

Boiling Temperature Measurements on the Binary Mixtures of *n*-Heptane with Some Aliphatic Alcohols

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Boiling temperatures at 95 kPa, over the entire composition range, are measured for the five binary systems formed by *n*-heptane with isopropanol, *n*-butanol, isobutanol, *sec*-butanol, and *tert*-butanol. A Swietoslowski-type ebulliometer was used for the measurements. The composition versus temperature measurements are well represented by the Wilson model.

Introduction

This investigation of 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 and alcohols.^{1,2} The measurements have been carried out at 95 kPa. Among the systems chosen for the present study, *n*-heptane (1) + *n*-butanol (2) is the most extensively investigated— isothermally at 50 °C by Aristovich *et al.*³ and Smith and Engel⁴ and isobarically at 760 mmHg by Sablyn,³ Hollo *et al.*,⁵ and Kogan *et al.*⁶ Vijayaraghavan *et al.*^{7,8} also studied the isobaric vapor–liquid equilibria of the *n*-heptane + *n*-butanol system at several pressures—684, 1445, 2205, 2965, and 3725 mmHg. The isopropanol (1) + *n*-heptane system has been investigated by Van Ness *et al.*⁹ Comparison of the present measurements with the literature data has also been carried out.

Experimental Section

A Swietoslowski-type ebulliometer, very similar to the one described by Hala *et al.*,¹⁰ was used for this experimental investigation. 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 ± 1 mmHg (± 1.013 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 certified by the National Bureau of Standards (now NIST). The liquid mixtures for the studies were prepared gravimetrically, with use of an electronic balance precise to ± 0.0001 g, and stirred well before being placed in the ebulliometer. The heating rate was adjusted to yield the desired condensate drop rate of 30 drops per minute 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. Each measurement was repeated several times, till at least two consecutive observations were within the stated limits of the experimental accuracy of ± 0.1 K, 1.013 kPa, and 0.0001 in liquid-phase composition.

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

substance	<i>D</i> (kg·m ⁻³)		<i>n</i>	
	this work	Riddick <i>et al.</i> ¹¹	this work	Riddick <i>et al.</i> ¹¹
<i>n</i> -heptane	679.5	679.46	1.3851	1.385 11
isopropanol	781.3	781.26	1.3752	1.375 20
<i>n</i> -butanol	805.8	805.75	1.3974	1.397 41
isobutanol	797.8	797.80	1.3939	1.393 89
<i>sec</i> -butanol	802.4	802.41	1.3953	1.395 30
<i>tert</i> -butanol	781.2	781.20	1.3852	1.385 20

Materials. The AR grade chemicals used in this study were further purified according to the easiest possible of the methods described in Riddick *et al.*¹¹ The purities of the chemicals were ascertained by measuring their densities and refractive indices, which compare favorably with the literature values as shown in Table 1.

Results and Discussion

The experimental liquid-phase composition (*x*₁) versus temperature (*T*) data, summarized in Table 2, are fitted to the Wilson model¹² in the form

$$\ln \gamma_1 = \ln(x_1 + \Delta_{12}x_2) + x_2 \left\{ \frac{\Delta_{12}}{x_1 + \Delta_{12}x_2} - \frac{\Delta_{21}}{x_2 + (x_2 + \Delta_{12}x_2)} \right\} \quad (1)$$

$$\ln \gamma_2 = \ln(x_2 + \Delta_{21}x_1) + x_1 \left\{ \frac{\Delta_{21}}{x_2 + \Delta_{21}x_1} - \frac{\Delta_{12}}{x_1 + (x_1 + \Delta_{12}x_2)} \right\} \quad (2)$$

where

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

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

*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 λ 's 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

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

Table 2. Boiling Temperature Measurements

isopropanol (1) + <i>n</i> -heptane (2)		<i>n</i> -heptane (1) + <i>n</i> -butanol (2)		<i>n</i> -heptane (1) + isobutanol (2)		<i>n</i> -heptane (1) + <i>sec</i> -butanol (2)		<i>tert</i> -butanol (1) + <i>n</i> -heptane (2)	
x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K
0.0000	369.35	0.0000	389.05	0.0000	379.35	0.0000	371.05	0.0000	369.45
0.1004	353.75	0.1005	378.05	0.1006	372.95	0.1007	361.85	0.1008	359.35
0.2005	349.75	0.2006	372.35	0.2007	368.85	0.2008	360.95	0.2009	356.15
0.3006	348.15	0.3007	369.15	0.3009	365.85	0.3008	360.55	0.3010	354.35
0.4007	347.35	0.4008	367.25	0.4009	364.05	0.4010	360.35	0.4011	353.45
0.5008	347.05	0.5009	366.15	0.5010	362.85	0.5011	360.35	0.5012	352.65
0.6009	346.85	0.6010	365.55	0.6011	362.15	0.6012	360.65	0.6013	352.35
0.7010	347.05	0.7011	365.15	0.7012	361.95	0.7012	360.65	0.7014	352.25
0.8011	347.15	0.8012	365.05	0.8013	361.95	0.8014	362.75	0.8015	352.35
0.9012	348.25	0.9013	365.55	0.9014	362.25	0.9015	365.25	0.9016	352.85
1.0000	353.75	1.0000	369.35	1.0000	369.45	1.0000	369.45	1.0000	353.85

Table 3. Antoine Constants for the Equation $\ln(P/kPa) = A - B/(TK) + C$

substance	A	B	C
<i>n</i> -heptane	13.8563	2911.31	-56.51
isopropanol	16.6755	3640.20	-53.54
<i>n</i> -butanol	15.1986	3137.02	-94.43
isobutanol	14.8538	2874.72	-100.30
<i>sec</i> -butanol	15.1928	3026.03	-86.65
<i>tert</i> -butanol	14.8374	2658.29	-95.50

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
isopropanol (1) + <i>n</i> -heptane (2)	382.43	581.84	0.06
<i>n</i> -heptane (1) + <i>n</i> -butanol (2)	204.80	652.55	0.05
<i>n</i> -heptane (1) + isobutanol (2)	79.80	1187.18	0.04
<i>n</i> -heptane (1) + <i>sec</i> -butanol (2)	1045.17	36.74	0.05
<i>n</i> -heptane (1) + <i>tert</i> -butanol (2)	447.11	43.84	0.04

where P_{cal} and P_{expt} stand for the calculated and experimental total pressures. The Nelder–Mead optimization technique described by Kuester and Mize¹³ was used. Vapor pressures needed in the computations are calculated from the Antoine constants collected from Reid *et al.*¹⁴ and noted in Table 3 for ready reference. The Antoine equation, with the constants noted in Table 3, has been used in the present work for the reduction of the equilibrium measurements. Prior to use, the Antoine equation with the constants noted in Table 3 was tested for its applicability. First, the available literature vapor pressure data were noted. A test was made to determine whether the Antoine equation could predict the experimental data to within the claimed accuracy of the particular set of data or with an average absolute deviation of 0.5%. This equation was 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 95 kPa. In all the cases the departures were found to be within the experimental accuracy of each set of measurements or they gave average absolute deviation of 0.5%. Hence, the Antoine equation for vapor pressure, with the set of constants for the six liquids noted in Table 3, satisfactorily represents the data.

The 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 Wilson¹² model, summarized in Table 4, indicate that the data and the representation are quite good. An attempt has been made to compare the

Table 5. Summary of the Comparisons with Literature Data

lit. source	conditions	avg abs dev in y_1
Van Ness <i>et al.</i> ⁹	Isopropanol (1) + <i>n</i> -Heptane (2) 60 °C	0.034
Aristovich <i>et al.</i> ³	<i>n</i> -Heptane (1) + <i>n</i> -Butanol (2) 50 °C and 760 mmHg	0.010
Smyth and Engler ⁴	50 °C	0.006
Hollo <i>et al.</i> ⁵	760 mmHg	0.022
Kogan <i>et al.</i> ⁶	760 mmHg	0.009
Vijayaraghavan <i>et al.</i> ⁷	684 mmHg	0.026
Vijayaraghavan <i>et al.</i> ⁸	1445 to 3725 mmHg	0.022

values of the vapor phase composition of the more volatile component (y_1), calculated from the Wilson parameters for the system derived from the present set of observations (and recorded in Table 4), with the experimental data from the literature under the conditions reported in the literature. 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.

Literature Cited

- (1) Vittal Prasad, T. E.; Kumari Vallabhaneni, G.; Krishna Sameera, M.; Praveena Bose, V.; Prasad, D. H. L. Bubble Temperature Measurements on *p*-Xylene with Methanol, Propan-1-ol and Butan-1-ol at 95.1 kPa. *J. Chem. Eng. Data* **1998**, *43*, 555–557.
- (2) Vital Prasad, T. E.; Chandrika, K.; Haritha, M.; Geetha, N. B.; Prasad, D. H. L. Bubble Temperature Measurements on Methanol with *o*-Xylene and Ethanol with *m*-Xylene and *p*-Xylene. *Fluid Phase Equilib.* **1998**, *149*, 121–125.
- (3) Aristovich, V. Yu.; Morachevsky, B. G.; Sablyn, I. I. Experimental Study and Equilibrium Calculations in the Ternary System – Methylene ketone – Butanol – Heptane. *Zh. Prikl. Khim.* **1965**, *38*, 2694–2700.
- (4) Smyth, C. P.; Engel, E. W. Molecular Orientation and Partial Vapor Pressures of Binary Mixtures II. Systems Containing an Alcohol. *J. Am. Chem. Soc.* **1929**, *51*, 2660–2670.
- (5) Hollo, J.; Lengyl, T. Vapor-Liquid Equilibria of Homoazeotropes. *Period. Polytech.* **1958**, *2*, 173–182.
- (6) Kogan, V. B.; Fridman, V. M.; Romanova, T. G. Phase Equilibria Formed in Systems of Paraffin Hydrocarbons with Fatty Alcohols. *Zh. Fiz. Khim.* **1959**, *33*, 1521–1525.
- (7) Vijayaraghavan, S. V.; Deshpande, P. K.; Kuloor, N. R. Isobaric Vapor Liquid Equilibrium of *n*-Heptane–*n*-Butanol System. *J. Chem. Eng. Data* **1966**, *11*, 147–149.
- (8) Vijayaraghavan, S. V.; Deshpande, P. K.; Kuloor, N. R. Vapor Liquid Equilibrium Data of the System *n*-Heptane–*n*-Butyl Alcohol at Medium Pressures. *J. Chem. Eng. Data* **1967**, *12*, 13–15.
- (9) Van Ness, H. C.; Soczek, C. A.; Reloquin, G. L.; Machado, R. L. Thermodynamic Excess Properties of Three Alcohol–Hydrocarbon Systems. *J. Chem. Eng. Data* **1967**, *12*, 217–224.
- (10) Hala, E.; Pick, J.; Fried, V.; Villim, O. *Vapor Liquid Equilibrium*; Pergamon: Oxford, 1958.

- (11) Riddick, J. A.; Bunger, W. S.; Sakano, T. K. *Organic Solvents: Physical Properties and Methods of Purification*, 4th ed.; Wiley: New York, 1973; Vol. 2.
- (12) 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.
- (13) Kuester, R. T.; Mize, J. H. *Optimization Techniques with Fortran*; McGraw-Hill: New York, 1973.
- (14) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977.

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