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Calculation of the activity coefficients at infinite dilution in binary aqueous systems of pyridine and its derivatives

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The activity coefficients at infinite dilution of binary mixtures formed by water and pyridine and its derivatives (2-methylpyridine, 3-ethylpyridine, 2,4,6-trimethylpyridine) have been calculated using the NRTLmKW model. The calculation have been performed for experimental isothermal data measured at T=353.15K in a very narrow range of concentration using the ebulliometric method. The calculated activity coefficients have been compared with the activity coefficients at infinite dilution obtained directly from the measured vapour pressures. The obtained results have been fully discussed from the point of view of intermolecular interactions in the solutions and some recommendations have been made on the use of the NRTLmKW model for such calculation.

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The purpose of this work is to provide the reliable and accurate model for description of phase equilibria for binary aqueous solutions of coal liquids important both for the industrial and environmental purposes.

The broad analysis of various methods applied to describe phase equilibria leads to a conclusion that regardless of many years of studies and achievements in this field there has been a failure in creating a general model that would describe equilibrium data with experimental accuracy. All methods of description (statistical, empirical, semi-empirical) are limited to particular classes of mixtures and different ranges of change in parameters of state (pressure and temperature).

On the other hand the prediction of equilibrium behaviour of fluids and fluid mixtures belong nowadays to the most challenging and perhaps also most significant tasks at the boundary between physical chemistry and physics. An enormous amount of data has been collected and correlated over the years but the rapid advance of technology into new fields seems always to maintain a significant gap between demand and availability. Therefore, the construction of new thermodynamic models with deep theoretical background is absolutely necessary both for the better understanding of behaviour of fluids and the proper design in the modern technologies.

One of the best tests for checking the accuracy of such model is its prediction of activity coefficients at infinite dilution from VLE data in various classes of binary systems.

As an example of such systems the binary mixtures of water and pyridines and its derivatives have been selected. Pyridine and methyl pyridines are fully miscible with water that is why a lot of vapour-liquid equilibrium data of these systems can be found in the literature[3-7]. The situation is much worse in the case of ethylopyridines and trimethylpyridine, which are only partially miscible with water[7-8].

Such selected data were are very useful both for thermodynamic description of multicomponent coal liquids (full and partial miscibility, very diluted region of experimental data, different kind and shape of molecules, different molecular interactions in solution) and for description of diluted aqueous solutions extremely important from the point of view environmental protection.

The Model

Thermodynamic definition of an activity coefficient in a liquid phase (γ) is connected with the concept of

excess functions which define the difference between values of thermodynamic functions of real mixtures and the values of these functions for ideal mixtures. The deviations of mixtures from ideality, what is measured by an activity coefficient, result from specific molecular interactions and the nature of forces acting between molecules of different types occurring in the solution. The key problem connected with the calculation of vapour-liquid equilibria is finding a formula that precisely defines the activity coefficient as a function of content, temperature and pressure for the studied mixture. The pressure dependence of the activity coefficient may be ignored for pressure not exceeding approx. 500 kPa (Ref. 2).

The general model for description of activity coefficients in the solution has to take into account the molecular interaction between components. As a good example of such approach the NRTLmKW model[1,9] can be proposed, where the activity coefficient of component *i* in a liquid phase for the multicomponent systems is expressed by:

$$\ln\gamma_i = (\ln\gamma_i)_{phys} + (\ln\gamma_i)_{chem} \quad \ldots (1)$$

The physical contribution to the activity coefficient is defined by the modified local composition and has the following form:

$$\ln(\gamma_i)_{phys} = \frac{g^E}{RT} + \frac{d}{dx_i}\left(\frac{g^E}{RT}\right) - \sum_{j=1}^{n} x_j \frac{d}{dx_j}\left(\frac{g^E}{RT}\right) \quad \ldots (2)$$

where:

$$\frac{g^E}{RT} = \sum_{i=1}^{n} x_i \frac{\sum_{j=1}^{n} Z_{ji}\tau_{ji} x_j^{1+(-1)^j \beta_{ji}}}{\sum_{k=1}^{n} Z_{ki} x_k^{1+(-1)^k \beta_{ki}}} \quad \ldots (3)$$

$$\frac{d}{dx_i}\left(\frac{g^E}{RT}\right) = \frac{\sum_{j=1}^{n} Z_{ji}\tau_{ji} x_j^{1+(-1)^j \beta_{ji}}}{\sum_{k=1}^{n} Z_{ki} x_k^{1+(-1)^k \beta_{ki}}} - \sum_{j=1}^{n}\left(\frac{(1+(-1)^j \beta_{ij}) x_i^{(-1)^j \beta_{ij}} x_j Z_{ij}}{\sum_{k=1}^{n} Z_{kj} x_k^{1+(-1)^k \beta_{kj}}}\left(\frac{\sum_{j=1}^{n} Z_{ji}\tau_{ji} x_j^{1+(-1)^j \beta_{ji}}}{\sum_{k=1}^{n} Z_{ki} x_k^{1+(-1)^k \beta_{ki}}} - \tau_{ij}\right)\right) \quad \ldots (4)$$

where:

$$Z_{ij} = A_{ij}\exp(-\alpha\tau_{ij}), \qquad \tau_{ij} = \frac{g_{ij} - g_{jj}}{RT},$$

$$\alpha = \beta = \frac{s}{150} \quad \text{or} \quad \alpha = -\beta = \frac{s}{150}$$

$$A_{ij} = \frac{[(2+\beta)/\alpha]^{1+\beta/2}}{[(2-\beta)/\alpha]^{1-\beta/2}} \quad \ldots (5)$$

$$A_{ji} = \frac{[(2-\beta)/\alpha]^{1-\beta/2}}{[(2+\beta)/\alpha]^{1+\beta/2}} \quad \ldots (6)$$

$$s = |s_i - s_j + 1| \quad \ldots (7)$$

where:

s_i, s_j - *s*-mers of component *i* and *j*, respectively, calculated from the following equation:

$$\ln K_i = \ln\frac{s_i}{s_i - 1} + (s_i - 1)\ln 2 \quad \ldots (8)$$

where: K_i – association constant of component *i*.

As it was proven[10], consideration of all possible *i*-*i*, *j*-*j*, *i*-*j*-mers in the solution, which complicates calculation, was unnecessary and it has been limited to the following reactions:

$$A_i + A = A_{i+1} \quad \ldots (9)$$

$$B_j + B = B_{j+1} \quad \ldots (10)$$

$$A_i + B_j = A_i B_j \quad \ldots (11)$$

For those reactions, assuming Kretschmer-Wiebe[11] association, the chemical contribution to activity coefficients can be derived using Nagata[12] method and will obtain the following form:

$$(\ln\gamma_i)_{chem} = \ln\frac{\Psi_i}{\Psi_i^0 x_i} - r_i\left(\frac{1}{Z_i^0} - \frac{1}{Z}\right) - \ln\frac{\phi_i}{x_i} - 1 + \frac{\phi_i}{x_i} \quad \ldots (12)$$

where:

$$\phi_i = \frac{r_i x_i}{\sum_{j=1}^{n} r_j x_j} \quad \ldots (13)$$

$$r = \frac{V_j}{V_i} \quad \ldots (14)$$

$$\Psi_i^0 = \frac{1 + 2K_i - \sqrt{1 + 4K_i}}{2K_i^2} \quad \ldots (15)$$

$$\frac{1}{Z_i^0} = \frac{1 - K_i \Psi_i^0}{r_i} \quad \ldots (16)$$

$$\frac{1}{Z} = \sum_{i=1}^{n} \frac{\Psi_i}{r_1(1 - K_i \Psi_i)} + \sum_{i=1}^{1} \sum_{j=1}^{n} \frac{K_{ij} \Psi_i \Psi_j}{(1 - K_i \Psi_i) r_1 (1 - K_j \Psi_j)} \quad \ldots (17)$$

where:

V_i, – molar volumes of pure components *i*,

x_i, – the mole fraction of components *i,*

Ψ_i^0 - the true volume fractions of monomer in pure components *i,*

Ψ_i - the true volume fractions of monomer in the components *i,*

Z - the true volume of the mixture,

n – number of components

$$K_{ij} = \sqrt{K_i K_j} \quad \ldots (18)$$

The mass balance equation of volume fractions of component *I* in the solution has the following form:

$$\phi_i = \frac{\Psi_i}{(1 - K_i \phi_i)^2} \left(1 + r_i \sum_{j=1}^{n} \frac{K_{ij} \phi_j}{(1 - K_j \phi_j)^2} \right) \quad \ldots (19)$$

For non-associating mixtures (K_i, K_j, K_{ij}=0) the NRTLmKW model is reduced only to the physical part of the activity coefficients.

The NRTLmKW model has, for binary systems, only two adjustable parameters (g_{ij},-g_{jj}) and all associating parameters are calculated from pure components data using the homomorph approach.

Calculation

The applicability of the proposed model has been checked on calculation of isothermal vapour-liquid equilibria for binary systems formed by water, pyridine and its derivatives[7]. The systems have been selected providing a possibility of comparison for binary systems in very diluted region of experimental data, different kind and shape of molecules and different molecular interactions in solution.

The activity coefficients at infinite dilution have been calculated from the experimental isothermal (T=353.15 K) binary VLE data[7] using the NRTLmKW[1,9] model for the following systems:

1) water + pyridine,
2) water +2-methylpyridine,
3) water + 3-ethylpyridine,
4) water + 2,4,6-trimethylpyridine.

In all cases the fugacity coefficients for the vapour phase were calculated from the virial equation of state using the O'Connell-Prausnitz method[13] for determination of the second virial coefficient. All auxiliary data needed for the calculations are given in **Table I**.

The calculated activity coefficients at infinite dilution have been compared with the values of activity coefficients at infinite dilution obtained directly from the experimental isothermal vapour-liquid equilibria[7].

The total vapour pressure was measured at solute mole fractions up to 0.01 for water + pyridine and water+2-methylpyridine. In two other cases (water+3-ethylpyridine and water + 2,4,6-trimethylpyridine) the range investigated was decreased to solute mole fraction below 0.005 because of their miscibility in water[7]. However, in all cases the total pressure of the systems was, according to Henry's law, a linear function of the solute mole fraction.

That is why, using the ebulliometric method[12], the activity coefficient at infinite dilution ($\gamma_i^{\infty exp}$) could be evaluated by the iterative procedure solving two of the following equations:

$$\gamma_1^{\infty \exp} = \frac{P_2^0 + z^{-1}(dp/dx)_T}{P_1^0 \varphi_1} \quad \ldots (20)$$

Table I — Saturated vapour pressures (P_i^0), molar volumes (V_{mi}) and second virial coefficient (B_{ii}) and (B_{1i})

Substance	P_i^0 / kPa	V_{mi} / (cm^3 mol^{-1})	-B_{ii} / (cm^3 mol^{-1})	-B_{1i} / (cm^3 mol^{-1})
Water (1)	47.207	18.7	603	
Pyridine	32.229	85.4	1265	781
2-methylpyridine	20.113	104.5	1857	840
3-ethylpyridine	5.758	120.3	2475	1040
2,4,6-trimethylpyridine	4.536	140.5	3633	1116

$$z = \frac{1+f}{1+(f(P_1^0/P_2^0)\gamma_1^{\infty \exp}} \quad \ldots (21)$$

where:

P_1^0, P_2^0 – are the saturated vapour pressures of pure water (1) and organic component(2), respectively,

φ_1 – is the coefficient taking into account non-ideality of the vapour phase (calculated from the virial equation of state)

$(dp/dx)_T$ – is the derivative calculated directly from the experiment[7],

f – the ebulliometer factor[2], in this work f = 0.05 was used[7].

The experimental (directly evaluated from the VLE data) and calculated (NRTLmKW model) values of activity coefficients at infinite dilution are presented in **Table II**. This table shows also the relative deviation of activity coefficients at infinite dilution ($D(\gamma^{\infty})$) calculated according to Eqn. 22.

$$D(\gamma^{\infty}) = \left| \frac{\gamma_i^{\infty \exp} - \gamma_i^{\infty cal}}{\gamma_i^{\infty \exp}} \right| 100 \quad \ldots (22)$$

where:

$\gamma_i^{\infty}exp$, $\gamma_i^{\infty}cal$ - the experimental and calculated activity coefficient at infinite dilution, respectively.

The experimental values of activity coefficients at infinite dilution show a big discrepancy between activity coefficients on the water and pyridine and its derivatives side, respectively. The values of activity coefficients in infinite dilution on the water side oscillating around 3 while on the pyridine and its derivatives side rises drastically from 25 up to 186.

This trend is perfectly reproduced by the NRTLmKW model. Moreover results of calculation of activity coefficients at infinite dilution vary from 2 to 4% and can be fully accepted and appreciated as very good. The NRTLmKW model gave very good results of calculation irrespectively of the kind and shape of calculated components, as well as irrespectively of the character of intermolecular interaction. This results allows us to recommend the NRTLmKW model for calculation of very diluted aqueous mixtures of organic compounds.

Conclusions

The activity coefficients in infinite dilution of pyridine and its derivatives in water are strongly dependent on the number and kind of alkyl substituents in the pyridine chain.

The results shows that introduction of the alkyl substituent into the pyridine chain for some pyridine derivatives raises and for others lowers the activity coefficient in infinite dilution in water. At higher temperature, the activity coefficients do not obey the simple rule proposed by Andon *et al*.[8] for room temperature concerning the relation between a number of alkyl substituents and the values of activity coefficients. This can be explain by the fact that at T = 353.15 K hydration of pyridine derivatives is much smaller that at T = 298.15 K.

Due to the strong temperature dependence of the Gibbs free energies of these aqueous mixtures, thermodynamic information obtained only from the low temperature measurements cannot be recognized as sufficient, therefore the thermodynamic model with a appropriate temperature dependence is absolutely needed for proper thermodynamic description of those systems in a wide range of temperatures.

The obtained results show that the NRTLmKW model fulfils all those criteria and can be recommended for description of very diluted aqueous mixtures of pyridine and its derivatives as well as other organic compounds.

The NRTLmKW model predicts the activity coefficients in infinite dilution with accuracy close to that achieved experimentally and has only two energetic parameters which have to be adjusted from experimental (VLE, LLE, SLE, cp^E, h^E) data.

Table II — Experimental and calculated activity coefficients at infinite dilution for all systems investigated at T = 353.15 K

System	γ_1^{∞}exp	γ_1^{∞}cal	γ_2^{∞}exp	γ_2^{∞}cal	D(γ_1^{∞})/[%]	D(γ_2^{∞}/[%])
water (1) + pyridine(2)	2.986	3.052	25.63	26.71	2.21	4.21
water (1) + 2-methylpyridine	3.203	3.117	56.87	58.92	2.68	2.24
water (1) + 3-ethylpyridine	3.024	2.956	79.03	77.91	2.25	1.14
water (1) + 2,4,6-trimethylpyridine	3.263	3.398	186.87	191.26	4.14	2.35

The flexibility of the NRTLmKW model can be still improved by adjusting of the association parameter what can be useful in the case of systems very difficult for correlation. However in this case we lose the predictive power of the NRTLmKW model. Results of the calculations of activity coefficients at infinite dilution confirm both the good temperature dependance of the NRTLmKW model and the proper relation between the physical and chemical part of the model as well as very good description possibilities of the model for very dilute region of concentration.

References

1 Gierycz P, *Polish J Chem*, 70, **1996**, 498.

2 Rogalski M & Malanowski S, *Fluid Phase Equilibria*, 5, **1980**, 97.

3 Yushkova I, Belavina T G & Kharlampovich G D, *Zh Prikl Khim*, 47, **1974**, 2313.

4 Abe J, Nakanishi K & Touhara H, *J Chem Thermodynamics,* 10, **1978**, 483.

5 Wóycicka M & Kurtyka Z, *Bull Acad Polon Sci, Ser Sci Chim*, 13, **1965**, 469.

6 Andon R J L, Cox J D J & Herington E F G, *Trans Faraday Soc*, 53, **1957**, 410.

7 Gierycz P, *J Chem Thermodynamics* 28, **1996**, 343.

8 Andon R J L, Cox J D J & Herington E F G, *J Chem Soc*, **1954**, 3188.

9 Gierycz P, *Polish J Chem*, 70, **1996**, 1193.

10 Gierycz P, *Thermodynamics of Fluids: Measurement and Correlation*, (World Scientific Publishing Company, Singapore) **1990**, pp 370-414.

11 Kehiaian H & Treszczanowicz A, *Bull Acad Polon Sci, Ser Sci Chim*, 11-12, **1970**,693.

12 Nagata I, *Fluid Phase Equlibria*, 19, **1985**, 153.

13 O'Connell J P & Prausnitz J M, *Ind Eng Chem Process Des Dev*, 6, **1967**, 245.