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Vapor–liquid equilibria of selected binary mixtures formed by 2-methylpyrazine at 94.7 kPa

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Vapor–liquid equilibria at 94.7 kPa, over the entire composition range are obtained for the binary mixtures formed by 2-methylpyrazine with 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, trichloroethylene, tetrachloroethylene, *N,N*-dimethylformamide and *N,N*-dimethylacetamide. A Swietoslawski type ebulliometer is used to measure the bubble point temperatures necessary to determine the vapor–liquid equilibria. The Wilson equation is used to represent measured liquid phase composition *versus* temperature data.

Keywords: Vapor–liquid equilibria; Bubble temperature; 2-Methylpyrazine; Chloroethanes; Chloroethylenes; Amides

1. Introduction

This investigation on the vapor–liquid equilibria of the binary mixtures formed by 2-methyl-pyrazine with the compounds noted in the abstract, is in continuation of our recent systematic studies leading to the phase equilibria of the binary mixtures formed by different types of compounds [1,2]. There are no published vapor–liquid equilibrium data on the systems chosen for the present study.

2. Experimental section

2.1. Method

Bubble point temperature are measured making use of a Swietoslawski type ebulliometer similar to the one described by Hala *et al.* [3] in construction and mentioned in some detail in our earlier article [1]. The ebulliometer is connected to

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a vacuum pump and a dry nitrogen gas cylinder, with a closed end manometer in line, to enable the measurement and maintenance of the total pressure of the system at 94.7 kPa, by adjusting the opening of the needle valve of the gas cylinder/the opening of the by-pass line of the vacuum pump. The total pressure in this set of experiments is maintained within ± 0.1 kPa of the chosen value, by frequently reading the mercury columns of the manometer and applying the needed corrective adjustment. A mercury-in-glass thermometer, calibrated by means of point-to-point comparison with a platinum resistance thermometer (certified by the National Institute of Standards and Technology, Boulder, USA) is used to measure the equilibrium temperature to an accuracy of ± 0.05 K. The thermometer is placed in a thermowell (in the apparatus), the outer surface of which is constantly impinged by equilibrium vapor-liquid mixture. The thermowell has a small quantity of mercury to provide for good contact. The mixtures to be studied are prepared gravimetrically, by weighing the required components making use of a Mettler balance accurate to 0.0001 g and are stirred well before being introduced to the apparatus. The heating rate is maintained at 30 K min^{-1} per minute, in accordance with the suggestion of Hala *et al.* [3] by carefully adjusting the energy supply to the heater. The technique of subjecting the test sample to the lowest pressure/highest temperature, proposed to be studied and reverting to the ambient conditions several times, before starting the actual experiment is followed to achieve and retain the constancy of composition throughout the experiment. A gas chromatograph is used to verify the constancy of the composition of the sample at the beginning and at the end of each experimental phase equilibrium measurement. Equilibrium temperature is recorded, after the steady state conditions (judged by the maintenance of a constant temperature and uniform boiling rate indicated by the maintenance of the chosen liquid drop rate of 30 min^{-1}) are observed for at least 30 min.

2.2. Materials

2-Methylpyrazine, Purum grade (Fluka Chemie AG & Rd H Laborchemikalien, GMBH Co. KG) is stored over molecular sieves for two days and fractionally distilled twice.

AR grade 1,2-dichloroethane (BDH Chemicals, Mumbai, India) is further purified by washing with dilute potassium hydroxide solution and water, dried over phosphorous pentoxide and fractionally distilled.

AR grade 1,1,1-trichloroethane (SD's Fine Chemicals, Boisar, India) is washed with concentrated hydrochloric acid, followed by washing with 10% sodium chloride solution and drying over calcium chloride. Before subjecting the sample to fractional distillations 0.5 g of phenol is added as stabilizer.

AR grade 1,1,2,2-tetrachloroethane (SD's Fine Chemicals, Boisar, India) is shaken with concentrated sulfuric acid for 10 min at 355 K. The discolored acid is removed and the acid washing is repeated several times until the acid discoloration stops. The product is then washed with water, dried over potassium carbonate and fractionally distilled.

Spectroscopic grade trichloroethylene (SD's Fine Chemicals, Boisar, India) is steam distilled from 10% calcium hydroxide slurry. The organic phase is collected at -30 to -50°C and the ice is removed by filtration. The filtrate is purified by

Table 1. Comparison of the density (d) and refractive-index (n_D) with literature data.

Substance	Temperature (K)	d (kg m^{-3})		n_D	
		This work	Literature [Ref]	This work	Literature [Ref]
2-Methylpyrazine	293.15	1029.00	1029.00 [6]	1.49530	1.49530 [6]
1,2-Dichloroethane	293.15	1252.1	1252.09 [4]	1.4448	1.44480 [4]
1,1,1-Trichloroethane	293.15	1338.1	1338.10 [4]	1.4380	1.43800 [4]
1,1,1,2-Tetrachloroethane	293.15	1594.5	1594.49 [4]	1.49400	1.49389 [4]
Trichloroethylene	293.15	1464.0	1464.00 [5]	1.47820	1.47820 [5]
Tetrachloroethylene	293.15	1622.8	1622.83 [4]	1.50575	1.50576 [4]
<i>N,N</i> -Dimethylformamide	298.15	943.87	943.87 [4]	1.42820	1.42817 [4]
<i>N,N</i> -Dimethylacetamide	298.15	936.34	936.337 [4]	1.43560	1.43560 [4]

fractional distillation. AR grade tetrachloroethylene (SD's Fine Chemicals, Boisar, India) is fractionally distilled after drying over anhydrous sodium sulfate.

AR grade *N,N*-dimethylformamide (Ranbaxy Fine Chemicals Limited, Mumbai, India) is dried over sodium bicarbonate and fractionally distilled. AR grade *N,N*-dimethylacetamide (Ranbaxy Fine Chemicals Limited, Mumbai, India) is dried over sodium hydroxide and fractionally distilled.

The final step of the purification of all the liquids (fractional distillation) is carried by means of a packed column of height equivalent to 30 theoretical plates – only a few hours before the commencement of the phase equilibrium experiment and enough care is taken to prevent the absorption of moisture, oxidation, etc. during the intervening period. Based on the non-appearance of multiple significant peaks in the gas chromatograms and the comparison of the physical properties data with the literature values [4–6] presented in table 1, the pure liquids used in the present work are expected to be at least 99.9% pure.

3. Results and discussion

The experimental composition (x_1) versus temperature (T) data, summarized in table 2, are fitted to the Wilson model, expressing the activity coefficients as

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

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

where

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

and

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

The optimum Wilson parameters are obtained by minimizing the objective function defined as

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

Table 2. Vapor-liquid equilibria of selected binary mixtures of 2-methylpyrazine at 94.7 kPa.

x_1	T (K)	y_1	x_1	T (K)	y_1	x_1	T (K)	y_1	x_1	T (K)	y_1
1,2-Dichloro-ethane(1) + 2-methylpyrazine(2)											
0.0000	396.65	0.0000	0.0000	396.65	0.0000	0.0000	416.95	0.0000	0.0000	416.95	0.0000
0.1036	386.35	0.3263	0.1520	384.45	0.4146	0.1387	415.85	0.1310	0.1501	389.55	0.3062
0.1886	382.05	0.4631	0.3100	374.75	0.6819	0.2871	414.75	0.2385	0.3101	382.95	0.5549
0.2570	379.25	0.5522	0.4500	367.05	0.8332	0.4461	411.75	0.4614	0.4502	377.45	0.7206
0.6980	363.95	0.9143	0.7501	352.75	0.9770	0.5962	404.20	0.8094	0.6001	371.65	0.8503
0.7490	362.35	0.9362	0.9002	347.55	0.9947	0.7470	401.45	0.8852	0.7502	366.05	0.9358
0.8520	359.15	0.9703	1.0000	345.35	1.0000	0.8985	398.45	0.9622	0.9002	360.75	0.9838
0.9200	357.25	0.9864									
1.0000	354.95	1.0000				1.0000	396.65	1.0000	1.0000	357.65	1.0000
Tetrachloro-ethylene(1) + 2-methylpyrazine(2)											
0.0000	396.65	0.0000	0.0000	415.35	0.0000	0.0000	424.15	0.0000	0.0000	424.15	0.0000
0.1502	392.75	0.2199	0.1501	401.25	0.4525	0.1502	408.85	0.4297	0.1502	392.75	0.2199
0.3003	391.15	0.3578	0.3002	397.05	0.5692	0.3002	403.15	0.5694	0.3002	391.15	0.3578
0.4501	390.45	0.4774	0.4503	395.15	0.6036	0.4503	400.15	0.6505	0.4503	390.45	0.4774
0.6002	390.25	0.5987	0.6001	394.05	0.6839	0.6002	398.25	0.7204	0.6002	390.25	0.5987
0.7502	390.45	0.7315	0.7501	393.75	0.7504	0.7501	397.05	0.7983	0.7501	390.45	0.7315
0.9004	391.15	0.8840	0.9002	394.55	0.8608	0.9001	396.45	0.9022	0.9001	391.15	0.8840
1.0000	391.85	1.0000	1.0000	396.65	1.0000	1.0000	396.65	1.0000	1.0000	391.85	1.0000
2-Methylpyrazine(1) + 2-Methylpyrazine(1) + 1,1,2,2-tetrachloroethane(2)											
0.0000	396.65	0.0000	0.0000	416.95	0.0000	0.0000	416.95	0.0000	0.0000	416.95	0.0000
0.1501	389.55	0.3101	0.1501	389.55	0.3101	0.1501	389.55	0.3101	0.1501	389.55	0.3101
0.4502	377.45	0.7206	0.4502	377.45	0.7206	0.4502	377.45	0.7206	0.4502	377.45	0.7206
0.6001	371.65	0.8503	0.6001	371.65	0.8503	0.6001	371.65	0.8503	0.6001	371.65	0.8503
0.7502	366.05	0.9358	0.7502	366.05	0.9358	0.7502	366.05	0.9358	0.7502	366.05	0.9358
0.9002	360.75	0.9838	0.9002	360.75	0.9838	0.9002	360.75	0.9838	0.9002	360.75	0.9838
1.0000	357.65	1.0000	1.0000	357.65	1.0000	1.0000	357.65	1.0000	1.0000	357.65	1.0000
2-Methylpyrazine(1) + N,N -dimethyl-formamide(2)											
0.0000	396.65	0.0000	0.0000	415.35	0.0000	0.0000	424.15	0.0000	0.0000	424.15	0.0000
0.1501	392.75	0.2199	0.1501	401.25	0.4525	0.1502	408.85	0.4297	0.1502	392.75	0.2199
0.3003	391.15	0.3578	0.3002	397.05	0.5692	0.3002	403.15	0.5694	0.3002	391.15	0.3578
0.4501	390.45	0.4774	0.4503	395.15	0.6036	0.4503	400.15	0.6505	0.4503	390.45	0.4774
0.6002	390.25	0.5987	0.6001	394.05	0.6839	0.6002	398.25	0.7204	0.6002	390.25	0.5987
0.7502	390.45	0.7315	0.7501	393.75	0.7504	0.7501	397.05	0.7983	0.7501	390.45	0.7315
0.9004	391.15	0.8840	0.9002	394.55	0.8608	0.9001	396.45	0.9022	0.9001	391.15	0.8840
1.0000	391.85	1.0000	1.0000	396.65	1.0000	1.0000	396.65	1.0000	1.0000	391.85	1.0000

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

Substance	A	B	C
2-Methylpyrazine	6.9322	216.92	− 305.47
1,2-Dichloroethane	14.1590	2927.17	− 50.22
1,1,1-Trichloroethane	13.9483	2802.75	− 48.15
1,1,2,2-Tetrachloroethane	14.0632	3374.13	− 62.15
Trichloroethylene	14.1654	3028.13	− 43.15
Tetrachloroethylene	14.1469	3259.27	− 52.15
<i>N,N</i> -Dimethylformamide	14.3536	3541.51	− 62.76
<i>N,N</i> -Dimethylacetamide	20.3700	7539.56	61.76

P = Vapor pressure, T = absolute temperature.

Table 4. Representation of the bubble point temperature measurements by Wilson Model.

Mixture	$[(\lambda_{12} - \lambda_{11})/R]/\text{K}$	$[(\lambda_{12} - \lambda_{22})/R]/\text{K}$	SD
1,2-Dichloroethane(1) + 2-Methylpyrazine(2)	722.87	− 331.80	0.03
1,1,1-Trichloroethane(1) + 2-Methylpyrazine(2)	− 376.34	1044.28	0.03
2-Methylpyrazine(1) + 1,1,2,2-Tetrachloroethane(2)	− 155.36	91.07	0.05
Trichloroethylene(1) + 2-Methylpyrazine(2)	− 207.99	174.73	0.03
Tetrachloroethylene(1) + 2-Methylpyrazine(2)	408.34	− 145.16	0.04
2-Methylpyrazine(1) + <i>N,N</i> -Dimethylformamide(2)	469.38	211.41	0.03
2-Methylpyrazine(1) + <i>N,N</i> -Dimethylacetamide(2)	421.20	90.20	0.03

SD = Standard deviation in temperature, K.

The Nelder–Mead optimization technique, described by Kuester and Mize [7] is used. Vapor pressures, needed in the computations are calculated from the Antoine equation with the constants noted in table 3 for ready reference. These constants are found to represent the available pure liquid vapor pressure data, including the pure liquid boiling temperatures of the present experiments, with an average absolute deviation of 0.5%. 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 Wilson model are summarized in table 4. The vapor phase compositions determined from the Wilson model are also noted in table 2. In view of the care taken in carrying out the measurements and good representation by the model, the results presented in this article are expected to be useful for design purposes.

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