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Bubble Temperature Measurements on the Binary Mixtures of *n*-Heptane or Nitrobenzene or Chlorobenzene with Some Chloroethanes and Chloroethylenes at (94.6 to 95.8) kPa

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Bubble point temperatures at (94.6 to 95.8) kPa, over the entire composition range, were measured for the binary mixtures formed by *n*-heptane or nitrobenzene or chlorobenzene with 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, trichloroethylene, and tetrachloroethylene by making use of a Swietoslawski type ebulliometer. The liquid-phase composition versus temperature measurements could be well represented by the Wilson model.

Introduction

This investigation leading to the vapor−liquid equilibria of the binary mixtures formed by *n*-heptane or nitrobenzene or chlorobenzene with some chloroethanes and chloroethylenes is aimed at exploring trends and the prospect of generalization in the phase equilibrium behavior due to successive chlorination of ethane/ethylene and nitro-/chloro-substitution to the benzene ring. Vapor−liquid equilibrium data on the systems chosen for the present study could not be located in the open literature, for comparison.

Experimental Section

Method. A Swietoslawski type ebulliometer, very similar to the one described by Hala et al.[1] and shown schematically in Figure 1, was used for the present set of experiments. The ebulliometer was connected to a vacuum pump and a dry nitrogen gas cylinder, with a closed end manometer in line. This arrangement enabled the measurement and maintenance of the total pressure of the system within ±0.1 kPa of the desired value by adjusting the opening of the needle valve of the gas cylinder (or the bypass line of the vacuum pump). The total pressure in this set of experiments was maintained within ±0.1 kPa of the chosen value, by frequently reading the mercury columns of the manometer (calibrated by means of a dead weight tester and found to be accurate to ±0.05 kPa) and applying the needed corrective adjustment. A mercury-in-glass thermometer, calibrated by means of point to point comparison with a standard platinum resistance thermometer (certified by the National Institute of Standards and Technology) was used to measure the equilibrium temperature to an accuracy of ±0.05 K. The thermometer is placed in the thermowell (as shown in Figure 1) whose outer surface was constantly impinged by the equlilbrium vapor−liquid mixture. The thermowell has a small quantity of mercury to facilitate the quick transfer of the equilibrium temper-

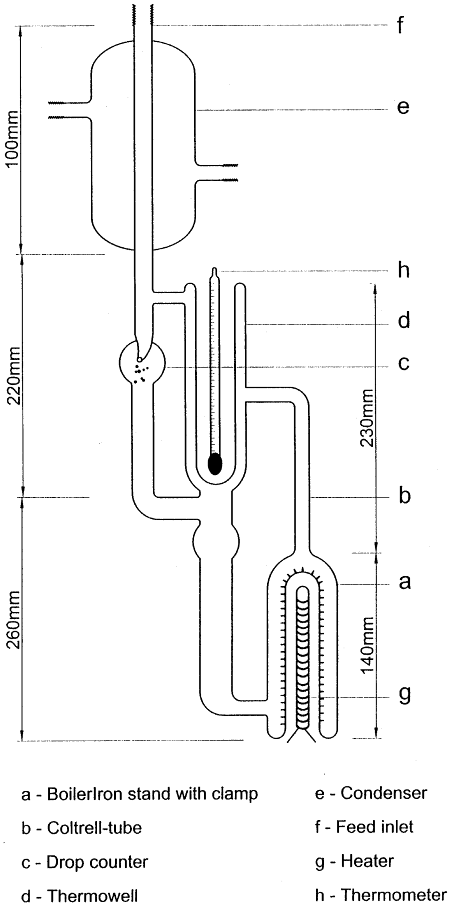

Figure 1. Schematic of the ebulliometer.

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Table 1. Comparison of the Density d and Refractive Index n_D with Literature Data

		d/kg·m^{-3}		n_D	
substance	T/K	this work	lit.^{ref}	this work	lit.^{ref}
n-heptane	298.15	679.5	679.46[2]	1.3851	1.385 11[2]
nitrobenzene	298.15	1198.0	1198.33[2]	1.5500	1.549 97[2]
chlorobenzene	293.15	1106.0	1106.30[2]	1.5248	1.524 81[2]
1,2-dichloroethane	298.15	1247.0	1246.37[2]	1.4421	1.442 10[2]
1,1,1-trichloroethane	298.15	1330.0	1329.90[2]	1.4360	1.435 90[2]
1,1,2,2-tetrachloroethane	298.15	1587.0	1586.66[2]	1.4940	1.494 40[2]
trichloroethylene	298.15	1464.0	1463.90[3]	1.4782	1.478 20[3]
tetrachloroethylene	298.15	1615.0	1614.32[2]	1.5050	1.503 20[2]

Table 2. Bubble Temperature Measurements on *n*-Heptane + Chloroethane or Chloroethylene Mixtures at 95.8 kPa

x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K
1,2-Dichloroethane (1) + *n*-Heptane (2)		1,1,1-Trichloroethane (2) + *n*-Heptane (2)		*n*-Heptane (1) + 1,1,2,2-Tetrachloroethane (2)		Trichloroethylene (1) + *n*-Heptane (2)		*n*-Heptane (1) + Tetrachloroethylene (2)	
0.0000	369.75	0.0000	369.75	0.0000	417.35	0.0000	369.78	0.0000	391.65
0.1650	362.95	0.1028	366.65	0.0937	409.45	0.1890	365.45	0.1664	386.15
0.2840	359.35	0.2913	361.05	0.1703	403.75	0.2590	364.25	0.2853	382.75
0.3689	357.35	0.4513	356.45	0.2911	396.05	0.3681	362.65	0.3745	380.65
0.4380	355.95	0.5069	354.85	0.4181	389.15	0.4492	361.85	0.4146	379.75
0.5173	354.75	0.6267	351.65	0.5571	382.75	0.6749	360.85	0.5500	376.95
0.6835	352.85	0.7705	348.15	0.6264	379.95	0.7654	359.75	0.6197	375.55
0.7641	352.65	0.8344	346.95	0.7155	376.75	0.8509	359.15	0.7562	373.15
0.8663	352.45	0.9097	345.95	0.8342	373.35	0.9195	358.85	0.8302	372.15
0.9284	352.95	1.0000	345.65	0.9197	371.35	1.0000	358.55	1.0000	369.75
1.0000	355.25			1.0000	369.75				

ature to the thermometer inserted into it. The mixtures to be studied were prepared gravimetrically by weighing the required components making use of a Mettler balance accurate to 0.0001 g and were stirred well before being introduced into the apparatus. The heating rate was maintained at the level required to produce a condensate drop rate of 30 drops per min, in accordance with the suggestion of Hala et al.,[1] by carefully adjusting the energy supply to the heater. The mixture was subjected to the highest temperature likely to be encountered in the experiment and brought back to the ambient conditions several times, before commencing the actual measurement, to achieve the constancy of composition during the experiment. A gas chromatograph was used to determine the composition of the sample at the beginning and the end of each phase equilibrium measurement, to confirm that the composition of the sample remained constant. The equilibrium temperature was recorded, after attaining the steady-state conditions (observation of a constant temperature and uniform boiling rate indicated by the maintenance of the chosen liquid drop rate of 30 per min for at least 30 min).

Materials. *n*-Heptane, GR (Loba Chemie, Mumbai, India), Extrapure AR grade nitrobenzene (SISCO Research Laboratories, Mumbai, India), and chlorobenzene (Ranbaxy Laboratories, SAS Nagar, Panjab, India) were stored over anhydrous phosphorus pentoxide for 2 days and fractionally distilled twice. AR grade 1,2-dichloroethane (BDH Chemicals, Bombay, India) was further purified by washing with dilute potassium hydroxide solution and water, drying over phosphorus pentoxide, and fractionally distilling twice. AR grade 1,1,1-trichloroethane (SD's Fine Chemicals, Boisar, India) was washed with concentrated hydrochloric acid, followed by washing with 10% sodium chloride solution and drying over calcium chloride. Phenol (0.5 g) was added as stabilizer before subjecting the sample to fractional distillations. AR grade 1,1,2,2-tetrachloroethane (SD's Fine Chemicals, Boisar, India) was shaken with concentrated sulfuric acid for 10 min at 355 K. The discolored acid was removed, and the acid washing was repeated several times until the acid discoloration stops. The product was then washed with water, dried over potassium carbonate, and fractionally distilled twice. Spectroscopic grade trichloroethylene (SD's Fine Chemicals, Boisar, India) was steam distilled from 10% calcium hydroxide slurry. The organic phase was collected at (−30 to −50) °C and the ice removed by filtration. The filtrate was fractionally distilled twice. AR grade tetrachloroethylene (SD's Fine Chemicals, Boisar, India) was distilled twice fractionally after drying over anhydrous sodium sulfate. Purification of all the liquids was carried out only a few hours before the commencement of the phase equilibrium experimentation. Enough care was taken to prevent the absorption of moisture and oxidation during the intervening period. On the basis of the good agreement of the density and refractive index data of the pure liquid samples used in the present work with the literature values given in refs 2 and 3 (presented in Table 1) and the observation of a single peak when injected to a GC column (SE-30, known to be capable of producing chromatograms by giving characteristic peaks for all the pure components involved in the present study) maintained under suitable conditions, the pure liquids used in the present work were expected to be at least 99.9% pure. The same GC column is used to ascertain the constancy of the composition of the mixture samples during the course of the experimentation, after establishing the optimum conditions for the separation, and calibration through studies on gravimetrically prepared samples of each binary mixture.

Results and Discussion

The experimental composition (x_1) versus temperature (T) data, summarized in Tables 2−4, were fitted to the Wilson model. Optimum Wilson parameters were obtained by minimizing the objective function defined as

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

The Nelder−Mead optimization technique, described by

Table 3. Boiling Temperature Measurements on Nitrobenzene + Chloroethane or Chloroethylene Mixtures at 94.6 kPa

x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K
1,2-Dichloroethane (1) + Nitrobenzene (2)		1,1,1-Trichloroethane (1) + Nitronenzene (2)		1,1,2,2-Tetrrachloroethane (1) + Nitrobenzene (2)		Trichloroethylene (1) + Nitrobenzene (2)		Tetrachloroethylene (1) + Nitrobenzene (2)	
0.0000	481.15	0.0000	481.15	0.0000	481.15	0.0000	481.15	0.0000	481.15
0.1775	417.25	0.1430	409.95	0.1395	465.85	0.1595	415.55	0.1428	439.05
0.3014	397.55	0.3342	379.35	0.3272	450.05	0.3627	388.05	0.3330	417.95
0.4632	381.65	0.4560	369.05	0.4477	441.85	0.4868	379.15	0.4545	410.65
0.5642	374.45	0.6009	360.55	0.5390	436.45	0.6306	371.65	0.6012	404.25
0.6609	368.85	0.7507	354.05	0.7450	426.55	0.6942	368.95	0.7513	399.05
0.7952	362.45	0.8576	349.95	0.8537	422.05	0.7735	365.85	0.9232	393.65
0.8859	358.85	1.0000	345.35	1.0000	416.95	0.8723	362.45	1.0000	391.25
1.0000	354.95					1.0000	358.25		

Table 4. Boiling Temperature Measurements on Chlorobenzene + Chloroethane or Chloroethylene Mixtures at 94.6 kPa

x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K
1,2-Dichloroethane (1) + Chlorobenzene (2)		1,1,1-Trichloroethane (1) + Chlorobenzene (2)		Chlorobenzene (1) + 1,1,2,2-Tetrachloroethane (2)		Trichloroethylene (1) + Chlorobenzene (2)		Tetrachloroethylene (1) + Chlorobenzene (2)	
0.0000	402.55	0.0000	402.55	0.0000	416.95	0.0000	402.55	0.0000	402.55
0.1550	389.25	0.1249	391.65	0.1288	416.15	0.1392	394.35	0.1243	400.85
0.2686	382.25	0.2221	383.95	0.2282	415.15	0.2443	388.65	0.2212	399.65
0.4238	374.55	0.3634	374.15	0.3073	414.25	0.3929	381.15	0.3622	397.85
0.5620	368.75	0.5382	363.85	0.4251	412.85	0.4929	376.65	0.5370	395.95
0.6920	364.05	0.6362	358.95	0.5470	411.15	0.5692	373.25	0.6350	394.85
0.8180	359.95	0.7776	352.85	0.6450	409.55	0.6640	369.45	0.7767	393.35
0.8990	357.65	0.8749	349.25	0.7837	406.95	0.7985	364.45	0.8743	392.45
1.0000	355.05	1.0000	345.25	0.8787	405.05	0.8479	361.45	1.0000	391.25
				1.0000	402.55	1.0000	358.25		

Table 5. Antoine Constants Used in $\ln[P/\text{kPa}] = A - B/[(T/\text{K}) + C]$

substance$^{\text{ref}}$	A	B	C	substance$^{\text{ref}}$	A	B	C
n-heptane^5	13.8563	2911.32	−56.51	1,1,1-trichloroethane^7	13.9845	2802.75	−48.15
nitrobenzene^6	14.3698	4022.42	−71.37	1,1,2,2-tetrachloroethane^7	14.0631	3374.13	−62.15
chlorobenzene^5	14.0502	3295.12	−55.60	trichloroethylene^5	14.1653	3028.13	−43.15
1,2-dichloroethane^5	14.1590	2927.17	−50.22	tetrachloroethylene^5	14.1642	3259.29	−52.15

Table 6. Representation of the Boiling Temperature Measurements by the Wilson Model

mixture	$[(\lambda_{12} - \lambda_{11})/R]$/K	$[(\lambda_{12} - \lambda_{22})/R]$/K	std dev in T/K
1,2-dichloroethane (1) + *n*-heptane (2)	−155.16	856.66	0.07
1,1,1-trichloroethane (1) + *n*-heptane (2)	−376.18	1203.38	0.04
n-heptane (1) + 1,1,2,2-tetrachloroethane (2)	−350.58	798.81	0.03
trichloroethylene (1) + *n*-heptane (2)	−376.45	794.91	0.05
n-heptane (1) + tetrachloroethylene (2)	−100.82	201.01	0.06
1,2-dichloroethane (1) + nitrobenzene (2)	−147.27	167.71	0.03
1,1,1-trichloroethane (1) + nitrobenzene (2)	12.01	83.08	0.05
1,1,2,2-tertrachloroethane (1) + nitrobenzene (2)	−259.34	353.57	0.06
trichloroethylene (1) + nitrobenzene (2)	35.87	110.67	0.04
tetrachloroethylene (1) + nitrobenzene (2)	177.32	102.22	0.02
1,2-dichloroethane (1) + chlorobenzene (2)	426.33	−264.62	0.05
1,1,1-trichloroethane (1) + chlorobenzene (2)	−104.68	0.00	0.05
chlorobenzene (1) + 1,1,2,2-tertrachloroethane (2)	−280.99	252.39	0.06
trichloroethylene (1) + chlorobenzene (2)	−148.85	89.59	0.04
tetrachloroethylene (1) + chlorobenzene (2)	−439.08	64.04	0.04

Kuester and Mize,[4] was used. Pure component vapor pressures needed in the computations were calculated from the Antoine equation with the constants collected from the literature[5−7] and noted in Table 5 for ready reference. These constants were 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, were 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 6. In view of the care taken in carrying out the measurements and good representation by the Wilson model, the results presented in the paper are expected to be useful for design purposes.

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