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Mutual Solubility of Hexadecane with Diethanolamine and with Bis(hydroxyethyl)piperazine

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Mutual solubilities were determined by the cloud point method for the hexadecane + diethanolamine and hexadecane + bis(hydroxyethyl) piperazine systems in the temperature ranges of (105.4 to 222.4) °C and (69.4 to 193.2) °C, respectively. The results were successfully interpreted using the NRTL model, and NRTL parameters were used to predict vapor−liquid equilibria.

Introduction

Aqueous alkanolamine solutions, which are extensively used in the gas-processing industries, become contaminated over time with amine degradation compounds, heat stable salts, corrosion products, and various other impurities. To recover the valuable amines, conventional flash separators and distillation have been considered, but they encounter operational problems when the solids content is high and the volatilities of degradation compounds are comparable to those of the amines. Furthermore, amines are subject to thermal degradation and should therefore not be preheated in conventional heat exchangers with extended residence times.

To overcome these problems, it has been proposed to mix the contaminated amine solutions with an immiscible, high boiling point, inert liquid prior to distillation (Abedinzadegan Abdi, 1997). The inert liquid can act as a rapid heat transfer medium and also increases the liquid flow in the lower section of the distillation column where the impurities predominate. The inert liquid should have the following characteristics: thermal stability, chemical inertness, low melting point, high boiling point, low specific gravity, low solubility of contaminants and amine, low toxicity and cost, good heat transfer properties, low corrosivity, and low viscosity. The high boiling point of the inert liquid minimizes its presence in the overhead product leaving the distillation column. The low specific gravity, low mutual solubility with the amines and their contaminants, and chemical inertness facilitate the recovery of the inert liquid in a recycle process. Hexadecane is a promising candidate as the inert liquid. Its boiling and melting points fall within ranges satisfying the requirements of amine distillation processes. It also has good thermal properties and is available in bulk at reasonable prices.

The design of amine-reclaiming systems based on distillation requires information on phase equilibria and related thermodynamic properties. By determining the mutual solubilities for the hexadecane−amine and hexadecane−amine degradation compound systems, the nonidealities of the liquid phases can be found and subsequently used to predict the vapor−liquid behavior of systems containing hexadecane, amine, amine degradation compounds, and water. The mutual solubilities of hexadecane + diethanolamine (DEA) and hexadecane + bis(hydroxyethyl) piperazine (BHEP) mixtures were therefore measured. BHEP is one of the major products of acid gas induced degradation of DEA (Kennard and Meisen, 1985). Its boiling point is relatively close to that of DEA, and it cannot be efficiently separated from DEA in a simple flash operation.

Experimental Section

The chemicals used in this study were supplied by Aldrich Chemical Co., and their purities exceeded 99%. BHEP is a white crystalline powder with a melting point of 137 °C; it becomes gradually discolored at temperatures above 170 °C. The solubility studies were therefore restricted to the temperature range of (69.4 to 193.2) °C for the hexadecane + BHEP system. Since DEA degrades rapidly at temperatures above 250 °C, the hexadecane + DEA studies were limited to (105.4−222.4) °C.

The “cloud point method” was selected to conduct the experiments. Binary mixtures of known compositions were prepared by weighing the compounds (with an accuracy of three significant figures) before sealing them into Pyrex glass vials (60 mm long, 13 mm i.d.) and placing them into a bath of Paratherm NF heat transfer oil supplied by Paratherm Corp. (Conshohocken, PA). The bath initial temperature was sufficiently elevated to ensure that a clear, homogeneous single-phase liquid resulted. The temperature was gradually lowered until phase separation occurred, which rendered the solution cloudy. By visual observation, the cloud point temperatures could be determined with an accuracy of ±0.2 °C. The mixtures were agitated by a stirrer bar, and the temperatures were monitored by K-type thermocouples. Details of the experimental procedure were reported by Abedinzadegan Abdi (1996, 1997).

All measurements were made near atmospheric pressure. For each mixture, the experiments were repeated at least three times, and, as the separation temperature was approached, attempts were made to keep the rate of cooling as low as possible.

Results and Discussion

The results of the solubility studies for the hexadecane + DEA and hexadecane + BHEP systems are given in Tables 1 and 2 and Figures 1 and 2, respectively. The compositions are expressed in mass fractions and are

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Table 1. Liquid−Liquid Equilibrium Data for Hexadecane (1) + DEA (2)

exptl values		estimated values	
$w_2{}^a \pm 0.0005$	$(t \pm 0.2)$/°C	w_2	t/°C
0.0088	105.4	0.0095	104.4
0.0151	127.2	0.0150	126.7
0.0198	140.5	0.0197	141.1
0.0250	158.2	0.0247	158.7
0.0257	163.5	0.0259	163.2
0.0288	172.3	0.0292	171.8
0.0372	190.5	0.0376	190.1
0.9800	222.4	0.9775	222.1
0.9855	210.5	0.9851	210.2
0.9902	196.3	0.9900	195.8
0.9927	182.3	0.9926	182.1
0.9944	172.4	0.9943	172.1
0.9962	156.3	0.9964	156.7
0.9981	135.2	0.9983	135.5

[a] w denotes the mass fraction.

Table 2. Liquid−Liquid Equilibrium Data for Hexadecane (1) + BHEP (2)

exptl values		estimated values	
$w_2 \pm 0.0005$	$(t \pm 0.2)$/°C	w_2	t/°C
0.0021	69.4		
0.0034	81.1		
0.0058	90.6		
0.0138	110.8		
0.0260	134.8		
0.0332	145.8	0.0327	145.1
0.0434	155.5	0.0430	155.2
0.0586	169.2	0.0591	168.7
0.0787	180.7	0.0781	181.1
0.9379	193.2	0.9362	192.8
0.9507	182.6	0.9489	182.1
0.9565	173.7	0.9574	174.2
0.9691	156.8	0.9699	157.5
0.9728	153.2	0.9733	153.6
0.9822	140.2	0.9811	140.0

accurate to at least three significant figures. Figures 1 and 2 also show the NRTL [nonrandom two-liquid (Renon and Prausnitz, 1968)] predictions for higher temperatures. The upper critical solution temperatures (UCST) can be estimated from these diagrams even though they cannot be measured because DEA and BHEP decompose rapidly at temperatures above 250 °C.

The NRTL activity coefficient model was used to regress the present data by means of the ASPEN PLUS simulator The NRTL model equations and related parameters are given in the Appendix. The regression method used in the ASPEN simulator is the generalized least-squares method based on the maximum likelihood principles. The Britt−Luecke algorithm (Britt and Luecke, 1973) is employed to obtain the model parameters. The nonrandomness parameter α in the NRTL model was set to 0.3 by default.

The adjustable parameters for the NRTL model are shown in Table 3. As is evident from Figure 1 and also Table 1, the NRTL model gave good fits for hexadecane + DEA. The same is also generally true for hexadecane + BHEP. Although the regression for hexadecane + BHEP was based on data collected above 138 °C, the NRTL model predicted the experimental measurements well for temperatures below 130 °C. Tables 1 and 2 also indicate that the errors between the estimated and experimental data are generally less than 1%.

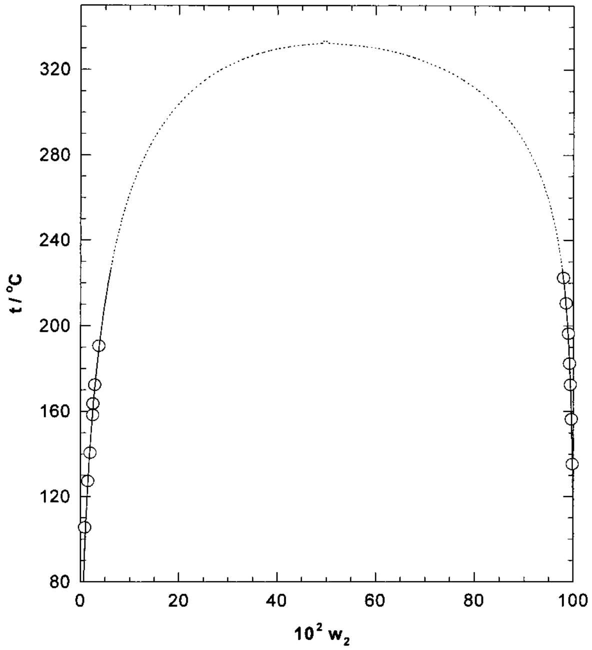

Figure 1. Hexadecane (1) + DEA (2) mass fraction solubility diagram; NRTL predictions were used for elevated temperatures: (○) present experimental data; (—) NRTL regression; (···) NRTL predictions for elevated temperatures.

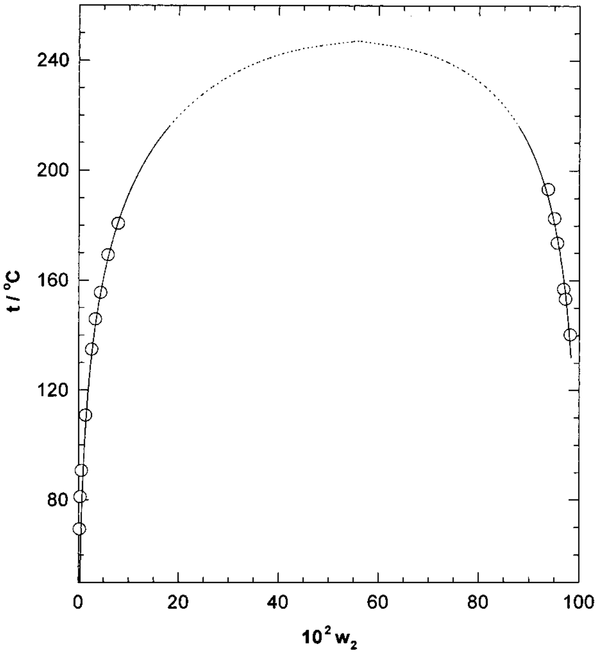

Figure 2. Hexadecane (1) + BHEP (2) solubility diagram; NRTL predictions were used for elevated temperatures: (○) present experimental data; (—) NRTL regression; (···) NRTL predictions for elevated temperatures

To gain insight into the likely effectiveness of distillation processes for the separation for hexadecane + DEA and hexadecane + BHEP mixtures, vapor−liquid equilibrium (VLE) information can be generated using the parameters obtained in the solubility studies. Figures 3 and 4 show the VLE predictions using the NRTL parameters for hexadecane + DEA and hexadecane + BHEP, respectively. Although the use of activity coefficients obtained from the liquid−liquid equilibrium studies is not common in estimating vapor−liquid equilibria, the closeness of the predictions based upon the parameters obtained from the solubility studies and the experimental results (see Figures 3 and 4) demonstrates that the equilibrium predictions using the NRTL parameters are sound (Abedinzadegan Abdi, 1997). The UNIFAC predictions for hexadecane + DEA are also shown in Figure 3. The UNIFAC estimates,

Table 3. Values of Adjustable NRTL Model Parameters and Standard Deviations for the Hexadecane + DEA and Hexadecane + BHEP Systems ($\alpha = 0.3$)

system	parameter[a]	estimate	standard deviation (σ)
DEA (1) + hexadecane (2)	a_{12}	−5.4080	0.9365
	a_{21}	−4.3107	0.8289
	b_{12}	4583.84	414.54
	b_{21}	2871.64	366.22
	RRMS	17.6	
	SSQ	41.5×10^3	
BHEP (1) + hexadecane (2)	a_{12}	−3.8173	0.4093
	a_{21}	−5.5447	0.3983
	b_{12}	2922.46	179.06
	b_{21}	3277.39	174.15
	RRMS	55.8	
	SSQ	21.8×10^3	

[a] *a* and *b* are ASPEN parameters and are given in SI units (see Appendix); RRMS and SSQ denote the residual root mean square and sum of squares of errors, respectively.

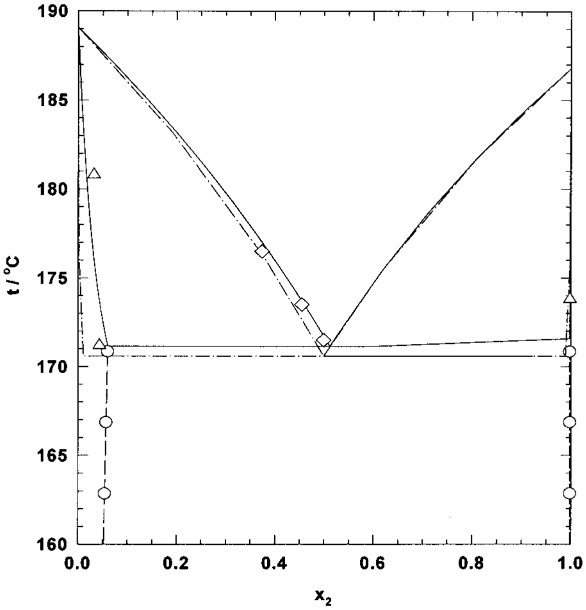

Figure 3. Equilibrium (*T*−*xy*) diagram for the hexadecane (1) + DEA (2) system at 6.7 kPa: (—) NRTL predictions; (○, - - -) present experimental data; (— —) UNIFAC predictions; (△) total pressure measurements, data from Abedinzadegan Abdi (1997); (◇) vapor circulation cell and distillation data from Abedinzadegan Abdi (1997).

especially near the azeotropic composition, show good agreement with experimental data and the NRTL predictions.

Distillation of a hexadecane + DEA mixture under total reflux at 6.7 kPa in a tall packed column (1 m high) yielded a top product with a DEA mole fraction of 0.4992 at 171.5 °C. These values closely correspond to the azeotrope predicted by the NRTL and UNIFAC methods shown in Figure 3 and Table 4. Measurements conducted by Abedinzadegan Abdi (1997) with a vapor circulating VLE cell using hexadecane + DEA and hexadecane + BHEP mixtures also gave results that corresponded closely to the NRTL predictions (see Table 5). Figure 5 depicts the bubble point surface plot for hexadecane + DEA + BHEP based on the NRTL model. The plot also demonstrates the relationships for the binary systems. The small mutual solubility of DEA and hexadecane is reflected in the constant temperature of the miscibility gap that sharply rises to the pure component boiling points at the diagram corners. The diagram shows the "imprint" of the two-liquid-phase region, and only very small changes in the bubble point temperature are exhibited within this region. Large increases in temperature occur at the binodal curve as the mixture becomes homogeneous. The same is true for hexadecane + BHEP. The constant bubble point temperature throughout the entire range of composition for hexadecane + BHEP indicates the small mutual solubility for this binary system. The parameters for DEA + BHEP were obtained using the same method of data reduction, and the VLE data were obtained and reported by Abedinzadegan Abdi (1997). Figure 6 shows the dew point surface plot for hexadecane + DEA + BHEP. The vapor-phase equilibrium lines for the binary systems of hexadecane + DEA, DEA + BHEP, and hexadecane + BHEP can be seen in the binary planes of the plot.

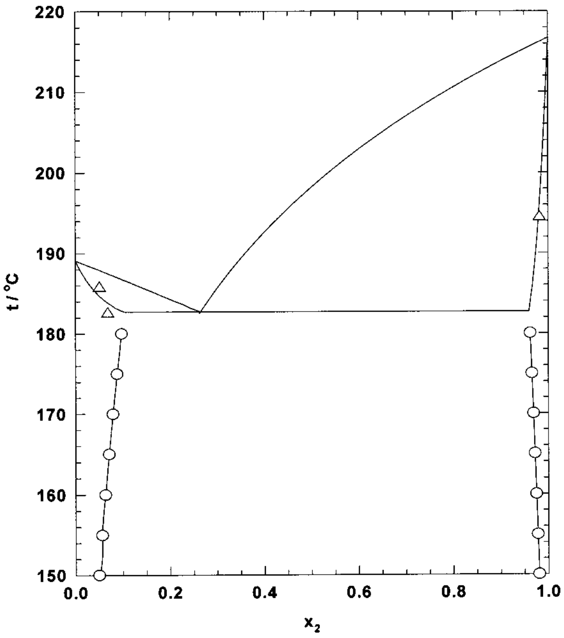

Figure 4. Equilibrium (*T*−*xy*) diagram for the hexadecane (1) + BHEP (2) system at 6.7 kPa: (—) NRTL VLE prediction; (○, —) present experimental LLE data; (△) bubble point measurements, data from Abedinzadegan Abdi (1997).

Table 4. Azeotrope Composition and Temperature of the Hexadecane (1) + DEA (2) System Determined Experimentally and by the NRTL and UNIFAC Methods at 6.7 kPa

method	azeotropic parameter	
	x_2	*t*/°C
present experimental work	0.4992	171.5
NRTL	0.5122	171.2
UNIFAC	0.4995	170.6

Table 5. Comparison of the NRTL Predictions and Bubble Point Measurements for the Hexadecane + DEA and Hexadecane + BHEP Systems at 6.7 kPa

	bubble point temperature/°C		
x_2	NRTL prediction	exptl result	absolute error (%)
	Hexadecane (1) + DEA (2)		
0.9978	173.1	173.8	0.40
0.0436	173.7	171.2	1.46
0.0321	176.1	180.8	2.67
	Hexadecane (1) + BHEP (2)		
0.9818	196.3	194.4	0.97
0.0682	183.5	182.5	0.55
0.0507	184.6	185.7	0.59

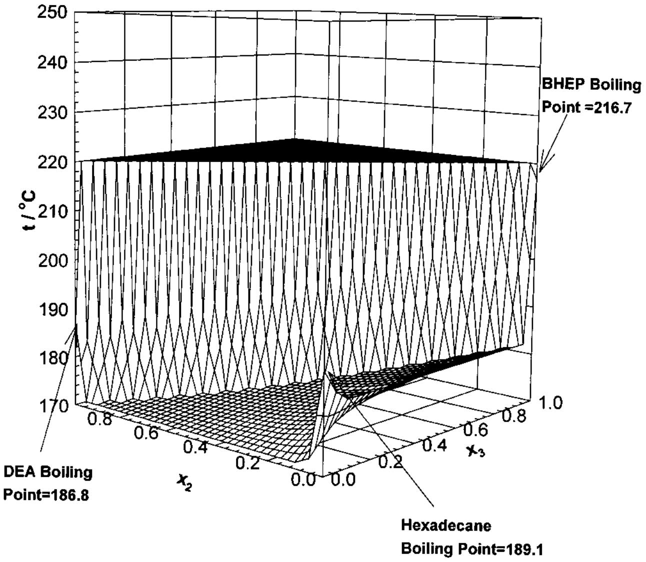

Figure 5. Bubble point surface generated with the NRTL model for the hexadecane (1) + DEA (2) + BHEP (3) ternary system at 6.7 kPa.

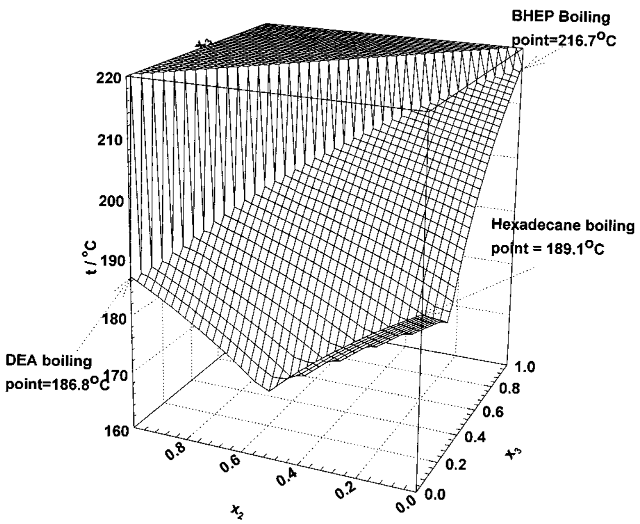

Figure 6. Dew point surface plot generated with the NRTL model for the hexadecane (1) + DEA (2) + BHEP (3) ternary system at 6.7 kPa.

Conclusions

Since hexadecane appears to be a promising liquid for reclaiming DEA from contaminated solutions by distillation, the solubilities of the hexadecane + DEA and hexadecane + BHEP systems were determined. The NRTL activity coefficient model was successfully used to represent the experimental data. The mutual solubilities of the hexadecane + DEA and hexadecane + BHEP systems are quite similar, with the solubility of BHEP in hexadecane being only somewhat higher than that of DEA in hexadecane. The solubility of BHEP in hexadecane is strongly temperature dependent, and its recovery from the inert liquid should be readily possible at near ambient temperatures. The somewhat higher solubility of BHEP in hexadecane can also improve the distillative separation of BHEP and DEA.

List of Symbols

a = constant in temperature-dependent equations for the model adjustable parameters (ASPEN parameters)

b = temperature coefficient in the temperature-dependent equations for model adjustable parameters (ASPEN parameters)

G = parameter in the NRTL model

g = binary interaction energy in the NRTL model

R = universal gas constant

RRMS = residual root mean square

SSQ = sum of squares of errors

T = temperature

w = mass fraction in the liquid phase

x = mole fraction in the liquid phase

Greek Letters

α = nonrandomness parameter in the NRTL model

γ = activity coefficient

σ = standard deviation

τ = NRTL binary interaction energy parameter

Subscripts

i, j = species i, j

1, 2 = components in binary systems

Appendix. NRTL Equation and Related Parameters

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

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

where

$$\tau_{12} = \frac{g_{12} - g_{22}}{RT} \qquad \tau_{21} = \frac{g_{21} - g_{11}}{RT}$$

$$G_{12} = \exp\{-\alpha_{12}\tau_{12}\} \qquad G_{21} = \exp\{-\alpha_{21}\tau_{21}\}$$

The NRTL parameters are related to the ASPEN "*a*" and "*b*" parameters as follows:

$$\tau_{ij} = a_{ij} + b_{ij}/T$$

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