

Modeling of isobaric vapor-liquid equilibrium for binary systems of methanol, ethanol and water

Modélisation de l'équilibre vapeur-liquide isobare pour les systèmes binaires de méthanol, éthanol et eau

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ABSTRACT. The present work exposes a thermodynamic framework of the modeling of the vapor-liquid equilibrium for the three binary systems composed of {methanol-water}, {methanol-ethanol} and {ethanol-cyclohexane} at 101.3 kPa. The experimental data were correlated using the extended UNIQUAC model. The deviations between the calculated and experimental vapor-phase compositions, liquid-phase compositions and bubble point temperatures have been determined. To improve the accuracy of the proposed model we determine the deviations between the calculated and experimental values with respect to all variables (i.e. vapor-phase compositions, liquid-phase compositions and bubble point temperatures). The calculated results of {methanol-water}, {methanol-ethanol} and {ethanol-cyclohexane} mixtures are compared with experimental data presented in literature showing minimum of deviations.

RÉSUMÉ. Le présent travail traite le cas thermodynamique de la modélisation de la vapeur-liquide pour les trois systèmes binaires composés de {méthanol-eau}, {méthanol-éthanol} et {éthanol-cyclohexane} à la pression de 101,3 kPa. Les données expérimentales ont été corrélées en utilisant le modèle UNIQUAC étendu. Les écarts entre les compositions en phase vapeur calculées et expérimentales, les compositions en phase liquide et les températures de point de bulle ont été déterminés. Pour améliorer la précision du modèle proposé, nous déterminons les écarts entre les valeurs calculées et expérimentales par rapport à toutes les variables (c'est-à-dire les compositions en phase vapeur, les compositions en phase liquide et les températures de point de bulle). Les résultats calculés des mélanges {méthanol-eau}, {méthanol-éthanol} et {éthanol-cyclohexane} sont comparés aux données expérimentales présentées dans la littérature montrant un minimum de déviations.

KEYWORDS. Vapor-liquid equilibrium, thermodynamic modeling, extended UNIQUAC model.

MOTS-CLÉS. Équilibre vapeur-liquide, modélisation thermodynamique, modèle UNIQUAC étendu.

1. Introduction

Much attention has been consecrated the area of thermodynamic modeling in the research works of various systems in the last years. These studies were often based on the development of thermodynamic models in order to determine the thermodynamic properties of the systems envisaged.

Because of its important role in chemical engineering in terms in studying, optimizing and controlling in distillation processes, many publications have been focussed on modeling of vapor-liquid equilibrium of varied systems that should be apt encountered in chemical industries.

A precise description of phase equilibrium of mixtures is an essential part of thermodynamic modeling. This requires the utilization of accurate and reliable thermodynamic model. That's why a great deal of work has been devoted to the development of thermodynamic models for studying and determining the phase equilibrium data of various mixtures.

Despite the large number of studies in the literature pertaining to correlate experimental data of vapor-liquid equilibrium of various systems, but often do not provide enough information in the result of correlation. For example in the modeling of vapor-liquid equilibrium at pressure constant, these

works have been not donate the deviations with respect to all variables which are important for testing the accurate of the model used.

In this work, we are interested for applying the Extended UNIQUAC model for modeling the isobaric vapor-liquid equilibrium for methanol-water, methanol-ethanol and ethanol-cyclohexane binary systems at 101.3 kPa, to study the performance of the model and comparing the obtained results with those of the literature. We signal that we have tried to determine the deviations with respect to all variables.

2. The thermodynamic model

We have used the Extended UNIQUAC that composed by combinatorial and residual terms. As we have in our study nonelectrolyte systems, only the short-range interactions are tacked into account.

The activity coefficient of combinatorial term of component (i) is:

$$\ln \gamma_i^{\text{Com}} = \ln \left(\frac{\varphi_i}{x_i} \right) - \frac{\varphi_i}{x_i} + 1 - \frac{Z}{2} q_i \left[\ln \left(\frac{\varphi_i}{\theta_i} \right) - \frac{\varphi_i}{\theta_i} + 1 \right] \quad [1]$$

The activity coefficient of residual term of component (i) is

$$\ln \gamma_i^{\text{Res}} = q_i \left[1 - \ln \left(\sum_j \theta_j \psi_{ji} \right) - \sum_j \frac{\theta_j \psi_{ij}}{\sum_l \theta_l \psi_{lj}} \right] \quad [2]$$

$Z=10$ is the co-ordination number, x_i is the mole fraction, φ_i and θ_i are respectively volume and surface area fractions of component (i). r_i and q_i are respectively volume and surface area parameters of component (i)

$$\varphi_i = \frac{r_i x_i}{\sum_k r_k x_k} \quad \theta_i = \frac{q_i x_i}{\sum_k q_k x_k} \quad [3]$$

The interaction parameter ψ_{ji} is given by:

$$\psi_{ji} = \exp \left(- \frac{\Delta u_{ji}}{RT} \right) \quad [4]$$

The activity coefficient of component (i) is:

$$\ln \gamma_i = \ln \gamma_i^{\text{Com}} + \ln \gamma_i^{\text{Res}} \quad [5]$$

3. Results and discussion

As cited previously, we have used the Extended UNIQUAC model. The experimental data reported in the literature for the three binary systems were correlated to adjust the interaction parameters. Table 1 and 2 summarize the Antoine coefficients and the structural parameters, respectively.

Components	A	B	C	References
Water	7.19	1730.63	-39.72	[KUR 93]
Methanol	7.20	1582.27	-33.42	[KUR 93]
Ethanol	7.28	1623.22	-44.17	[KUR 93]
Cyclohexane	6.85	1206.47	223.13	[CUI 04]

Table 1. Antoine coefficients

Components	r	q	References
Water	0.92	1.40	[AND 78]
Methanol	1.43	1.43	[AND 78]
Ethanol	2.11	1.97	[AND 78]
Cyclohexane	3.97	3.01	[CHE 14]

Table 2. UNIQUAC structural parameters

The interaction parameters of methanol-water and methanol-ethanol binary systems were obtained by applying the model to vapor-liquid equilibrium data reported in [KUR 93]. The reported data in [KUA 63] are used to determine the interaction parameters for ethanol-cyclohexane binary system. The minimization of the Following function was carried out by the numerical method in [MOR 78] to adjust the interaction parameters for the studied binary systems.

$$of = \sum_{i=1}^N \left[(T^{cal} - T^{exp})_i^2 \right] \quad [6]$$

Table 1 presents the obtained interaction parameters. In table 4, the mean absolute deviations between the experimental data and the calculated ones in this work. For a better representation of the experimental data, we have tacked into account to determine the mean absolute deviations with respect to all variables. As can be seen from table 4, the deviations between the calculated values and experimental data are small.

Systems	interaction parameters	
	ψ_{ji}	ψ_{ij}
Mehanol-Water	9.27	18.54
Methanol-Ethanol	10.38	20.76
Ethanol- cyclohexane	13.90	27.81

Table 3. UNIQUAC interaction parameters

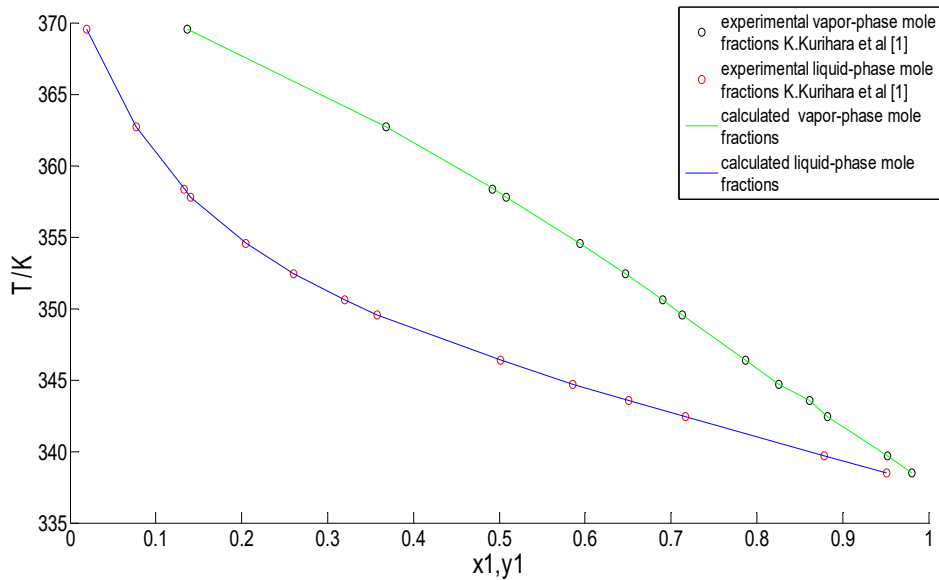


Figure 1. Temperature-composition diagram for methanol(1)-water(2) binary system at 101.3kPa

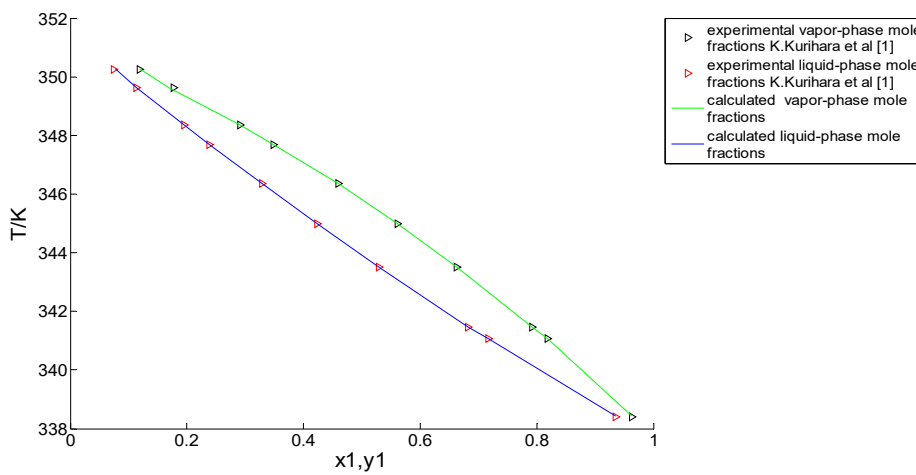


Figure 2. Temperature-composition diagram for methanol(1)-ethanol(2) binary system at 101.3kPa

Authors	K.KURIHARA et al [KUR 93]			Our study			S.KOBUCHI et al [KOB 11]		
	ΔT^a	Δy_1^b	Δx_1^c	ΔT^a	Δy_1^b	Δx_1^c	ΔT^a	Δy_1^b	Δx_1^c
Binary systems (1)-(2)									
Methanol-Water	0.18	0.008		0.002	0.00007	0.0002			
Methanol-Ethanol	0.04	0.005		0.003	0.0009	0.0004			
Ethanol-Cyclohexane				0.0029	0.0007	0.00035	0.3	0.01	

Tableau 4. Mean absolute deviations between the calculated and experimental data of vapor-phase mole fractions, liquid-phase mole fractions and equilibrium temperatures

$$\Delta T^a = \frac{\sum_k |T_{\text{expt}} - T_{\text{calc}}|_k}{N}$$

$$\Delta x_1^c = \frac{\sum_k |x_{1,\text{expt}} - x_{1,\text{calc}}|_k}{N}$$

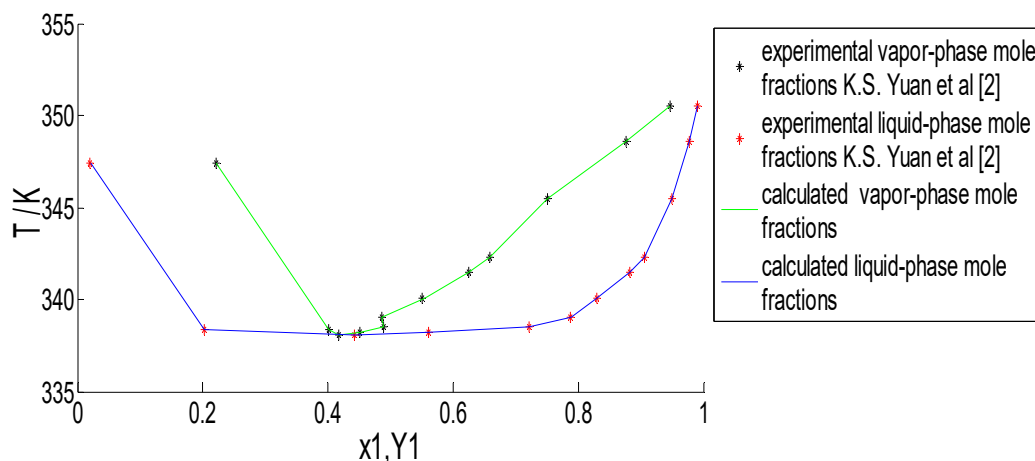


Figure 3. Temperature-composition diagram for ethanol (1)-cyclohexane (2) binary system at 101.3kPa

The calculated and experimental vapor-liquid equilibrium of methanol(1)-water(2), methanol(1)-ethanol(2) and ethanol(1)-cyclohexane(2) data are plotted on (T, x_1, y_1) diagrams in figs.1-3. As can be seen from these figs, the calculated values are in good agreement with experimental data.

4. Conclusion

The modeling of isobaric vapor-liquid equilibrium for binary systems is studied in this work. The interaction parameters of the Extended UNIQUAC model for methanol-water, methanol-ethanol and ethanol-cyclohexane were determined by the correlation of the experimental data. A determination of the mean absolute deviations with respect to all variables such as: temperature and compositions in both phases is widely considered for representing adequately the experimental data.

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