RESULTS

The experimental vapor-liquid equilibrium data are presented in Table II. The liquid-phase activity coefficients were evaluated using the classical thermodynamic relationship:

$$\ln \gamma_i = \ln \left(\frac{\pi y_i}{x_i P_i{}^\circ} \right) + \frac{(\beta_i - v_2{}^L)(\pi - P_i{}^\circ)}{RT} \qquad i = 1,2 \tag{1}$$

Equation 1 allows for the effect of pressure on the liquid fugacity, and for the nonideality in the gas phase. For the latter, the virial equation was truncated to the second term. Wohl's (5) equation was employed to estimate the values of the second virial coefficients. Volumetric data were taken from the literature. For our systems, the contribution of the second term on the right-hand side of Equation 1 was very small.

During the experimental determinations, some difficulty was experienced in establishing the equilibrium pressure. Though pressures could be read accurately, pressure changes of 10–15 mm Hg showed no observable effect on the temperature. This was particularly true for the systems containing di-n-propyl ether. The following procedure was therefore adopted to determine the equilibrium pressure. The pressure was deliberately changed in small steps until the measured equilibrium temperature differed from 90°C. This gave pressures corresponding to temperatures of approximately 90 ± 0.05°C, and the mean pressure was taken to be the equilibrium pressure at 90°C.

The activity coefficients for these systems are close to unity. Considerable scatter was noted in the activity coefficient data, possibly due, at least in part, to the uncertainty in pressure. The equilibrium data were compared with ideal values calculated from

$$y_i = \frac{P_i{}^\circ x_i}{\Sigma P_i{}^\circ x_i} \qquad i = 1,2 \tag{2}$$

and are shown in Figures 2–4.

NOMENCLATURE

P° = pure component vapor pressure, mm Hg
R = gas constant, (mm Hg)(cc)/(g mol)(°K)
T = temp, °K
v = molal volume, cc/g mol
x = mole fraction in liquid
y = mole fraction in vapor

GREEK LETTERS

β = second virial coefficient
γ = activity coefficient
π = total pressure, mm Hg

SUBSCRIPTS

1,2,i = component 1, 2, or i

SUPERSCRIPT

L = liquid

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Vapor-Liquid Equilibria of Methyl Propanoate–Methanol and Methyl Propanoate–Ethanol Systems at 25°C

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Vapor-liquid equilibria of the systems methyl propanoate–methanol and methyl propanoate–ethanol measured at 25°C are reported along with the results of the volumes of mixing at the same temperature.

$\mathbf{V}$apor-liquid equilibria at 25°C for the two binary systems, methyl propanoate–methanol and methyl propanoate–ethanol, were measured by a circulation method. The experimental equilibrium pressures and compositions, together with the liquid activity coefficients and excess Gibbs free energies, are presented. The excess volumes of the systems were calculated using the density values obtained by means of a pycnometer at 25°C.

EXPERIMENTAL

The method and equipment used in this study were described in earlier articles (8, 10).

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A circulation still with a total capacity of about 150 ml was used for the determination of vapor-liquid equilibrium compositions. When the temperature of 25°C was obtained in the still head, this temperature was maintained for 3 hr to ensure the establishment of equilibrium. Samples of the liquid and condensed vapor phases were taken immediately after boiling was discontinued, and analyses of both phases were made by measuring their densities in calibrated 5-ml capillary-stem pycnometers. The temperature of the still, as measured with a calibrated Beckmann thermometer, was maintained within ±0.005°C, and the pressure, as measured with a Texas Instrument Pressure gage, was read with a precision of ±0.04 mm Hg.

The concentrations of the samples were determined by mea-

Component	Density, d_4^{25}, cm³ mol⁻¹		Vapor pressure, mm Hg		Second virial coefficient, cm³ mol⁻¹ᵃ
	Measured	Lit.	Measured	Lit.	
Methyl propanoate	0.90890	0.9090 (12)	86.34	86.30 (9)	−2260 (5)
Methanol	0.78662	0.78662 (13)	126.96	127.04 (1)	−2090 (6)
Ethanol	0.78511	0.78508 (13)	58.99	59.03 (1)	−3020 (3)

ᵃ Extrapolated values.

suring their densities at 25.000° ± 0.002°C. The variation of the density with concentration was established from measurements on a series of mixtures of known compositions. The precision of the density measurements was ±0.0001 cm³ mol⁻¹ for mixtures and ±0.00005 cm³ mol⁻¹ for the pure components. The precision of the concentration determinations was therefore about ±0.00021 mol fraction for the system methyl propanoate–methanol, and ±0.00036 mol fraction for the system methyl propanoate–ethanol.

MATERIALS

"Chromatoquality" methanol, supplied by Matheson Coleman and Bell, was used without further purification. Ethanol, supplied by Canadian Industrial Alcohols and Chemicals Ltd., was dried over Drierite and distilled immediately before use. Methyl propanoate, supplied by Matheson Coleman and Bell, was dried over Drierite and twice distilled before use. Physical properties of these materials are compared with literature values in Table I.

RESULTS

The equilibrium pressures and compositions of the liquid and vapor phases are listed in Table II along with the calculated Raoult's law activity coefficients and molar excess Gibbs free energies. The activity coefficients were calculated from the equation:

$$\gamma_i = \frac{y_i p}{x_i p_i^\circ} + \exp\,[(B_{ii} - v_i^\circ)(p - p_i^\circ)/RT +$$

$$(1 - y_i)^2 p \delta /RT]\quad (1)$$

where

$$\delta = 2\,B_{12} - B_{11} - B_{22}\quad (2)$$
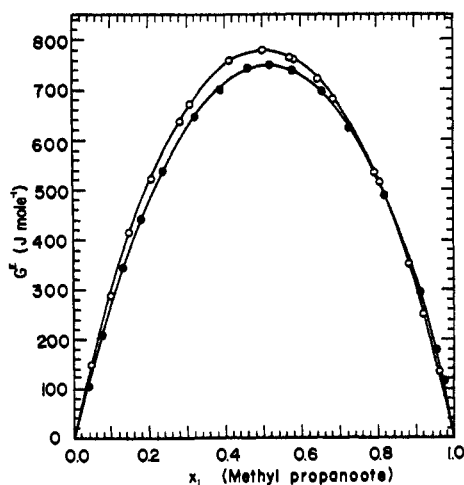

Figure 1. Molar excess Gibbs free energies at 25°C

○ Methyl propanoate–methanol ● Methyl propanoate–ethanol

The Gibbs excess free energy is given by the formula

$$G^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2)\quad (3)$$

Numerical values of G^E for the two systems are shown in Figure 1. The physical constants required for these calculations are given in Table I. The second virial coefficients for these materials at 25°C were obtained by extrapolating the literature values by means of the Stockmayer potential function. The mixed virial coefficients were estimated by the correlation of O'Connell and Prausntiz (7). The molecular parameters used were those reported in ref. 7, and the critical constants used in the calculation were those compiled by Kudchadker et al. (4). The values obtained for B_{12} are −2170 cm³ mol⁻¹ for the methyl propanoate–methanol system and −2240 cm³ mol⁻¹ for the methyl propanoate–ethanol system.

The area test of Redlich and Kister (11) was applied to both systems. The difference between the positive and negative areas of the ln (γ_1/γ_2) vs. x_1 curve expressed as a percentage of the total area is 3.0% for the system methyl propanoate–

Table II. Vapor-Liquid Equilibria Data at 25°C

Methyl Propanoate (1)–Methanol (2)

x_1	y_1	p, mm Hg	γ_1	γ_2	G^E, J mol⁻¹
0.0465	0.0963	134.95	3.217	1.007	151
0.0979	0.1692	140.46	2.793	1.018	289
0.1508	0.2229	144.31	2.453	1.039	415
0.2066	0.2675	146.68	2.183	1.065	523
0.2821	0.3108	148.16	1.876	1.118	639
0.3099	0.3255	148.36	1.791	1.140	672
0.4128	0.3705	148.08	1.527	1.248	756
0.4992	0.4053	146.68	1.369	1.370	779
0.5726	0.4349	144.71	1.264	1.505	765
0.5800	0.4395	144.31	1.257	1.515	762
0.6438	0.4667	141.97	1.184	1.672	723
0.6821	0.4828	139.97	1.140	1.792	681
0.7894	0.5491	132.41	1.061	2.233	534
0.8028	0.5636	130.91	1.058	2.282	516
0.8817	0.6445	120.96	1.020	2.867	351
0.9163	0.7000	114.07	1.006	3.227	256
0.9594	0.7986	103.64	0.997	4.063	134

Methyl Propanoate (1)–Ethanol (2)

x_1	y_1	p, mm Hg	γ_1	γ_2	G^E, J mol⁻¹
0.0368	0.1441	66.75	3.041	1.002	106
0.0743	0.2426	73.16	2.776	1.010	212
0.1325	0.3471	80.68	2.453	1.024	345
0.1784	0.3998	84.98	2.209	1.046	442
0.2364	0.4562	89.37	1.999	1.072	538
0.3181	0.5085	93.55	1.732	1.135	648
0.3800	0.5427	95.87	1.585	1.190	702
0.4587	0.5777	97.94	1.428	1.286	742
0.5142	0.6029	99.06	1.344	1.363	750
0.5759	0.6272	99.92	1.259	1.478	740
0.6531	0.6610	100.50	1.177	1.653	695
0.7229	0.6926	100.48	1.113	1.876	625
0.8151	0.7492	99.45	1.057	2.272	489
0.9049	0.8231	96.54	1.016	3.027	296
0.9520	0.8883	93.73	1.012	3.680	183
0.9722	0.9161	92.20	1.005	4.696	120

Table III. Excess Molar Volumes at 25°C

Methyl Propanoate (1)–Methanol (2)

x_1	V^E, cm³ mol⁻¹
0.0987	−0.028
0.2020	−0.045
0.3005	−0.052
0.4013	−0.057
0.4985	−0.075
0.5993	−0.059
0.7052	−0.026
0.8083	−0.022
0.8963	−0.031

Methyl Propanoate (1)–Ethanol (2)

x_1	V^E, cm³ mol⁻¹
0.0983	0.024
0.2007	0.067
0.3034	0.080
0.4032	0.099
0.5012	0.124
0.6013	0.114
0.7040	0.126
0.8052	0.090
0.9043	0.055
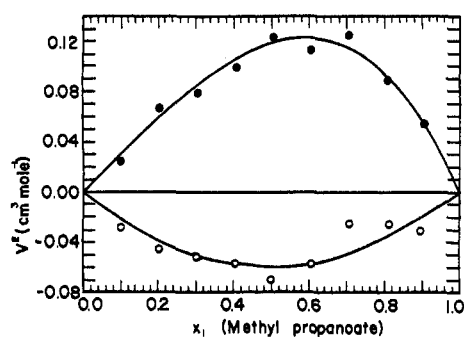
Figure 2. Molar excess volumes at 25°C

O Methyl propanoate–methanol ● Methyl propanoate–ethanol

methanol and 3.2% for the system methyl propanoate–ethanol. The G^E values were correlated using the equation

$$G^E = x_1(1 - x_1) \sum_{i=1}^{3} c_i(1 - 2 x_1)^{i-1} \qquad (4)$$

where x_1 refers to the mole fraction of the methyl propanoate. The coefficients were determined by a least-squares fitting procedure. The resulting coefficients in the order, c_1, c_2, c_3 for the system methyl propanoate–methanol are 3112 ± 2.8, −34.51 ± 7.7, 309.3 ± 13.6 with a standard deviation of 2.6 J mol⁻¹, and for the system methyl propanoate–ethanol are 2985 ± 13.4, −200.2 ± 38.0, 422.8 ± 66.1 with a standard deviation of 10.2 J mol⁻¹. The estimated uncertainties in G^E are ±1.6 J mol⁻¹ for the system methyl propanoate–methanol and ±2.1 J mol⁻¹ for the system methyl propanoate–ethanol.

The densities of binary systems, determined primarily to measure the concentrations of vapor-liquid equilibria samples, were also used to calculate the excess volumes of the two systems. Their numerical values are listed in Table III and graphically shown in Figure 2. The excess volumes were also expressed by the right-hand side of Equation 4 but with only two coefficients. For the methyl propanoate–methanol system $c_1 = -0.238 \pm 0.019$ and $c_2 = -0.083 \pm 0.050$ with a standard deviation of 0.01 cm³ mol⁻¹. This gives the excess volume at $x_1 = x_2 = 0.5$, $V_{0.5}^E = -0.06$ cm³ mol⁻¹. Similarly for the methyl propanoate–ethanol system, $c_1 = 0.473 \pm 0.013$

and $c_2 = -0.197 \pm 0.035$ with a standard deviation of 0.008 cm³ mol⁻¹. At $x_1 = 0.5$, $V_{0.5}^E = 0.118$ cm³ mol⁻¹. The estimated uncertainty in V^E is ±0.01 cm³ mol⁻¹ for both systems.

When the results of this work were compared with those obtained in work previously done on two similar systems, with methyl formate in place of methyl propanoate (8), it is seen that the G^E values of all the systems do not differ by much, but in the present case, the system with methanol, unlike those before has a larger G^E than the system with ethanol. The excess volumes are again negative for the methyl propanoate–methanol system and positive for the methyl propanoate–ethanol system.

ACKNOWLEDGMENT

NOMENCLATURE

B_{ii} = second virial coefficient of pure component i, cm³ mol⁻¹

B_{12} = cross virial coefficient, cm³ mol⁻¹

c_1, c_2, c_3 = coefficients in Redlich-Kister equation (4), J mol⁻¹ for G^E and cm³ mol⁻¹ for V^E

G^E = molar excess Gibbs free energy, J mol⁻¹

p = total vapor pressure, mm Hg

$p_i°$ = vapor pressure of pure component i, mm Hg

R = gas constant

T = absolute temperature, K

V^E = molar excess values, cm³ mol⁻¹

$v_i°$ = molar volume of pure component, cm³ mol⁻¹

x_i = mole fraction of component i in liquid phase

y_i = mole fraction of component i in vapor phase

GREEK LETTERS

δ = difference of virial coefficients as defined by Equation 2, cm³ mol⁻¹

γ_i = activity coefficient of component i in liquid phase

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