PREDICTION OF FINITE CONCENTRATIONBEHAVIOR FROM INFINITE DILUTION EGUILIBRIUM DATA

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ABSTRACT

Experimental activity coefficients at infinite dilution are particularly useful for calculating the parameters needed in an expression for the excess Gibbs energy. If reliable values of $\gamma\infty 1$ and $\gamma\infty 2$ are available, either from direct experiment or from a correlation, it is possible to predict the composition of the azeotrope and vapor-liquid equilibrium over the entire range of composition. These can be used to evaluate two adjustable constants in any desired expression for G E. In this study MOSCED model and SPACE model are two different methods were used to calculate $\gamma\infty 1$ and $\gamma\infty 2$

INTRODUCTION

Activity coefficients at infinite dilution have many uses, some of them: calculating the Vapor Liquid Equilibrium for any mixture, finding the azeotrope composition and pressure; and the estimation of mutual solubility. These calculations are carried out by finding the two adjustable parameters of any desired expression for GE (Wilson [1], NRTL [2] and UNTQUAC [3] equations.

Wilson equation has two adjustable constants $\lambda 12$ and $\lambda 21$ (energy parameters) where they can be found from the $\gamma\infty$ by solving the equations for the two component simultaneously. But NRTL or UNIQUAC

equations have three parameters. For NRTL equation parameters are τ_{12}, τ_{21} and α_{22} where α_{12} is related to the non randomness in the mixture, the others are considered as energy parameters. The UNIQUAC equation contains three parameters, u_{12} and u_{21} adjustable binary energy parameters and the third parameter is considered as coordination number designated as Z.

All parameters for activity coefficient equations (Wilson, NRTL and UNIQUAC) for most binary mixtures are not available in the literature. Hence, another method was advocated to calculate these parameters which

serve to calculate the activity coefficient at infinite dilution γ∞.

Several methods were developed for the measurement of activities coefficients at infinite dilution (γ∞). The most important methods are: gas- liquid chromatography (GLC), non-steady-state gas-liquid chromatography, differential ebulliometry, static methods and the dilutor method. The simple experimental method for rapid determination of activity coefficients at infinite dilution is based on gas-liquid chromatography.

Principal aim of this work is to adopt the activities coefficients at infinite dilution for finding the parameters of different models (i.e., Wilson, NRTL, and UNIQUAC) which are not easy to find. The other aim is to evaluate the uses of the activities coefficients at infinite dilution (γ∞) and the methods that can be used and compare between them.

Mosced model

Mosced (modified separation of cohesive energy density) is a model proposed by Thomas and Eckert [4] for predicting limiting activity coefficients from pure component parameters only. It is essential]y an extension of regular solution theory to polar and associating systems. The extension is based on the assumption that forces contributing to the cohesive energy density are additive. Those forces included are dispersion, orientation, induction, and hydrogen bonding. The five parameters associated with these forces are the dispersion parameters.

A list of the parameters for 15 substances at 20 0C is given in [5]. In a binary mixture, the activity coefficient for component 2 at infinite dilution is calculated from:

$$\ln\gamma_2^\infty = \frac{V_2}{RT}\left[(\lambda_1-\lambda_2)^2 + \frac{q_1^2 q_2^2(\tau_1-\tau_2)^2}{\psi_1} + \frac{(\alpha_1-\alpha_2)(\beta_1-\beta_2)}{\xi_1}\right] + d_{12} \quad (1)$$

$$d_{12} = \ln\left(\frac{V_2}{V_1}\right)^{aa} + 1 - \left(\frac{V_2}{V_1}\right)^{aa} \quad (2)$$

$$\tau_T = \tau_{293}\left(\frac{293}{T}\right)^{0.4}$$

$$;\quad \alpha_T = \alpha_{293}\left(\frac{293}{T}\right)^{0.8}$$

$$;\quad \beta_T = \beta_{293}\left(\frac{293}{T}\right)^{0.8} \quad (3)$$

$$\psi = POL + 0.011\alpha_T\beta_T \quad (4)$$

$$\xi = 0.68(POL-1) + \left\{3.4 - 2.4\exp\left[-0.023(\alpha_o\beta_o)^{1.5}\right]\right\}t^2 \quad (5)$$

Where
POL=q4 [1.15 -1.15 exp (-0.020 τ ^{3}T)] + 1 (6)

And where τ = 293/T (T in Kelvin). Subscript 0 refers to 20°C (293 K), and subscript T refers to system temperature
aa = 0.953 — (0.00968)(τ_2^2 + α_2 β_2) (7)

where τ, α_2 and β are at system temperature T.

Space model

A predictive method for estimating γ^∞ is provided by the solvatochromic correlation of Bush and Eckert (2000) [6] through the SPACE equation. SPACE stands for Solvatochromic Parameters for Activity Coefficient Estimation. The SPACE formulation for solvent 1 is:

$$\ln\gamma_2^\infty = \frac{V_2}{RT}\left[(\lambda_1-\lambda_2)^2 + (\tau_1-\tau_{2eff})^2 + (\alpha_1-\alpha_{2eff})(\beta_1-\beta_{2eff})\right]$$

$$+\ln\left(\frac{V_2}{V_1}\right)^{0.936} + 1 - \left(\frac{V_2}{V_1}\right)^{0.936} \quad (8)$$

The dispersion terms are calculated as functions of the molar refractivity index (n_D):

$$\lambda = k\left(\frac{n_D^2 - 1}{n_D^2 + 2}\right) \quad\quad (9)$$

Where constant k is 15.418 for aliphatic compounds, 15.314 for aromatics, and 17.478 for halogen compounds [6]. R is 1.987,1 is in Kelvin, and V is in cm/mol.

The polarity and hydrogen-bond parameters for the solvent are

$$\tau_1 = \left|\frac{A_1\pi_1^{*KT} + B}{\sqrt{V_1}}\right| \quad ;$$

$$\alpha_1 = \left|\frac{C_1\alpha_1^{KT} + D_1}{\sqrt{V_1}}\right| \quad ;$$

$$\beta_1 = \left|\frac{E_1\beta_1^{KT} + F_1}{\sqrt{V_1}}\right| \quad\quad (10)$$

Parameters τ_{2eff} , α_{2eff}, and β_{2eff} are for the solute. Subscript eff means they are normalized such that limiting activity coefficients for a solute in itself must be unity. Calculation of these quantities requires both solvent and solute parameters for the solute.

$$\tau_{2eff} = \tau_2^o + \left(\tau_2 - \tau_2^o\right)\frac{\left|\pi_1^{*kT} - \pi_2^{*KT}\right|}{1.33} \quad (11)$$

$$\alpha_{2eff} = \alpha_2^o + \left(\alpha_2 - \alpha_2^o\right)\frac{\left|\alpha_1^{kT} - \alpha_2^{KT}\right|}{1.20} \quad (12)$$

$$\beta_{2eff} = \beta_2^o + \left(\beta_2 - \beta_2^o\right)\frac{\left|\beta_1^{kT} - \beta_2^{KT}\right|}{0.95} \quad (13)$$

where, $\quad \tau_2 = \left|\frac{A_2\pi_2^{*H} + B}{\sqrt{V_2}}\right| \quad ;$

$$\alpha_2 = \left|\frac{C_2\alpha_2^{H} + D_2}{\sqrt{V_2}}\right| \quad ;$$

$$\beta_2 = \left|\frac{E_2\beta_2^{H} + F_2}{\sqrt{V_2}}\right|$$

(14)

and $\quad \tau_2^o = \left|\frac{A_1\pi_2^{*KT} + B}{\sqrt{V_2}}\right| \quad ;$

$$\alpha_2^o = \left|\frac{C_1\alpha_2^{KT} + D_1}{\sqrt{V_2}}\right| \quad ;$$

$$\beta_2^o = \left|\frac{E_1\beta_2^{KT} + F_1}{\sqrt{V_2}}\right| \quad\quad (15)$$

Parameters are given in [6] for 15 components. Superscription 0 means that properties for the solute in its solvent - like state

Calculation of Activity coefficients at Infinite dilution

The calculation that carried out by using MOSCED and SPACE models is shown in Table 1 noting that the experimental data are extracted from literatures.

The overall average deviation results show that SPACE model equation gives better results than
Mosced model equation.

Space is similar to MOSCED, but reduces the three adjustable parameters of each component to 0 and adds 7 adjustable parameters per functionality of compound. Thus, for a database containing 100 different solvents, MOSCED will have 300 parameters (i.e, equivalent to 3 parameters for each solvent) while, SPACE has about 100 parameters. The main advantage of SPACE over MOSCED is the prediction of activities coefficients of compounds that were not in the original database provided they have the same functionality as others in the database as well as the required solvent and solute parameters. The SPACE method is probably the best universal available method for estimating activities coefficients at infinite dilution.

Calculation of the Uses of Activity Coefficient at in finite Dilution

Steps of Calculation for Azeotropic Composition and Pressure:
a. Determining the parameters of the activity

coefficient equations (Wilson, NRTL, and UNIQUAC) from experimental $\gamma\infty$.

b. Calculating of the vapor pressure of pure component at specified temperature using Wagner equation "see Appendix A".

c. At Azeotrope the relation volatility ($\square$ 12) is one, hence according to modified Rault's law

$$\frac{P_2^{sat}}{P_1^{sat}} = \frac{\gamma_1}{\gamma_2} \qquad (16)$$

d. Substitution of $\ln(\gamma_1/\gamma_2)$ with the activity coefficient model used.

e. Solving the composition (x1 and x2) by trial and error.

f. Calculation of activity coefficient at the azeotropic composition.

g. Calculation of azeotropic pressure by the following equation

$$P^{az} = \gamma_i^{az} P_i^{sat} \qquad (17)$$

Table 1 Experimental and Calculated γ^{∞}_1 and γ^{∞}_2 by using MOSCED and SPACE modes

System	T°C	Experimental data		By MOSCED model		By SPACE model	
		γ^{∞}_1	γ^{∞}_2	γ^{∞}_1	γ^{∞}_2	γ^{∞}_1	γ^{∞}_2
Acetone— Acetonitrile	45	1.05	1.04	1.105	1.1	0.9954	1.0061
Acetone—Benzene	45	1.65	1.52	1.48061	1.3809	1.4475	1.5476
Acetone —Carbon tetrachioride	45	3.00	2.15	2.64655	2.0804	2.5052	2.1490
Acetone—Methyl acetate	50	1.32	1.18	1.0417	1.0376	1.044	1.0472
Acetone —nitro methane	50	0.94	0.96	1.0377	1.0362	1.0499	0.7709
Acetonitrile — Benzene	100	3.20	3.00	2.3056	2.0093	2.9103	2.3198
Acetonitrile — nitro methane	40	0.96	1.00	0.9839	0.9838	0.9173	0.9691
Benzene—n-heptane	30	1.35	1.82	1.55136	1.95156	1.3591	1.8565
Carbon tetrachioride - Acetonitrile	60	5.66	9.30	5.2169	7.0278	4.4317	8.816
Chloroform—Methanol	50	2.00	9.40	3.23174	5.34556	2.1859	7.7311
Ethanol—Benzene	45	10.6	4.45	13.9057	4.6284	12.9898	5.1616
n-Hexane—Benzene	69	1.68	1.49	1.73638	1.4944	1.6637	1.3251
n-Hexane—Methylcyclopentane	69	1.17	1.03	1.01697	1.01402	1.0795	1.0668
Met hylcyclopenane—Benzene	72	1.47	1.34	1.5328	1.44367	1.2499	1.161
Nitroethane—Benzene	25	2.78	1.91	2.20598	1.72945	2.2299	1.8874
Nitromethane — Benzene	25	3.20	3.72	4.00663	3.064	3.5746	3.2465
Nitro methane — Benzene	45	3.20	3.40	3.42507	2.67778	3.2797	2.9901
2-Nitropropane - carbon tetrachioride	25	3.24	1.92	4.73716	2.54479	4.7714	2.1122
Over all average absolute deviation				0.5794	0.5799	0.4526	0.3042

Table 2 Calculated and experimental azeotrope composition and pressure using Wilson equation of one and two parameters models (γ^{∞}_1 and γ^{∞}_2)

System	T^oC	α_{12}	X_1 wt% at azeotrope exp.	X_1 wt% at azeotrope cal. with one parameter.	X_1 wt% at azeotrope exp. cal. with two parameters	P^{az} Exp. (bar)	P^{az} cal. with one parameter. (bar)	P^{az} cal. with two parameters (bar)
Acetone – Carbon tetrachloride	45	0.47	91	92.62	83.0338	0.68421	0.7045251	0.68578
Acetone – Chloroform	50	0.3	22.9	23.6269	19.2754	0.60662	0.6117064	0.59379
Acetonitrile - Benzene	45	0.47	30.7	30.2309	31.9997	0.37064	0.3752523	0.38272
Carbontetrachloride - Acetonitrile	45	0.47	84.5	82.1122	84.1988	0.49489	0.4544587	0.49205
Chloroform - Methanol	50	0.47	87.8	87.9172	90.8768	0.83598	0.7432916	0.83946
Methyl cyclopentane - Benzene	72	0.47	91	84.9816	93.8899	0.69861	1.026725	1.01761
Nitromethane - Benzene	25	0.47	6.4	4.44970	6.326	0.13026	0.1273378	0.12777
System	T^oC	α_{12}	X_1 wt% at azeotrope exp.	X_1 wt% at azeotrope cal. with one parameter	X_1 wt% at azeotrope exp. cal. with two parameters	P^{az} Exp. (bar)	P^{az} cal. with one parameter. (bar)	P^{az} cal. with two parameters (bar)
Nitromethane - Benzene	45	0.47	9.6	6.89904	9.8254	0.30398	0.3011422	0.30282
Nitromethane - Carbontetrachloride	45	0.4	10.6	8.44299	9.7866	0.40397	0.3863205	0.39316
n-Hexane - Benzene	69	0.47	99.8	87.4161	95.1542	0.76660	1.030297	1.02179
%Over All Average Absolute Deviation				**3.053157**	**2.4917**		**0.077836**	**0.062145**

While, when we apply similar calculation procedure but with NRTL equation the following results are obtained Table 3.

Table 3 Calculated and Experimental Azeotrope Composition and Pressure Using NRTL Equation of One and Two Parameters γ^{∞}_1 and γ^{∞}_2

System	T^oC	α_{12}	X_1 wt% at Azeo. Exp.	X_1 wt % at Azeo. Cal. with One Parameter	X_1 wt % at Azeo. Cal. with Two Parameters	$P_{Exp.}$ (bar)	P^{az} Cal. with One Parameter (bar)	P^{az} Cal. with Two Parameters (bar)
Acetone - Carbon tetrachloride	45	0.47	91	88.258 7	90.8 107	0.68421	0.70284	0.684 72
Acetone - Chloroform	50	0.3	22.9	26.7476	25.7412	0.60662	0.59908	0.59934
Acetonitrile - Benzene	45	0.47	30.7	17.5476	30.0615	0.37064	0.32809	0.35051
Carbonleirachioride - Acetonitrile	45	0.47	84.5	80.4428	84.3994	0.49489	0.43264	0.49401
Chloroform - Methanol	50	0.47	87.8	91.365 7	90.3624	0.83598	0.69886	0.86534
Methyl cyclopentane - Benzene	72	0.47	91	91.7786	93.7580	0.69861	1.00296	1.00203
Nitromethane - Benzene	25	0.47	6.4	8.1236	6.7034	0.13026	0.12 795	0.12 773
Nitromethane - Benzene	45	0.47	9.6	12.5 794	9.5541	0.30398	0.30424	0.30265
Nitromethane - Carbontetrachloride	45	0.4	10.6	13.8429	10.7995	0.4039 7	0.41330	0.40086
n-hexane - Benzene	69	0.47	99.8	99.9238	99.9208	0.76660	1.01256	1.01257
%Over all Absolute Average deviation				**2.4917**	**0.97596**		**0.08303**	**0.061452**

When UNIQAC model is applied the results will change to:

Table 4 Calculated and Experimental Azeotrope Composition and Pressure Using UNIQUAC Equation of One and Two Parameters γ^{∞}_1 and γ^{∞}_2

System	T^oC	α_{12}	X_1 wt% at Azeo. Exp.	X_1 wt % at Azeo. Cal. with One Parameter	X_1 wt % at Azeo. Cal. with Two Parameters	$P_{Exp.}$ (bar)	P^{az} Cal. with One Parameter (bar)	P^{az} Cal. with Two Parameters (bar)
Acetone - Carbon tetrachloride	45	0.8	91	90.55 75	90.8730	0.6842]	0.6842 7	0.68408
Acetone - chloroform	50	3.9	22.9	24.2491	22.9058	0.60662	0.6871	0.59263
Acetonitrile - Benzene	45	0.65	30.7	30.7088	30.7092	0.3 7064	0.15446	0.38309

Carbontetrachloride - Acetonitrile	45	1.4	84.5	84.4917	84.5021	0.49489	0.01852	0.505 12
Chloroform - Methanol	50	0.01	87.8	8 7.8072	89.8536	0.83598	0.88632	0.85041
Methyl cyclopentane - Benzene	72	0.01	91	89.2809	93.8282	0.69861	1.00765	1.00202
Nitromethane - Benzene	25	6	6.4	3.3 7393	6.3678	0.13026	0.12 714	0.13016
Nitromethane - Benzene	45	3.5	9.6	5.28095	9.5828	0.30398	0.30020	0.30789
Nitromethane - carbontetrachloride	45	2.5	10.6	6.60830	10.7628	0.4039 7	0.3 7879	0.40511
n-hexane - Benzene	69	0.36	99.8	99.6282	99.8332	0.76660	1.01256	1.01255
%Over all Absolute Average deviation				*1.50436*	*0.52713*		*0.133212*	*0.06057*

Vapor Liquid Equilibrium Calculation

The Vapor Liquid Equilibrium (VLE) data can be calculated from the activities coefficients at infinite dilution ($\gamma\infty1$, $\gamma\infty2$) for any binary system. The equations of Vapor Liquid Equilibrium are calculated using suitable equation of state (EOS). Peng Robinson equation of state [7] is selected to calculate VLE since it is the more reliable equation for the calculation. The VLE data for 13 systems has been calculated by using Wilson, NRTL

Table 5 Vapor liquid equilibrium Systems data

and UNIQUAC equations for one parameter and two parameters.

Experimental Data

From the experimental data can be determined the accuracy of any calculation and this can be done by calculating the deviation between the experimental data and the calculated results. The experimental data for Vapor Liquid Equilibrium obtained from literature for 13 systems are shown in Table 5:

	System	*P(mmHg) or T in (^{O}C)*	*No. of data points*	*Reference*
1	*Benzene (1) - Acetonitrile (2)*	*T= 70*	*21*	*8*
2	*Methanol (1) - Water (2)*	*P= 760*	*26*	*9*
3	*Acetone(1)-Carbon tetrachloride (2)*	*P =450*	*24*	*10*
4	*Hexane (1) - Benzene (2)*	*P=735*	*11*	*11*
5	*Acetone (1) - Benzene (2)*	*P= 738*	*10*	*12*
6	*Acetone (1) - Water (2)*	*P=760*	*13*	*13*
7	*Methelcyclopentane (1) - Benzene (2)*	*P= 760*	*15*	*14*
8	*Benzene (1) - Heptane (2)*	*P= 760*	*18*	*15*
9	*Acetone (1) - Benzene (2)*	*T=45*	*11*	*16*
10	*Acetone (1) - Acetonitrile (2)*	*T=45*	*10*	*17*
11	*Acetonitrile (1) - Nitro methane (2)*	*T=60*	*10*	*18*
12	*Nitro methane (1) - Carbon tetrachloride (2)*	*T==45*	*12*	*19*
13	*Carbon tetrachloride (1) - Acetonitri/e(2)*	*T=45*	*13*	*20*

Steps of Calculation of VLE Data

1. Calculating the parameters of the activity coefficient equations (Wilson, NRTL and UNIQUAC) from experimental $\gamma\infty$.

2. For each point of the VLE data (x1) the following steps were taken

a.Finding the pure-component saturated vapor pressure Psat1, Psat2 at temperature of that point using Wagner equation appendix "A".

b.Calculating the constants of the e~} nation at that temperature corresponding to that point

c.Calculating the activity coefficients ($\gamma\infty1$, $\gamma\infty2$) at that point from the employed equation (Wilson, NRTL or UNIQUAC)

d.Calculating VLi from Rackett eqtiation which has the form:

$$V_i^{sat} = V_C Z_C^{(1-Tr)^{0.2857}}$$
(18)

e.Solving the following equation where ϕi sat and ϕ_i^V must be calculated using Peng ― Robinson equation of state.

$$y_i P \overset{\wedge}{\phi}_i^V = x_i V_i P_i^{sat} \phi_i^{sat} \exp\left[\frac{V_i^L(P-P_i^{sat})}{RT}\right]$$
(19)

f. Calculating y_1 from the following equation

$$y_i = \left(\frac{x_i \gamma_i P_i^{sat} \phi_i^{sat}}{P \phi_i^V}\right) \exp\left(\frac{V_i^L\left(P-P_i^{sat}\right)}{RT}\right)$$
(20)

These steps are repeated for each point of VLE data (for each x_1) by preparing suitable computer program.

Steps of Investigation for VLE Calculation

The steps of investigation were carried out on 13 different systems some of them are Isothermal and the others are Isobaric by the three models of Wilson, NRTL, and UNIQUAC models and the following results are obtained:

Table 6 Average absolute deviation for VLE calculation when Wilson, NRTL, and UNIQUAC models are applied for the following systems:

System	P(mmHg) or T (^{O}C)	No.of data points	Wilson Parameters		NRTL Parameters		UNIQUAC Parameters	
			One	Two	One	Two	One	Two
Benzene (1) - Acetonitrile (2)	Isothermal T=70	21	0.019294	0.019044	0.02 7988	0.017167	0.016661	0.0161 63
Methanol (1) - Water (2)	Isobaric P=760	26	0.032758	0.02 1413	0.024775	0.020513	0.019821	0.015083
Acetone(1) - Carbon tetrachioride (2)	Isobaric P=450	24	0.007259	0.003249	0.038627	0.020761	0.003735	0.002005
Hexane (1) - Benzene (2)	Isobaric P=735	11	0.0233 79	0.00672 7	0.018 786	0.00 7361	0.053490	0.006812
Acetone (1) - Benzene (2)	Isobaric P=738	10	0.018799	0.008494	0.011519	0.020163	0.008019	0.7854
Acetone (1) - Water (2)	Isobaric P=760	13	0.012 764	0.010586	0.020921	0.012743	0.011605	0.7809
Methelcyclopentane (1) - Benzene (2)	Isobaric P=760	15	0.004823	0.003538	0.011235	0.006554	0.003601	0.004110
Benzene (1) - Heptane (2)	Isobaric P=760	18	0.098944	0.004573	0.014158	0.006411	0.005809	0.004804
Acetone (1) - Benzene (2)	Isothermal T=45	11	0.004832	0.003964	0.031053	0.007277	0.004547	0.003527
Acetone (1) - Acetonitrile (2)	Isothermal T=45	10	0.00 7607	0.007518	0.00 7776	0.00 7738	0.007467	0.00 7153
Acetonitrile (1) - Nitro methane (2)	Isothermal T=60	10	0.025060	0.003938	0.007455	0.005826	0.004469	0.003910
Nitromethane (1) - Carbon tetrachloride (2)	Isothermal T=45	12	0.009516	0.007698	0.034571	0.006849	0.012256	0.005957
Carbon tetrachloride(1) – Acetonitrile (2)	Isothermal T=45	13	0.042118	0.005674	0.018375	0.0183 75	0.019538	0.017218
%Over all Average Absolute Deviation		194	0.023627	0.008186	0.022892	0.012134	0.013155	0.007877

Also; the results of application of Wilson, NRTL, and UNIQUAC relations can be represented on a graph for range of composition for a selected systems which are taken as a sample of calculation for one and two parameters as follows:
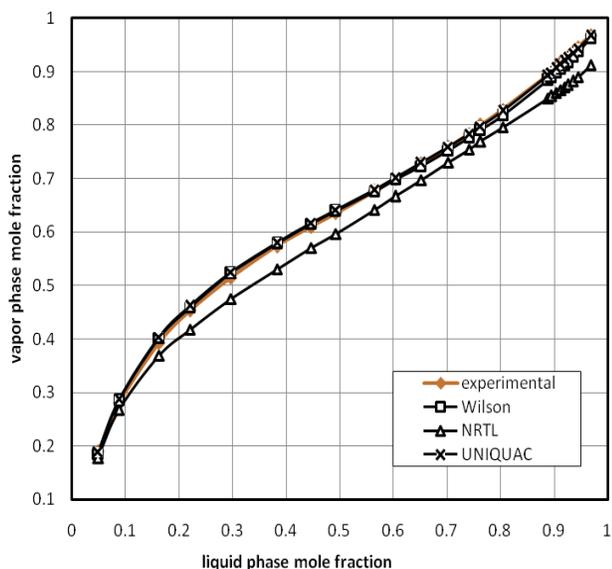
Fig. 1 VLE for Acetone-Carbon tetrachloride at P=450mmHg by using different models of one parameter
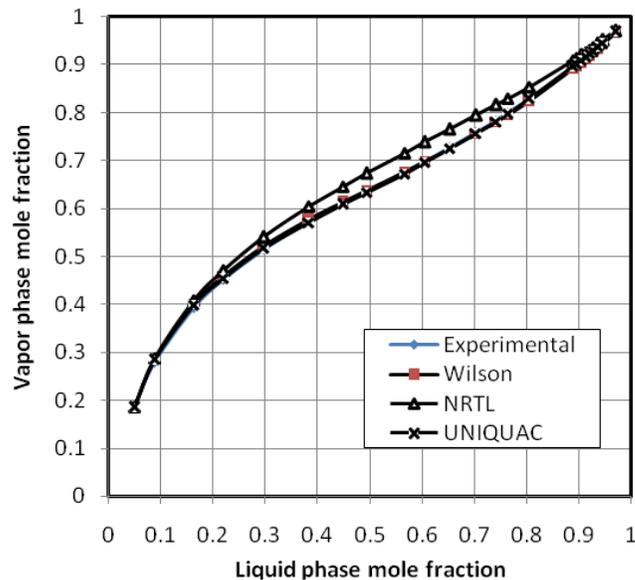
Fig. 2 VLE for Acetone-Carbon tetrachloride at P=450mmHg by using different models of two parameter
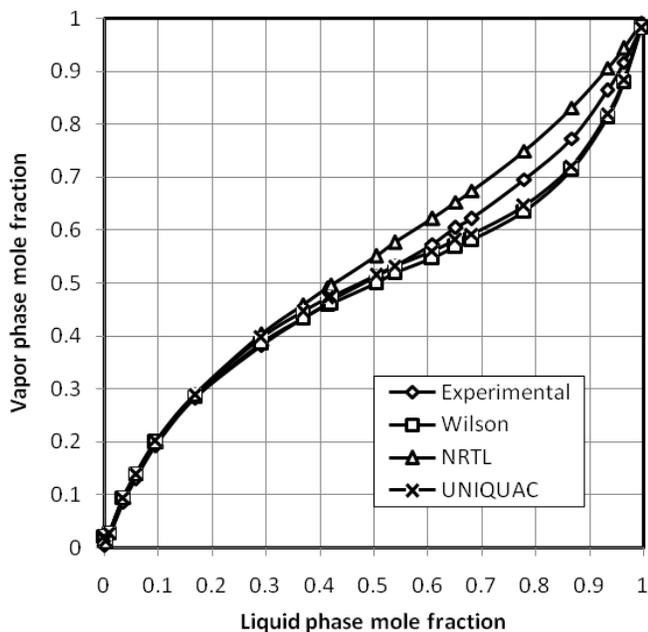
Fig. 3 VLE for Benzene – Acetonitrile at T=70°C by using different models of one parameter
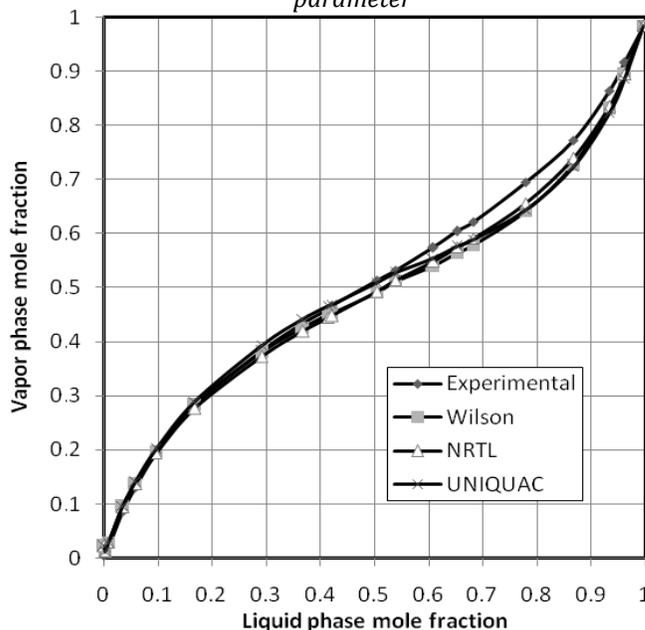
Fig. 4 VLE for Benzene – Acetonitrile at T=70°C by using different models of Two parameter
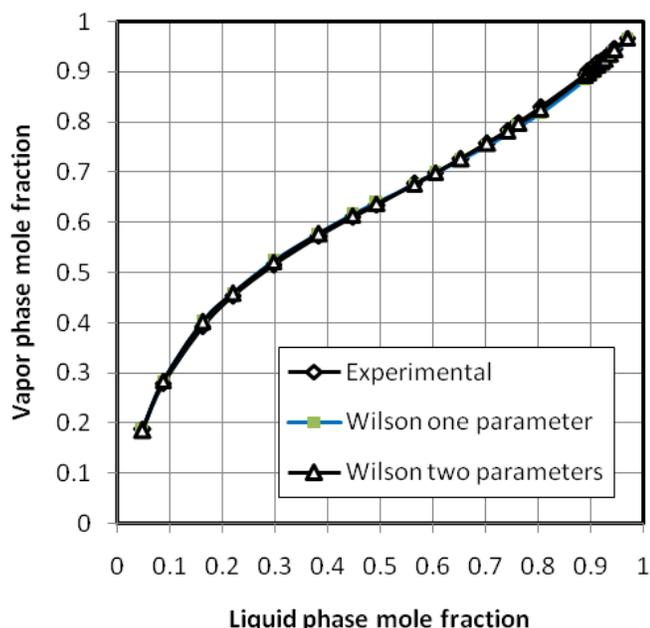
Fig. 5 VLE for Acetone-Carbon tetrachloride at P=450mmHg by using Wilson models of one and two parameters
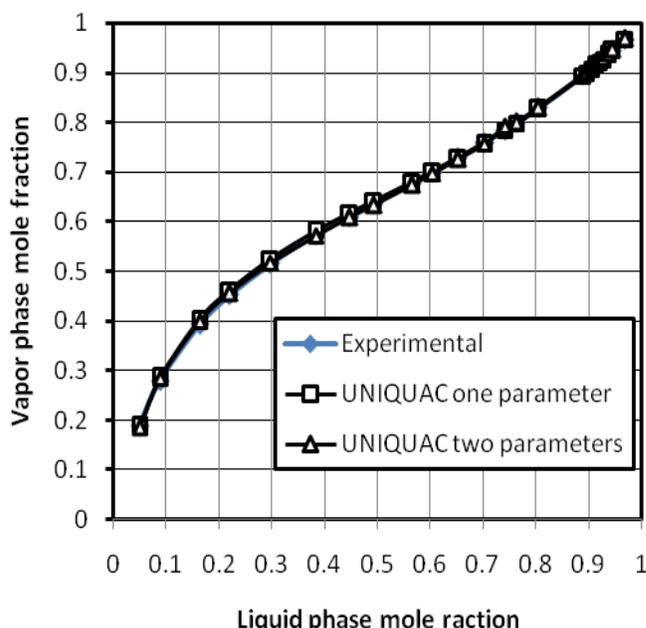
Fig. 7 VLE for Acetone-Carbon tetrachloride at P=450mmHg by using UNIQUAC models of one and two parameters
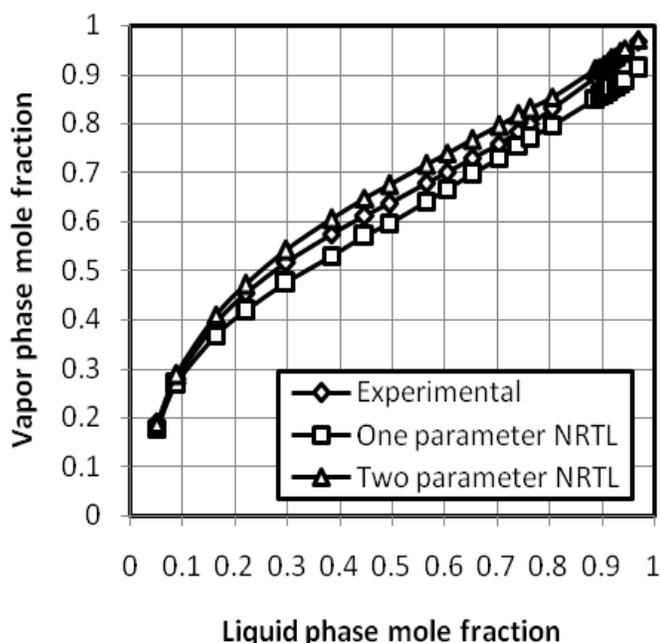
Fig. 6 VLE for Acetone-Carbon tetrachloride at P=450mmHg by using NRTL models of one and two parameters

Discussion

The principle aim in this work is to show if it is possible to use the activities coefficients at infinite dilution to find the parameters of different models.

It was suggested two modem methods for calculating the activities coefficients at infinite dilution ($\gamma\infty$), MOSCED method (modified separation of cohesive energy density) and SPACE method (Solvatochromic Parameters for Activity Coefficient Estimation). The two equations are applied to 18 systems and SPACE model gives better results than MOSCED equation.

This work presents the evaluation of the uses of activities coefficients at infinite dilution, $\gamma\infty$, to calculate the parameters of different equations: Wilson, NRTL and UNIQUAC. One of the uses is azeotropic calculation where it is applied for

10 different binary systems from the experimental $\gamma\infty$ and the results when compared with the experimental data for azeotrope at the same temperature show as nearly as good if using the actual parameters of the equations. The other use is the calculation of Vapor Liquid Equilibrium data where it applied for 13 different binary systems (194 data points) from the experimental γ^{∞} and the results also show as high accuracy as if using the actual parameters of the equations. From these calculations IJNIQUAC model gives the highest accuracy than the other models (Wilson, NRTL).

In the system that only one γ^{∞} is available one parameter equation is used for Wilson, NRTL and UNIQUAC equation which it gives result closer accuracy to the two parameters equation. For more details and comparison for all systems which are investigated in this work you can see appendix "B"

The results which appeared in the previous Tables with their absolute deviations show

1. The most important two methods for calculating the activities coefficients at infinite dilution are SPACE method and MOSCED method. And it was found that SPACE method is better than MOSCED where SPACE gives Average Absolute Deviation *0.4526,* 0.3042 for γ^{∞}_{1} and γ^{∞}_{2} respectively and MOSCED equation give Average Absolute Deviation equal to *0.5794, 0.5* 799 for 'y' respectively.
2. One of the uses of activities coefficients at infinite dilution is the calculation of azeotropic properties (azeotropic composition and pressure). The equations used are Wilson, NRTL and UNIQUAC where UNIQUAC equation gives better results than NRTL and Wilson equations.
3. The other uses of activities coefficients at infinite dilution is the calculation of VLE and the same equation are used (Wilson,

NRTL and UNIQUAC).UNIQUAC equation also gives the best results than the others.
4. In the system that has only one γ^{∞} available, the use of one parameter equation gives result with accuracy near to the two parameters equation which is accepted.

Conclusions

1. SPACE and MOSCED are good estimated methods to predict or calculate values of parameters which serve the calculation of activity coefficients at infinite dilution (γ^{∞}).
2. Wilson equation of two parameters is the easier method to calculate activity coefficients at infinite dilution (γ^{∞}) since it contain only two parameters. While, NRTL and UNIQUAC models contains three adjustable parameters which make the program which designed to calculate the parameters more difficult.
3. When the obtained parameters applied to calculate activity coefficients at infinite dilution (γ^{∞}) and then calculate vapor liquid equilibrium, azeotropic composition and pressure good agreement with the experimental data are obtained for all applications.
4. When Wilson model is applied; the affect of increasing adjustable parameters from one to two parameters will be appeared in azeotropic composition calculation; while it would not had a great affect in the calculation of azeotropic pressure. The same thing is happened when NRTL and UNIQUAC equations are applied for the calculation.
5. The comparison between the Wilson, NRTL, UNIQUAC equations for azeotropic composition and pressure calculation; UNIQUAC equation gives best results

comparing with the experimental data than NRTL and Wilson equation which gives the less accurate results.

6. Wilson, NRTL, and UNIQUAC models are applied to calculate VLE for thirteen different binary mixtures with 194 data points at different temperatures gives very good accuracies for one parameter and excellent results for two parameters i.e. increasing the number of parameters will increase the accuracy.

7. Also, like the calculation of azeotropic composition and pressure the two parameters model gives better results compared with the one parameter models for Wilson, NRTL, and UNIQUAC equations with slightly different accuracies. UNIQUAC, NRTL, and Wilson models give reasonable accuracy comparing with the experimental data for one and two parameters when VLE calculation is adopted.

8. The calculated results show that prediction of VLE from activity coefficients at infinite dilution (γ^{∞}) when SPACE and MOSCED models adopted are excellent.

9. For azeotropic calculation of composition and pressure a very good results are obtained for two parameters models especially for UNIQUAC model. While; reasonable results are obtained for one parameter model. Also, UNIQUAC gives more accurate results when compared with Wilson and NRTL equations.

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Appendix "A"

Wagner equation to calculate pure component vapor pressure

Equation "1" $ln(P/Pc) = (1-x)^{-1}[Ax + Bx^{1.5} + Cx^3 + Dx^6]$ *where x=1-(T/Tc)*   *(A-1)*

Equation "2" $lnP = A - (B/T) \pm Cln(T) + DP/T^2$ *(A-2)*

Component	A	B	C	D	Eq. no.
Acetone	-7.45514	1.2)2	-2.43926	-3.3559	1
Acetonii~rile	40.774	5392.43	-4.357	2615	2
Benzene	-6.98273	1.33213	-2.62863	-3.33399	1
Carbon tetrachioride	-7.07139	1.71497	-2.8993	-2.49466	1
Chloroform	-6.95546	1.16225	-2.1397	-3.44421	1
Water	-7.76451	1.45838	-2.7758	-1.23303	1
Methanol	-8.54796	0.76982	-3.10850	1.54481	1
Methylcyclopentane	-7.15937	1.48017	-2.92482	-1.98377	1
n-Heptane	-7.67468	l.37068	-3.53620	-3.20243	1
n-Hexane	-7.46765	1.44211	-3.28222	-2.50941	1
Nitromethane	-8.41688	2.76466	-3.65341	-1.01376	

Nomenclature

P	pressure
T	temperature
V	volume
Z	Compressibility factor
x	Mole fraction in the liquid phase
y	Mole fraction in the gas or vapor phase
R	gas constant
EOS	Equation of state
n_D	Refractive index
C, D, E, and F	Equation constants
G	Gibbs free energy
R	Gas constant
f	Fugacity
u	UNIQUAC parameter
x	Mole fraction in liquid phase
y	Mole fraction in vapor or gas phase

Latinic symbols

γ	Activity coefficient
φ	Fugacity coefficient
α	NRTL parameter
β	Proportionality factor
λ	Wilson parameter calculated from energy parameter
ξ	Parameter calculated by an equation
π	Parameter in SPACE MODEL

Subscript

0	System at 1 atmosphere and 20°C
1	Component one in the system
2	Component two in the system
C	critical
i	Component "*i*"
r	Reduced condition
T	System temperature

Superscript

∞	*Infinite dilution*
sat	*Saturation*
ʌ	*Physical property of component in the solution or mixture*
V	*Vapor phase*
L	*Liquid phase*
az	*Azeotropic condition*

E	Excess	H	Solute state
KT	Solvent state		

التنبؤ بتصرف المواد عند تراكيز محددة في التخفيف اللانهائي لمعلومات التعادل الفيزيائي

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الخلاصة:

γ^∞ المختبري عند التخفيف اللانهائي مهم وضروري جدا" لحساب المعامل الضرورية لمحتوى الطاقة الفائض الحر لكَبس G^E. اذا كان لدينا قيم موثوقة لكل من $\left(\gamma_1^\infty, \gamma_2^\infty\right)$ سواء كانت هذه القيم محسوبة من التجارب او من العلاقات تؤدي الى امكانية استنتاج عند نقطة الـazeotrope الضغط والنسب لكل من السائل و البخار كذلك تمكننا من حساب كميات التوازن لكل من السائل و البخار عند ظروف التشغيل. هذا يفتح المجال لحساب G^E.

قد طبقت في هذا البحث لحساب ثوابت كل من (Wilson, NRTL, UNIQUAC). أختير موديل كل من MOSCEDو SPACE لحساب كل من $\left(\gamma_1^\infty, \gamma_2^\infty\right)$