Boiling Temperature Measurements on the Binary Mixtures of Cyclohexane with Some Alcohols and Chlorohydrocarbons

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Boiling temperatures at 95 kPa, over the entire composition range, are measured for the eight binary systems formed by cyclohexane with *n*-butanol, isobutanol, 2-methyl-1-butanol, 3-methyl-1-butanol, 1,2-dichloroethane, trichloroethylene, chloroform, and carbon tetrachloride. A Swietoslawski-type ebulliometer was used for the measurements. The composition versus temperature measurements are well represented by the Wilson model.

Introduction

This investigation on the boiling temperature measurements of the binary mixtures noted in the abstract is in continuation of our recent studies on the phase equilibria of the binary mixtures containing hydrocarbons, alcohols, and chlorohydrocarbons.[1−6] The measurements have been carried out at 95 kPa. The cyclohexane (1) + *n*-butanol (2) system has been studied isobarically by Subba Rao and Venkata Rao[7] and Zong et al.[8] and isothermally by Ramalho and Delmas,[9] Vonka et al.,[10] and Smirnov and Kurtynina.[11] The cyclohexane (1) + isobutanol (2) system has been investigated isobarically by Zong et al.[8] and Nataraj and Raja Rao.[12]

The cyclohexane (1) + 1,2-dichloroethane (2) system has been investigated isobarically by Mesagne and Marsan,[13] Mato et al.,[14] and Fordyce and Simonsen[15] and isothermally by Kato.[16] The cyclohexane (1) + trichloroethylene (2) system has been investigated isobarically by Jayarama Rao et al.[17] The cyclohexane (1) + chloroform (2) system has been investigated isobarically by Norrish and Twigg.[18] The carbon tetrachloride (1) + cyclohexane (2) system has been investigated isobarically by Norrish and Twigg,[18] Jayarama Rao et al.,[19] Yuan and Lu,[20] Rodger et al.,[21] and Fordyce and Simonsen[15] and isothermally by Brown and Ewald,[22] Dvorak and Boublik,[23] and Scatchard et al.[24] Comparisons of the present work with the literature data have also been carried out.

Experimental Section

A Swietoswski-type ebulliometer, very similar to the one described by Hala et al.,[25] was used for this experimental investigation. The experimental procedure and the details of the method adopted for the measurements are as described in Vijaya Kumar et al.[1] All of the analytical reagent grade chemicals used in this study were further purified according to the easiest possible of the methods described in Riddick et al.[26] The purity of the chemicals was ascertained by measuring their density and refractive index, which compare favorably with the literature values as shown in Table 1.

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.[25] at 293.15 K

	D/(kg/m^{-3})		*n*	
substance	this work	Riddick et al.[25]	this work	Riddick et al.[25]
cyclohexane	779.0	779.10	1.4260	1.425 99
n-butanol	809.7	809.56	1.3992	1.399 29
isobutanol	802.1	802.09	1.3978	1.397 79
2-methyl-1-butanol	819.0	819.10	1.4090	1.409 00
3-methyl-1-butanol	810.0	810.10	1.4060	1.406 10
1,2-dichloroethane	1253.0	1252.92	1.4196	1.419 59
trichloroethylene	1462.0	1462.10	1.4765	1.476 49
chloroform	1492.0	1492.09	1.4460	1.445 99
carbon tetrachloride	1594.0	1594.10	1.4595	1.459 49

Results and Discussion

The experimental liquid-phase composition (x_1) versus temperature (T) data, summarized in Table 2, are fitted to the Wilson model.[27] The optimum Wilson parameters are obtained by minimizing the objective function defined as

$$\varphi = \sum[(P_{cal}/P_{expt}) - 1]^2 \qquad (1)$$

where P_{cal} and P_{expt} stand for the calculated and experimental total pressures. The Nelder−Mead optimization technique described by Kuester amd Mize[28] was used. Vapor pressures needed in the computations are calculated from the Antoine constants collected from Reid et al.[29] and noted in Table 3 for ready reference. The Antoine equation, with the constants noted in Table 3, represents the literature vapor pressure data as well as the present measurements with an average absolute deviation of 0.5%, for the nine pure liquids of the present study. The molar volumes of the pure liquids calculated from the density measurements of this study (recorded in Table 1) are used as the input in obtaining the optimum Wilson parameters. The results of the representation of the phase equilibrium

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Table 2. Boiling Temperature Measurements

cyclohexane (1) + *n*-butanol (2)		cyclohexane (1) + isobutanol (2)		cyclohexane (1) + 2-methyl-1-butanol (2)		cyclohexane (1) + 3-methyl-1-butanol (2)	
x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K
0.0000	389.05	0.0000	379.35	0.0000	399.95	0.0000	402.55
0.1034	372.15	0.1044	366.55	0.0926	385.25	0.0936	388.55
0.2018	363.65	0.2028	359.65	0.1993	379.35	0.2012	383.55
0.3038	358.65	0.3048	355.85	0.2992	375.95	0.3014	378.95
0.3995	355.85	0.4005	353.35	0.3991	371.25	0.4017	374.45
0.4986	354.05	0.4998	351.95	0.4991	367.65	0.5018	370.05
0.6009	352.75	0.6019	350.85	0.5991	364.15	0.6017	365.75
0.7165	351.85	0.7174	350.15	0.6992	360.75	0.7015	361.75
0.7907	351.45	0.7918	349.95	0.7994	357.53	0.8011	358.95
0.9389	350.95	0.9399	349.85	0.8996	354.55	0.9007	354.65
1.0000	351.65	1.0000	351.65	1.0000	351.65	1.0000	351.65

cyclohexane (1) + 1,2-dichloroethane (2)		cyclohexane (1) + trichloroethylene (2)		chloroform (1) + cyclohexane (2)		carbon tetrachloride (1) + cyclohexane (2)	
x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K
0.0000	354.95	0.0000	358.15	0.0000	351.65	0.0000	351.65
0.1502	348.95	0.1504	355.65	0.1506	347.05	0.1502	350.55
0.3003	347.05	0.4502	353.05	0.3005	342.65	0.3003	349.55
0.4502	346.25	0.6003	352.35	0.4504	339.65	0.4504	348.85
0.6003	346.05	0.7502	351.85	0.6004	337.35	0.6005	348.25
0.7502	346.95	0.9001	351.75	0.7505	335.45	0.7506	347.95
0.9003	349.05	1.0000	351.65	0.9001	333.85	0.9007	347.85
1.0000	351.65			1.0000	332.85	1.0000	347.75

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

substance	*A*	*B*	*C*
cyclohexane	13.7882	2776.63	−50.50
n-butanol	15.0689	3137.02	−94.43
isobutanol	14.7672	2874.73	−100.30
2-methyl-1-butanol	14.2416	2752.19	−116.30
3-methyl-1-butanol	14.6284	3026.43	−104.10
1,2-dichloroethane	14.1590	2929.16	−50.22
trichloroethylene	14.1645	3028.13	−43.15
chloroform	13.9812	2696.79	−46.16
carbon tetrachloride	13.8944	2808.19	−45.99

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) + *n*-butanol (2)	187.10	633.65	0.02
cyclohexane (1) + isobutanol (2)	180.92	617.29	0.05
cyclohexane (1) + 2-methyl-1-butanol (2)	898.29	−2621.22	0.04
cyclohexane (1) + 3-methyl-1-butanol (2)	1803.04	−370.74	0.08
cyclohexane (1) + 1,2-dichloroethane (2)	308.33	68.62	0.06
cyclohexane (1) + trichloroethylene (2)	191.21	−82.04	0.03
chloroform (1) + cyclohexane (2)	−56.14	173.82	0.17
carbon tetrachloride (1) + cyclohexane (2)	−7.54	61.71	0.01

data by the Wilson[27] model, summarized in Table 4, indicate that the data and the representation are quite good. An attempt has been made to compare the values of the vapor-phase composition of the more volatile component (y_1) from the Wilson parameters for the system presented in Table 4 with the experimental data from the literature under the same conditions. The results of such extensive comparisons, summarized in Table 5, show good results with a few exceptions shown in the table. The data and the representation presented in the paper are expected to be useful for engineering design purposes.

Table 5. Summary of the Comparisons with Literature Data

literature source	condition	% avg abs dev in y_1
Cyclohexane (1) + *n*-Butanol (2)		
Subba Rao and Venkata Rao[7]	760 mmHg	0.005
Zong et al.[8]	760 mmHg	0.017
Ramalho and Delmas[9]	80−100 °C	0.022
Vonka et al.[10]	50−70 °C	0.012
Smirnov and Kurtynina[11]	25−45 °C	0.012
Cyclohexane (1) + Isobutanol (2)		
Zong et al.[8]	760 mmHg	0.032
Nataraj and Raja Rao[12]	760 mmHg	0.007
Cyclohexane (1) + 1,2-Dichloroethane (2)		
Mesagne and Marsan[13]	760 mmHg	0.010
Mato et al.[14]	760 mmHg	0.005
Fardyce and Simonsen[15]	760 mmHg	0.043
Kato[16]	25 °C	0.086
Cyclohexane (1) + Trichloroethylene (2)		
Jayarama Rao et al.[17]	760 mmHg	0.006
Chloroform (1) + Cyclohexane (2)		
Norrish and Twigg[18]	300 and 760 mmHg	0.013
Carbon Tetrachloride (1) + Cyclohexane (2)		
Fordyce and Simonsen[15]	760 mmHg	0.008
Norrish and Twigg[18]	400 and 760 mmHg	0.005
Jayarama Rao et al.[19]	760 mmHg	0.067
Rodger et al.[21]	760 mmHg	0.006
Brown and Ewald[22]	70 °C	0.005
Dvorak and Boublik[23]	10 and 60 °C	0.006
Scatchard et al.[24]	40 and 70 °C	0.013

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