Table III. Standard Enthalpies of Solution of Glucose and Xylose in Ethanol + Water Mixtures at 45 °C

	$\Delta H°$, kJ/mol	
% water	glucose	xylose
0	30.2 ± 0.2	30.4 ± 0.4
2		29.9 ± 0.4
5	29.1 ± 0.2	29.4 ± 0.3
10	27.9 ± 0.2	28.0 ± 0.3

linear extrapolations of the data for sugar concentrations below 1% and are listed in Table III. There is remarkable agreement between the values for the two sugars in ethanol-rich mixtures, within experimental uncertainty, though the values for xylose are consistently about 0.2 kJ/mol greater than those for glucose. The effect of added water on the differential enthalpy of solution of these sugars is essentially the same, while the effect of added sugar is significantly greater for glucose than for xylose.

Literature Cited

(1) Bertrand, G. L.; Dickneite, B. R.; Sitton, O. C. *J. Chem. Eng. Data*, preceding paper in this issue.

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Vapor-Liquid Equilibrium of Ethanol/Water/*N*,*N*-Dimethylformamide

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The low-pressure isothermal vapor-liquid equilibrium of ethanol/water/*N*,*N*-dimethylformamide (DMF) at 85 and 90 °C has been measured. The main finding is that the addition of DMF breaks the ethanol/water azeotrope. In ethanol-rich mixtures containing 30-70 mol % DMF, the lowest relative volatility of ethanol to water is 1.3 and this occurs at infinite dilution of water in ethanol. This suggests that ethanol and water can easily be separated by extractive distillation using DMF. A comparison with our ternary data is made of the predictions of the UNIFAC and a recently proposed solute aggregation activity coefficient model using parameters obtained from binary data.

Introduction

Recent work at the University of Delaware and the Technical University of Berlin has indicated that *N*,*N*-dimethylformamide (DMF) can be used to affect the relative volatility of polar organic mixtures (*1*). DMF is a Lewis base, and previous studies have shown that the phase behavior of solutions containing DMF are influenced by its chemically basic behavior (*2*). Since water is a stronger Lewis acid than are alcohols, we anticipated that DMF would selectively lower the vapor pressure of water in solutions with alcohols. Thus, if water is the less volatile component, the addition of DMF should increase the relative volatility of the alcohol with respect to water and, therefore, make the separation by distillation easier. In this work we have studied the vapor-liquid equilibrium of the ethanol/water/DMF mixture, because of the widespread use of ethanol as a fuel and solvent.

Experiments

DMF is embryotoxic to laboratory animals and should not be inhaled or allowed to contact skin. Since DMF is such a good solvent, care must be exercised in the choice of materials which contact it.

Table I. VLE Data at 85.00 and 90.00 °C for Ethanol (1)/Water (2)/DMF (3)

T, °C	x_{DMF}[a]	x_1[b]	y_1[b]	y_{DMF}	y_1x_2/y_2x_1	P, kPa
			$x_{\mathrm{DMF}} \cong 0.50$			
85	0.4954	0.0306	0.1029	0.1382	3.67	37.15
85	0.5049	0.1202	0.2634	0.1116	2.62	41.90
85	0.5191	0.2511	0.4337	0.0948	2.28	46.40
85	0.4947	0.4121	0.5874	0.0639	2.03	54.45
85	0.5108	0.5600	0.6991	0.0448	1.83	56.74
85	0.5024	0.5608	0.7021	0.0520	1.85	56.88
85	0.5169	0.6165	0.7423	0.0522	1.79	58.86
85	0.5136	0.6781	0.7885	0.0502	1.77	64.45
85	0.4784	0.7871	0.8564	0.0408	1.61	[c]
90	0.545	0.748	0.830	0.0749	1.64	70.24
90	0.526	0.779	0.850	0.0672	1.61	66.30
90	0.520	0.827	0.880	0.0702	1.53	73.26
90	0.515	0.910	0.935	0.0665	1.42	74.68
90	0.505	0.945	0.961	0.0663	1.43	75.11
			Ethanol/Water ≅ 4/1			
90	0.3169	0.8001	0.8390	0.0054	1.30	105.2
90	0.4164	0.7898	0.8457	0.0307	1.46	88.60
90	0.5650	0.7872	0.8514	0.0946	1.55	65.58
90	0.7114	0.7862	0.8526	0.2037	1.57	45.05
			Ethanol/Water ≅ 9/1			
90	0.3146	0.8909	0.9196	0.0044	1.40	106.89
90	0.5202	0.8987	0.9238	0.0672	1.37	74.17
90	0.6171	0.8994	0.9224	0.1174	1.33	60.09
90	0.7361	0.8892	0.9141	0.2186	1.33	43.36
			Ethanol/Water ≅ 18/1			
90	0.328	0.943	0.953	0.0087	1.23	106.2
90	0.408	0.947	0.957	0.0290	1.25	91.97
90	0.526	0.943	0.957	0.0705	1.35	74.12
90	0.628	0.940	0.957	0.1279	1.42	58.92
90	0.633	0.942	0.957	0.1243	1.37	59.52

[a] Ternary. [b] DMF-free basis. [c] Pressure inadvertently not recorded for this point.

The experimental procedures, equipment, and analytical methods used have been discussed in an earlier paper (*1*). High-purity Aldrich gold-label DMF was used and required no further purification, but as it is very hygroscopic it was not contacted with air. The water used was filtered, distilled, and deionized, and gave vapor pressures that agreed to within ±0.05 kPa with literature values (*3*). Punctilious ethanol from National Distillers required no further purification. The gas chromatograph was calibrated for ternary mixtures by using previously described techniques (*1*), and measured phase compositions are accurate and reproducible to within ±0.003 mole fraction. To ensure approximately constant mole fractions of DMF in the liquid phase, all experimental data were measured from separate gravimetrically prepared solutions. Thus, the still

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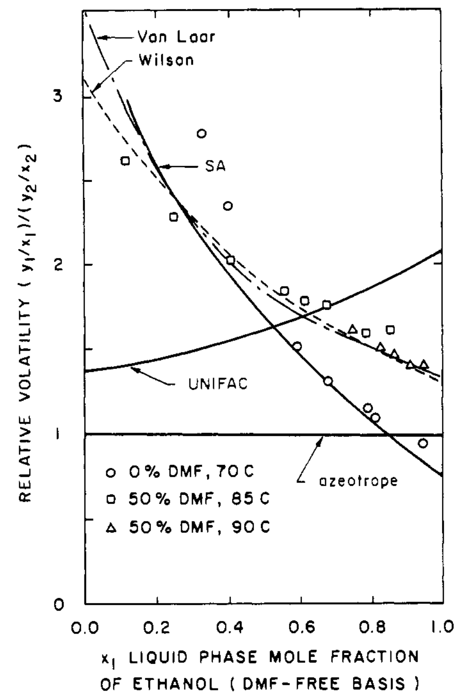

Figure 1. The relative volatility of ethanol (1) to water (2) vs. liquid-phase mole fraction of ethanol on a DMF-free basis. Also shown are the correlations of UNIFAC, SA, Wilson, and van Laar models.

was emptied and refilled with a new charge for each data point.

Results and Discussion

The experimental results are given in Table I and are graphically presented in Figure 1. Because of the dilution of the ethanol and water by the DMF, and the small errors in composition measurement, we estimate the calculated ethanol to water relative volatilities to have an uncertainty of ±0.04 at DMF liquid-phase mole fractions of approximately 0.3, increasing to an uncertainty of ±0.12 at DMF mole fractions of 0.7. Therefore, for a fixed ethanol-to-water ratio, there is no discernible dependence of the relative volatility on DMF concentrations for the DMF concentration range considered. Figure 1 shows that, for a solution containing approximately 50 mol % DMF, the minimum value of relative volatility is approximately 1.3 and, therefore, the ethanol/water azeotrope is broken. Further, the ethanol/water relative volatility is sufficiently high that an easy distillative separation to produce anhydrous ethanol can be accomplished (*4*). Note that for solutions with less than a 9/1 ratio of ethanol to water the enhancement of relative volatility is sensitive to the amount of DMF in the liquid phase. However, the enhancement of relative volatility for solutions with ethanol-to-water ratios of greater than 9/1 was found to be relatively insensitive to the amount of DMF for the concentrations we studied. The addition of DMF decreases slightly the relative volatility of ethanol with respect to water for water-rich solutions; however, the relative volatility is considerably greater than unity even in this region.

The UNIFAC model (*5*) and reported parameters (*6*) were used to predict the behavior of the ethanol/water/DMF system. This model fits the available data for the ethanol/water (*7*) and ethanol/diethylformamide (*8*) systems well but does not describe either the published water/DMF (*9*) or our ternary data satisfactorily. Since both water and DMF are considered single groups in UNIFAC, and since UNIFAC reduces to the UNIQUAC model in this case (*10*), the reported UNIQUAC parameters were used for the water/DMF UNIFAC interaction parameters in this calculation. All parameters used are given in Tables II and III. The resulting predictions, shown in Figure 1 for 50 mol % DMF, are satisfactory at ethanol-rich concentrations but poor in water-rich solutions.

Table II. Group Parameters Used in UNIFAC To Predict H_2O/EtOH/DMF Vapor-Liquid Equilibrium

group name	R	Q
CH_3	0.9011	0.848
CH_2	0.6744	0.54
OH	1.0	1.2
H_2O	0.92	1.4
DMF	3.0856	2.736

Table III. UNIFAC Interaction Parameters A_{mn} (K) Used in the Calculations

group	CH_3	CH_2	OH	H_2O	DMF
CH_3	0	0	986.5	1318	485.3
CH_2	0	0	986.5	1318	485.3
OH	156.4	156.4	0	353.5	−143.9
H_2O	300	300	−229.1	0	319.0
DMF	−31.95	−31.95	64.16	−287.1	0

Table IV. Solute Aggregation Model Binary Mixture Parameters[a]

$B = 40$		
water (1)/ethanol (2)	$A = 0.70$	$C = 1.15$
water (1)/DMF (3)	$A = 0.90$	$C = 0.40$
ethanol (2)/DMF (3)	$\Lambda_{23} = -0.48$	$\Lambda_{32} = -0.70$

[a] The water-ethanol and water-DMF parameters were obtained from the correlation of binary vapor-liquid equilibrium data, while the ethanol-DMF parameters were obtained from the predictions of the UNIFAC model.

Recently a new thermodynamic model for aqueous solutions has been proposed (*11*) based on the idea that the solute molecules in such a solution form clusters or aggregates at low concentrations. Much data supporting this hypothesis of the formulation of micellar-like solutions at low solute concentrations are given in ref *11*. The binary form of the resulting model is

$$\frac{G^{EX}}{RTx_1x_2} = C + (A - 1)x_1(1 - \exp[-Bx_2]) \ln x_2 \qquad (1)$$

where A, B, and C are adjustable parameters and subscript 2 denotes the solute. This model, with B equal to a constant ($B = 40$), has been found (*11*) to accurately correlate both the vapor-liquid and liquid-liquid equilibria of aqueous/organic solutions with a single set of parameters. We have used this model to predict the ethanol/water/DMF behavior by fitting the adjustable parameters to data for the water/ethanol and water/DMF binary systems. As no data are available for the ethanol/DMF binary mixtures, the SA model parameters were fit to the UNIFAC predictions for this systems. The correlation shown in Figure 1 was obtained by using the parameters in Table IV and the multicomponent form of the solute aggregation (SA) model appropriate to aqueous-nonaqueous (a-n) and nonaqueous-nonaqueous (n-n) interactions

$$\frac{G^{EX}}{RT} = \left(\frac{G^{EX}}{RT}\right)_{a-n} + \left(\frac{G^{EX}}{RT}\right)_{n-n} \qquad (2)$$

where

$$\left(\frac{G^{EX}}{RT}\right)_{a-n} = x_1^2(1 - x_1)\left[\frac{\sum_{i=2}^{m} A_{ij}x_i}{\sum_{i=2}^{m} x_i} - 1\right] \times$$
$$[1 - \exp(-B(-x_1))] \ln (1 - x_1) + \sum_{i=2}^{m} C_i x_1 x_i$$

$$\left(\frac{G^{EX}}{RT}\right)_{n-n} = \sum_{\substack{i\neq j\\ i\neq 1}} \sum x_i x_j (\Lambda_{ij}x_i + \Lambda_{ji}x_j) \qquad (3)$$

Table V. Parameters in the van Laar Model

	ethanol	water	DMF
ethanol	0	1.6648	-0.2224
water	0.9401	0	0.1042
DMF	-0.2531	0.3646	0

In this equation x_1 is the mole fraction of water, and $B = 40$. The expressions for the activity coefficients for the binary and ternary forms of this model are given in the Appendix. As can be seen in the figure, the SA model correctly predicts the decreasing trend of the ethanol/water relative volatility with increasing ethanol concentration but does not correctly predict the breaking of the azeotrope.

Finally, instead of predictions based only on binary data as above, we have also correlated out data with the ternary van Laar equation which can be written as

$$\ln \gamma_i = A/B^2 \tag{4}$$

where

$$A = x_i + x_j(A_{ji}/A_{ij}) + x_k(A_{ki}/A_{ik})$$

$$B = x_j^{\,2}A_{ij}(A_{ji}/A_{ij})^2 + x_k^{\,2}A_{ik}(A_{ki}/A_{ik})^2 + x_jx_k\frac{A_{ji}A_{ki}}{A_{ij}A_{ik}}\left(A_{ij} + A_{ik} - \frac{A_{jk}A_{ij}}{A_{ji}}\right) \tag{5}$$

The ethanol–water and DMF–water parameters were obtained from the correlation of binary data, while the ethanol–DMF parameters were gotten by correlating our ternary data treating them as the only adjustable parameters. The parameters so obtained are given in Table V. The results of this correlation, as shown in Figure 1, are in best agreement with our data. This is not surprising since ternary data were used in obtaining the parameters. Using the same procedure, a correlation of the ternary data of similar quality was also obtained by using the ternary form of the Wilson equation, and this also is shown in the figure.

Industrial Application

An old method for the industrial dehydration of ethanol is azeotropic distillation using benzene (*12*). The disadvantages of this process are that the added solvent must be vaporized, and benzene is a recognized carcinogen. Extractive distillation using ethylene glycol (*13*) has recently gained attention because the solvent is not vaporized and is safer to use. The disadvantage of ethylene glycol is that it has a high normal boiling point (197 °C). Therefore, the column that separates ethylene glycol from water must operate at subatmospheric pressures to avoid high operating temperatures. A solvent that can be used as an extractive distillation agent and boils at a lower temperature but still breaks the water/ethanol azeotrope may, therefore, be an economical alternative to ethylene glycol.

DMF (bp = 153 °C) breaks the ethanol/water azeotrope when used as an extractive distillation agent, and as it boils at a lower temperature than ethylene glycol at equivalent operating pressures, DMF requires lower operating temperatures. An important consideration in the comparison between DMF and ethylene glycol is the effect each solvent has on the relative volatility of ethanol/water. Unfortunately, no published experimental data for the ethanol/water/ethylene glycol system are readily available, so we could not make this comparison. However, our data show that a relatively easy distillative separation of ethanol and water is obtained when DMF is used.

DMF is known to hydrolyze, and this could negate its advantage as an extractive distillation solvent. To examine this, we boiled 50 mol % aqueous solutions of DMF for 5 h at 100 °C and observed no sign of a change in boiling temperature at constant pressure or extra peaks in the chromatographic analysis. Thus, we conclude that there was no sign of short-term degradation. Finally, as mentioned above, DMF decreases the relative volatility of water-rich solutions. This effect should be unimportant industrially because the feed into the extractive distillation tower is ethanol-rich, and the ethanol-to-water relative volatility is greater than 1.3 over the whole column.

Conclusions

Our data show that DMF breaks the ethanol/water azeotrope resulting in a minimum relative volatility of 1.3 when the liquid-phase mole fraction of DMF is at least 0.40. DMF may be a more economical extractive distillation agent than ethylene glycol because it is more volatile and therefore requires a lower operating temperature. Further, hydrolysis of aqueous DMF solutions was not observed over a 5-h period at 100 °C. Finally, the recently proposed solute aggregation model was found to predict the behavior of ethanol/water/DMF ternary mixture well in water-rich solutions, while the UNIFAC model did not. Neither model, however, was successful in predicting accurate low-pressure vapor-liquid equilibrium over the whole composition range.

Acknowledgment

The advice during the course of this work from Professor H. Knapp and his co-workers at the Technical University of Berlin (West) is gratefully acknowledged, as is the assistance with some of the calculations provided by Mr. Roukang Li.

Appendix

Activity Coefficient Expressions for the Solute Aggregation Model. For binary solutions, combination of eq 1 with

$$RT \ln \lambda_i = G_i^{\mathrm{E}} = \left.\frac{\partial(nG^{E/RT})}{\partial n_i}\right|_{T,P,n_j} = G^{\mathrm{EX}} - \sum_{k\neq i} x_k\left(\frac{\partial G^{\mathrm{EX}}}{\partial x_k}\right)_{T,P,x_{1\neq i,k}} \tag{A1}$$

yields

$$\ln \gamma_1 = 2S\,\frac{(1-x_1)}{x_1} - W(1-x_1) + C(1-x_1)^2$$

$$\ln \gamma_2 = S\,\frac{(2x_1-1)}{(1-x_1)} + Wx_1 + Cx_1^{\,2}$$

where

$$S = x_1^{\,2}(1-x_1)(A-1)(1-Z)\ln(1-x_1)$$

$$W = x_1^{\,2}(1-x_1)(A-1)\left[\frac{(1-Z)}{(1-x_1)} + BZ\ln(1-x_1)\right]$$

$$Z = \exp[-B(1-x_1)] \tag{A2}$$

Here x_1 is the mole fraction of water. The combination of eq A1 and 2 yield, for a mixture containing M components

$$\ln \gamma_1 = 2S\,\frac{(1-x_1)}{x_1} - (1-x_1)W + \sum_{i=2}^{m} x_i\sum_{j=2}^{m} C_ix_j - 2\sum_{j=3}^{m}\sum_{i=2}^{j-1}(x_i^{\,2}x_j\Lambda_{ij} + x_j^{\,2}x_i\Lambda_{ji}) \tag{A3}$$

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$$\ln \gamma_n = S\frac{(2x_1 - 1)}{1 - x_1} + x_1W - \frac{x_1^2}{1 - x_1}(1 - Z)\ln(1 - x_1)\sum_{i \neq 1,n}^{m} x_i(A_i - A_n) + x_1C_n - x_1\sum_{i=2}^{m} x_iC_i + \sum_{j=2}^{m}[2\Lambda_{nj}x_nx_j(1 - x_n) + x_j^2\Lambda_{jn}(1 - 2x_n)]_{(j\neq n)} - 2\sum_{j=3}^{m}\sum_{i=2}^{m}(x_i^2x_j\Lambda_{ij} + x_j^2x_i\Lambda_{ji})_{i,j\neq n} \tag{A4}$$

where S, W, and Z are defined above and

$$A = \sum_{i=2}^{m}\frac{A_ix_i}{\sum_{2}^{m}x_i}$$

Registry No. DMF, 68-12-2; ethanol, 64-17-5.

Literature Cited

(1) Shealy, G. S.; Bauer, J. T.; Sandler, S. I.; Kassman, K. D.; Hauschild, T.; Knapp, H. *J. Chem. Eng. Data* **1985**, *31*, 457.
(2) Shealy, G. S.; Sandler, S. I. *J. Chem. Eng. Data* **1985**, *30*, 455.
(3) Riddick, J. A.; Bunger, W. A. *Organic Solvents*; Wiley-Interscience: New York, 1970.
(4) Shealy, G. S.; Sandler, S. I. U.S. Patent Application, Serial No. 06/829,252. Filed February 14, 1986.
(5) Fredenslund, A.; Jones, R. L.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 1086.
(6) Gmehling, J.; Rasmussen, P.; Fredenslund, A. *Ind. Eng. Chem. Process Des. Dev.* **1982**, *21*, 118.
(7) Gmehling, J.; Onken, U. *Vapor-Liquid Equilibrium Data Collection*; DECHEMA: Frankfurt, 1977; Vol. I, Part 1, p 172.
(8) Gmehling, J.; Onken, U.; Arlt, W. *Vapor-Liquid Equilibrium Data Collection*; DECHEMA; Frankfurt, 1982; Vol. I, Part 2C, p 372.
(9) Page 275 of ref *7*.
(10) Magloe, B. M.Sc. Thesis, Instituttet for Kemiteknik, The Technical University of Denmark, Lyngby, Denmark, 1979.
(11) Shealy, G. S. Ph.D. Thesis, University of Delaware, December 1985.
(12) Shreve, R. N. *Chemical Process Industries*, 2nd ed.; McGraw-Hill: New York, 1956; p 678.
(13) Brandt, H. W.; Steude, H.; Bruns, L.; Koehler, H. D. Ger. Offen. DE 3 038 497, 1982.

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Equilibrium Phase Compositions, Phase Densities, and Interfacial Tensions for CO_2 + Hydrocarbon Systems. 3. CO_2 + Cyclohexane. 4. CO_2 + Benzene

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Experimental vapor–liquid equilibrium phase compositions, phase densities, and interfacial tensions are presented for CO_2 + cyclohexane and for CO_2 + benzene at 160 °F at pressures from 1000 psia to the critical point (interfacial tensions as low as 0.009 mN/m). These data for CO_2 with a naphthenic and an aromatic hydrocarbon complement our earlier work on binary mixtures of CO_2 with the paraffins *n*-butane and *n*-decane.

Introduction

The work presented here on CO_2 + cyclohexane and CO_2 + benzene is the third in a planned series of studies on CO_2 + hydrocarbon systems which will include measurements on CO_2 with other pure and mixed hydrocarbons and with reservoir oils. The previous two parts of this series presented data on CO_2 + *n*-butane (*1*) and CO_2 + *n*-decane (*2*). These new data on interfacial tensions (IFT) in CO_2 + hydrocarbon systems provide additional information on the effects of temperature, pressure, and composition on the IFT in such systems, which could lead to improved understanding of the process of miscible (or near-miscible, low-IFT) displacement of reservoir oils by CO_2 injection.

Experimental Method

The apparatus and procedures used in the present measurements have been described in detail previously (*1*, *2*). The only change in procedures from those used in the study of CO_2 + *n*-decane involved the chromatographic analysis of compositions, where 10 ft of 0V101 at 170 °C was used to separate CO_2 from cyclohexane or benzene. Response factors of 0.553 and 0.609 were used in the analyses of the cyclohexane and benzene systems, respectively, based on volumetrically prepared calibration mixtures.

Table I. Pure Component Equilibrium Phase Properties at 160 °F

vapor pressure, psia	phase densities, (kg/m³) × 10⁻³ liquid	vapor	ref
	Cyclohexane		
11.0	0.7282	0.0038	this work
10.9	0.7294		*3*, *4*
	Benzene		
11.0	0.8225	0.0042	this work
11.0	0.8237	0.0021	*3*, *4*

Materials

The CO_2 was supplied by Union Carbide Linde Division and had a stated purity of 99.99%. The cyclohexane and benzene were from Phillips Petroleum Co. (Research Grade) with purities of 99.9%. The chemicals were used without further purification.

Experimental Results

The complete data appear in Tables I–III. As part of the measurements, phase compositions and densities of pure cyclohexane and benzene were measured. They are compared in Table I with values interpolated from the literature (*3*, *4*).

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