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Vapor-Liquid Equilibria

Systems 1,2-Dichloroethane–Ethylbenzene and 1,2-Dichloroethane–p-Xylene

BHUSHAN KUMAR and K. S. N. RAJU[1]
Department of Chemical Engineering and Technology, Panjab University, Chandigarh-14, India

Vapor-liquid equilibrium data were obtained for the wide-boiling systems 1,2-dichloroethane–ethylbenzene and 1,2-dichloroethane–*p*-xylene at 735 mm of Hg pressure using a vapor recirculating type of equilibrium still. The experimental equilibrium compositions were compared with those calculated by Raoult's law. The vapor-phase nonideality was estimated and found to be moderate.

This work is part of an investigation on the evaluation of vapor-liquid equilibrium characteristics of systems involving close-boiling hydrocarbons and other compounds. Isobaric vapor-liquid equilibria at 735 mm of Hg pressure were determined for two binary systems.

EXPERIMENTAL

The purification of materials and apparatus has already been described (*2*). Table I gives the physical properties of 1,2-dichloroethane whereas the physical properties of ethylbenzene and *p*-xylene are given in Table I of ref. *2*. The atmospheric pressure during the runs remained constant at 735 mm of Hg with a variation of ±2 mm of Hg. A standard mercury barometer was used to measure the atmospheric pressure to within ±0.1 mm of Hg. Temperatures were measured by means of calibrated 24-gage copper-constantan thermocouples in conjunction with an OSAW Vernier potentiometer with an accuracy of 0.00002 V and an OSAW spot-reflecting galvanometer having a sensitivity of 0.04 to 0.05 μA per mm of scale division. The accuracy of temperature measurements was of the order of ±0.1°C.

Table I. Physical Properties of 1,2-Dichloroethane

Molecular weight		98.97
Normal bp, °C	Exptl	83.47
	Lit	83.50 (*4*)
Refractive index, 30°C	Exptl	1.4402
	Lit	......
Density, 30°C	Exptl	1.2360
	Lit	......

Table II. Refractive Index–Composition Data at 30°C

1,2-Dichloroethane–ethylbenzene system		1,2-Dichloroethane–*p*-xylene system	
Mole fraction, 1,2-dichloroethane	Refractive index	Mole fraction, 1,2-dichloroethane	Refractive index
0.0000	1.4922	0.0000	1.4904
0.0751	1.4892	0.0788	1.4876
0.1487	1.4857	0.1488	1.4850
0.2607	1.4808	0.2130	1.4822
0.2764	1.4802	0.2807	1.4791
0.3430	1.4777	0.3454	1.4763
0.4000	1.4745	0.4036	1.4732
0.4584	1.4725	0.4579	1.4707
0.5094	1.4690	0.5019	1.4681
0.5582	1.4670	0.5615	1.4655
0.6049	1.4644	0.6053	1.4634
0.6489	1.4621	0.6569	1.4608
0.7005	1.4593	0.6950	1.4584
0.7453	1.4568	0.7459	1.4559
0.7839	1.4543	0.7952	1.4529
0.8194	1.4520	0.8262	1.4513
0.8605	1.4496	0.8574	1.4491
0.8966	1.4470	0.8978	1.4467
0.9330	1.4449	0.9332	1.4445
0.9678	1.4425	0.9742	1.4414
1.0000	1.4402	1.0000	1.4402

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[1] To whom correspondence should be addressed.

The equilibrium mixtures were analyzed by the refractive index method using a Bausch and Lomb Abbé-3L refractometer calibrated by means of a standard glass test piece having a nominal refractive index of 1.5126, using 1-bromonaphthalene as contacting liquid. The prism temperatures were maintained to within ±0.1°C by the use of a Precision Scientific constant temperature circulating bath. The accuracy of the refractive index measurements was of the order of ±0.0002. Table II gives the refractive index-composition data for the binary mixtures.

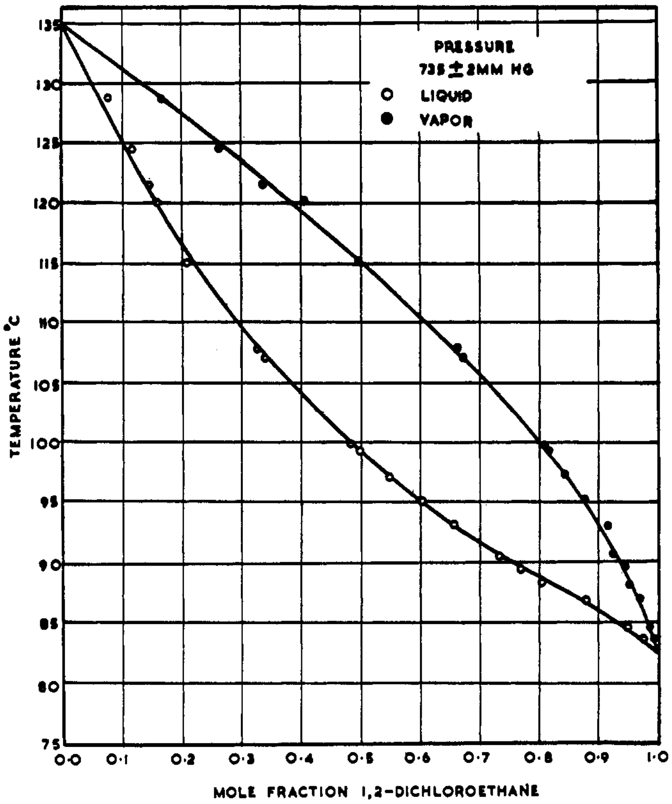

Figure 1. Boiling point–composition diagram for 1,2-dichloroethane–ethylbenzene system

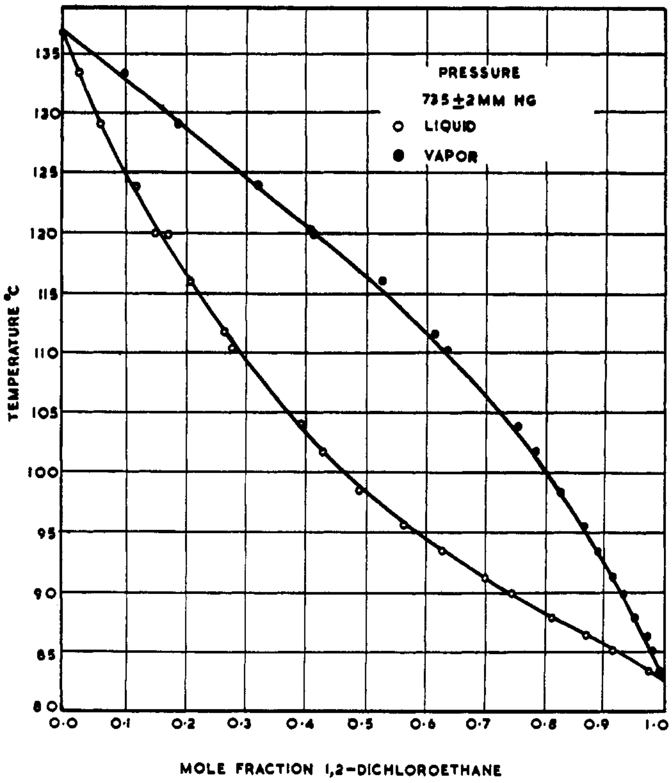

Figure 2. Boiling point–composition diagram for 1,2-dichloroethane–*p*-xylene system

Figures 1 and 2 represent the boiling point-composition diagrams for the two systems, 1,2-dichloroethane-ethylbenzene and 1,2-dichloroethane-*p*-xylene, respectively.

RESULTS

Table III gives the vapor-liquid equilibrium data for the systems 1,2-dichloroethane–ethylbenzene and 1,2-dichloroethane–*p*-xylene. The differences between the experimental composition and the composition calculated by means of Raoult's law are also included. Figures 3 and 4 give x vs. $y - x$ relationships. The dotted lines represent the relationships corresponding to the vapor compositions calculated from Raoult's law. The differences are not large, the average deviations being 0.016 mole fraction in x and 0.031 mole fraction in y for the 1,2-dichloroethane–ethylbenzene system and 0.014 mole fraction in x and 0.025 mole fraction in y for the 1,2-dichloroethane–*p*-xylene system, indicating that the systems obey Raoult's law to a large measure.

Table III. Vapor–Liquid Equilibrium Data at 735 ± 2 Mm of Hg Pressure

t, °C	x_1	y_1	$x_1 - x_1^{*a}$	$y_1 - y_1^{*a}$	z_1	z_2
System 1,2-Dichloroethane(1)–Ethylbenzene(2)						
128.65	0.080	0.168	0.031	−0.104	1.038	0.992
124.35	0.120	0.261	0.035	−0.108	1.034	0.988
121.35	0.149	0.334	0.032	−0.093	1.030	0.984
119.85	0.160	0.405	0.013	−0.037	1.029	0.982
114.85	0.210	0.505	0.003	−0.008	1.025	0.977
107.75	0.325	0.660	0.002	−0.004	1.019	0.969
107.00	0.336	0.670	0.007	−0.004	1.018	0.968
99.65	0.483	0.810	−0.008	0.013	1.012	0.961
97.00	0.548	0.844	−0.001	0.001	1.010	0.958
95.00	0.605	0.879	0.002	−0.003	1.009	0.956
92.80	0.654	0.916	−0.015	0.020	1.007	0.954
90.50	0.733	0.924	0.014	−0.018	1.006	0.951
89.30	0.768	0.944	0.008	−0.010	1.005	0.950
88.05	0.803	0.953	0.008	−0.010	1.004	0.949
86.60	0.878	0.971	0.033	−0.038	1.003	0.947
84.45	0.946	0.988	0.032	−0.035	1.002	0.945
83.40	0.980	0.997	0.029	−0.030	1.001	0.947
System 1,2-Dichloroethane(1)–*p*-Xylene(2)						
133.25	0.026	0.109	−0.003	0.011	1.043	0.995
129.05	0.062	0.191	0.006	−0.020	1.039	0.990
123.80	0.124	0.324	0.017	−0.053	1.033	0.984
120.00	0.152	0.410	0.004	−0.010	1.030	0.980
119.85	0.175	0.416	0.024	−0.067	1.029	0.980
115.95	0.214	0.530	0.002	−0.006	1.026	0.975
111.70	0.270	0.620	−0.004	0.009	1.022	0.971
110.20	0.278	0.641	−0.017	0.037	1.021	0.969
103.85	0.396	0.759	−0.015	0.027	1.016	0.962
101.60	0.431	0.790	−0.023	0.040	1.014	0.960
98.40	0.494	0.832	−0.027	0.043	1.012	0.957
95.65	0.566	0.869	−0.020	0.029	1.009	0.954
93.50	0.632	0.893	−0.007	0.009	1.008	0.951
91.25	0.704	0.918	0.005	−0.006	1.006	0.949
89.85	0.749	0.938	0.006	−0.007	1.005	0.948
87.85	0.814	0.953	0.015	−0.018	1.004	0.945
86.40	0.873	0.976	0.019	−0.022	1.003	0.944
85.10	0.919	0.984	0.026	−0.028	1.002	0.942
83.40	0.978	0.998	0.026	−0.027	1.001	0.941

[a] Difference between the experimental and Raoult's law composition.

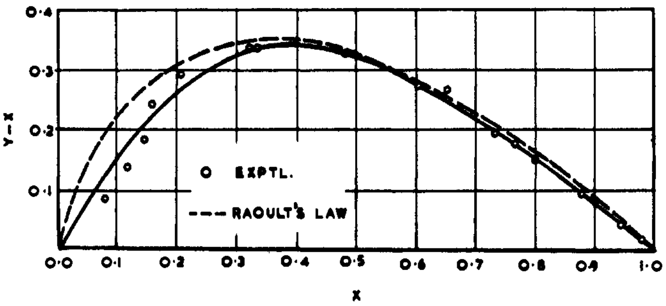

Figure 3. *x* vs. *y-x* diagram for 1,2-dichloroethane–ethylbenzene system

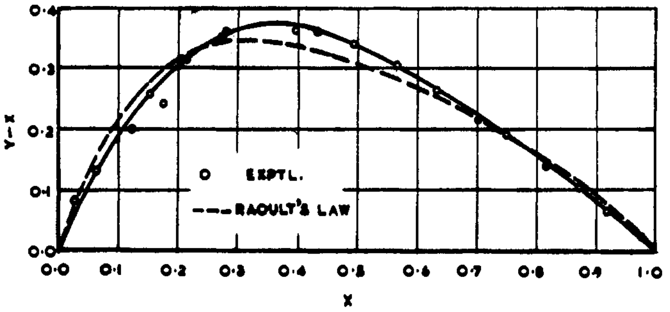

Figure 4. *x* vs. *y-x* diagram for 1,2-dichloroethane–*p*-xylene system

The deviations of the vapor phase from the perfect gas laws were estimated using the following equation:

$$z_i = \exp\left[(\pi - P_i^\circ)(B_i - V_i)/RT\right]$$

For ethylbenzene and *p*-xylene vapor pressures, second virial coefficients and liquid molar volumes were estimated by the correlations referred to (*2*). Vapor pressures of 1,2-dichloroethane were estimated using the Wrede equation (*5*) with the constants obtained (*1*). The average absolute deviations between the calculated and literature (*3*) vapor pressures for 1,2-dichloroethane over the temperature range 82–184°C were estimated to be 8.29 mm of Hg. The O'Connell and Prausnitz correlation and Yen and Woods correlation (*2*) were used for the estimation of its second virial coefficients and liquid molar volumes, respectively.

The assumption that the vapors follow the ideal gas laws yields errors in the relative volatility up to a maximum of about 6% for the two systems, the values of the relative volatility being higher than the corresponding values for the real vapor phase. This departure from the perfect gas laws is primarily due to the large differences in the boiling points of the constituents of the mixtures. The calculated vapor-phase imperfection coefficients are given in Table III.

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The authors gratefully acknowledge the encouragement and helpful suggestions of Bimalendu Ghosh.

NOMENCLATURE

z = vapor-phase imperfection coefficient

Nomenclature for the remaining terms appearing in the text is the same as given in ref. *2*.

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Gas-Liquid Equilibrium of Oxygen–Carbon Dioxide System

AAGE FREDENSLUND,[1] JØRGEN MOLLERUP, and OLE PERSSON
Institute of Chemical Technology, The Technical University of Denmark, Building 229, 2800 Lyngby, Denmark

Gas–liquid equilibrium compositions for the O_2–CO_2 system were determined for the −49.4°C isotherm over the complete pressure range from the vapor pressure of CO_2 at −49.4°C, 6.92 atm abs, to the maximum pressure of the system, 142.4 atm abs. Activity coefficients are calculated, and a thermodynamic consistency test is applied.

The gas-liquid equilibrium of the O_2–CO_2 system at low temperatures has been studied in detail previously (*2*, *4*, *6*). Partly to verify and partly to complete the previous work (*2*) where the high-pressure range of the isotherm is missing, a series of gas- and liquid-phase equilibrium compositions were determined at −49.4°C for pressure up to the maximum, 142.4 atm abs. Activity coefficients based on the unsymmetric normalization are calculated, and a thermodynamic consistency test is performed.

EXPERIMENTAL

The apparatus used here is of the vapor-recirculation type and is discussed in detail elsewhere (*1*). The central unit of the vapor-recirculation apparatus is the cell containing a sta-

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[1] To whom correspondence should be addressed.