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Bubble-Temperature Measurements on Some Binary Mixtures Formed by Tetrahydrofuran or Amyl Alcohol with Hydrocarbons, Chlorohydrocarbons, or Butanols at (94.6 or 95.8) kPa

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Bubble temperatures at 94.6 kPa for the binary mixtures formed by tetrahydrofuran with *n*-heptane, cyclohexane, methylethyl ketone, and amyl alcohol with 1,2-dichloroethane, 1,1,1-trichloroethane, and 1,1,2,2-tetrachloroethane, and 95.8 kPa for the binary mixtures formed by tetrahydrofuran with 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, trichloroethylene, tetrachloroethylene, and *n*-, iso-, *sec*-, and *tert*- butanols were measured over the entire composition range. A Swietoslawski-type ebulliometer is used for the experiments, and the Wilson model is found to represent the data well.

Introduction

The importance of vapor−liquid equilibrium data for the design of separation processes needs no fresh emphasis. This investigation on the bubble temperatures noted in the abstract is in continuation of our recent studies aiming at the phase equilibria of the binary mixtures formed by hydrocarbons, chlorohydrocarbons, and alcohols.[1−3] There is no published vapor−liquid equilibrium data on the systems chosen for the present study in the open literature.

Experimental Section

Apparatus and Method. A brief description of the apparatus and the method followed for the main measurement (bubble temperature) and the measurements carried out to ascertain the purity (density and refractive index) is provided below.

Bubble Temperature. A Swietoslawski-type ebulliometer, very similar to the one described in Hala et al.[4] and mentioned in some detail in our earlier publication,[3] was used for this set of experimental investigations. Connection of the ebulliometer to a good vacuum system and dry nitrogen gas cylinder, through an inline mercury manometer, facilitated the creation and the maintenance of the chosen pressure within ±0.1 kPa by reading the manometer frequently and carefully adjusting the opening of the needle valve attached to a nitrogen gas cylinder or the bypass line of the vacuum system, as needed. Equilibrium temperatures were measured to an accuracy of ± 0.1 K by means of a platinum-resistance thermometer, calibrated by means of point-to-point comparison with a Standard Platinum-Resistance Thermometer certified by the National Bureau of Standards (USA). The liquid mixtures for the studies are prepared gravimetrically by using an electronic balance precise to ±0.0001 g and stirred well before being placed in the ebulliometer. The liquid-phase mole fractions of the samples were calculated from the masses of the two pure liquids mixed and their respective molecular masses. The heating rate was adjusted to yield the desired condensate drop rate of 30 drops per minute, following the suggestion of Hala et al.[4] The equilibrium temperature was recorded after a steady drop rate and a constant temperature were maintained for at least 30 min. Each measurement was repeated several times, until at least two consecutive observations are within the estimated limits of the experimental uncertainties of ±0.1 K (temperature), 0.1 kPa (pressure) and 0.0005 (in liquid-phase mole fraction).

Table 1. Comparison of the Density (*D*) and Refractive Index (*n*) of the Pure Substances Used in This Study with Literature Data from Riddick et al.[5] at 298.15 K

	D/(kg.m^{-3})		n	
substance	this work	Riddick et al.[5]	this work	Riddick et al.[5]
tetrahydrofuran[a]	889.2	889.20	1.4072	1.40716
1,2-dichloroethane	1246.4	1246.37	1.4421	1.44210
1,1,1-trichloroethane	1329.9	1329.90	1.4359	1.43590
1,1,2,2-tetrachloroethane	1586.7	1586.66	1.4914	1.49140
trichloroethylene	1451.4[b]	1451.40[b]	1.4750	1.47500
tetrachloroethylene	1614.3	1614.32	1.5032	1.50320
n-butanol	805.8	805.75	1.3974	1.39741
isobutanol	798.0	797.80	1.3939	1.39389
sec-butanol	802.4	802.41	1.3953	1.39530
tert-butanol	781.2	781.20	1.3850	1.38520
amyl alcohol	811.0	810.80	1.4080	1.40800
n-heptane	679.5	679.46	1.3851	1.38511
cyclohexane	773.9	773.89	1.4235	1.42354
methylethyl ketone	799.7	799.70	1.3769	1.37685

[a] At 293.15 K. [b] At 303.15 K.

Density. A carefully calibrated pycnometer (of about 10 mL volume) filled with the test liquid is immersed in an

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Table 2. Bubble-Temperature Measurements at 94.6 kPa

x_1	T/K	x_1	T/K	x_1	T/K
Tetrahydrofuran (1) + *n*-Heptane (2)		Tetrahydrofuran (1) + Cyclohexane (2)		Tetrahydrofuran (1) + Methylethyl Ketone (2)	
0.0000	369.35	0.0000	351.75	0.0000	350.75
0.1411	362.05	0.2103	345.65	0.1810	347.05
0.3301	354.05	0.3990	341.85	0.3985	345.35
0.4508	349.95	0.6313	338.65	0.6120	342.75
0.6002	345.35	0.7998	337.45	0.8466	338.95
0.7831	340.95	1.0000	337.15	1.0000	337.15
0.9002	338.75				
1.0000	337.15				
1,2-Dichloroethane (1) + Amyl Alcohol (2)		1,1,1-Trichloroetane (1) + Amyl Alcohol (2)		Amyl Alcohol (1) + 1,1,2,2-Tetrachloroethane (2)	
0.0000	400.35	0.0000	400.35	0.0000	417.35
0.1626	384.35	0.1745	374.05	0.1052	412.35
0.2798	377.95	0.2971	364.85	0.2278	409.85
0.4372	371.25	0.4581	357.45	0.3199	405.15
0.6133	365.55	0.5376	354.95	0.4137	402.95
0.7041	362.85	0.6379	352.55	0.7967	397.65
0.8263	359.65	0.7854	349.65	0.8546	397.45
0.9049	357.65	0.8409	348.65	0.9216	397.45
1.0000	355.25	1.0000	345.65	1.0000	400.35

Table 3. Bubble-Temperature Measurements at 95.8 kPa

x_1	T/K	x_1	T/K	x_1	T/K
Tetrahydrofuran (1) + 1,2-Dichloroethane (2)		Tetrahydrofuran (1) + 1,1,1-Trichloroethane (2)		Tetrahydrofuran (1) + 1,1,2,2-Tetrachloroethane (2)	
0.0000	355.25	0.0000	345.65	0.0000	417.45
0.1024	354.35	0.1521	344.95	0.1565	406.55
0.2181	352.95	0.3498	343.85	0.3576	390.45
0.2949	351.95	0.4177	343.35	0.4812	379.65
0.4108	350.05	0.4728	342.85	0.6024	368.75
0.4939	348.45	0.6374	341.45	0.6944	360.35
0.6507	344.85	0.7455	340.35	0.8197	348.85
0.7736	341.75	0.8978	338.65	0.9009	341.75
0.8723	338.95	1.0000	337.55	1.0000	355.95
1.0000	335.55				
Tetrahyofuran (1) + Trichloroethylene (2)		Tetrahydrofuran (1) + Tetrachloroethylene (2)		Tetrahydrofuran (1) + *n*-Butanol (2)	
0.0000	357.95	0.0000	393.25	0.0000	389.45
0.1367	356.25	0.1528	378.65	0.1338	370.65
0.3220	353.25	0.2650	366.45	0.2436	360.45
0.4480	350.85	0.3570	360.45	0.3257	354.75
0.6080	346.85	0.4741	353.65	0.3918	350.95
0.7211	343.55	0.5955	347.35	0.4460	348.25
0.7950	341.55	0.6883	347.05	0.4914	346.35
0.8858	338.75	0.8154	314.65	0.6123	342.15
1.0000	335.55	1.0000	311.45	0.6637	340.75
				0.7247	340.75
				0.8206	333.35
				0.8876	337.75
				1.0000	337.55
Tetrahydrofuran (1) + Isobutanol (2)		Tetrahydrofuran (1) + *sec*-Butanol (2)		Tetrahydrofuran (1) + *tert*-Butanol (2)	
0.0000	379.65	0.0000	371.35	0.0000	354.15
0.1367	373.15	0.1072	366.45	0.1423	351.75
0.2456	367.85	0.1847	363.15	0.2491	349.95
0.3281	363.95	0.2536	360.45	0.3323	348.55
0.3943	361.35	0.3615	356.25	0.4534	346.45
0.4487	358.45	0.5047	351.25	0.5753	344.45
0.4941	356.45	0.6132	347.85	0.6702	342.85
0.5707	353.05	0.7257	344.65	0.8904	339.25
0.6147	351.25	0.7984	342.65	1.0000	337.55
0.6660	349.15	0.8880	340.24		
0.7995	343.95	1.0000	337.55		
0.8886	340.85				
1.0000	337.55				

electronically controlled thermostat maintained within ±0.05 K of the desired value for at least half an hour and is carefully cleaned on the outer surface and weighed on an electronic balance precise to ±0.0001 g. From a knowledge of the mass of the empty pycnometer, it was possible to determine the density of the liquid sample. Care was taken that air bubbles did not exist in the pycnometer during experimentation and that the liquids were filled exactly up to the fixed mark in the pycnometer. The estimated uncertainty in the density measurements using

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

substance	*A*	*B*	*C*
tetrahydrofuran[a]	14.0895	2768.37	−48.90
1,2-dichloroethane	14.1590	2929.16	−50.22
1,1,1-trichloroethane	13.9897	2802.75	−48.15
1,1,2,2-tetrachloroethane	14.0633	3341.88	−62.15
trichloroethylene	14.1555	3023.13	−43.15
tetrachloroethylene	14.1468	3259.27	−52.15
n-butanol	15.1986	3137.02	−95.13
isobutanol	14.8538	2874.72	−100.30
sec-butanol	15.1928	3026.03	−86.65
tert-butanol	14.8374	2658.29	−95.40
amyl alcohol	14.2435	2752.19	−116.30
n-heptane	13.8565	2911.31	−56.51
cyclohexane	13.7253	2352.10	−50.50
methylethyl ketone	14.1569	3150.41	−36.65

the pycnometer and method used in the present work is ±0.05%.

Refractive Index. An Abbe-type refractometer, with provision to circulate water at the desired temperature to enable the maintenance of the desired temperature and a sodium vapor lamp are the main constituents of the apparatus used for the measurement of refractive index. The sample was maintained within ±0.05 K of the desired temperature by circulating water (maintained at the desired temperature) from an electronically controlled thermostat for about half an hour. The estimated uncertainty in the present refractive index measurements is ±0.05%.

The uncertainties mentioned in all the measured variables are based on the comparisons of the measurements on a large number of liquids and conditions, carried out incidental to the physical property measurements on pure liquids as well as a result of comparisons with some known or evaluated standards.

Materials. AR-grade chemicals used in this study were further purified according to the easiest possible method described in the treatise.[5] The purity of each chemical was ascertained by measuring its density and refractive index, which compare favorably with the evaluated literature values given by Riddick et al.,[5] as shown in Table 1.

Results and Discussion

The experimental liquid-phase composition (x_1) vs temperature (T) data, summarized in Tables 2 and 3, are fitted to the activity coefficient model proposed by Wilson[6] in the form

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

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

where

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

and

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

V_1^L and V_2^L are the pure liquid molar volumes, and $[(\lambda_{12} - \lambda_{11})/R]$ and $[(\lambda_{12} - \lambda_{22})/R]$ are the Wilson parameters with λs giving the energies of interaction between the molecules denoted by the subscripts. The optimum Wilson parameters are obtained by minimizing the objective function defined as

$$\varphi = \sum[(P_{cal}/P_{exp}) - 1]^2 \quad (5)$$

where P_{cal} and P_{exp} stand for the calculated and experimental total pressures. The Nelder−Mead optimization technique described in the book of Kuester and Mize[7] was used. Pure liquid vapor pressures needed in the computations are calculated from the Antoine equation with the constants noted in Table 4. Prior to use, the Antoine equation with the constants noted in Table 4 was tested for its applicability. First, all the available literature vapor pressure data were collected. It was examined whether the Antoine equation can predict the measured data to within the claimed accuracy of the particular set of data or with an average absolute deviation of 0.5%. The equation is also applied to predict the vapor pressure of each pure liquid of the present study, at the pure liquid boiling temperature observed in the present study at (94.6 or 95.8) kPa. In all the cases, the departures are within the experimental accuracy of the set of measurements or average absolute deviation of 0.5%. Hence, the Antoine equation for vapor pressure, with the set of constants for the 14 liquids noted in Table 4, representing the data well has been used. The

Table 5. Representation of the Measurements by the Wilson Model for the Systems Investigated a 94.6 kPa

system	$[(\lambda_{12} - \lambda_{11})/R]$/K	$[(\lambda_{12} - \lambda_{22})/R]$/K	std dev in *T*/K
tetrahydrofuran (1) + *n*-heptane (2)	−265.84	523.07	0.05
tetrahydrofuran (1) + cyclohexane (2)	−142.96	392.79	0.05
tetrahydrofuran 1) + methylethyl ketone (2)	554.72	−282.42	0.03
1,2-dichloroethane (1) + amyl alcohol (2)	276.33	−60.13	0.08
1,1,1-trichloroethane (1) + amyl alcohol (2)	26.86	391.85	0.04
amyl alcohol (1) + 1,1,2,2-tetrachloroethane (2)	−271.19	2594.66	0.03

Table 6. Representation of the Measurements by Wilson Model for the Systems Investigated at 95.8 kPa

system	$[(\lambda_{12} - \lambda_{11})/R]$/K	$[(\lambda_{12} - \lambda_{22})/R]$/K	std dev in *T*/K
tetrahydrofuran (1) + 1,2-dichloroethane (2)	−348.37	332.44	0.04
tetrahydrofuran (1) + 1,1,1-trichloroethane (2)	−131.58	90.37	0.03
tetrahydrofuran (1) + 1,1,2,2-tetrachloroethane (2)	−615.30	195.55	0.06
tetrahydrofuran (1) + trichloroethylene (2)	−341.06	292.67	0.08
tetrahydrofuran (1) + tetrachloroethylene (2)	−295.73	297.82	0.05
tetrahydrofuran (1) + *n*-butanol (2)	−178.37	5785.54	0.06
tetrahydrofuran (1) + isobutanol (2)	−292.29	323.84	0.04
tetrahydrofuran (1) + *sec*-butanol (2)	−46.09	57.37	0.05
tetrahydrofuran (1) + *tert*-butanol (2)	168.30	−137.13	0.03

molar volumes of the pure liquids calculated from the density measurements of this study (recorded in Table 1) were used as the input to obtain the optimum Wilson parameters. The results of the representation of the phase equilibrium data by the Wilson model, summarized in Tables 5 and 6, indicate that the data and the representation are quite good and can be used for engineering design purposes.

Literature Cited

(1) Vittal Prasad, T. E.; Reddi Prasad Naidu, B.; Madhukiran, D.; Prasad, D. H. L. Boiling Temperature Measurements on the Binary Mixtures of Cyclohexanel with Some Alcohols and Chlorohydrocarbons. *J. Chem. Eng. Data* **2001**, *46*, 416−418.
(2) Vittal Prasad, T. E.: Mythili, R.; Nirmala, G. S.; Prasad, D. H. L. Vapor Liquid Equilibria in Trichloroethylene + Ethanol, + Isopropanol and Tetrachloroethylene + Methanol. *J. Chem. Eng. Data* **2002**, *47*, 816−818.
(3) Vittal Prasad, T. E.; Sravan Kumar, A.; Prasad, D. H. L. Boiling Temperature Measurements on the Binary Mixtures formed by Acetonirile with Some Chloroethanes and Chloroethylenes at 94.6 kPa. *Fluid Phase Equilib.* **2002**, *201*, 47−55.
(4) Hala, E.; Pick, J.; Fried, V.; Villim, O. *Vapor Liquid Equilibrium*; Pergamon: Oxford, 1958.
(5) Riddick, J. A.; Bunger, W. S.; Sakano, T. K. *Organic Solvents. Physical Properties and Methods of Purification*, 4th ed.; Wiley: New York, 1986.
(6) Wilson, G. M. Vapor-Liquid Equilibrium. XI. A New Expression for the Excess Free Energy of Mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127−130.
(7) Kuester, R. T.; Mize, J. H. *Optimization Techniques with Fortran*; McGraw-Hill: New York, 1973.

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