Vapor−Liquid Equilibria for the Binary Systems of Dimethoxymethane with Some Fuel Oxygenates

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Isobaric vapor−liquid equilibrium data at 95.96 kPa for the three binary systems of dimethoxymethane with methyl *tert*-butyl ether, diisopropyl ether, and 2-propanol are determined. A Swietoslawski-type ebulliometer is used for the measurements. The experimental $T-x$ data are used to estimate Wilson parameters, and the parameters is in turn are used to calculate vapor compositions and activity coefficients. The activity coefficients are useful for calculating the excess Gibbs function (G^E/RT). None of the systems studied here exhibit azeotropes. Excess Gibbs function values are positive over the entire range of composition for all of the systems.

1. Introduction

Recently, several fuel oxygenates have been used to enhance the octane number of gasoline and to improve air quality by reducing air pollution. Generally, ethers and alkanols are added to gasoline as oxygenates to replace lead antiknock agents. Methyl *tert*-butyl ether (MTBE) has been used extensively as a gasoline additive, but it dissolves easily in water and causes a health risk by contaminating drinking water.[1] In addition, it is resistant to microbial decomposition. These facts have promoted research on the possible use of several oxygenates that have low solubility in water and are harmless to the environment. Diisopropyl ether (DIPE), dimethoxymethane (DMM), 2-propanol, dimethyl carbonate (DMC), and diethyl carbonate (DEC) have some advantages over MTBE. Diisopropyl ether is effective in reducing automobile CO emissions and has been considered to be a good alternative to MTBE. Dimethoxymethane (DMM) is a potential oxygenate for diesel fuel.[2] Test results indicate that the addition of 30% DMM to diesel fuel results in a reduction of particulate matter; however, NO_x emissions remain unaffected.[3]

Phase equilibrium data of these oxygenated mixtures are important for predicting the vapor-phase composition that would be in equilibrium with hydrocarbons. Recently, several papers have been published on the VLE of binary systems of oxygenates. Rodriguez et al.[4] have reported isobaric phase equilibria of diethyl carbonate with five alcohols at 101.3 kPa. Sojinpark et al.[5] have reported isothermal and isobaric VLE data for the binary systems of MTBE with C_1 to C_4 alcohols. Juan Antoni et al.[6] studied isothermal VLE data for the binary systems of MTBE with methanol and 1-butanol at 298.15 K. Jaime Wisnaik et al.[7] have reported isobaric vapor−liquid equilibria for the binary systems of MTBE + 2,2′-oxybis (propane) and MTBE + 1,3-dioxolane at 94 kPa. Wisnaik[8] has reported isobaric vapor−liquid equilibria data for the binary systems of oxolane + MTBE and oxolane + 2-propanol at 94 kPa, and Francesconi et al.[9] have reported isothermal vapor−liquid equilibria for the binary systems of MTBE with dialkyl carbonates at 298.15 K. In the present work, we report new experimental data for the isobaric vapor−liquid equilibrium for the binary systems of dimethoxymethane + methyl *tert*-butyl ether, dimethoxymethane + diisopropyl ether, and dimethoxymethane + 2-propanol at 95.96 kPa. A search of the literature indicates that no VLE data have been reported for these systems.

Table 1. Comparison of the Density ρ at 298.15 K and the Boiling Points of the Pure Components with Literature Data

	T_{bp}/K		ρ/kg·m^{-3}	
component	expt	lit	expt	lit
dimethoxymethane	315.25	315.45[a]	847.51	847.45[a]
methyl *tert*-butyl ether	328.25	328.35[b]	735.42	735.28[c]
diisopropyl ether	341.35	341.45[a]	718.14	718.2[a]
2-propanol	355.15	355.35[a]	781.38	781.26[a]

[a] Riddick et al.[10] [b] TRC, 1996.[11] [c] Daubert et al.[12]

2. Experimental Section

Materials. All of the chemicals except 2-propanol are from the Merck Company with a guaranteed purity of 99.5%. HPLC-grade 2-propanol was supplied by Spectrochem Pvt. Ltd. (Mumbai, India). The reagents were used without further purification after gas chromatography failed to show any significant impurities. The purity of the samples was checked by comparing the measured densities and boiling points of the components with those reported in the literature.[10−12] The data are presented in Table 1. The densities were measured with a bicapillary pycnometer described by Rao and Naidu.[13] The values are reproducible to $\pm 5 \times 10^{-2}$ kg·m^3.

Apparatus and Procedure. A Swietoslawski ebulliometer, similar to the one described by Hala et al.,[14] was used for the experimental investigation. The ebulliometer was connected to a pressure-controlling system. The pressure was controlled by a Cartesian diver and was measured with an accuracy of ±1 mmHg. The equilibrium temperatures were measured with an accuracy of ±0.1 K by means of a resistance thermometer carefully calibrated by means of a point-to-point comparison with a standard platinum resistance thermometer certified by the National Bureau

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Table 2. T−x_1−y_1 Data, Activity Coefficients, and Dimensionless Excess Gibbs Function for Dimethoxymethane (1) + Methyl *tert*-Butyl Ether (2) at 95.96 kPa

x_1	T_{exptl}/K	T_{calcd}/K	$y_{1,\mathrm{calcd}}$	γ_1	γ_2	G^E/RT
0.0000	326.55	326.55	0.0000	1.3483	1.0000	0
0.1034	323.65	323.75	0.1814	1.2436	1.0044	0.026
0.1813	322.05	322.15	0.2868	1.1843	1.0127	0.041
0.2571	320.95	320.85	0.3744	1.1388	1.0240	0.051
0.3498	319.55	319.45	0.4685	1.0961	1.0413	0.058
0.4800	317.95	317.95	0.5860	1.0539	1.0707	0.061
0.5764	316.85	316.95	0.6667	1.0327	1.0955	0.057
0.6750	316.15	316.05	0.7460	1.0177	1.1227	0.049
0.7687	315.35	315.35	0.8197	1.0083	1.1501	0.038
0.8493	314.65	314.75	0.8826	1.0033	1.1745	0.027
0.9432	314.15	314.15	0.9557	1.0004	1.2038	0.011
1.0000	313.75	313.75	1.0000	1.0000	1.2218	0

Table 3. T−x_1−y_1 Data, Activity Coefficients, and Dimensionless Excess Gibbs Function for the System Dimethoxymethane (1) + Diisopropyl Ether (2) at 95.96 kPa

x_1	T_{exptl}/K	T_{calcd}/K	$y_{1,\mathrm{calcd}}$	γ_1	γ_2	G^E/RT
0.0000	339.95	339.95	0.0000	2.1796	1.0000	0
0.0564	334.45	334.45	0.2087	1.8604	1.0048	0.039
0.1207	330.65	330.65	0.3426	1.6093	1.0194	0.074
0.2245	326.75	326.75	0.4750	1.3583	1.0563	0.111
0.3545	323.55	323.55	0.5889	1.1867	1.1158	0.131
0.4516	321.55	321.55	0.6598	1.1126	1.1656	0.132
0.5534	319.85	319.85	0.7281	1.0632	1.2203	0.123
0.6870	317.85	317.85	0.8129	1.0256	1.2936	0.098
0.7981	316.35	316.35	0.8807	1.0092	1.3545	0.068
0.9081	314.85	314.85	0.9463	1.0017	1.4140	0.033
1.0000	313.75	313.75	1.0000	1.0000	1.4627	0

Table 4. T−x_1−y_1 Data, Activity Coefficients, and Dimensionless Excess Gibbs Function for the System Dimethoxymethane (1) + 2-Propanol (2) at 95.96 kPa

x_1	T_{exptl}/K	T_{calcd}/K	$y_{1,\mathrm{calcd}}$	γ_1	γ_2	G^E/RT
0.0000	354.05	354.05	0.0000	1.8723	1.0000	0
0.0654	345.95	345.95	0.3320	1.8142	1.0011	0.039
0.1294	339.55	339.55	0.5282	1.7579	1.0044	0.076
0.2710	329.35	329.35	0.7501	1.6337	1.0231	0.149
0.3497	325.35	325.35	0.8136	1.5642	1.0432	0.184
0.4264	322.25	322.25	0.8556	1.4960	1.0732	0.212
0.5014	319.85	319.85	0.8849	1.4286	1.1171	0.234
0.5723	317.95	317.95	0.9054	1.3643	1.1787	0.248
0.6817	315.85	315.85	0.9284	1.2642	1.3427	0.253
0.8426	314.05	314.05	0.9510	1.1166	2.0504	0.206
0.9187	313.65	313.65	0.9603	1.0499	3.2930	0.141
1.0000	313.75	313.75	1.0000	1.0000	15.1160	0

Table 5. Antoine Constants of the Components

component	A	B	C
dimethoxymethane[a]	7.10401	1162.58	233.15
methyl *tert*-butyl ether[b]	6.89117	1126.59	225.86
diisopropyl ether[a]	6.85188	1143.07	219.34
2-propanol[a]	7.74128	1360.13	197.59

[a] Riddick et al.[10] [b] Aim et al.[17]

Table 6. Representation of the Measurements by the Wilson Model

system	$[\Delta\lambda_{12}/R]$/K	$[\Delta\lambda_{21}/R]$/K	σ/K
dimethoxymethane (1) + methyl *tert*-butyl ether (2)	214.8	−108.23	0.079
dimethoxymethane (1) + diisopropyl ether (2)	415.75	−134.96	0.034
dimethoxymethane (1) + 2-propanol (2)	−72.4	944.4	0.018

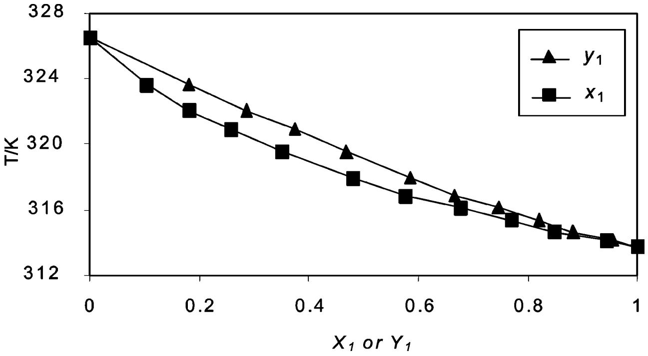

Figure 1. T−x_1−y_1 data for dimethoxymethane (1) + methyl *tert*-butyl ether (2).

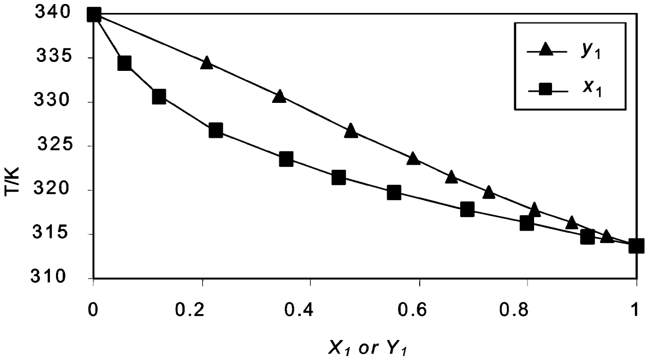

Figure 2. T−x_1−y_1 data for dimethoxymethane (1) + diisopropyl ether (2).

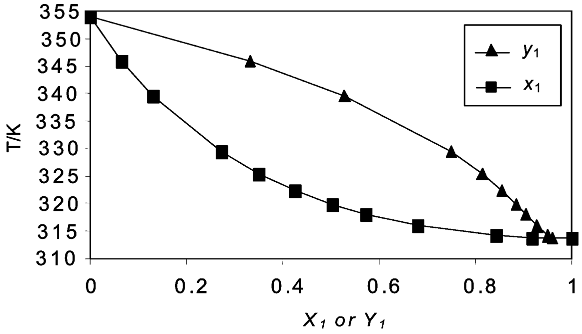

Figure 3. T−x_1−y_1 data for dimethoxymethane (1) + 2-propanol (2).

of Standards (now NIST). Liquid mixtures of the required compositions were prepared gravimetrically with the use of an electronic balance that was precise to ±0.0001 g. The ebulliometer was charged with the mixture of the desired composition, and the boiler was heated by a Nichrome wire wound on the boiler. After the liquid started boiling, the bubbles along with the drops of liquid spurted on the thermowell. After adjusting the pressure to a desired value when vapor−liquid equilibrium was attained, the temperature was measured. Precautions were taken to minimize the loss of components due to evaporation during the preparation and subsequent measurements.

3. Results and Discussion

The experimental liquid mole fraction of DMM (x_1) and boiling temperature (T) for three binary systems are given in Tables 2 to 4. The liquid-phase composition versus temperature data were fitted to the Wilson model[15] in the form of

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

$$l_n\gamma_2 = -l_n(x_2 + \Lambda_{21}x_1) + x_1\left[\frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} - \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2}\right] \quad (2)$$

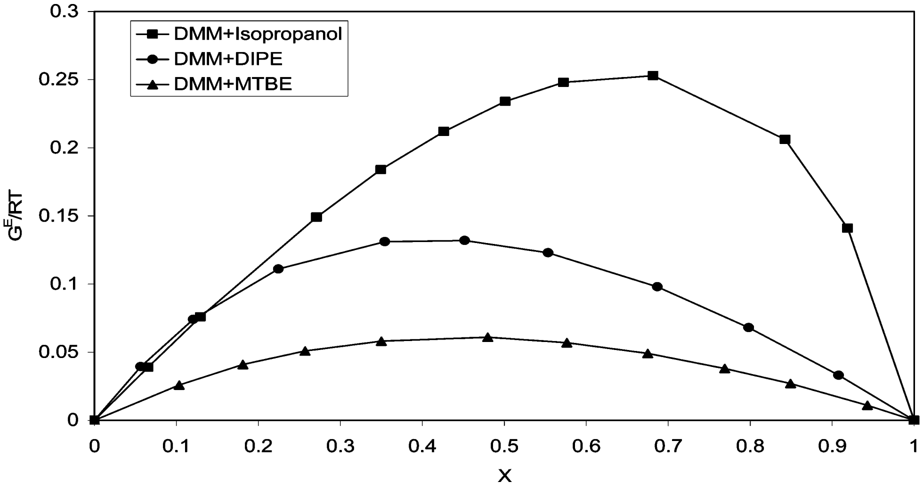

Figure 4. Excess Gibbs function (G^E/RT) vs DMM liquid mole fraction (x_1) for three binary systems.

where

$$\Lambda_{12} = \frac{V_2^L}{V_1^L}\exp\left[-\frac{\Delta\lambda_{12}}{RT}\right] \tag{3}$$

$$\Lambda_{21} = \frac{V_1^L}{V_2^L}\exp\left[-\frac{\Delta\lambda_{21}}{RT}\right] \tag{4}$$

Here V_1^L and V_2^L are the liquid molar volumes and $\Delta\lambda_{12}$ and $\Delta\lambda_{21}$ are the Wilson model constants. The optimum Wilson parameters were obtained by minimizing the objective function defined as

$$S = \Sigma\left[\left(\frac{P_{\text{calcd}}}{P_{\text{exptl}}}\right) - 1\right]^2 \tag{5}$$

where P_{exptl} and P_{calcd} are the experimental and calculated values of the total pressure. The Nelder–Mead optimization technique described by Kuester and Mize[16] was used. Vapor pressure needed in the computations was calculated from the Antoine constants derived from the compilation in the data bank of Riddick et al.[10] and Aim et al.[17] The Antoine constants are given in Table 5 for ready reference. The vapor pressure of compounds was calculated using the Antoine equation.

$$\log[P/\text{mm Hg}] = A - \left[\frac{B}{(t/^\circ\text{C}) + C}\right] \tag{6}$$

The vapor-pressure data of pure liquids obtained using eq 6 are in agreement with the experimental values with an average absolute deviation of 0.6%. Molar volumes of liquids were calculated from the liquid density data of the present work recorded in Table 1. Critical properties and the other input data required for the estimation are collected from Ried et al.[18] The values of Wilson parameters along with standard deviations are given in Table 6.

Activity coefficients computed on the basis of the Wilson model are used to evaluate the excess Gibbs free energy at 95.96 kPa for three binary systems over the entire range of composition. Calculated boiling points (T_{calcd}), vapor-phase mole fractions (y_1) of DMM, the liquid-phase activity coefficients (γ_1 and γ_2), and dimensionless excess Gibbs functions (G^E/RT) are included in Tables 2 to 4. The $T-x_1-y_1$ plots are shown in Figures 1 to 3, and plots of the Gibbs free energy versus the liquid-phase mole fraction of DMM (x_1) are given in Figure 4. An observation of the plots in Figures 1 to 3 indicates that the binary system dimethoxymethane + methyl *tert*-butyl ether deviates slightly from ideal behavior, dimethoxymethane + diisopropyl ether deviates moderately from ideal behavior, and dimethoxymethane + 2-propanol behaves as a regular solution. None of the systems studied here exhibits an azeotrope. The excess Gibbs function values are positive over the entire range of composition for all of the systems. G^E/RT values follow the order DMM (1) + 2-propanol (2) > DMM (1) + DIPE (2) > DMM (1) + MTBE (2). Positive excess Gibbs functions have been reported by Wisnaik[8] for the systems MTBE + oxolane and 2-propanol + oxolane. G^E/RT is maximized at an equimolar fraction in systems of DMM with ethers, and the maximum value shifts to about 0.68 mole fraction of DMM in the mixture of DMM with 2-propanol.

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