Short Articles

Vapor−Liquid Equilibrium and Excess Gibbs Energies of Hexane + *N*,*N*-Dimethyl Formamide, 2-Methylpropan-2-ol + 2-Aminophenol, *N*,*N*-Dimethyl Formamide, and 2-Propanol + Diisopropyl Amine at 94.4 kPa

M. Shyam Sunder and Dasika H. L. Prasad*

Properties Group, Chemical Engineering Laboratory, Indian Institute of Chemical Technology, Hyderabad - 500 007, India

Vapor−liquid equilibria at 94.4 kPa, over the entire composition range, were measured for the binary mixtures hexane (1) + *N*,*N*-dimethyl formamide (2), 2-methylpropan-2-ol (1) + 2-aminoethanol (2), 2-methylpropan-2-ol (1) + *N*,*N*-dimethyl formamide (2), and 2-propanol (1) + diisopropyl amine (2). A Swietoslawski-type ebulliometer was used to measure the bubble point temperatures necessary to determine the vapor−liquid equilibrium. The Wilson equation was used to represent the measured liquid-phase composition versus temperature data. Values of the vapor-phase mole fraction, activity coefficients, and excess Gibbs' energy computed from the model are also presented and discussed.

Introduction

During a multistep process for the preparation of λ-cyhalotherin (an important insecticide) and separation of the intermediate components at various stages, mixtures of hexane + *N*,*N*-dimethyl formamide; 2-methylpropan-2-ol + aminoethanol, and *N*,*N*-dimethyl formamide; and 2-propanol + diisopropyl amine are formed and need be separated into their pure components for reuse in the process for economic reasons. This investigation on the vapor−liquid equilibrium of the binary mixtures of hexane (1) + *N*,*N*-dimethyl formamide (2), 2-methylpropan-2-ol (1) + *N*,*N*-dimethyl formamide (2) and 2-methylpropan-2-ol (1) + 2-aminoethanol (2), and 2-propanol (1) + diisopropyl amine (2) was undertaken, because of potential direct application in the separation processes for the pure components by distillation at the conditions where the ambient pressure is close to 94.4 kPa, and is a continuation of some of our recent studies.[1,2] Komarov and Krichevtsov[3] studied the 2-propanol (1) + diidopropyl amine (2) system at 101.3 kPa, whereas the hexane (1) + *N*,*N*-dimethyl formamide (2) system was studied at 101.3 kPa by Blanco et al.[4] Hollenshed and van Winkle investigated the effect of the concentration of *N*,*N*-dimethyl formamide on the relative volatilities of the components in the mixtures formed by hexane with hexene, 4-methyl-1-pentene, and 2-methyl-1-pentene. There are no published vapor−liquid equilibrium data on the other systems chosen for the present study. The present work has been compared with the available literature data.

Experimental Section

The Swietoslawski-type apparatus used and the method of experimentation were essentially the same as those described in our earlier publication.[1] About 100 mL of the liquid mixture sample required to conduct an experiment was prepared by weighing the pure components, using an electronic balance precise to 0.0001 g. Gas chromatography was used to determine the composition of the liquid sample at the beginning and the end of each phase equilibrium experiment to verify whether the liquid sample of the desired composition has actually been prepared and also to ascertain whether the composition of the liquid phase remained the same during the experiment. Careful maintenance of the total pressure within ± 0.1 kPa and control of the energy supply to the heater contributed to the accuracy of the measurements. The experimental uncertainties in the measured variables are expected to be ± 0.05 K in temperature, ± 0.1 kPa in pressure, and ± 0.0005 in liquid-phase mole fraction.

Table 1. Comparison of the Density (ρ) and Refractive Index (n_D) with Literature Data[6]

substance	T/K	ρ/kg·m^{-3} this work	ρ/kg·m^{-3} lit.	n_D this work	n_D lit.
2-amino ethanol	298.15	1013.0	1012.70	1.4525	1.45250
diisopropyl amine	293.15	715.3	715.30	1.3924	1.39236
N,*N*-dimethyl formamide	298.15	943.9	943.87	1.4282	1.42817
hexane	298.15	654.8	654.84	1.3723	1.37226
2-methylpropan-2-ol	298.15	781.2	781.20	1.3852	1.38520
2-propanol	298.15	781.3	781.26	1.3752	1.37520

Materials. Purum grade 2-aminophenol (Fluka Chemie AG & Rd H Laborchemikalien, GMBH Co. KG.) was stored over molecular sieves for 2 days and fractionally distilled twice. Purum grade diisopropyl amine (Fluka Chemie AG & Rd H Laborchemikalien, GMBH Co. KG.) was boiled with calcium hydroxide for (2 to 3) h and stored over molecular sieves for 2 days and fractionally distilled twice. AR grade *N*,*N*-dimethyl formamide (Ranbaxy Fine Chemicals Limited, Mumbai, India) was dried over sodium bicarbonate and fractionally distilled. Laboratory reagent grade hexane (Ranbaxy Laboratories, SAS Nagar, Punjab, India) was purified by drying over anhydrous calcium chloride for 2 days and subjected to fractional distil-

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* Corresponding author. Email: dasika@iict.res.in; dhlprasad@yahoo.com.

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Table 2. Liquid-Phase Mole Fraction (x_1) and Bubble Point (T) Measurements and Computed Values of Vapor-Phase Mole Fraction (y_1), Liquid-Phase Activity Coefficients (γ_1 and γ_2), and Excess Gibbs Energy (G^E) of the Mixtures at 94.4 kPa from the Wilson Model

x_1	T/K	y_1	γ_1	γ_2	G^E	x_1	T/K	y_1	γ_1	γ_2	G^E
Hexane (1) + *N*,*N*-Dimethyl Formamide (2)											
0.0000	423.95	0.0000	−	1.0000	0	0.5890	347.05	0.9673	1.3101	1.1276	601.5
0.0502	404.75	0.4519	1.6570	1.0004	94.3	0.7041	343.65	0.9773	1.2293	1.2666	615.1
0.0905	393.85	0.6275	1.6247	1.0013	147.3	0.7818	342.05	0.9820	1.1700	1.4620	584.8
0.2299	370.65	0.8574	1.5311	1.0095	324.2	0.8775	340.55	0.9865	1.0918	2.0746	471.4
0.3323	360.95	0.9142	1.4696	1.0231	429.7	0.9502	340.15	0.9897	1.0306	4.0090	276.6
0.4988	350.65	0.9556	1.3686	1.0724	558.5	1.0000	339.75	1.0000	1.0000	−	0
2-Methylpropan-2-ol (1) + *N*,*N*-Dimethyl Formamide (2)											
0.0000	423.95	0.0000	−	1.0000	0	0.5199	365.25	0.9247	1.1528	1.0517	298.0
0.0585	406.45	0.4290	1.2888	1.0003	52.1	0.6189	361.95	0.9454	1.1188	1.0942	308.9
0.1192	395.05	0.6236	1.2705	1.0014	103.6	0.7090	359.55	0.9598	1.0859	1.1611	325.7
0.2130	383.75	0.7687	1.2441	1.0049	160.7	0.8297	356.95	0.9755	1.0413	1.3417	248.2
0.3512	373.25	0.8670	1.2051	1.0167	237.9	0.9069	355.55	0.9851	1.0160	1.5844	169.5
0.4036	370.35	0.8894	1.1896	1.0243	260.2	1.0000	353.85	1.0000	1.0000	−	0
2-Methylpropan-2-ol (1) + Monoethanol Amine (2)											
0.0000	441.45	0.0000	−	1.0000	0	0.4325	362.15	0.9746	1.6666	1.1519	906.8
0.0957	392.55	0.8473	2.3207	1.0044	275.8	0.4879	360.55	0.9776	1.5640	1.2171	955.8
0.1747	378.65	0.9251	2.1702	1.0159	467.1	0.5595	359.15	0.9803	1.4386	1.3361	988.7
0.2410	371.95	0.9496	2.0403	1.0334	608.6	0.6558	357.55	0.9828	1.2871	1.5914	967.5
0.2975	368.05	0.9610	1.9288	1.0558	714.7	0.7921	356.15	0.9857	1.1171	2.3261	779.2
0.3461	365.45	0.9674	1.8332	1.0823	795.3	0.9105	355.25	0.9904	1.0246	3.8689	422.5
0.3884	363.65	0.9714	1.7509	1.1122	856.0	1.0000	354.15	1.0000	1.0000	−	0
2-Propanol (1) + Diisopropyl Amine (2)											
0.0000	355.05	0.0000	−	1.0000	0	0.5164	351.65	0.5118	1.0965	1.1267	307.8
0.0721	354.85	0.1045	1.4615	1.0026	80.4	0.6282	351.85	0.6026	1.0545	1.1869	283.8
0.1324	353.05	0.1766	1.3861	1.0088	147.6	0.7094	352.05	0.6732	1.0323	1.2387	247.7
0.2338	352.35	0.2788	1.2815	1.0268	229.3	0.8146	352.55	0.7747	1.0127	1.3164	179.5
0.3140	351.95	0.3494	1.2150	1.0478	272.5	0.9165	353.25	0.8892	1.0025	1.4042	90.0
0.4327	351.65	0.4457	1.1381	1.0895	305.8	1.0000	354.05	1.0000	1.0000	−	0

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

substance	A	B	C	ref
2-amino ethanol	15.8000	3988.33	−86.93	6
diisopropyl amine	15.9559	4092.82	0.00	7
N,*N*-dimethyl formamide	14.3536	3541.51	−62.76	8
hexane	13.8192	2697.55	−48.78	6
2-methylpropan-2-ol	14.8373	2658.28	−95.45	6
2-propanol	16.6754	3640.19	−53.54	6

Table 4. Representation of the Bubble Point Temperature Measurements by the Wilson Model

	$[(\lambda_{12} - \lambda_{11})/R]$	$[(\lambda_{12} - \lambda_{22})/R]$	std. dev.
mixture	K	K	T/K
hexane (1) + monoethanol amine (2)	−175.13	1237.09	0.05
2-methylpropan-2-ol (1) + *N*,*N*-dimethyl formamide (2)	−194.24	550.95	0.03
2-methylpropan-2-ol (1) + 2-aminoethanol (2)	1248.94	−48.93	0.03
2-propanol (1) + diisopropyl amine (2)	128.10	32.80	0.02

lation twice. AR grade 2-methylpropan-2-ol (Ranbaxy Fine Chemicals Limited, Mumbai, India) was dried over phosphorus pentoxide and fractionally distilled twice. Guaranteed reagent grade 2-propanol (Loba Chemie Pvt. Ltd, Mumbai, India) was dried over calcium chloride followed by barium oxide and fractionally distilled twice.

The final step of the purification of all the liquids (fractional distillation) was carried out by means of a packed column of a height equivalent to 30 theoretical plates only a few hours before starting the phase equilibrium experiment, and enough care is taken to prevent the absorption of moisture, oxidation, etc., during the intervening period. On the basis of the non-appearance of multiple significant peaks in the gas chromatograms and the comparison of the physical properties data with the literature values,[6] presented in Table 1, the pure liquids used in the present work are expected to be at least 99.9 % pure.

Results and Discussion

The experimental composition (x_1) vs temperature (T) data, summarized in Table 2, are fitted to the Wilson model, in the manner described in our earlier works.[1,2] Vapor pressures, needed in the computations, are calculated from the Antoine equation with the constants collected from the literature[6−8] and noted in Table 3 for ready reference. Molar volumes of the pure liquids, calculated from the liquid density data given in Table 1, are used as inputs to the calculation of the Wilson parameters. The results of the representation of the data by the Wilson model are summarized in Table 4. The vapor-phase compositions determined from the Wilson model are also noted in Table 2, along with the values of activity coefficients and the excess Gibbs' energies.

Wilson parameters given in Table 4, for the hexane (1) + *N*,*N*-dimethyl formamide system, have been employed to predict the vapor-phase mole fractions at the conditions for which data have been reported by Blanco et al.[4] The predicted values agree with the vapor-phase mole fractions reported in the paper with an average absolute deviation of 0.015.

A similar effort for the 2-propanol (1) + diisopropyl amine (2) system produced vapor-phase mole fractions with an average absolute deviation of 0.013, compared to the literature data of Komarov and Krischevtsov.[5]

The activity coefficients of the more volatile component (γ_1) for all the four systems are positive, indicating positive deviations from Raoult's law. Values of γ_1 corresponding to equimolar mixtures follow the order 2-propanol (1) + diisopropyl amine (2) < 2-methylpropan-2-ol (1) + *N*,*N*-dimethyl formamide (2) < hexane + *N*,*N*-dimethyl formamide (2) < 2-methylpropan-2-ol (1) + 2-amino ethanol (2).

The values of excess Gibbs' energy are also all positive, and the values corresponding to equimolar mixtures follow the order 2-methylpropan-2-ol (1) + *N*,*N*-dimethyl formamide (2) <

2-propanol (1) + diisopropyl amine (2) < hexane (1) + *N*,*N*-dimethyl formamide (2) < 2-methylpropan-2-ol (1) + 2-amino ethanol (2).

In view of the care taken in carrying out the measurements, good representation by the model, and satisfactory agreement with the literature data, the results presented in the paper are expected to be useful for design purposes.

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