Vapor−Liquid Equilibria and Excess Enthalpies for Binary Systems of Dimethoxymethane with Hydrocarbons

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Isobaric vapor−liquid equilibrium data at 95.96 kPa for the three binary systems of dimethoxymethane with hexane, cyclohexane, and benzene are determined. A Swietoslawski-type ebulliometer is used for the measurements. The experimental $T-x$ data are used to estimate Wilson parameters, and these parameters in turn are used to calculate vapor-phase compositions and activity coefficients. The activity coefficients are useful to calculate excess Gibbs function (G^E/RT). All the systems studied here do not exhibit azeotropes. Excess Gibbs function values are positive over the entire range of composition for all the systems. Excess enthalpies are reported for the binary systems of dimethoxymethane with hexane, cyclohexane, and benzene at 298.15 K. The H^E data are interpreted on the basis of intermolecular interactions between unlike molecules.

Introduction

Modern environmentally beneficial methods of reformulating motor gasoline often use ethers and alcohols as octane enhancers and also to improve air quality by reducing pollutants in the atmosphere. Methyl *tert*-butyl ether (MTBE) has been used extensively as gasoline additive. However, it dissolves easily in water and causes health risk by the contamination of 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 (IPA), dimethyl carbonate (DMC), and diethyl carbonate (DEC) have some advantages over MTBE. Dimethoxymethane (DMM) is a potential oxygenate for diesel fuel.[2] Test results indicate that addition of 30 % DMM to diesel fuel results in reduction of particulate matter, while 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. The heat of mixing of two components is of importance in design calculations involving chemical separation and fluid flow and is a direct measure of their molecular interactions. As a part of our work on thermodynamic and transport properties of octane boosters,[4−6] this paper reports new experimental data for isobaric vapor−liquid equilibrium (VLE) at 95.96 kPa and excess enthalpy data on the binary systems of dimethoxymethane with C_6 hydrocarbons at 298.15 K. A search in the literature indicates that Treszczanowicz et al.[7−12] reported VLE data for some binary systems of dimethoxymethane with hydrocarbons.

Experimental Section

Materials. All the chemicals except dimethoxymethane are from S. D. Fine Chemicals (Mumbai, India) with purity greater than 99.5 mass %. Dimethoxymethane with purity 99 mass % was supplied by E. Merk 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 by Riddick et al.[13] The experimental values agree well with literature values. The densities were measured with a bicapillary pycnometer previously described by Rao and Naidu.[14] The values are reproducible to $\pm 5 \times 10^{-2}$ kg·m^{-3} and have an uncertainty of 0.1 kg·m^{-3}. The data are presented in Table 1.

Table 1. Boiling Points (T_{bp}) and Densities (ρ) at 298.15 K of the Pure Components

	T_{bp}/K		ρ/kg·m^{-3}	
component	expt	lit	expt	lit
dimethoxymethane	315.25	315.45	847.51	847.45
hexane	341.85	341.89	654.90	654.81
cyclohexane	353.95	353.87	773.98	773.89
benzene	353.15	353.25	873.64	873.70

Apparatus and Procedure. A Swietoslawski ebulliometer, similar to the one described by Hala et al.,[15] was used for the VLE measurements. The ebulliometer was connected to a pressure controlling system. The pressure was controlled by Cartesian diver and was measured with an accuracy of ± 0.13 kPa. The equilibrium temperatures were measured to an accuracy of ± 0.1 K by means of a resistance thermometer, carefully calibrated by means of point-to-point comparison with a standard platinum resistance thermometer certified by the National Bureau of Standards (now NIST). The liquid mixtures of required composition were prepared gravimetrically, with the use of an electronic balance that was precise to ± 0.0001 g. The values of mole fraction were reproducible to ± 0.0001 and have uncertainty of 0.1 %. The ebulliometer was charged with the mixture of desired composition, and the boiler was then heated by Nichrome wire wound around the boiler. After the liquid mixture started boiling, the bubbles along with the drops of liquid spurted on the thermowell. After adjusting the pressure to a desired value and when VLE was attained, the temperature was measured. All the precautions were taken to minimize the

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Table 2. $T-x_1-y_1$ Data, Activity Coefficients, and Dimensionless Excess Gibbs Function for Dimethoxymethane (1) + Hexane (2) at 95.96 kPa

x_1	T_{expt}/K	T_{cal}/K	$y_{1,\mathrm{cal}}$	γ_1	γ_2	G^{E}/RT
0	340.15	340.15	0	2.4356	1.0000	0
0.1128	328.55	328.55	0.3893	2.0899	1.0108	0.092
0.2457	321.95	321.95	0.5712	1.7507	1.0539	0.177
0.3372	319.35	319.35	0.6408	1.5649	1.1058	0.217
0.4120	317.75	317.75	0.6828	1.4383	1.1649	0.239
0.5043	316.35	316.35	0.7247	1.3093	1.2635	0.252
0.5964	315.45	315.35	0.7613	1.2060	1.3996	0.247
0.6959	314.45	314.35	0.8001	1.1194	1.6067	0.222
0.7855	313.95	313.95	0.8391	1.0614	1.8733	0.181
0.9015	313.55	313.55	0.9066	1.0139	2.4067	0.098
1	313.75	313.75	1	1.0000	3.1578	0

Table 3. $T-x_1-y_1$ Data, Activity Coefficients, and Dimensionless Excess Gibbs Function for Dimethoxymethane (1) + Cyclohexane (2) at 95.96 kPa

x_1	T_{expt}/K	T_{cal}/K	$y_{1,\mathrm{cal}}$	γ_1	γ_2	G^{E}/RT
0	352.05	352.05	0	2.0706	1.0000	0
0.0782	340.35	340.35	0.3631	1.9546	1.0030	0.055
0.1736	331.55	331.55	0.5705	1.8089	1.0158	0.115
0.2508	326.85	326.85	0.6642	1.6944	1.0355	0.158
0.3444	322.95	322.85	0.7371	1.5631	1.0736	0.200
0.4567	319.45	319.55	0.7941	1.4192	1.1483	0.235
0.5517	317.55	317.65	0.8285	1.3100	1.2486	0.248
0.6511	316.25	316.15	0.8573	1.2087	1.4137	0.244
0.7516	315.15	315.05	0.8834	1.1211	1.6928	0.217
0.8832	314.15	314.05	0.9234	1.0341	2.4625	0.137
0.9298	313.85	313.95	0.9447	1.0138	2.9926	0.089
1	313.75	313.75	1	1.0000	4.4604	0

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

x_1	T_{expt}/K	T_{cal}/K	$y_{1,\mathrm{cal}}$	γ_1	γ_2	G^{E}/RT
0	350.85	350.85	0	2.7074	1.0000	0
0.0615	339.75	339.75	0.3423	2.3867	1.0050	0.058
0.1456	331.75	331.75	0.5359	2.0146	1.0271	0.124
0.2135	327.95	327.95	0.6163	1.7820	1.0569	0.166
0.3003	324.75	324.75	0.6816	1.5559	1.1100	0.205
0.4071	322.05	322.05	0.7369	1.3575	1.1985	0.231
0.4785	320.65	320.65	0.7669	1.2603	1.2732	0.236
0.5617	319.25	319.25	0.7992	1.1731	1.3782	0.230
0.6384	318.15	318.15	0.828	1.1127	1.4942	0.213
0.7555	316.65	316.55	0.8749	1.0489	1.7150	0.167
0.8607	315.25	315.25	0.9221	1.0154	1.9703	0.107
1	313.75	313.75	1	1.0000	2.4211	0

loss of components due to evaporation during the preparation and subsequent measurements. Excess enthalpies were measured using Parr 1451 solution calorimeter. The details of the calorimeter and experimental procedure have been described previously by Krishnaiah et al.[16] The values of H^{E} are reproducible to within ± 1 % and have an uncertainty of 2 %.

Results and Discussion

The experimental liquid mole fraction of DMM (x_1) and boiling temperature (T) data are given in Tables 2 to 4. The liquid-phase composition versus temperature data are fitted to the Wilson model[17] in the form of

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

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

where

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

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

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

$$S = \sum[(P_{\mathrm{cal}}/P_{\mathrm{exp}}) - 1]^2 \quad (5)$$

where P_{exp} and P_{cal} are experimental and calculated values respectively of the total pressure. The Nelder−Mead optimization technique described by Kuester and Mize[18] was used. Here the vapor phase is assumed to be ideal in the evaluation of vapor-phase composition; this assumption is justified as the phase behavior is studied at low pressure.[19] The vapor composition (y_{A}) is calculated from the following equation:

$$y_{\mathrm{A}} = \frac{x_{\mathrm{A}}\gamma_{\mathrm{A}}p_{\mathrm{A}}^{\mathrm{s}}}{p_{\mathrm{cal}}} \quad (6)$$

where

$$p_{\mathrm{cal}} = \sum x_i\gamma_i p_i^{\mathrm{S}}$$

where p_i^{S} is the saturation vapor pressure of component i at temperature T. Vapor pressures needed in the computations were calculated from the Antoine constants derived from the compilation in the data bank of Riddick et al.,[13] and the values of Antoine constants are given in Table 5. The vapor pressure P of compounds (in mmHg) was calculated using the Antoine equation:

$$\log[P/\mathrm{mmHg}] = A - \left[\frac{B}{T/\mathrm{K} + C}\right] \quad (8)$$

where A, B, and C are Antoine constants and T is temperature in Kelvin. The vapor pressure data of pure liquids obtained using eq 8 are in agreement with the experimental values with an average absolute deviation of 0.7 % and maximum deviation of 1.86 %. Molar volumes of liquids were calculated from the liquid density data of the present work. Critical properties and the other input data required for the estimation were collected from Reid et al.[20] The values of Wilson parameters along with standard deviations are given in Table 6. $T-x_1-y_1$ plots for the three binary systems of DMM with C_6 hydrocarbons are shown in Figures 1 to 3. An observation of the plots in Figures 1 to 3 indicates that the binary systems of dimethoxymethane with C_6 hydrocarbons exhibit positive deviation from ideal behavior. All the systems studied here do not form azeotropes. The same behavior was observed by Treszczanowicz et al. for the binary systems of DMM (1) + cyclohexane (2)[7] and DMM (1) + hexane (2).[10] Activity coefficients computed on the basis of Wilson model were used to evaluate dimensionless excess Gibbs function at 95.96 kPa for three binary systems over the entire range of composition. Calculated boiling points (T_{cal}), vapor-phase mole fractions (y_1) of DMM, the liquid-phase activity coefficients (γ_1 and γ_2), and dimensionless excess Gibbs function (G^{E}/RT) are included in Tables 2 to 4. The plots of excess Gibbs function (G^{E}/RT) versus liquid-phase mole fraction of DMM (x_1) are given in Figure 4. The excess Gibbs function

Table 5. Antoine Constants[a] of the Components

component	*A*	*B*	*C*
dimethoxymethane	7.10401	1162.58	−40
hexane	6.87601	1171.17	−48.74
cyclohexane	6.83917	1200.31	−50.65
benzene	6.89710	1206.53	−52.24

[a] $\log [P/\text{mmHg}] = A - [B/(T/\text{K} + C)]$.

Table 6. Representation of the Measurements by the Wilson Model

system	$[\Delta\lambda_{12}/R]$/K	$[\Delta\lambda_{21}/R]$/K	σ^a/K
dimethoxymethane (1) + hexane (2)	156.2	225.8	0.04
dimethoxymethane (1) + cyclohexane (2)	33.30	435.8	0.07
dimethoxymethane (1) + benzene (2)	297.5	65.56	0.03

[a] $\sigma/\text{K} = [(\sum(T_{\text{exp}} - T_{\text{cal}})^2)/n]^{1/2}$.

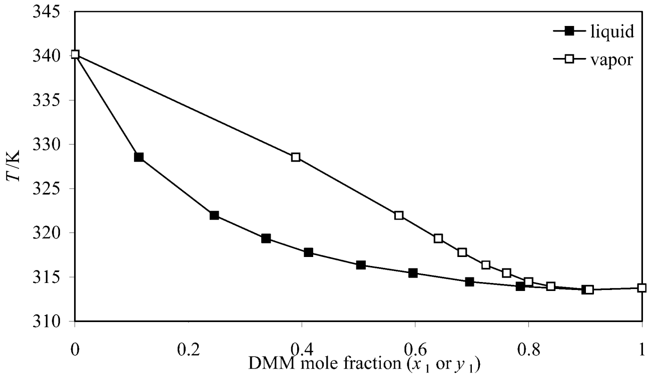

Figure 1. $T-x_1-y_1$ data for DMM (1) + hexane (2) at 95.96 kPa.

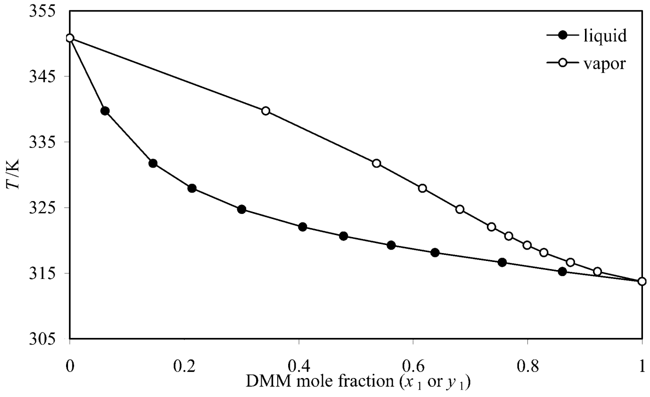

Figure 2. $T-x_1-y_1$ data for DMM (1) + cyclohexane (2) at 95.96 kPa.

values are positive over the entire range of composition for all the systems. G^E/RT values follow the order DMM (1) + hexane (2) > DMM (1) + cyclohexane (2) > DMM (1) + benzene (2). G^E/RT is maximized at an equimolar fraction in systems of DMM with benzene and hexane, and the maximum value is skewed toward high ether mole fraction range in case of DMM with cyclohexane. The VLE data presented in Tables 2 to 4 were found to be thermodynamically consistent by the area test method of Herington.[19] The Wilson parameters determined in this work have been utilized to predict the vapor-phase mole fraction for the binary mixtures of DMM (1) + cyclohexane (2) and DMM (1) + benzene (2) systems at the conditions given by Treszczanowicz et al.[7,10] The vapor-phase mole fractions predicted from the present work deviated from the vapor-phase composition reported by Treszczanowicz et al.[7,10] with average absolute deviations of 0.013 and 0.063 respectively for the DMM (1) + cyclohexane (2) and DMM (1) + benzene (2).

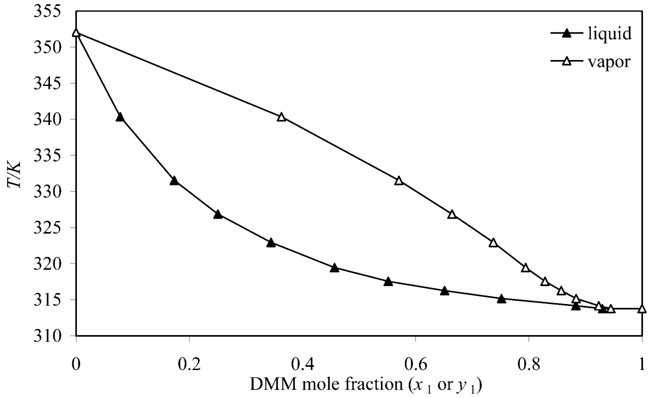

Figure 3. $T-x_1-y_1$ data for DMM (1) + benzene (2) at 95.96 kPa.

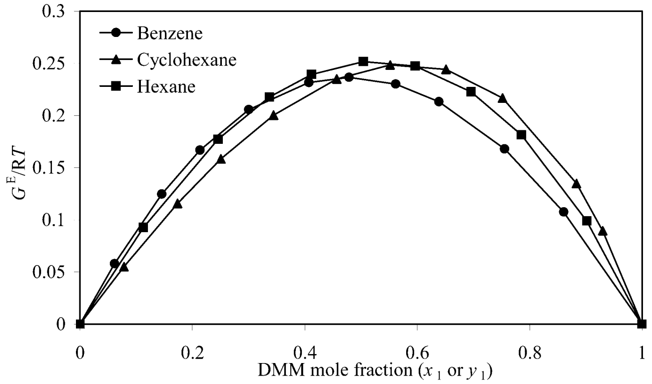

Figure 4. Excess Gibbs functions (G^E/RT) vs DMM mole fraction (x_1) for three binary systems.

Table 7. Mole Fraction of DMM and Excess Enthalpy H^E for the Binary Systems of DMM with C_6 Hydrocarbons at 298.15 K

DMM (1) + hexane (2)		DMM (1) + cyclohexane (2)		DMM (1) + benzene (2)	
x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
0.0576	277	0.0659	341	0.0561	42
0.1238	538	0.1321	630	0.1140	70
0.1942	757	0.2046	870	0.1671	88
0.3159	1033	0.2797	1068	0.2700	113
0.3900	1128	0.3488	1191	0.3228	118
0.5076	1205	0.4173	1279	0.3836	119
0.5787	1196	0.4784	1322	0.4404	117
0.6973	935	0.5335	1325	0.6190	104
0.7374	863	0.5851	1303	0.6685	97
0.8112	695	0.6481	1101	0.7134	88
0.8393	607	0.7360	943	0.7550	78
0.8788	475	0.7727	852	0.8018	61
0.9522	210	0.8132	744	0.9471	15
		0.8538	615		
		0.9008	428		
		0.9471	235		

The experimental values of H^E are given in Table 7. The data are fitted to an empirical equation in the form of

$$H^E = x(1-x)\Big[\sum_{i=0}^{3} h_i(2x-1)^i\Big] \qquad (9)$$

where *x* is the mole fraction of dimethoxymethane. The values of parameters h_i have been determined using the method of least squares and are listed in Table 8 along with values of percentage standard deviation. The dependence of excess enthalpy on composition is illustrated graphically in Figure 5. The excess enthalpy versus mole fraction curves are symmetric in all the systems. The values of excess enthalpies are positive over the entire range of composition in all the systems. The positive

Table 8. Estimated Parameters of Equation 9 and Percentage of Standard Deviation [% $\sigma(H^E)$] at 298. 15 K

system	h_0	h_1	h_2	h_3	[% $\sigma(H^E)$][a]
DMM +	J·mol^{-1}	J·mol^{-1}	J·mol^{-1}	J·mol^{-1}	J·mol^{-1}
hexane	4703.6	−353.9	82.14	85.52	2.73
cyclohexane	5211.7	−417.8	−121.8	−43.5	2.43
benzene	472.9	−109.7	88.7	−205.1	2.08

[a] $\% \sigma(H^E) = [\sum((H_{exp}^E - H_{cal}^E)/H_{exp}^E \times 100)^2/n - p]^{1/2}$.

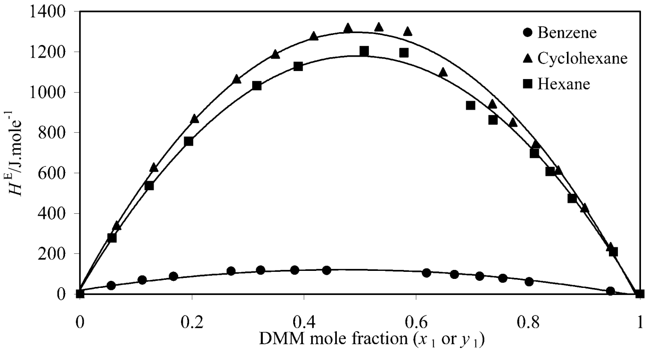

Figure 5. Excess enthalpies (H^E) for the binary systems of dimethoxymethane (1) with hydrocarbons (2) at 298.15 K.

values of H^E may be due to the dispersion forces operating between unlike molecules. The positive H^E values indicate that the interactions between unlike molecules are weaker than those between similar molecules. The H^E data of dimethoxymethane with hydrocarbons increase in the following order: benzene < hexane < cyclohexane.

The lower H^E values in the case of benzene may be attributed to the $n-\pi$ interactions between DMM and benzene. A similar trend is observed by several authors in the case of mono ethers with hydrocarbons.[21−23]

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