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Thermodynamic Properties of Four Ester–Hydrocarbon Mixtures

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Vapor–liquid equilibrium data were presented for the systems of ethyl formate–benzene and ethyl formate–cyclohexane at 323.15 K and 66.66 kPa (500 mmHg) and for the systems of ethyl acetate–benzene and ethyl acetate–cyclohexane at 328.15 K. Heat of mixing data were obtained for the former two systems. These two kinds of thermodynamic quantities for each system were simultaneously well correlated with the Wilson and UNIQUAC equations having temperature-dependent parameters.

Introduction

This paper presents the experimental data on vapor–liquid equilibrium for the binary systems ethyl formate–benzene and ethyl formate–cyclohexane at 323.15 K and 66.66 kPa (500 mmHg) and ethyl acetate–benzene and ethyl acetate–cyclohexane at 328.15 K and on heats of mixing for the systems ethyl formate–benzene at 298.15, 308.15, and 318.15 K and ethyl formate–cyclohexane at 298.15 and 308.15 K. The equilibrium data of mixtures of ethyl acetate with benzene and cyclohexane have been reported on isobaric vapor-liquid equilibrium (*3*) and heats of mixing at 308.15 K (*13*). These two equilibrium data for the four systems were simultaneously correlated with the Wilson and UNIQUAC equations, whose energy parameters were assumed to be a quadratic function of temperature.

Experimental Procedures

Materials. Guaranteed reagent grade ethyl formate was used without further purification. Ethyl acetate was purified in accordance with the procedure of Hurd and Strong (*15*). Chemically pure benzene was subjected to repeated recrystallization. Guaranteed reagent grade cyclohexane was passed through a 1.2 m by 30 mm i.d. glass column packed with silica gel of chromatographic quality. Values of the boiling points, densities, and refractive indices of the purified materials are compared with the literature values in Table I.

Apparatus. The still used to obtain vapor–liquid equilibrium data was a Scatchard vapor-recirculation still (*16*), with minor modifications suggested by Renon and Prausnitz (*14*). Vapor and liquid samples were analyzed by using refractive index measurements at 298.15 K. The measurements of heats of mixing were carried out in two types of calorimeters (*6*, *8*). Further details on the apparatus and experimental technique have been reported previously (*6–8*).

Experimental Results and Data Analysis

Table II presents vapor-liquid equilibrium data for four binary systems. The liquid-phase activity coefficients were obtained by taking vapor-phase nonideality into account.

$$\gamma_i = \frac{\psi_i y_i P}{\psi_i^{s} x_i P_i^{s} \exp[v_i^{L}(P - P_i^{s})/RT]} \qquad (1)$$

Table I. Physical Properties of Compounds

	ethyl formate	ethyl acetate	benzene	cyclohexane
boiling point, K				
exptl	327.15	350.25	353.25	353.95
lit.	327.30[a]	350.264[a]	353.25[a]	353.87[a]
density at 298.15 K, g/cm^3				
exptl	0.9201[b]	0.8946	0.8735	0.7739
lit.	. . .	0.89455[a]	0.87364[a]	0.7737[a]
refractive index at 298.15 K				
exptl	1.35998[b]	1.3698	1.4979	1.4236
lit.	1.35994[a,b]	1.36979[a]	1.49792[a]	1.42354[a]
Antoine constants				
A	7.00902[c]	7.08520[d]	6.90565[a]	6.84498[a]
B	1123.943	1231.47	1211.033	1203.526
C	218.247	215.84	220.790	222.863

[a] Reference 15. [b] At 293.15 K. [c] Reference 2. [d] Reference 5.

where the vapor-phase fugacity coefficients were obtained from the virial equation truncated after the second term (*12*). Second virial coefficients for pure components and cross coefficients were estimated by using the method of O'Connell and Prausnitz (*11*). The liquid molar volumes of each component at three temperatures are available in the literature: benzene and cyclohexane, ref 12; ethyl formate and ethyl acetate, calculated by an equation given by Francis (*4*). These data were used to determine the constants of a quadratic equation representing the volume–temperature points. Then, the molar volume of each component at any temperature could be calculated. The pure vapor pressure data were taken from the Antoine equation whose constants are given in Table I. The excess Gibbs free energy is calculated by

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

Azeotropic data interpolated from smoothed experimental values are given in Table III.

Table IV lists experimental heat of mixing data for the systems of ethyl formate with benzene and cyclohexane.

The experimental data were analyzed by using the Wilson (*12*) and UNIQUAC (*1*) equations. These equations give expressions for g^E, γ, and h^E as follows.

The Wilson equation:

$$g^{E}/RT = -x_1 \ln (x_1 + \Lambda_{12}x_2) - x_2 \ln (x_2 + \Lambda_{21}x_1) \qquad (3)$$

$$\ln \gamma_1 = -\ln (x_1 + \Lambda_{12}x_2) + x_2[\Lambda_{12}/(x_1 + \Lambda_{12}x_2) - \Lambda_{21}/(x_2 + \Lambda_{21}x_1)] \qquad (4)$$

$$\ln \gamma_2 = -\ln (x_2 + \Lambda_{21}x_1) - x_1[\Lambda_{12}/(x_1 + \Lambda_{12}x_2) - \Lambda_{21}/(x_2 + \Lambda_{21}x_1)] \qquad (5)$$

$$h^{E}/R = x_1x_2[\Lambda_{12}(\tau_{12}' - \rho_{12}')/(x_1 + \Lambda_{12}x_2) + \Lambda_{21}(\tau_{21}' - \rho_{21}')/(x_2 + \Lambda_{21}x_1)] \qquad (6)$$

where

$$\Lambda_{ij} = (v_j^{L}/v_i^{L}) \exp[-(\lambda_{ij} - \lambda_{ii})/RT] \qquad (7)$$

$$\tau_{ij} = (\lambda_{ij} - \lambda_{ii})/RT \qquad (8)$$

$$\tau_{ij}' = \partial\tau_{ij}/\partial(1/T) \qquad (9)$$

$$\rho_{ij} = v_j^{L}/v_i^{L} \qquad (10)$$

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

x_1	y_1	P, kPa	T, K	γ_1	γ_2	ψ_1	ψ_2	g^E, J/mol
Ethyl Formate (1)-Benzene (2) at 323.15 K								
0.026	0.091	38.65	323.15	1.590	1.003	0.986	0.983	41.0
0.162	0.364	48.33		1.270	1.016	0.982	0.979	139.3
0.294	0.536	56.82		1.206	1.031	0.977	0.976	205.4
0.356	0.588	59.85		1.149	1.056	0.976	0.974	226.4
0.470	0.668	64.97		1.071	1.120	0.974	0.973	247.3
0.594	0.752	70.71		1.035	1.186	0.971	0.971	241.0
0.679	0.808	74.71		1.026	1.226	0.969	0.970	221.8
0.742	0.850	77.30		1.020	1.232	0.968	0.969	184.5
0.830	0.898	80.65		1.004	1.325	0.967	0.968	136.8
0.939	0.964	84.86		1.000	1.370	0.965	0.968	52.3
Ethyl Formate (1)-Benzene (2) at 66.66 kPa (500 mmHg)								
0.109	0.275	66.66	334.55	1.337	0.991	0.978	0.974	65.3
0.212	0.429		330.55	1.219	1.014	0.976	0.973	146.4
0.312	0.538		327.65	1.143	1.043	0.975	0.973	192.0
0.565	0.739		322.35	1.038	1.134	0.973	0.972	203.3
0.656	0.798		320.75	1.022	1.179	0.972	0.972	188.3
0.767	0.864		319.05	1.005	1.251	0.971	0.973	148.5
0.820	0.895		318.35	0.998	1.285	0.971	0.973	115.9
0.934	0.957		316.85	0.990	1.522	0.970	0.973	47.3
Ethyl Formate (1)-Cyclohexane (2) at 323.15 K								
0.069	0.378	55.34	323.15	3.535	1.017	0.979	0.972	276.6
0.207	0.568	73.63		2.335	1.093	0.971	0.964	661.5
0.367	0.652	83.26		1.701	1.242	0.966	0.960	892.4
0.457	0.682	85.87		1.472	1.363	0.965	0.959	926.3
0.573	0.720	88.41		1.274	1.570	0.964	0.958	889.9
0.626	0.742	89.97		1.222	1.679	0.963	0.957	858.1
0.796	0.809	91.59		1.066	2.320	0.962	0.957	597.5
0.850	0.842	91.14		1.034	2.599	0.962	0.958	460.7
0.978	0.961	88.61		0.998	4.265	0.963	0.961	80.3
Ethyl Formate (1)-Cyclohexane (2) at 66.66 kPa (500 mmHg)								
0.082	0.419	66.66	326.95	3.469	1.007	0.976	0.968	293.3
0.205	0.578		320.45	2.395	1.069	0.972	0.966	618.8
0.396	0.666		317.25	1.602	1.257	0.971	0.966	856.5
0.444	0.673		316.65	1.476	1.368	0.971	0.966	913.4
0.530	0.705		316.05	1.324	1.494	0.970	0.966	886.6
0.599	0.727		315.45	1.235	1.659	0.970	0.966	863.6
0.654	0.738		315.45	1.148	1.845	0.970	0.966	792.4
0.792	0.799		315.05	1.041	2.393	0.969	0.966	559.4
0.911	0.881		315.25	0.991	3.289	0.969	0.967	255.2
Ethyl Acetate (1)-Benzene (2) at 328.15 K								
0.122	0.133	44.12	328.15	1.047	1.006	0.978	0.981	30.5
0.341	0.359	44.86		1.026	1.008	0.976	0.982	38.5
0.486	0.500	45.22		1.009	1.017	0.975	0.982	36.0
0.602	0.610	45.50		0.999	1.032	0.974	0.983	32.6
0.709	0.710	45.81		0.994	1.057	0.973	0.984	31.4
0.836	0.837	45.93		0.996	1.058	0.973	0.985	15.1
Ethyl Acetate (1)-Cyclohexane (2) at 328.15 K								
0.049	0.129	47.17	328.15	2.699	0.998	0.977	0.977	127.2
0.119	0.235	51.70		2.211	1.035	0.973	0.975	339.7
0.180	0.310	54.01		2.010	1.046	0.971	0.974	444.3
0.210	0.329	54.92		1.858	1.074	0.971	0.974	507.9
0.241	0.352	55.44		1.747	1.089	0.970	0.974	543.9
0.355	0.425	57.09		1.472	1.171	0.968	0.973	652.3
0.448	0.468	57.85		1.301	1.282	0.968	0.973	696.2
0.527	0.521	58.01		1.234	1.352	0.967	0.974	691.2
0.549	0.528	57.81		1.196	1.392	0.967	0.974	675.7
0.603	0.563	57.64		1.158	1.461	0.967	0.974	651.0
0.668	0.601	57.20		1.107	1.583	0.967	0.975	601.7
0.735	0.644	56.16		1.059	1.739	0.967	0.976	515.1
0.764	0.672	55.46		1.050	1.778	0.968	0.976	472.8
0.821	0.722	53.46		1.013	1.919	0.969	0.978	347.7
0.930	0.869	49.90		1.007	2.165	0.970	0.981	164.4
0.966	0.924	48.57		1.004	2.520	0.971	0.982	95.8

Table III. Azeotropic Data for Binary Systems

system (1-2)	T, K	x_1	P, kPa
ethyl formate-cyclohexane	323.15	0.821	91.46
	314.95	0.815	66.66
ethyl acetate-cyclohexane	328.15	0.510	57.93

$$\rho_{ij}' = (1/\rho_{ij})\partial\rho_{ij}/\partial(1/T) \tag{11}$$

The UNIQUAC equation:

$$g^E/RT = x_1 \ln(\phi_1/x_1) + x_2 \ln(\phi_2/x_2) + (Z/2)[q_1x_1 \ln(\theta_1/\phi_1) + q_2x_2 \ln(\theta_2/\phi_2)] - q_1x_1 \ln(\theta_1 + \theta_2\nu_{21}) - q_2x_2 \ln(\theta_2 + \theta_1\nu_{12}) \tag{12}$$

Table IV. Experimental Heat of Mixing Data for Two Binary Systems

Ethyl Formate (1)-Benzene (2)[a]

298.15 K		308.15 K		318.15 K	
x_1	h^E, J/mol	x_1	h^E, J/mol	x_1	h^E, J/mol
0.0691	143.9	0.1094	169.0	0.1133	160.7
0.1609	284.5	0.2112	272.4	0.2036	243.5
0.2089	331.8	0.3063	331.4	0.2531	282.0
0.3142	389.9	0.3985	363.6	0.2978	307.1
0.3826	399.2	0.4044	362.8	0.4126	339.3
0.4555	407.5	0.4909	374.5	0.4284	341.8
0.4969	406.7	0.5797	352.3	0.5558	341.4
0.6999	330.5	0.5869	350.2	0.6019	325.9
0.8093	238.1	0.6936	311.3	0.7139	274.9
0.8478	200.8	0.7963	236.8	0.7973	221.3
0.8891	149.8	0.8991	136.4	0.7995	221.8
0.9485	77.8			0.8963	130.5

Ethyl Formate (1)-Cyclohexane (2)[b]

298.15 K		308.15 K	
x_1	h^E, J/mol	x_1	h^E, J/mol
0.0518	405.0	0.0345	278.2
0.1083	749.4	0.0720	533.0
0.1723	1041.8	0.1123	764.4
0.2331	1251.4	0.1552	969.9
0.2987	1410.8	0.2003	1146.8
0.3639	1516.7	0.2473	1294.9
0.4296	1571.9	0.2958	1413.4
0.4841	1582.0	0.3453	1501.2
0.5272	1566.9	0.3955	1558.5
0.5528	1548.9	0.4464	1587.0
0.5844	1515.0	0.4833	1589.9
0.6041	1489.9	0.5082	1583.2
0.6469	1419.6	0.6163	1482.4
0.6942	1319.6	0.6469	1429.3
0.7448	1184.5	0.6820	1356.0
0.7957	1018.0	0.7174	1267.8
0.8462	819.6	0.7534	1163.6
0.8525	792.9	0.7891	1044.7
0.9025	559.4	0.8247	910.0
0.9515	295.0	0.8602	759.8
		0.8956	593.3
		0.9308	411.3
		0.9657	213.4

[a] Obtained by using the Larkin and McGlashan type calorimeter (*8*). [b] Obtained by using the Van Ness type calorimeter (*6*).

$$\ln \gamma_1 = \ln (\phi_1/x_1) + (Z/2)q_1 \ln (\theta_1/\phi_1) + \phi_2[l_1 - (r_1/r_2)l_2] - q_1 \ln (\theta_1 + \theta_2\nu_{21}) + \theta_2 q_1[\nu_{21}/(\theta_1 + \theta_2\nu_{21}) - \nu_{12}/(\theta_2 + \theta_1\nu_{12})] \quad (13)$$

$$\ln \gamma_2 = \ln (\phi_2/x_2) + (Z/2)q_2 \ln (\theta_2/\phi_2) + \phi_1[l_2 - (r_2/r_1)l_1] - q_2 \ln (\theta_2 + \theta_1\nu_{12}) + \theta_1 q_2[\nu_{12}/(\theta_2 + \theta_1\nu_{12}) - \nu_{21}/(\theta_1 + \theta_2\nu_{21})] \quad (14)$$

$$h^E/R = -q_1x_1\theta_2/(\theta_1 + \theta_2\nu_{21})\nu_{21}' - q_2x_2\theta_1/(\theta_2 + \theta_1\nu_{12})\nu_{12}' \quad (15)$$

where

$$\nu_{ij} = \exp[-(u_{ij} - u_{jj})/RT] \quad (16)$$

$$\nu_{ij}' = \partial\nu_{ij}/\partial(1/T) \quad (17)$$

$$\theta_i = q_ix_i/\sum_j (q_jx_j) \quad (18)$$

$$\phi_i = r_ix_i/\sum_j (r_jx_j) \quad (19)$$

Table V. Binary Constants of Wilson and UNIQUAC Equations and Root-Mean-Square Deviations for Binary Systems

	binary constants										
	Wilson			UNIQUAC						root-mean-square devns, J/mol	
system	C_1/R C_2/R, K	D_1/R D_2/R	$E_1/R \times 100$ $E_2/R \times 100$, 1/K	C_1/R C_2/R, K	D_1/R D_2/R	$E_1/R \times 100$ $E_2/R \times 100$, 1/K	excess functions	temp or pressure	no. of data points	Wilson	UNIQUAC	ref
ethyl formate (1)-benzene (2)	133.80 2.71	−0.3637 −0.2081	−0.4784 0.8665	39.23 −12.67	−1.2197 0.8438	−0.0705 0.4112	g^E	323.15 K	10	13.4	14.6	this work
							g^E	66.66 kPa (500 mmHg)	8	18.0	16.3	this work
							h^E	298.15 K	12	14.6	15.9	this work
							h^E	308.15 K	11	11.3	10.9	this work
							h^E	318.15 K	12	7.1	8.8	this work
ethyl formate (1)-cyclohexane (2)	502.63 194.76	−0.8421 −2.6670	−1.2199 2.5319	222.32 −22.40	0.5703 −0.8849	−0.5472 0.3344	g^E	323.15 K	9	25.5	22.6	this work
							g^E	66.66 kPa (500 mmHg)	9	20.5	23.4	this work
							h^E	298.15 K	20	16.3	30.1	this work
							h^E	308.15 K	23	12.1	28.0	this work
ethyl acetate (1)-benzene (2)	144.01 −57.20	−0.7075 −0.9565	−0.5918 1.9120	−49.64 64.75	−1.2652 0.0380	3.2586 −2.1235	g^E	328.15 K	6	5.0	7.1	this work
							g^E	101.325 kPa (760 mmHg)	13	9.2	10.5	3
							h^E	308.15 K	7	13.0	15.5	13
ethyl acetate (1)-cyclohexane (2)	310.45 227.29	0.4504 −3.3727	−0.9102 1.8008	36.26 89.60	−1.4255 1.1087	1.8103 −2.2712	g^E	328.15 K	16	13.8	37.2	this work
							g^E	101.325 kPa (760 mmHg)	13	6.7	24.7	3
							h^E	308.15 K	13	30.5	44.4	13

$$l_i = (Z/2)(r_i - q_i) - (r_i - 1) \qquad (20)$$

A simultaneous fit of g^E and h^E data was attempted by using the Wilson equation (and also the UNIQUAC equation) whose energy parameter differences were assumed to be expressed by a quadratic function of temperature as shown by Nagata and Yamada (*9*).

$$\lambda_{ij} - \lambda_{ii} = C_i + D_i(T - 273.15) + E_i(T - 273.15)^2 \qquad (21)$$

The constants, C, D, and E, were determined by using the simplex method (*10*) which minimized the sum of squares of deviations in g^E plus that in h^E data points. Calculated results for four binary systems agree reasonably well with the experimental values as shown in Table V. The table also indicates that the Wilson equation gives slightly better results than the UNIQUAC equation for two ester-cyclohexane systems.

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Glossary

C, D, E	constants of eq 21
g^E	excess Gibbs free energy, J/mol
h^E	excess enthalpy of mixing, J/mol
l	bulk factor defined by eq 20
P_i^s	vapor pressure of pure component i, kPa
P	total pressure, kPa
q	pure component area parameter
R	gas constant
r	pure component volume parameter
T	absolute temperature, K
u_{ij}	UNIQUAC binary interaction parameter, J/mol
v_i^L	liquid molar volume of pure component i, cm^3/mol
x	liquid-phase mole fraction
y	vapor-phase mole fraction
Z	lattice coordination number, a constant set equal to 10

Greek Letters

γ_i	activity coefficient of component i
θ_i	area fraction defined by eq 18
Λ_{ij}	coefficient defined by eq 7
λ_{ij}	Wilson binary interaction parameter, J/mol
ρ_{ij}	volume ratio defined by eq 10
τ_{ij}	coefficient defined by eq 8
ν_{ij}	coefficient defined by eq 16
ϕ_i	volume fraction defined by eq 19
ψ_i^s	fugacity coefficient of pure component i at system temperature and P_i^s
ψ_i	fugacity coefficient of component i

Subscript

i	component

Superscripts

E	excess
s	saturation

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