

Activity Coefficients and Excess Gibbs Free Energies of 1,2-Dichloroethane with Isomeric Butanols

Abburli Krishnalah*

Department of Chemistry, S. V. U. College of Engineering, Tirupati 517 502, India

V. Nettam Choudary

Department of Chemical Engineering, I. I. T., Bombay 400 076, India

Isobaric boiling point data for the binary liquid mixtures of 1,2-dichloroethane with 1-butanol, isobutyl alcohol, *sec*-butyl alcohol, and *tert*-butyl alcohol are obtained over the entire composition range by using standard Swietoslowski-type ebullometer at 760 mmHg. The experimental $t-x$ data are used to estimate Wilson parameters and also used to calculate the equilibrium vapor compositions for these systems. These Wilson parameters are used to calculate activity coefficients and these in turn are used to compute excess Gibbs free energy. Excess Gibbs free energies are positive over the entire range of composition in all the systems. Further, these properties are also obtained by using the UNIFAC model.

Introduction

Distillation has been used as an effective means of separation in chemical processing. Evidently an accurate and complete knowledge of vapor-liquid equilibrium data on the mixture under consideration is necessary for the design of separation equipment. Generally vapor-liquid equilibrium data are obtained under two fixed conditions, namely, isothermal and isobaric. Most distillation processes are carried out at constant pressure rather than at constant temperature, so that the temperature-composition curves are more practical in making calculations such as the number of plates, although for theoretical consideration the pressure-composition curves are preferable. Hence, an attempt is made to determine the isobaric boiling points and to calculate vapor compositions, activity coefficients, and excess Gibbs free energies for the systems of 1,2-dichloroethane with isomeric butanols at 760 mmHg.

Experimental Section

The isobaric vapor-liquid equilibrium measurements are made in a Swietoslowski ebullometer (1). The ebullometer is connected to a pressure controlling system. The pressure is measured with a mercury-filled U-tube manometer with an accuracy of ± 1 mmHg. The equilibrium temperatures are measured by a standard mercury-in-glass thermometer having an accuracy of ± 0.1 °C. In order to obtain a more reliable equilibrium temperature, stem correction is made for the mercury thermometer readings. The detailed procedure is described elsewhere (1).

The boiling points for the systems of 1,2-dichloroethane with isomeric butanols are determined over the entire range of composition. Mixtures of different compositions are made by taking suitable quantities (by weight) of the pure materials. The equilibrium compositions are not determined experimentally. The liquid compositions are assumed from the gravimetric composition of the mixture. Vapor compositions are estimated by using Wilson equations. The boiling points for the known

Table I. Boiling Points and Densities (at 303.15 K) of Pure Components

component	boiling point, °C		density, g cm ⁻³	
	present work	lit.	present work	lit.
1,2-dichloroethane	83.4	83.5	1.238 30	1.238 31
<i>n</i> -butyl alcohol	117.6	117.7	0.802 03	0.802 06
isobutyl alcohol	107.7	107.7	0.794 32	0.794 37
<i>sec</i> -butyl alcohol	99.5	99.6	0.798 91	0.798 95
<i>tert</i> -butyl alcohol	82.4	82.4	0.775 64	0.775 70

binary composition are measured at 760 mmHg.

Purification of Materials. 1,2-Dichloroethane (BDH) is further purified by the standard method described by Riddick and Bunger (2). 1-Butanol (Glaxo, AR), isobutyl alcohol (SD, AR), *sec*-butyl alcohol (BDH), and *tert*-butyl alcohol (Glaxo, AR) are dried over Drierite and fractionally distilled. The purity of the samples is checked by measuring densities and boiling points. The densities are measured with a bicapillary pycnometer with an accuracy of $\pm 5 \times 10^{-5}$ g cm⁻³. The measured values are in good agreement with the literature values (2, 3). The data are shown in Table I.

Results and Discussion

The experimentally determined $t-x$ values are used for the data reduction. The model for expressing the composition and temperature dependence is chosen to be the Wilson equation (4).

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

$$\ln \lambda_2 = -(\ln x_2 + \Lambda_{21}x_1) - x_1 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right] \quad (2)$$

The Wilson parameters Λ_{12} and Λ_{21} are given by

$$\Lambda_{12} = \frac{v_2^L}{v_1^L} \exp \left[-\frac{(\lambda_{12} - \lambda_{11})}{RT} \right] \quad (3)$$

$$\Lambda_{21} = \frac{v_1^L}{v_2^L} \exp \left[-\frac{(\lambda_{21} - \lambda_{22})}{RT} \right] \quad (4)$$

where v_1^L and v_2^L are liquid molar volumes, $(\lambda_{12} - \lambda_{11})$ and $(\lambda_{12} - \lambda_{22})$ are temperature-independent (to some extent) Wilson parameters. λ 's are the energies of interaction between the molecules designated in the subscripts. The optimum Wilson parameters λ_{12} and λ_{21} are obtained by minimizing the objective

Table II. Values of the Wilson's Parameters

system	Λ_{12}	Λ_{21}
1,2-DCE + 1-butanol	153.83	821.17
1,2-DCE + isobutyl alcohol	150.75	869.01
1,2-DCE + <i>sec</i> -butyl alcohol	396.45	351.29
1,2-DCE + <i>tert</i> -butyl alcohol	582.22	122.84

Table III. Average Deviation from Experimental Data

system	av deviation	
	temp, °C	press., mmHg
1,2-dichloroethane + 1-butanol	0.23	6.3
1,2-dichloroethane + isobutyl alcohol	0.23	6.1
1,2-dichloroethane + <i>sec</i> -butyl alcohol	0.22	5.8
1,2-dichloroethane + <i>tert</i> -butyl alcohol	0.25	6.4

function ϕ , using Nelder-Mead optimization techniques (5). The objective function is defined as

$$\phi = \left[\frac{P_{\text{calcd}}}{P_{\text{exptl}}} - 1.0 \right]^2 \quad (5)$$

Wilson parameters so obtained are included in Table II. The estimated temperatures and pressures, using Wilson's con-

stants, are compared with the experimental data and the average deviations are shown in Table III.

Since the prediction of vapor-liquid equilibrium data involves the vapor pressure data of the pure components, the same are determined for 1,2-dichloroethane and isomeric butanols. If vapor-phase nonidealities are neglected, which is justified, the vapor compositions can be obtained by using the following equation

$$y_1 = \frac{x_1 P_1^s \gamma_1^s}{P_{\text{calcd}}} \quad (6)$$

The data are checked for thermodynamic consistency in terms of area test.

The excess Gibbs free energies are calculated from the activity coefficients by using the equation

$$G^E/RT = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \quad (7)$$

The boiling points, liquid composition, and vapor composition along with the activity coefficients, and excess Gibbs free energy predicted both on the basis of Wilson parameters and UNIFAC model are presented in Table IV.

The excess Gibbs free energies are positive over the entire range of composition. The values of G^E fall in the order isobutyl

Table IV. T - x_1 - y_1 - γ_1 - γ_2 - G^E Data for 1,2-Dichloroethane with Isomeric Butanols at 760 mmHg

T, °C	x_1	y_1	Wilson			UNIFAC		
			γ_1	γ_2	G^E , cal mol ⁻¹	γ_1	γ_2	G^E , cal mol ⁻¹
1,2-DCE + 1-Butyl Alcohol								
113.2	0.0201	0.0981	1.9852	1.0002	10.5	2.2098	1.0002	12.4
112.5	0.0496	0.2138	1.9153	1.0011	25.5	2.1426	1.0014	30.0
108.2	0.1028	0.3748	1.8396	1.0049	50.8	2.0393	1.0063	59.8
98.1	0.2566	0.6370	1.6304	1.0350	111.4	1.7551	1.0456	130.9
91.2	0.4443	0.7777	1.4003	1.1297	157.4	1.4505	1.1695	182.6
87.4	0.6076	0.8440	1.2315	1.3107	166.7	1.2413	1.4027	189.2
86.0	0.7525	0.8861	1.1099	1.6445	143.9	1.1042	1.8110	158.1
84.4	0.8949	0.9333	1.0256	2.4171	88.2	1.0212	2.6420	86.0
83.8	0.9526	0.9626	1.0059	3.0696	41.7	1.0046	3.2346	42.6
83.6	0.9806	0.9825	1.0011	3.5387	18.1	1.0008	3.6103	18.2
1,2-DCE + Isobutyl Alcohol								
106.2	0.0258	0.0970	1.9939	1.0003	13.6	2.0110	1.0003	13.8
103.9	0.0563	0.1947	1.9479	1.0014	29.1	1.9592	1.0017	29.6
100.3	0.1028	0.3166	1.8795	1.0049	51.4	1.8828	1.0059	52.2
93.2	0.2579	0.5648	1.6559	1.0359	113.7	1.6310	1.0423	114.2
88.3	0.4046	0.6906	1.4661	1.1041	153.5	1.4246	1.1206	151.6
85.6	0.5987	0.7855	1.2511	1.3031	171.3	1.2059	1.3347	162.5
84.1	0.7521	0.8413	1.1164	1.6633	148.3	1.0846	1.6744	134.1
83.1	0.9011	0.9060	1.0245	2.5526	81.1	1.0149	2.3187	68.3
83.2	0.9510	0.9418	1.0068	3.1818	44.7	1.0038	2.6605	36.5
83.3	0.9808	0.9730	1.0011	3.7390	18.7	1.0006	2.9118	15.0
1,2-DCE + <i>sec</i> -Butyl Alcohol								
98.5	0.0213	0.0712	2.1901	1.0003	12.6	2.2815	1.0003	13.2
95.6	0.0559	0.1698	2.0960	1.0023	31.9	2.2085	1.0019	33.7
93.3	0.1077	0.2833	1.9585	1.0088	58.5	2.0925	1.0072	62.7
89.2	0.2528	0.4806	1.6380	1.0511	116.7	1.7897	1.0451	129.7
86.1	0.4015	0.5982	1.3966	1.1387	151.2	1.5269	1.1334	174.8
83.6	0.6020	0.7079	1.1747	1.3609	155.7	1.2483	1.3930	189.5
82.8	0.7809	0.8021	1.0552	1.7369	115.2	1.0841	1.9403	147.3
83.0	0.8999	0.8870	1.0122	2.1651	62.4	1.0193	2.6939	82.4
83.1	0.9455	0.9314	1.0037	2.3933	36.1	1.0060	3.1513	48.3
83.3	0.9804	0.9728	1.0005	2.6011	13.6	1.0006	3.6413	25.4
1,2-DCE + <i>tert</i> -Butyl Alcohol								
81.5	0.0248	0.0546	2.3557	1.0006	15.4			
80.7	0.0658	0.1295	2.1855	1.0043	39.0			
80.1	0.1084	0.1923	2.0301	1.0115	61.0			
77.4	0.2603	0.3476	1.6179	1.0659	120.1			
76.7	0.4063	0.4454	1.3603	1.1628	149.2			
76.8	0.6056	0.5601	1.1460	1.3856	146.8			
78.0	0.7547	0.6613	1.0549	1.6501	113.9			
80.4	0.8987	0.8111	1.0093	2.0300	56.3			
81.8	0.9437	0.8811	1.0029	2.1830	31.0			
82.7	0.9788	0.9501	1.0004	2.3183	12.9			

alcohol > 1-butanol > *sec*-butyl alcohol > *tert*-butyl alcohol. A comparison of γ 's and G^E obtained from Wilson parameters with those computed by using the UNIFAC model (6) indicates that the UNIFAC method provides a reasonable estimate of the solution behavior. In the case of 1,2-dichloroethane + *tert*-butyl alcohol, the properties are not predicted on the basis of UNIFAC model as the interaction parameters for methyl groups in *tert*-butyl alcohol are not available.

Acknowledgment

We are thankful to Prof. A. P. Kudchadkar and Dr. (Mrs.) Mukhopadhyay, Department of Chemical Engineering, I. I. T., Bombay, for providing the necessary facilities to carry out this work.

Glossary

x	mole fraction in liquid phase
y	vapor composition
T	temperature, K
t	temperature, °C

Greek Letters

γ	activity coefficient
Λ	Wilson parameter

Subscripts

1	1,2-dichloroethane
2	isomeric butanols

Superscripts

G^E	excess Gibbs free energy
-------	--------------------------

Registry No. *n*-Butyl alcohol, 71-36-3; isobutyl alcohol, 78-83-1; *sec*-butyl alcohol, 78-92-2; *tert*-butyl alcohol, 75-65-0; 1,2-dichloroethane, 107-06-2.

Literature Cited

- (1) Hala, E.; Pick, J.; Fried, V.; Villim, O. *Vapour-Liquid Equilibrium*; Pergamon: Oxford, 1967.
- (2) Riddick, J. A.; Bunger, W. B. *Organic Solvents*; Wiley-Interscience: New York, 1970.
- (3) Timmermans, J. *Physico-chemical Constants of Pure Organic Compounds*; Elsevier: New York, 1965.
- (4) Wilson, G. M. *J. Am. Chem. Soc.* **1964**, *86*, 127.
- (5) Kuester, R. T.; Mize, J. H. *Optimization Techniques with Fortran*; McGraw-Hill: New York, 1973.
- (6) Francesconi, R.; Trevisol, C. *Chem. Eng. Sci.* **1966**, *21*, 123.

Received for review May 7, 1986. Revised manuscript received October 3, 1986. Accepted December 10, 1986.

Isobaric Vapor-Liquid Equilibria for Binary Mixtures of Ethylbenzene and *p*-Xylene with Dimethylformamide

O. P. Bagga,* Virender K. Rattan, Sukhmehar Singh, Bhupinder P. S. Sethi, and K. S. N. Raju†

Department of Chemical Engineering and Technology, Panjab University, Chandigarh 160 014, India

Isobaric vapor-liquid equilibrium data for the systems ethylbenzene-dimethylformamide and *p*-xylene-dimethylformamide were obtained at 760 mmHg pressure by using a vapor recirculating type of equilibrium still. Both the systems form minimum-boiling azeotropes. The activity coefficient data were tested for thermodynamic consistency by the methods of Herrington, Black, and Norrish and Twigg and correlated by the van Laar, Wilson, and Redlich-Kister equations.

Introduction

Petroleum fractions, especially from the catalytic reforming processes, are sources of C_8 aromatics. Mixtures of C_8 aromatics containing xylene and ethylbenzene are difficult to separate into pure components as the isomers are close boiling, having a relative volatility close to unity. *p*-Xylene and ethylbenzene form the closest boiling pair with about 2 °C difference in the boiling points. Knowledge of vapor-liquid equilibria between ethylbenzene or *p*-xylene and different classes of compounds will be of importance in the development of alternative distillation processes for their separation. Isobaric vapor-liquid equilibrium data were obtained for the systems ethylbenzene-dimethylformamide and *p*-xylene-dimethylformamide at 760 ± 2 mmHg pressure by using a vapor recirculating type of equi-

librium still. Experimental data for these systems have not been reported in the literature.

Experimental Section

Ethylbenzene from British Drug House, England, *p*-xylene from Riedel, Germany, and dimethylformamide, also from Riedel, were first dried by keeping over anhydrous magnesium sulfate for 48 h with occasional shaking. Ethylbenzene and *p*-xylene were further dried with metallic sodium whereas dimethylformamide (DMF) was dried with phosphorus pentoxide for extreme desiccation (1). The dried and filtered materials were further purified by distillation in a glass column described elsewhere (2). Ethylbenzene and *p*-xylene were distilled at the prevailing atmospheric pressure whereas dimethylformamide was distilled under vacuum. The vacuum was adjusted to collect the purified sample at 78 °C. Table I summarizes some of the physical properties of the reagents used.

A modified version of the equilibrium still described by Rao and co-workers (6) was used for obtaining the vapor-liquid equilibrium data. The equilibrated mixtures were analyzed at 35 ± 0.1 °C by density measurements. Density measurements were made with a pycnometer calibrated with conductivity water. Triplicate density measurements were identical within ±0.0003 g/mL.

The samples were maintained at the temperature of analyses in an ultrathermostat (Metrimpex, Hungary). The temperature was controlled to within ±0.1 °C by means of a "merc-to-merc" magnetically adjusted thermoregulator supplied by the

* Presently Visiting Professor and Chairman, Department of Chemical Engineering, Bright Star University of Technology, Ajdabia, Libya.