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Bubble point temperatures of the binary mixtures of cyclohexanone with C₁-C₄ aliphatic alcohols at 94.8 kPa

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Bubble point temperatures of the binary mixtures of cyclohexanone with C₁–C₄ aliphatic alcohols at 94.8 kPa

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Bubble point temperatures at 94.8 kPa, over the entire composition range, are measured for the binary mixtures of cyclohexanone with: methanol, ethanol, *n*-propanol, *iso*-propanol, and *n*-, *iso*-, *sec*-, and *tert*-butanols – using a Swietoslowski-type ebulliometer. The liquid phase composition *versus* bubble point temperature measurements are well represented by the Wilson model.

Keywords: Bubble point temperatures; Cyclohexanone; Aliphatic alcohols; Vapor-liquid equilibria

1. Introduction

Cyclohexanone is an intermediate in nylon manufacture, besides being used as solvent and thinner for lacquers and a variety of other substances of importance like synthetic resins and polymers, pharmaceuticals, insecticides, and herbicides. Information leading to the phase equilibria on the mixtures formed by cyclohexanone is expected to be of use in the design and operation of the separation equipments and processes for the compounds present in the mixtures. This investigation on the bubble point temperatures of the binary mixtures noted in the abstract is a continuation of our recent studies leading to the vapor-liquid equilibria of the binary mixtures containing hydrocarbons and alcohols [1,2]. The measurements have been carried out at 94.8 kPa.

Among the systems chosen for the present study:

- (a) isobaric studies at 101 kPa on the ethanol (1) + cyclohexanone (2) mixture have been carried out by Marchenko *et al.* [3] and solution total pressures at 291.15 K have been determined by Weissberger *et al.* [4],

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- (b) *n*-propanol (1) + cyclohexanone (2) mixtures at 101 kPa have been investigated by Marchenko *et al.* [3],
- (c) the *n*-butanol (1) + cyclohexanone (2) mixture at 101 kPa have been investigated by Marchenko *et al.* [3,5] and Ukhin *et al.* [6], and
- (d) *tert*-butanol (1) + cyclohexanone (2) mixture has been studied at 398.15 and 448.15 K by Leu and Robinson [7]. An attempt has been made to compare the available literature with the present work.

2. Experimental section

2.1. Method

A Swietoslowski-type ebulliometer, very similar to the one described by Hala *et al.* [8], is used for this experimental investigation. Connection of the ebulliometer to a good vacuum system and dry nitrogen gas cylinder helped in the creation and maintenance of the chosen pressure within ± 0.1 kPa. An open end manometer provided in line is read frequently and the needed corrective action of adjusting the opening of the needle valve attached to the gas cylinder or the by pass line of the vacuum pump is performed according to the requirement.

Equilibrium temperatures are measured to an accuracy of ± 0.05 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 Institute of Standards and Technology, Boulder, USA. Liquid mixtures for the studies are prepared gravimetrically, making use of electronic balance precise to ± 0.0001 g and stirred well before being placed in the ebulliometer. The heating rate is adjusted to yield the desired condensate drop rate of 30 drops per minute, in accordance with the suggestion of Hala *et al.* [8]. The equilibrium temperatures reported are those measured after the steady condensate drop rate and constancy of temperature are maintained for at least 30 min.

2.2. Materials

Extrapure AR (Analytical Reagent) grade cyclohexanone, SISCO Research Laboratories, Mumbai, (India) is fractionally distilled, after prior drying over silica gel for 2 days. Spectroscopic grade methanol, SDS Fine Chemicals, Boisar (India) is fractionally distilled after drying over silica gel and molecular sieves. Anhydrous ethanol, Aldrich Chemical Co., Gillingham (England) is dried over silica gel and fractionally distilled. AR grade *n*-propanol, SD's Fine-Chem. Ltd., Poicha (India) is dried over anhydrous sodium. GR grade *iso*-propanol, Loba Chemie, Mumbai (India) is dried over calcium chloride followed by barium oxide and fractionally distilled.

GR (Guarenteed Reagent) grade *n*-butanol procured from Loba Chemie Pvt.Ltd., Mumbai (India) is fractionally distilled after initial overnight drying over silica gel. Extrapure AR grade *iso*-butanol procured from SISCO Research Laboratories, Mumbai (India) is purified by drying over silica gel and fractional distillation. Extrapure AR grade *sec*-butanol purchased from SISCO Research Laboratories, Mumbai (India) is fractionally distilled twice, after drying over silica gel. *tert*-Butanol

Table 1. Comparison of the density (D) and refractive-index (n) of the pure liquids used in this study with literature data of Riddick *et al.* at 298.15 K.

Substance	D (kg m ⁻³)		n	
	This work	Literature	This work	Literature
Cyclohexanone ^a	945.2	945.20	1.4510	1.45097
Methanol	786.4	786.37	1.3265	1.32652
Ethanol	784.9	784.93	1.3594	1.35941
<i>n</i> -Propanol	799.6	799.60	1.3837	1.38370
<i>iso</i> -Propanol	781.3	781.26	1.3752	1.37520
<i>n</i> -Butanol	805.8	805.75	1.3974	1.39741
<i>iso</i> -Butanol	797.8	797.80	1.3939	1.39389
<i>sec</i> -Butanol	802.4	802.41	1.3953	1.39530
<i>tert</i> -Butanol	781.2	781.20	1.3852	1.38520

^aAt 293.15 K.

supplied by Ranbaxy Laboratories, SAS Nagar, Punjab (India) is dried over phosphorous pentoxide and fractionally distilled twice.

The fractional distillations are carried out using a packed column of length equivalent to 30 theoretical plates. The middle fractions of the second distillations are collected in amber colored bottles for use in the experiments. The final distillations of the substances are performed only a few hours before the commencement of the phase equilibrium experiments and enough care is taken to prevent absorption of moisture, oxidation, etc., during the intervening period. The purity of the chemicals is ascertained by measuring their density and refractive-index, which compare favorably with the literature values of Riddick *et al.* [9] as shown in table 1. GC-FID test showed no significant additional peaks and the samples used are expected to be free from moisture.

3. Results and discussion

The experimental liquid phase composition (x_1) *versus* temperature (T) data, summarized in table 2, are fitted to the Wilson [10] model.

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

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

where

$$\Lambda_{12} = \left(\frac{V_2^L}{V_1^L} \right) \exp \left[- \left\{ \frac{(\lambda_{12} - \lambda_{11})}{RT} \right\} \right]. \quad (3)$$

$$\Lambda_{21} = \left(\frac{V_1^L}{V_2^L} \right) \exp \left[- \left\{ \frac{(\lambda_{12} - \lambda_{22})}{RT} \right\} \right]. \quad (4)$$

Table 2. Bubble point temperatures of select binary cyclohexanone + alcohol mixtures at 94.8 kPa.

x_1	T (K)	x_1	T (K)	x_1	T (K)	x_1	T (K)
Methanol (1) + cyclohexanone (2)		Ethanol (1) + cyclohexanone (2)		<i>n</i> -Propanol (1) + cyclohexanone (2)		<i>iso</i> -Propanol (1) + cyclohexanone (2)	
0.0000	426.15	0.0000	426.15	0.0000	426.15	0.0000	426.15
0.1545	367.45	0.1626	376.65	0.1653	396.65	0.1726	387.65
0.3541	354.95	0.2828	369.95	0.3311	388.25	0.2943	379.95
0.4775	350.35	0.4409	364.15	0.4712	382.85	0.4548	371.55
0.5938	346.65	0.6083	359.25	0.6179	378.15	0.6126	365.05
0.7543	342.15	0.7565	355.35	0.7638	374.15	0.7598	360.05
0.9109	338.15	0.8923	352.05	0.9065	370.75	0.9047	356.05
1.0000	336.05	1.0000	349.75	1.0000	368.75	1.0000	353.85
<i>n</i> -Butanol (1) + cyclohexanone (2)		<i>iso</i> -Butanol (1) + cyclohexanone (2)		<i>sec</i> -Butanol (1) + cyclohexanone (2)		<i>tert</i> -Butanol (1) + cyclohexanone (2)	
0.0000	426.15	0.0000	426.15	0.0000	426.15	0.0000	426.15
0.1390	414.05	0.1471	410.35	0.1583	409.35	0.1340	395.95
0.2877	408.05	0.3013	401.55	0.3193	397.75	0.2803	383.45
0.4469	402.75	0.4631	394.65	0.4584	390.25	0.4379	373.45
0.6129	397.85	0.6109	389.45	0.6198	383.05	0.6291	365.05
0.7600	394.15	0.5054	385.15	0.7458	378.35	0.7533	360.65
0.8870	391.35	0.6073	381.85	0.8800	374.25	0.8841	356.85
1.0000	389.15	0.7052	379.45	1.0000	370.95	1.0000	353.95

V_1^L and V_2^L being the liquid molar volumes of the pure components and λ 's are the energies of interaction between the molecules designated by the subscripts. As can be seen from the functional forms, the temperature variation of the Wilson parameters is effective through the changes in the pure liquid molar volumes (not considered in the present work) and also in the exponential term. The optimum Wilson parameters are obtained by minimizing the objective function φ defined as

$$\varphi = \sum \left[\frac{(P_{\text{Calcd(Wilson parameter)}} - P_{\text{expt}})}{P_{\text{expt}}} - 1 \right]^2, \quad (5)$$

where $P_{\text{Calcd(Wilson parameter)}}$ is the total pressure calculated from the equation

$$P_{\text{Calcd(Wilson parameter)}} = \gamma_{1(\text{Wilson})} x_1 P_1^0 + \gamma_{2(\text{Wilson})} x_2 P_2^0 \quad (6)$$

with $\gamma_{1(\text{Wilson})}$ and $\gamma_{2(\text{Wilson})}$ calculated from the trial values of the Wilson parameters chosen for regression and P_{expt} stands for the calculated and experimental total pressures. The Nelder–Mead optimization technique described by Kuester and Mize [11] is used. Pure component vapor pressures needed in the computations are calculated from the Antoine constants noted in table 3. The Antoine equation, with the constants [9,12] noted in table 3, represents the literature vapor pressure data as well the present measurements on pure liquids with an average absolute deviation of 0.5%. 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 data by the Wilson [10] model, summarized in table 4, indicate that the data and the representation are quite good.

The optimum Wilson parameters determined as described above and noted in table 4 are used to re-evaluate the phase diagram at 94.8 kPa. The activity coefficients at the observed liquid phase compositions are first calculated and subsequently used to regress

Table 3. Antoine constants for the equation $\ln(P/k\text{ Pa}) = A - B/[(T/K) + C]$.

Substance	A	B	C	Temperature range (K)	Reference
Cyclohexanone	14.0539	3444.16	-64.60	363–439	Riddick <i>et al.</i> [9]
Methanol	16.5723	3626.55	-34.29	257–364	Reid <i>et al.</i> [12]
Ethanol	16.8945	3803.98	-41.68	210–369	Reid <i>et al.</i> [12]
<i>n</i> -Propanol	15.5287	3166.38	-80.15	285–400	Reid <i>et al.</i> [12]
<i>iso</i> -Propanol	16.6755	3640.20	-53.54	273–374	Reid <i>et al.</i> [12]
<i>n</i> -Butanol	15.1985	3137.01	-94.43	288–404	Reid <i>et al.</i> [12]
<i>iso</i> -Butanol	14.8538	2658.28	-95.50	293–376	Reid <i>et al.</i> [12]
<i>sec</i> -Butanol	15.1928	3026.03	-86.65	288–404	Reid <i>et al.</i> [12]
<i>tert</i> -Butanol	14.8734	2658.28	-95.50	293–376	Reid <i>et al.</i> [12]

Table 4. Representation of the measurements by Wilson model.

System	$[(\lambda_{12}-\lambda_{11})/R]$ (K)	$[(\lambda_{12}-\lambda_{22})/R]$ (K)	SD in T (K)
Methanol (1) + cyclohexanone (2)	514.41	-98.25	0.02
Ethanol (1) + cyclohexanone (2)	658.26	-130.09	0.04
<i>n</i> -Propanol (1) + cyclohexanone (2)	798.67	-296.47	0.03
<i>iso</i> -Propanol (1) + cyclohexanone (2)	1339.85	-366.49	0.03
<i>n</i> -Butanol (1) + cyclohexanone (2)	971.58	-409.83	0.03
<i>iso</i> -Butanol (1) + cyclohexanone (2)	643.89	-356.68	0.02
<i>sec</i> -Butanol (1) + cyclohexanone (2)	-238.20	225.83	0.06
<i>tert</i> -Butanol (1) + cyclohexanone (2)	832.89	-386.26	0.03

At the conditions observed by Leu and Ribinson [7].

the bubble point temperatures and the vapor phase compositions at the observed total pressure, making use of the other necessary input data like vapor pressures and molar volumes. The SD of the predicted bubble temperatures are compared with the experimentally observed values and a summary of the comparisons is also noted in table 4.

4. Conclusion

Phase equilibria in the binary mixtures of cyclohexanone with methanol, ethanol, *n*-propanol *iso*-propanol, and *n*-, *iso*-, *sec*-, and *tert*-butanols have been investigated. The observed values of the liquid phase mole fraction *versus* bubble point on all the mixtures investigated could be well represented by the Wilson model. Values of x_1 *versus* T for the ethanol, *n*-propanol, *n*-butanol mixtures with cyclohexanone available in the literature at 101 kPa as well as the present work at 94.8 kPa have been plotted and found to agree satisfactorily – departures being of the order of the pure liquid boiling temperatures of the pure liquids at the different pressures. Isothermal vapor phase compositions of the *tert*-butanol mixture have been computed from the Wilson parameters given in table 4. The values of y_1 are predicted with an average deviation of 0.0156. In view of the care taken during the experimentation and the satisfactory agreement with the literature, the data and representation are reliable and are expected to be useful for design purposes.

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