Table IV. Constants for Excess Properties Equation, Standard Error, and Maximum Error, Cal Mol^{-1}, 25.0°C

Mixture	A_0	A_1	A_2	A_3	A_4	σ_{ave}	σ_{max}
Benzene(1)–1-hexanol(2)	1091.0	493.8	−12.3	604.5	898.4	3.28	6.5
Benzene(1)–2-methyl-2-butanol(2)	1494.3	388.6	277.8	539.8	605.2	1.63	2.6
Toluene(1)–2-methyl-2-butanol(2)[a]	1320.3	333.6	248.7	567.5	690.1	0.57	0.7
Toluene(1)–2-methyl-2-butanol(2)[b]	1322.2	327.8	226.3	596.4	749.8	2.95	6.3
1,3,5-Trimethylbenzene(1)–2-methyl-2-butanol(2)	1286.9	310.3	489.0	563.4	467.3	2.49	4.3
n-Hexane(1)–nitroethane(2)[c]	1341.8	−32.8	1990.3	402.9	−1199.5	2.08	5.3
Cyclohexane(1)–nitroethane(2)	1608.7	−66.0	738.5	514.9	...	1.19	2.4
Methylcyclohexane(1)–nitroethane(2)	1545.6	−19.3	894.5	261.7	−204.0	1.04	1.6
2,2,4-Trimethylpentane(1)–nitroethane(2)[d]	1560.8	−19.3	937.7	201.8	...	1.86	3.5
n-Hexane(1)–2-nitropropane(2)	1399.5	113.5	323.7	308.0	163.9	0.78	0.9
Cyclohexane(1)–2-nitropropane(2)	1412.4	159.9	228.5	298.5	264.2	1.04	1.7
Methylcyclohexane(1)–2-nitroethane(2)	1371.4	127.9	320.8	292.5	79.1	1.09	2.1
2,2,4-Trimethylpentane(1)–2-nitropropane(2)	1393.9	102.1	345.3	200.4	120.0	1.44	3.3

[a] Excludes measurements at mole fractions of 0.0619 and 0.9133. [b] Includes all measurements. [c] For liquid miscible ranges of 0.0–0.3 and 0.78–1.0 mole fraction nitroethane. [d] For liquid miscible ranges of 0.0–0.3 and 0.82–1.0 mole fraction nitroethane.

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

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Isothermal vapor-liquid equilibrium data for the methanol–ethyl acetate, ethyl acetate–ethanol, ethyl acetate–1-propanol, and ethyl acetate–2-propanol systems are presented at 55°C. Heat of mixing data are also obtained for the ethyl acetate–1-propanol system at 25°, 35°, and 45°C and for the other systems at 25° and 35°C. A simultaneous fit of the excess Gibbs free energies and heats of mixing is successfully represented by the Wilson equation whose energy parameter differences are assumed to be a quadratic function of temperature.

As part of a continuing study of thermodynamic properties of binary alcohol mixtures including such solvents as esters and ketones, vapor-liquid equilibrium data at 55°C for the four binary systems, methanol–ethyl acetate, ethanol–ethyl acetate, ethyl acetate–1-propanol, and ethyl acetate–2-propanol, were measured by a Scatchard still. The experimental data are compared with those of other investigations (*4, 6*) using the Wilson equation. Heat of mixing data are presented for the ethyl acetate–1-propanol system at 25°, 35°, and 45°C and for the other three systems at 25° and 35°C. Both excess Gibbs free energies and heat of mixing data are simultaneously correlated by the Wilson equation whose energy parameter differences are given by a quadratic function of temperature.

Experimental Procedure

Materials purchased for experimental work were of chemically pure grade. The alcohols used were mainly purified by fractional distillation in a glass column packed with McMahon packings. The alcohols were first treated with drying materials: methanol (anhydrous calcium sulfate), ethanol (calcium oxide), and propanols (copper sulfate anhydride). Ethyl acetate was purified according

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Table I. Physical Properties of Compounds

	Ethyl acetate	Methanol	Ethanol	1-Propanol	2-Propanol
Boiling point, °C					
Experimental	77.1	64.7	78.3	97.2	82.3
Literature	77.114 (*12*)	64.7 (*12*)	78.29 (*12*)	97.20 (*12*)	82.26 (*12*)
Density at 25°C					
Experimental	0.8946	0.7868	0.7853	0.7995	0.7811
Literature	0.89455 (*12*)	0.78664 (*12*)	0.78504 (*12*)	0.79975 (*12*)	0.78126 (*12*)
Refractive index at 25°C					
Experimental	1.3698	1.3265	1.3592	1.3828	1.3749
Literature	1.36979 (*12*)	1.32652 (*12*)	1.35941 (*12*)	1.38370 (*12*)	1.3752 (*12*)
Antoine constants					
A	7.08520 (*4*)	7.89750 (*12*)	8.21337 (*1*)	7.61924 (*1*)	8.11778 (*12*)
B	1231.47	1474.08	1652.05	1375.14	1580.92
C	215.84	229.13	231.48	193.00	219.61

Table II. Experimental Isothermal Vapor-Liquid Equilibrium Data for Four Binary Systems at 55°C

x_1	y_1	P, mm Hg	γ_1	γ_2	ϕ_1	ϕ_2	g^E, cal/mol
			Methanol(1)–ethyl acetate(2)				
0.031	0.116	381.0	2.740	1.000	0.974	0.970	20.2
0.166	0.364	477.6	2.001	1.038	0.968	0.962	95.6
0.206	0.406	493.6	1.857	1.051	0.967	0.960	109.0
0.339	0.513	534.4	1.540	1.117	0.965	0.957	142.9
0.455	0.573	554.6	1.328	1.230	0.964	0.955	157.6
0.541	0.615	563.9	1.218	1.337	0.963	0.954	156.6
0.604	0.649	568.1	1.160	1.423	0.963	0.953	149.4
0.660	0.675	571.1	1.110	1.542	0.963	0.953	140.7
0.739	0.725	571.7	1.066	1.701	0.963	0.953	121.0
0.862	0.815	562.3	1.011	2.130	0.964	0.953	74.0
0.900	0.856	553.5	1.002	2.253	0.964	0.954	53.9
			Ethyl acetate(1)–ethanol(2)				
0.081	0.189	323.2	2.178	0.997	0.973	0.976	39.6
0.112	0.240	338.8	2.094	1.013	0.972	0.975	61.3
0.165	0.313	355.4	1.942	1.020	0.971	0.973	82.1
0.273	0.406	379.7	1.623	1.080	0.969	0.971	122.7
0.385	0.489	395.0	1.441	1.141	0.968	0.970	144.5
0.428	0.511	398.9	1.367	1.185	0.968	0.970	150.6
0.495	0.546	402.8	1.275	1.258	0.968	0.970	154.0
0.594	0.604	404.2	1.180	1.369	0.968	0.969	147.1
0.708	0.672	403.5	1.099	1.574	0.968	0.969	130.0
0.814	0.749	393.8	1.041	1.846	0.969	0.970	95.7
0.890	0.825	376.9	1.005	2.085	0.970	0.971	55.8
			Ethyl acetate(1)–1-propanol(2)				
0.108	0.389	178.5	1.882	1.017	0.986	0.987	54.3
0.275	0.623	242.7	1.602	1.045	0.981	0.983	105.3
0.359	0.667	266.5	1.439	1.144	0.979	0.981	141.3
0.438	0.710	278.6	1.311	1.187	0.978	0.980	140.0
0.525	0.755	297.9	1.242	1.267	0.976	0.979	147.2
0.584	0.771	303.4	1.160	1.376	0.976	0.979	143.1
0.647	0.800	312.9	1.120	1.460	0.975	0.978	134.7
0.695	0.822	320.4	1.096	1.539	0.975	0.978	127.2
0.770	0.856	325.5	1.046	1.677	0.974	0.977	100.0
0.839	0.895	330.5	1.019	1.773	0.974	0.977	70.2
0.896	0.927	337.0	1.007	1.945	0.973	0.976	49.0
0.946	0.958	339.3	0.992	2.169	0.973	0.976	22.3
			Ethyl acetate(1)–2-propanol(2)				
0.080	0.186	260.5	1.761	0.980	0.979	0.984	17.3
0.159	0.315	288.9	1.660	0.999	0.977	0.982	51.7
0.260	0.420	313.4	1.465	1.041	0.975	0.981	83.9
0.358	0.505	329.5	1.343	1.075	0.974	0.980	99.2
0.450	0.566	341.6	1.240	1.140	0.973	0.979	110.1
0.525	0.611	351.2	1.179	1.215	0.972	0.978	116.8
0.569	0.646	354.7	1.161	1.231	0.972	0.978	113.8
0.640	0.682	360.4	1.107	1.345	0.971	0.978	118.2
0.696	0.716	360.0	1.067	1.420	0.971	0.978	99.1
0.778	0.776	362.9	1.043	1.546	0.971	0.978	84.4
0.845	0.829	360.5	1.019	1.680	0.971	0.978	62.9
0.923	0.900	356.4	1.002	1.956	0.972	0.978	34.7

to the procedure of Hurd and Strong (*12*). Values of the densities, refractive indices, and boiling points of the purified components are compared with the literature values in Table I.

The vapor-recirculating still used to obtain vapor-liquid equilibrium data in this study was originally designed by Scatchard and Ticknor (*13*) and modified by Renon and Prausnitz (*11*) who used a longer coiled Cottrell pump between a boiler and a thermometer well. The still has no stopcocks in contact with the liquid and needs a relatively small sample size (about 50 ml).

Analyses of the liquid and the vapor phase for the methanol–ethyl acetate system were made by measuring their refractive indices at 25°C with a Shimadzu Pulfrich refractometer with an accuracy of ±0.00005. Liquid and vapor samples for the other three systems were analyzed by measuring their densities at 25°C with 10 cm^3 Lypkin pycnometers which had been calibrated with distilled water. The precision of the density measurements was ±0.0001 grams. Boiling temperature measurements were made using copper–constantan thermocouples which had been calibrated against a mercury thermometer certified by the National Research Laboratory of Metrology, Tokyo, with a precision of 0.05°C. A mercury manometer and a cathetometer were used to read off the pressure in the still with an accuracy of 0.1 mm Hg. All observed readings of pressure were corrected to give the height of a mercury column at 0°C and standard gravity.

The calorimeter (*8*) used for measuring the heat of mixing of liquids is analogous to that described by Larkin and McGlashan (*3*). It consists of a glass mixing cell with two compartments in its upper half and a side arm. The cell also contains a thermistor and an electrical heater for calibration. The two liquids to be mixed are confined separately in the compartments by filling mercury in the rest of the cell and the side arm in the complete absence of vapor spaces. The cell is loaded in a sealed plastic vessel submerged in a water thermostat with inner and outer baths controlled separately. The temperature of the cell was maintained within ±0.005°C of specified temperature. The errors of the obtained heat of mixing data were estimated to be of the order of ±1.0%.

Results

Table II lists isothermal vapor-liquid equilibrium data for four binary systems. The liquid-phase activity coefficients were calculated from the following equation which involves corrections for vapor-phase nonideality:

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

using experimental x, y, P, and T data and the methods described by Prausnitz et al. (*10*) to calculate the vapor-phase fugacity coefficients. The pure vapor-pressure data were obtained from the Antoine equation whose constants are listed in Table I.

The excess Gibbs free energy is obtained by

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

Isothermal vapor-liquid equilibrium data for the ethyl acetate–ethanol system were reported by Murti and Van Winkle (*6*) at 40° and 60°C and by Mertl (*4*) at 40°, 55°, and 70°C. Isothermal experimental data for the other three systems were also obtained by Murti and Van Winkle (*6*). Table II represents the results at 55°C.

The area test was used to examine the thermodynamic consistency of the data by preparing a plot of ln (γ_1/γ_2) vs. x_1. Prausnitz (*9*) suggested that a given set of data is thermodynamically consistent if 0.02 > |(area above x-axis − area below x-axis)/(area above x-axis + area below x-axis)|.

Results obtained for the present data are less than this criterion: methanol–ethyl acetate (0.001), ethyl acetate–ethanol (0.005), ethyl acetate–1-propanol (0.013), and ethyl acetate–2-propanol (0.006).

The Wilson equation used for data reduction is given by

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

Table III. Parameters of Wilson Equation and Root-Mean-Square Deviations for Binary Systems

System	°C	No. of data points	Parameters, cal/mol		Root-mean-square deviations			Ref.
			$\lambda_{12} - \lambda_{11}$	$\lambda_{21} - \lambda_{22}$	Vapor mole fraction × 1000	Relative dev in press × 1000	Absolute dev in press, mm Hg	
Methanol(1)–ethyl acetate(2)	40	14	1223	−338	16	15	4	(*6*)
	50	13	1007	−250	14	7	3	(*6*)
	60	15	1190	−420	15	8	5	(*6*)
	55	11	1052	−299	4	2	1	This work
	55	11	1059	−313	5	2	1	This work[a]
Ethyl acetate(1)–ethanol(2)	40	18	−40	845	9	9	2	(*6*)
	60	19	−131	778	10	12	5	(*6*)
	40	14	20	730	5	3	1	(*4*)
	55	14	25	660	6	5	2	(*4*)
	70	15	−53	665	7	5	4	(*4*)
	55	11	2	702	5	3	2	This work
	55	11	−119	852	8	6	3	This work[a]
Ethyl acetate(1)–1-propanol(2)	40	12	5	635	9	12	1	(*6*)
	60	14	−2	500	12	6	3	(*6*)
	55	12	143	502	10	6	3	This work
	55	12	167	493	15	8	4	This work[a]
Ethyl acetate(1)–2-propanol(2)	40	14	0	610	12	12	2	(*6*)
	60	19	−130	625	13	9	4	(*6*)
	55	12	−39	557	6	5	2	This work
	55	12	−87	620	6	5	2	This work[a]

[a] A simultaneous fit of g^E and h^E data.

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

Temp, °C	x_1	h^E, cal/mol	Temp, °C	x_1	h^E, cal/mol	Temp, °C	x_1	h^E, cal/mol	Temp, °C	x_1	h^E, cal/mol
Methanol(1)-ethyl acetate(2)			Ethanol(1)-ethyl acetate(2)			1-Propanol(1)-ethyl acetate(2)			2-Propanol(1)-ethyl acetate(2)		
25.00	0.0123	18.1	25.00	0.0384	65.9	25.00	0.0353	64.3	25.00	0.0354	66.9
	0.0524	67.3		0.0932	135.7		0.0652	109.7		0.0625	112.9
	0.1150	125.9		0.1105	154.0		0.1538	220.4		0.0935	162.8
	0.1706	160.7		0.1879	214.2		0.1737	243.1		0.1632	258.1
	0.3042	225.2		0.2844	269.7		0.3054	345.0		0.2764	359.6
	0.3846	242.2		0.3807	300.2		0.3925	379.5		0.4470	422.6
	0.4853	252.7		0.4810	306.2		0.4830	383.6		0.5723	406.3
	0.5930	233.8		0.5903	289.4		0.6018	352.6		0.5593	411.4
	0.7019	185.0		0.6769	257.8		0.7179	294.7		0.6818	358.4
	0.8067	132.6		0.7679	213.5		0.8112	222.4		0.7007	347.1
	0.9026	70.9		0.8975	113.0		0.8957	138.5		0.7629	301.5
	0.9345	50.2		0.9461	63.7		0.9067	127.8		0.8340	236.3
	0.9617	30.8		0.9859	17.9		0.9489	77.8		0.8937	164.2
										0.9502	83.6
35.00	0.0569	73.6	35.00	0.0601	104.6	35.00	0.0502	88.2			
	0.1065	116.4		0.0669	110.3		0.0535	92.4	35.00	0.0491	96.2
	0.2057	187.6		0.1115	172.2		0.1032	167.0		0.0999	182.9
	0.3030	232.7		0.2037	246.7		0.1994	275.4		0.1001	182.5
	0.3056	234.8		0.2311	269.4		0.2009	280.1		0.1972	301.2
	0.3986	242.0		0.2725	288.4		0.2046	283.2		0.2004	302.9
	0.4850	246.3		0.3071	294.0		0.3061	342.8		0.2979	379.2
	0.5610	238.5		0.3869	323.1		0.3866	377.6		0.3975	422.5
	0.6414	218.8		9.4080	326.6		0.5068	379.2		0.4985	425.8
	0.7314	183.3		0.4986	317.5		0.6307	343.3		0.5065	427.7
	0.8370	131.3		0.5049	317.8		0.7073	306.4		0.5079	431.4
	0.9569	45.0		0.5824	309.1		0.7095	303.1		0.6060	401.5
	0.9576	43.1		0.5865	297.0		0.7965	241.6		0.6093	397.4
				0.6797	272.8		0.8082	228.7		0.7046	337.4
				0.7711	228.5		0.9001	130.3		0.7046	345.7
				0.8181	198.5		0.9013	130.2		0.7994	265.1
				0.9131	118.8		0.9021	132.7		0.8011	262.7
							0.9467	76.2		0.8957	161.6
							0.9479	73.7		0.9209	124.9
							0.9481	74.4		0.9453	89.7
						45.00	0.1043	174.2			
							0.2051	286.4			
							0.2524	327.4			
							0.2990	362.5			
							0.3953	392.3			
							0.4389	399.5			
							0.5420	389.5			
							0.5920	374.3			
							0.6853	327.4			
							0.7929	251 2			
							0.7932	250.4			
							0.8905	151.6			

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

System	C_1 C_2	D_1 D_2	$E_1 \times 1000$ $E_2 \times 1000$	g^E or h^E	°C	Dev, cal/mol
Methanol(1)-ethyl	1051.64	0.2066	−1.408	g^E	55	1.4
acetate(2)	−173.98	−2.6615	2.478	h^E	25	4.9
				h^E	35	4.5
Ethyl acetate(1)-	311.27	−2.7427	0.308	g^E	55	4.3
ethanol(2)	907.61	−0.3605	−11.718	h^E	25	3.9
				h^E	35	9.6
Ethyl acetate(1)-	285.74	−3.4493	23.317	g^E	55	5.7
1-propanol(2)	640.39	−1.6924	−17.977	h^E	25	4.5
				h^E	35	3.3
				h^E	45	4.0
Ethyl acetate(1)-	135.71	−4.9714	16.751	g^E	55	4.4
2-propanol(2)	699.60	−0.7080	−13.527	h^E	25	3.6
				h^E	35	3.9

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

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

where

$$\Lambda_{ij} = (V_j^L/V_i^L) \exp [-(\lambda_{ij} - \lambda_{ii})/RT] \quad (6)$$

The Wilson parameters were determined by using a nonlinear least-squares regression program which minimizes the sum of squares of deviations in the vapor mole fraction plus the sum of squares of relative deviations in pressure for all data points. Table III lists the numerical values of the Wilson parameters and the root-mean-square deviations calculated from experimental results, showing that the present data have smaller deviations than the previous data. Table IV shows experimental heat of mixing data obtained in this work. Murti and Van Winkle (5) and Grolier and Viallard (2) reported data at 25°C. Their smoothed data were compared with the present smoothed experimental data. Data smoothing was made using the three-constant Redlich-Kister equation. The absolute arithmetic average deviations of these literature values from our smoothed data at nine points of the interval of 0.1 mole fraction are given as follows:

	Deviation, cal/mol	
System	Data of ref. *4*	Data of ref. *2*
Methanol–ethyl acetate	6	13
Ethyl acetate–ethanol	27	4
Ethyl acetate–1-propanol	8	11
Ethyl acetate–2-propanol	5	4

Substitution of Equation 3 into the Gibbs-Helmholtz relation gives

$$h^E/R = x_1x_2[\Lambda_{12}(\tau_{12}' - \rho_{12}')/(x_1 + \Lambda_{12}x_2) + \Lambda_{21}(\tau_{21}' - \rho_{21}')/(x_2 + \Lambda_{21}x_1)] \quad (7)$$

where $\tau_{ij}' = \partial\tau_{ij}/\partial(1/T)$ and $\rho_{ij}' = (1/\rho_{ij})\partial\rho_{ij}/\partial(1/T)$. A simultaneous fit of g^E and h^E data was attempted by using the Wilson equation whose parameters are assumed to be a quadratic function of temperature as shown by Nagata and Yamada (*7*).

$$\lambda_{ij} - \lambda_{ii} = C_i + D_i(T - 273.15) + E_i(T - 273.15)^2 \quad (8)$$

A Simplex pattern search procedure was used to obtain constants *C*, *D*, and *E* listed in Table V by minimizing the sum of squares of deviations in g^E plus that in h^E data points.

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Nomenclature

C, D, E = constants of Equation 7
g^E = excess Gibbs free energy, cal/mol
h^E = excess enthalpy of mixing, cal/mol
P = total pressure, atm
P_i^S = vapor pressure of pure component i at system temperature, atm
R = gas constant, 1.987 cal/mol K
T = absolute temperature, K
V^L = molar liquid volume, ml/mol
x = liquid-phase mole fraction
y = vapor-phase mole fraction

Greek Letters

γ = activity coefficient
ρ = ratio of molar liquid volume as defined by $\rho_{ij} = V_j^L/V_i^L$
τ_{ij} = coefficient as defined by $\tau_{ij} = (\lambda_{ij} - \lambda_{ii})/RT$
$\lambda_{ij} - \lambda_{ii}$ = Wilson parameter, cal/mol
Λ_{ij} = coefficient as defined by $\Lambda_{ij} = (V_j^L/V_i^L) \exp [-(\lambda_{ij} - \lambda_{ii})/RT]$
ϕ_i = vapor-phase fugacity coefficient of component i
ϕ_i^S = vapor-phase fugacity coefficient of pure component i at system temperature and P_i^S

Subscript

i = component

Superscripts

E = excess property
L = liquid state
S = saturation condition

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