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USE OF THE NRTL EQUATION FOR SIMULTANEOUS CORRELATION OF VAPOUR-LIQUID EQUILIBRIA AND EXCESS ENTHALPY

Applications to aqueous alkanolamine systems

K. A. G. Schmidt[1], *Y. Maham*[2] *and A. E. Mather*[2*]

[1]Department of Physics and Technology, University of Bergen, Allegatén 55, 5007 Bergen, Norway
[2]Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, T6G 2G6, Canada

The NRTL model has been used to correlate the data for the aqueous alkanolamine systems of (MEA+H_2O), (DEA+H_2O) and (MDEA+H_2O). The model was successfully applied to correlate simultaneously the excess enthalpy, vapour-liquid equilibria, and low temperature activity coefficients. A large database of data was collected for the investigation and it covers a wide range of composition, temperature and pressures. It was found that the form of the binary interaction parameters used by Posey (1996) with a variable non-randomness parameter gave the best results.

Keywords: *diethanolamine, excess properties, infinite dilution, methyldiethanolamine, modelling, monoethanolamine, NRTL, VLE*

Introduction

Aqueous alkanolamine solutions are widely used to remove acid gases (H_2S, CO_2, SO_2, etc.) from gaseous (such as natural gas) and liquefied (such as LPG) hydrocarbon streams. The most common removal process involves the absorption of the acid gas into aqueous solutions at low temperatures and then the subsequent stripping of the acid gas from the resulting mixtures at a higher temperature. During the design of these absorption/stripping facilities, accurate information regarding the vapour-liquid equilibrium, the physicochemical and thermodynamic properties, the kinetics of mass transfer and the chemical reaction equilibrium of these mixtures is required. However, as pointed out by Oscarson *et al.* [1], the design of these facilities is often based on empirical models due to a lack of thermodynamically consistent models.

Recently (in the past fifteen years) many models have been proposed for the correlation and prediction of the vapour-liquid equilibrium and enthalpies of acid gases in aqueous alkanolamine solutions. These models have used the extensive (acid gas+water+alkanolamine) mixture data available in the literature to determine the binary interaction parameters inherent in each model. As such, the investigators have gone into great detail to determine the (acid gas+alkanolamine) and the (acid gas+water) binary interaction parameters used to model the equilibrium between the components. Less detail has gone into the determination of the (alkanolamine+water) binary interaction parameters.

Chang *et al.* [2] have shown that the activity coefficients for alkanolamine and water at low acid gas loading conditions have a significant effect on the predictions of CO_2 and H_2S vapour-liquid equilibrium (VLE) in this region. Despite the importance of the (alkanolamine+water) equilibrium, most investigators have modelled this system with a simple excess Gibbs free energy model. Often the binary parameters, when not used from previous investigations, are fit with pseudo-data or with incomplete data sets [3–14]. This investigation will focus on determining the properties of the neglected (alkanolamine+water) system.

The initial objective of this work is to collect the relevant data available in the public domain for relevant aqueous alkanolamine solutions, which are commonly used in industry. Secondly, to update the NRTL model used to estimate the necessary thermodynamic properties of these systems required in the design of gas treating facilities. Thirdly, to create an algorithm that can be used to determine the (alkanolamine+water) binary interaction parameters of this model from the collected data. Finally, to test the capability of the proposed model to correlate and/or predict the required properties over the composition, temperature and pressure ranges found in industrial acid gas separation plants.

Literature review

A comprehensive literature review revealed relatively few investigations into the thermodynamic properties

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[*] Author for correspondence: alan.mather@ualberta.ca

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Table 1 Experimental investigations of the thermodynamic properties of aqueous MEA, DEA and MDEA systems

Investigators	Year	Components	Data type	Comments	Acronym–reference
Leibush and Shorina	1947	MEA, DEA	VLE		LS47–[15]
Conners	1958	MEA	VLE	Figures only	C58–[16]
Martin *et al.*	1969	DEA	VLE	Smoothed data	MDE69–[17]
Lychkin *et al.*	1973	MEA	γ	Figures only	LAA73–[18]
Danilov *et al.*	1974	MEA, DEA	γ	Calculated from Leibush & Shorina	DMR74–[19]
Wohland	1976	MEA	VLE		W76–[20]
de Oliveira *et al.*	1980	MEA, DEA	G^E	Figures only	DAMCV80–[21]
Touhara *et al.*	1982	MEA	VLE, H^E		TOOTIN82–[22]
Nath and Bender	1983	MEA	VLE		NB83–[23]
Buslaeva *et al.*	1983	MEA	H^E		BTMK83–[24]
Kuwairi	1983	MDEA	VLE		K83–[25]
Kennard and Meisen	1984	DEA	VLE		KM84–[26]
Lenard *et al.*	1987	MEA	VLE		LRT87–[27]
Kim *et al.*	1987	MEA, DEA, MDEA	H^E		KDH87–[28]
Kling and Maurer	1991	MEA	VLE		KM91–[29]
Wilding *et al.*	1991	DEA	VLE		WWW91–[30]
Xu *et al.*	1991	MDEA	VLE		XQZZC91–[31]
Chang *et al.*	1993	MEA, DEA, MDEA	γ		CPR93–[2]
Sandall *et al.*	1993	DEA, MDEA	VLE		SRA93–[32]
Dohnal *et al.*	1994	MEA	H^E		DRH94–[33]
Posey	1996	MEA, DEA, MDEA	H^E		P96–[34]
Cai *et al.*	1996	MEA, DEA	VLE		CXW96–[35]
Kuranov *et al.*	1996	MDEA	VLE		KRSM96–[36]
Maham *et al.*	1997	MEA, MDEA	H^E		MMH97–[37]
Park and Lee	1997	MEA	VLE		PL97–[38]
Tochigi *et al.*	1999	MEA	VLE		TAOLK99–[39]
Abedizadegan and Meisen	1999	DEA	VLE		AM99–[40]
Maham *et al.*	2000	DEA, MDEA	H^E		MMM00–[41]
Tanaka *et al.*	2001	MEA	VLE		TKYK01–[42]
Vrachnos *et al.*	2004	MDEA	VLE		VVML04–[43]
Sidi–Boumedine *et al.*	2004	MDEA	VLE		SHFPFG04–[44]

of aqueous alkanolamine solutions. The systems with the most published data sets were the aqueous systems of the three of the most widely used alkanolamines in industrial acid gas removal processes: monoethanolamine, C_2H_7NO, (MEA), diethanolamine, $C_4H_{11}NO_2$, (DEA) and methyldiethanolamine $C_5H_{13}NO_2$ (MDEA). In this investigation, only excess enthalpy and VLE data were considered.

In this investigation, only activity coefficient, excess enthalpy (H^E) and VLE data were considered. These three types of data (presented in Table 1) are valuable in the determination of the binary parameters found in most models. The additional physical properties will be considred in a separate and subsequent review. A complete list of the data sets used in this investigation is presented in Table 1. As can be seen, a number of published reports, articles and data compilations only present smoothed data in tables and figures. As interpretation of this type of data is highly speculative.

Vapour liquid equilibrium

In this investigation, liquid phase fugacities were determined with the activity coefficient model approach

$$y_\mathrm{i}\hat{\phi}_\mathrm{i}^\mathrm{V} P=\gamma_\mathrm{i} x_\mathrm{i} f_\mathrm{i}^\mathrm{oL}\exp\left[\int_{P^\mathrm{REF}}^{P}\frac{\bar{V}_\mathrm{i}^\mathrm{L}}{RT}\mathrm{d}P\right] \tag{1}$$

where y_i, $\hat{\phi}_\mathrm{i}^\mathrm{V}$, γ_i, f_i^oL and $\bar{V}_\mathrm{i}^\mathrm{L}$ are the vapour mole fraction, fugacity coefficient, liquid mole fraction, activity coefficient, standard state fugacity, partial molar liquid volume of component *i* and *R*, *P*, and P^REF are the gas constant, total pressure and reference pressure respectively.

To determine the fugacity of a species in a liquid mixture using this approach, the expression for the standard state fugacity needs to be determined. In case of non-condensable compounds (i.e. liquids at standard conditions) the standard state fugacity is determined by

$$f_\mathrm{i}^\mathrm{oL}=P_\mathrm{i}^\mathrm{SAT}\phi_\mathrm{i}^\mathrm{SAT}\exp\left[\int_{P^\mathrm{SAT}}^{P^\mathrm{REF}}\frac{\underline{V}_\mathrm{i}^\mathrm{L}}{RT}\mathrm{d}P\right] \tag{2}$$

where ϕ_i is liquid fugacity coefficient, $\underline{V}_\mathrm{i}^\mathrm{L}$ the molar volume of the pure component *i* and the superscript SAT represents the property at saturation conditions. The pure component liquid fugacity coefficient may be determined by an equation of state. With these definitions the complete ensemble for the this approach becomes:

$$y_\mathrm{i}\hat{\phi}_\mathrm{i}^\mathrm{V} P=\gamma_\mathrm{i} x_\mathrm{i} P_\mathrm{i}^\mathrm{SAT}\exp\left[\int_{P^\mathrm{SAT}}^{P^\mathrm{REF}}\frac{\underline{V}_\mathrm{i}^\mathrm{L}}{RT}\mathrm{d}P\right]\exp\left[\int_{P^\mathrm{REF}}^{P}\frac{\bar{V}_\mathrm{i}^\mathrm{L}}{RT}\mathrm{d}P\right] \tag{3}$$

Assuming the liquid molar volume and the partial molar volume are independent of pressure and composition, Prausnitz *et al.* [45] state that $\bar{V}_\mathrm{i}^\mathrm{L}=\underline{V}_\mathrm{i}^\mathrm{L}$. Hence Eq. (3) becomes

$$y_\mathrm{i}\hat{\phi}_\mathrm{i}^\mathrm{V} P=\gamma_\mathrm{i} x_\mathrm{i} P_\mathrm{i}^\mathrm{SAT}\phi_\mathrm{i}^\mathrm{SAT}\exp\left[\int_{P^\mathrm{SAT}}^{P^\mathrm{REF}}\frac{\underline{V}_\mathrm{i}^\mathrm{L}}{RT}\mathrm{d}P\right]\exp\left[\int_{P^\mathrm{REF}}^{P}\frac{\underline{V}_\mathrm{i}^\mathrm{L}}{RT}\mathrm{d}P\right] \tag{4}$$

and if the liquid molar volume is also assumed to be independent of pressure this reduces down to:

$$y_\mathrm{i}\hat{\phi}_\mathrm{i}^\mathrm{V} P=\gamma_\mathrm{i} x_\mathrm{i} P_\mathrm{i}^\mathrm{SAT}\phi_\mathrm{i}^\mathrm{SAT}\exp\left[\frac{\underline{V}_\mathrm{i}^\mathrm{L}}{RT}(P^\mathrm{REF}-P^\mathrm{SAT})\right]\exp\left[\frac{\underline{V}_\mathrm{i}^\mathrm{L}}{RT}(P-P^\mathrm{REF})\right] \tag{5}$$

Activity coefficient model

The NRTL model was selected for the current study because of its wide use and simple implementation [46] and because of the success Rochelle and co-workers [2, 14, 34, 47] have had representing the excess Gibbs energy and excess enthalpy of these systems.

The NRTL (non-random, two-liquid) model was an empirical equation proposed by Renon and Prausnitz, [48–50] based on the local composition representation of the excess Gibbs energy, G^E, of liquid mixtures. The NRTL expression for the Gibbs energy is:

$$G^\mathrm{E}=x_1x_2\left(\frac{\tau_{21}G_{21}}{x_1+x_2G_{21}}+\frac{\tau_{12}G_{12}}{x_2+x_1G_{12}}\right) \tag{6}$$

where

$$\tau_{12}=\frac{g_{12}-g_{22}}{RT},\ \tau_{21}=\frac{g_{21}-g_{11}}{RT} \tag{7}$$

and

$$G_{12}=\exp(-\alpha_{12}\tau_{12}),\ G_{21}=\exp(-\alpha_{12}\tau_{21}) \tag{8}$$

In Eqs (6)–(8), g_ij and g_ij is the energies of interactions between the *ii* or *ij* component pairs and α_{12} is the non-randomness parameter.

$$RT\ln\gamma_\mathrm{i}=G^\mathrm{E}-\sum_{\mathrm{k}\neq\mathrm{i}}\left(\frac{\partial G^\mathrm{E}}{\partial x_\mathrm{i}}\right)_{\mathrm{T,\,P,\,x}_{\mathrm{j}\neq\mathrm{ik}}} \tag{9}$$

Therefore, the resulting expressions for the activity coefficients of component 1 and 2 in a binary mixture are:

$$\ln\gamma_1=x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1+x_2G_{21}}\right)^2+\left(\frac{\tau_{12}G_{12}}{\left(x_2+x_1G_{12}\right)^2}\right)\right] \tag{10}$$

$$\ln\gamma_2=x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2+x_1G_{12}}\right)^2+\left(\frac{\tau_{21}G_{21}}{\left(x_1+x_2G_{21}\right)^2}\right)\right] \tag{11}$$

The expressions for the multi-component representation and a comprehensive review of the model may be found in Walas [51]. The excess enthalpy, which indicates the temperature dependence of the Gibbs energy, and hence also the activity coefficients, can be determined via the Gibbs–Helmholtz relation.

$$\left(\frac{\partial(G^\mathrm{E}/T)}{\partial T}\right)_{\mathrm{P,\,x}}=-\frac{H^\mathrm{E}}{T^2} \tag{12}$$

Once the excess Gibbs energy and excess enthalpy, S^E, have been determined the isothermal excess entropy can be calculated by the fundamental thermodynamic relationship

$$TS^{\mathrm{E}} = H^{\mathrm{E}} - G^{\mathrm{E}} \tag{13}$$

Binary interaction parameters

In this investigation the inherent binary parameters and non-randomness parameters were treated in two different ways. Initially, the binary parameters and the non-randomness parameters were those suggested by Posey [34] which are the forms found in the ASPEN process simulator.

$$\begin{aligned}\tau_{12} &= a_{12} + \frac{b_{12}}{T}\\ \tau_{21} &= a_{21} + \frac{b_{21}}{T}\end{aligned} \tag{14}$$

The non-randomness parameter was specified to be a fixed value of 0.2. Based on these binary parameters and the temperature independent non-randomness parameter the Gibbs–Helmholtz relation gives

$$H^{\mathrm{E}} = -R\left(\begin{aligned}&\frac{x_1x_2b_{21}G_{21}[x_1(\alpha_{12}\tau_{21}-1)-x_2G_{21}]}{(x_1+x_2G_{21})^2}+\\ &+\frac{x_1x_2b_{12}G_{12}[x_2(\alpha_{12}\tau_{12}-1)-x_1G_{12}]}{(x_2+x_1G_{12})^2}\end{aligned}\right) \tag{15}$$

for the excess enthalpy.

Further investigation into the binary interaction showed that the energy parameters g_{12} and g_{21} were originally suggested [49] to be weak functions of temperature, but during subsequent testing of the model these interaction parameters were found to vary linearly with temperature. In subsequent works, Renon and co-workers [50, 52, 53], further developed the linear dependence of the binary interaction parameters and the non-randomness parameter. An advantage of assuming the additional temperature dependence of these parameters was the improved ability of the model to correlate and predict the excess enthalpy and the excess Gibbs free energy of non-ideal mixtures.

Murthy and Zudkevitch [54], Hanks *et al.* [55] and Wilkinson [56] have shown, that the NRTL equation could not correlate both G^{E} and H^{E} for a system when the heat of mixing was greater than a determinable maximum value of H^{E} at any given temperature. However as discussed by Demirel and Gecegormez [57] and Murthy and Zudkevitch [54], this limitation can be eliminated when the binary interaction parameters are treated as linear (and non-linear) functions of temperature and they are determined from both VLE and H^{E} data [58].

Demirel and Gecegormez [59] suggest the linear temperature dependence of the parameters was not suitable for excess heat capacity calculations, which involved the differentiation of the excess enthalpy with respect to temperature. They also stated, the heat of mixing for systems with strong hydrogen bonding was not satisfactorily correlated well with this form of the interaction parameters. Demirel and co-workers subsequently proposed to extend the temperature dependence of the NRTL parameters in order to correlate/predict the excess heat capacity of liquid mixtures. Instead of a linear dependence, a non-linear relationship with temperature was proposed.

$$\begin{aligned}\Delta g_{21} &= c_1 + c_2/(T-T_{\mathrm{base}})\\ \Delta g_{12} &= c_3 + c_4/(T-T_{\mathrm{base}})\\ \alpha_{12} &= c_5 + c_6/(T-T_{\mathrm{base}})\end{aligned} \tag{16}$$

which, results in a new expression for the excess enthalpy of mixing.

$$\begin{aligned}H^{\mathrm{E}} = {} & \frac{T(x_1x_2G_{21})}{T'(x_1+x_2G_{21})}\left[\left(1-\frac{\alpha_{12}\tau_{21}x_1}{(x_1+x_2G_{21})}\right)(c_2+RT'\tau_{21})-\right.\\ & \left.-\frac{c_6x_1\tau_{21}^2RT^2}{(x_1+x_2G_{21})}\right]+\\ & +\frac{T(x_1x_2G_{12})}{T'(x_2+x_1G_{12})}\left[\left(1-\frac{\alpha_{12}\tau_{12}x_2}{(x_2+x_1G_{12})}\right)(c_4-RT'\tau_{12})-\right.\\ & \left.-\frac{c_6x_2\tau_{12}^2RT^2}{(x_2+x_1G_{12})}\right]\end{aligned} \tag{17}$$

where $T'=(T-T_{\mathrm{base}})^2$. In the original works by Demirel T_{base} was set to 273.15 K.

Demirel [60] showed the correlation of the excess enthalpy with the non-linear temperature dependence was better for correlating the excess enthalpy of associating mixtures than when correlated with the linearly dependent parameters. An investigation by Demirel [60] was then performed to test which of the forms, linear or non-linear, correlated/predicted the excess enthalpy and infinite dilution properties of a wide range of systems (including associating and partially miscible systems) the best. Results from the correlation of 55 binary systems indicated that the NRTL model performed better with the inclusion of the non-linear temperature dependence in the interaction parameters.

Estimation of parameters

The estimation of the parameters in the NRTL equation, was performed by minimizing the following objective function

$$F_{\mathrm{OBJ}}=\frac{W_{\mathrm{P}}}{L}\left\{\sum^{L}\left[\frac{P_{\mathrm{i,EXP}}-P_{\mathrm{i,CALC}}}{P_{\mathrm{i,EXP}}}\right]^{2}\right\}+ \\ +\frac{W_{\mathrm{H^E}}}{N}\left\{\sum^{N}\left[\frac{H^{\mathrm{E}}_{\mathrm{i,EXP}}-H^{\mathrm{E}}_{\mathrm{i,CALC}}}{H^{\mathrm{E}}_{\mathrm{i,EXP}}}\right]^{2}\right\}+ \\ +\frac{w_{\gamma}}{I}\left\{1000\sum^{I}\left[\frac{\gamma^{\mathrm{E}}_{\mathrm{i,EXP}}-\gamma^{\mathrm{E}}_{\mathrm{i,CALC}}}{\gamma^{\mathrm{E}}_{\mathrm{i,EXP}}}\right]^{2}\right\} \quad (18)$$

where *I*, *L*, and *N* are the total number of experimentally determined, activity coefficient, VLE and excess enthalpy. In this investigation the data weighting factor, w_j=1, was used in all the parameter estimations. If, say for example, no VLE data was used in the parameter optimisation, the data weighting factor w_p was set to zero.

The objective function was minimized with a hybrid algorithm consisting of the simulated annealing optimisation algorithm [61] and either the Simplex [62] Levenberg-Marquardt algorithm [63–64] or Powell's dog-leg method [65]. The simulated annealing method, with enough time should ultimately find the global optimal solution; however due to practical CPU time limitations, a rough (essentially the global minimum) global minimum will most likely be obtained from the algorithm.

In order to optimise the computational effort, the parameters, determined at the rough global optimum can be further refined to obtain the global optimum with the use of standard non-linear optimisation technique. This technique, however, will work sufficiently well only if the simulated annealing algorithm has determined a good starting point, i.e. sufficiently close to the global optimum (as required by all non-stochastic optimisation algorithms, [66]). This hybrid approach has also been used and recommended by [66–68] amongst others. The 'optimal' parameters determined from the simulated annealing algorithm were used as the starting point in the local optimization algorithm. Throughout the parameter optimisation, the values that dictated the performance of the simulated annealing algorithm (number of iterations, cooling schedule, etc.) were those recommended by Goffe [66].

The calculated excess enthalpies were determined directly from the respective forms of the NRTL equation Eqs (15) and (17), and the activity coefficients were determined with Eqs (10) and (11). Equation (5) was used to calculate the pressure. As can be seen, Eq. (5) requires the vapour phase compositions. As most of the vapour-liquid equilibrium measurements were total (or vapour) pressure measurements the vapour phase compositions were not measured. Therefore, the vapour phase compositions needed to be estimated in order to determine the left hand side of Eq. (5). For completeness (accounting for all vapour-phase non-idealities), the pressure and vapour composition were determined from the experimental liquid composition and temperature with an iterative bubble point calculation involving Eq. (5). The bubble point algorithm, suggested by Sandler [69] was used in this investigation.

As the pressure range of the systems investigated were low, the fugacity coefficient of pure component *i*, ϕ_i and of component *i* in the vapour phase, $\hat{\phi}^{\mathrm{V}}_{\mathrm{i}}$, were calculated with the virial equation of state truncated after the second term.

$$\ln\hat{\phi}^{\mathrm{V}}_{\mathrm{i}}=\left(2\sum_{j=1}^{m}y_{\mathrm{j}}B_{\mathrm{ij}}-B_{\mathrm{mix}}\right)\frac{P}{RT} \quad (19)$$

where B_{mix} is defined as

$$B_{\mathrm{mix}}=\sum_{i=1}^{m}\sum_{j=1}^{m}y_{\mathrm{i}}\,y_{\mathrm{j}}B_{\mathrm{ij}} \quad (20)$$

The second virial coefficient of pure component *i*, B_{ii}, and the cross second virial coefficient, B_{ij}, were determined from the Hayden and O'Connell [70] correlation. The critical properties, dipole moment and the mean radius of gyration required in the Hayden and O'Connell correlation were obtained from the DIPPR database [71]. The parameter describing the association of like and unlike molecules was taken from the recommended values in [45] except for pure water, which was obtained from Stein and Miller [72].

The pure component saturation pressures, $P_{\mathrm{i}}^{\mathrm{SAT}}$, liquid molar volumes, $\underline{V}_{\mathrm{i}}^{\mathrm{L}}$ (except for water) were calculated from the correlations of [71]. The saturation pressure of water and its molar volume were calculated with the correlations of Saul and Wagner [73]. Since, the excess enthalpy and activity coefficient data used in this study were all performed at 1.013 bar. The reference pressure in the Poynting correction term found in Eq. (5) was set to 1.013 bar. During the parameter estimation, the Poynting correction terms, and the corrections for the vapour phase non-idealities were negligible in all the systems considered.

During the parameter estimation, the quality of the fit was determined by the average absolute percentage difference of the fit. The average absolute percentage difference were calculated from

$$S_{\mathrm{P}}=\frac{100}{L}\sum^{L}\left|\left[\frac{P_{\mathrm{i,EXP}}-P_{\mathrm{i,CALC}}}{P_{\mathrm{i,EXP}}}\right]\right| \quad (21)$$

$$S_{\mathrm{h^E}}=\frac{100}{N}\sum^{N}\left|\left[\frac{H^{\mathrm{E}}_{\mathrm{i,EXP}}-H^{\mathrm{E}}_{\mathrm{i,CALC}}}{H^{\mathrm{E}}_{\mathrm{i,EXP}}}\right]\right| \quad (22)$$

$$S_{\gamma}=\frac{100}{I}\sum^{I}\left[\left|\frac{\gamma^{E}_{i,EXP}-\gamma^{E}_{i,CALC}}{\gamma^{E}_{i,EXP}}\right|\right] \tag{23}$$

Regression procedure

Before the ability of the NRTL model was tested to simultaneously correlate all the available aqueous MEA and aqueous DEA mixture data (Table 1), the three individual types of data: activity coefficient, total pressure, and excess enthalpy were regressed individually to ascertain the scatter in the data. In all cases, any data sets that significantly deviated from the regression results were rejected. In this work a rather liberal tolerance of 20% deviation from the regression value was used to reject out-lying data points. Following this initial data reduction the model was used to simultaneously correlate the remaining data. In the preliminary data screening for the (DEA+H_2O) system, two data sets were determined to be excluded in the overall correlation data set: [35, 74] and [40]. In addition, due to apparent inconsistencies in the data from [15] the data were not used in this investigation.

Results and discussion (MEA+H_2O), (DEA+H_2O) and (MDEA+H_2O) systems

As described earlier, the form of binary interaction parameters suggested by Posey [34] was used in the NRTL equation. In this case the four parameters a_{12}, b_{12}, a_{21}, and b_{21} were determined from the available excess enthalpy, VLE and activity coefficient data simultaneously. The non-randomness parameter, α_{12} was fixed at 0.2. The regressed parameters for the (DEA+H_2O), (MEA+H_2O) and (MDEA+H_2O) individual property regressions are presented in Table 2. A comparison of the regression statistics; the number of points and the average absolute percentage difference of each system are presented in Tables 3 to 5.

As can be seen the results are quite good. As discussed by Tassios [75] and Mato *et al.* [76] the non-randomness parameter is largely an empirical parameter and may not follow the rules set out by Renon. Tassios states that the NRTL equation should be considered an empirical model and the best results are obtained when the non-randomness is obtained from regression of the available experimental data. This was also suggested by van Bochove, who pointed out that values from 0.01 to 100 can be found from correlations of experimental data [77].

Table 2 Temperature dependent parameters of the NRTL model (Posey form) of the (MEA+H_2O), (DEA+H_2O) and (MDEA+H_2O) systems; α_{12}=0.2

	MEA	DEA	MDEA
a_{21}	0.6011	6.062	8.421
b_{21}/K	1036	–1108	–1658
a_{12}	0.0607	–1.585	–2.212
b_{12}/K	–887.3	–190.5	–182.2
T_{min}/K	252.6	262.7	259.3
T_{max}/K	466.4	483.2	458.7

Table 3 Comparison of the regression results of the (MEA+H_2O) system; Posey form, α_{12}=0.2

	γ	P	H^E
Np	39	211	73
S/%	0.2	5.9	2.9

Table 4 Comparison of the regression results of the (DEA+H_2O) system; Posey form, α_{12}=0.2

	γ	P	H^E
Np	25	97	57
S/%	0.1	6.6	7.0

Table 5 Comparison of the regression results of the (MDEA+H_2O) system; Posey form, α_{12}=0.2

	γ	P	H^E
Np	31	113	54
S/%	0.2	6.6	6.5

Based on this reasoning, the non-randomness parameter, in addition to the four temperature dependent binary interaction parameters, was regressed to all the experimental data. The results are presented in Tables 6 to 9.

The additional degree of freedom reduced the overall deviations for all the data sets considered. In all cases the obtained non-randomness parameters values were in the range suggested in the literature to maintain some physical meaning of the parameters. Walas [51] and Demirel and Paksoy [78] suggest that the non-randomness parameter should be forced to vary between 0.1–0.9.

Table 6 Temperature dependent parameters of the NRTL model (Posey form) of the (MEA+H_2O), (DEA+H_2O) and (MDEA+H_2O) systems; variable α_{12}

	MEA	DEA	MDEA
a_{21}	0.8807	0.0733	3.812
b_{21}/K	1012	450.3	–925.7
a_{12}	–0.0390	0.5489	0.1012
b_{12}/K	–909.4	–483.7	–341.1
α_{12}	0.1823	0.8184	0.7522
T_{min}/K	252.6	262.7	259.3
T_{max}/K	466.4	483.2	458.7

Table 7 Comparison of the regression results of the ($MEA+H_2O$) system; Posey form, variable α_{12}

	γ	P	H^E
Np	39	211	73
S/%	0.2	5.9	3.0

Table 8 Comparison of the regression results of the ($DEA+H_2O$) system; Posey form, variable α_{12}

	γ	P	H^E
Np	25	97	57
S/%	0.1	5.8	5.2

Table 9 Comparison of the regression results of the ($MDEA+H_2O$) system; Posey form, variable α_{12}

	γ	P	H^E
Np	31	113	54
S/%	0.2	4.5	5.6

Table 10 Temperature dependent parameters of the NRTL model (Demirel form) of the ($DEA+H_2O$), ($MEA+H_2O$) and ($MDEA+H_2O$) systems

	MEA	DEA	MDEA
c_1/kJ mol^{-1}	14.86	14.46	10.24
c_2/kJ K mol^{-1}	–107.3	–445.2	–370.4
c_3/kJ mol^{-1}	–10.14	–8.767	–5.872
c_4/kJ K mol^{-1}	33.62	132.5	58.63
c_5 (α_{12})	0.1310	0.1533	0.3014
T_{min}/K	252.6	262.7	259.3
T_{max}/K	466.4	483.2	458.7

In addition, the forms of the binary interaction parameters and non-randomness parameter proposed by Demirel and co-workers were also regressed for the ($DEA+H_2O$), ($MEA+H_2O$) and ($MDEA+H_2O$) systems. However, to have the same degrees of freedom as the other modelling approaches only 5 parameters were fit to the experimental data. The temperature dependence of the non-randomness parameter, c_6 was set to zero. In order to accommodate the low temperature data the base temperature in Demirel's modification of the NRTL model was set to 223.15 K. This ensured no discontinuity of the parameters over the temperature range considered. The relatively low percentage differences of each property used in the correlation indicate the ability of the non-linear NRTL model proposed by Demirel and co-workers to simultaneously correlate the data (considering the quality of the data). The results are presented in Tables 10 to 13.

Table 11 Comparison of the regression results of the ($MEA+H_2O$) system; Demirel form

	γ	P	H^E
Np	39	211	73
S/%	0.2	6.2	3.3

Table 12 Comparison of the regression results of the ($DEA+H_2O$) system; Demirel form

	γ	P	H^E
Np	25	97	57
S/%	0.1	6.1	5.6

Table 13 Comparison of the regression results of the ($MDEA+H_2O$) system; Demirel form

	γ	P	H^E
Np	31	113	54
S/%	0.2	5.1	5.9

As can be seen by the low average absolute percentage differences, the NRTL model, with both forms of the binary interaction and variable non-randomness parameter were quite successful in simultaneously correlating the VLE data, excess enthalpy and the low temperature activity coefficient data. The success of the NRTL model is exhibited over the large temperature range (~200 K) for each of the systems considered.

Based on the overall results, the form of the binary interaction parameters used by Posey [34] with a variable non-randomness parameter gave the best results. This form of the NRTL model is recommended, due to its simplicity, accuracy, and it does not suffer from the discontinuity problem of the model proposed by Demirel and co-workers. Comparison of the calculated results, with this model and the obtained parameters, and the experimental excess enthalpy, vapour pressure and low temperature activity coefficient results are presented in Figs 1 to 9. The differences between the experimental and calculated results, for the data sets considered, are lower than those obtained with the parameters presented in Posey [34]. The results for the ($DEA+H_2O$) system were significantly improved.

As discussed by Nagata [79], Demirel and Gecegormez [58], Demirel *et al.* [59], Huang and Lee [80], Demirel *et al.* [81] and Demirel [82] the quality of data, the type of data and the temperature range of data used in the parameter estimation, dictates the ability of the semi-theoretical (or empirical) model (regardless of the assumed temperature dependence) to simultaneously correlate and/or to predict (when no data were used in the regression) the other

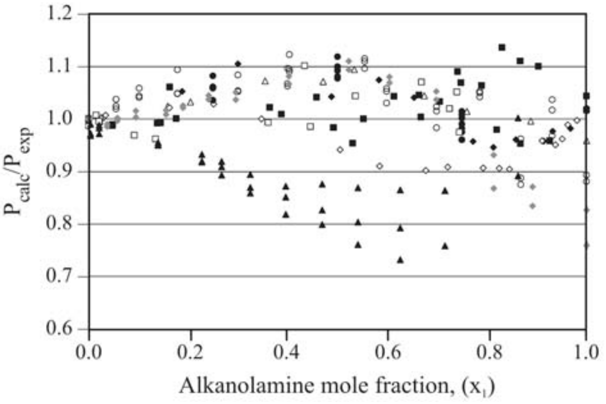

Fig. 1 Comparison of the calculated and the experimental vapour pressures (MEA+H2O): ◆ – TKYK01, ◇ – PL97, ● – KM91, ○ – NB93, ▲ – W76, △ – TAOLK99, ■ – CXW96, □ – LRT87, grey ◇ – TOOTIN82

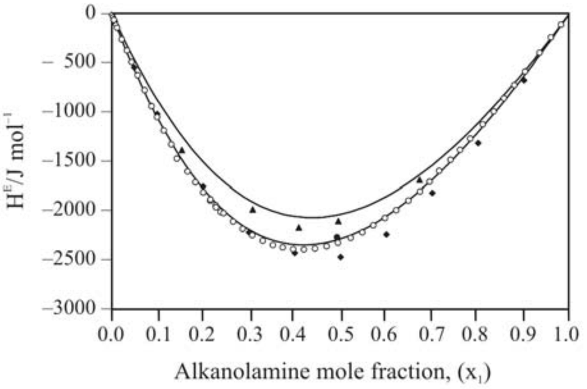

Fig. 2 Comparison of the calculated and the experimental excess enthalpies (MEA+H$_2$O): ◆ – 298.0 K BTMK83, ◇ – 298.15 K DRH94, ● – 298.15 PR96, ○ – 298.15 TOOTIN82, ▲ – 342.55 K PR96

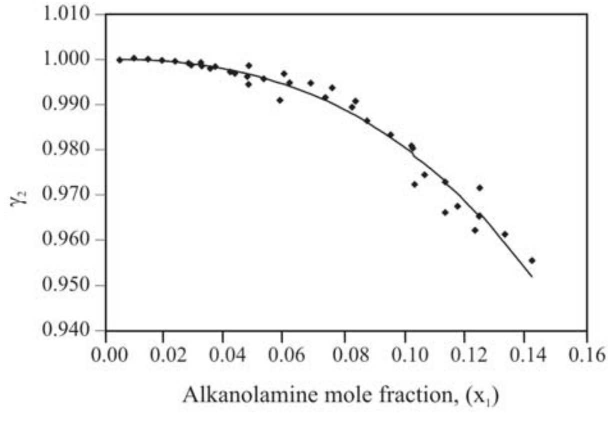

Fig. 3 Comparison of the calculated and the experimental water activity coefficients (MEA+H$_2$O): ◆ – CPR93

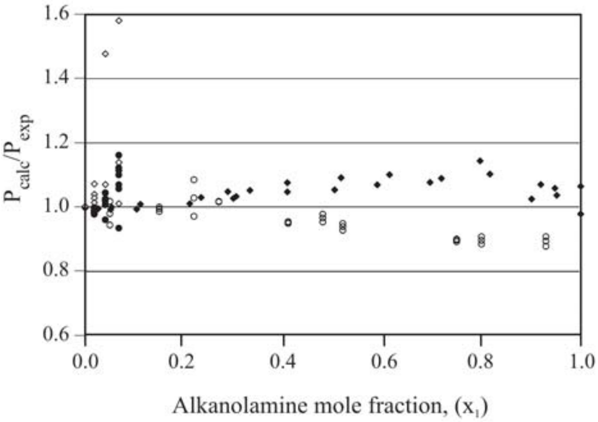

Fig. 4 Comparison of the calculated and the experimental vapour pressures (DEA+H$_2$O): ◆ – WWW91, ◇ – SRA93, ● – KM84, ○ – MDE69

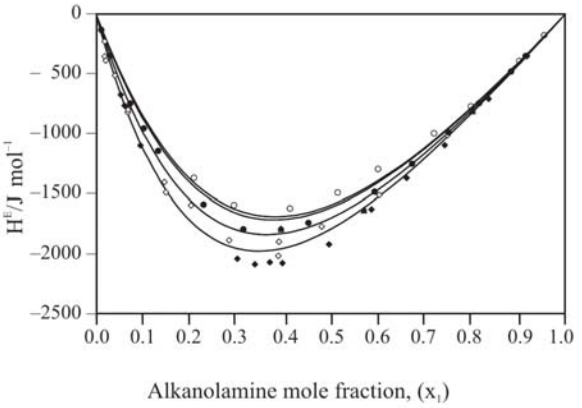

Fig. 5 Comparison of the calculated and the experimental excess enthalpies (DEA+H$_2$O): ◆ – 298.15 K MMH97, ◇ – 298.15 K PR96, ● – 318.15 MMH00, ○ – 338.15 MMH00, ▲ – 342.55 K PR96

excess properties. In addition, the quality of the overall fit is directly related to the accuracy of the pure component vapour pressure. The water vapour pressure [73] is quite accurate compared to the alkanolamine vapour pressures (~10%). The coefficients of these alkanolamine vapour pressure models may need to be revised with some new high precision vapour pressure measurements.

Table 14 compares the average absolute percentage deviation of each data set used in the regression. As can be seen, certain data sets appear to be of higher accuracy and/or consistency when compared to the other data sets.

Presented in Figs 10, 11 and 12 are the excess Gibbs energy, excess enthalpy and excess entropy, determined with the parameters in Table 6 at 298.15 K for the (MEA+H$_2$O), (DEA+H$_2$O) and (MDEA+H$_2$O) systems respectively. These figures give a good indication of the non-ideality of the respective systems.

To ensure the results had physical significance, the obtained parameters were used to predict the infinite dilution excess enthalpy and activity coefficients. Properties at infinite dilution are of interest as they usually indicate the maximum non-ideality of the system. The two properties of interest for the gas processing industry are the excess enthalpy and the activity coefficient of the amine at infinite dilution. These properties can be determined via the following equations.

$$\ln(\gamma_1^{\infty})=\tau_{21}+\tau_{12}G_{12} \tag{24}$$

Posey form:

$$H_1^{\mathrm{E},\infty}=-R\{-b_{21}+b_{21}G_{12}[\alpha_{12}\tau_{12}-1]\} \tag{25}$$

Demirel form:

$$\begin{aligned} H_1^{\mathrm{E},\infty}=\frac{T}{T'}\{&c_2+\tau_{21}RT'+\\ &+G_{12}[(c_4+\tau_{12}RT)(1-\tau_{12}\alpha_{12})-RT\tau_{12}^2c_6]\}\end{aligned} \tag{26}$$

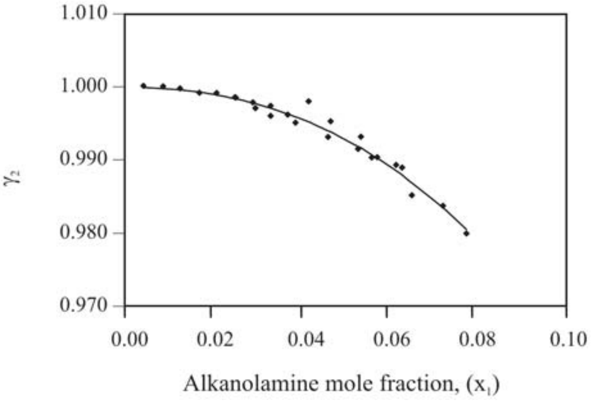

Fig. 6 Comparison of the calculated and the experimental water activity coefficients (DEA+H_2O): ◆ – CPR93

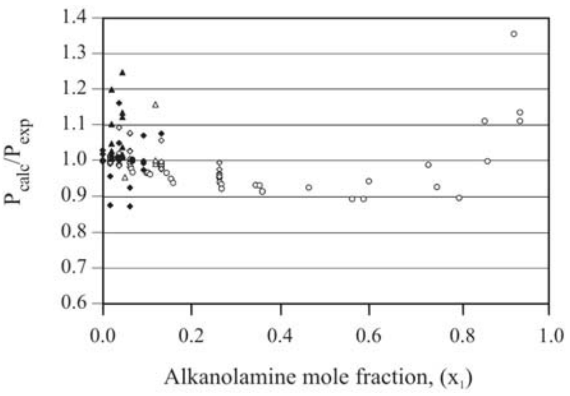

Fig. 7 Comparison of the calculated and the experimental vapour pressures (MDEA+H_2O): ◆ – SRA93, ◇ – ZQZZC91, • – KRSM96, ○ – VVML04, ▲ – K83, △ – SHFPFG04

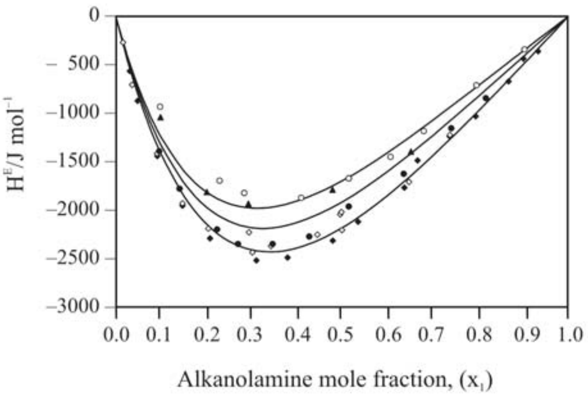

Fig. 8 Comparison of the calculated and the experimental excess enthalpies (MDEA+H_2O): ◆ – 298.15 K MMH97, ◇ – 298.15 K PR96, • – 313.15 MMH97, ○ – 338.15 MMH00, ▲ – 342.55 K PR96

Table 14 Comparison of the average absolute percentage deviation of the data sets used in the regression

	MEA	DEA	MDEA	Data type
DRH94	5.0	–	–	H^E
PR96	4.3	8.7	5.7	H^E
BTMK83	5.1	–	–	H^E
TOOTIN82	2.2	–	–	H^E
TKYK01	4.3	–	–	VLE
TAOLK99	3.7	–	–	VLE
PL97	4.6	–	–	VLE
CXW96	3.8	–	–	VLE
KM91	5.4	4.6	–	VLE
LRT87	2.8	–	–	VLE
NB83	5.9	–	–	VLE
TOOTIN82	6.0	–	–	VLE
W76	11.1	–	–	VLE
CPR93	0.2	0.1	0.2	γ
MMM00	–	3.5	7.2	H^E
MMH97	–	3.5	5.1	H^E
WWW91	–	4.6	–	VLE
SRA93	–	10.0	3.8	VLE
KM84	–	4.6	–	VLE
MDE69	–	5.6	–	VLE
XQZZC91	–	–	2.5	VLE
KRSM96	–	–	0.5	VLE
VVML04	–	–	7.4	VLE
SHFPFG04	–	–	5.3	VLE
K83	–	–	5.2	VLE

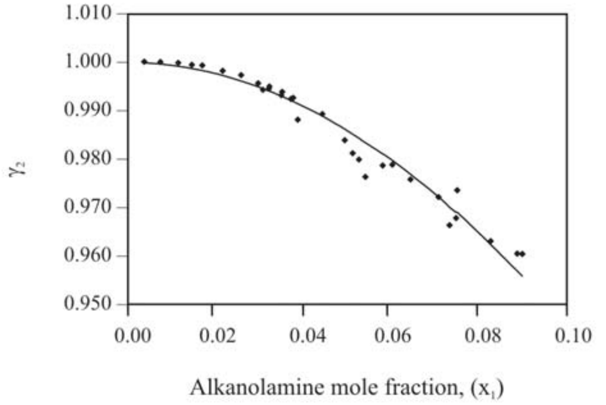

Fig. 9 Comparison of the calculated and the experimental water activity coefficients (MDEA+H_2O):◆ – CPR93

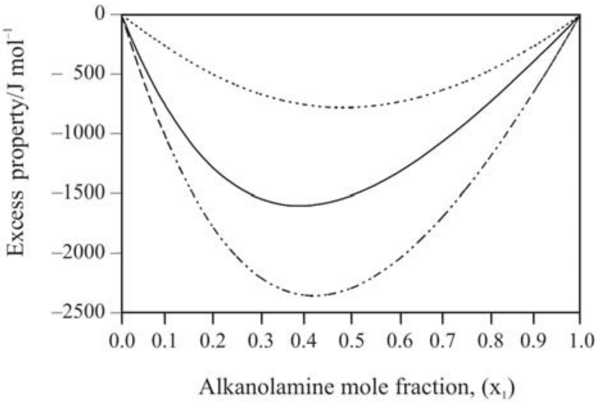

Fig. 10 Calculated excess Gibbs energy, excess enthalpy and excess entropy (MEA+H_2O): dashed line – G^E, dash-solid line – H^E, solid line – TS^E

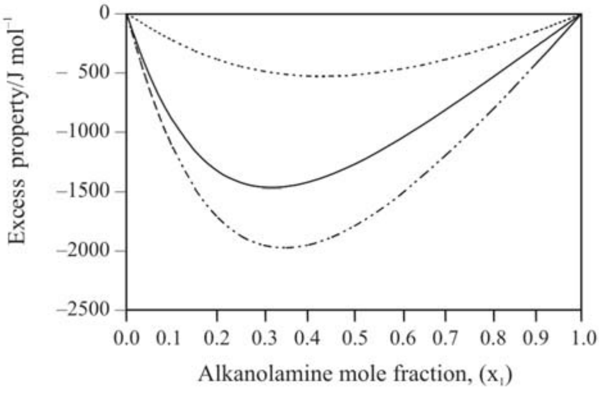

Fig. 11 Calculated excess Gibbs energy, excess enthalpy and excess entropy (DEA+H_2O): dashed line – G^E, dash-solid line – H^E, solid line – TS^E

Table 15 Alkanolamine excess enthalpy and activity coefficient at infinite dilution at 298.15 K

	MEA	DEA	MDEA
$H_1^{E,\infty}$/kJ mol^{-1}	–12.3	–14.4	–18.8
γ_1^∞	0.32	0.37	0.21

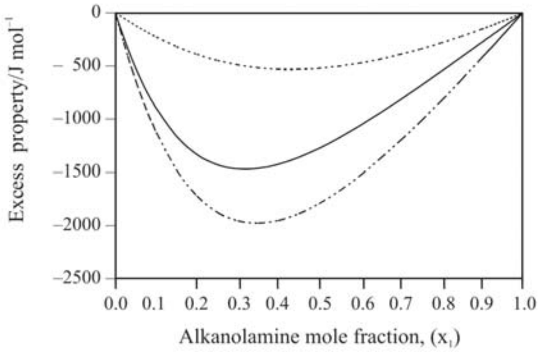

Fig. 12 Calculated excess Gibbs energy, excess enthalpy and excess entropy (MDEA+H_2O): dashed line – G^E, dash-solid line – H^E, solid line – TS^E

Table 16 Comparison of the alkanolamine excess enthalpy and activity coefficient at infinite dilution obtained from Austgen [83], Chang *et al.* [2] and Posey [34] at 298.15 K

Austgen	MEA	DEA	MDEA
$H_1^{E,\infty}$/kJ mol^{-1}	–12.0	–6.8	–
γ_1^∞	0.18	0.11	0.86

Chang *et al.*	MEA	DEA	MDEA
$H_1^{E,\infty}$/kJ mol^{-1}	–10.1	–3.3	–27.3
γ_1^∞	0.27	0.21	0.14

Posey	MEA	DEA	MDEA
$H_1^{E,\infty}$/kJ mol^{-1}	–12.8	–14.2	–19.2
γ_1^∞	0.32	0.14	0.24

Table 17 Comparison of the alkanolamine excess enthalpy at infinite dilution obtained from literature

	MEA	DEA	MDEA	Investigator
$H_1^{E,\infty}$/kJ mol^{-1}	–11.4	–14.5	–	KDH87
$H_1^{E,\infty}$/kJ mol^{-1}	–12.6	–	–	TOOTIN82
$H_1^{E,\infty}$/kJ mol^{-1}	–12.8	–14.5	–20.0	MMM97
$H_1^{E,\infty}$/kJ mol^{-1}	–11.7	–	–	DRH94

Presented in Table 15 are the results at 298.15 K obtained from the best fit parameters regressed from all the available data.

The results compare favourably to those obtained from Posey [34]. The exception is the difference in the infinite dilution activity coefficient in the (DEA+H_2O) system. The difference most likely occurs due to the VLE data set used in the parameter correlation. The data set used in this investigation only uses data published in the open literature and not those graphically presented in trade books.

The obtained heats of mixing at infinite dilution also compare well with those determined by Touhara *et al.* [22], Kim *et al.* [28], Maham *et al.* [37] and [41], and Dohnal *et al.* [34]. These are presented in Table 17.

Conclusions

A data bank, with the relevant data to determine the binary NRTL interaction parameters of (MEA+H_2O), (DEA+H_2O) and (MDEA+H_2O) mixtures, has been created. An optimization algorithm, based on the simulated annealing algorithm, has been developed to optimise the binary interaction parameters in the NRTL model from activity coefficient, VLE and excess enthalpy data. The model was quite successful in simultaneously correlating the activity coefficient, VLE, and excess enthalpy data of the systems investigated. The difference in the goodness of fit between the systems can be explained by the quality of data found for each system. At 298.15 K, the excess enthalpy and the activity coefficients at infinite dilution agree well with previous investigations and those determined experimentally.

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