higher the f values. Figures 5–7 show a comparison of the predicted and experimental data for the adsorption of n-hexadecane at 283, 295, and 303 K. The adsorption isotherms calculated from parameters determined by a nonlinear least-squares fitting procedure are in fairly good agreement with the experimental data. From the results presented, the Langmuir isotherm equation appears to provide a better fit to the experimental data than the Freundlich model. The average absolute deviations between the predicted and the experimental data range from 5.3% to 19.2% for the Freundlich isotherm and from 4.4% to 18.8% for the Langmuir isotherm equation. The poor fit of the Freundlich isotherm equation is due to systematic deviations between the predicted values and the experimental data. That is, the predicted values are higher than the experimental ones in both regions of lower and higher concentrations, while in the region of medium concentration the predicted values are lower than the experimental ones. The BET isotherm equation provides a good overall correlation of the experimental data. The values of the parameters in Tables IV–VI show a considerable scatter among the adsorbates. The temperature dependence of the parameters is also questionable. Although any two parameter model would provide a good fit to the data, there remains a problem of whether the parameters for the Langmuir, Freundlich and BET equations can be related to the adsorption process.

Glossary

a_1, a_2	parameters of the Langmuir isotherm
A	surface area
C	equilibrium concentration, mol/m^3
D_e	effective diffusion coefficient
E_a	apparent activation energy
f	separation coefficient
k_1	a parameter of the Freundlich isotherm equation
n	constant in the Freundlich isotherm equation
q_t	amount of n-alkane adsorbed at time t
q_e	amount adsorbed at equilibrium
q_m	amount adsorbed in the monolayer
R	gas constant
T	temperature
V	unit volume
X	equilibrium concentration, mole fraction
β	coefficient of mutual displacement of the components

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Isobaric Vapor–Liquid Equilibria for the Binary Systems of Benzene/Triethylamine, Benzene/Trimethyl Phosphite, and Triethylamine/Trimethyl Phosphite[†]

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Isobaric boiling point data for the binary liquid mixtures of benzene with triethylamine, benzene with trimethyl phosphite, and triethylamine with trimethyl phosphite are obtained at 100- and 200-mmHg pressures. The data are found to be well represented by the Wilson and the NRTL models.

Introduction

The importance of benzene, triethylamine, trimethyl phosphite, and their mixtures in plastic, detergent, drug, dye, and pesticide industries is well-known. Among the binary combination of this group of important compounds, only the isothermal VLE measurements on benzene–triethylamine system are reported in the literature (*1*, *2*). Hence, the present work on isobaric VLE measurements is undertaken. The method of fitting the experimental temperature–liquid composition (t–x) measurements to the well-tested models for predicting the liquid-phase activity coefficients is employed in this study. The advantages of this method are as follows: (i) quicker estimation and (ii) minimization of the effort as well as errors involved in the measurement of vapor composition.

Experimental Section

The apparatus consists of a Swietoslawski-type ebulliometer described by Hala et al. (*3*), a Cenco high-vacuum pump, a U-tube mercury manometer, a double surface condenser, and a 2-L capacity buffer vessel for dampening the pressure fluctuations. An externally wound nichrome wire supplies the heat to the ebulliometer so that the apparatus could be used for corrosive liquids also. Nucleation for the boiling process is provided by fine glass pieces fused inside the ebulliometer. Cold water circulated at an appropriate flow rate in the double-walled condenser ensures the complete condensation of the vapors. Temperature measurements, with use of a calibrated mercury-in-glass thermometer, are to an accuracy of 0.1 °C while the pressures are maintained and measured to an accuracy of 1 mmHg.

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Table I. Physical Properties of the Compounds Used

compound	refractive index at 20 °C present work	refractive index at 20 °C reported value	ref	density at 20 °C, g/mL present work	density at 20 °C, g/mL reported value	ref
benzene	1.5010	1.50112	4	0.878	0.87901	4
trimethyl phosphite	1.4084	1.40836	5	1.049		
triethylamine	1.4008	1.4010	6	0.7275	0.7276	7

About 130 mL of the binary mixture to be studied, prepared from weighed components, are charged to the ebulliometer. Pressure is maintained at the desired level by proper manipulation of the vacuum section of the apparatus and the needle valves therein. The heating rate is adjusted to yield a drop rate of 20–30/min in conformity with the suggestion of Hala et al. (*3*). Attainment of equilibrium is assumed and the measurements are recorded when a steady reading on the thermometer together with a steady drop rate on the counter is observed.

Materials

Trimethyl phosphite and triethylamine supplied by Merck Co., Germany (98% pure), are separately fractionated in a 18-mm-diameter, 1-m-length packed column at a reflux ratio of 16:1, and the middle cuts used in the experiments have the physical properties shown in Table I. AnalaR-grade benzene (supplied by B.D.H. Co., U.K.) used in the present work has the physical properties given in Table I. Literature values (*4–7*) of the physical properties are also given in Table I for a comparison.

Results and Discussion

Experimental data of this work are given in Tables II–IV. The present total pressures of this work on the benzene/triethylamine system are in agreement with the isothermal data of Siedler et al. (*1*) within ±2 mmHg.

The total pressure π can be calculated from

$$\pi_{\text{calc}} = x_1\gamma_1P_1 + x_2\gamma_2P_2 \qquad (1)$$

Antoine constants for benzene given by Boublik et al. (*8*) have been used. Vapor pressure measurements carried out in this laboratory have been used to determine the Antoine constants of trimethyl phosphite and triethylamine, given in Table V. The Antoine equation with the coefficients given in Table V has been used to calculate the vapor pressure of the pure liquids for use in eq 1. The Antoine constants of triethylamine and trimethyl phosphite reported in Table V have been determined from the vapor pressure measurements reported in Table VI, by the method of Rose et al. (*9*).

Activity coefficients γ_1 and γ_2 of eq 1 are determined by using the Wilson and NRTL models (*10*), and the two sets of the model constants (Λ_{12} and Λ_{21} for Wilson and τ_{12}, τ_{21}, and α_{12} for NRTL) obtained are reported in Tables II–IV. The activity coefficients, γ_1 and γ_2, are reported in Table II for the system benzene/triethylamine, by including the excess enthalpy data of Fenby (*11*) and Velasco et al. (*12*), in the calculations. The activity coefficient data are not reported for the other two systems because of the nonavailability of the excess enthalpy data.

The boiling point (t) vs liquid mole fraction (x) data are used to minimize the objective function, ϕ, with the equation

$$\phi = \sum_{i=1}^{n}(\pi - \pi_{i,\text{calc}})^2 \qquad (2)$$

applying the Fletcher and Reeves conjugate gradient method

Table II. VLE Data for the System Benzene (1)–Triethylamine (2) at 100 and 200 mmHg

Model Constants

pressure, mmHg	Wilson Λ_{12}	Wilson Λ_{21}	Wilson $\bar{e}$	NRTL τ_{12}	NRTL τ_{21}	NRTL α_{12}	NRTL $\bar{e}$
100	0.0606	1.9685	0.76	0.21035	0.49195	0.19195	0.97
200	0.1072	2.1091	0.55	0.17997	0.48003	0.33003	1.85

Model Results of 21 Experimental Points

100 mmHg t, °C	100 mmHg x_1	γ_1 Wilson	γ_1 NRTL	γ_2 Wilson	γ_2 NRTL	200 mmHg t, °C	200 mmHg x_1	γ_1 Wilson	γ_1 NRTL	γ_2 Wilson	γ_2 NRTL
33.7	0.000					50.5	0.000				
32.6	0.025	3.685	1.929	1.006	1.000	48.9	0.025	2.339	1.849	1.003	1.000
32.4	0.050	2.677	1.862	1.018	1.001	48.5	0.050	1.929	1.788	1.010	1.002
31.6	0.100	1.831	1.740	1.048	1.007	47.8	0.100	1.506	1.677	1.030	1.007
31.0	0.150	1.486	1.633	1.080	1.016	47.2	0.150	1.301	1.580	1.051	1.016
30.5	0.200	1.307	1.539	1.019	1.029	46.7	0.200	1.187	1.495	1.072	1.028
30.1	0.250	1.202	1.457	1.136	1.045	46.3	0.250	1.118	1.420	1.090	1.044
29.6	0.300	1.136	1.384	1.161	1.066	45.9	0.300	1.075	1.354	1.107	1.063
29.2	0.350	1.092	1.321	1.183	1.090	45.5	0.350	1.047	1.296	1.121	1.085
28.9	0.400	1.063	1.266	1.202	1.119	45.2	0.400	1.029	1.246	1.133	1.111
28.5	0.450	1.042	1.217	1.219	1.152	44.8	0.450	1.017	1.201	1.142	1.141
28.3	0.500	1.028	1.175	1.234	1.189	44.5	0.500	1.009	1.163	1.150	1.175
27.8	0.550	1.018	1.138	1.248	1.232	44.3	0.550	1.004	1.129	1.156	1.214
27.7	0.600	1.012	1.107	1.259	1.280	44.0	0.600	1.001	1.100	1.151	1.256
27.5	0.650	1.007	1.080	1.268	1.334	43.8	0.650	1.000	1.075	1.164	1.304
27.3	0.700	1.004	1.058	1.277	1.394	43.6	0.700	0.999	1.054	1.166	1.356
27.0	0.750	1.002	1.040	1.283	1.461	43.4	0.750	0.999	1.037	1.167	1.414
26.8	0.800	1.001	1.025	1.289	1.536	43.2	0.800	0.999	1.023	1.167	1.478
26.7	0.850	1.000	1.013	1.293	1.620	43.1	0.850	0.999	1.013	1.165	1.548
26.4	0.900	1.000	1.006	1.296	1.712	42.9	0.900	0.999	1.005	1.163	1.625
26.2	0.950	1.000	1.002	1.298	1.816	42.7	0.950	0.999	1.001	1.161	1.710
26.1	0.975	1.000	1.000	1.299	1.872	42.5	0.975	0.999	1.000	1.159	1.755
26.1	1.00					42.2	1.000				

Table III. VLE Data for the System Triethylamine (1)–Trimethyl Phosphite (2) at 100 and 200 mmHg

Model Constants

pressure, mmHg	Wilson			NRTL			
	Λ_{12}	Λ_{21}	$\bar{e}$	τ_{12}	τ_{21}	α_{12}	$\bar{e}$
100	1.5295	0.2258	0.55	0.084 79	0.572 46	0.766 65	1.34
200	1.1414	0.3177	0.69	0.159 97	0.599 97	0.249 97	1.54

Model Results of 19 Experimental Points

100 mmHg		200 mmHg	
t, °C	x_1	t, °C	x_1
52.3	0.000	70.5	0.000
48.0	0.100	64.3	0.100
46.3	0.150	61.9	0.150
44.7	0.200	60.0	0.200
43.4	0.250	58.3	0.250
42.2	0.300	57.0	0.300
41.1	0.350	56.9	0.350
40.1	0.400	55.0	0.400
39.2	0.450	54.2	0.450
38.4	0.500	53.5	0.500
37.7	0.550	52.9	0.550
37.0	0.600	52.4	0.600
36.3	0.650	51.9	0.650
35.8	0.700	51.5	0.700
35.2	0.750	51.1	0.750
34.7	0.800	50.7	0.800
34.3	0.850	50.5	0.850
33.9	0.900	50.0	0.900
33.8	0.920	49.9	0.920
33.6	0.940	50.0	0.940
33.7	1.000	50.5	1.000

Table IV. VLE Data for the System Trimethyl Phosphite (1)–Benzene (2) at 100 and 200 mmHg

Model Constants

pressure, mmHg	Wilson			NRTL			
	Λ_{12}	Λ_{21}	$\bar{e}$	τ_{12}	τ_{21}	α_{12}	$\bar{e}$
100	1.6610	0.6022	0.56	0.569 99	0.480 00	0.080 00	0.43
200	1.5267	0.7878	1.38	−0.572 71	0.397 29	0.277 29	0.43

Model Results of 21 Experimental Points

100 mmHg		200 mmHg	
t, °C	x_1	t, °C	x_1
26.1	0.000	42.2	0.000
26.5	0.025	42.5	0.025
26.8	0.050	43.0	0.050
27.7	0.100	44.0	0.100
28.2	0.150	45.0	0.150
29.5	0.200	46.1	0.200
30.5	0.250	47.3	0.250
31.5	0.300	48.5	0.300
32.7	0.350	49.8	0.350
33.9	0.400	51.2	0.400
35.2	0.450	52.6	0.450
36.6	0.500	54.2	0.500
38.0	0.550	55.6	0.550
39.5	0.600	57.1	0.600
41.0	0.650	58.7	0.650
42.6	0.700	60.2	0.700
44.2	0.750	61.8	0.750
45.8	0.800	63.5	0.800
47.4	0.850	65.2	0.850
49.1	0.900	67.0	0.900
50.7	0.950	68.8	0.950
51.4	0.975	69.6	0.975
52.3	1.000	70.5	1.000

(*13*). The Wilson and NRTL sets of constants are reported in Tables II–IV.

Tables II–IV list the average errors obtained in the prediction of total pressure (π) with use of the Wilson and NRTL models. It could be seen from the tables that both the models represent the t–x data adequately.

Table V. Constants of the Antoine Equation log (P/mmHg) = $A - B/((t/°C) + C)$

substance	pressure range, mmHg	temp range, °C	A	B	C
benzene (*8*)	57–779	14.5–80.9	6.892 72	1203.531	219.888
triethylamine	80–350	28.6–65.4	6.883 82	1245.190	221.247
trimethyl phosphite	30–200	29.2–68.6	4.263 20	268.819	66.528

Table VI. Vapor Pressure Data on Triethylamine and Trimethyl Phosphite[a]

triethylamine			trimethyl phosphite		
temp, °C	vapor pressure, mmHg	% dev on pressure	temp, °C	vapor pressure, mmHg	% dev on pressure
28.6	80	+0.71	29.2	30.0	+4.95
31.2	90	+0.67	34.9	40.0	−2.52
33.5	100	+0.95	34.9	41.0	−0.02
35.0	106	+0.19	39.6	55.0	+2.44
35.7	110	+0.84	41.0	57.0	−1.71
38.2	120	−1.21	44.9	71.0	+0.13
40.1	130	−1.24	45.2	72.0	+0.03
42.1	140	−2.18	49.9	88.0	−2.29
43.3	150	−0.20	50.1	93.0	+2.32
44.8	160	+0.15	51.9	101.0	+2.50
46.2	170	+0.57	53.9	107.0	−0.38
47.7	180	+0.30	56.0	119.0	+1.44
49.1	190	+0.19	58.6	130.0	−0.21
49.8	195	+0.01	59.9	139.0	+0.67
50.7	200	−0.92	61.2	148.0	+2.65
65.4	350	+0.92	61.9	152.0	+2.68
			66.4	169.0	−3.05
			68.7	185.0	−1.89
			70.3	200.0	+0.57
overall % dev		0.71			1.71

[a] The data are fitted with the Antoine Constants reported in Table V.

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Glossary

A	Antoine constant
$\Lambda_{12},\Lambda_{21}$	parameters of Wilson equation
B,C	Antoine constants
τ_{12},τ_{21}	parameters of the NRTL equation
i,j	subscripts
n	number of T–x data points
P	pure component vapor pressure, mmHg
t	temperature, °C
x	liquid-phase mole fraction
y	vapor-phase mole fraction
α_{12}	nonrandomness parameter in NRTL equation
γ	activity coefficient
π	observed isobaric pressure
π_{calc}	calculated isobaric pressure
ϕ	objective function

Registry No. Triethylamine, 121-44-8; trimethyl phosphite, 121-45-9; benzene, 71-43-2.

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Thermal Conductivity of Poly(ethylene glycols) and Their Binary Mixtures

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A transient hot-wire method was used to measure the thermal conductivities of the first six members of the poly(ethylene glycol) series at 1 atm and in the temperature range 295-480 K. The method was used on a relative basis, and the accuracy of the measurements is estimated to be ±2%. The thermal conductivities of the binary systems ethylene glycol + tri(ethylene glycol), di(ethylene glycol) + tri(ethylene glycol), and di(ethylene glycol) + hexa(ethylene glycol) were also measured over the whole composition range at 1 atm and 295-480 K. The pure liquid data were correlated with use of a carbon number approach, and a linear mixing rule was used to extend the correlation to mixtures of poly(ethylene glycols). Agreement between prediction and experiment was within experimental error.

1. Introduction

The poly(ethylene glycols) ($HOCH_2CH_2(OCH_2CH_2)_nOH$) are industrially important chemicals that have found widespread application in the manufacture of explosives and as antifreezes, solvents, hygroscopic agents, plasticizers, lubricants, and conditioning agents. The large variety of uses for these glycols makes it necessary to have reliable physical-properties data for these substances. Vapor pressures of the glycols up to tetra(ethylene glycol) and molecular weights up to hepta(ethylene glycol) have been reported by Gallaugher and Hilbert (*1*, *2*). Densities, viscosities, and thermal conductivities of the lower glycols have been studied by a number of workers (*3*-*5*). The present work reports thermal conductivities of six glycols and three binary mixtures of glycols. The thermal conductivity of the pure liquids is interesting in that it exhibits a maximum when plotted against the temperature. Additionally, the glycols are known to be thermally unstable at the higher temperatures studied in this work (*1*). This provides an interesting challenge in the development of correlations for the thermal conductivity.

2. Apparatus and Procedure

The transient hot-wire apparatus employed in this work is shown in Figure 1 and consisted of a Wheatstone bridge, a power supply, and a data acquisition system. The Wheatstone bridge consisted of two $100 \pm 0.01\ \Omega$ precision resistors, a General Radio (Model 1433 U) decade box with a range of $0-111.11\ \Omega$, and a hot-wire cell. The hot-wire cell was fabricated from 0.01-m-diameter Pyrex (7740) tubing with a 0.002 m inside diameter glass sleeve at each end. The sleeves act to center two 0.001-m-diameter platinum lead wires. The lead wires protruded beyond the sleeves on the inside and outside of the cell and were sealed into place by melting the ends of the sleeves. A platinum filament 0.000 025 m in diameter (Englehard; 99.9%) was spot-welded between the leads inside the cell. The length of the filament was 0.099 95 ± 0.0005 m as determined with a cathetometer. On the outside of the cell, silver wires were soldered to each lead and, in turn, connected to an amphenol plug. The plug was directly attached to the bridge. The cell itself was attached to a 0.125-in. thermocouple to ensure that it remained vertical. The cell and thermocouple were then inserted into a stainless steel enclosure as shown in Figure 2.

The bridge was powered by a Hewlett-Packard (Model 6213A) power supply used as a constant voltage source. The supply was used to both balance the bridge and provide the voltage for heating. A Fluke multimeter (Model 8840A) was used to indicate a balanced condition in the bridge. A data acquisition system consisting of an IBM PC XT with a Strawberry Tree analog-to-digital (A/D) converter card (ACPC-16) was used to read both the offset voltage and the applied voltage.

The test fluid was loaded into the glass cell mounted in a stainless steel housing. The whole assembly was then placed in a Techne fluidized sand bath (Model SBL-2D) that maintained the temperature to ±0.1 K. A type K thermocouple, calibrated against a PRT, was used to determine the stability of the bath and the sample temperatures. After temperature equilibrium had been achieved, the air flow to the sand bath was stopped to prevent any vibration of the cell during measurement.

The procedure for each measurement was as follows. The bridge was first balanced and the computer program started. The program initiated a step input to the bridge with a relay (Magnecraft W172DIP-1). The relay settled in less than 0.3 ms. The program sampled the offset voltage on one channel and then switched channels to sample the applied voltage to ensure its constancy. The time between any two samples was 0.0084 s and that between two successive readings of the same channel was 0.0168 s. The delay between the closing of the relay and the first sampling was found experimentally to be 0.0132 s. There were 50 points measured during each run, and the experiment lasted about 0.9 s. From a previous calibration of the temperature versus resistance, the temperature of the wire was found. A plot of ΔT versus $\ln t$ was made, and the slope in the time interval from 0.1 to 0.8 s was calculated by

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