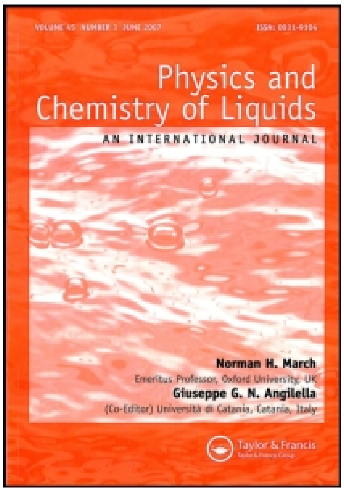

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Activity coefficients and excess Gibbs' energies of the binary mixtures formed by 2-cyanopyrazine with some chloroaliphatics at 95.5 kPa

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Bubble points at a pressure of 95.5 kPa, over the entire composition range are measured for the binary mixtures formed by 2-cyanopyrazine with: 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, trichloroethylene and tetrachloroethylene making use of a Swietoslawski type ebulliometer. The liquid phase composition *versus* temperature measurements are found to be well represented by the Wilson model. Computed values of the activity coefficients and excess Gibbs' energies are also presented along with the phase equilibrium data.

Keywords: 2-Cyanopyrazine; Chloroethanes; Chloroethylenes; Vapor + liquid equilibria

1. Introduction

2-Cyanopyrazine is an intermediate in the manufacture of pyrazine amide, besides use in other applications. Bubble temperature measurements, the vapor–liquid equilibria, and other derived information are expected to be useful in the design and operation of conventional separation processes involving the compounds. This investigation leading to the vapor–liquid equilibria of the binary mixtures formed by 2-cyanopyrazine with the chloroethanes, chloroethylenes is in continuation of our recent systematic studies leading to the phase equilibria of the binary mixtures formed by alcohols, hydrocarbons and halohydrocarbons [1,2]. We could not locate any phase equilibrium data on the systems chosen for the present study.

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2. Experimental section

2.1. *Method*

A Swietoslawski type ebulliometer, very similar to the one described by Hala *et al.* [3] and mentioned in some detail in our earlier publication [1] is used for the present work. The ebulliometer is connected to 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 95.5 kPa, by adjusting the opening of the needle valve attached to the gas cylinder or the opening of the bypass line of the vacuum pump. The total pressure in this set of experiments is maintained within a pressure interval of ±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. For accurate reading of the equilibrium temperature, the thermometer is placed in a thermowell (in the apparatus) whose outer surface 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 a level capable of producing a condensate drop rate of 30 drops per minute, as suggested in Hala *et al.* [3], by carefully adjusting the energy supply to the heater. Constancy of the liquid phase composition is achieved and maintained by subjecting the test sample to the highest temperature, proposed to be studied and reverting to the ambient conditions several times, before starting the actual experiment. A gas chromatograph is used to verify the constancy of the composition of the sample at the beginning and end of each 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 per minute) are observed for at least 30 min.

2.2. *Materials*

2-Cyanopyrazine (Southern Petrochemical Industries Corporation, Tuticorin, India) is 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 phosphorus pentoxide and fractional distillation.

AR grade 1,1,2,2-tetrachloroethane (SD's Fine chemicals, Boisar, India) is shaken with concentrated sulfuric acid for 10 min at a temperature of $T = 355$ K. 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.

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

		ρ (kg m^{-3})		n_D	
Substance	T (K)	This work	literature [Ref.]	This work	literature [Ref.]
2-Cyanopyrazine	293.15	1174.00	1174.00 [5]	1.53400	1.53400 [5]
1,2-Dichloroethane	293.15	1252.90	1252.92 [4]	1.41960	1.41959 [4]
1,1,2,2-Tetrachloroethane	293.15	1593.00	1593.02 [4]	1.49400	1.49389 [4]
Trichloroethylene	303.15	1451.30	1451.40 [4]	1.4750*	1.4750 [4]*
Tetrachloroethylene	293.15	1623.00	1622.83 [4]	1.50575	1.50576 [4]

*At 297.75 K.

The organic phase is collected in the temperature range of $T = 223$ to 243 K and the ice formed removed by filtration. The filtrate is subjected to fractional distillation.

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

The purification of all the liquids is carried out 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.

To ascertain the purity of the pure liquid samples used in the present work, their densitity and refractive index at the selected temperature (as indicated in table 1) has been measured and compared with the literature data.

A carefully calibrated pyknometer, filled with the test liquid, is immersed in a thermostat maintained at the selected temperature within an interval of $T = \pm 0.01$ K for 1 hr, and is weighed employing an electronic balance precise to ±0.0001 g, to determine the weight of liquid occupying known volume, in connection with the determination of density.

Refractive-index of the test sample is measured by means of an Abbe type refractometer, maintained within a temperature interval of ±0.01 K of the selected temperature, by circulating water from an electronically controlled water bath for at least 15 min, employing sodium-D line.

Based on the non-appearance of multiple singnificant peaks in the gas chromatograms, and the comparison of the physical properties data with the literature values [4,5] 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. The optimum Wilson parameters are obtained by minimizing the objective function defined as

$$\varphi = \sum \left[\left(\frac{p_{\text{cal}}}{p_{\text{expt}}} \right) - 1 \right]^2 \tag{1}$$

The Nelder–Mead optimization technique, described by Kuester and Mize [6] is used.

Vapor pressures, needed in the computations are calculated from the Antoine equation with the constants noted in table 3 for ready reference. Prior to use the

Table 2. Boiling temperature (T) measurements and derived phase equilibrium information at a total pressure of 95.5 kPa.

x_1	T (K)	y_1	γ_1	γ_2	G^{E} (J mol^{-1})	x_1	T (K)	y_1	γ_1	γ_2	G_{E} (J mol^{-1})
1,2-Dichloroethane (**1**) + 2-cyanopyrazine (**2**)						1,1,2,2-Tetrachloroethane (**1**) + 2-cyanopyrazine (**2**)					
0.0000	476.35	0.0000	–	1.0000	0	0.0000	476.35	0.0000	–	1.0000	0
0.1001	422.85	0.7962	1.3940	1.0004	48	0.1002	439.95	0.6395	3.6071	1.0297	567
0.1702	405.55	0.9000	1.3580	1.0009	178	0.1305	436.55	0.6787	3.1794	1.0480	696
0.2002	400.05	0.9226	1.3461	1.0012	201	0.2002	432.15	0.7294	2.4846	1.1024	935
0.3001	386.45	0.9627	1.3143	1.0030	270	0.2313	430.85	0.7437	2.2640	1.1318	1018
0.3502	381.15	0.9729	1.3008	1.0046	301	0.3101	428.35	0.7703	1.8565	1.2199	1172
0.3801	378.75	0.9773	1.2931	1.0060	319	0.4004	426.45	0.7933	1.5560	1.3463	1260
0.4502	373.35	0.9847	1.2750	1.0111	346	0.4301	425.95	0.8002	1.4820	1.3944	1270
0.5002	370.15	0.9883	1.2616	1.0171	384	0.5003	424.75	0.8163	1.3409	1.5229	1261
0.6004	364.85	0.9929	1.2315	1.0403	427	0.6002	423.15	0.8402	1.1994	1.7482	1250
0.6702	361.95	0.9949	1.2063	1.0732	448	0.7003	421.55	0.8675	1.1052	2.0387	1124
0.7002	360.85	0.9956	1.1940	1.0951	454	0.7504	420.75	0.8832	1.0714	2.2157	865
0.7505	359.65	0.9965	1.1710	1.1492	454	0.8002	419.95	0.9006	1.0450	2.4176	739
0.8602	356.65	0.9979	1.1079	1.4544	417	0.9002	418.55	0.9430	1.0110	2.9229	407
1.0000	355.15	1.0000	1.0000	–	0	1.0000	417.25	1.0000	1.0000	–	0
Trichloroethylene (**1**) + 2-cyanopyrazine (**2**)						Tetrachloroethylene (**1**) + 2-cyanopyrazine (**2**)					
0.0000	476.35	0.0000	–	1.0000	0	0.0000	476.35	0.0000	–	1.0000	0
0.1001	402.95	0.9010	2.7027	1.0101	364	0.1011	424.55	0.7806	3.3476	1.0142	476
0.1501	391.05	0.9430	2.5170	1.0235	515	0.1302	418.85	0.8242	3.1525	1.0238	592
0.2002	383.45	0.9616	2.3330	1.0429	648	0.2002	409.95	0.8791	2.7270	1.0571	836
0.3100	374.05	0.9782	1.9759	1.1099	880	0.2401	406.75	0.8961	2.5172	1.0831	955
0.4004	369.75	0.9838	1.7357	1.1964	1009	0.3003	403.25	0.9127	2.2431	1.1328	1106
0.4301	368.65	0.9851	1.6666	1.2326	1039	0.3903	399.95	0.9274	1.9136	1.2352	1281
0.4702	367.45	0.9864	1.5801	1.2893	1069	0.4401	398.75	0.9328	1.7646	1.3100	1323
0.5002	366.65	0.9873	1.5204	1.3382	1083	0.5001	397.65	0.9379	1.6104	1.4226	1370
0.6100	364.65	0.9897	1.3328	1.5834	1075	0.6101	396.15	0.9449	1.3849	1.7221	1352
0.7001	363.05	0.9912	1.2113	1.9051	989	0.7501	395.25	0.9499	1.2429	2.1205	1239
0.7302	362.45	0.9917	1.1764	2.0521	942	0.8004	394.85	0.9527	1.1786	2.4426	1137
0.8402	361.25	0.9937	1.0722	2.9056	688	0.9005	394.35	0.9561	1.1224	2.8959	999
0.9001	360.15	0.9951	1.0138	3.7780	482	0.9501	393.35	0.9668	1.0374	4.5895	604
1.0000	357.85	1.0000	1.0000	–	0	1.0000	392.15	1.0000	1.0000	–	0

Table 3. Antoine constants for the equation: $\ln[p/\mathrm{kPa}] = A - B/[T\ (\mathrm{K}) + C]$.

Substance	A	B	C
2-Cyanopyrazine	11.2459	1970.03	−181.66
1,2-Dichloroethane	14.1590	2927.17	−50.22
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

Antoine equation with the constants noted in table 3, has been used to test the applicability to the available literature vapor pressure data. The available pure liquid vapor pressure data, including the pure liquid boiling temperatures of the present experiments, are found to be represented 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 in the calculation of the Wilson parameters. Results of the representation of the data by Wilson model are summarized in table 4.

Table 4. Representation of the boiling temperature measurements by Wilson model.

Mixture	$[(\lambda_{12}-\lambda_{11})/R]$ (K)	$[(\lambda_{21}-\lambda_{22})/R]$ (K)	σ (K)
1,2-Dichloroethane (**1**) + 2-cyanopyrazine (**2**)	−272.57	1730.31	0.07
1,1,2,2-Tetrachloroethane (**1**) + 2-cyanopyrazine (**2**)	663.13	203.65	0.05
Trichloroethylene (**1**) + 2-cyanopyrazine (**2**)	171.51	574.41	0.09
Tetrachloroethylene (**1**) + 2-cyanopyrazine (**2**)	283.61	700.42	0.03

The computational methodology followed in brief is as follows. The equation

$$p_{\text{expt}} = p_1^0 x_1 \gamma_1 + p_2^0 x_2 \gamma_2 \tag{2}$$

where p_{expt} is total pressure maintained, p_1^0 and p_2^0 are the vapor pressures of the two pure components at the temperature of the mixture, x_1 and x_2 are the liquid phase mole fractions and γ_1 and γ_2 are the activity coefficients of the species 1 and 2, is used to optimally to determine the values of γ_1 and γ_2 according to the Wilson model equations

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12} x_2) + x_2 \left[\left\{ \frac{\Lambda_{12}}{(\Lambda_{12} x_2 + x_1)} \right\} - \left\{ \frac{\Lambda_{21}}{(x_2 + \Lambda_{21} x_1)} \right\} \right] \tag{3}$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21} x_1) + x_1 \left[\left\{ \frac{\Lambda_{21}}{(\Lambda_{21} x_1 + x_2)} \right\} - \left\{ \frac{\Lambda_{12}}{(x_1 + \Lambda_{12} x_2)} \right\} \right] \tag{4}$$

where

$$\Lambda_{12} = \left(\frac{V_2^{\mathrm{L}}}{V_1^{\mathrm{L}}} \right) \exp\left[-\frac{\lambda_{12} - \lambda_{11}}{RT} \right] \tag{5}$$

$$\Lambda_{21} = \frac{V_1^{\mathrm{L}}}{V_2^{\mathrm{L}}} \exp\left[-\frac{\lambda_{21} - \lambda_{22}}{RT} \right] \tag{6}$$

V_1^{L} and V_2^{L} being the molar volumes of the pure liquids and λ's being the energies of interaction between the molecules denoted by the subscripts, by trial and error type solution to optimize the objective function, defined by equation (1) making use of all the other needed input information. The optimum Wilson parameters are used to calculate the bubble point temperatures for each mixture composition studied under the total pressure of 95.5 kPa (by trial and error) from equation (2) plugging in all the required data. Computed values of the bubble point temperature are compared with their measured values and the standard deviations are also noted in table 4.

The optimum values of the Wilson parameters (noted in table 4) are subsequently used to calculate the activity coefficient γ_1 employing equation (3) and inserted in to the following equation to calculate the vapor phase composition (y_1) corresponding to each liquid phase mole fraction (x_1).

$$\phi_1 y_1 p_{\text{expt}} = \gamma_1 x_1 p_1^0 \tag{7}$$

assuming the vapor phase imperfection coefficient (ϕ_1) to be unity.

During this investigation, binary mixtures formed by 2-cyanopyrazine with two chloroethanes (1,2-dichloro- and 1,1,2,2-tetrachloro-) and two chloroethylenes (tri- and tetra-) have been studied over the entire composition range.

The results can be discussed in terms of the patterns of the equilibrium vapor phase compositions and the activity coefficients and the excess Gibbs' energies, for the two groups of compounds studied as one of the compounds of binary mixtures formed with 2-cyanopyrazine as the other component.

For the mixtures formed by 2-cyanopyrazine with chloroethanes – the equilibrium vapor phase compositions at the lower mole fractions of the more volatile components are in the order: 1,1,2,2-tetrachloroethane < 1,2-dichloroethane. The same pattern is maintained at higher mole fractions also. The departures of the activity coefficients of the more volatile component from unity for this set of compounds is in the reverse order. The mixtures formed with chloroethylenes also follow similar pattern, in the sense that the equilibrium vapor phase mole fractions of the more volatile component for tetrachloroethylene mixtures are lower than those for trichloroethylene mixtures and the departures of the activity coefficients of the more volatile components from unity are in the reverse order. All the activity coefficients have values greater than unity, indicating positive deviations from the Raoult's law.

The excess Gibbs' energies for all the four systems have positive values. The numerical values of excess Gibbs' energies at equimolar composition are in the order: 1,2-dichloroethane < trichloroethylene < 1,1,2,2-tetrachloroethane < tetrachloroethylene.

In view of the care taken in carrying out the measurements and good representation by the model, the results presented in the article are expected to be useful for design purposes.

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