Purification of Phosphoric Acid by Liquid-Liquid Equilibrium

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Additional information is available at the end of the chapter

Abstract

Various ternary and quaternary liquid-liquid phase equilibrium data for water + phosphoric acid + solvent(s) have been reported. Salting-out, solvent, and temperature effects on the binodal curve and the tie lines have been highlighted and the capability of solvents with different functional groups to extract phosphoric acid from water has been compared. Studying of influence of magnetic, electromagnetic, and ultrasonic fields on the separation factors and distribution coefficients of aqueous phosphoric acid mixtures has been proposed. Moreover, a summary of the optimized binary interaction values, which resulted from non-random two-liquid (NRTL) and universal quasi-chemical (UNIQUAC) thermodynamic models using genetic algorithm (GA), bee algorithm (BA), and simulated annealing (SA), has been presented. Group method of data handling (GMDH) and linear solvation energy relationship (LSER) methods for the correlation of experimental liquid-liquid equilibrium (LLE) data have been used.

Keywords: phosphoric acid, LLE, optimization algorithms, GMDH, LSER

1. Introduction

The phosphoric acid due to its potential applications in various industries attracted a great deal of attention in the area of petrochemical operations, pharmaceutical productions, food industry, detergents, insecticides, and agricultural fertilizers. Generally, there are two basic methods in commercial use for the production of phosphoric acid—thermal and wet processes. The thermal process produces a pure acid with huge energy consumption, whereas the wet process is economic and practiced everywhere in the world [1]. Nevertheless, phosphoric acid produced from both methods contains a variety of impurities, which could affect quantity and the quality of the product. Therefore, for efficient removal and decreasing the impurities to below acceptable regulatory levels, not only suitable studies but also using and developing

new different techniques and technologies are required. For this purpose, some of the common selective methods such as liquid-liquid extraction, solid-liquid extraction, crystallization, concentration, addition of additives, and so on, have been investigated [2–4].

Liquid-liquid extraction or solvent extraction is now one of the most important and widely employed separation techniques in the modern process industries. It is well known due to various practical characteristics, including simplicity, rapid method development, and reasonable selectivity. Moreover, it can be used for several purposes, for instance, to separate the systems with similar boiling points, high boiling points, and temperature-sensitive components [2].

Success of liquid-liquid extraction and accurate understanding of the performance of that is measured through the liquid-liquid equilibrium (LLE) data. LLE is described with the separation of components of a feed solution, containing the carrier and extract components, using an additional liquid solvent, as the mixture of feed and solvent—if enough solvent is added—forms two immiscible liquid phases. LLE is based on the differences in solubility and equilibrium distribution of these components between the two produced immiscible—or partially miscible—phases. In other words, it depends on the mass transfer of the component to be extracted from the carrier to the solvent. For having an effective extraction, the extract component should more preferably dissolve in the solvent. After settling the two phases, the raffinate and the extract phases are formed. The raffinate phase contains mostly the carrier, as well as a residue of the extracted component and solved solvent, whereas the extract phase consists of the main the solvent, a part of the extracted component, and solved carrier. Solvent extraction is a separation process aiming to purify the feed or to recover one or more components from it [5]. Nowadays, enormous amounts of acid, specifically high-purity phosphoric acid, can be commercially produced through liquid-liquid equilibrium process.

2. Phase diagram of multicomponent liquid mixtures: measurement and visualization

Only systems with at least three components and a miscibility gap can be used for extractions. Phase behavior of such systems at a constant temperature and pressure is conveniently represented on an equilateral triangular diagram, which its corners indicate the pure components, binary compositions are along the edges, and ternary mixtures are located inside the triangle. A common phase diagram is type I system and shown in **Figure 1**, where a pair of components propylene carbonate and water are partially miscible, and liquid phosphoric acid dissolves completely in propylene carbonate or water [6]. In this figure, the boundaries that each one of them separates the single-phase region from the two-phase region are named binodal (solubility) curves. The two-phase region is included inside below the curved envelope. The binodal curve results are determined by cloud-point titration method [7]. According to this method, a binary mixture of known composition was titrated with the third component at each mixture using non-sealed glass vessels. The transition point is taken as the appearance/disappearance of turbidity in the sample and it is defined as a cloud point. The mixture temperature is regulated by a thermostatic thermometer with an accuracy of ± 0.1 K. Every point on the binodal curve also has another corresponding point on the binodal curve, as these two points represent the phase equilibrium. The lines between these two equilibrium points
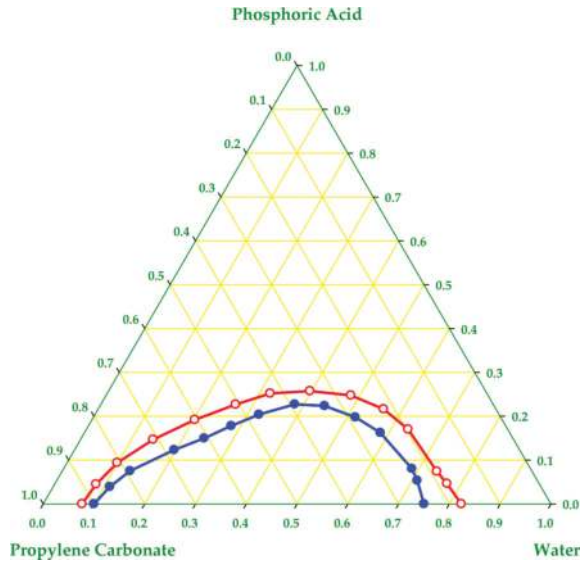
Figure 1. Binodal curves for (water + phosphoric acid + propylene carbonate) mixture at two different temperatures and atmospheric pressure: (-O-) T = 298.2 K, and (-●-) T = 318.2 K [6].

are called tie lines. The tie lines are usually not parallel and their slopes can increase and decrease drastically. Tie line experiments were carried out in a jacketed 150 ml glass cell. The biphasic mixture with known compositions was placed in the extraction cell and was vigorously agitated by a magnetic stirrer for 4 h, and then left to settle for minimum 4 h for phase
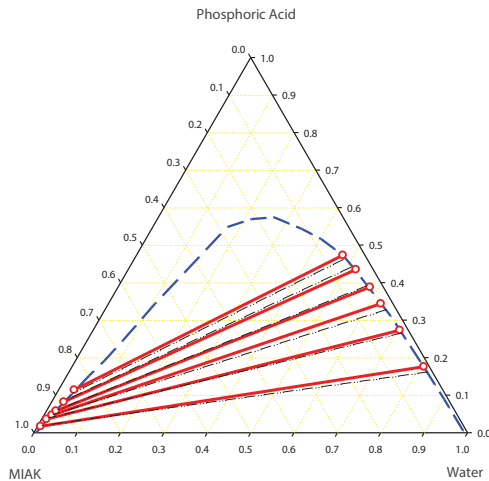
Figure 2. Tie lines of the system water + phosphoric acid + MIAK at two different temperatures and atmospheric pressure: (-O-) T = 308.2 K, and (-··-), T = 318.2 K [9].

separation. After separation, samples of both phases were transparent and were carefully weighed and analyzed to determine their compositions. Then, the concentrations of the acid in both the phases were obtained by potentiometric NaOH titration [6]. Besides, the water content of the organic phase was measured by the Karl-Fisher method [6] and the water contained in the aqueous layer was determined using refractive index measurement method [8]. The obtained tie line data for (water + phosphoric acid + methyl isoamyl ketone (MIAK)) [9] and (water + phosphoric acid + dichloromethane (DCM)) [10] ternary systems are presented in **Figure 2** and **Table 1**, respectively. As either the temperature or pressure is varied, the location of the binodal curve and slopes of the tie lines may change (see **Figures 1** and **2**).

Aqueous phase (raffinate) mass percent			Organic phase (extract) mass percent			D_1	D_2	S
W_{11}	W_{21}	W_{31}	W_{13}	W_{23}	W_{33}			
70.48	15.00	14.52	6.14	1.40	92.46	0.087	0.093	1.071
66.82	16.39	16.79	6.49	1.67	91.84	0.097	0.101	1.049
58.19	19.78	22.03	6.60	2.01	91.39	0.113	0.102	0.896
50.89	23.28	25.83	6.78	2.92	90.30	0.133	0.125	0.941
45.74	24.33	29.93	6.80	3.31	89.89	0.149	0.136	0.915

[*]GMDH is used to predict the tie lines.

Table 1. Calculated tie line data, distribution coefficient, and separation factor for the ternary system of water (1) + phosphoric acid (2) + DCM (3), according to the GMDH[*] results [10].

3. Separation factor and distribution coefficients

In order to evaluate the extracting capability of the solvent for the separation of components from feed solutions with liquid-liquid extraction, the separation factor, S, is calculated. The separation factor is defined as the ratio of distribution coefficients of extract component, 2, to carrier one, 1, $S = D_2/D_1$. Additionally, distribution coefficient is the ratio of concentrations of a component in a mixture of two immiscible phases at equilibrium. This ratio is therefore a measure of the difference in the component solubilities in these two phases (see **Table 1**). Depending on the system, the distribution coefficient and separation factor can be a function of temperature, the concentration of chemical species in the system, and a large number of other parameters. **Figure 3** gives the distribution coefficient as a function of the mass percent of phosphoric acid in aqueous phase for water + phosphoric acid + mixed-solvent (dichloromethane + 1,2-dichloroethane (DCE)) system at different ratios of mixed solvent [11]. Generally, if the separation factor is greater than one ($S > 1$) for the systems investigated, it means that the component can be extracted by the proposed solvent—for example, according to the reported S for studied system in **Table 1**, DCM can be considered as a possible candidate for the recovery of the aqueous phosphoric acid solutions.
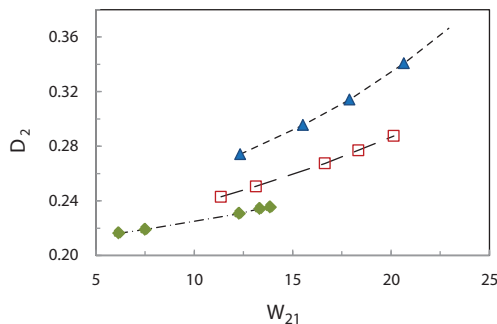
Figure 3. Distribution coefficients D2 of phosphoric acid as a function of the mass percent W_{21} of acid in aqueous phase for NRTL LLE data of {water + phosphoric acid + mixed-solvent (DCM + DCE)} system at temperature T = 298.15 K: (25% DCM + 75% DCE); ◆, (50% DCM + 50% DCE); □, (75% DCM + 25% DCE); ▲ [11].

In recent years, significant investigations on LLE measurements and the extraction of phosphoric acid from aqueous solutions have been carried out, while many solvents have mainly been tested, in order to understand and provide further information for accurate interpretation of phase equilibria of the different multicomponent mixtures with phosphoric acid [12–27]. As a detailed evaluation of extraction abilities of the different solvents reported in the literature, including alcohols, esters, ethers, ketones, and hydrocarbons to extract phosphoric acid from aqueous solutions, a comparative study is listed in **Table 2**. **Figure 3** also highlights the definitive effects of different chemical structures present in solvents on recovering of the acid. As it is drawn, results show the following order of effectiveness of solvent for systems containing phosphoric acid: methylcyclohexane > ethyl benzene > isoamyl acetate > n-pentane > 1-octanol > bis(2-methylpropyl) ether. From the obtained experimental results, it can be concluded that methylcyclohexane is the most appropriate solvent for the separation of a mixture of water and phosphoric acid. It is also apparent from **Figure 4** that bis(2-methylpropyl) ether is a less favorable solvating agent for phosphoric acid.

In addition, the presence of dissolved salt changes the phase equilibrium behavior of a mixture significantly [28–31]. Recently, Govindarajan and Sabarathinam [32], Mohsen-Nia et al. [33], and Santos et al. [34] have investigated effects of some inorganic salts such as Na_2SO_4, $ZnSO_4$, $(NH_4)_2SO_4$, NaCl, KCl, KBr, and $NaNO_3$ on the ternary liquid-liquid equilibria data. Similarly, by considering the importance of the salting effect on the extraction of phosphoric acid from aqueous mixtures, it is worthwhile to study LLE of mixtures of (water + phosphoric acid + solvent + salt). In particular, as can be seen in **Table 2**, maximum values of separation factor for (water + phosphoric acid + DCM + 10 wt% NaCl and 10 wt% $CaCl_2$) solutions are improved compared with those in the absence of added salts [26].

Although solvents with high separation are considered as potential candidates to carry out the extraction, due to the economic, environmental, and technical factors, the suitable solvent at optimum conditions is proposed to be chosen for the extraction of phosphoric acid from aqueous mixtures. Meanwhile, it seems that the measurement of the (liquid + liquid) equilibrium data of

System	Solvent type	T/K	S	Ref.
Water + phosphoric acid + 1-butanol	Alcohol	308.2	1.65	[12]
Water + phosphoric acid + 2-methyl-2-butanol	Alcohol	298.2	1.82	[13]
Water + phosphoric acid + isoamy1 alcohol	Alcohol	308.2	1.82	[14]
Water + phosphoric acid + 2-ethyl-1-hexanol	Alcohol	298.2	1.46	[15]
Water + phosphoric acid + 1-octanol	Alcohol	298.2	6.35	[16]
Water + phosphoric acid + 1-nanonol	Alcohol	298.2	3.54	[17]
Water + phosphoric acid + 1-decanol	Alcohol	303.2	3.80	[18]
Water + phosphoric acid + 1-dodecanol	Alcohol	303.2	4.30	[18]
Water + phosphoric acid + cyclohexanol	Alcohol, cyclic alcohol	308.2	1.57	[14]
Water + phosphoric acid + 1-dodecanethiol	Thiol, aliphatic thiol	303.2	18.20	[18]
Water + phosphoric acid + butyl acetate	Ester	308.2	5.78	[12]
Water + phosphoric acid + isobutyl acetate	Ester	298.2	7.46	[13]
Water + phosphoric acid + isoamyl acetate	Ester	298.2	19.70	[9]
Water + phosphoric acid + hexyl acetate	Ester	298.2	7.00	[19]
Water + phosphoric acid + cyclohexyl acetate	Ester	298.2	6.20	[19]
Water + phosphoric acid + propylene carbonate	Ester	298.2	2.82	[6]
Water + phosphoric acid + tributyl phosphate	Ester	298.2	3.40	[20]
Water + phosphoric acid + diisopropyl ether	Ether	293.2	1.89	[21]
Water + phosphoric acid + bis(2-methylpropyl) ether	Ether	298.2	3.76	[22]
Water + phosphoric acid + n-pentane	Hydrocarbon	308.2	15.08	[23]
Water + phosphoric acid + 2-methylpentane	Hydrocarbon	308.2	3.36	[23]
Water + phosphoric acid + n-hexane	Hydrocarbon	308.2	4.60	[23]
Water + phosphoric acid + cyclohexane	Hydrocarbon, cycloalkane	308.2	15.30	[24]
Water + phosphoric acid + methyl cyclohexane	Hydrocarbon, cycloalkane	308.2	43.10	[24]
Water + phosphoric acid + toluene	Hydrocarbon, aromatic hydrocarbon	308.2	26.50	[24]
Water + phosphoric acid + ethyl benzene	Hydrocarbon, aromatic hydrocarbon	298.2	32.70	[25]
Water + phosphoric acid + isopropyl benzene	Hydrocarbon, aromatic hydrocarbon	298.2	23.70	[25]
Water + phosphoric acid + dichloromethane (DCM)	Halogenated aliphatic hydrocarbon	298.2	1.04	[26]
Water + phosphoric acid + DCM + 10 wt% NaCl	Halogenated aliphatic hydrocarbon + salt	298.2	2.20	[26]
Water + phosphoric acid + DCM + 10 wt% $CaCl_2$	Halogenated aliphatic hydrocarbon + salt	298.2	1.39	[26]
Water + phosphoric acid + 1,2-dichloroethane (DCE)	Halogenated aliphatic hydrocarbon	298.2	1.10	[26]
Water + phosphoric acid + DCE + 10 wt% NaCl	Halogenated aliphatic hydrocarbon + salt	298.2	2.35	[26]
Water + phosphoric acid + DCE + 10 wt% $CaCl_2$	Halogenated aliphatic hydrocarbon + salt	298.2	2.13	[26]
Water + phosphoric acid + methyl isobutyl ketone	Ketone	308.2	1.26	[14]
Water + phosphoric acid + methyl isoamyl ketone	Ketone	298.2	11.00	[9]
Water + phosphoric acid + methyl ethyl ketone	Ketone	308.2	0.91	[27]

Table 2. The maximum values of separation factors for the (water + phosphoric acid + solvent) ternary systems.
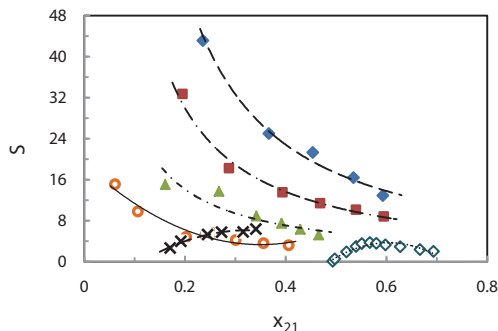
Figure 4. The effects of solvents with various functional groups on separation factor S for {water + phosphoric acid + solvent} system at mentioned temperature: (methylcyclohexane, 308.2 K [24]), ◆; (ethyl benzene, 298.2 K [25]), ■; (isoamyl acetate, 308.2 K [9]), ▲; (n-pantane, 308.2 K [23]), ○; (1-octanol, 298.2 K [16]), ✕; bis(2-methylpropyl) ether, 298.2 K [22]), ◇.

the mixtures with a mixed solvent has become the turning point topic of the chemistry investigations in recent years [11, 35–42]. As an illustration, **Figure 3** compares distribution coefficients of phosphoric acid for three quaternary systems of (water + phosphoric acid + mixed solvent (25% DCM + 75% DCE) or (50% DCM + 50% DCE) or (75% DCM + 25% DCE)) [11]. The results confirm the different effects of the dichloromethane as co-solvent on 1,2-dichloroethane for the extraction of phosphoric acid from aqueous mixtures. The comparison between the experimental separation factors obtained for the mixed solvent (DCM + DCE) with various ratios also indicates that mixed solvent (25% DCM, 75% DCE) has a higher separation factor than the other mixed solvents at $T = 298.15$ K, which means that the extraction of phosphoric acid by mixed solvent (25% DCM, 75% DCE) is more suitable.

Besides, it is anticipated that the magnetic, electromagnetic, and ultrasonic fields as external factors can affect LLE data by influencing solvents properties such as polarity and permittivity, especially for polar solvents. Therefore, the application of them to the phase separation in the solvent extraction process has been considered from the technical and economical viewpoints. For studying this purpose, the effect of the applied different fields on phase behavior of several ternary systems has been obtained and reported [43–48]. There are a number of effective potentials for future research to evaluate the effects of the magnetic, electromagnetic, and ultrasonic fields on the extraction of phosphoric acid from aqueous mixtures.

The linear solvation energy relationship (LSER) models [49] such as Kamlet (Eq. (1)) and Katritzky (Eq. (2)) equations [50, 51] were used to correlate separation factor for several ternary LLE systems with phosphoric acid, reporting in references [16, 19, 24]. Kamlet LSER model with the solvatochromic parameters is defined according to the following equation:

$$\log S = \log S_0 + s(x\pi^* + dx\delta) + ax\alpha + bx\beta \tag{1}$$

where π^* is a measure of solvent dipolarity/polarizability, δ is a discontinuous polarizability correction term, α is a measure of the solvent hydrogen-bond donor acidity, and β is a measure

of the hydrogen-bond acceptor basicity. The coefficients S_0, s, d, a, and b include the properties of solute and are derived from regression. The values of Kamlet-Taft solvatochromic parameters (α, β, and π^*) of the solvents are obtained from literature [49].

Katritzky [51] introduced a multiparameter polarity scale with combination of Riechardt's solvent polarity, E_T^N, the dielectric constant, ε, and the index of refraction, n, functions. The Katritzky equation (Eq. (2)) allows one to estimate independent description of solvent dipolarity, polarizability, and specific interactions (such as hydrogen bonding, π-π interaction). The coefficients, a, b, c, and d measure the relative susceptibilities of log (S) to the indicated solvent parameters and are regressed using experimental data. E_T^N, ε, and n values of solvents are also present in literature [49]. A modified form of the Katritzky equation may be used, consisting of the addition of a dimensionless term as T/298.2 that characterizes temperature effect

$$\log S = \log S_0 + a \cdot E_T^N + b \cdot \left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right) + c \cdot \left(\frac{n^2 - 1}{2n^2 + 1}\right) + d \cdot \left(\frac{T}{298.2}\right) \tag{2}$$

The LSER model values showed a good regression of the experimental data for all investigated systems. The temperature susceptibility coefficient, d, shows that all the systems in references [24] are temperature sensitive.

4. LLE correlation

Various thermodynamic models with different abilities can be used to accurately describe the multicomponent LLE systems. Aided by these activity coefficient equations and a parameter fit, it is possible to reproduce the measurement and control the data. The non-random two-liquid (NRTL) [52] and the universal quasi-chemical (UNIQUAC) [53] methods have been successfully applied for the correlation of many ternary and quaternary liquid-liquid phase equilibrium solutions [12, 16–19, 24–26], while a group contribution approach (UNIFAC) [54] may be utilized to predict the LLE mixtures.

4.1. NRTL equation

The basic idea in NRTL equation follows from the concept of local composition which was used by Renon and Prausnitz [52]. Renon's equation is applicable to partially miscible liquid mixtures, and for the binary mixtures the excess Gibbs energy is

$$\frac{G^E}{RT} = x_1 x_2 \left(\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}}\right) \tag{3}$$

where

$$G_{12} = \exp\left(-\alpha_{12}\tau_{12}\right); \ G_{21} = \exp\left(-\alpha_{21}\tau_{21}\right) \tag{4}$$

$$\tau_{12} = \frac{g_{12} - g_{22}}{RT} \ ; \ \tau_{21} = \frac{g_{21} - g_{11}}{RT} \tag{5}$$

The significance of g_{ij} is an energy parameter characteristic of the *i-j* interaction. Parameter α_{12} is related to the nonrandomness in the mixture; when α_{12} is zero, the mixture is completely random and Eq. (1) reduces to the two-suffix Margules equation [55]. The NRTL equation contains three parameters, but reduction of experimental data for a large number of binary systems indicates that α_{12} varies from about 0.20 to 0.47; when experimental data are scarce, the value of α_{12} can often be set arbitrarily; a typical choice is $\alpha_{12} = 0.3$. From Eq. (3), the activity coefficients are

$$\ln\gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right] \tag{6}$$

$$\ln\gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right] \tag{7}$$

For strongly nonideal mixtures and especially for partially immiscible systems [56], the NRTL equation often provides a good representation of experimental data if care is exercised in data reduction to obtain the adjustable parameters.

The equations discussed are readily to as many components as desired without any additional assumptions and without introducing any constants other than those obtained from binary data. For a solution of *m* components, the NRTL equation is

$$\frac{G^E}{RT} = \sum_{i=1}^{m} x_i \frac{\sum_{j=1}^{m} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{m} G_{li} x_1} \tag{8}$$

where

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT}, \qquad \tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} \tag{9}$$

$$G_{ji} = \exp\left(-\alpha_{ji}\tau_{ji}\right) \quad (\alpha_{ji} = \alpha_{ij}) \tag{10}$$

The activity coefficient for any component *i* is given by

$$\ln\gamma_i = \frac{\sum_{j=1}^{m} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{m} G_{li} x_l} + \sum_{j=1}^{m} \left[\frac{x_j G_{ij}}{\sum_{l=1}^{m} G_{ij} x_l} \left(\tau_{ij} - \frac{\sum_{r=1}^{m} x_r \tau_{rj} G_{rj}}{\sum_{l=1}^{m} G_{lj} x_l} \right) \right] \tag{11}$$

Eqs. (8) and (11) contain only parameters obtained from binary data. The experimental tie line LLE data of multicomponent mixtures can be correlated using the NRTL model within well-known simulation software such as Aspen Plus. The quality of the correlation is measured by the root-mean-square deviation (RMSD) [16]. Many NRTL LLE values for the ternary and quaternary systems containing water, phosphoric acid, and solvent have appeared in the

i-j	A_{ij}(K) *	A_{ji}(K)
1–2	7.01	62.86
1–3	996.58	334.13
2–3	230.64	270.65

*g_{ij} (J mol^{-1}) = A_{ij} (K)/RT.

Table 3. Correlated LLE results from the NRTL ($\alpha_{12} = 0.3$) model using SA; the corresponding binary interaction parameters, A_{ij} and A_{ji}, for ternary system water (1) + phosphoric acid (2) + DCE (3) + 10 wt% CaCl$_2$ at temperature $T = 298.15$ K.

i-j	A_{ij}(K)	A_{ji}(K)
1–2	2492.75	−419.50
1–3	2303.05	1212.55
1–4	7.56	−3652.94
2–3	2466.50	4329.12
2–4	−2316.04	−2817.74
3–4	−854.74	−3413.39

Table 4. NRTL ($\alpha_{12} = 0.3$) interaction parameters, A_{ij} and A_{ji}, using BA for quaternary LLE system water (1) + phosphoric acid (2) + (50% DCM (3) + 50% DCE (4)) at temperature $T = 298.15$ K.

available literature [11, 16, 17]. For example, in **Figure 3**, the calculated NRTL data have been used to plot and show the variation of distribution coefficients of acid for (water + phosphoric acid + mixed-solvent (DCM + DCE)) system at temperature $T = 298.15$ K. Furthermore, several optimization algorithms such as genetic algorithm (GA) [57], bee algorithm (BA) [58], and simulated annealing (SA) [59] can be applied to predict the binary interaction parameters. As can be seen in **Table 3**, the SA and NRTL models have been used to estimate the optimized binary interaction parameters for an aqueous ternary system containing phosphoric acid [60]. **Table 4** reports 12 NRTL binary interaction parameters obtained using BA for the quaternary aqueous mixture including phosphoric acid and (50% DCM + 50% DCE) [61].

4.2. UNIQUAC equation

A critical examination of the derivation of the NRTL equation shows that this equation is more suitable for H^E than G^E [53]. Abrams derived an equation that, in a sense, extends the quasi-chemical theory of Guggenhiem [56] for nonrandom mixtures to solutions containing molecules of different size. This extension was therefore called the universal quasi-chemical theory or, in short, UNIQUAC. The UNIQUAC equation for G^E consists of two parts: a combinatorial part that attempts to describe the dominant entropic contribution and a residual part that is due primarily to intermolecular forces that are responsible for the enthalpy of mixing. The combinatorial part is determined only by the composition and by the sizes and shapes of the molecules; it requires only pure-component data. The residual part, however, depends also on

intermolecular forces; the two adjustable binary parameters, therefore, appear only in the residual part. The UNIQUAC equation is

$$\frac{G^E}{RT} = \left(\frac{G^E}{RT}\right)_{combinatorial} + \left(\frac{G^E}{RT}\right)_{residual} \tag{12}$$

For a binary mixture,

$$\left(\frac{G^E}{RT}\right)_{combinatorial} = x_1 \ln\frac{\Phi_1}{x_1} + x_2 \ln\frac{\Phi_2}{x_2} + \frac{z}{2}\left(x_1 q_1 \ln\frac{\theta_1}{\Phi_1} + x_2 q_2 \ln\frac{\theta_2}{\Phi_2}\right) \tag{13}$$

$$\left(\frac{G^E}{RT}\right)_{residual} = -x_1 q'_1 \ln\left(\theta'_1 + \theta'_2 \tau_{21}\right) - x_2 q'_2 \ln\left(\theta'_2 + \theta'_1 \tau_{12}\right) \tag{14}$$

where the coordination number z is set equal to 10. Segment fraction, Φ, and area fraction, θ and θ', are given by

$$\Phi_1 = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2}, \qquad \Phi_2 = \frac{x_2 r_2}{x_1 r_1 + x_2 r_2} \tag{15}$$

$$\theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2}, \qquad \theta_2 = \frac{x_2 q_2}{x_1 q_1 + x_2 q_2} \tag{16}$$

$$\theta'_1 = \frac{x_1 q'_1}{x_1 q'_1 + x_2 q'_2}, \qquad \theta'_2 = \frac{x_2 q'_2}{x_1 q'_1 + x_2 q'_2} \tag{17}$$

where

$$l_j = \frac{z}{2}(r_j - q_j) - (r_j - 1) \tag{18}$$

Parameters r, q, and q' are pure component molecular structure constants depending on molecular size and external surface areas. In the original formulation, $q = q'$. To obtain better agreement for systems containing water or lower alcohols, q' values for water and alcohols were adjusted empirically by Anderson [62] to give an optimum fit to a variety of systems containing these components. For alcohols, the surface of interaction q' is smaller than the geometric external surface q, suggesting that intermolecular attraction is dominated by the OH group (hydrogen bonding). For fluids other than water or lower alcohols, $q = q'$.

For each binary mixture, there are two adjustable parameters, τ_{12} and τ_{21}. These, in turn, are given in terms of characteristic energies Δu_{12} and Δu_{21}, by

$$\tau_{12} = \exp\left(-\frac{\Delta u_{12}}{RT}\right) \equiv \exp\left(-\frac{a_{12}}{T}\right) \tag{19}$$

$$\tau_{21} = \exp\left(-\frac{\Delta u_{21}}{RT}\right) \equiv \exp\left(-\frac{a_{21}}{T}\right) \tag{20}$$

For many cases, Eqs. (19) and (20) give the primary effect of temperature on τ_{12} and τ_{21}. Characteristic energies Δu_{12} and Δu_{21} are often only weakly dependent on temperature.

$$\ln\gamma_1 = \ln\frac{\Phi_1}{x_1} + \frac{z}{2}q_1 ln\frac{\theta_1}{\Phi_1} + \Phi_1\left(l_1 - \frac{r_1}{r_2}l_2\right) - q_1'\ln(\theta_1' + \theta_2'\tau_{21}) + \theta_2'q_1'\left(\frac{\tau_{21}}{\theta_1' + \theta_2'\tau_{21}} - \frac{\tau_{12}}{\theta_2' + \theta_1'\tau_{12}}\right)$$
(21)

$$\ln\gamma_2 = \ln\frac{\Phi_2}{x_2} + \frac{z}{2}q_2 ln\frac{\theta_2}{\Phi_2} + \Phi_2\left(l_2 - \frac{r_2}{r_1}l_1\right) - q_2'\ln(\theta_2' + \theta_1'\tau_{12}) + \theta_1'q_2'\left(\frac{\tau_{12}}{\theta_2' + \theta_1'\tau_{12}} - \frac{\tau_{21}}{\theta_1' + \theta_2'\tau_{21}}\right)$$
(22)

For a multicomponent system, the UNIQUAC equation for the molar excess Gibbs energy is given by the sum of

$$\frac{G^E(\text{combinatorial})}{RT} = \sum_{i=1}^{m} x_i\ln\frac{\Phi_i}{x_i} + \frac{z}{2}\sum_{i=1}^{m} q_i x_i\ln\frac{\theta_i}{\Phi_i}$$
(23)

and

$$\frac{G^E(\text{residual})}{RT} = -\sum_{i=1}^{m} q_i' x_i\ln\left(\sum_{j=1}^{m} \theta_j'\tau_{ji}\right)$$
(24)

where segment fraction Φ and area fractions θ and θ' are given by

$$\Phi_i = \frac{x_i r_i}{\sum_j x_j r_j}, \qquad \theta_i = \frac{q_i x_i}{\sum_{j=1}^{m} q_j x_j}, \qquad \theta_i' = \frac{q_i' x_i}{\sum_{j=1}^{m} q_j' x_j}$$
(25)

The activity coefficient for any component i is given by

$$\ln\gamma_i = \ln\frac{\Phi_i}{x_i} + \frac{z}{2}q_i\ln\frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i}\sum_{j=1}^{m} x_j l_j - q_i'\ln\left(\sum_{j=1}^{m} \theta_j'\tau_{ji}\right) + q_i' - q_i'\sum_{j=1}^{m} \frac{\theta_j'\tau_{ij}}{\sum_{k=1}^{m} \theta_k'\tau_{kj}}$$
(26)

i-j	$u_{ij}(\text{J mol}^{-1})$	$u_{ji}(\text{J mol}^{-1})$
1–2	3589.99	−2835.91
1–3	909.55	4182.19
2–3	3043.92	−4435.44
*$r_1 = 0.920$, $r_2 = 3.000$, $r_3 = 4.827$		*$q_1 = 1.400$, $q_2 = 4.000$, $q_3 = 4.196$

*r_i and q_i are the UN1QUAC structural parameters.

Table 5. Optimized UNIQUAC binary interaction energy parameters, u_{ij} and u_{ji}(J mol^{-1}), for water (1) + phosphoric acid (2) + butyl acetate (3) ternary system at $T = 308.2$ K [12].

The molecular interaction-based model of UNIQUAC successfully has correlated many LLE data of ternary and quaternary systems [10, 15–17, 24] within Aspen Plus—for example, see **Table 5**; however, as previously mentioned, during the last 10 years, many LLE-based algorithm—GA, SA, and BA—have been developed and introduced in the literature [57, 60, 61]. Recently, a study on *improved binary parameters using GA for ternary mixtures: UNIQUAC model* has been carried out by Hamidi [63].

4.3. GMDH-type neural network

It is observed that usually LLE measurements are successfully correlated using common models such as NRTL and UNIQUAC. However, these conventional thermodynamic methods for data prediction of complex systems are tedious and involve a certain amount of empiricism. Recently, a new prediction method, the group method of data handling, was developed to predict LLE and VLE data in order to avoid these limitations [64, 65]. Namely, the GMDH tie line data for the ternary system of water + phosphoric acid + dichloromethane have been illustrated in **Table 1** [10, 26]. Furthermore, the reliability of the presented tie line results can be tested through the Othmer-Tobias [66] and Bachman [67] correlation equations.

Acknowledgements

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