

Phase Behavior Modeling of Alkyl Amine + Hydrocarbon and Alkyl Amine + Alcohol Systems Using a Group Contribution Associating Equation of State

Francisco A. Sánchez,[†] Amir H. Mohammadi,[‡] Alfonsina Andreatta,[†] Selva Pereda,[†] Esteban Brignole,^{*,†} and Dominique Richon^{*,‡}

Planta Piloto de Ingeniería Química, Universidad Nacional del Sur, CONICET, CC 717-8000, Bahía Blanca, Argentina, and MINES ParisTech, CEP/TEP - Centre 35, Rue Saint Honoré, 77305 Fontainebleau, France

In this work, a group contribution-associating equation of state namely GCA-EoS, is extended to model the phase behavior of alkyl amine + hydrocarbon and alkyl amine + alcohol systems while considering the association of functional groups. A generalized routine has been implemented to quantify the association effects through functional groups with associating sites. The predictions of the model are found in good agreement with experimental data reported in the literature. The model parameters were estimated in the temperature range 218–428 K and pressures up to 735 kPa.

1. Introduction

Natural gases often contain quantities of acid gases like CO₂ and H₂S. The presence of acid gases can cause corrosion and other operational problems during production, transportation, and processing of natural gases. To avoid these problems, acid gases are normally separated through amine absorption units. Alcohols are added to aqueous alkanolamine solutions when significant physical absorption is desired. Design and optimization of these units naturally require accurate knowledge of phase behavior in natural gas components + amine aqueous solution systems. For the continuous representation of properties, in particular, of phase equilibria of the above-mentioned systems, it is necessary to rely on accurate and reliable thermodynamic models. Existing thermodynamic models based on group contribution and cubic equations of state (EoS) like SRK with the modified Huron–Vidal mixing rule MHV2^{1,2} may be used for modeling amine aqueous solutions containing systems; however, in this type of model, the association and solvation effects are normally ignored. Nevertheless, these effects have an important contribution to the nonideality of the water- and amine-containing systems. A well-known concept applied in modeling associating solutions is the chemical theory, which postulates the existence of distinct chemical species in solution. A different approach is to apply statistical-mechanics such as in Wertheim's perturbation theory³ for fluids with highly oriented attractive forces. Wertheim's theory has been used in equations of state such as the statistical associating fluid theory (SAFT) based equations of state^{4,5} and the group contribution associating equation of state (GCA)^{6–9} to account explicitly for association effects. In contrast with the approach used in this work, researchers using SAFT family models assumed that amines present self-association.^{10–13} Other researchers¹⁴ have developed a cubic plus association equation of state (like SAFT, molecular based, and it is accounted for amine self-association) that has been applied to phase equilibrium correlation of amine vapor pressure and vapor–liquid equilibria of amines or alkanolamines with water, alcohol, and alkanes.^{15,16}

This study is part of a project for measuring and predicting phase equilibria in natural gas treating units of removing acid

* To whom correspondence should be addressed. E-mail: ebrignole@plapiqui.edu.ar and dominique.richon@mines-paristech.fr.

[†] Universidad Nacional del Sur.

[‡] MINES ParisTech.

gases using aqueous solutions of alkanol amines. In the previous works, the solubilities of hydrocarbons in water were measured, and their correlation and prediction were studied.^{17,18}

The aim of the present work is to study the capability of the GCA-EoS to model the phase behavior of alkane + alkyl amine and alkyl amine + alcohol systems. A detailed description of

Table 1. Pure Group Parameters

group	<i>q</i>	<i>T</i> [*] /K	<i>g</i> [*] /atm· cm ⁶ ·mol ⁻²	<i>g</i> '	<i>g</i> ''	ref
Paraffins						
CH ₃	0.848	600	316910	-0.9274	0	20
CH ₂	0.54	600	356080	-0.8755	0	20
CH=CH ₂	1.176	600	337980	-0.6764	0	21
Alcohols						
CH ₃ OH	1.432	512.6	547424.9	-0.6195	0.2488	22
CH ₂ OH	1.124	512.6	547424.9	-0.6195	0.2488	22
CH ₃ CH ₂ OH	1.972	514.00	438928.6	-0.6945	0.1448	22
Primary Amines						
CH ₃ NH ₂	1.544	430.05	704426	-0.325	-0.2543	this work
CH ₂ NH ₂	1.236	430.05	768254	-0.451	-0.0581	this work
CHNH ₂	0.942	430.05	768254	-0.451	-0.0581	this work
Secondary Amines						
CH ₃ NH	1.244	430.05	738872	-0.7057	0	this work
CH ₂ NH	0.936	430.05	738872	-0.7057	0	this work
CHNH	0.624	430.05	738872	-0.7057	0	this work
Tertiary Amines						
CH ₃ N	0.94	430.05	558334.6	-0.4789	0	this work
CH ₂ N	0.632	430.05	558334.6	-0.4789	0	this work

Table 2. Binary Interactions Parameters of Primary, Secondary, and Tertiary Amine Groups with Hydrocarbons and between Amine Groups

group <i>i</i>	group <i>j</i>	<i>k</i> _{ij} [*]	<i>k</i> _{ij} [']	α_{ij}	α_{ji}
Paraffins - Primary Amines					
CH ₃ /CH ₂ /CH	CH ₃ NH ₂	0.8705	-0.0227	1.2736	1.2736
CH ₃ /CH ₂ /CH	CH ₂ NH ₂ /CHNH ₂	0.8608	-0.0219	1.0000	1.0000
CH=CH ₂	CH ₂ NH ₂ /CHNH ₂	0.8608	-0.0219	1.0000	1.0000
Paraffins - Secondary Amines					
CH ₃ /CH ₂ /CH	CH ₃ NH/CH ₂ NH/CHNH	0.9242	0.0675	0.9574	0.9574
CH=CH ₂	CH ₂ NH/CHNH	0.9242	0.0675	0.9574	0.9574
Paraffins - Tertiary Amines					
CH ₃ /CH ₂	CH ₃ N/CH ₂ N	1	0	0	0
CH=CH ₂	CH ₃ N	1	0	0	0

Table 3. GCA-EoS Vapor Pressure Correlation of Alkyl Amines^a

alkyl amine	T_r	$\Delta p\%$	$d_c^b/\text{cm}\cdot\text{mol}^{-1}$
methylamine	0.57–1 ^c	0.42	3.4997 ^c
ethyldiamine	0.48–0.99	2.9	4.1235
ethylamine	0.58–0.99	1.6	3.8653
<i>n</i> -propyl amine	0.52–0.96	2.2	4.2333
<i>sec</i> -butylamine	0.50–0.95	5.4	4.5432
<i>iso</i> -butylamine	0.49–0.95	1.3	4.5871
diethylamine	0.45–0.97	2.9	4.6218
di- <i>n</i> -propylamine	0.49–0.99	4.1	5.2477
di- <i>iso</i> -propylamine	0.58–0.95	5.3	5.2998
trimethylamine	0.60–0.99	0.7	4.2933

^a Relative error ($\Delta p\%$) is indicated in the correlated temperature range (reduced temperature, T_r). ^b Critical diameter fitted to the normal boiling point except for methylamine. ^c In compounds formed by a single group, the critical diameter is calculated to exactly represent the critical point.

Table 4. GCA-EoS Vapor Pressure Prediction of Alkyl Amines^a

alkyl amine	T_r	$\Delta p\%$	$d_c^b/\text{cm}\cdot\text{mol}^{-1}$
<i>iso</i> -propyl amine	0.5–0.99	3.5	4.1943
<i>n</i> -butylamine	0.49–0.98	4.5	4.5615
<i>n</i> -pentylamine	0.48–0.99	2.2	4.8667
<i>n</i> -hexylamine	0.43–0.98	3.8	5.1519
<i>n</i> -nonylamine	0.55–0.99	3.1	5.8848
dimethylamine	0.51–0.99	2.4	3.9709
di- <i>n</i> -butylamine	0.48–0.99	3.3	5.7587
di- <i>iso</i> -butylamine	0.50–0.97	7.0	5.8550
triethylamine	0.50–0.97	4.0	5.2500
dimethylbutylamine	0.50–0.95	5.7	5.2079

^a Relative error ($\Delta p\%$) is indicated in the predicted temperature range (reduced temperature, T_r). ^b Critical diameter fitted to the normal boiling point.

Table 5. GCA-EoS Model Correlation of Systems Containing Amines + Hydrocarbons^a

compound		T/K	P/kPa	$\Delta p\%$	$\Delta y_1\%$	data points	ref
Primary amines							
methylamine	<i>n</i> -butane	288	180–315	1.1	–	21	24
methylamine	<i>n</i> -hexane	253–293 ^b	5–287	3.2	–	63	25
ethylamine	<i>n</i> -hexane	273–293 ^c	6–115	3.7	–	49	24
<i>n</i> -propylamine	<i>n</i> -hexane	253	2–5	5.2	–	22	24
<i>n</i> -butylamine	<i>n</i> -heptane	328, 348	23–93	0.5	0.8	28	26
Secondary amines							
diethylamine	<i>n</i> -hexane	333	8–12	1	0.1	6	27
di- <i>n</i> -propylamine	<i>n</i> -hexane	333	2–7	0.4	0.2	7	27

^a The temperature and pressure ranges of experimental data and the reference source are reported together with the relative errors of the model correlation. ^b Isotherms at 263 and 283 K of this source were not used for correlating. ^c Isotherms at 253 and 273 K were not used for correlating.

this equation of state is given in the Appendix. Using pure compound and binary equilibrium data reported in the literature, the parameters of the GCA-EoS are adjusted in the temperature range 218–428 K and pressures up to 735 kPa. The model predictions are compared with experimental data from the literature not used in the parameter fitting procedure.

2. Results and Discussion

Alkyl Amine + Alkane Systems. The GCA-EoS was applied to calculate phase equilibria in alkyl amine + hydrocarbon systems. The self-association effect of the alkyl amines is disregarded in this work; therefore, only parameters for the dispersive contribution of the GCA-EoS for the new amine groups are estimated. The groups for primary, secondary, and tertiary amines were defined. Table 1 reports all

Table 6. GCA-EoS Model Prediction of Systems Containing Amines + Hydrocarbons^a

compound		T/K	P/kPa	$\Delta z^b\%$	$\Delta y_1\%$	data points	ref
Primary amines + Paraffins							
methylamine	<i>n</i> -butane	233–273	45–182	4.0	–	66	24
methylamine	<i>n</i> -hexane	263, 283	7–198	2.8	–	42	25
ethylamine	<i>n</i> -butane	218–293	2–223	2.4	–	90	24
<i>n</i> -propylamine	<i>n</i> -hexane	273, 293	6–34	1.3	–	44	24
<i>n</i> -butylamine	<i>n</i> -hexane	333	83–64	4.1	0.5	7	27
<i>n</i> -butylamine	1-hexene	333	64–91	0.5	0.7	7	27
<i>n</i> -hexylamine	<i>n</i> -hexane	333	69–18	1.5	1.5	6	27
<i>n</i> -hexylamine	1-hexene	333	19–82	0.7	0.6	7	27
Secondary amines + Paraffins							
dimethylamine	<i>n</i> -hexane	233, 293	1–185	4.5	–	63	28
diethylamine	1-hexene	333	95–117	1.1	5.1	7	27
diethylamine	<i>n</i> -heptane	308, 328	11–100	1.2	0.2	14	26
di- <i>n</i> -propylamine	1-hexene	333	24–83	0.8	0.5	8	27
di- <i>iso</i> -propylamine	<i>n</i> -hexane	333	50–73	0.8	0.7	7	27
di- <i>iso</i> -propylamine	1-hexene	333	52–86	0.7	0.7	7	27
Tertiary amines + Paraffins							
trimethylamine	<i>n</i> -hexane	223–293	1–185	3.8	–	63	29
triethylamine	<i>n</i> -hexane	333	40–74	0.8	0.5	7	27
triethylamine	1-hexene	333	43–85	0.8	0.4	7	27
triethylamine	<i>n</i> -heptane	333	30–39	0.6	0.3	19	26
triethylamine	<i>n</i> -heptane	353	70–76	0.2	0.1	19	26

^a The temperature and pressure ranges of experimental data and the reference source are reported together with the relative errors of the model predictions. ^b $\Delta z\%$ corresponds to pressure for isothermal data and to temperature for isobaric data.

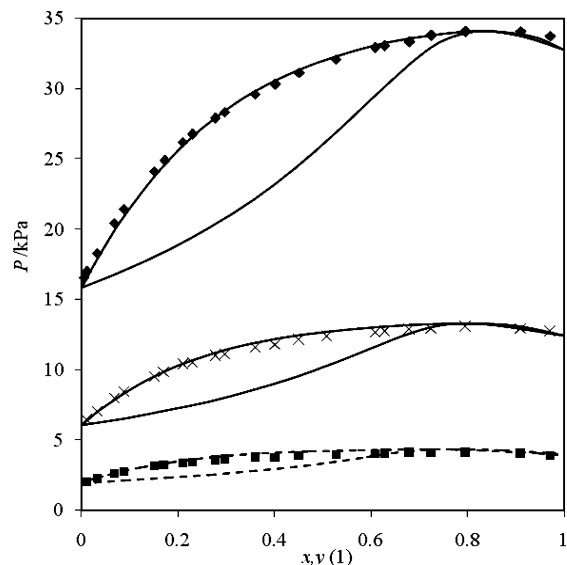


Figure 1. Vapor–liquid equilibrium of the *n*-propylamine (1) + hexane (2) binary system. Experimental data²⁴ at (■) 253.15 K, (×) 273.15 K, and (◆) 293.15 K. (– –) GCA-EoS correlation. (–) GCA-EoS prediction.

pure-group parameters to be applied in the attractive term of the equation in this work. These are the attractive energy parameters (g^* , g' , and g''), the reference temperature (T^*), and the normalized van der Waals group surface area (q). Also, the reference source for each set is indicated. The temperature-dependent attractive energy parameters estimated in this work were obtained from vapor pressure data for molecular groups (methylamine) and from binary phase equilibria and vapor pressure data for functional groups. Vapor pressures of the different amines were taken from the DIPPR Data Bank¹⁹ in the range of reduced temperature 0.5–0.99. Parameters for aliphatic, olefinic, and alcohol groups are from refs 20, 21, and 22, respectively.

Table 2 contains the values of the binary interaction parameters between hydrocarbon and amine groups (k_{ij}' and

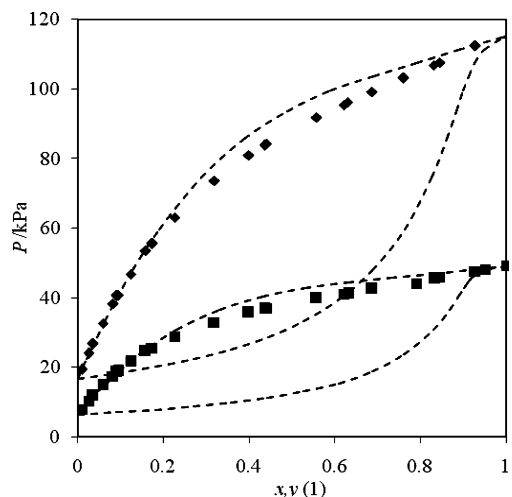


Figure 2. Vapor–liquid equilibrium of the ethylamine (1) + *n*-hexane (2) binary system. Experimental data²⁴ at (■) 273.15 K, (◆) 293.15 K. Dashed lines: GCA-EoS correlation.

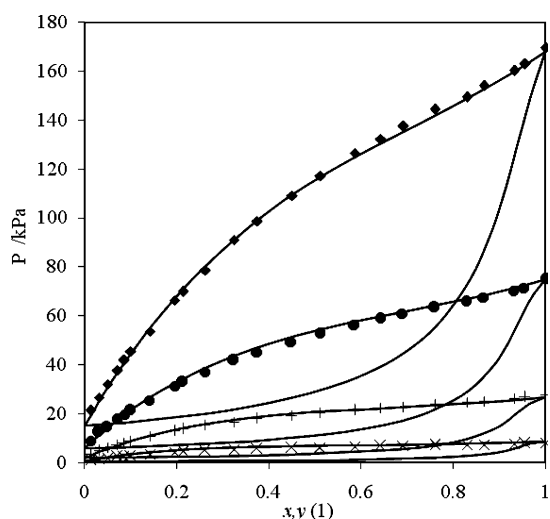


Figure 3. Vapor–liquid equilibrium of dimethylamine (1) + *n*-hexane (2) binary system. Experimental data²⁸ at (×) 233.15 K, (+) 253.15 K, (●) 273.15 K, and (◆) 293.15 K. Solid lines: GCA-EoS prediction.

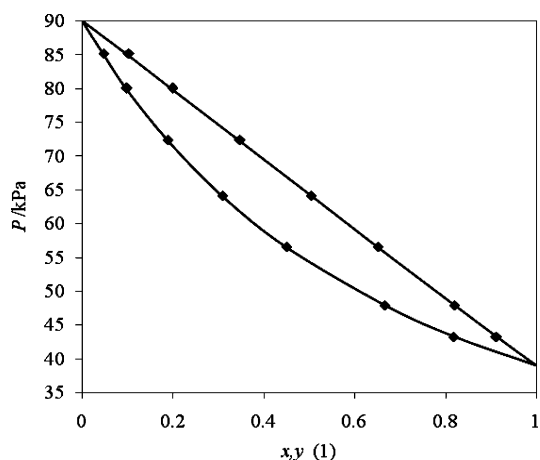


Figure 4. Vapor–liquid equilibrium of the triethylamine (1) + 1-hexene (2) binary system. Experimental data²⁷ at (◆) 333.15 K. Solid lines: GCA-EoS predictions.

k_{ij}'' , used to calculate the attractive energy between unlike interactions (g_{ji}). This table also reports the values of the nonrandomness parameters α_{ij} and α_{ji} , which quantify devia-

Table 7. Binary Interactions Parameters of the Alcohol Group with Paraffins and Primary, Secondary, and Tertiary Amine Groups

group <i>i</i>	group <i>j</i>	k_{ij}^*	k_{ij}'	α_{ij}	α_{ji}
Paraffins - alcohols ^a					
CH ₃	CH ₃ OH	0.91	-0.05	3	1
CH ₂	CH ₃ OH	0.98	-0.05	6	3
CH ₃ /CH ₂	CH ₃ CH ₂ OH	1	0	0	0
CH ₃	CH ₂ OH	0.93	-0.08	0	0
CH ₂	CH ₂ OH	0.93	0	0	0
Primary amines - alcohols					
CH ₂ NH ₂	CH ₃ OH/CH ₂ OH	1	0	0	0
CH ₂ NH ₂	CH ₃ CH ₂ OH	0.97	0	0	0
Secondary amines - alcohols					
CH ₃ NH/CH ₂ NH	CH ₃ OH	1.2062	0.1587	0	0
CH ₃ NH/CH ₂ NH	CH ₃ CH ₂ OH	1	0	0	0
CH ₃ NH/CH ₂ NH	CH ₂ OH	1	0	0	0
Tertiary amines - alcohols					
CH ₂ N	CH ₃ OH	1.200	0	0	0
CH ₂ N	CH ₂ OH	1	0	0	0

^a Binary interaction parameters from Soria.²²

Table 8. Energy (ϵ) and Volume (κ) of Association Parameters for the OH Group Self Association and for the Cross Association of the OH Group with the Amine Group

associating site ^a	associating group ^b	associating site <i>l</i>	associating group <i>j</i>	$\epsilon^{k,i,l,j}/K$	$\kappa^{k,i,l,j}/\text{cm}^3 \text{mol}^{-1}$
A	NH _x	A	NH _x	0	0
A	NH _x	A	OH	0	0
A	NH ₂	B	OH	3049	0.5418
A	NH	B	OH	3775	0.03614
A	N	B	OH	3775	0.02926
A	OH	A	OH	0	0
A	OH	B	OH	2759	0.8709
B	OH	B	OH	0	0

^a A: electronegative site. B: electropositive site. ^b *x* refers to 2, 1, and 0, for primary, secondary, and tertiary amines, respectively.

Table 9. GCA-EoS Model Correlation of Systems Containing Amines + Alcohols^a

compound		<i>T</i> /K	<i>P</i> /kPa	$\Delta z\%$	$\Delta y_1\%$	data points	ref
Primary amines + primary alcohols							
<i>n</i> -butylamine	1-propanol	318	9–26	1.8	2.0	10	30
<i>n</i> -butylamine	1-butanol	353–388	101	0.1	1.6	10	31
methanol	ethylendiamine	337–386	99	0.1	0.8	10	32
<i>n</i> -butylamine	ethanol	313	16–23	0.1	0.6	8	33
Secondary amines + primary alcohols							
1-propanol	di- <i>n</i> -propylamine	298	2–4	1.1	0.4	8	34
1-butanol	di- <i>n</i> -butylamina	393–428	101	0.2	1.2	8	31
diethylamine	methanol	298, 399	14–735	1.8	1.1	37	35
Tertiary amines + primary alcohols							
triethylamine	1-propanol	343	35–55	1.1	-	22	36
triethylamine	1-butanol	363	81–104	1.3	-	13	36
methanol	triethylamine	293	8–13	3.8	-	20	37

^a The temperature and pressure ranges of experimental data and the reference source are reported together with the relative errors of the model correlations. ^b $\Delta z\%$ corresponds to the error in pressure for isothermal data and to the error in temperature for isobaric data.

tions from second-order mixing rules. The parameters of Table 2 were estimated on the basis of binary vapor–liquid equilibrium data as indicated in the table together with vapor pressure information of amines from the DIPPR database.¹⁹ Table 3 presents the percent average relative deviations ($\Delta p\%$) of the correlation of vapor pressures of amines with the GCA-EoS model, and Table 4 reports the $\Delta p\%$ in vapor pressure predictions. Table 5 contains a summary of the

Table 10. GCA-EoS Model Prediction of Systems Containing Amines + Alcohols^a

compound		T/K	P/kPa	$\Delta z\%$	$\Delta y_1\%$	data points	reference
1	2						
Primary amines + primary alcohols							
methanol	<i>n</i> -butylamine	341–351	101	0.2	1.3	9	38
ethanol	ethylendiamine	357–381	99	0.2	1.5	10	32
<i>n</i> -propylamine	1-propanol	318	42–83	4.5	–	16	39
<i>n</i> -butylamine	1-propanol	313, 328–338	15–62	2.3	1.1	29	30, 33
<i>n</i> -butylamine	1-butanol	313	3–21	10.8	5.5	8	40
Secondary amines + primary alcohols							
dimethylamine	methanol	293–313	99–119	4.7	–	16	41
methanol	diethylamine	329–339	101	0.2	1.4	45	38, 42
methanol	di- <i>n</i> -propylamine	337–370	99	0.5	1.5	10	32
diethylamine	ethanol	313	19–50	2	1.9	9	42
ethanol	di- <i>n</i> -propylamine	351–373	99	0.3	0.8	10	32
1-propanol	di- <i>n</i> -propylamine	303–318	4–10	0.8	0.6	38	34
di- <i>n</i> -propylamine	1-propanol	380–372	101	0.2	2.2	8	43
Tertiary amines + primary alcohols							
methanol	triethylamine	338–356	101	0.2	1.6	18	38
triethylamine	1-propanol	353, 363	57–104	0.9	–	32	36
triethylamine	1-butanol	338, 352	13–70	0.7	–	13	36

^a The temperature and pressure ranges of experimental data and the reference source are reported together with the relative errors of the model predictions. ^b $\Delta z\%$ corresponds to the error in pressure for isothermal data and to the error in temperature for isobaric data.

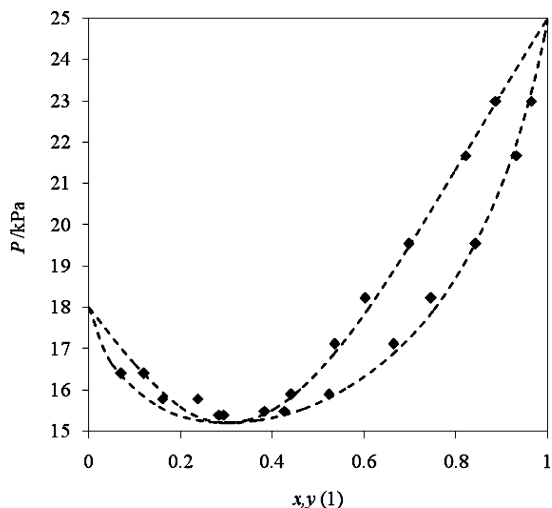


Figure 5. Vapor–liquid equilibrium of the *n*-butylamine (1) + ethanol (2) binary system. Experimental data³³ at (◆) 313.15 K. Dashed lines: GCA-EoS correlation.

GCA-EoS model vapor–liquid equilibrium correlation of experimental data of alkanes with primary, secondary, and tertiary amines and the relative errors of the correlation. Table 6 shows GCA-EoS predictive capacity for several binary hydrocarbon + amine systems. Figures 1–4 compare selected vapor–liquid equilibrium data with GCA-EoS correlation (dashed lines) and predictions (solid lines). The effect of self-association is normally dominant in determining the value of the activity coefficient at infinite dilution. It can be seen from Figures 1–4 that disregarding the self-association of the amine group has not hampered the predictions of vapor–liquid equilibria at low amine concentrations. These results are in agreement with the claim of Funke et al.²³ that the self-association effect in alkyl amines is several orders of magnitude lower than in alcohols.

Alkyl Amine + Alcohol Systems. In the case of alcohol + alkyl amine system, the self-association of the alcohols and the cross association between the active hydrogen of the alcohol and the electron donor site of the amine group are

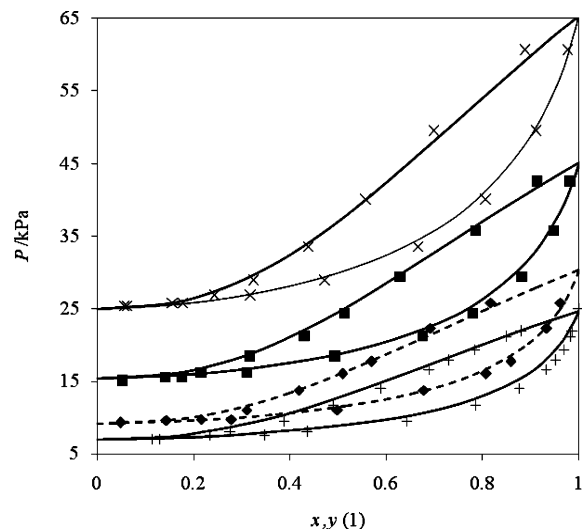


Figure 6. Vapor–liquid equilibrium of the *n*-butylamine (1) + *n*-propanol (2) binary system. Experimental data^{30,33} at (◆) 318.15 K; (■) 328.15 K; (×) 338.15. (---) GCA-EoS correlation. (—) GCA-EoS prediction.

considered. On the basis of spectroscopic information, Soria²² determined new values for the self-associating energy and volume parameters of the alcohol hydroxyl group. On the other hand, this author also determined the energy parameters for molecular description of methanol and ethanol (g^* , g' , and g'' reported in Table 1). In the present work, this new description of the associating methanol group is also used for the alcohol group CH₂OH. The dispersive interaction parameters of amine and paraffins with alcohol groups are given in Table 7.

In Table 8 are given the energy and volume of association parameters for the alcohol self-association and for the cross-association between the amine and the alcohol groups. It is interesting to note the rather large value of the energy of cross association between the alcohol and the amine groups. There was no need of binary interaction energy parameters for the primary, secondary, and tertiary amine + alcohol. However, methanol did require an interaction parameter with

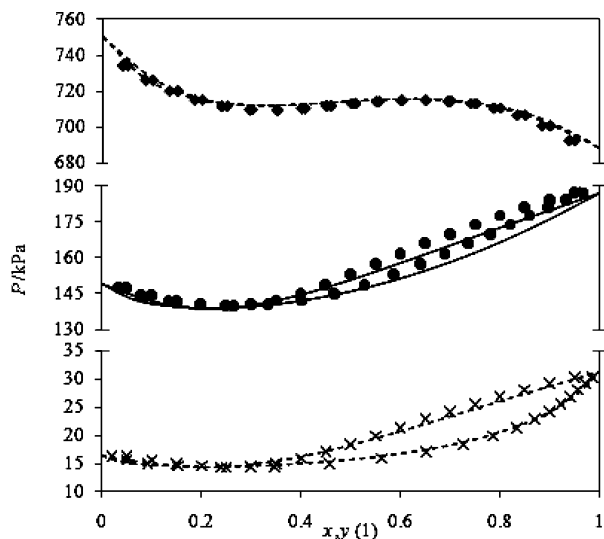


Figure 7. Vapor–liquid equilibrium of methanol (1) + diethylamine (2). Experimental data³⁵ at (x) 297.7 K; (●) 348.1 K; (◆) 398.8 K. (---) GCA-EoS correlation and (—) GCA-EoS prediction.

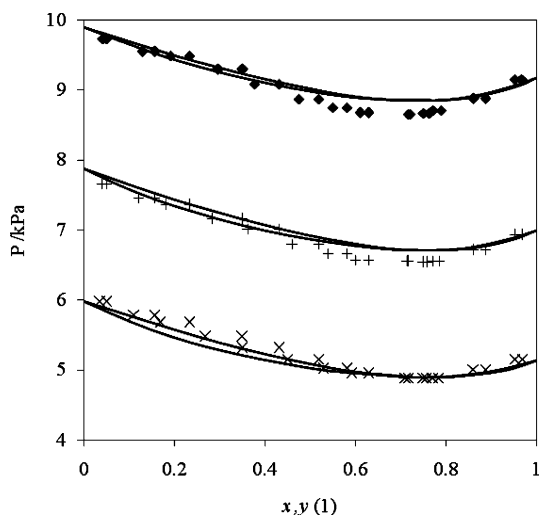


Figure 8. Vapor–liquid equilibrium of 1-propanol (1) + di-*n*-propylamine (2) binary. Experimental data³⁴ at (x) 308.15 K; (+) 313.15 K; (◆) 318.15 K. Solid lines: GCA-EoS predictions.

secondary and tertiary amines which is common for the first component of the series. Table 9 presents a summary of the GCA-EoS model correlation of vapor–liquid equilibrium data of alcohols with primary, secondary, and tertiary amines and the relative errors of the model. GCA-EoS predictions of selected alcohol + amine binaries are given in Table 10. Figures 5–10 compare selected vapor–liquid equilibrium data with GCA-EoS correlation (dashed lines) and predictions (solid lines). It is interesting to note the almost ideal behavior of the *n*-butanol + triethyl amine binary.

3. Conclusions

In this paper, a group contribution associating equation of state was extended to take into account association and solvation effects, to properly model the phase behavior of alkyl amine + hydrocarbon and alkyl amine + alcohol systems. New values for associating groups were defined. Acceptable representation of vapor–liquid equilibria was achieved in binary systems of

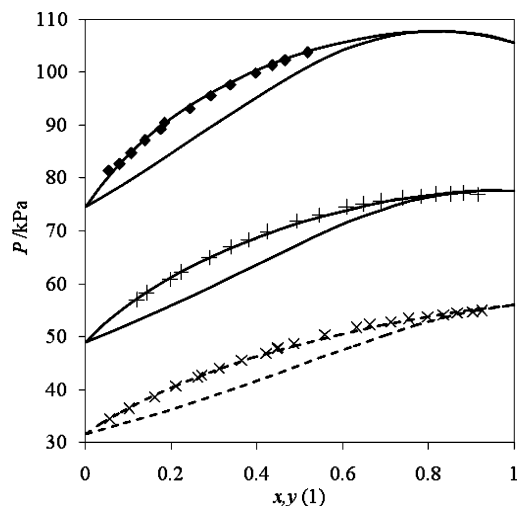


Figure 9. Vapor–liquid equilibrium of the triethylamine (1) + 1-propanol (2) binary system. Experimental data³⁶ at (x) 343.2 K, (+) 352.2 K, (◆) 362.2 K, (---) GCA correlation, (—) GCA prediction.

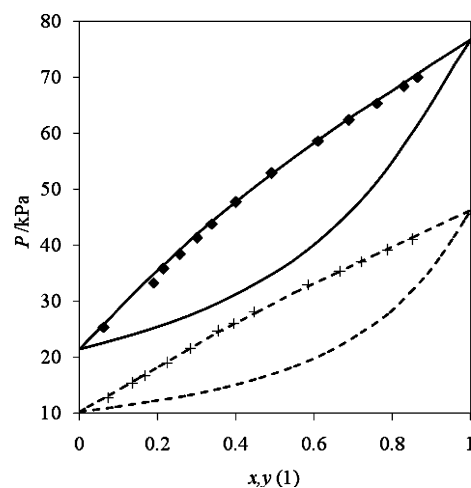


Figure 10. Vapor–liquid equilibrium of the triethylamine (1) + 1-butanol (2) binary system. Experimental data³⁶ at (+) 337.65 K, (◆) 353.95 K, (---) GCA correlation, (—) GCA prediction.

alkyl amine + hydrocarbon and alkyl amine + alcohol binaries, and good predictions of vapor pressures of alkylamines were obtained.

Acknowledgment

The financial support by the ECOS-SUD program that provided the opportunity for this joint work is gratefully acknowledged. The authors also acknowledge the support of CONICET, Universidad Nacional del Sur and Ministerio de Ciencia y Tecnología de Argentina.

Appendix

Group-Contribution Associating Equation of State, GCA-EoS

The GCA-EoS^{6–9} is based on the group contribution expression for the configurational Helmholtz function, A^c . All thermodynamic phase equilibrium properties may be derived from A^c by differentiation with respect to composition or volume.

The Helmholtz energy is considered as composed of two parts: the first describes the ideal gas behavior, A^{ideal} , and the

second part takes into account the intermolecular forces, which can be evaluated by a repulsive or free volume term, A^{fv} , a contribution from attractive intermolecular forces, A^{att} , and an associative term, A^{assoc}

$$A = A^{ideal} + (A^{fv} + A^{att} + A^{assoc}) \quad (A.1)$$

The free volume contribution is modeled by assuming a hard sphere behavior for the molecules, characterizing each substance i by a hard sphere diameter d_i . A Carnahan–Starling⁴⁴ type of hard sphere expression for mixtures is adopted

$$(A/RT)^{fv} = 3(\lambda_1\lambda_2/\lambda_3)(Y - 1) + (\lambda_2^3/\lambda_3^2)(Y^2 - Y - \ln Y) + n \ln Y \quad (A.2)$$

with

$$Y = \left(1 - \frac{\pi\lambda_3}{6V}\right)^{-1} \quad (A.3)$$

$$\lambda_k = \sum_j^{NC} n_j d_j^k \quad (A.4)$$

where n_i is the number of moles of component i ; NC stands for the number of components; V represents the total volume; R stands for universal gas constant; and T is temperature.

The following generalized expression is assumed for the hard sphere diameter temperature dependence

$$d_i = 1.065655d_{ci}\{1 - 0.12 \exp[-2T_{ci}/(3T)]\} \quad (A.5)$$

where d_c is the value of the hard sphere diameter at the critical temperature, T_c , for the pure component.

For the evaluation of the attractive contribution to the Helmholtz energy, a group contribution version of a density-dependent NRTL-type expression⁴⁵ is derived

$$(A/RT)^{att} = -\frac{z}{2} \sum_{i=1}^{NC} n_i \sum_{j=1}^{NG} v_j^i q_j \frac{\sum_{k=1}^{NG} \theta_k g_{kj} \tilde{q} \tau_{kj} / (RTV)}{\sum_{i=1}^{NG} \theta_i \tau_{ij}} \quad (A.6)$$

where

$$\theta_j = (q_j/\tilde{q}) \sum_i^{NC} n_i v_j^i \quad (A.7)$$

$$\tilde{q} = \sum_i^{NC} n_i \sum_j^{NG} v_j^i q_j \quad (A.8)$$

$$\tau_{ij} = \exp(a_{ij} \Delta g_{ij} \tilde{q} / (RTV)) \quad (A.9)$$

$$\Delta g_{ij} = g_{ij} - g_{jj} \quad (A.10)$$

where z is the number of nearest neighbors to any segment (set to 10); v_j^i is the number of groups type j in molecule i ; q_j stands for the number of surface segments assigned to group j ; θ_k represents the surface fraction of group k ; \tilde{q} is the total number of surface segments; g_{ij} stands for the attraction energy parameter

for interactions between groups i and j ; and α_{ij} is the NRTL nonrandomness parameter.

The interactions between unlike groups are calculated from

$$g_{ij} = k_{ij}(g_{ii}g_{jj})^{1/2} \quad (k_{ij} = k_{ji}) \quad (A.11)$$

with the following temperature dependence for the interaction parameters

$$g_{ij} = g_{ij}^* [1 + g'_{ij}(T/T_j^* - 1) + g''_{ij} \ln(T/T_j^*)] \quad (A.12)$$

and

$$k_{ij} = k_{ij}^* \left[1 + k'_{ij} \ln\left(\frac{2T}{T_i^* + T_j^*}\right)\right] \quad (A.13)$$

where g_{ij}^* is the interaction parameter for reference temperature T_i^* .

The Helmholtz function due to association is calculated with a modified form of the expression used in the SAFT equation⁴ and is formulated in terms of associating groups

$$\frac{A^{assoc}}{RT} = \sum_{i=1}^{NGA} n_i^* \left[\sum_{k=1}^{M_i} \left(\ln X^{(k,i)} - \frac{X^{(k,i)}}{2} \right) + \frac{1}{2} M_i \right] \quad (A.14)$$

where NGA represents the number of associating groups; n_i is the total number of moles of associating group i ; $X^{(k,i)}$ stands for the mole fraction of group i not bonded at site k ; and M_i is the number of associating sites assigned to group i . The number of moles of the associating group is

$$n_i^* = \sum_{m=1}^{NC} v_{assoc}^{(i,m)} n_m \quad (A.15)$$

where $v_{assoc}^{(i,m)}$ represents the number of associating groups i in molecule m and n_m is the total number of moles of molecules m ; the summation includes all the NC components in the mixture.

The mole fraction of group i not bonded at site k is determined by

$$X^{(k,i)} = \left[1 + \sum_{j=1}^{NGA} \sum_{l=1}^{M_j} \rho_j X^{(l,j)} \Delta^{(k,i,l,j)}\right]^{-1} \quad (A.16)$$

$X^{(k,i)}$ depends on the molar density of the associating group j , $\rho_j = n_j^*/V$, and on the association strength between site k of group i and site l of group j

$$\Delta^{(k,i,l,j)} = \kappa^{(k,i,l,j)} [\exp(e^{(k,i,l,j)}/kT) - 1] \quad (A.17)$$

The associating strength is a function of the temperature and characteristic association parameters ε (association energy) and κ (associating volume).

List of Symbols

A = Helmholtz energy ($\text{J} \cdot \text{mol}^{-1}$)

A^{ideal} = Helmholtz energy term describing ideal behavior part ($\text{J} \cdot \text{mol}^{-1}$)

A^{fv} = Helmholtz energy term describing free volume part ($\text{J} \cdot \text{mol}^{-1}$)

A^{att} = Helmholtz energy term describing attractive part ($\text{J} \cdot \text{mol}^{-1}$)

A^{assoc} = Helmholtz energy term describing association part ($\text{J} \cdot \text{mol}^{-1}$)

d_i = diameter of the component i ($\text{cm} \cdot \text{mol}^{-1}$)

d_{ci} = hard sphere diameter of the component i ($\text{cm} \cdot \text{mol}^{-1}$)
 g_{ij} = attractive energy parameter for interactions between groups i and j ($\text{atm} \cdot \text{cm}^6 \cdot \text{mol}^{-1}$)
 k = Boltzmann constant
 k_{ij}, k_{ji} = binary interaction parameters
 M_i = number of associating sites assigned to group i
 NC = number of components in the mixture
 NGA = number of associating groups
 n_i = number of moles of component i
 n_j^* = number of moles of associating group j
 q = surface-area segments per mole
 q_j = number of surface segments assigned to group j
 \tilde{q} = total number of surface segments
 T = temperature (K)
 T_{ci} = critical temperature of component i (K)
 R = ideal gas constant ($8.314 \text{ (J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$)
 V = volume (m^3)
 x_i = mole fraction in liquid phase of component i
 $X^{(k,i)}$ = fraction of not bonded site k of group i
 y_i = mole fraction in vapor phase of component i
 z = number of nearest neighbors to any segment
Greek Letters
 α_{ij}, α_{ji} = nonrandomness parameters
 $\Delta^{(k,i,l,j)}$ = association strength between site k of group i and site l of group j ($\text{cm}^3 \cdot \text{mol}^{-1}$)
 $\Delta z\%$ = average relative deviation $100 \cdot \sum_N [(z_{\text{calc}} - z_{\text{exp}})/z_{\text{exp}}]^2 / N$
 $\varepsilon^{(k,i,l,j)}$ = association energy between site k of group i and site l of group j (J)
 $\kappa^{(k,i,l,j)}$ = association volume between site k of group i and site l of group j ($\text{cm}^3 \cdot \text{mol}^{-1}$)
 ν_j^i = number of groups j in molecule i
 $\nu_{\text{assoc}}^{(i,m)}$ = number of associating group i in molecule m
 ρ = density ($\text{mol} \cdot \text{cm}^{-3}$)
 ρ_j = molar density of the associating group j ($\text{mol} \cdot \text{cm}^{-3}$)
 θ_j = surface fraction of group j

Literature Cited

- Michelsen, M. L. A Method for Incorporating Excess Gibbs Energy Models in Equations of State. *Fluid Phase Equilib.* **1990**, *60*, 47–58.
- Dahl, S.; Michelsen, M. L. High-Pressure Vapor-Liquid Equilibrium with a UNIFAC-Based Equation of State. *AIChE J.* **1990**, *36*, 1829–1836.
- Wertheim, M. S. Fluids with Highly Directional Attractive Forces. IV. Equilibrium Polymerization. *J. Stat. Phys.* **1986**, *42*, 477–492.
- Chapman, W. G.; Gubbins, K. E.; Jackson, G.; Radosz, M. SAFT: Equation-of-state solution model for associating fluids. *Fluid Phase Equilib.* **1989**, *52*, 31–38.
- Chapman, W. G.; Gubbins, K. E.; Jackson, G.; Radosz, M. New reference equation of state for associating liquids. *Ind. Eng. Chem. Res.* **1990**, *29*, 1709–1721.
- Zabaloy, M. S.; Mabe, G. D. B.; Bottini, S. B.; Brignole, E. A. Vapor-liquid equilibria in ternary mixtures of water-alcohol-non polar gases. *Fluid Phase Equilib.* **1993**, *83*, 159–166.
- Gross, H. P.; Bottini, S. B.; Brignole, E. A. A group contribution equation of state for associating mixtures. *Fluid Phase Equilib.* **1996**, *116*, 535–544.
- Ferreira, O.; Macedo, E. A.; Brignole, E. A. Application of the GCA-EoS model to the supercritical processing of fatty oil derivatives. *J. Food Eng.* **2005**, *70* (4), 579–587.
- Ferreira, O.; Brignole, E. A.; Macedo, E. A. Modelling Phase Equilibria with an Equation of State. *J. Chem. Thermodyn.* **2004**, *36*, 1105–1117.
- Huang, S. H.; Radoz, M. Equation of State for Small, Large, Polydisperse, and Associating Molecules. *Ind. Eng. Chem. Res.* **1990**, *29*, 2284–2294.
- Gross, J.; Sadowski, G. Application of the Perturbed Chain SAFT Equation of State to Associating Systems. *Ind. Eng. Chem. Res.* **2002**, *41*, 5510–5515.
- Grenner, A.; Schmelzer, J.; von Solms, N.; Kontogeorgis, G. M. Comparison of Two Association Models (Elliott-Suresh-Donohue and Simplified PC-SAFT) for Complex Phase Equilibria of Hydrocarbon-Water and Amine-Containing Mixtures. *Ind. Eng. Chem. Res.* **2006**, *45*, 8170–8179.
- Elliott, J. R., Jr. Efficient Implementation of Wertheim's Theory for Multicomponent Mixtures of Polysegmented Species. *Ind. Eng. Chem. Res.* **1996**, *35*, 1624–1629.
- Kontogeorgis, G. M.; E. C.; Voutsas, I. V.; Yakoumis, D. P. Tassios, An Equation of State for Associating Fluids. *Ind. Eng. Chem. Res.* **1996**, *35*, 4310–4318.
- Kaarsholm, M.; Derawi, S. O.; Michelsen, M. L.; Kontogeorgis, G. M. Extension of the Cubic-plus-Association (CPA) Equation of State to Amines. *Ind. Eng. Chem. Res.* **2005**, *44*, 4406–4413.
- Avlund, A. S.; Michelsen, M. L.; Kontogeorgis, G. M. Michelsen Modeling Systems Containing Alkanolamines with the CPA Equation of State. *Ind. Eng. Chem. Res.* **2008**, *47* (19), 7441–7446.
- Mokraoui, S.; Coquelet, C.; Valtz, A.; Hegel, P. E.; Richon, D. New Solubility Data of Hydrocarbons in Water and Modeling Concerning Vapor-Liquid-Liquid Binary Systems. *Ind. Eng. Chem. Res.* **2007**, *46*(26), 9257–9262.
- Pereda, S.; Awan, J. A.; Mohammadi, A. H.; Valtz, A.; Coquelet, C.; Brignole, E. A.; Richon, D. Solubility of hydrocarbons in water: Experimental measurements and modeling using a group contribution with association equation of state (GCA-EoS). *Fluid Phase Equilib.* **2008**, *275*, 52–59.
- DIPPR801-Database. Thermophysical Properties Database, 1998.
- Steen-Jørgensen, S. Group Contribution Equation of State (GC-EOS): A predictive Method for Phase Equilibrium Computations over Wide Ranges of Temperatures and Pressures up to 30 MPa. *Ind. Eng. Chem. Res.* **1988**, *27*, 110–118.
- Pusch, J.; Schmelzer, J. Extension of the Group-Contribution Equation of State parameter matrix for the prediction of phase equilibria containing argon, ammonia propane and other alkanes. *Ber. Bunsen-Ges. Phys.* **1993**, *97* (4), 597–603.
- Soria, T. Personal communication, 2008.
- Funke, H.; Wetzel, M.; Heintz, A. New applications of the ERAS model. Thermodynamics of amine + alkane and alcohol + amine mixtures. *Pure Appl. Chem.* **1989**, *61* (8), 1429–1439.
- Wolff, H.; Hoepfner, A.; Hoepfner, H. M. Die Assoziation von Methyl-, Aethyl- und Propylamin in gesättigten aliphatischen Kohlenwasserstoffen. *Ber. Bunsen-Ges. Phys. Chem.* **1964**, *68*, 410–417.
- Wolff, H.; Hoepfner, A. Die Wasserstoffbrückenassoziation von Methylamin in n-Hexan (nach Dampfdruckmessungen). *Z. Elektrochem.* **1962**, *66*, 149–159.
- Letcher, T. T.; Bayles, J. M. J. Thermodynamics of some binary liquid mixtures containing aliphatic amines. *J. Chem. Eng. Data.* **1971**, *16*, 266.
- Humphrey, J. L.; Van Winkle, M. Vapor-liquid equilibrium at 60 °C for n-hexane-alkyl amines and 1-hexene-alkyl amines. *J. Chem. Eng. Data* **1967**, *12*, 526–531.
- Wolff, H.; Hoepfel, H.-E. Wasserstoffbrückenassoziation und Komplexbildung von Dimethylamin in n-Hexan und Tetrachlorkohlenstoff (nach Dampfdruckmessungen). *Ber. Bunsen-Ges. Phys. Chem.* **1966**, *70*, 874–883.
- Wolff, H.; Wuertz, R. Komplexbildung und Wasserstoffbrückenassoziation von Trimethyl- und Methylamin in Tetrachlorkohlenstoff und Hexan (nach Dampfdruckmessungen). *Ber. Bunsen-Ges. Phys. Chem.* **1968**, *72*, 101–110.
- Pradhan, S. D. *Indian J. Technol.* **1979**, *17*, 324 (as quoted in DECHEMA Data Series).
- Komarov, V. M.; Krichevstov, B. K. *Zh. Prikl. Khim.* **1966**, *39*, 2836–2838 (as quoted in DECHEMA Data Series).
- Kato, M.; Tanaka, H. Vapor-Liquid Equilibrium Determination with a Flow-Type Ebulliometer for Six Binary Systems Made of Alcohol and Amine. *J. Chem. Eng. Data* **1989**, *34*, 203–206.
- Dutta-Choudhury, M. K. Excess Free Energy of Binary Mixtures of n-Butylamine with Ethyl alcohol and n-Propyl alcohol. *Indian J. Chem.* **1976**, *14A*, 553–556.
- Villa, S.; Garriga, R.; Pérez, P.; García, M.; González, J. A.; García de la Fuente, I.; Cobos, J. C. Thermodynamics of mixtures with strongly negative deviations from Raoult's Law, Part 9: Vapor - liquid equilibria for the system 1-propanol + di-n-propylamine at six temperatures between 293.15 and 318.15 K. *Fluid Phase Equilib.* **2005**, *231*, 211–220.
- Srivastava, R.; Smith, B. D. Total-Pressure Vapor-Liquid Equilibrium Data for Binary Systems of Diethylamine with Acetone, Acetonitrile, and Methanol. *J. Chem. Eng. Data* **1985**, *30*, 308–313.
- Copp, J. L.; Findlay, T. J. V. Thermodynamics of binary systems containing amines. Part 4. *Trans. Faraday Soc.* **1960**, *56*, 13–22.
- Chun, K. W.; Davison, R. R. Thermodynamic Properties of Binary Mixtures of Triethylamine with Methyl and Ethyl Alcohol. *J. Chem. Eng. Data* **1972**, *17*, 307–310.

(38) Nakanishi, K.; Shirai, H.; Minamiyama, T. Vapor-liquid Equilibria of Binary Systems Containing Alcohols: Methanol with Aliphatic Amines. *J. Chem. Eng. Data* **1967**, *12* (4), 591–594.

(39) Kristoif, E.; Orszaig, I.; Ratkovics, F. Static Vapour-Liquid Equilibrium Studies On $\{x_{\text{C}_3\text{H}_7\text{NH}_2} + (1-x)_{\text{C}_3\text{H}_7\text{OH}}\}$. *J. Chem. Thermodyn.* **1981**, *13*, 557–562.

(40) Ratkovics, F.; Liszi, J.; Laszlo, M.; Szeiler, B.; Devay, J. *Acta. Chim. Acad. Sci. Hung.* **1973**, *77*, 249–265 (as quoted in DECHEMA Data Series).

(41) Niepel, W.; Novak, J. P.; Matous, J.; Sobr, J. *Chem. Zvesti* **1972**, *26*, 44 (as quoted in DECHEMA Data Series).

(42) Aucejo, A.; Loras, S.; Muñoz, R.; Wisniak, J.; Segura, H. Phase Equilibria and Multiple Azeotropy in the Associating System Methanol + Diethylamine. *J. Chem. Eng. Data* **1997**, *42*, 1201–1207.

(43) Krichevtsov, B. K.; Komarov, V. M. Correlation of thermodynamic properties of systems consisting of aliphatic amines and alcohols. *Zh. Prikl. Khim.* **1970**, *43* (2), 295–301.

(44) Carnahan, N. F.; Starling, K. E. Equation of state for nonattracting rigid spheres. *J. Chem. Phys.* **1969**, *51*, 635–636.

(45) Renon, H.; Prausnitz, J. M. Local composition in thermodynamic functions for liquid mixtures. *AIChE J.* **1968**, *14*, 135–44.

Received for review December 29, 2008
Revised manuscript received June 17, 2009
Accepted July 8, 2009

IE802004V