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Phase Equilibria of Water + Furfural and Dichloromethane + *n*-Hexane

M. Shyam Sunder and D. H. L. Prasad*

Chemical Engineering Laboratory, Indian Institute of Chemical Technology, Hyderabad 500 007, India

Bubble temperature measurements over the whole composition range have been carried out for the binary mixtures of water(1) + furfural(2) and dichloroethane(1) + *n*-hexane(2) at 94.6 kPa. The measurements on the first system are well represented by the NRTL model, and the measurements on the second system are well represented by both the Wilson and NRTL models.

Introduction

A steam distillation technique is often used in the manufacture of furfural from rice husk. Furfural produced by this process is likely to contain moisture at levels unacceptable for the requirements of the pharmaceutical industry. Phase equilibrium data for the water(1) + furfural(2) system will be of help in the design of distillation equipment for the purification of furfural. Methanol and *n*-hexane are among the solvents in common use for the extraction of medicinal or pesticidal chemicals such as azadiractin from neem oil. Economic as well as other technical factors may point to the use of mixed solvents. Phase equilibrium data on the methanol(1) + *n*-hexane(2) system will be useful in optimizing separation processes to obtain active components from natural products. It has therefore been decided to determine the phase equilibria of these two systems isobarically at the local pressure of 94.6 kPa, by an ebulliometric method to measure the bubble point temperatures of gravimetrically prepared mixtures. Among studies on the phase equilibria of the water(1) + furfural(2) mixtures are isobaric measurements at 101.3 kPa by Mains,[1,2] at 101.3 to 1823.4 kPa by Milnikov and Tsirlin[3], at 605.3−964.3 kPa by Curtiss and Hatt,[4] at 40 kPa by Andreev and Tsrlin,[5] and at 310.93 to 366.48 by Pearce and Gerster.[6] Lecat[7] reported the formation of an azetrope at 371 K for 101.3 kPa pressure. Comparisons of the present work with literature data have been summarized.

Experimental Section

Apparatus. A Swietoslawski-type ebulliometer, very similar to the one described by Hala et al.[8] was used for this investigation. The ebulliometer is connected to a vacuum pump and a dry nitrogen gas cylinder with a closed-end manometer in line. This enabled the measurement and maintenance of the pressure in the ebullimeter, within ±0.1 kPa of the chosen value of 94.6, by adjusting the opening of the needle valve attached to the gas cylinder or the opening of the bypass line of the vacuum pump. The total pressure of the system was maintained at the desired value by frequently reading the manometer and carrying out the required corrective adjustment of the valve attached to the gas cylinder or the vacuum pump. A platinum resistance thermometer, calibrated by means of point to point comparison with a standard platinum resistance thermometer (certified by the National Institute of Standards and Technology) was used in these experiments to measure the temperatures with an accuracy of ±0.1 K. The thermometer bulb was placed in a thermo-well (filled with mercury) located at a point in the apparatus where the gas liquid mixture was in close contact.

Materials. Laboratory Reagent grade dichloromethane and *n*-hexane (Ranbaxy Laboratories, SAS Nagar, Punjab,-India) were dried over anhydrous calcium chloride for 2 days and fractionally distilled twice. The middle fractions of the second distillations were stored in amber colored bottles for use in the experiments. Furfural (Delta Agro-Chemicals, Hanuman Junction,Vijayawada, India) was stored overnight over anhydrous sodium hydroxide and fractionally distilled twice. The middle fraction of the second distillation was stored in amber colored bottles for use in the experiments. Double distilled, demineralized water was used in these studies. The purification, particularly the second distillation of the organic substances used in this study, was carried out by means of a packed fractionation column, of length equal to 30 theoretical plates, only a few hours before the commencement of the phase equilibrium experiments. Sufficient care is taken to prevent absorption of moisture, oxidation, etc., during the intervening period. Based on a comparison of the density and refractive-index with the literature data of Riddick et al.[9] (presented in Table 1), the substances used in this study are believed to be at least 99.8% pure.

Method. The mixture samples to be studied were prepared gravimetrically by weighing the required amounts of the two components into a clean and dry conical flask and stirring them well before charging them to the apparatus. A Mettler balance, accurate to ±0.0001 g, was used to measure all of the required weights. The heating rate was adjusted to yield the desired drop rate of about 30 per minute, in accordance with the suggestion of Hala et al.[8] The test mixture was subjected to the probable highest temperature and lowest pressure and then returned to the ambient conditions several times before commencing the actual experiment to ensure a constant composition during the experiment. A gas chromatograph was used to verify the constancy of composition at the beginning and the end of each experiment. The equilibrium temperature was recorded after the steady-state conditions

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* To whom correspondence should be addressed. E-mail: dasika@iict.ap.nic.in.

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Table 1. Comparison of the Density (*D*) and Refractive Index (*n*) with the Literaturature Data of Riddick et al.[9] at 293.15 K

	D/(kg. m^{-3})		n	
substance	this work	literature	this work	literature
dichloromethane	1489.0	1489.11	1.4459	1.44590
furfural	659.3	659.33	1.3749	1.37480
n-hexane	1128.5	1128.50	1.4868	1.48680
water	998.2	998.21	1.3330	1.33299

Table 2. Vapor−Liquid Equilibria for Water(1) + Furfural(2) at 94.6 kPa

T/K	x_1	y_1 (NRTL)	γ_1(NRTL)	γ_2 (NRTL)
432.05	0.0000	0.0000	3.9286	1.0000
410.05	0.0625	0.6229	3.7111	1.0023
390.05	0.1193	0.7643	3.4923	1.0089
382.65	0.1688	0.8227	3.2971	1.0193
377.95	0.2132	0.8554	3.1198	1.0332
375.05	0.2529	0.8737	2.9603	1.0503
373.35	0.2889	0.8865	2.8155	1.0705
372.05	0.3218	0.8954	2.6838	1.0938
370.45	0.3787	0.9064	2.4590	1.1476
369.25	0.4375	0.9134	2.2338	1.2272
369.25	0.4790	0.9164	2.0811	1.3035
369.25	0.5250	0.9181	1.9196	1.4147
369.25	0.5632	0.9184	1.7927	1.5352
369.25	0.5958	0.9179	1.6903	1.6649
369.25	0.6970	0.9124	1.4106	2.3222
369.25	0.7870	0.9036	1.2162	3.5654
369.25	0.9149	0.9026	1.0393	8.9590
369.45	0.9767	0.9492	1.0032	16.7032
370.15	0.9880	0.9698	1.0009	18.9829
370.75	0.9950	0.9862	1.0002	20.5891
371.25	1.0000	1.0000	1.0000	21.8372

Table 3. Vapor−Liquid Equilibria of Dichloromethane(1) + *n*-Hexane(2) at 94.6 kPa

		y_1		γ_1		γ_2	
T/K	x_1	Wilson	NRTL	Wilson	NRTL	Wilson	NRTL
339.75	0.0000	0.0000	0.0000	2.9758	2.8950	1.0000	1.0000
326.75	0.0969	0.4047	0.4036	2.4306	2.4181	1.0123	1.0113
321.65	0.1848	0.5428	0.5445	2.0424	2.0512	1.0439	1.0416
316.85	0.3377	0.6571	0.6585	1.5863	1.5937	1.1415	1.1434
314.75	0.4660	0.7145	0.7140	1.3462	1.3459	1.2814	1.2842
312.85	0.6253	0.7751	0.7730	1.1581	1.1530	1.5390	1.5503
311.55	0.7912	0.8475	0.8464	1.0476	1.0439	1.9684	1.9778
311.05	0.9483	0.9506	0.9514	1.0030	1.0026	2.6412	2.5917
311.05	1.0000	1.0000	1.0000	1.0000	1.0000	2.9536	2.8539

Table 4. Antoine Constants in the Equation ln(*P*/kPa) = *A* − [{*B*/(*T*/K) + *C*}]

substance	A	B	C	ref
dichloromethane	14.2877	2622.44	−41.70	11
furfural	13.1391	2759.92	−110.21	12
n-hexane	13.8205	2697.55	−48.78	11
water	16.2884	3816.44	−46.13	11

Table 5. Representation of the Data by the Models

system	model	parameters	std. dev. in T/K
water(1) + furfural(2)	NRTL	$\Delta g_{12} = 1683.3$ K	
		$\Delta g_{21} = -463.5$ K	0.50
dichloromethane(1) + *n*-hexane(2)	NRTL	$\Delta g_{12} = 48.1$ K	
		$\Delta g_{21} = 313.9$ K	0.15
	WILSON	$(\lambda_{12} - \lambda_{11})/R = 270.4$ K	
		$(\lambda_{12} - \lambda_{22})/R = 137.8$ K	0.10

as judged by the constancy of temperature and maintenance of a uniform condensate drop rate for at least 30 min were achieved.

Results and Discussion

The experimental composition (x_1) versus temperature (T) measurements, summarized in Tables 2 and 3, are fitted to the Wilson model

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}\, x_2) + x_2[\{\Lambda_{12}/(x_1 + \Lambda_{12}\, x_2)\} - \{\Lambda_{21}/(x_2 + \Lambda_{21}\, x_1)\}] \quad (1)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}\, x_1) + x_1[\{\Lambda_{21}/(x_2 + \Lambda_{21}\, x_1)\} - \{\Lambda_{12}/(x_1 + \Lambda_{12}\, x_2)\}] \quad (2)$$

where

$$\Lambda_{12} = (V_2/V_1) \exp[-(\lambda_{12} - \lambda_{11})/RT] \quad (3)$$

and

$$\Lambda_{21} = (V_1/V_2) \exp[-(\lambda_{12} - \lambda_{22})/RT] \quad (4)$$

V_1 and V_2 are the molar volumes of the pure liquids, and the NRTL model is given by

$$\ln \gamma_1 = x_2^{\,2}[\tau_{21}\{G_{21}/(x_1 + x_2G_{21})\}^2 + \{\tau_{12}G_{12}/(x_2 + x_1G_{12})^2\}] \quad (5)$$

$$\ln \gamma_2 = x_1^{\,2}[\tau_{12}\{G_{12}/(x_2 + x_1G_{12})\}^2 + \{\tau_{21}G_{21}/(x_1 + x_2G_{21})^2\}] \quad (6)$$

where

$$\ln G_{12} = -\alpha_{12}\tau_{12} \quad (7)$$

$$\ln G_{21} = -\alpha_{12}\tau_{21} \quad (8)$$

$$\tau_{12} = \Delta g_{12}/RT \quad (9)$$

$$\tau_{21} = \Delta g_{21}/RT \quad (10)$$

and

$$\alpha_{12} = 0.12 \quad (11)$$

The energies of interaction between the different species of molecules are designated by λ's in the Wilson model, whereas they are designated by g's in the NRTL model. The optimum model parameters are computed by minimizing the objective function defined as

$$\Phi = \sum[(P_{\mathrm{cal}}/P_{\mathrm{expt}}) - 1]^2 \quad (12)$$

The Nelder−Mead optimization technique, described in detail by Kuester and Mize[10] was used. Vapor pressures required in the computations are calculated from the Antoine equation

$$\ln(P/\mathrm{kPa}) = A - B/[(T/\mathrm{K}) + C\,] \quad (13)$$

with the constants derived from evaluated literature data and given in Table 4, for ready reference. In these calculations, the vapor phase is assumed to be ideal. The calculated values of the vapor phase composition and the activity coefficients are also included in Tables 2 and 3. The model parameter and the nature of representation are summarized in Table 5. The NRTL parameters obtained for the water(1) + furfural(2) system are used to calculate the vapor phase mole fractions of the literature observations. Comparisons of the calculated mole fractions with the literature data are summarized in Table 6, which indicates satisfactory agreement at 101.3 kPa and disagreement at

Table 6. Comparison with Literature Vapor−Liquid Equilibrium Data on Water(1) + Furfural System

authors(s)	ref	condition	average abs. dev. in y_1
Mains	1,2	101.3 kPa	0.019
Melnikov & Tsirlin	3	101.3 kPa	0.037
Melnikov & Tsirlin	3	303.9 kPa	0.033
Melnikov & Tsirlin	3	582.5 kPa	0.027
Melnikov & Tsirlin	3	709.1 kPa	0.027
Melnikov & Tsirlin	3	911.7 kPa	0.027
Melnikov & Tsirlin	3	1418.2 kPa	0.022
Melnikov & Tsirlin	3	1823.4 kPa	0.020
Curtiss & Hatt	4	605.3 kPa	0.080
Curtiss & Hatt	4	765.2 kPa	0.095
Curtiss & Hatt	4	964.3 kPa	0.047
Andrev & Tsirlin	5	40.0 kPa	0.075
Pearce & Gerster	6	310.95 K	0.059
Pearce & Gerster	6	338.74 K	0.070
Pearce & Gerster	6	366.45 K	0.103

the other conditions. The data and their representation are expected to be useful for engineering design purposes.

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