KPU International Journal of Engineering & Technology
Volume 4, Issue2, Sep. 2024
e-ISSN:2790-0819, p-ISSN:2790-0800

Date Received: 2023-12-25
Date Accepted: 2024-08-25
Date Published: 2024-09-30

Thermodynamic investigation of the vapor-liquid equilibrium for isobaric water, acetic acid, and sodium acetate ternary system using modified UNIQUAC mode

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Abstract

In this work a modification of the UNIQUAC model was used to describe the excess Gibbs energy of electrolyte systems; the capability of the model in the correlation of vapor-liquid equilibria (VLE) in water + acetic acid + sodium acetate ternary system was investigated. The modified UNIQUAC model (M–UNIQUAC) is composed of the original UNIQUAC model and the Pitzer–Debye–Hückel (PDH) law. The Peng Robinson equation of state (PR EOS) was applied for the vapor phase calculations. In this work the experimental data at the temperature range of 373.35 to 393.85 ºK were used to obtain the binary interaction parameters; in summary, 173 data points were correlated satisfactorily. The results show that the quality of the model is in good agreement with the experimental data. In this work, a comparison between the M–UNIQUAC and the original UNIQUAC was carried out and it proves that using the M–UNIQUAC model for the liquid phase and PR EOS for vapor phase calculation could be suitable for the correlation of phase behavior in VLE with total Average Absolute Deviation (%AAD) of 7.6%.

Keywords: Vapor-Liquid Equilibrium, Electrolyte System, Modified UNIQUAC Model

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1. Introduction

Phase equilibria of electrolyte systems are of great importance for the different separation processes in chemical industries such as distillation of salt–containing liquids, liquid-liquid extraction of salt mixtures, salt precipitation from mixed solvents, etc. [1-3]; therefore, recently there has emerged an industrial interest in electrolyte systems. The presence of salts in the solution can change the properties of the mixture such as boiling point and the equilibrium composition of the vapor phase; thus, a lot of experimental data is required to obtain the properties of the electrolyte system. Nowadays, a large number of data on mixed solvent electrolyte systems are available. To develop, design, and optimization of chemical plants, thermodynamic models are needed [4]. Theoretically, the correlation of the vapor-liquid equilibria (VLE) for these systems by applying an appropriate thermodynamic model is beneficial. The excess Gibbs energy models such as Wilson, the–random two–liquid (NRTL), TK–Wilson, and UNIQUAC models [1] are widely used to describe the mentioned thermodynamic systems; which have presented good results in some cases. Because of the special interaction between ions, in recent decades various modifications have been proposed to enable these models to correlate and even predict the equilibrium properties of electrolyte systems. As an example, NRTL and electrolyte non–random–two–liquid (eNRTL) equations have been used for the correlation of Vapor-liquid equilibrium (VLE) data by Dongshun et al. [5]. A generalized strong electrolyte LIQUAC model has been also presented to describe the VLE, osmotic coefficients, mean ionic activity coefficients, and solid-liquid equilibria (SLE) for the single and mixed solvent electrolyte systems [6, 7]. To correlate the electrolyte systems, it is better to use thermodynamic models that combine with a term for long-range interactions. Sander and his co-workers combined a term of the Debye–Hückel type with a UNIQUAC equation with concentration-dependent parameters [8] which is known as extended UNIQUAC. The extended UNIQUAC model has been applied to aqueous salt systems to demonstrate its ability to represent the solid-liquid–vapor (SLV) equilibrium and thermal property data [3]. In this way, using the Debye–Hückel law is very useful [9]. In 2010 and 2011 Pirahmadi et al. [10, 11] presented a modified UNIQUAC model to correlate liquid-liquid equilibria (LLE) of electrolyte systems. Recently, Hamta et al. [12] correlated a ternary system composed of water, polyethylene glycol, and sodium carbonate at different temperatures using extended UNIQUAC. It seems that M–UNIQUAC, may also successfully correlate the experimental data of VLE. Therefore, this work aims to examine the M–UNIQUAC model to describe the VLE data of water + acetic acid + sodium acetate ternary systems.

2. Thermodynamic model

To obtain an activity coefficient model for the salt–containing systems the local composition strategy was followed. The model that is used in this work is composed of three distinct contributions; the original UNIQUAC term by Abrams and Prausnitz [13] considers the effect of short-range entropy and enthalpy effects. The contribution of long-range interaction in the electrolyte solution is modeled by the Pitzaer–Debye–

Hückel (PDH) equation [14]. Therefore, the total excess Gibbs free energy can be calculated as follows:

$$\frac{G^E}{RT} = \frac{G^{E,UNIQUAC}}{RT} + \frac{G^{E,PDH}}{RT}$$

(1)

Equation (1), $G^{E,UNIQUAC}$ is the original UNIQUAC equation.

To find the activity coefficient of ions and solvents equations (2) and (3) can be used, respectively.

$$ln\gamma_i^* = ln\gamma_i^{*UNIQUAC} + ln\gamma_i^{*PDH}$$

(2)

$$ln\gamma_j = ln\gamma_j^{UNIQUAC} + ln\gamma_j^{PDH}$$

(3)

Where j and I refer to solvent and ions, and the asterisk determines the activity coefficients of the ions that are defined using the asymmetric convention [10]. The activity coefficient of solvents can be derived by straight–forward differentiation of excess Gibbs function as follows:

$$ln\gamma_j^{PDH} = \frac{2A_x I^{'3/2}}{1+\rho I_x^{'1/2}} + \frac{4I_x A_x}{\rho}\ln\left(1+\rho I_x^{1/2}\right)\left[\frac{1}{2M_s}\frac{\left(M_j - M_s\right)}{\sum_{solvent} x_{solvent}} - \frac{1}{2d_s}\frac{\partial d_s}{\partial x_j} + \frac{3}{2D_s}\frac{\partial D_s}{\partial x_j}\right]$$

(4)

$$ln\gamma_j^{UNIQUAC} = 1 - \frac{\phi_j}{x_i} + \ln\left(\frac{\phi_j}{x_i}\right) - 5q_j\left[\ln\left(\frac{\phi_j}{x_i}\right) + 1 - \frac{\phi_j}{x_i}\right] + q_j\left[1 - \ln\left(\sum_k \theta_k \psi_{kj}\right) - \sum_k \frac{\theta_k \psi_{jk}}{\sum_l \theta_l \psi_{lk}}\right]$$

(5)

The following equations can be used to calculate the asymmetrical activity coefficient of ions:

$$ln\gamma_i^{*PDH} = -\frac{2A_x z_i^2}{\rho}\ln\left(1+\rho I_x^{1/2}\right) - \frac{2A_x I_x^{1/2} z_i^2}{1+\rho I_x^{1/2}}$$

(6)

$$ln\gamma_i^{*UNIQUAC} = ln\gamma_i^{UNIQUAC} - ln\gamma_i^{\infty UNIQUAC}$$

(7)

Activity coefficients at infinite dilution can also be calculated using Eq. (10).

$$ln\gamma_i^{\infty UNIQUAC} = \ln\frac{r_i}{r_w} + 1 - \frac{r_i}{r_w} - 5q_i\left[ln\frac{r_i q_w}{r_w q_i} + 1 - \frac{r_i q_w}{r_w q_i}\right] + q_i\left[1 - \ln\psi_{wi} - \psi_{iw}\right] \qquad (8)$$

Where the ionic strength I_x, and the Debye–Hückel parameter on a mole fraction basis (A_x), are defined as follows:

$$I_x = \frac{1}{2}\sum z_i^2 x_i$$

(9)

$$A_x = \frac{1}{3}\left(\frac{1000}{M_s}\right)^{\frac{1}{2}}\left(\frac{2\pi N_A d_s}{1000}\right)^{\frac{1}{2}}\left(\frac{e^2}{4\pi\varepsilon_0 D_s kT}\right)^{\frac{3}{2}}$$

(10)

In these equations e is the electronic charge, N_A is Avogadro's number, ε_0 is the vacuum permittivity and *k* is Boltzmann's constant.

To calculate the molar mass (M_s), density (d_s), and dielectric constant of mixed solvent (D_s) the following equations can be used.

$$M_s = \sum_j x_j' M_j$$

(11)

$$d_s = \frac{M_s}{\sum_j (x_j' M_j / d_j)}$$

(12)

$$D_s = \sum_j \omega_j' D_j$$

(13)

In Eqs. (14–16) ω_j' and x_j' are the salt-free mass fraction and mole fraction of solvent *j*, and M_j, d_j, and D_j are the molar mass, density, and dielectric constant of solvent *j*. The parameter ρ is related to a hardcore collision diameter or the distance of the closest approach of ions in solution. The ϕ and θ parameters are the surface and volume fractions. These parameters are functions of the size and the volume area parameters *r* and *q*:

$$\phi_i = \frac{x_i r_i}{\sum_i x_i r_i}$$

(14)

$$\theta_i = \frac{x_i q_i}{\sum_i x_i q_i}$$

(15)

Also, ψ_{kj} is defined in terms of the binary energy interaction parameter (a_{kl}):

$$u_{kl} = u_{kl}^0 + u_{kl}^t \left(T - 298.15\right)$$

(16)

$$\psi_{kl} = \exp\left(\frac{-u_{kl} - u_{ll}}{T}\right) = \exp\left(-\frac{a_{kl}}{T}\right)$$

(17)

$$u_{kl}{}^0 = u_{lk}{}^0, u_{kl}{}^t = u_{lk}{}^t, u_{kk}{}^0 = u_{ll}{}^0 \neq 0, u_{kk}{}^t = u_{ll}{}^t \neq 0$$

(18)

Where $a_{kl} \neq a_{lk}$ and $a_{kk} = a_{ll} = 0$ [11].

The structural parameters of the UNIQUAC equation, r_i and q_i, for water, acetic acid, and sodium acetate were taken from Abrams et al.[12], A1–Muhtaseb et al. [15] and Kikic et al. [16], respectively.

3. Results and discussions

In this work, thermodynamic modeling of VLE data is investigated using modified UNIQUAC. The VLE is calculated by using the criteria of chemical potential equality in two phases:

$$\mu_i^I = \mu_i^{II}$$

(19)

Accordingly:

$$x_i \gamma_i P_i^{sat} = y_i \varphi_i P$$

(20)

Where φ_i is the fugacity coefficient of component *I*, P_i^{sat} is the saturation pressure and P is the total pressure of the vapor phase. To calculate the activity coefficient of species in the liquid phase the original UNIQUAC and M–UNIQUAC models were used. For this purpose, binary interaction parameters of species are required. The binary interaction parameters of water + acetic acid + sodium acetate ternary system were determined by using VLE experimental data at atmospheric pressure. The isobaric VLE data was obtained from the experimental data reported by Vercher et al. [17] in the 373–395 K range. The adjustable parameters of the M–UNIQUAC model were fitted to experimental data. It must be mentioned that the Peng–Robinson EOS was applied to the calculation of the fugacity coefficient in the vapor phase. To determine the interaction parameters in the function of temperature, all data in the literature mentioned above was used. The shuffled Complex Evolution (SCE) optimization algorithm was used to adjust the binary interaction parameters of components in the thermodynamic model. To fit the VLE data of the Water + Acetic Acid + Sodium Acetate system the objective function that is defined as follows was minimized [11, 18]:

$$OF_w = \sum_{j=1}^{M}\sum_{i=1}^{N}\left(\left(W_{ij}^{I,cal} - W_{ij}^{I,exp}\right)^2 + \left(W_{ij}^{II,cal} - W_{ij}^{II,exp}\right)^2\right)$$

(21)

Where *M* is the number of tie lines and *N* is the number of components. Also, W_{ij}^k is the mass fraction of component *i* in the phase *k* for *j*–th tie line. Superscripts "*cal*" and "*exp*" represent the calculated values by the model and experimental ones. The correlation of VLE was tested by using the Rachford–Rice flash calculation algorithm.

It must be mentioned that the all parameters in this work are the UNIQUAC parameters and there are no parameters for PDH low and PR EOS. The values of volume (*r*) and surface area (*q*) parameters can be adjusted to the VLE data but to reduce the number of fitting parameters, the *r* and *q* for water and acetic acid were used from the Al–Muhtaseb et al. [15] and the same for sodium and acetate ions were taken from Kikic et al. [16]; These parameters have been shown in Table 1.

Table 1. The volume (r) and surface area (q) parameters for the UNIQUAC model [15, 16]

	water	acetic acid	Na^+	acetate
r	0.92	2.2024	3	2.05
q	1.4	2.072	3	1.9

In the following, the parameters were adjusted and after that, the equilibrium values were calculated. The experimental values were compared with the calculated ones. In each case, the Average Absolute Deviation (*%AAD*) of calculated values from experimental data was determined according to:

$$\%AAD = 100\left(\frac{\sum_{j=1}^{M}\sum_{i=1}^{N}\left(\left(W_{ij}^{I,cal} - W_{ij}^{I,exp}\right)^2 + \left(W_{ij}^{II,cal} - W_{ij}^{II,exp}\right)^2\right)}{2MN}\right)^{\frac{1}{2}}$$

(22)

The M–UNIQUAC interaction parameters for the aqueous solution containing acetic acid and sodium acetate are reported in Table 2 and Table 3. Figure 1 shows the ability of the M–UNIQUAC model to correlate the mentioned system by comparing experimental data and modeling results.

Table 2. $uij^0 = uji^0$ parameters for calculating binary interaction parameters of the modified extended UNIQUAC model for the system containing water + acetic acid + Na^+ + acetate

uij0	water	acetic acid	Na+	acetate
water	3079.397	1425.568	809.419	2075.221
acetic acid	-	1413.164	2551.028	2393.4215
Na+	-	-	126.452	1640.33
acetate	-	-	-	1619.327

Table 3. $uij^t = uji^t$ parameters for calculating binary interaction parameters of the modified extended UNIQUAC model for the system containing water + acetic acid + Na^+ + acetate

uijt	water	acetic acid	Na+	acetate
water	2.661	192.753	219.623	2.919
acetic acid	-	199.23	177.018	207.344
Na+	-	-	730.633	0.0011
acetate	-	-	-	77.49159

As can be seen from Fig.1 the model has predicted the compositions well over the studied temperature range and only trivial deviations between experimental and calculated values are observed.

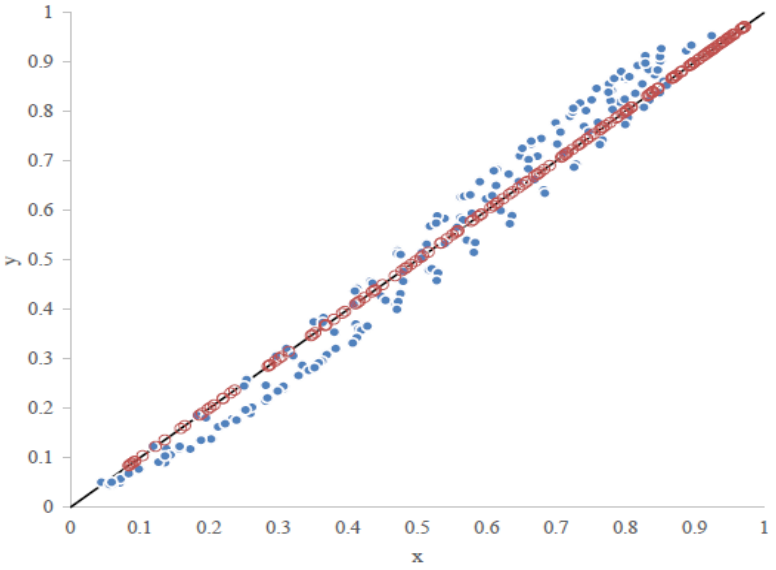


Fig. 1. Experimental and calculated x–y diagram for water + acetic acid + sodium acetate ternary

the system at atmospheric pressure

To study the effect of each term in the mentioned model, a comparison between modified and original UNIQUAC models was carried out. The *%AAD* of all studied models is listed in Table 4. As shown in Table 4, the results of the M–UNIQUAC model that be used in this work, show a good agreement with the experimental data. The value of *%AAD* for Water + Acetic Acid + Sodium Acetate ternary system for M–UNIQUAC is about 7.6%. Therefore, the accuracy of this model is better than other models and it can reproduce the compositions satisfactorily.

Table 4. Average absolute deviation in calculated compositions (see Eq. (25)) for the water + acetic acid + sodium acetate ternary system at atmospheric pressure

	This work	Original UNIQUAC	modified UNIQUAC
%AAD	7.67	10.3	7.35

4. Conclusions

In the present study, the VLE experimental data of the Water + Acetic Acid + Sodium Acetate ternary system were correlated. In this way, the M–UNIQUAC and Peng–Robinson equation of state (PR EOS) were used to calculate the activity coefficient in the liquid phase and fugacity coefficient in the vapor phase, respectively. The result showed that using the original UNIQUAC model correlated the experimental data suitably but the M–UNIQUAC model is better. In this modification, PDH law was used

for considering long-range interactions. To check the ability of this model to correlate the vapor-liquid equilibrium of this system more than 170 data were evaluated. Results show that adding the PDH law has a significant role in reducing the error. It was also proved that the M–UNIQUAC model properly described the VLE of this system at a wide range of temperatures at atmospheric pressure. The average absolute deviation (*%AAD*) of the mentioned model is about 7%, however, the *%AAD* for the original UNIQUAC model is about 10.3%. Therefore, the results indicate that the M–UNIQUAC model can correlate the experimental data satisfactorily.

References

[1] I.-M. Shiah, W.-L. Weng, and M.-C. Wang, "An activity coefficient model for predicting salt effects on vapor–liquid equilibria of mixed solvent systems," *Fluid Phase Equilibria,* vol. 170, pp. 297–308, 2000.

[2] M. C. Iliuta, I. Iliuta, and F. Larachi, "Vapour-liquid equilibrium data analysis for mixed solvent-electrolyte systems using neural network models," *Chemical Engineering Science,* vol. 55, pp. 2813-2825, 2000.

[3] M. C. Iliuta, K. Thomsen, and P. Rasmussen, "Extended UNIQUAC model for correlation and prediction of vapour-liquid-solid equilibria in aqueous salt systems containing non-electrolytes. Part A. Methanol-water-salt systems," *Chemical Engineering Science,* vol. 55, pp. 2673-2686, 2000.

[4] P. Moilanen, P. Uusi-Kyyny, J.-P. Pokki, M. Pakkanen, and J. Aittamaa, "Vapor–Liquid Equilibrium for Butane + Methanol, + Ethanol, + 2-Propanol, + 2-Butanol, and + 2-Methyl-2-Propanol (TBA) at 323 K," *Journal of Chemical & Engineering Data,* vol. 53, pp. 83-88, 2008/01/01 2008.

[5] D. Dongshun, W. Rufa, Z. Lianzhong, G. Yun, and J. Jianbing, "Vapor-Liquid Equilibrium Measurements and Modeling for Ternary System Water + Ethanol + 1-Butyl-3-methylimidazolium Acetate," *Chinese Journal of Chemical Engineering,* vol. 19, pp. 703-708, 2011.

[6] M.-Y. Li, L.-S. Wang, B. Jiang, and J. Gmehling, "Generalized LIQUAC Model for the Single- and Mixed-Solvent Strong Electrolyte Systems," *AIChE Journal,* vol. 57, pp. 2535-2546, 2010.

[7] W. Yan, M. Topphoff, C. Rose, and J. Gmehling, "Prediction of vapor–liquid equilibria in mixed-solvent electrolyte systems using the group contribution concept," *Fluid Phase Equilibria,* vol. 162, pp. 97-113, 1999.

[8] B. Sander, A. Fredenslund, and P. Rasmussen, "calculation of Vapor-Liquid equilibria in mixed solvent/salt system using an extended UNIQUAC equation," *Chemical Engineering Science,* vol. 41, pp. 1171-1183, 1986.

[9] B. Sander, A. Fredenslund, and P. Rasmussen, "Calculation of vapour-liquid equilibria in mixed solvent/salt systems using an extended UNIQUAC equation," *Chemical Engineering Science,* vol. 41, pp. 1171-1183, 1986/01/01 1986.

[10] F. Pirahmadi, M. R. Dehghani, and B. Behzadi, "Experimental and theoretical study on liquid–liquid equilibrium of 1-butanol + water + NH4Cl at 298.15, 308.15 and 318.15 K," *Fluid Phase Equilibria,* vol. 325, pp. 1-5, 2012.

[11] F. Pirahmadi, M. R. Dehghani, B. Behzadi, S. M. Seyedi, and H. Rabiee, "Experimental and theoretical study on liquid-liquid equilibrium of 1-butanol + water +NaNO3 at 25 and 35 C," *Fluid Phase Equilibria,* vol. 299, pp. 122-126, 2010.

[12] A. Hamta, M. R. Dehghani, M. Gholami, "Novel experimental data on aqueous two–phase system containing PEG–6000 and Na2CO3 at T = (293.15, 303.15 and 313.15) K". Journal of Molecular Liquids.

[13] D. S. Abrams and J. m. Prausnitz, "Statistical thermodynamics of liquid mixtures: A new expression for the excess gibbs energy of partly or completely miscible systems," *AIChE Journal,* vol. 21, pp. 116-128, 1975.

[14] K. S. Pitzer, "Electrolytes. From Dilute Solutions to Fused Salts," *Journal of the American Chemical Society,* vol. 102, pp. 2902-2906, 1980.

[15] S. A. Al-Muhtaseb and M. A. Fahim, "Phase equilibria of the ternary system water/acetic acid/2-pentanol," *Fluid Phase Equilibria,* vol. 123, pp. 189-203, 1996.

[16] I. Kikic, M. Fermeglia, and P. Rasmussen, "Unifac prediction of vapor—liquid equilibria in mixed solvent—salt systems," *Chemical Engineering Science,* vol. 46, pp. 2775-2780, 1991.

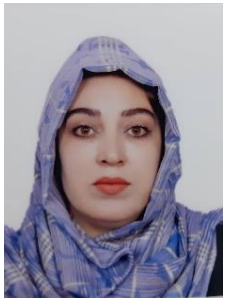
[17] E. Vercher, M. I. Vázquez, and A. Martínez-Andreu, "Isobaric Vapor-Liquid Equilibria for Water + Acetic Acid + Sodium Acetate," *Journal of Chemical & Engineering Data*, vol. 48, pp. 217-220, 2003.

[18] R. C. Basso, F. H. Miyake, A. J. d. A. Meirelles, and E. A. C. Batista, "Liquid–liquid equilibrium data and thermodynamic modeling, at T/K = 298.2, in the washing step of ethyl biodiesel production from crambe, fodder radish and macauba pulp oils," *Fuel*, vol. 117, pp. 590-597, 2014.

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