Representation of nonideality in concentrated electrolyte solutions using the Electrolyte NRTL model with concentration-dependent parameters

V. Abovsky, Y. Liu* , and S. Watanasiri

Aspen Technology, Inc., Ten Canal Park, Cambridge, MA 02141

Abstract

The Electrolyte NRTL model proposed by Chen et al. [1, 2] has been modified to include concentration dependence of interaction parameters in order to enhance the capability of the model in representing the nonideality of concentrated electrolyte solutions. The concentration-dependent interaction parameter is based on the concept that the multi-body effect should be considered in determining the local composition when the electrolyte concentration is high. In this work, a linear concentration dependence is assumed and the activity-coefficient expressions for cations, anions and molecular species are derived from the excess Gibbs energy expression through the thermodynamic relationship. Therefore, the activity-coefficient expressions are consistent and satisfy the Gibbs-Duhem equation. The experimental mean-ionic-activity-coefficient of highly soluble aqueous electrolyte systems have been used to regress the concentration-dependent parameters. The calculated values and experimental data are in excellent agreement. The deviations are usually within experimental uncertainty and significantly smaller than those using the original model. The modified model is completely compatible with the original model because it reduces to the original model when the concentration dependent term is zero.

Keywords: Activity Coefficient Model; Electrolytes; Aqueous Solutions; Data Regression

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* To whom correspondence should be addressed

Introduction

There is a wide variety of important industrial processes involving electrolyte solutions. Wasterwater treatment, seawater desalination, gas scrubbing, extractive distillation, normal or extractive crystallization and hydro-metallurgical process are a few such examples. Modeling the thermodynamic properties of electrolyte solutions is essential for design and simulation of these processes. For some processes, property modeling in the dilute or intermediate concentration range of electrolytes is all that is required, while for others modeling in the high concentration range is of great importance.

Although in the last few decades many thermodynamic models for electrolyte solutions have been proposed [3], most of them have applicable concentration limit around 6 m for the aqueous electrolytes of uni-uni valence (for nonuni-uni valent electrolytes, the limit is even lower). Only a few models claimed to be able to model the entire concentration range for those electrolytes which have solubility far above the usual applicable limit. Among the few, one is the Electrolyte NRTL model proposed by Chen et al. [1, 2]. Since its publication in 1982, the model has been successfully applied to model the phase-equilibria of a broad range of electrolyte systems including high concentration electrolyte systems and is widely used in the chemical and other industries. However, for some high concentration electrolyte systems such as $LiBr-H_2O$ and $CaCl_2-H_2O$ where nonideality in the high concentration range is large, the results using the Electrolyte NRTL model is not satisfactory. There is still a need for further improvement.

The objective of the present work is to improve the capability of the Electrolyte NRTL model for high concentration electrolyte systems by introducing concentration-dependent interaction parameters. The interaction-parameter concentration dependency is introduced by considering the multi-body effect in determining the local composition. The experimental mean-ionic-activity-coefficient data of highly soluble aqueous electrolyte systems are fitted using the Electrolyte NRTL model with and without the interaction-parameter concentration dependency and the results are compared.

Electrolyte NRTL Model

The Electrolyte NRTL model proposed by Chen et al. [1, 2] assumes the excess Gibbs energy to be the sum of two interaction contributions, one long range and one short range. The long-range interaction contribution is represented by the Pitzer-Debye-Huckel equation [4], which accounts for the contribution due to the electrostatic forces among all ions. The short-range interaction contribution is represented by the electrolyte NRTL expression, which accounts for the contribution due to short-range interaction forces among all species. The electrolyte NRTL expression was developed based on the Non-Random-Two-Liquid local-composition concept [5], the like-ion repulsion assumption and the local electro-neutrality assumption. Later, Chen and coworkers [6] introduced a Born contribution to the model to extend its capacity to the mixed-solvent electrolyte systems. The Born contribution accounts for the change of Gibbs energy associated with moving the ionic species from a mixed-solvent reference state to an aqueous reference state. After proper consideration of unsymmetric convention, the excess Gibbs energy expression of the three-contribution Electrolyte NRTL model is given as follows:

$$g^{ex*} = g^{ex*,PDH} + g^{ex*,Born} + g^{ex*,lc} \tag{1}$$

For detailed information on the complete excess Gibbs energy expression of the three-contribution Electrolyte NRTL model, please refer to reference [6].

Concentration-dependent Interaction Parameters

In 1986, Sander, Rasmussen and Fredenslund [7] introduced the concentration-dependent interaction parameters into an electrolyte UNIQUAC expression by an empirical way. In this work, we introduced interaction parameter concentration dependency into the electrolyte NRTL expression by considering the multi-body effect in the local composition determination. In deriving of the electrolyte NRTL expression with interaction-parameter concentration dependency, we considered not only the Non-Random-Two-Liquid local-composition concept, the like-ion repulsion assumption and the local electroneutrality assumption but also the followings:

1. In the high concentration region, the mole ratio of solvents to ions is low. The probability of an ion being immediately surrounded by ions of opposite charge becomes significant.
2. The amount of the ions in the immediate surrounding of a central ion varies with the electrolyte concentration.
3. The interaction energy between a central ion and the ions in the immediate surrounding is affected by the amount of ions in the immediate surrounding.
4. For simplicity, this multi-ion effect in the immediate surrounding is assumed to be a linear function of a key solvent.
5. Since the high concentration electrolyte systems are basically the aqueous electrolyte systems, we assume the key solvent is water.

Following the derivation steps outlined by Chen and Evans [2], we obtained the electrolyte NRTL excess-Gibbs-energy expression with interaction-parameter concentration dependency as follows:

$$\frac{g^{ex,lc}}{RT}=\sum_m X_m \frac{\sum_j X_j G_{jm}\tau_{jm}}{\sum_k X_k G_{km}}+\sum_c X_c \sum_{a'}\left(\frac{X_{a'}}{\sum_{a''} X_{a''}}\right)\frac{\sum_j X_j G_{jc,a'c}\tau_{jc,a'c}}{\sum_k X_k G_{kc,a'c}}+\sum_a X_a \sum_{c'}\left(\frac{X_{c'}}{\sum_{c''} X_{c''}}\right)\frac{\sum_j X_j G_{ja,c'a}\tau_{ja,c'a}}{\sum_k X_k G_{ka,c'a}} \tag{2}$$

where:

$$G_{jm}=\exp\left(-\alpha_{jm}\tau_{jm}\right) \tag{2a}$$

$$G_{jc,ac}=\exp\left(-\alpha_{jc,ac}\tau_{jc,ac}\right) \tag{2b}$$

$$G_{ja,ca}=\exp\left(-\alpha_{ja,ca}\tau_{ja,ca}\right) \tag{2c}$$

$$G_{cm}=\frac{\sum_a X_a G_{ca,m}}{\sum_{a'} X_{a'}} \tag{2d}$$

$$G_{am}=\frac{\sum_c X_c G_{ca,m}}{\sum_{c'} X_{c'}} \tag{2e}$$

$$\alpha_{cm}=\frac{\sum_a X_a \alpha_{ca,m}}{\sum_{a'} X_{a'}} \tag{2f}$$

$$\alpha_{am}=\frac{\sum_c X_c \alpha_{ca,m}}{\sum_{c'} X_{c'}} \tag{2g}$$

$$\tau_{mc,ac} = \tau_{cm} - \tau_{ca,m} + \tau_{m,ca} \tag{2h}$$

$$\tau_{ma,ca} = \tau_{am} - \tau_{ca,m} + \tau_{m,ca} \tag{2i}$$

$$\tau_{ca,m} = C_{ca,m} + \frac{D_{ca,m}}{T} + E_{ca,m}\left[\frac{(Tr-T)}{T} + \ln\left(\frac{Tr}{T}\right)\right] + F_{ca,m} X_w \tag{2j}$$

$$\tau_{m.ca} = C_{m,ca} + \frac{D_{m,ca}}{T} + E_{m,ca}\left[\frac{(Tr-T)}{T} + \ln\left(\frac{Tr}{T}\right)\right] + F_{m,ca} X_w \tag{2k}$$

The variables τ_{cm} and τ_{am} are computed from G_{cm} and G_{am} according to Eq. (2a), (2d) and (2e). *C, D, E* and *F* are adjustable parameters where *D* and *E* are related to temperature dependency and *F* is related to concentration dependency. For simplicity, we assume there is no concentration dependency for the interaction parameters between ion pairs and non-water molecular species. Therefore only when the molecular species, m, is water, *F* can be applied. Otherwise *F* is set to zero.

The short-range NRTL activity-coefficient expressions for cations, anions and molecular species are obtained through the thermodynamic relation:

$$\left(\frac{\partial N_T g^{ex,lc}}{N_i}\right)_{T,P,N_{i\neq j}} = RT \ln \gamma_i \tag{3}$$

where N_i is the mole number of species i and N_T is the total mole number for all species in the system. The effective mole fraction of species i is defined as $X_i = N_i A_i / N_T$. For ionic species, A_i is equal to the absolute value of the charge for ion i. For molecular species, A_i is equal to unity. For detailed information on the short-range NRTL activity-coefficient expressions with parameter-concentration dependency, please refer to reference [6]. As pointed out by reference [8] and [9], the equation-of-state expressions or activity-coefficient expressions should be invariant when a component is divided into two or more identical subcomponents. We did an invariant analysis on the newly derived expressions and found they satisfied the invariant condition.

Data Correlation and Discussion

The mean-ionic-activity-coefficient data of aqueous electrolytes have been correlated using the Electrolyte NRTL model with and without parameter-concentration dependency. In

this work the data correlation was carried out based on the least-squares analysis using the following objective function:

$$OF = \sum_{i}^{n} \left(\ln \gamma_{\pm,i}^{cal.} - \ln \gamma_{\pm,i}^{\exp.}\right)^2 \tag{4}$$

where n is the total number of experimental data points.

Table 1 shows the results of correlation for molality mean-ionic-activity-coefficient data of 38 concentrated aqueous electrolytes at 25 °C using the original model (without parameter-concentration dependency) and the modified model (with parameter-concentration dependency). The NRTL nonrandomness factor is set at the conventional value of 0.2. The root-mean-squares relative deviation, $\sigma_{\gamma\pm}$, in the table is defined as:

$$\sigma_{\gamma\pm} = \sqrt{\frac{\sum_{i}^{n}\left[\left(\gamma_{\pm,i}^{cal.} - \gamma_{\pm,i}^{\exp.}\right)/\gamma_{\pm,i}^{\exp.}\right]^2}{n}} \tag{5}$$

It can be seen clearly that the modified model reduces the deviation by an order of magnitude in most cases. The correlation results for aqueous lithium bromide and nitric acid are also shown in Figure 1 and 2. Plot (a) in Figure 1 displays the experimental and calculated mean ionic activity coefficient of aqueous lithium bromide at 0 - 20 m and 25 °C. Plot (b) in Figure 1 displays the experimental and calculated osmotic coefficient of aqueous lithium bromide at 0 - 20 m and 25 °C. The osmotic coefficient is calculated using the parameter values regressed solely from the mean-ionic-activity-coefficient data. The excellent representation of the osmotic coefficient evidently proves that the modified model satisfies Gibbs-Duhem thermodynamic relationship.

Plot (a) and (b) in Figure 2 display the mean ionic activity coefficient and osmotic coefficient, respectively, of aqueous nitric acid at 0 - 28 m and 25 °C. Although the concentration is very high, the results from the original model is reasonable. This is because the nonideality of aqueous nitric acid in the high concentration range is not large. Its maximum mean-ionic-activity-coefficient value is only about 2.81, which is much smaller than the maximum value of 485.0 for aqueous lithium bromide. For aqueous electrolytes of

nonuni-uni valence, because of deficiency of the Debye-Hückel theory, there are also significant deviations at the low concentration range when using the original model. By introducing parameter-concentration dependency, the modified model is more flexible and is capable of providing adequate fit of data at both low and high concentration ranges for aqueous nonuni-uni electrolytes. A such example is shown in Figure 3.

Figure 4 illustrates the linear concentration dependency of interaction parameter $\tau_{m,ca}$ and $\tau_{ca,m}$ for aqueous lithium chloride using the modified model. It is a typical pattern of concentration dependency of interaction parameter for aqueous 1-1 electrolytes. For comparison, the corresponding $\tau_{m,ca}$ and $\tau_{ca,m}$ using the original model is also shown. Although the parameter-concentration dependency is assumed to be proportional to the mole fraction of water, for more direct analysis, we set the abscissa in Figure 4 as mole fraction of the salt. From a close examination of the parameter values in Table 1, we notice that the parameter-concentration dependency of aqueous sodium nitrate does not follow the general pattern of other 1-1 electrolytes. This needs further investigation.

Table 2 and Figure 5 show the results of fitting the mean-ionic-activity-coefficient data of aqueous potassium hydroxide at the temperature range of 0 - 80 °C and concentration range up to 17 m using the original and modified models. Six adjustable parameters are regressed for the original model while eight are used for the modified model. One order of magnitude improvement on deviation is also observed for the modified model. In this work, we assume the parameter concentration dependency is the same at different temperature. This appears to work well for aqueous potassium hydroxide system. However, many more systems need to be studied before we can conclude that the parameter-concentration dependency is not a temperature function.

Conclusion

The Electrolyte NRTL model has been successfully modified by including a linear concentration dependency of interaction parameters. The parameter-concentration dependency is based on the concept that the multi-body effect should be considered in

determining the local composition when the electrolyte concentration is high. The experimental mean-ionic-activity-coefficient of highly soluble aqueous electrolyte systems have been fitted using both the original and modified models. The results indicate that the parameter-concentration dependency can greatly enhance the capability of the Electrolyte NRTL model in representing the nonideality of the concentrated electrolyte solutions. The modified model is consistent and satisfies the Gibbs-Duhem thermodynamic relationship. Furthermore, it is completely compatible with the original model because it will reduce to the original model when the concentration dependent term is set to zero. Work is in progress to apply the modified model to vapor-liquid and liquid-liquid equilibria of industrial systems with multi-electrolytes and multi-solvents.

Notation

C, D, E, F = parameters defined in Eq. 2

G = quantity defined in Eq. 2

N = number of moles

R = gas constant

T = temperature, K

X = effective mole fraction

g = Gibbs energy

m = molality

n = number of data points

Greek letters

α = NRTL nonrandomness factor

γ = activity coefficient

σ = root mean squares relative deviation

τ = NRTL interaction parameter

Superscripts

* = unsymmetric convention

Born = Born contribution

cal = calculated value

ex = excess property

exp = experimental value

lc = local-composition NRTL equation

PDH = Pitzer-Debye-HÜckel equation

Subscripts:

± = mean ionic

a, a', a" = anion

c, c', c" = cation

ca = electrolyte ca

i, j, k = any species

m = molecular species

r = reference

w = water

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Figure captions

Figure 1. Mean ionic activity coefficient (a) and osmotic coefficient (b) of aqueous lithium bromide at 25 °C. (o): experimental data ; (- -): calculated by the original model; (—): calculated by the modified model

Figure 2. Mean ionic activity coefficient (a) and osmotic coefficient (b) of aqueous nitric acid at 25 °C. (o): experimental data ; (- -): calculated by the original model; (—): calculated by the modified model

Figure 3. Mean ionic activity coefficient (a) and osmotic coefficient (b) of aqueous

samarium chloride at 25 °C. (o): experimental data ; (- -): calculated by the original model; (—): calculated by the modified model

Figure 4. Concentration dependency of interaction parameter $\tau_{m,ca}$ (1) and $\tau_{ca,m}$ (2) for aqueous lithium chloride at 25 °C

Figure 5. Mean ionic activity coefficient of aqueous potassium hydroxide at temperature range of 0 - 80 °C

Table 1. Results of fit for molality mean-ionic-activity-coefficient data of concentrated aqueous electrolytes at 25 °C using the original and modified Electrolyte NRTL models

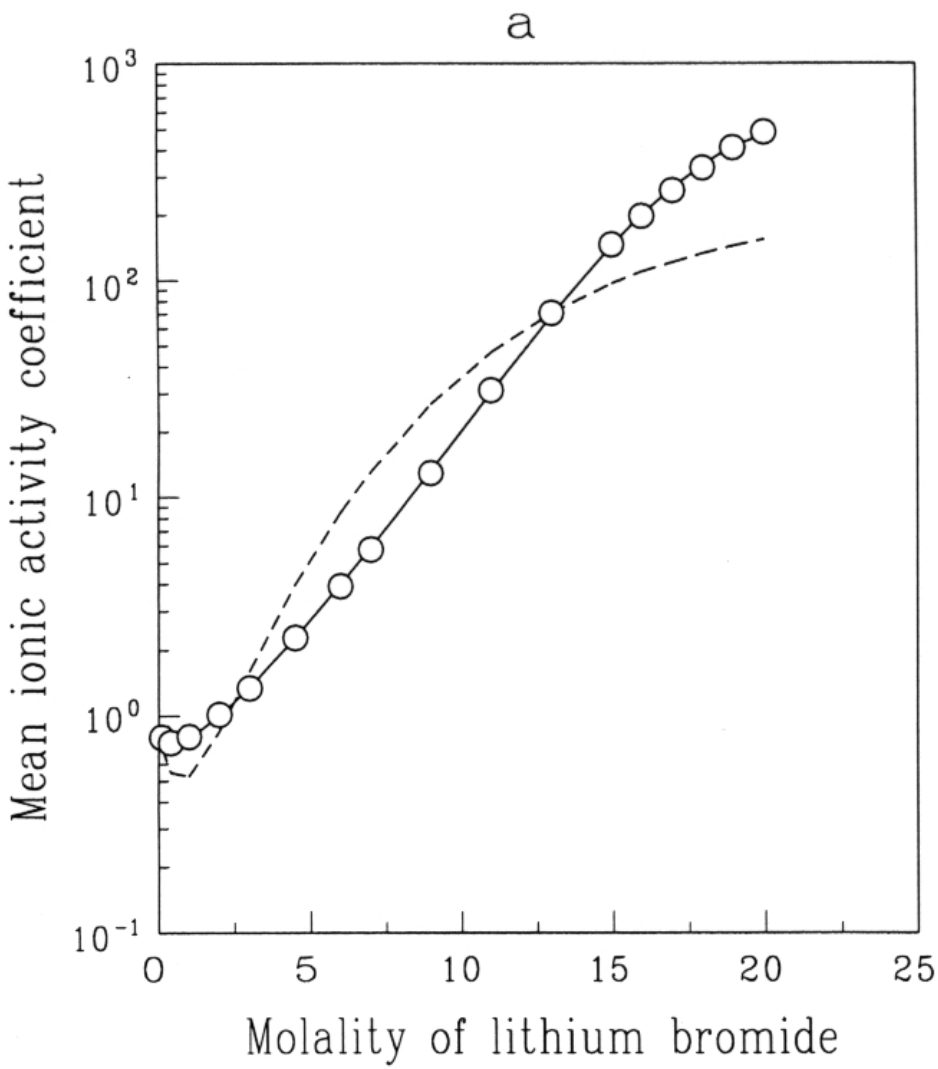
		The original			***The modified***					
1-1 Electrolyte	***max. m***	$C_{m,ca}$	$C_{ca,m}$	$\sigma_{\gamma\pm}$	$C_{m,ca}$	$C_{ca,m}$	$F_{m,ca}$	$F_{ca,m}$	$\sigma_{\gamma\pm}$	***Ref.***
HBr	**11.0**	11.615	-5.794	**0.213**	20.990	-7.604	-9.708	1.739	**0.022**	[11]
HCl	**16.0**	11.343	-5.629	**0.211**	16.016	-6.790	-5.869	1.491	**0.005**	[10]
$HClO_4$	**16.0**	12.625	-6.081	**0.560**	15.659	-7.872	-7.547	3.434	**0.007**	[10]
HI	**10.0**	11.500	-5.807	**0.179**	20.315	-7.723	-9.448	1.991	**0.006**	[11]
HNO_3	**28.0**	9.246	-4.746	**0.051**	17.254	-6.054	-6.228	0.387	**0.005**	[11]
KF	**17.5**	10.115	-4.999	**0.112**	15.769	-6.143	-5.488	0.909	**0.007**	[11]
LiBr	**20.0**	12.703	-6.079	**0.648**	19.749	-7.592	-9.144	2.062	**0.045**	[10]
LiCl	**20.0**	11.721	-5.719	**0.303**	22.313	-7.262	-10.499	1.923	**0.024**	[10]
$LiNO_3$	**20.0**	9.756	-4.975	**0.072**	15.060	-5.955	-4.664	0.585	**0.013**	[11]
NaI	**12.0**	10.244	-5.164	**0.099**	16.742	-6.557	-6.373	1.199	**0.003**	[11]
$NaNO_3$	**11.0**	8.641	-4.207	**0.090**	22.492	-12.373	-24.294	13.476	**0.007**	[11]
NaOH	**20.0**	11.242	-5.441	**0.291**	18.696	-6.858	-8.068	1.412	**0.022**	[10]
2-1 Electrolyte										
$Ba(ClO_4)_2$	**5.0**	9.117	-4.788	**0.061**	24.692	-6.947	-12.728	0.793	**0.007**	[10]
$CaBr_2$	**9.2**	12.379	-5.959	**0.911**	25.212	-8.159	-14.132	2.368	**0.063**	[12]
$CaCl_2$	**10.0**	11.176	-5.510	**0.312**	29.316	-7.711	-16.932	1.348	**0.036**	[10]
$Ca(ClO_4)_2$	**6.0**	11.223	-5.656	**0.251**	26.063	-7.897	-14.287	1.769	**0.015**	[10]
CoI_2	**10.0**	11.504	-5.800	**0.216**	40.676	-8.401	-26.801	1.247	**0.077**	[13]
$Cu(NO_3)_2$	**7.8**	10.070	-5.073	**0.130**	21.739	-6.917	-10.583	1.163	**0.010**	[14]

Table 1. (Concluded)

		The original			*The modified*					
2-1 Electrolyte	***max. m***	$C_{m,ca}$	$C_{ca,m}$	$\sigma_{\gamma\pm}$	$C_{m,ca}$	$C_{ca,m}$	$F_{m,ca}$	$F_{ca,m}$	$\sigma_{\gamma\pm}$	***Ref.***
$MgBr_2$	**5.0**	11.155	-5.629	**0.219**	22.230	-8.031	-11.576	2.425	**0.012**	[12]
$MgCl_2$	**5.0**	10.774	-5.434	**0.182**	22.833	-7.776	-11.896	2.086	**0.012**	[10]
MgI_2	**5.0**	11.617	-5.840	**0.288**	23.478	-8.464	-12.783	2.792	**0.020**	[10]
$Mg(NO_2)_2$	**6.5**	9.622	-4.918	**0.134**	14.597	-7.362	-9.486	4.180	**0.013**	[15]
$Mg(NO_3)_2$	**5.0**	9.938	-5.108	**0.111**	21.861	-7.222	-10.847	1.503	**0.007**	[10]
$Sr(ClO_4)_2$	**8.0**	10.988	-5.522	**0.232**	23.598	-7.383	-11.974	1.370	**0.007**	[16]
UO_2Cl_2	**3.0**	8.632	-4.685	**0.035**	29.769	-7.111	-16.774	0.448	**0.008**	[10]
$UO_2(ClO_4)_2$	**5.5**	12.499	-6.222	**0.437**	30.772	-8.791	-18.349	2.288	**0.015**	[10]
$ZnBr_2$	**6.0**	6.411	-3.772	**0.107**	19.902	-6.570	-9.935	1.245	**0.008**	[10]
$ZnCl_2$	**23.2**	9.842	-4.803	**0.463**	19.056	-6.462	-9.299	1.370	**0.026**	[17]
$Zn(ClO_4)_2$	**4.0**	11.312	-5.756	**0.190**	28.886	-8.414	-16.707	2.077	**0.013**	[10]
ZnI_2	**12.0**	8.784	-4.727	**0.299**	17.854	-6.613	-9.213	1.714	**0.022**	[17]
$Zn(NO_3)_2$	**6.0**	10.002	-5.123	**0.131**	22.374	-7.145	-11.163	1.334	**0.012**	[10]
3-1 Electrolyte										
$SmCl_3$	**3.6**	10.348	-5.281	**0.174**	29.917	-7.796	-17.719	1.484	**0.012**	[18]
$Sm(ClO_4)_3$	**4.5**	12.374	-6.060	**0.698**	28.775	-8.720	-17.385	2.678	**0.039**	[19]
$Sm(NO_3)_3$	**4.3**	8.761	-4.569	**0.091**	24.994	-6.935	-13.462	0.989	**0.015**	[20]
$Tb(ClO_4)_3$	**4.5**	12.468	-6.103	**0.721**	30.083	-8.785	-18.444	2.621	**0.034**	[21]
$Tb(NO_3)_3$	**4.5**	8.908	-4.665	**0.114**	24.827	-7.012	-13.421	1.094	**0.015**	[20]
$YbCl_3$	**4.0**	10.828	-5.465	**0.266**	29.883	-8.019	-17.890	1.775	**0.019**	[18]
$Yb(ClO_4)_3$	**4.6**	12.586	-6.141	**0.779**	29.692	-8.848	-18.160	2.733	**0.033**	[21]

Table 2. Results of fit for molality mean-ionic-activity-coefficient data of aqueous potassium hydroxide at the temperature range of 0 - 80 °C and concentration range up to 17 m using the original and modified Electrolyte NRTL models (data from Harned and Owen, [22])

	The original	***The modified***		***The original***	***The modified***
$C_{m,ca}$	8.054	6.293	$\sigma_{\gamma\pm}$ *(0 °C)*	0.290	0.008
$C_{ca,m}$	-4.354	-4.568	$\sigma_{\gamma\pm}$ *(10 °C)*	0.270	0.007
$D_{m,ca}$	977.599	1422.298	$\sigma_{\gamma\pm}$ *(20 °C)*	0.252	0.006
$D_{ca,m}$	-360.448	-541.833	$\sigma_{\gamma\pm}$ *(30 °C)*	0.236	0.007
$E_{m,ca}$	-3.458	2.417	$\sigma_{\gamma\pm}$ *(40 °C)*	0.224	0.005
$E_{ca,m}$	2.765	2.582	$\sigma_{\gamma\pm}$ *(50 °C)*	0.213	0.006
$F_{m,ca}$		-3.860	$\sigma_{\gamma\pm}$ *(60 °C)*	0.202	0.006
$F_{ca,m}$		2.429	$\sigma_{\gamma\pm}$ *(70 °C)*	0.194	0.010
			$\sigma_{\gamma\pm}$ *(80 °C)*	0.168	0.015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Mean ionic activity coefficient
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10^1
10^0
10^{-1}
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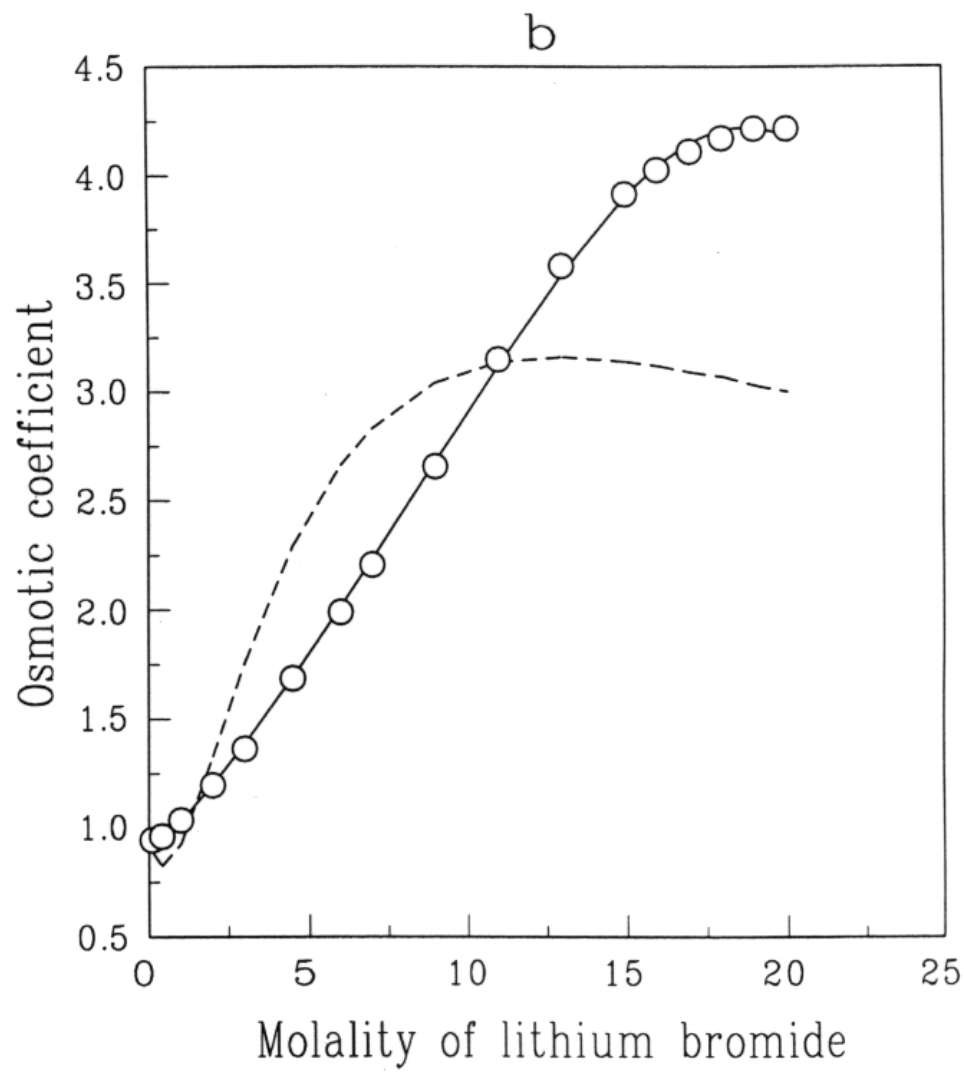
5
10
15
20
25
Molality of lithium bromide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Osmotic coefficient
4.5
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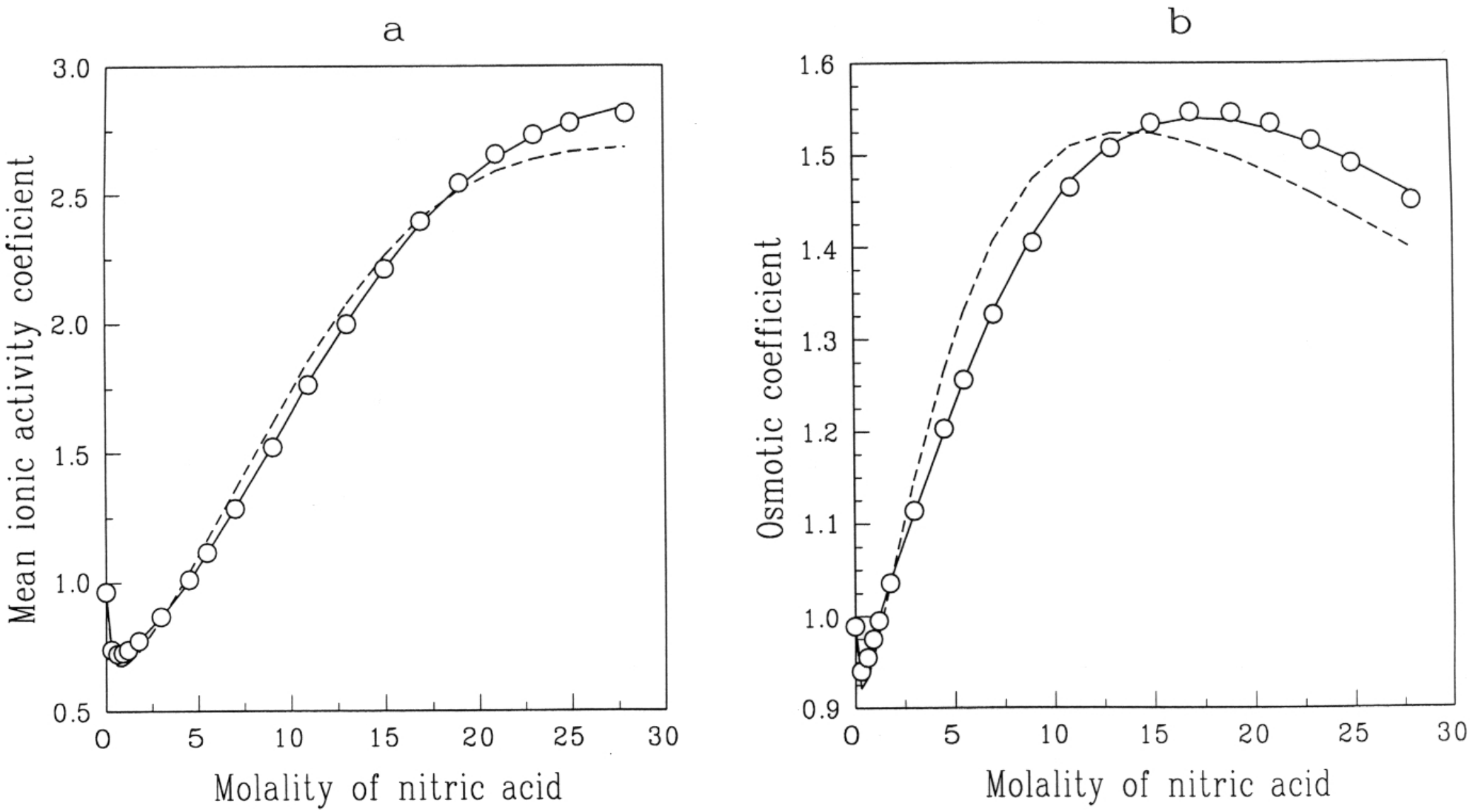
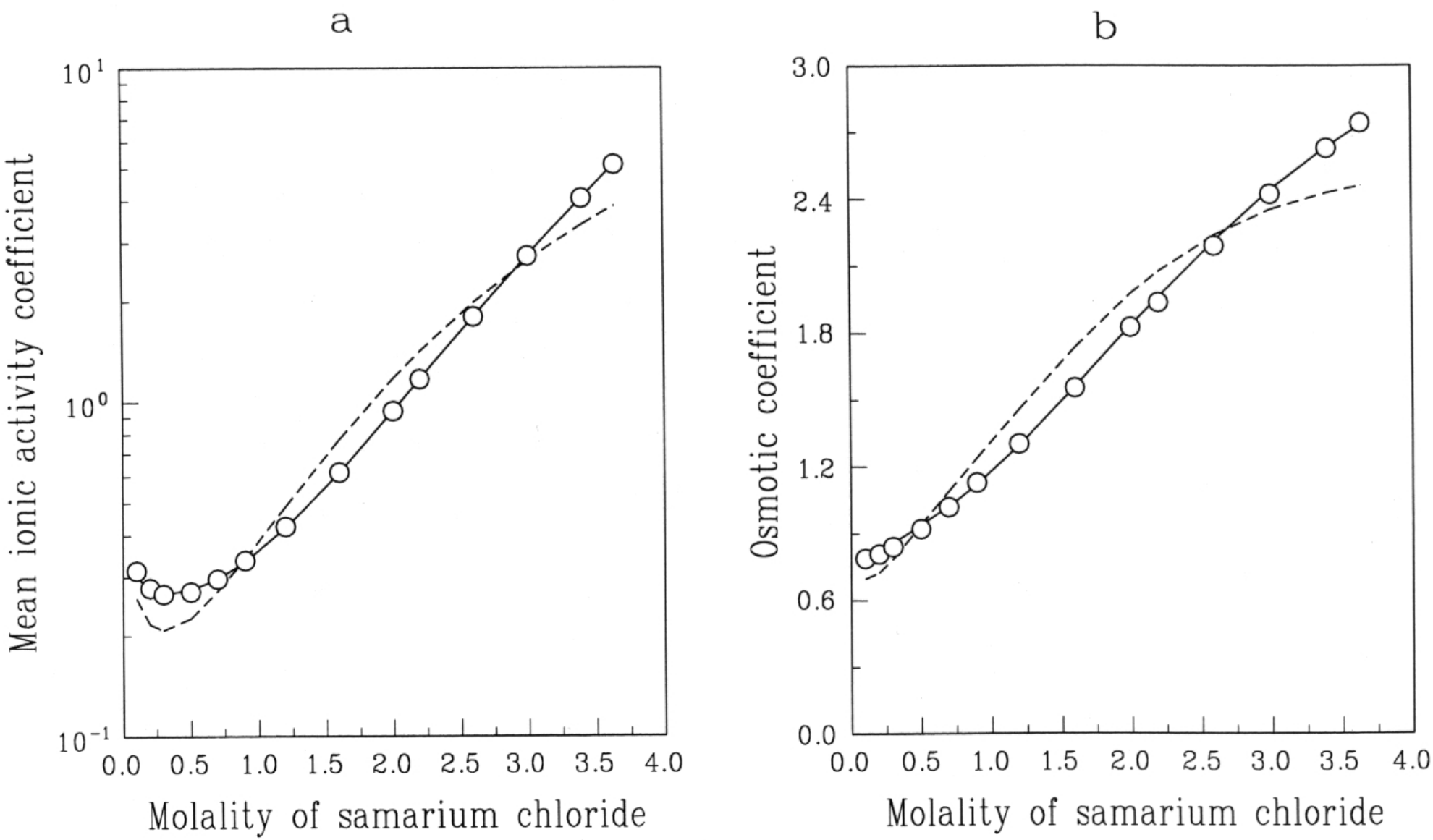
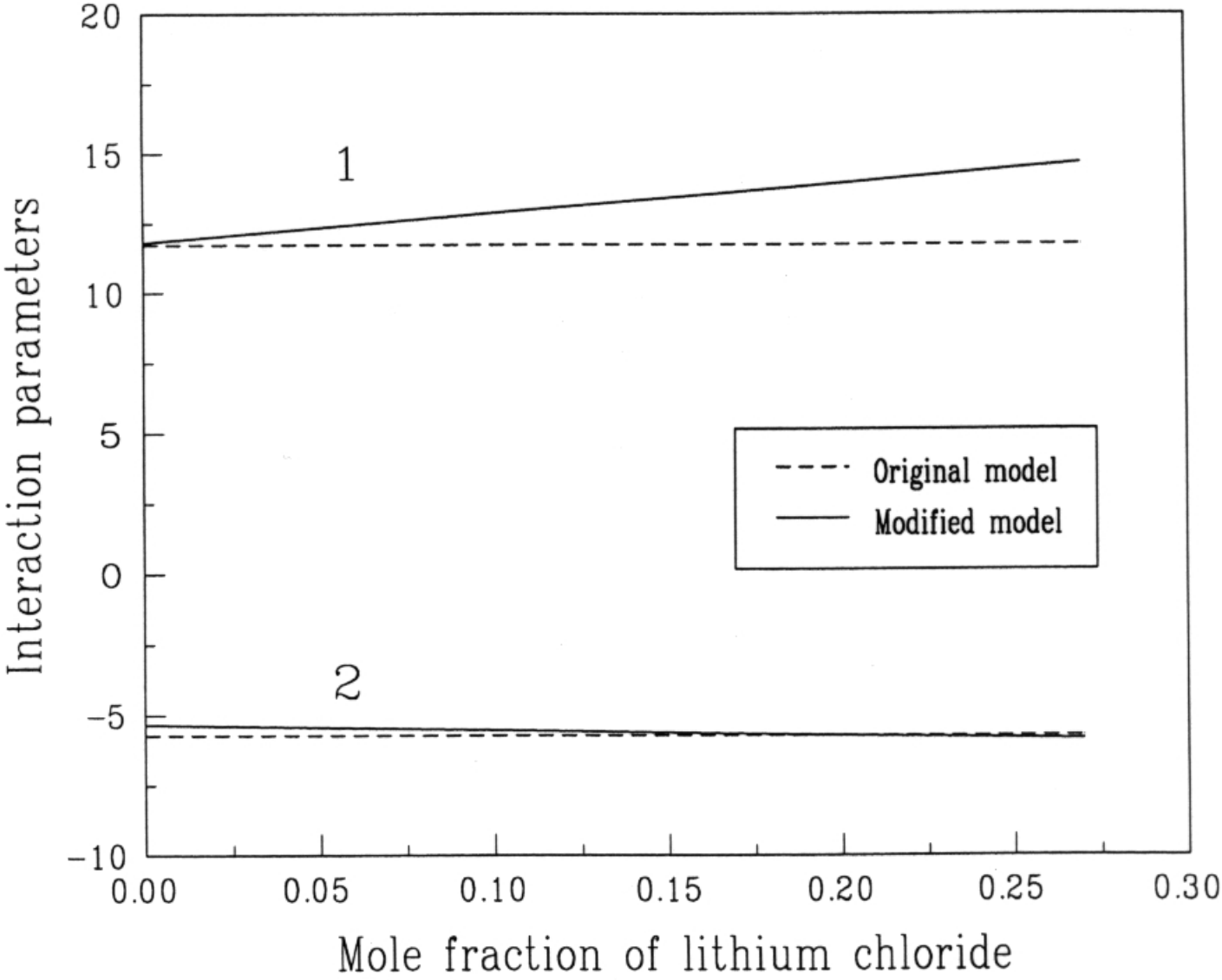
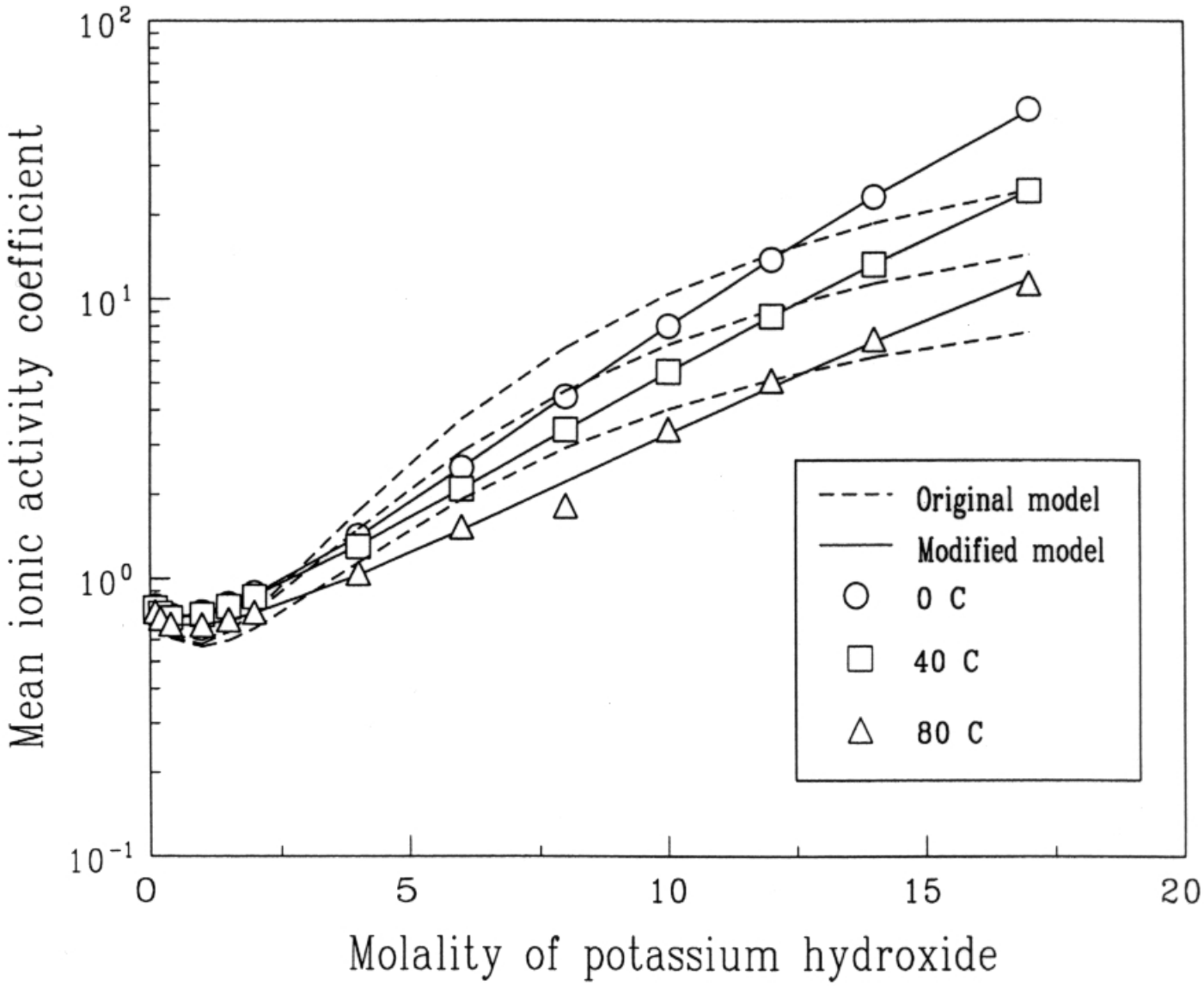
25
Molality of lithium bromide


a
Mean ionic activity coeficient
3.0
2.5
2.0
1.5
1.0
0.5
0
5
10
15
20
25
30
Molality of nitric acid
b
Osmotic coefficient
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0
5
10
15
20
25
30
Molality of nitric acid


a
b
Mean ionic activity coefficient
Osmotic coefficient
Molality of samarium chloride
Molality of samarium chloride
10^1
10^0
10^{-1}
3.0
2.4
1.8
1.2
0.6
0.0
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0


20
15
10
5
0
−5
−10
0.00
0.05
0.10
0.15
0.20
0.25
0.30
Interaction parameters
Mole fraction of lithium chloride
1
2
Original model
Modified model


Mean ionic activity coefficient
10^2
10^1
10^0
10^{-1}
0
5
10
15
20
Molality of potassium hydroxide
Original model
Modified model
0 C
40 C
80 C