Excess Gibbs Free Energies and Heats of Mixing for Binary Systems: Ethyl Formate with Methanol, Ethanol, 1-Propanol, and 2-Propanol

Isamu Nagata,* Tatsuhiko Ohta, Michio Ogura, and Shuhei Yasuda[†]
Department of Chemical Engineering, Kanazawa University, Kanazawa, 920, Japan

Isothermal vapor–liquid equilibrium data are determined for ethyl formate–1-propanol at 50 °C and three other systems at 45 °C. The ethyl formate–methanol system forms an azeotrope with 0.700 mol fraction ethyl formate at 610.1 mmHg. Heat of mixing data are obtained for the four systems at 25, 35, and 45 °C. The NRTL equation with temperature-dependent parameters fits simultaneously vapor–liquid equilibrium and heat of mixing data for each system.

Isothermal vapor–liquid equilibrium data of mixtures of ethyl formate with alcohols were measured at 45 or 50 °C and heats of mixing of the mixtures were observed at 25, 35, and 45 °C. The coexistence equation was used to check thermodynamic consistency of vapor–liquid equilibrium data and the NRTL (nonrandom two-liquid) equation whose parameters were assumed to be a linear function of temperature was used to obtain a simultaneous fit of vapor–liquid equilibrium data and heat of mixing data.

Experimental Procedures

Materials. Chemically pure materials were purified for experimental work. The alcohols were distilled in a 1.2-m tall glass distillation column packed with McMahon packings after they were treated with drying materials: methanol (anhydrous calcium sulfate), ethanol (calcium oxide), propanols (copper sulfate anhydride). Ethyl formate was purified in accordance with the method of Hurd and Strong (*7*). Table I compares the densities, refractive indices, and vapor pressures of purified materials with literature values.

Apparatus. Isothermal vapor–liquid equilibrium data were determined by using a Scatchard still (*8*), with minor modifications of Renon and Prausnitz (*6*). A copper–constantan thermocouple was calibrated by intercomparison with a mercury thermometer that has been calibrated at the National Research Laboratory of Metrology, Tokyo. Temperatures could be measured within ±0.1 °C. A vacuum system was controlled by a cartesian manostat connected with a vapor condenser. The pressure in the still was measured by a mercury manometer and a cathetometer with an accuracy of ±0.1 mmHg. All observed pressures were corrected to give the equivalent height of a mercury column at 0 °C and standard gravity. Times required for reaching equilibrium varied between 3 and 4 h. Lypkin pycnometers were used to obtain densities of vapor and liquid samples at 25 °C with an accuracy of ±0.0001 g. The concentration data accuracy could be estimated to be 0.001 mol fraction.

A calorimeter was similar to that of Larkin and McGlashan (*4*). A mixing vessel included a thermistor (Shibaura Electric Co., Model NB, resistance at 25 °C was about 27 kΩ) and a heater consisted of about 220 cm of manganin wire wound on a porcelain insulator of 2 mm diameter. The heater was calibrated by Japan Electric Meters Inspection Corporation, Tokyo. The thermistor was used as a temperature sensitive material by combining use of a dc bridge (Yokogawa Electric Co., Model 2755), an amplifier (Ohkura Electric Co., Model A.M. 100), and a recorder (Yokogawa Electric Co., Model LER 12A). The mixing vessel was filled with mercury in the complete absence of vapor spaces and weighed quantities of the two liquids to be mixed were injected into their compartments through hypodermic syringes. The temperature in the mixing vessel was maintained within ±0.005 °C in a thermostated bath. The errors in observed heat of mixing data were estimated to be of the order of ±1%.

Experimental Results and Analysis of Data

Tables II and III list, respectively, experimental vapor–liquid equilibrium data and heat mixing data for the four systems. Only the ethyl formate–methanol system presents an azeotrope at 610.1 mmHg and 70.0 mol % ethyl formate. The liquid-phase activity coefficients were calculated by taking vapor-phase nonideality into account in accordance with the methods of Prausnitz et al. (*5*).

$$\gamma_i = \frac{\phi_i y_i P}{\phi_i^s x_i P_i^s \exp[V_i^L(P - P_i^s)/RT]} \tag{1}$$

The excess Gibbs free energy is calculated by

$$g^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \tag{2}$$

Van Ness et al. (*10*) recommended that the reliable thermodynamic consistency test for experimental data is to compare vapor-phase compositions calculated from isothermal total pressure–liquid composition data with those experimentally obtained. We used the isothermal coexistence equation to calculate the vapor-phase compositions.

The isothermal coexistence equation at low pressures (*9*) is expressed by

Table I. Physical Constants of Compounds at 25 °C

	Density		Refractive index		Vapor pressure	
Compound	Exptl	Lit. (*7*)	Exptl	Lit. (*7*)	Exptl	Lit.
Ethyl formate	0.9201 (20 °C)	. . .	1.35998 (20 °C)	1.35994	549.1 (45 °C)	548.89 (2)
					659.4 (50 °C)	659.27 (2)
Methanol	0.7868	0.78664	1.3265	1.32652	331.0 (45 °C)	331.28 (7)
Ethanol	0.7852	0.78504	1.3594	1.35941	174.2 (45 °C)	174.00 (7)
1-Propanol	0.7995	0.79975	1.3835	1.38370	91.5(50 °C)	91.2 (7)
2-Propanol	0.7811	0.78126	1.3752	1.3752	139.2 (45 °C)	139.08 (7)

[†] Present address, Toray Co., Nagoya, 455, Japan.

Table II. Experimental Isothermal Vapor-Liquid Equilibrium Data for Four Binary Systems

x_1	y_1	P, mmHg	γ_1	γ_2	ϕ_1	ϕ_2	g^E, cal/mol	$\Delta y^a \times 10^3$	ΔP,[b] %
Ethyl Formate (1)-Methanol (2) at 45 °C									
0.073	0.245	419.7	2.603	1.006	0.973	0.969	47.8	3	0.50
0.165	0.402	490.1	2.197	1.027	0.970	0.963	96.2	4	0.50
0.269	0.496	539.6	1.826	1.084	0.967	0.959	139.5	−3	0.12
0.361	0.553	569.3	1.597	1.157	0.965	0.956	165.8	−4	0.18
0.435	0.592	584.3	1.455	1.224	0.965	0.955	175.4	−2	−0.03
0.503	0.631	592.2	1.359	1.274	0.964	0.954	173.7	8	−0.50
0.596	0.668	602.6	1.235	1.434	0.964	0.953	171.5	7	−0.37
0.668	0.694	608.8	1.156	1.623	0.964	0.952	163.0	2	0.02
0.798	0.767	607.8	1.068	2.027	0.964	0.952	123.5	6	0.27
0.824	0.789	605.2	1.060	2.098	0.964	0.952	112.7	10	0.28
0.898	0.846	590.1	1.018	2.578	0.965	0.953	71.1	2	0.10
0.931	0.885	578.5	1.008	2.792	0.966	0.953	49.3	2	−0.10
Ethyl Formate (1)-Ethanol (2) at 45 °C									
0.051	0.313	246.9	2.836	1.003	0.985	0.979	35.2	2	0.40
0.155	0.554	345.7	2.298	1.014	0.979	0.970	89.0	3	−0.30
0.201	0.612	379.8	2.146	1.022	0.977	0.967	107.9	9	0.23
0.248	0.647	407.0	1.967	1.056	0.976	0.964	131.8	5	0.24
0.369	0.715	452.9	1.621	1.125	0.973	0.960	159.7	6	−0.83
0.410	0.733	468.4	1.545	1.164	0.972	0.959	169.5	8	−0.20
0.429	0.740	473.2	1.506	1.183	0.972	0.958	171.6	8	−0.31
0.582	0.787	509.5	1.268	1.420	0.970	0.955	180.0	7	0.25
0.635	0.805	516.0	1.204	1.507	0.969	0.954	168.9	9	−0.23
0.773	0.849	536.7	1.083	1.947	0.968	0.952	134.6	6	0.05
0.891	0.905	547.3	1.021	2.598	0.968	0.951	77.3	2	0.08
0.950	0.954	549.8	1.014	2.754	0.968	0.951	40.1	6	0.38
Ethyl Formate (1)-1-Propanol (2) at 50 °C									
0.088	0.604	213.5	2.301	0.996	0.988	0.984	44.5	3	−0.28
0.156	0.718	282.7	2.035	1.009	0.985	0.979	76.0	4	0.12
0.384	0.833	424.3	1.427	1.215	0.977	0.969	164.8	−8	−0.17
0.419	0.845	439.1	1.372	1.236	0.976	0.968	164.1	−6	−0.30
0.588	0.886	505.0	1.174	1.467	0.972	0.963	161.9	−5	0.05
0.674	0.905	537.2	1.111	1.639	0.970	0.961	148.9	−5	0.52
0.737	0.918	557.9	1.069	1.819	0.969	0.959	132.4	−5	0.35
0.869	0.955	600.8	1.013	2.150	0.967	0.956	71.5	−1	−0.32
0.911	0.963	614.8	0.996	2.660	0.966	0.955	53.5	−6	−0.59
Ethyl Formate (1)-2-Propanol (2) at 45 °C									
0.039	0.307	196.1	2.900	0.990	0.989	0.986	20.1	8	0.02
0.132	0.557	284.8	2.245	1.011	0.983	0.980	73.4	2	−0.69
0.205	0.649	336.1	1.981	1.028	0.980	0.976	102.4	10	0.39
0.347	0.732	394.6	1.544	1.117	0.977	0.972	140.9	5	−0.85
0.444	0.767	429.5	1.373	1.238	0.975	0.970	164.0	1	0.15
0.540	0.802	453.5	1.244	1.340	0.973	0.968	159.8	4	−0.17
0.662	0.837	480.5	1.120	1.588	0.972	0.966	146.4	−1	−0.37
0.726	0.859	498.2	1.086	1.755	0.971	0.965	135.2	−1	0.48
0.809	0.900	513.0	1.050	1.836	0.970	0.964	98.5	8	0.13
0.859	0.919	525.8	1.034	2.063	0.969	0.963	82.9	4	0.78
0.955	0.970	544.3	1.015	2.475	0.968	0.962	35.0	2	1.18

[a] $\Delta y = y_{1\mathrm{exptl}} - y_{1\mathrm{calcd}}$. [b] $\Delta P = 100(P_{\mathrm{exptl}} - P_{\mathrm{calcd}})/P_{\mathrm{exptl}}$.

$$\frac{\mathrm{d}y_1}{\mathrm{d}P} = \frac{\psi - (1 - 2y_1)(y_1 - x_1)(\delta_{12}/RT)}{\dfrac{y_1 - x_1}{y_1(1 - y_1)} - (y_1 - x_1)(2P\delta_{12}/RT)} \qquad (3)$$

where

$$\psi = \frac{y_1 y_2 \delta_{12} - V^L + x_1 B_{11} + x_2 B_{22}}{RT} + \frac{1}{P} \qquad (4)$$

Second virial coefficients were estimated using procedures described by Prausnitz et al. (*5*). The liquid molar volumes were assumed to be a linear mole fraction average of the molar volumes for the pure components. The total pressure vs. x data were correlated by the orthogonal polynomials of Hutchison and Fletcher (*3*). P–y curves were calculated from the P–x curves by numerical integration of eq 3. The fourth-order Runge–Kutta-Gill integration technique was used to perform the integrations in the direction of increasing pressure. Calculated results show that the present data seem to be thermodynamically consistent (Table IV).

The NRTL equation was used to fit simultaneously the experimental vapor-liquid equilibrium and heat of mixing data. The NRTL equation presents the activity coefficients.

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right] \qquad (5)$$

$$\ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right] \qquad (6)$$

where $\tau_{12} = (g_{12} - g_{22})/RT$; $\tau_{21} = (g_{21} - g_{11})/RT$; $G_{12} = \exp(-\alpha_{12}\tau_{12})$; and $G_{21} = \exp(-\alpha_{12}\tau_{21})$. Asselineau and Renon

Table III. Experimental Heats of Mixing for Four Binary Systems

Temp, °C	x_1	h^E cal/mol	Δh^a cal/mol
Ethyl formate (1)–methanol (2)			
25.00	0.1012	58.4	−3.2
	0.1996	102.7	−2.8
	0.2980	136.3	−0.7
	0.3931	157.0	−0.9
	0.4946	166.5	−4.5
	0.5883	170.6	−3.5
	0.6873	165.9	−0.2
	0.7864	137.9	−4.4
	0.8901	86.5	−6.6
35.00	0.0474	32.2	−1.0
	0.0955	62.0	−0.8
	0.1996	119.3	4.7
	0.2913	153.1	4.7
	0.3205	164.3	7.2
	0.3903	179.2	5.2
	0.4901	188.0	−0.9
	0.5872	197.1	4.9
	0.6830	191.4	8.8
	0.7745	164.7	6.4
	0.8229	143.3	5.4
	0.9283	71.7	1.7
45.00	0.1002	67.4	−2.4
	0.1974	122.6	0.1
	0.2913	158.2	−2.8
	0.3960	187.6	−3.4
	0.4991	199.4	−7.6
	0.5919	206.9	−2.0
	0.6878	194.2	−2.2
	0.7644	174.9	1.3
	0.8213	144.2	−3.5
	0.8976	97.9	−0.7

Temp, °C	x_1	h^E cal/mol	Δh cal/mol
Ethyl formate (1)–ethanol (2)			
25.00	0.1134	99.2	−5.9
	0.1970	155.1	−6.1
	0.2990	205.0	−4.8
	0.3927	238.5	0.1
	0.4947	249.2	−4.8
	0.5927	249.2	−4.2
	0.6955	226.8	−7.5
	0.7816	192.7	−7.6
	0.8811	126.9	−6.9
35.00	0.0513	56.3	1.1
	0.0678	71.2	−0.1
	0.1814	166.4	3.3
	0.2907	231.6	7.4
	0.3927	266.8	6.6
	0.4890	283.8	6.6
	0.4976	287.9	10.0
	0.5947	288.1	11.9
	0.6895	260.6	4.7
	0.7089	257.3	8.0
	0.7828	221.8	7.3
	0.8361	187.8	8.5
	0.8846	144.1	5.6
	0.9500	71.9	3.9
45.00	0.0527	59.5	−0.1
	0.1973	187.4	2.0
	0.2994	243.7	−1.4
	0.3938	279.3	−1.9
	0.5432	292.2	−9.3
	0.5888	289.8	−8.6
	0.6672	271.9	−10.1
	0.6914	272.3	1.4
	0.7995	213.8	−3.5
	0.8299	194.0	−0.8
	0.8944	135.1	−0.6

Temp, °C	x_1	h^E cal/mol	Δh cal/mol
Ethyl formate (1)–1-propanol (2)			
25.00	0.1013	122.8	−5.8
	0.1993	209.4	−5.9
	0.3037	272.3	−5.5
	0.4033	305.3	−3.5
	0.4993	319.2	−4.3
	0.5922	315.1	−3.8
	0.6972	283.3	−1.2
	0.7825	236.6	−1.8
	0.8984	133.7	−2.1
35.00	0.0539	76.1	3.6
	0.0954	126.2	5.0
	0.2024	225.2	3.2
	0.3122	303.2	6.3
	0.4000	341.9	10.1
	0.4422	346.2	7.1
	0.5022	352.8	6.3
	0.5964	346.4	6.0
	0.6931	318.2	11.3
	0.7884	257.0	6.2
	0.8400	210.2	−2.1
	0.8875	162.6	0.8
	0.9360	100.8	0.8
45.00	0.1079	148.1	0.6
	0.2049	243.4	−3.4
	0.3039	309.6	−0.6
	0.4028	343.5	−3.2
	0.4544	360.0	−5.5
	0.5448	363.8	−3.3
	0.6018	352.6	−3.8
	0.6933	321.3	−8.9
	0.7957	255.6	−1.5
	0.7961	252.5	0.7
	0.8968	152.6	1.5

Temp, °C	x_1	h^E cal/mol	Δh cal/mol
Ethyl formate (1)–2-propanol			
25.00	0.1004	150.3	−2.7
	0.1515	211.2	1.2
	0.1998	250.6	−3.0
	0.3055	325.4	5.0
	0.3978	353.8	1.1
	0.3989	353.3	0.4
	0.4907	362.9	−1.4
	0.4917	361.4	−2.9
	0.5673	359.3	0.3
	0.5832	357.4	1.1
	0.6893	319.4	−2.3
	0.7914	263.0	4.5
	0.8853	163.6	−4.2
35.00	0.0962	150.2	−3.6
	0.1977	264.0	−0.8
	0.2931	332.5	−0.1
	0.3832	367.4	−3.2
	0.5237	388.9	2.5
	0.5852	376.5	−1.1
	0.6837	337.6	−5.0
	0.7548	303.4	3.8
	0.7964	269.2	2.5
	0.8255	245.1	5.1
	0.8814	180.3	1.3
	0.9436	94.7	0.3
45.00	0.0980	161.4	−1.0
	0.2046	287.6	3.6
	0.3012	359.1	3.8
	0.3945	392.0	−3.1
	0.4908	415.4	5.7
	0.5933	396.6	−0.3
	0.6914	350.7	−5.5
	0.7048	346.9	−1.5
	0.7935	279.7	−1.6
	0.8506	221.4	−1.4
	0.9010	159.7	−0.1

[a] $\Delta h = h^E_{\text{exptl}} - h^E_{\text{calcd}}$.

Table IV. Data Analysis by the Coexistence Equation

System	Absolute arithmetic deviation	
	Pressure, mmHg	Vapor mole fraction
Ethyl formate–methanol	0.4	0.007
Ethyl formate–ethanol	0.8	0.005
Ethyl formate-1-propanol	0.2	0.005
Ethyl formate-2-propanol	1.3	0.003

(*1*) proposed that the three parameters of the NRTL equation could be expressed by a linear function of temperature.

$$g_{21} - g_{11} = C_1 + D_1(T - 273.15) \tag{7}$$

$$g_{12} - g_{22} = C_2 + D_2(T - 273.15) \tag{8}$$

$$\alpha_{12} = C_3 + D_3(T - 273.15) \tag{9}$$

Then, the heat of mixing is given by

$$h^E = \frac{x_1 x_2 \exp(-\alpha_{12}\tau_{21})}{x_1 + x_2 \exp(-\alpha_{12}\tau_{21})}\left[\left(1 - \frac{\alpha_{12}\tau_{21}x_1}{x_1 + x_2\exp(-\alpha_{12}\tau_{21})}\right) \times (C_1 - 273.15D_1) + \frac{\tau_{21}{}^2 x_1 D_3 R T^2}{x_1 + x_2 \exp(-\alpha_{12}\tau_{21})}\right] + \frac{x_1 x_2 \exp(-\alpha_{12}\tau_{12})}{x_2 + x_1 \exp(-\alpha_{12}\tau_{12})}\left[\left(1 - \frac{\alpha_{12}\tau_{12}x_2}{x_2 + x_1\exp(-\alpha_{12}\tau_{12})}\right) \times (C_2 - 273.15D_2) + \frac{\tau_{12}{}^2 x_2 D_3 R T^2}{x_2 + x_1 \exp(-\alpha_{12}\tau_{12})}\right] \tag{10}$$

Best fitting was obtained by minimizing the following objective function as suggested by Asselineau and Renon.

$$Q = \sum\{100(y_{\text{exptl}} - y_{\text{calcd}})\}^2 + \sum\left\{100\frac{(P_{\text{exptl}} - P_{\text{calcd}})}{P_{\text{exptl}}}\right\}^2 + \sum\left\{\frac{h^E{}_{\text{exptl}} - h^E{}_{\text{calcd}}}{5}\right\}^2 \tag{11}$$

Tables II and III include each point to point deviation of calculated results from experimental data. Table V presents the constants of the NRTL parameters and the root-mean-square deviations of calculated values from experimental results.

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Nomenclature

B_{ij} = second virial coefficient, ml/mol
C, D = constants of eq 7–9
g^E = excess Gibbs free energy, cal/mol
g_{ij} = energies of interaction between an i–j pair of molecules, cal/mol
G_{ij} = coefficient as defined by $G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$
h^E = excess enthalpy of mixing, cal/mol
P_i^s = vapor pressure of pure component i at system temperature, atm
P = total pressure, atm
Q = objective function as defined by eq 10
R = gas constant, 1.987 cal/(mol K)
T = absolute temperature, K
V_i^L = liquid molar volume of pure component i, ml/mol
V^L = liquid molar volume of mixture, ml/mol
x = liquid-phase mole fraction
y = vapor-phase mole fraction

Greek Letters

α = nonrandomness constant
γ = activity coefficient
δ_{12} = coefficient as defined by $\delta_{12} = 2B_{12} - (B_{11} + B_{22})$
τ_{ij} = coefficient as defined by $\tau_{ij} = (g_{ij} - g_{jj})/RT$
ϕ_i^s = fugacity coefficient of pure saturated component i at system temperature and P_i^s
ϕ_i = fugacity coefficient of component i
ψ = coefficient as defined by eq 4

Subscript

i = component

Superscript

E = excess

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Table V. Binary Constants of NRTL Equation and Root-Mean-Square Deviations

System	C_1, cal/mol	C_2, cal/mol	C_3	D_1, cal/(mol K)	D_2, cal/(mol K)	D_3, K^{-1}	$\Delta y^a \times 10^3$	ΔP,^{b} %	Δh,^{c} cal/mol
Ethyl formate (1)–methanol (2)	365.64	577.71	0.5561	−1.3281	−0.8991	−0.003132	5	0.3	4
Ethyl formate (1)–ethanol (2)	433.16	621.03	0.5270	−1.9387	−1.6445	−0.002091	7	0.3	6
Ethyl formate (1)-1-propanol (2)	484.96	521.25	0.5962	−1.8551	−2.9460	−0.000520	5	0.3	5
Ethyl formate (1)-2-propanol (2)	593.41	534.09	0.6245	−2.8169	−3.1702	0.000885	5	0.6	3

[a] $\Delta y = y_{1\text{exptl}} - y_{1\text{calcd}}$. [b] $\Delta P = 100(P_{\text{exptl}} - P_{\text{calcd}})/P_{\text{exptl}}$. [c] $\Delta h = h^E{}_{\text{exptl}} - h^E{}_{\text{calcd}}$.