Measurement of the Liquid−Liquid Equilibria for Mixtures of Water + Sodium Hydroxide + an Alkanol or Dimethyl Ether Using Near-Infrared Spectroscopy

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Here we use near-infrared spectroscopy and chemometric methods of analysis for the measurement of ternary liquid−liquid equilibria. We report data for mixtures of water + sodium hydroxide + an alkanol at 298.15 K and mixtures of water + sodium hydroxide + dimethyl ether at 343.15 K. The alkanols studied were 1-butanol, 2-butanol, 1-pentanol, 2-pentanol, and 2-methyl-1-propanol. The advantage of the method is that all analyses are done in situ, without the need for sampling.

Introduction

The distribution of the components of a mixture between two or more phases is important in the design of separation processes.[1] Central to liquid−liquid extraction processes is the distribution of the components between two liquid phases at equilibrium, so that a knowledge of the liquid−liquid equilibrium is crucial.[2]

The determination of the compositions of the conjugate phases in liquid−liquid equilibria can be accomplished using the direct analytical method or the titration method.[2,3] In the direct analytical method,[3] mixtures whose overall compositions lie in the two-phase region are prepared and samples of both phases are taken after equilibrium is achieved for composition analysis, usually by gas−liquid chromatography. The titration method[4] is based on the determination of the cloud point by the addition of the third component to a known composition of the other two components in the ternary mixture, until the appearance or disappearance of turbidity is observed.

The above techniques are not suitable for the measurement of liquid−liquid equilibria when the components of the mixture are volatile or difficult to handle. The analysis of such systems has required sophisticated sampling equipment and analytical techniques. A better approach to analyze such systems is to determine the composition of the conjugate phases in situ. In situ approaches for the measurement of the phase equilibria have been reported previously. Typically these include the use of spectroscopy; a review of the use of spectroscopy for the determination of binary and ternary liquid−liquid equilibria has been given by Schneider et al.[5]

In this work we introduce a new in situ method for the measurement of ternary liquid−liquid equilibria based on near-infrared spectroscopy (NIR). Here we demonstrate this method first by considering mixtures of water, sodium hydroxide, and dimethyl ether (DME) at 343.15 K. This is a challenging system to study for several reasons. First, because of the volatility of DME (vapor pressure at T = 386.15 K is 1.8 MPa), samples would partially vaporize if reduced to atmospheric pressure. Also, since the liquid−liquid equilibrium shifts with temperature, cooling the samples obtained from the equilibrium phases would result in an additional liquid−liquid-phase separation. Finally, samples could not be analyzed, for example, by gas chromatography because of the presence of sodium hydroxide. In situ NIR analysis resolved all the difficulties. As a further demonstration of the method, we have also measured the liquid−liquid equilibria for the simpler mixtures of water + sodium hydroxide + an alkanol at 298.15 K where an alkanol is 1-butanol, 2-butanol, 1-pentanol, 2-pentanol, or 1-methyl-2-propanol.

In this work sophisticated chemometric methods[6,7] of analysis are used to relate the concentration of the mixtures to the near-infrared spectra. It should be noted that previous work using NIR to determine phase equilibrium has been carried out.[8] That work, however, made use of both NIR and infrared spectroscopy and did not apply chemometric methods to resolve the spectral complexities and overlapping peaks which were encountered in the measurements here.

Experimental Section

Chemicals. Dimethyl ether was supplied by Sigma-Aldrich with a purity greater than 99.5% by mass. Sodium hydroxide was supplied by Fisher with a purity of 98.7%. Distilled, deionized water was used in this work. The alkanols were supplied by Sigma-Aldrich, with purities better than 99.0% by mass. The alkanols were analyzed using a Karl Fischer method and found to have water contents of less than 0.1% by mass.

Apparatus. Two different equilibrium cells were used to make the measurements. Solutions of known composition were prepared gravimetrically. For the system containing DME, a 50 cm^3 316 stainless steel vessel was used as the equilibration cell. A fitting to accept a probe was

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Table 1. Compositions of the Conjugate Phases for the Mixtures {H_2O (1) + NaOH (2) + CH_3OCH_3 (3)} at T = 343.15 K[a]

feed composition		water-rich phase		dimethyl ether-rich phase	
$100w_1$	$100w_2$	$100w_1'$	$100w_2'$	$100w_1''$	$100w_2''$
H_2O (1) + NaOH (2) + CH_3OCH_3 (3)					
59.1	0.0	70.6	0.0	13.2	0.0
66.2	1.8	78.1	2.2	7.3	<0.1
71.7	2.5	81.8	2.9	7.3	<0.1
73.9	7.4	83.4	8.4	7.1	<0.1
67.7	9.4	82.0	13.1	5.0	<0.1
58.9	21.5	73.0	27.0	2.5	<0.1
42.0	37.7	52.6	47.4	1.2	<0.1

[a] All data are in mass percent, 100*w*.

Table 2. Compositions of the Conjugate Phases for the Mixtures {H_2O (1) + NaOH (2) + [$CH_3(CH_2)_3OH$ or $CH_3CH(OH)CH_2CH_3$ or $CH_3(CH_2)_4OH$ or $CH_3CH(OH)CH_2CH_2CH_3$ or $(CH_3)_2CH(OH)CH_3$] (3)} at T = 298.15 K[a]

feed composition		water-rich phase		alkanol-rich phase	
$100w_1$	$100w_2$	$100w_1'$	$100w_2'$	$100w_1''$	$100w_2''$
H_2O (1) + NaOH (2) + $CH_3(CH_2)_3OH$ (3)					
80.4	0.0	92.5	0.0	18.8	0.0
80.0	0.5	92.2	0.7	15.5	<0.1
78.8	0.7	92.5	1.0	14.2	<0.1
53.4	4.3	89.3	8.0	10.6	<0.1
79.8	5.1	90.3	6.4	11.0	<0.1
57.3	8.0	85.6	13.2	8.1	<0.1
77.7	8.1	88.0	10.2	9.7	<0.1
60.5	11.5	82.4	16.8	5.9	<0.1
52.3	14.2	77.3	22.4	6.3	0.3
52.1	16.3	75.3	24.6	5.8	0.7
63.4	21.1	74.4	25.6	5.3	0.9
H_2O (1) + NaOH (2) + $CH_3CH(OH)CH_2CH_3$ (3)					
72.0	0.0	87.5	0.0	44.1	0.0
51.8	0.6	83.3	1.2	18.1	<0.1
59.3	2.9	85.9	4.9	14.4	<0.1
52.9	6.7	85.9	12.4	12.8	<0.1
42.3	8.4	81.2	18.3	11.5	0.1
61.1	8.8	84.8	14.0	11.5	<0.1
34.3	9.3	77.8	22.1	5.4	0.4
46.3	10.6	79.7	20.0	9.2	0.2
33.6	11.4	74.1	25.8	4.4	0.7
H_2O (1) + NaOH (2) + $CH_3(CH_2)_4OH$ (3)					
62.4	0.0	98.0	0.0	7.5	0.0
69.2	0.4	97.6	0.6	7.7	<0.1
70.4	1.5	96.4	2.2	9.6	<0.1
62.1	2.0	95.6	3.3	8.3	<0.1
40.9	4.4	89.0	10.4	6.9	<0.1
45.6	4.4	90.0	9.1	5.2	<0.1
38.8	5.2	87.3	12.3	4.6	0.1
45.9	9.3	82.4	17.3	6.4	0.6
61.8	10.0	85.2	14.3	4.0	0.2
40.1	10.7	78.2	21.8	5.9	0.7
H_2O (1) + NaOH (2) + $CH_3CH(OH)CH_2CH_2CH_3$ (3)					
53.6	1.1	95.2	1.1	12.2	1.1
55.4	2.0	94.2	2.7	12.6	1.2
45.6	2.4	93.8	4.2	13.2	1.3
46.7	3.2	92.7	5.8	14.0	1.6
46.9	6.1	88.1	11.2	12.2	1.9
40.4	8.5	82.5	17.3	9.3	2.1
62.7	9.4	86.7	12.9	10.9	1.8
56.8	9.9	84.9	14.8	9.2	1.6
38.3	10.1	79.2	20.7	9.5	2.5
42.5	14.4	74.7	25.3	8.6	3.1
H_2O (1) + NaOH (2) + $(CH_3)_2CH(OH)CH_3$ (3)					
42.6	0.0	89.9	0.0	15.5	0.0
61.1	0.2	91.1	0.3	13.8	<0.1
64.3	0.7	91.2	1.1	13.4	<0.1
64.2	1.7	91.0	2.7	12.4	<0.1
71.0	2.8	90.7	4.1	12.9	<0.1
59.7	5.6	88.6	9.2	9.3	0.0
56.1	6.3	87.4	10.8	8.5	0.0
39.0	6.5	84.1	15.1	7.4	0.1
51.2	7.1	85.9	12.9	7.8	0.1
49.8	10.5	81.5	18.1	6.3	0.3
43.0	11.8	77.7	22.2	7.7	1.3

[a] All data are in mass percent, 100*w*.

welded near the bottom of the cell. The empty vessel was weighed, and then known masses of water or aqueous sodium hydroxide were added to the vessel. The mixing vessel was cooled with liquid nitrogen, and dimethyl ether was added to the cold vessel. The mixing vessel was then allowed to reach room temperature, the external surface was dried, and the vessel was reweighed to give the total mass of the contents. As a result of this procedure, the amounts (and concentrations) of water, sodium hydroxide, and the organic compound were known. The uncertainty in the concentration of these standard solutions was better than 0.1 mass %.

The mixing vessel was again cooled with liquid nitrogen, and a fiber optic probe was inserted into the vessel. The vessel and the probe were put into an air bath controlled to within ±0.3 K of the set temperature. The temperature was measured with a Hewlett-Packard platinum resistance thermometer. After equilibration, the spectrum of the dense phase was recorded. The cell was then inverted (so now the probe was near the top of the cell), the phases were allowed to disengage, and the spectrum of the less dense phase was recorded.

For the alcohol systems, a glass Erlenmeyer flask with a stopper was used as the sample vessel. The NIR probe could be inserted through the stopper into each of the phases. The stopper not only held the probe in the correct position but it also prevented the loss of material due to evaporation.

The spectra were recorded using a Guided Wave Insite III fiber optic near-infrared spectrometer with a fiber optic probe, model EQDP-1/4 PL2-F supplied by CIC Photonics. The probe, which has an optical path length of 2 mm, made of stainless steel and sealed with Kalrez O-rings, was connected to the spectrometer with a low-hydroxide quartz fiber optic cable with a fiber diameter of 400 μm and standard SMA connections. All optical material in the probe was made of low-hydroxide quartz. The range of the instrument was from 800 to 1700 nm.

Method. The first and most tedious step in the determination of the ternary liquid−liquid equilibrium using near-infrared spectroscopy involves a calibration relating the NIR spectra to the concentration using the advanced chemometric method of analysis mentioned below. The second step entails the preparation of mixtures with concentrations in the two-phase region and the recording of the spectra of both phases. These spectra were then used to compute the concentrations of both liquid phases using the calibration information.

The calibration was carried out as follows. Single-phase mixtures of known concentrations were prepared gravimetrically. These mixtures were placed in a water bath that was controlled at 298.15 K to within 0.3 K with a Tronac temperature controller used in conjunction with a Systemteknik AB S 1220 platinum resistance thermometer. Five replicate spectra of each mixture were recorded, and these were averaged to give one spectrum that was used in the calibration. Generally, ternary mixtures were used in the calibration; however, spectra for some binary mixtures and for the pure alkanols and pure water were also used in the calibration.

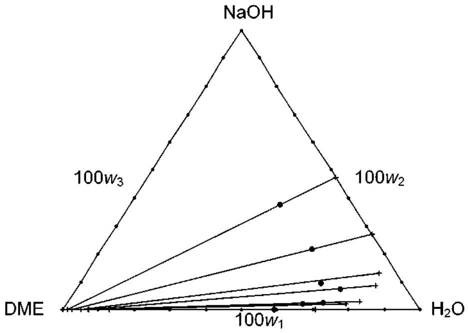

Figure 1. Phase diagram for the mixtures {H_2O (1) + NaOH (2) + CH_3OCH_3 (3)} at T = 343.15 K. Filled dots represent the feed compositions.

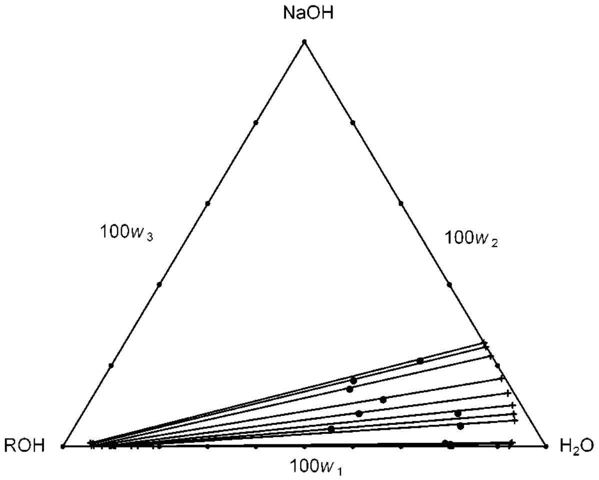

Figure 2. Phase diagram for the mixtures {H_2O (1) + NaOH (2) + $CH_3(CH_2)_3OH$ (3)} at T = 298.15 K. Filled dots represent the feed compositions.

The near-infrared spectra of these mixtures were complex, and it was not possible to assign separate peaks to each component. Consequently, the spectra and gravimetrically prepared concentration data were used in a chemometric analysis with the commercially available GRAMS/32 software, version 5.22, with the PLSplus/IQ add-in. (See www.galactic.com for a demonstration version of GRAMS/32 and www.camo.com for an alternate version of the chemometric software. Both contain a detailed description of the PLS method.) The spectra were related to the concentrations of the components of the mixture using a partial least squares (PLS) method of analysis. A crossvalidation method was used to provide the most rigorous calibration, and a first-order differential was applied to the data to eliminate the effects of the change in the refractive index with concentration, especially for those solutions containing high concentrations of sodium hydroxide. The entire spectrum ranging from 800 nm to 1700 nm was used in the calibration. The standard error of the calibration was <0.3 mass %.

Results

The compositions of the phases at equilibrium for mixtures of water + sodium hydroxide + dimethyl ether are reported in Table 1, and those for mixtures of water + sodium hydroxide + an alkanol are reported in Table 2 and are shown in Figures 1−6. The compositions are reported in mass percent, 100w, with the symbol 100w_i' indicating the mass percent of constituent i in the water-rich phase and 100w_i'' indicating the mass percent of constituent i in the alkanol-rich or ether-rich phase.

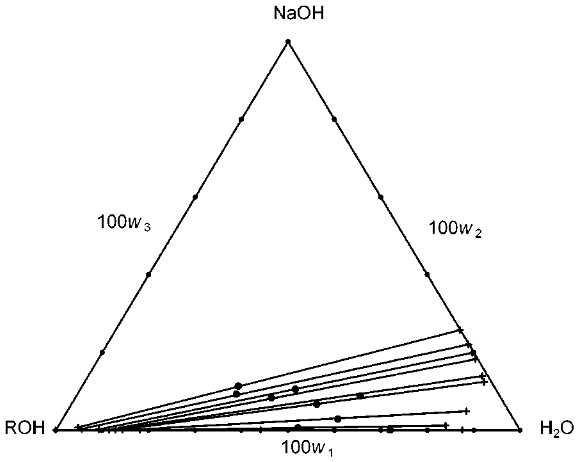

Figure 3. Phase diagram for the mixtures {H_2O (1) + NaOH (2) + $CH_3CH(OH)CH_2CH_3$ (3)} at T = 298.15 K. Filled dots represent the feed compositions.

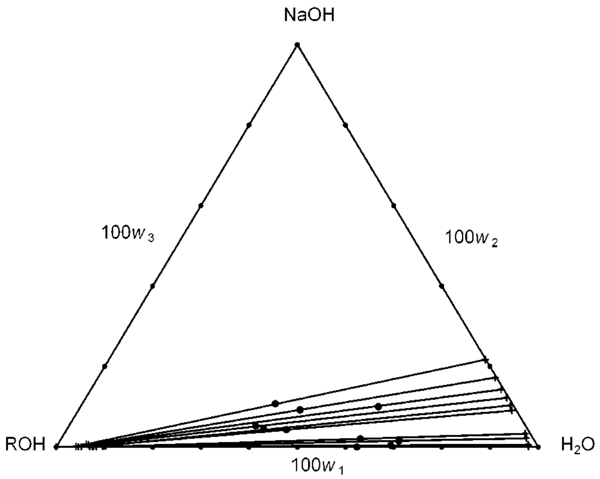

Figure 4. Phase diagram for the mixtures {H_2O (1) + NaOH (2) + $CH_3(CH_2)_4OH$ (3)} at T = 298.15 K. Filled dots represent the feed compositions.

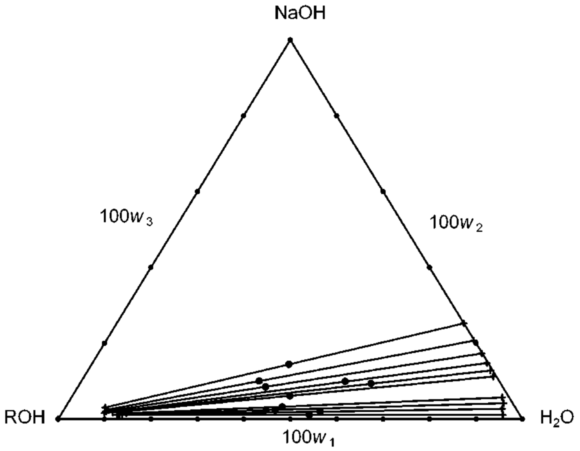

Figure 5. Phase diagram for the mixtures {H_2O (1) + NaOH (2) + $CH_3CH(OH)CH_2CH_2CH_3$ (3)} at T = 298.15 K. Filled dots represent the feed compositions.

Discussion

The liquid−liquid equilibrium results for all mixtures show that sodium hydroxide has a salting out effect. As the sodium hydroxide concentration is increased, there is a decrease in the mutual solubility of water and the organic compound.

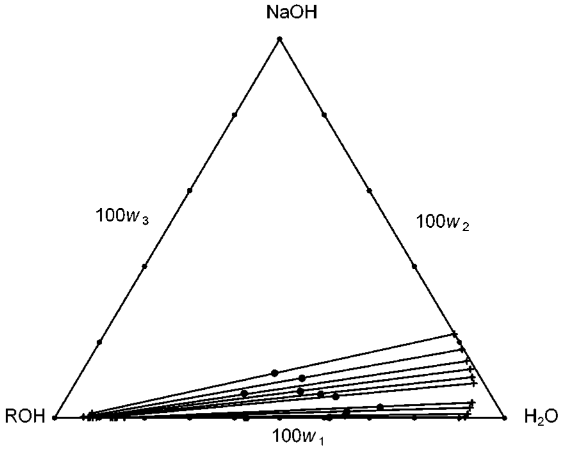

Figure 6. Phase diagram for the mixtures {H_2O (1) + NaOH (2) + $(CH_3)_2CH(OH)CH_3$ (3)} at T = 298.15 K. Filled dots represent the feed compositions.

Our results also show that the concentration of sodium hydroxide in the alkanol phase is very low. This is expected because of the limited solubility of sodium hydroxide in alkanols. The only published data for mixtures of the type investigated here are for the mixture {H_2O (1) + NaOH (2) + $CH_3(CH_2)_3OH$ (3)} at T = 298.15 K.[9] The results from this work and the published data agree to within than 0.5 mass %, which is within the combined errors of both work. The published data were determined using gas−liquid chromatography and the Karl Fischer titration method. While those methods are much more time-intensive than the one used here, the favorable comparison serves to validate the method used here. Also, the chromatographic/titration method could not be used because of the elevated temperature and pressure of the corrosive system studied here. This suggests that near-infrared spectroscopy is a suitable technique for use in the determination of liquid−liquid equilibria, especially for mixtures that contain volatile components or other difficult systems.

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Literature Cited

(1) Perry, R. H.; Green, D. W. *Perry's Chemical Engineers Handbook*, 7th ed.; McGraw-Hill: New York, 1997.
(2) Novak, J. P.; Matous, J.; Pick, J. *Liquid−Liquid Equilibria;* Elsevier: Amsterdam, Holland, 1987.
(3) Thornton, J. D. *Science and Practice of Liquid−Liquid Extraction, Vol. 1;* Clarendon-Press: Oxford, Great Britain, 1992.
(4) Briggs, S. W.; Comings, E. W. Tie Line Correlations and Plait Point Determinations. *Ind. Eng. Chem.* **1943**, *35*, 411−415.
(5) Schneider, G. M.; Ellert, J.; Haarhaus, U.; Hoelscher, I. F.; Katzenski-Ohling, G.; Kopner, A.; Kulka, J.; Nickel, D.; Ruebesamen, J.; Wilsch, A. Thermodynamic, Spectroscopic and Phase Equilibrium Investigations on Polar Fluid Mixtures at High Pressures. *Pure Appl. Chem.* **1987**, *59* (9), 1115−1126.
(6) Kramer, R. *Chemometric techniques for quantitative analysis;* Marcel Dekker: New York, 1998.
(7) Stewart, J. E. *Infrared spectroscopy; experimental methods and techniques;* Marcel Dekker: New York, 1970.
(8) Buback, M. Near Infrared Spectroscopy of Fluid Phases. *J. Mol. Struct.* **1995**, *347*, 113−129.
(9) Yui, N.; Kurokawa, Y.; Sakuraba, I. Equilibrium composition of 1-butanol-water-alkali hydroxide system and the distribution of the base. *Bull. Chem. Soc. Jpn.* **1973**, *46* (7), 1915−1918.

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