Use of an electrolyte equations of state to the calculation of vapor-liquid equilibria and mean activity coefficients in water-alcohol electrolyte systems

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Abstract

In a previous paper [1] a new electrolyte equation of state has been developed and applied to aqueous strong electrolyte solutions. One of the original features of this equation was that all ionic parameters could be determined using correlations related to experimental solvation properties which leads to a predictive model. Later, Zuo and Fürst [2] extended it to predict vapor pressure and mean ionic activity coefficients for various nonaqueous electrolyte systems. In this work the model has been extended to mixed-solvent electrolyte systems. This has been done by deducing most of the ionic parameters from experimental solvation properties and by developing mixing rules to represent preferential solvations in mixed-solvents, the aim being to minimize the number of adjusted parameters. Vapor-liquid equilibrium data relative to 26 water-alcohol-salt systems and mean ionic activity coefficients relative to 8 water-alcohol-salt systems have been represented using only 18 parameters. The obtained deviations for VLE are similar to those obtained by other authors, but with less adjustable parameters. Furthermore it could represent mean ionic activity coefficients as well. Finally the model has been used to predict VLE for 12 other mixed-solvent electrolyte systems with satisfactory results.

Key words: Equation of state; Vapor-liquid equilibria; Electrolyte; Mixed-solvent

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1. Introduction

Mixed-solvent systems are present in many industrial processes. This explains that in the past few years an increasing number of papers has been devoted to their thermodynamic modeling. An analysis of previous papers shows that quite all the authors used an excess Gibbs energy framework, representing essentially vapor-liquid equilibria (VLE).

In 1993 we derived [1] a new equation of state (EOS) adapted to aqueous electrolyte systems. The first step was to test the equations on strong aqueous electrolyte systems. The most original result was that the use of correlations between all adjustable parameters and experimental diameters representative of solvation allowed us to obtain a predictive method which has been successfully tested. Since that time, the model has been extended and applied to various systems such as the salting out effect of salts on gas solubilities at high pressures [3]. Recently, Zuo and Fürst [2] have successfully extended the EOS to the representation of vapor pressure and mean ionic activity coefficients relative to numerous nonaqueous electrolyte systems without or with a very limited number of fitted parameters.

The aim of this work is to extend our EOS to mixed-solvent electrolyte systems.

2. Main features of the electrolyte equation of state

The basis of the EOS derived by Fürst and Renon [1] is an expression for the Helmholtz energy which contains four contributions:

$$\left(\frac{\Delta a}{RT}\right)=\left(\frac{\Delta a}{RT}\right)_{RF}+\left(\frac{\Delta a}{RT}\right)_{SR1}+\left(\frac{\Delta a}{RT}\right)_{SR2}+\left(\frac{\Delta a}{RT}\right)_{LR} \qquad (1)$$

The first term (RF) is relative to repulsive forces, the second one (SR1) represents attractive short-range interactions involving no ions. The two last terms are specific to ionic contributions, the first one (SR2) representing solvation interactions and the second one (LR) being related to long-range interactions.

In fact our model may be considered as an extension of a classical cubic non-electrolyte EOS and the RF and SR1 terms being similar to the corresponding terms of

the SRK equation of state. The LR contribution is expressed using a simplified version of the MSA model. The SR2 term is a specific one and involves symmetrical cation-solvent (W_{cs}) and cation-anion (W_{ca}) interaction parameters. The other interactions involving ions (cation-cation, anion-anion or anion-solvent) are ignored due to charge repulsive effects and low solvation of anions (if compared to cations). The others ionic adjustable parameters are the anionic (b_a) and cationic (b_c) covolumes. Hence the model contains up to four kinds of adjustable ionic parameters. However, it has been shown [1] that all these parameters could be related to Stokes diameters σ_c^S (for cations) and Pauling diameters σ_a^P (for anions):

$$b_c = \lambda_1 \left(\sigma_c^S\right)^3 + \lambda_2 \qquad and \qquad b_a = \lambda_1 \left(\sigma_a^P\right)^3 + \lambda_2 \tag{2}$$

And, for interaction parameters:

$$W_{cs} = \lambda_3 \sigma_c^S + \lambda_4 \qquad and \qquad W_{ca} = \lambda_5 \left(\sigma_c^S + \sigma_a^P\right)^4 + \lambda_6 \tag{3}$$

The use of Pauling diameters in the case of anions is justified by their lower solvation. Correlation coefficients λ_1-λ_6 have been deduced from a data treatment of numerous experimental coefficients relative to halide and non-halide systems.

The EOS proposed by Fürst and Renon [1] has been extended for the representation of vapor pressures and mean activity coefficients relative to various nonaqueous by Zuo and Fürst [2]. In their paper, two methods have been proposed. The first one is entirely predictive; it is just an extrapolation of the results obtained in the case of aqueous solutions, the Stokes diameters determined in water being replaced by Stokes diameters determined experimentally in the appropriate solvents.

In method II, it is assumed that the values of ionic covolumes in nonaqueous electrolyte solutions are the same as in aqueous electrolyte solutions. On the contrary, binary interaction parameters (W_{ij}) are solvent dependent and estimated from Eq. (3), using Stokes diameters determined in the solvent. This method is no more entirely predictive because it is assumed that λ_5 and λ_6 coefficients (in Eq. (3)) are adjustable parameters. They have been determined by fitting experimental vapor pressure data restricted to binary salt-ethanol mixtures at 298.15 K. The obtained λ_5 and λ_6 values are

then used for the prediction of thermodynamic properties relative to the other nonaqueous solvents (methanol, propanol and acetonitrile). The detailed results are given elsewhere [2]. This second method although not entirely predictive is more suitable for the extrapolation to mixed-solvent systems and has been used in this work.

3. Extension of the electrolyte EOS to mixed-solvent electrolyte systems

To apply our electrolyte EOS to mixed-solvent systems, the first step is to choose a mixing rule for the non-ionic part of the model. The Wong-Sandler mixing rule [4] associated to the UNIQUAC model has been used. The corresponding adjustable parameters ($k_{ij}=k_{ji}$, τ_{ij} and τ_{ji}) are determined by fitting VLE data. It has also to be mentioned that the dielectric constant of the mixture is calculated using a linear mixing rule over solvent volume fractions.

The next step concerns the determination of mixing rules for ionic parameters. As the ionic parameters are related to solvation properties, the mixing rule problem is strongly connected with the preferential solvation problem in mixed-solvents. To get an idea of this phenomena, we dispose of experimental limiting conductance for Na^+, K^+, Cs^+ and Li^+ ions in ethanol-water systems at 25°C [5]. Applying the Stokes law, these data may be converted into Stokes diameter values. Figure 1 shows the variation of these values as a function of solvent mixture composition.

As the electrolyte EOS was able to represent experimental values with low deviations in nonaqueous solvents as well as in aqueous solutions, using parameters related to Stokes diameters, the same approach has been assumed in the case of mixed-solvent systems. This implies that the Stokes diameters in mixed-solvents σ_m could be calculated as a function of the solvent composition and of σ_1 and σ_2, the corresponding values in pure solvents. For this purpose, the following equation has been used:

$$\ln\sigma_m = x_1^{(0)3}\ln\sigma_1 + x_2^{(0)3}\ln\sigma_2 - x_1^{(0)}x_2^{(0)}\left\{A_{12} - B_{12}\left[\left(M_1/M_2\right)^2 x_1^{(0)} + x_2^{(0)}\right]^{-1}\right\} \qquad (4)$$

This expression is based on an expression used to express the viscosity variation in mixed-solvent systems [6]. In this equation M_i is the molecular weight of solvent i and

$x_i^{(0)}$ is the salt-free mole fraction of solvent i. It also involves two adjustable parameters A_{12} and B_{12}, which are obviously ion dependent (see Figure 1) but also probably solvent dependent, although we have no data concerning experimental Stokes diameters in other solvent mixtures. If we adopt the approach defined above as method II, the ionic covolumes are set to their values in water. Interaction parameters between cation and water are related by Eq. 3 to the Stokes diameters deduced from Eq. 4, correlation parameters λ_3 and λ_4 being the same as in water.

The next step is to find a mixing rule to express $\lambda_5^{(m)}$ and $\lambda_6^{(m)}$ in mixed-solvent solution as a function of their values in both pure solvent ($\lambda^{(i)}$and $\lambda^{(j)}$). For this purpose, we use an expression similar to one published by Schwartzentruber [7] for the mixing rule associated to non-electrolyte systems:

$$\lambda_k^{(m)} = \sum_{i=1}^{NS}\sum_{j=1}^{NS} x_i^{(0)} x_j^{(0)} \frac{\lambda_k^{(i)} + \lambda_k^{(j)}}{2}\left[1 - k_{ij} - l_{ij}\frac{m_{ij}x_i^{(0)} - m_{ji}x_j^{(0)}}{m_{ij}x_i^{(0)} + m_{ji}x_j^{(0)}}\left(x_i^{(0)} + x_j^{(0)}\right)\right] \quad (5)$$

In this equation, k_{ij}, l_{ij} and m_{ij} are adjustable parameters (with $k_{ij}= k_{ji}$, $l_{ij}=-l_{ij}$ and $m_{ij}+m_{ji}=1$) which are only solvent dependent and, hence, have the same value for all ions. Obviously, if the three types of parameters are set to zero, the mixing rule is reduced to a linear mixing rule of the salt-free mole fraction of solvents.

Firstly, we tried to use a predictive approach to represent equilibrium data relative to mixed solvent systems. The corresponding method is the following:

- A_{12} and B_{12} parameters (Eq. 4) are determined by fitting experimental Stokes diameters in water-ethanol solvents [5].
- In the case of systems where experimental Stokes diameters in solvent mixtures are not available (ethanol - water solutions with Ca^{2+} and all the systems containing other solvent mixtures, see Tables 4 and 5), a linear mixing rule is used to deduce σ_m from σ_1, σ_2 and $x_i^{(0)}$.
- a linear mixing rule is use for the determination of $\lambda_5^{(m)}$ and $\lambda_6^{(m)}$ ($k_{ij}= l_{ij}= m_{ij} =0$)

The agreement between calculated values and experimental VLE data is good excepted in the case of water-propanol electrolyte systems. In this case the linear mixing

rule of the Stokes diameters is inadequate since the preferential solvation between ions and water is much stronger than that in water-methanol systems. It can also be seen from Figure 1 that the Stokes diameters in water-propanol are far away from the linear mixing rule.

Hence, to get a modeling valid for all the considered systems, an approach involving adjustable parameters has been used. The model parameters are not only A_{12} and B_{12} but also k_{ij}, l_{ij} and m_{ij}. All these parameters have been adjusted using experimental VLE data. As said above, it appears that A_{12} and B_{12} are solvent dependent (and ion dependent). However it may be shown that, for water-alcohol systems, when the following equation is used to correlate the preceding parameters to the alcohol critical compressibility factor :

$$A_{12} = A_{12}^{(0)} Z_c + A_{12}^{(1)} \qquad and \qquad B_{12} = B_{12}^{(0)} Z_c + B_{12}^{(1)} \tag{6}$$

New parameters $A^{(0)}$, $A^{(1)}$, $B^{(0)}$ and $B^{(1)}$ are introduced which are only ion dependent, reducing the number of adjustable parameters. A combination of Eq. 4 and Eq. 6 is used in the case of water-methanol, water-ethanol and water-propanol electrolyte systems.

The values of the adjusted parameters are given in Tables 1 and 2 and the deviations between calculated and experimental data VLE are summarized in Tables 3 and 4. It has to be noticed that not only VLE data are well represented with a limited number of adjustable parameters compared to the large number of systems considered but also that the deviation associated to the calculation of the few mean ionic activity coefficient data sets are consistent to corresponding experimental deviations.

Furthermore, we have also considered 12 mixed-solvent systems different from water-alcohol mixtures. In this case a linear mixing rule is used for the Stokes diameters and for λ_5 and λ_6 has been used resulting in a predictive modeling. The predicted results are given in Table 5. The predictions are in very good agreement with experimental data.

Our results have been then compared to those obtained by Ye et al. [8], those of Sander et al. and Macedo et al.[9, 10] and those which can be obtained using the

electrolyte NRTL model of Chen [11,12]. The comparison between our method and the preceding ones shows that our deviations are lower or of the same order of magnitude as what is obtained with the other modelings, but with less parameters.

Ye et al. [8] calculated mean ionic activity coefficients of NaBr in methanol-water and in ethanol-water by a modified Pitzer model. The reported deviations are 2.78% and 4.81%, respectively, instead of 2.64% and 1.80% for our modeling. To compare our approach to the results obtained with C. C. Chen electrolyte NRTL equations [11], we applied the corresponding model to the representation of data detailed in Table 4. In this case, the alcohol-salt nonrandomness factor has been set equal to the best value obtained by Mock et al. [12]. Two interaction parameters per salt - alcohol have be determined by fitting VLE data. The deviations are very close to the deviations reported in Table 4. For instance the deviations on vapor mole fractions associated to the use of NRTL electrolyte model is 0.01824 instead of 0.01812. The models of Sander et al. and Macedo et al.[9, 10] have also been applied to predict VLE for some mixed-solvent electrolyte systems taking into account the parameter values given by the authors. The results of the comparison of both models with our EOS is given in Table 6. In this case, the results are comparable.

4. Conclusion

In this work, the EOS developed by Fürst and Renon [1] has been extended to mixed-solvent electrolyte systems. A mixing rule has been developed for representing preferential solvations. The extended EOS has been tested on the prediction/correlation of mean ionic activity coefficients and vapor-liquid equilibria for a number of mixed-solvent salt systems. The results are quite satisfactory. In addition a comparison with what is obtained using previously published models (Ye et al. [8], Sander et al. [9], Macedo et al. [10] and the electrolyte NRTL model [11]) shows that, with a lower number of adjustable parameters, our approach gives lower or similar deviations.

Furthermore, our EOS could be used, in some cases to predict VLE equilibria. This is the case for all water - alcohol systems excepted water-propanol mixtures.

Acknowledgments

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Table 1 Adjustable coefficients ($A^{(0)}$, $A^{(1)}$, $B^{(0)}$ and $B^{(1)}$)*

Ion	$A^{(0)}$	$A^{(1)}$	$B^{(0)}$	$B^{(1)}$
Na^+	-39.0310	3.04526	5.26552	-0.237177
K^+	-78.3695	12.8623	33.0985	-7.050890
Li^+	29.1667	-13.5333	4.16667	-0.033334

* For Ca^{2+} in methanol-water and ethanol-water, the linear mixing rule is used for the Stokes diameter. For Ca^{2+} in propanol-water, A_{12} = -6.456, B_{12} = 0.3926.

Table 2 Adjustable coefficients k_{ij}, l_{ij} and m_{ij}*

System	k_{12}	l_{12}	m_{12}
water (1)-methanol (2)	0.06519	-0.6200	0.1254
water (1)-ethanol (2)	-0.6825	-1.0720	0.07184

* For other systems, k_{12}=0, l_{12}=0 and m_{12}=0.

Table 3 Deviations of the calculated mean activity coefficients for water-alcohol electrolyte solutions at 298.15 K

System		Max.	N_p	$\Delta\gamma_\pm/\gamma_\pm$	Ref.
Alcohol	Salt	Molality		%	
Ethanol	NaBr	4.86	138	1.80	[13]
Ethanol	NaBr	1.00	100	1.87	[14]
Ethanol	NaCl	2.00	123	4.21	[15]
Methanol	KCl	3.87	122	3.79	[16]
Methanol	NaBr	3.05	126	2.64	[13]
Methanol	CsCl	0.20	25	2.24	[17]
Methanol	KCl	0.20	30	0.67	[17]
Methanol	NaCl	0.20	30	2.49	[17]
Methanol	RbCl	0.20	30	0.65	[17]
Methanol	LiCl	0.20	30	1.74	[17]
Overall			754	2.64	

Table 4 Deviations of the calculated VLE for water-alcohol electrolyte systems

System		T, or	Max.	N_p	$\Delta P/P$	ΔT	Δy_1	Ref.
Alcohol	Salt	P	x_{salt}		%	K		
Methanol	$CaCl_2$	298.15 K	0.04641	40	1.91		0.01006	[18]
Methanol	$CaCl_2$	1.013 bar	0.05245	12		0.69	0.00813	[19]
Methanol	KCl	1.013 bar	0.03455	32		0.72	0.03025	[20]
Methanol	KCl	1.013 bar	0.06497	36			0.02998	[21]
Methanol	KBr	1.013 bar	0.09195	26			0.02663	[21]
Methanol	LiCl	1.013 bar	0.03348	16		0.93	0.01925	[20]
Methanol	NaBr	1.013 bar	0.06564	23		0.52	0.01779	[20]
Methanol	NaBr	1.013 bar	0.09195	19			0.01084	[21]
Methanol	NaCl	1.013 bar	0.07101	33			0.02011	[21]
Ethanol	$CaCl_2$	1.013 bar	0.07248	12		1.69	0.02117	[19]
Ethanol	$CaCl_2$	298.15 k	0.02011	9	1.02		0.01524	[22]
Ethanol	$CaCl_2$	298.15 k	0.06042	20	1.96		0.02814	[18]
Ethanol	$Ca(NO_3)_2$	0.55 bar	0.08193	45		1.26	0.01959	[23]
Ethanol	NaI	298.15 K	0.02828	9	0.62		0.00871	[22]
Ethanol	NH_4I	298.15 K	0.02881	9	2.85		0.01059	[22]
Ethanol	NaCl	298.15 K	0.02155	22	1.44			[24]
Ethanol	KCl	298.15 K	0.02155	20	2.12			[24]
Ethanol	NH_4Br	1.01 bar	0.08920	27		0.89	0.01367	[25]
Ethanol	KBr	1.01 bar	0.09147	35		0.53	0.00879	[25]
Ethanol	KI	1.01 bar	0.08813	14		0.38	0.00342	[26]
Ethanol	NaAc	1.01 bar	0.13000	10		2.97	0.01179	[26]
Ethanol	KAc	1.01 bar	0.08750	14		1.29	0.01310	[26]
1 Propanol	NaBr	1.013 bar	0.11696	22		0.81	0.01194	[21]
1 Propanol	NaCl	1.013 bar	0.10596	35		0.62	0.01886	[21]
1 Propanol	KBr	1.013 bar	0.10204	27		1.23	0.01942	[21]
2 Propanol	$CaCl_2$	1.013 bar	0.02214	27		0.33	0.01826	[27]
2 Propanol	NaCl	1.013 bar	0.04919	56		0.75	0.01608	[28]
2 Propanol	NaBr	1.013 bar	0.11099	53		0.61	0.02503	[21]
2 Propanol	LiCl	348.25 K	0.11235	20	3.81		0.01217	[29]
2 Propanol	LiCl	1.013 bar	0.11010	27		0.70	0.02080	[30]
2 Propanol	LiBr	348.15 K	0.1111	18	5.27		0.01428	[29]
2 Propanol	LiBr	1.013 bar	0.10300	27		0.63	0.02011	[30]
2 Propanol	$Ca(NO_3)_2$	0.55 bar	0.09233	43		2.36	0.02610	[23]
Overall				838	2.40	0.94	0.01812	

Table 5 Deviations of the calculated VLE for mixed-solvent electrolyte mixtures

System		T, or	Max.	N_p	$\Delta P/P$	ΔT	Δy_1	Ref
Solvent	Salt	P	x_{salt}		%	K		
Methanol - Ethanol	$CaCl_2$	298.15 K	0.06434	20	0.94		0.01212	[18]
Methanol - Ethanol	$CaCl_2$	1.013 bar	0.07683	27		1.10	0.01224	[27,31]
Methanol - Ethanol	$CuCl_2$	303.15 K	0.11380	49	2.14			[32]
Methanol - 1 Propanol	$CaCl_2$	298.15 K	0.08348	36	2.11		0.00962	[18]
Ethanol - 1 Propanol	$CaCl_2$	298.15 K	0.08535	36	0.94		0.00467	[18]
1 Propanol - 2 Propanol	$CaCl_2$	1.013 bar	0.09794	48		0.99	0.01608	[19]
Tetrahydrofuran - Water	$CaCl_2$	1.013 bar	0.05679	12		0.44	0.02344	[33]
Tetrahydrofuran - Water	LiCl	1.013 bar	0.11110	9		0.80	0.01847	[33]
Tetrahydrofuran - Water	NaCl	1.013 bar	0.04932	12		0.51	0.01609	[33]
Ethyl Acetate - Ethanol	$CaCl_2$	1.013 bar	0.08068	14		3.59	0.02267	[34]
Methanol - Methyl Acetate	$CaCl_2$	1.013 bar	0.11699	16		1.52	0.01217	[34]
Methanol - Ethyl Acetate	$CaCl_2$	1.013 bar	0.10523	33		1.75	0.01255	[35]
Acetone - Methanol	$CaCl_2$	1.013 bar	0.08235	28		1.17	0.02032	[36]
Overall				340	1.66	1.31	0.01373	

Table 6 Comparison of our EOS with the Models of Macedo et al. and Sander et al. for Mixed-Solvent Electrolyte Systems

	Deviations								
No. of Systems	Our Model			Macedo et al.			Sander et al.		
	$\Delta P/P$, %	ΔT K	Δy_1	$\Delta P/P$, %	ΔT K	Δy_1	$\Delta P/P$, %	ΔT K	Δy_1
19	2.81	0.66	0.01434	4.88	0.65	0.01901			
15	2.95	0.78	0.01421				3.77	0.52	0.01608

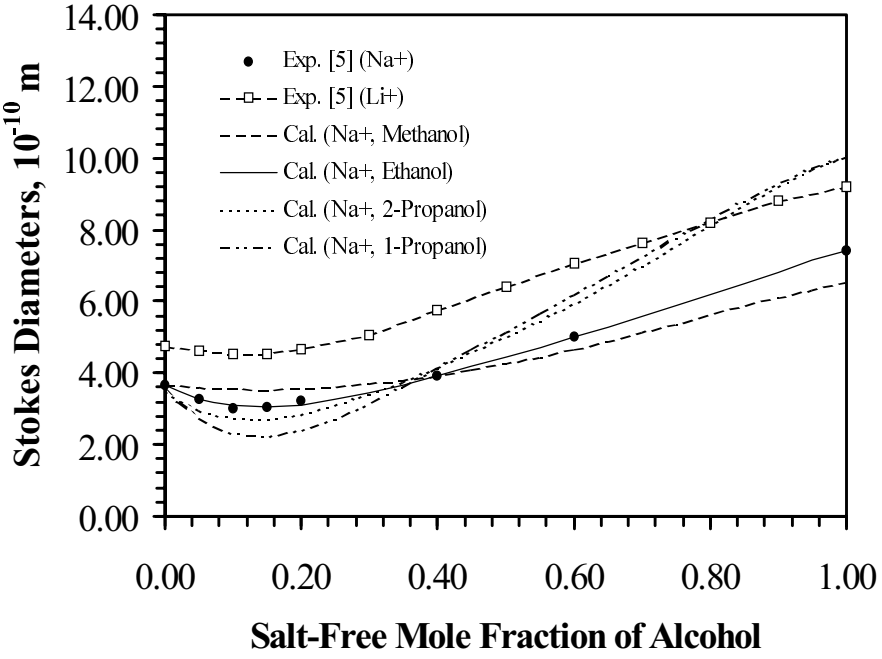

Figure 1 Stokes diameters of Na^+ and Li^+ in water-alcohol mixtures at 298.15 K