic mixtures and can be predicted by various theories such as hydration of salt ions in solution, internal pressure effect, electrostatic theory and van der Waals force [7]. These theories require the experimental ternary vapor liquid equilibrium data of the azeotropic mixtures and salts. The lack of availability of experimental data on the phase equilibria of methyl acetate–methanol-salt results in these theories unsuitable for the prediction of salting coefficients. Scaled particle theory can be used for screening of suitable salts in vapor–liquid equilibria of methyl acetate–methanol system since it requires only molecular parameters which are readily available.

Many experimental investigations have been reported on the applications of scaled particle theory in order to calculate the salting coefficient for non-polar aqueous systems [13,14], the

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Nomenclature

c	concentration of salt, mol/l
k_s	salting coefficient
$k_\alpha, k_\beta, k_\gamma$	contributions to salting coefficient
M	molecular weight (g/mol)
N	Avogadro number
S	solubility of non-electrolyte in salt solution
S_o	solubility of non-electrolyte in pure methanol
T	temperature, °C
x'_i	salt free mole fraction of component *i* in liquid
y_i	mole fraction of component *i* in vapor
z	salt mole fraction
α_1	polarizability of non-electrolyte
ε/κ	interaction energy parameter (K)
φ°	apparent molal volume of salt at infinite dilution (cc/mol)
γ_i	activity coefficient of component i in liquid
ρ_i	density of the components (g/cc)
σ	molecule size or ion diameter (°A)

salting coefficients of organic and inorganic electrolyte solutions of non-polar systems were found to be in good agreement with experimental results [15,16]. In recent years, scaled particle theory has also been applied to the case of polar systems in aqueous media [17–19], and a reasonable agreement with experimental data was observed. In a previous study, nitrate salts such as zinc, calcium and magnesium nitrate were examined experimentally for breaking the ethyl acetate–ethanol azeotrope and the salting coefficients were calculated using scaled particle theory and satisfactory agreement was found between experiment and theoretical predictions [20]. However, prediction of phase behavior of salt for polar non-aqueous systems is limited.

The objective of the present work is to study experimentally the salt effect on methyl acetate–methanol system using a modified Othmer still. The isobaric vapor–liquid equilibrium data with various bivalent chloride and nitrate salts at different salt concentrations are obtained. An attempt is made to characterize the salting phenomenon with inorganic electrolytes by using scaled particle theory. The experimental vapor–liquid equilibrium data with salt is compared with that calculated using the scaled particle theory.

2. Experimental

2.1. Chemicals

In the present study, the methyl acetate and methanol (HPLC grade) with a minimum purity of 99.99 wt% was used. Methyl acetate and methanol were used without further purification since no impurities were detected by the gas chromatography. Salts of magnesium nitrate, calcium nitrate and magnesium chloride (Rankem) with a minimum assay of 98 wt% purity and zinc nitrate (S-d fine chemicals) with an assay of 99 wt% purity were used. They were of analytical grade, vacuum-dried before use and the water content was less than 0.1% as analysed by the Karl Fischer method. A refractometer was also used as a quick test. The information of the chemicals used in the present study is given in Table 1.

The densities of known molalites of magnesium, calcium and zinc nitrates and magnesium chloride in methanol solution were measured using an oscillation type density meter (Rudolph Automatic Density Meter, DDM2910) at 25 °C and are given in the supplementary data. The operating principle of density meter is based on the law of harmonic oscillation and mass-spring model. The experimental uncertainty of density meter is $\pm 1 \times 10^{-2}$ kg m^{-3}. The density of double distilled water is measured as a reference fluid for calibrating each experiment.

2.2. Apparatus and procedure

The apparatus and procedure has been described earlier by Dhanalakshmi et al. [20]. The modified Othmer still described earlier [21] was used to obtain the isobaric vapor–liquid equilibrium data for various salt concentrations. The liquid phase composition was measured for different combinations of methyl acetate–methanol and for each experiment with a particular composition, the corresponding liquid phase compositions analysed earlier (binary system) was used in the ternary system as well and is given in Tables 2 to 5.

3. Results and discussion

3.1. Experimental results

3.1.1. Benchmarking of the binary system

Initially benchmarking was done on the binary methyl acetate–methanol system using isobaric vapor–liquid equilibrium data obtained in an earlier study and reported by Dhanalakshmi et al. [20]. The liquid and vapor phase composition of methyl acetate was compared with the measurements reported by Topphoff et al. [12] and Orchilles et al. [22] and the agreement was good.

3.1.2. Effect of different inorganic salts on the binary system

The isobaric vapor–liquid equilibrium data for ternary methyl acetate (1)–methanol (2)–salt (3) system with different nitrate salts and magnesium chloride were measured at a fixed salt concentration and are given in Tables 2 to 5. In this study, the composition of methyl acetate in liquid phase is expressed on salt free basis. When the salt addition was added to the binary methyl acetate–methanol system, an increase in the equilibrium temperature and vapor phase mole fraction was observed. The effect of salt on the vapor–liquid equilibrium of the methyl acetate–methanol system with different inorganic salts is shown in Fig. 5.2, in which the three nitrate salts zinc, calcium and magnesium nitrate and magnesium chloride showed a salting out effect. On the other hand, complete elimination of the azeotrope was not achieved with magnesium chloride despite exhibiting a salting out effect. Zinc nitrate may be considered as the “best entrainer” because of the significant increase in the vapor phase mole fraction of methyl acetate while compared to other nitrate salts, namely calcium and magnesium. Thus, the azeotropic composition shifted towards higher methyl acetate concentration due to increase in the methyl acetate mole fraction in the vapor phase (Fig. 1).

3.1.3. Effect of salt concentration on the phase equilibrium

The salt effect on the vapor–liquid equilibrium of methyl acetate–methanol system for various inorganic salts was studied at different concentrations of 2, 5, 7 and 10 wt% and the corresponding experimental results are shown in Figs. 2 to 5. In all these figures the salt free data is included. A considerable increase in the mole fraction of methyl acetate in the vapor phase with increasing salt concentration is observed. The azeotrope of methyl acetate–methanol disappears as the concentration of the salt increases and a rise in methyl acetate concentrations was observed. The elimination of the azeotrope for the binary system is accomplished with salt concentration of 5 wt%, 7 wt% and 10 wt% of zinc, calcium and magnesium nitrates respectively. This indicates that zinc nitrate is more effective and a higher salting out effect at a lower salt concentration than the other two nitrate salts