Water activity in poly(ethylene glycol) aqueous solutions

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Abstract

Water activities of binary and ternary poly(ethylene glycol)s (PEGs) solutions, at 298 K, were measured with an Aqua Lab CX-2 dew point device. The concentration was varied in the range 5–90 wt% or the solubility limit for each polymer (PEG molecular weights 200, 400, 600, 1000, 1450, 6000, 8000, 10 000 and 20 000). The group contribution method UNIFAC was used for correlating and predicting the experimental data of PEG solutions. Using own experimental data of binary solutions and some data obtained from literature sources, the interaction parameters for a new specific group [–CH$_2$CH$_2$O–] were estimated including a linear temperature dependence. This correlation provides a 0.527% mean deviation between experimental and calculated a_w values. The prediction of water activity for ternary systems results in mean deviation of 0.290%. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Water activity; Poly(ethylene glycol); UNIFAC

1. Introduction

Poly(ethylene glycol)s comprehend a series of water soluble, nonirritating, linear chain polymers of oxyethylene units, with low toxicity. These properties enable their use for commercial and technological applications such as purification of biological materials, pharmaceutical drugs, edible films for food coating and water treatment [1,2]. The property of the aqueous solutions of poly(ethylene glycol)s has been studied by various authors. Sabadini et al. [3] studied the excess volume of solutions of low molecular weight poly(ethylene glycol)s in water and in benzene. The stoichiometry of water molecules per

oxyethylene unit was determined. Herskowitz and Gottlieb [4] employed an isopiestic method to measure the water activity in aqueous solutions of PEG at three different temperatures and use the UNIFAC model to predict the experimental values, but the predictions are not in good agreement with the experimental results.

Water activity (a_w) is a physicochemical property defined as the ratio between the partial pressure of water in a sample and the vapor pressure of pure water at the same temperature. It is important in food engineering since many chemical, enzymatic and microbiological reactions which influence food stability are dependent on the availability of water.

Thermodynamic models of group contribution have been used to correlate and predict the water activity in solutions of sugars, salts, and other biochemical solutes [5–9].

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2. Materials and methods

2.1. Experimental water activities

The water activities of PEG solutions were measured with an AQUA-LAB CX-2 dew point device (Decagon, USA), coupled to a water bath at 25°C and controlled within ±0.1°C. The instrument was previously calibrated with saturated salt solutions over the relative humidity range from 100% to 34.2%. Measurements were made in triplicate, with a resultant mean standard deviation of ±0.001 a_w units. The PEGs used were analytical grade reagents from Sigma (purity higher than 99%) with molecular weights 200, 400, 600, 1000, 1450, 6000, 8000, 10 000 and 20 000. All solutions were prepared with distilled water and a weight precision of ±0.1 mg, using an analytical balance (Sartorius, Germany). Karl Fisher titration was used to determine water content in pure PEGs. This amount of water ranges from 0.20 to 0.75 wt% and it was considered for calculating the water concentration in solutions. Experimental data for binary mixtures are reported in Table 1.

Water activity for some ternary systems containing PEGs with different molecular weights were also measured and used for testing the prediction capability

Table 1
Experimental a_w in binary PEG solutions at 298 K

PEG 200		PEG 400		PEG 600		PEG 1000	
w	a_w	w	a_w	w	a_w	w	a_w
0.0502	0.996	0.0499	0.998	0.0498	0.999	0.0493	0.999
0.0995	0.991	0.0999	0.995	0.0995	0.997	0.0986	0.998
0.1500	0.983	0.1495	0.991	0.1497	0.993	0.1478	0.995
0.1882	0.976	0.1997	0.986	0.1994	0.990	0.1971	0.993
0.2995	0.954	0.2993	0.968	0.2993	0.976	0.2957	0.978
0.4016	0.921	0.4026	0.943	0.3985	0.953	0.3943	0.961
0.4989	0.874	0.4989	0.901	0.4988	0.913	0.4929	0.921
0.5988	0.805	0.5986	0.841	0.5984	0.855		
0.6972	0.717	0.6970	0.760	0.6979	0.777		
0.7983	0.587	0.7989	0.648	0.7976	0.692		
0.8981	0.393	0.8980	0.477	0.8972	0.523		

PEG 1450		PEG 3350		PEG 6000	
w	a_w	w	a_w	w	a_w
0.0496	0.998	0.0497	1.000	0.0497	1.000
0.0993	0.997	0.0993	0.998	0.0995	0.999
0.1489	0.996	0.1489	0.997	0.1489	0.998
0.1985	0.994	0.1988	0.993	0.1987	0.996
0.2978	0.983	0.2980	0.985	0.2980	0.987
0.3975	0.962	0.3972	0.965	0.3972	0.969
0.4962	0.925	0.4964	0.930	0.4970	0.934
0.5985	0.870				
0.6941	0.795				

PEG 8000		PEG 10 000		PEG 20 000	
w	a_w	w	a_w	w	a_w
0.0499	0.999	0.0497	0.999	0.0497	1.000
0.0997	0.998	0.0993	0.998	0.0994	0.999
0.1495	0.997	0.1490	0.996	0.1491	0.999
0.1994	0.996	0.1986	0.996	0.1988	0.997
0.2990	0.986	0.2980	0.985	0.2983	0.988
0.3987	0.968	0.3974	0.970	0.3978	0.969
0.4984	0.932	0.4967	0.932	0.4971	0.935

Table 2
Experimental a_w in ternary PEG solutions at 298 K

PEG 6000 (1)+PEG 20 000 (2)			PEG 400 (1)+PEG 20 000 (2)		
w_1	w_2	a_w	w_1	w_2	a_w
0.0494	0.0494	0.999	0.0499	0.0498	0.996
0.0986	0.0987	0.996	0.1004	0.0995	0.988
0.1397	0.1401	0.988	0.1490	0.1488	0.977
0.1970	0.1970	0.965	0.1997	0.1985	0.954
0.2462	0.2462	0.933	0.2496	0.2483	0.916
PEG 200 (1)+PEG 1450 (2)			PEG 200 (1) + PEG 600 (2)		
w_1	w_2	a_w	w_1	w_2	a_w
0.0500	0.0497	0.993	0.0500	0.0500	0.993
0.1066	0.1015	0.982	0.1004	0.1008	0.981
0.2008	0.1993	0.939	0.1495	0.1483	0.964
0.2482	0.2468	0.901	0.1997	0.2001	0.935
0.2990	0.2982	0.837	0.2500	0.2490	0.892
0.3492	0.3478	0.754	0.2996	0.3091	0.822
			0.3493	0.3493	0.745
			0.3992	0.3997	0.628
PEG 1000 (1)+PEG 10 000 (2)			PEG 1000 (1)+8000 (2)		
w_1	w_2	a_w	w_1	w_2	a_w
0.0490	0.0497	0.998	0.0495	0.0495	0.998
0.0976	0.0990	0.993	0.0984	0.1032	0.993
0.1461	0.1480	0.983	0.1501	0.1471	0.984
0.1930	0.1954	0.964	0.1936	0.1978	0.964
0.2265	0.2420	0.937	0.2373	0.2431	0.933

of UNIFAC model. The experimental data are presented in Table 2.

2.2. Thermodynamic concept of water activity

Water activity is defined as the ratio between the fugacity of water in a sample and the fugacity of pure water at the same temperature and pressure

$$a_w = \frac{f_w(T,P,x_w)}{f_w^0(T,P)} = x_w \gamma_w, \tag{1}$$

where a_w is the water activity; γ_w the activity coefficient of water; x_w mole fraction of water; f_w the fugacity of water in a sample; f_w^0 is the fugacity of pure water at reference conditions.

At moderated conditions of temperature and pressure, the vapor phase behaves ideally and the ratio between the fugacities can be represented as the ratio of partial pressures of water in a sample and pure water at reference conditions.

The activity coefficient of water (γ_w) can be calculated by UNIFAC group contribution method and then, the water activity can be estimated using Eq. (1).

2.3. UNIFAC group contribution method

In the UNIFAC model, the activity coefficient can be calculated as the sum of two contributions: a combinatorial (due to differences in sizes and shapes of solutes and solvents) and a residual, that computes the energetic interactions between groups of the molecules in mixture

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R. \tag{2}$$

The combinatorial part uses the pure component properties such as volume and surface area to calculate the activity coefficients

$$\ln \gamma_i^C = \ln \frac{\Theta_i}{x_i} + \frac{z}{2} q_i \ln \frac{\Theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_j x_j l_j, \tag{3}$$

where

$$\Phi_i = \frac{r_i x_i}{\sum_j r_j x_j}; \quad \Theta_i = \frac{q_i x_i}{\sum_j q_j x_j};$$

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1); \quad r_i = \sum_k v_k^{(i)} R_k;$$

$$q_i = \sum_k v_k^{(i)} Q_k.$$

The van der Waals volume and surface area for water (V_k and A_k, respectively) were calculated directly from molecular structure, e.g. atomic sizes and bond lengths as suggested by Breivi [10].

A relation between the volume parameter $r(n)$ for a n-mer polymer and R_k for the monomer, was proposed by Zhong et al. [11] based on excluded volumes. This relation was considered in the present work for calculating the volume parameter r_i for the polymer molecule, as shown below

$$r_i = r(n) + \sum_j v_j^i R_j = 0.6586 v_k^i R_k + 0.3712 R_k + \sum_j v_j^i R_j, \tag{4}$$

where R_k is the volume parameter for the monomer of an n-mer polymer and R_j are the volume parameters for the end groups of the polymer chain.

The residual part of the activity is a function of group area fractions and energetic interactions between the constituent groups in pure component and in mixture:

$$\ln \gamma_i^R = \sum_k v_k^{(i)} \left[\ln \Gamma_k - \ln \Gamma_k^{(i)} \right], \qquad (5)$$

where Γ_k is the group residual activity coefficient and $\Gamma_k^{(i)}$ is the group residual activity coefficient in a reference solution containing only molecules of type i.

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_m \Omega_m \Psi_{mk} \right) - \sum_m \left(\Omega_m \Psi_{km} \bigg/ \sum_n \Omega_n \Psi_{mn} \right) \right] \qquad (6)$$

and

$$\Omega_m = \frac{Q_m X_m}{\sum_n Q_n X_n}, \quad X_m = \frac{\sum_j V_m^j x_j}{\sum_j X_j \sum_m V_m^j},$$

$$\Psi_{mn} = \exp \left[-\left(\frac{a_{mn} + b_{mn} T}{T} \right) \right],$$

where Ω_m is the area fraction of the group m; X_m the group fraction in the mixture; Ψ_{mn} is the interaction parameter between m and n groups.

The coefficients a_{mn} and b_{mn} were introduced to represent the temperature dependence for the interaction parameters.

Table 3
Values of the group volume and surface area parameters

	R_k	Q_k
Water	0.766[a]	0.874[a]
Oxyethylene	1.5927	1.320

[a]From Ref. [10].

3. Group interaction parameters

For the mixtures PEG/water, the constituent UNIFAC groups were CH_2CH_2O, CH_2, OH and H_2O. In comparison to the original UNIFAC [12], the oxyethylene [$-CH_2CH_2O-$] units of PEG was included as an additional group. To calculate the pair of parameters a_{mn} and b_{mn} between the oxyethylene group and the other conventional UNIFAC groups, a non-linear Marquardt method in the statistical analysis system (SAS) package (Cary, NC, USA) was used. Experimental data measured in the present work (at 298 K) and those reported in the literature [4] (at 293, 313 and 333 K) were used to determine a single set of these parameters.

In the calculation of the combinatorial part, the values of R_k and Q_k for the oxyethylene group were calculated as the sum of R_k and Q_k, corresponding to the groups CH_2 and O. The values of R_k and Q_k can be calculated using the van der Waals volume and surface area determined by a structural group contribution method suggested by Bondi [13]. For structural groups that are not bonded to a carbon atom, this calculation method could result in larger deviations. Thus, the

Table 4
UNIFAC interaction parameters with calculated values and obtained from literature

		CH_2CH_2O	CH_2	OH	H_2O
CH_2CH_2O	a_{mn}	–	3073.80325	413.551994	−140.19436
	b_{mn}	–	−10.126922	−2.245686	2.277
CH_2	a_{mn}	2205.20255	–	986.5[a]	1318.0[a]
	b_{mn}	0.7644	–	–	–
OH	a_{mn}	−2654.907089	156.4[a]	–	353.5[a]
	b_{mn}	9.647	–	–	–
H_2O	a_{mn}	−371.717	300.0[a]	−229.1[a]	–
	b_{mn}	0.617100	–	–	–

[a]Parameters obtained from Ref. [12].

parameter should be calculated directly from molecular structure for molecules as water, ammonia, and hydrogen chloride [10]. Table 3 shows the values of R_k and Q_k for oxyethylene and water used in the present work.

The new interaction parameters calculated for UNIFAC and those from literature [14] are listed in Table 4.

4. Discussion

Fig. 1 shows the comparison between experimental and calculated values by UNIFAC model for PEG 200 at the temperatures of 293, 298, 313 and 333 K. A slight temperature dependence on a_w values is observed along the concentration range studied. The introduction of temperature dependent parameters in the UNIFAC model express this behavior in a very good agreement with experimental data.

The correlations obtained for PEGs with different molecular weights at 298 K are represented in Fig. 2. The ratio between terminal OH groups and the entire

molecule is larger in low molecular weight PEGs than in higher molecular weight PEGs. Thus, PEGs with low molecular weight depress water activity more than those with high molecular weights.

The prediction capability of the proposed method was assessed using the water activities in the ternary systems reported in this work, whose experimental data were not used for the correlation of the interaction parameters. Fig. 3 presents these predictions for a temperature of 298 K in the ternary system PEG 200/PEG 1450/water.

The average relative deviations between calculated and experimental a_w values using UNIFAC model for the binary mixtures were in the range 0.206–1.037%. These results are listed in Table 5. For the ternary mixtures the mean deviation, at 298 K, between experimental and predicted values were 0.290%. Table 6 presents predictions for the ternary mixtures studied in this work. The applicability of the model to predict a_w measured by different techniques is shown in Table 7, which also includes the measurement techniques and the mean deviation between experimental and predicted values.
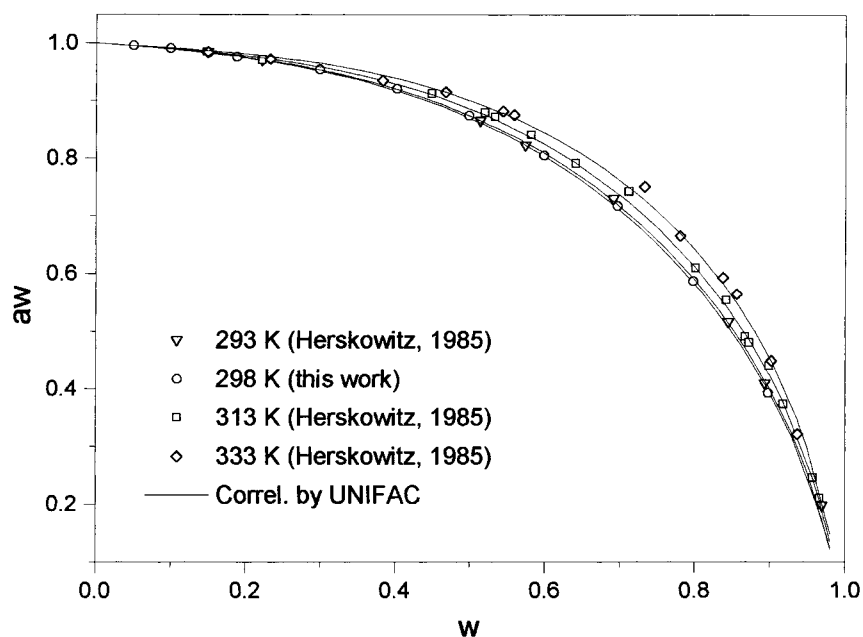

Fig. 1. Experimental ((∇) 293 K [3]; ($\bigcirc$) 298 K (*this work*); ($\square$) 313 K [3]; ($\blacksquare$) 333 K [3]) and calculated water activities for PEG 200 at four different temperatures.
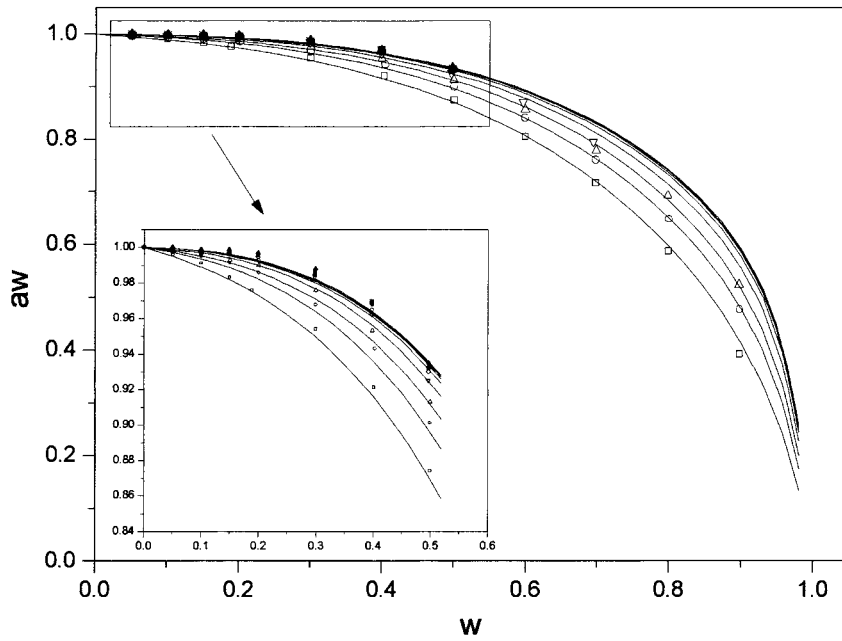
Fig. 2. Experimental water activities at 298 K ((□) PEG 200; (○) PEG 400; (△) PEG 600; (▽) PEG 1450; (◇) PEG 3350; (*) PEG 6000; (•) PEG 8000; (■) PEG 10 000; (▲) PEG 20 000) and correlated by UNIFAC model (———).
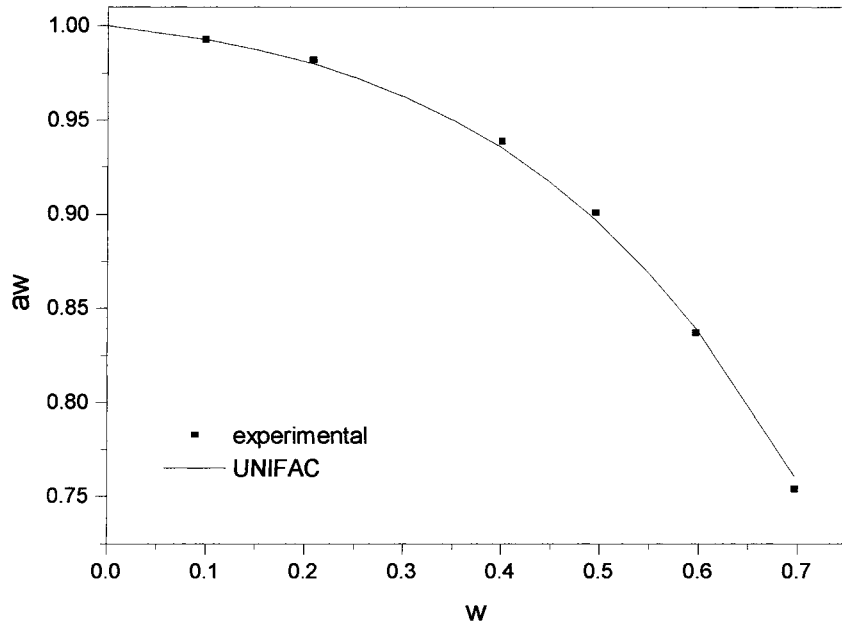

Fig. 3. Water activity prediction in a mixture PEG 200+PEG 1450, at 298 K, by UNIFAC model.

Table 5
Mean deviations between experimental and calculated data of a_w

PEG (mw)	Temperature range (K)	Concentration range	Deviation (%)
200	293–333	0.05–0.97	1.036
400	298	0.05–0.90	0.414
600	293–333	0.05–0.98	1.037
1000	298	0.05–0.50	0.255
1450	298	0.05–0.70	0.585
1500	293–333	0.35–0.98	0.811
3350	298	0.05–0.50	0.206
6000	298–333	0.05–0.98	0.655
8000	298	0.05–0.50	0.251
10 000	298	0.05–0.50	0.253
20 000	298	0.05–0.50	0.289

Table 7
a_w Prediction in PEG ternary mixtures at 298 K

PEG mixtures	a_w Range	Mean deviation (%)
6000+20 000	0.999–0.933	0.252
400+20 000	0.996–0.916	0.195
200+1450	0.993–0.754	0.380
200+600	0.993+0.628	0.416
1000+10 000	0.998–0.937	0.221
1000+8000	0.998–0.933	0.274

5. Conclusion

The proposed method described is in very good agreement with the experimental a_w for the binary and ternary systems studied in this work, including some data available in the literature. The adjustment of new interaction parameters for the oxyethylene group and the use of suitable structural parameters for water and oxyethylene units improve the correlation as well as prediction capabilities of the UNIFAC model.

6. Nomenclature

a_{mn}, b_{mn}	group interaction parameters
A_k	van der Waals area
a_w	water activity
f_w^0	fugacity of pure water
f_w	fugacity of water in a sample
P	pressure
PEG	poly(ethylene glycol)
Q_k	group area parameter
V_k	van der Waals volume
$r(n)$	volume parameter for a n-mer polymer
T	temperature
v_k	number of groups of type k in molecule I
x_w	mole fraction of water
x_i	mole fraction of component i
Φ_i	component volume fraction
γ_i	activity coefficient of component i
γ_i^C	combinatorial activity coefficient
γ_i^R	residual activity coefficient
Γ_k	group residual activity coefficient
$\Gamma_k^{(i)}$	group residual activity coefficient in a reference solution
Θ_i	component area fraction
Ω_m	area fraction of group m
Ψ_{mn}	interaction parameter between m and n groups

Table 6
a_w Prediction in PEG binary solutions compared to reported literature data at 298 K

Measurement method	PEG molecular weight range	a_w Range	Mean deviation (%)	Reference
Hygrometer Novasina	200–20 000	0.746–0.996	0.442	[15]
Microclimats	82–35 000	0.734–0.947	0.959	[15]
Cryometry	200–35 000	0.978–0.996	0.084	[15]
Isopiestic	1000/4000	0.943–0.990	0.317	[16]
	1000/8000	0.966–0.994	0.807	[17]

Acknowledgements

References

[1] R.L. Davidson, Handbook of Water-soluble Gums and Resins, McGraw-Hill, New York, 1980, p. 18.

[2] L.H.M. Silva, J.S.R. Coimbra, A.J.A. Meirelles, J. Chem. Eng. Data 42 (1997) 398.

[3] E. Sabadini, E.M. Assano, T.D.Z. Atvans, J. Appl. Polym. Sci. 63 (1997) 301.

[4] M. Herskowitz, M. Gottlieb, J. Chem. Eng. Data 30 (1985) 233.

[5] G. Achard, J.B. Gros, C.G. Dussap, Industries Alimentares et Agricoles 109 (1992) 93.

[6] A. Correa, J.F. Comesaña, A. Sereno, Fluid Phase Equilibria 98 (1994) 189.

[7] H. Kuramochi, H. Noritomi, D. Hoshino, K. Nagahama, Fluid Phase Equilibria 130 (1997) 117.

[8] C. Velezmoro, A.J.A. Meirelles, Drying Technology 16 (1998), in press.

[9] C. Velezmoro, A.J.A. Meirelles, A. Vitali, Engineering and food at ICEF 7, Proceedings of the Seventh International Congress on Engineering and Food, Part 1, Brighton, UK, 1997, p. A145.

[10] S.W. Breivi, Ind. Eng. Chem. Process Des. Dev. 21 (1982) 367.

[11] C. Zhong, Y. Sato, H. Masuoka, X. Chen, Fluid Phase Equilibria 123 (1996) 97.

[12] A. Fredenslund, R.L. Jones, J.M. Prausnitz, AIChE J. 21 (1975) 1086.

[13] A. Bondi, Physical Properties of Molecular Crystals, Liquids and Glasses, Wiley, New York, 1968, p. 450.

[14] S.S. Jorgensen, B. Kolbe, J. Gmehling, P. Rasmussen, Ind. Eng. Chem. Process Des. Dev. 18 (1979) 714.

[15] A. Voilley, G. Blond, G. Chevallier, Lebens. Wiss. u. Technol. 22 (1989) 32.

[16] D-Q. Lin, L.-H. Mei, Z.-Q. Zhu, Z.-X. Han, Fluid Phase Equilibria 118 (1996) 241.

[17] L.R. Ochs, M. Kabiri-Badr, H. Cabezas Jr., , AIChE J. 36 (1990) 1908.