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Bubble Temperature Measurements on Binary Mixtures Formed by Cyclohexane at 94.7 kPa

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Bubble temperatures at 94.7 k Pa, over the entire composition range, are measured for eight binary mixtures formed by cyclohexane with 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, epichlorohydrin, 1,2-dimethoxyethane, 1,4-dioxane, 2-picoline, *N*,*N*-dimethylformamide, and dimethylacetamide. A Swietoslawski-type ebulliometer was used for the measurements. The liquid-phase mole fraction versus temperature measurements were represented by the Wilson model.

Introduction

This investigation of the bubble temperatures of the binary mixtures noted in the abstract is in continuation of our recent studies on the phase equilibria of binary mixtures containing hydrocarbons and alcohols.[1−3] The measurements have been carried out at 94.7 kPa. Among the mixtures chosen for the present work, (a) the cyclohexane + 1,2-dimethoxyethane system has been investigated at 298.15 K by Lepori et al.,[4] (b) the cyclohexane + 1,4-dioxane system has been studied (i) at 308.15 K by Calvo et al.[5] and (ii) at 293.15, 303.15, and 313.15 K by Vierk,[6] and (c) the cyclohexane + *N*,*N*-dimethylformamide system has been investigated (i) by Blanko et al.[7] at 101.33 kPa, (ii) by Lepori et al.[8] at 298.15 K, and (iii) by Geier et al.[9] in the range 298.15−348.15 K. Comparisons of the present work with the available data are also presented.

Experimental Section

A Swietoslawski-type ebulliometer, very similar to the one described by Hala et al.,[10] was used for this study. Connection of the ebulliometer to a good vacuum system, through an in-line mercury manometer, facilitated the creation and the maintenance of the chosen pressure within ±0.1 kPa. The equilibrium temperatures were measured to an accuracy of ±0.1 K, by means of a platinum resistance thermometer, carefully calibrated by means of point-to-point comparison with a standard platinum resistance thermometer (IPTS-68). The liquid mixtures were prepared gravimetrically making use of an electronic balance precise to ±0.0001 g. They were stirred well before being placed in the ebulliometer. The heating rate was adjusted to yield the desired condensate drop rate of 30 drops per min, in accordance with the suggestion of Hala et al.[10] The equilibrium temperature was measured after a steady drop rate and a constant temperature were maintained for at least 30 min. The constancy of the liquid-phase composition during each experiment was ensured by injecting the liquid mixture sample into a gas chromatograph at the beginning and the end of each phase equilibrium experiment. Each measurement was repeated several times, till at least two consecutive observations were within the stated limits of the experimental error of ±0.1 K in temperature, ±0.1 kPa in pressure, and ±0.0001 in the liquid-phase mole fraction.

Table 1. Comparison of the Densities (ρ) and Refractive Indexes (n) of the Pure Substances Used in This Study with Literature Data from Riddick et al.[11] at 298.15 K

	ρ/kg·m^{-3}		n	
substance	this work	Riddick et al.[11]	this work	Riddick et al.[11]
cyclohexane	773.9	773.89	1.4235	1.423 54
1,1,1-trichloroethane	1329.9	1329.90	1.4359	1.435 90
1,1,2,2-tetrachloroethane	1586.7	1586.66	1.4914	1.491 40
epichlorohydrin	1174.6	1174.55	1.4358	1.435 80
1,2-dimethoxyethane	863.7	863.70	1.3781	1.378 11
1,4-dioxane	1028.0	1027.97	1.4203	1.420 25
2-picoline	939.8	939.81	1.4984	1.498 39
dimethylformamide	943.9	943.87	1.4282	1.428 17
dimethylacetamide	936.3	936.34	1.4356	1.435 60

Materials

AR grade chemicals used in this study were further purified according to the easiest possible methods described in ref 11. The purities of the chemicals were ascertained by measuring their densities and refractive indexes, which compare favorably with the literature data, as shown in Table 1.

Results and Discussion

The experimental liquid-phase composition mole fraction (x_1) versus temperature (T) data, summarized in Table 2, were fitted to the Wilson equation[12] in the form

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Table 2. Bubble Temperature Measurements

x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K
1,1,1-Trichloroethane (1) + Cyclohexane (2)		Cyclohexane (1) + 1,1,2,2-Tetrachloroethane (2)		Cyclohexane (1) + Epichlorohydrin (2)		Cyclohexane (1) + 1,2-Dimethoxyethane (2)	
0.0000	351.75	0.0000	416.95	0.0000	388.85	0.0000	356.65
0.1517	349.95	0.1399	391.25	0.1533	358.55	0.0643	353.95
0.3003	348.35	0.2808	377.35	0.2805	354.75	0.1382	352.45
0.4459	347.05	0.4226	368.45	0.4695	352.65	0.2774	350.55
0.5885	346.05	0.6373	360.25	0.6282	351.55	0.4191	349.85
0.7284	345.55	0.7816	356.55	0.7433	350.95	0.5619	349.65
0.8655	345.35	0.9269	353.45	0.8669	350.65	0.7063	349.85
1.0000	345.25	1.0000	351.75	0.9323	350.75	0.8523	350.55
				0.9726	351.15	0.9013	350.85
				1.0000	351.75	0.9505	351.35
						1.0000	351.75
Cyclohexane (1) + 1,4-Dioxane (2)		Cyclohexane (1) + 2-Picoline (2)		Cyclohexane (1) + Dimethylformamide (2)		Cyclohexane (1) + Dimethylacetamide (2)	
0.0000	373.05	0.0000	400.25	0.0000	423.95	0.0000	399.25
0.0570	360.85	0.1460	377.95	0.1400	366.75	0.1511	375.45
0.1420	357.35	0.2950	368.55	0.3020	358.05	0.3032	364.25
0.3020	355.05	0.4490	363.15	0.4100	356.05	0.4484	358.35
0.4500	353.55	0.5930	359.65	0.6000	354.45	0.6077	354.65
0.6020	352.45	0.7550	356.35	0.7460	353.55	0.7439	352.85
0.7430	351.65	0.9070	353.55	0.9050	352.45	0.9018	351.75
0.8630	351.45	1.0000	351.75	1.0000	351.75	0.9505	351.35
0.9640	351.65	1.0000	351.75				
1.0000	351.75						

Table 3. Antoine Constants for the Equation $\ln(P/\mathrm{kPa}) = A - B/[(T/\mathrm{K}) + C]$

substance	ref	A	B	C
cyclohexane	14	13.7882	2776.63	−50.50
1,1,1-trichloroethane	15	13.9897	2802.75	−48.15
1,1,2,2-tetrachloroethane	15	14.0633	3341.88	−62.15
epichlorohydrin	15	16.1716	3568.29	−43.75
1,2-dimethoxyethane	14	12.9968	2869.71	−53.15
1,4-dioxane	14	14.0855	2966.68	−62.15
2-picoline	15	14.1732	3264.69	−51.28
dimethylformamide	15	14.3437	3531.51	−62.76
dimethylacetamide	15	14.2092	3271.35	−71.15

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

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

where

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

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

$V_1{}^{\mathrm{L}}$ and $V_2{}^{\mathrm{L}}$ are the pure liquid molar volumes, and $[(\lambda_{12} - \lambda_{11})/R]$ and $[(\lambda_{12} - \lambda_{22})/R]$ are the Wilson parameters with λ values 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

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

where P_{cal} and P_{expt} are the calculated and experimental total pressures. The Nelder−Mead otimization technique described by Kuester and Mize[13] was used. Vapor pressures of the pure substances were calculated from the Antoine equation with the constants collected from the literature[14,15] and noted in Table 3 for ready reference. Prior to use, the Antoine equation with the constants noted in Table 3 was tested for its applicability. First, all the available literature vapor pressure data were noted. Then it was examined whether the Antoine equation could predict the experimental data to within the claimed accuracy of the particular set of data or within an average absolute deviation of 0.5%. The equation was also used to calculate the vapor pressure of each pure liquid of the present study, at the pure liquid boiling point observed in the present study and compared with the observed value of 94.7 kPa. In all cases the departures are within the experimental accuracy of the set of measurements or an average absolute deviation of 0.5%. Hence, the Antoine equation for vapor pressure with the set of constants for the nine liquids noted in Table 3 represents the data well and has been used. The molar volumes of the pure liquids calculated from the densities of this study (recorded in Table 1) were used as the input to obtain the optimum Wilson parameters. The results of representation of the phase equilibrium data by the Wilson[12] equation are summarized in Table 4. The Wilson parameters given in Table 4 were used to predict

Table 4. Representation of the Measurements by the Wilson Model

system	$[(\lambda_{12} - \lambda_{11})/R]$/K	$[(\lambda_{12} - \lambda_{22})/R]$/K	std dev in T/K
cyclohexane (1) + 1,1,1-trichloroethane (2)	−122.13	242.51	0.09
cyclohexane (1) + 1,1,2,2-tetrachloroethane (2)	−82.99	412.10	0.06
cyclohexane (1) + epichlorohydrin (2)	523.11	373.80	0.05
cyclohexane (1) + 1,2-dimethoxyethane (2)	410.13	−89.98	0.07
cyclohexane (1) + 1,4-dioxane (2)	898.27	−37.14	0.08
cyclohexane (1) + 2-picoline (2)	234.73	115.05	0.05
cyclohexane (1) + dimethylformamide (2)	436.89	606.21	0.06
cyclohexane (1) + dimethylacetamide (2)	−13.60	765.25	0.06

Table 5. Summary of the Comparisons with Literature Phase Equilibrium Data

system	ref	avg abs dev in y_1
cyclohexane (1) + 1,2-dimethoxyethane (2)	4	0.03
cyclohexane (1) + 1,4-dioxane (2)	5	0.03
cyclohexane (1) + *N*,*N*-dimethylformamide (2)	7	0.02
	8	0.02

the vapor-phase compositions at the conditions of the available literature data. A summary of the comparisons is presented in Table 5. The satisfactory agreement with the exceptions of data at the low concentrations of the more volatile component indicates that the data and the representation are quite good.

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