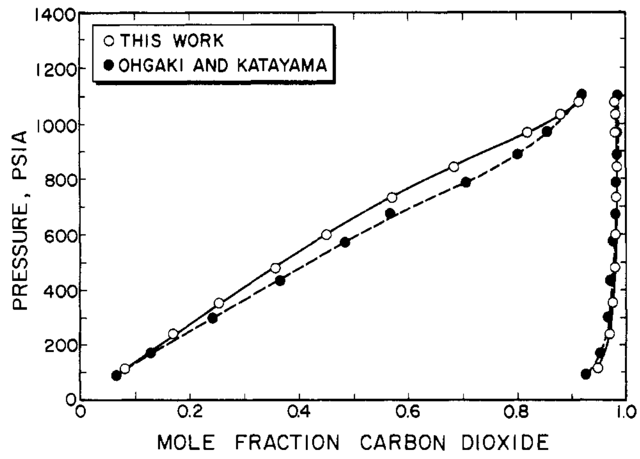

Figure 3. Comparison of pressure-composition data at 40 °C for carbon dioxide–*n*-hexane.

study are lower in *n*-hexane than those of the present study. At 500 psia, this difference is 6 mol %, and the difference in the *K* values for *n*-hexane is ~25%.

Correlation

The data from the present work have been correlated by the Soave equation of state (*3*), with the mixing rules

$$a = \sum_{i=1}^{N} \sum_{j=1}^{N} y_i y_j a_{ij}$$

$$b = \sum_{i=1}^{N} y_i b_i$$

$$a_{ij} = (a_i a_j)^{1/2}(1 - C_{ij})$$

where C_{ij} is an empirical interaction parameter. In this work, the value C_{ij} was determined by minimizing the sum of squares, SS, of errors in the predicted phase compositions at fixed temperature and pressure

$$SS = \sum_{i=1}^{M} \{(\Delta x)^2 + (\Delta y)^2\}_i$$

Table II presents values of C_{ij} evaluated from the data of the present work at each separate isotherm and from all of the data treated simultaneously. Also shown is the result of similar treatment of the data of Ohgaki and Katayama at 40 °C. As shown in Table II, when all data from the present work are treated simultaneously, root-mean-square (rms) errors of 0.012 and 0.009 result in the liquid- and vapor-phase mole fractions, respectively.

Table II. Soave Correlation of Carbon Dioxide–*n*-Hexane Data

temp, °C	optimum C_{ij}	rms error in mole fraction: liquid	rms error in mole fraction: vapor
	Present Work		
40	0.125	0.011	0.002
80	0.130	0.009	0.004
120	0.139	0.006	0.013
all	0.131	0.012	0.009
	Oghaki and Katayama		
40	0.090	0.018	0.006

Careful analysis of the data from the present work reveals increased scatter in the data near the critical point. The data were reanalyzed by deleting data points at the two highest pressures on each isotherm; the optimum C_{ij} was unaffected (0.131), but errors in the predicted vapor mole fraction were reduced by a factor of 2 (to 0.005) while the liquid-phase prediction was unaffected. In this case, average absolute errors in the predicted *K* values are 5% for CO_2 and 6% for *n*-hexane. When all data are included, the errors are 4 and 13%, respectively.

Glossary

a, *b*	parameters in Soave equation of state
C_{ij}	empirical interaction parameter in Soave equation
M	total number of data points
N	total number of components in mixture
x	mole fraction CO_2 in liquid phase
y	mole fraction CO_2 in vapor phase
Δ	difference between experimental and calculated value

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Excess Gibbs Energy for Eight Oleic Acid–Solvent and Triolein–Solvent Mixtures at 318.15 K

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Vapor pressures of eight oleic acid–solvent and triolein–solvent mixtures have been determined on a static apparatus at 318.15 K. Activity coefficients and excess Gibbs energies have been derived from the data. The solvents with oleic acid are methanol, ethanol, 2-propanol, acetone, and *n*-hexane, while the solvents with triolein are 2-propanol, acetone, and *n*-hexane.

Introduction

The C_{17} and C_{18} fatty acids and their glycerides are of considerable importance in the soap and food industries. The separation of these high-molecular-weight compounds is generally effected by energy-intensive processes such as fractional crystallization. Alternative methods of separation are liquid extraction and extractive distillation. We therefore examine the excess thermodynamic properties of some fatty acid–solvent and glyceride–solvent systems, to help assess the suitability of these methods.

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Table I. Solvent Properties at 318.15 K

	P/kPa		B/(cm^3 mol^{-1})	V/(cm^3 mol^{-1})
	exptl	lit.[a]		
methanol	44.47	44.43	−1464	41.73
ethanol	23.00	23.00	−1872	59.99
2-propanol	18.15	18.13	−2126	78.66
acetone	68.10	68.15	−1606	76.25
hexane	44.92	44.92	−1617	135.23

[a] Reference *1*.

In this paper we report the vapor pressures of eight oleic acid–solvent and triolein–solvent systems at 318.15 K, determined on a static vapor-pressure apparatus. The solvents chosen for study are methanol, ethanol, 2-propanol, acetone, and *n*-hexane. Triolein is partially miscible in methanol and ethanol at 318.15 K, so these solvents have been excluded from the triolein–solvent group.

Materials

Absolute ethanol was of 99% purity. The remaining solvents were of BDH "Analar" grade and were used without further purification. Oleic acid (99%) was supplied by Unilever Research. Triolein, supplied by BDH Chemicals, was estimated

Table II. Vapor Pressure P, Activity Coefficients f, and Excess Gibbs Energies of Mixing for Oleic Acid- and Triolein-Solvent Systems at 318.15 K

x_1	P/kPa	f_1	f_2	G^E/(J mol^{-1})
x_1 Methanol + x_2 Oleic Acid				
0.000			1.000	0.0
0.029	2.94	2.331	1.005	78.8
0.051	4.85	2.187	1.010	130.4
0.071	6.27	2.029	1.018	176.5
0.089	7.56	1.950	1.023	210.7
0.167	13.63	1.868	1.028	337.2
0.268	18.86	1.606	1.065	458.0
0.354	22.63	1.457	1.111	531.8
0.456	27.10	1.349	1.164	579.0
0.581	31.69	1.235	1.269	588.3
0.713	36.35	1.152	1.442	543.7
0.812	39.66	1.101	1.648	454.6
0.930	43.13	1.043	2.048	236.1
1.000	44.47	1.000		0.0
x_1 Ethanol + x_2 Oleic Acid				
0.000			1.000	0.0
0.052	1.89	1.604	1.001	67.4
0.083	2.96	1.572	1.002	104.1
0.131	4.52	1.521	1.006	158.9
0.195	6.49	1.464	1.014	226.0
0.286	8.96	1.376	1.037	310.3
0.376	11.21	1.307	1.068	375.7
0.493	13.95	1.238	1.113	421.6
0.615	16.35	1.162	1.187	418.2
0.700	17.89	1.115	1.268	389.6
0.814	19.68	1.053	1.502	311.2
0.936	21.67	1.007	2.129	145.1
1.000	23.00	1.000		0.0
x_1 2-Propanol + x_2 Oleic Acid				
0.000			1.000	0.0
0.041	1.02	1.385	1.006	51.3
0.065	1.59	1.364	1.010	76.8
0.084	2.02	1.344	1.011	92.3
0.156	3.67	1.310	1.017	149.0
0.261	5.70	1.215	1.036	204.5
0.365	7.77	1.183	1.048	240.8
0.474	9.63	1.127	1.085	263.1
0.575	11.39	1.099	1.109	259.6
0.662	12.64	1.057	1.180	244.8
0.738	14.09	1.055	1.194	227.2
0.882	16.52	1.034	1.308	161.6
0.927	17.49	1.018	1.459	116.6
1.000	18.15	1.000		0.0
x_1 Acetone + x_2 Oleic Acid				
0.000			1.000	0.0
0.031	2.86	1.414	1.001	30.9
0.056	5.16	1.407	1.002	55.5
0.082	7.43	1.383	1.003	77.5
0.117	10.45	1.359	1.004	104.2
0.211	17.96	1.290	1.014	171.1
0.309	25.28	1.235	1.031	228.8
0.421	33.73	1.202	1.049	277.9
0.471	36.58	1.163	1.077	291.6
0.598	44.75	1.115	1.128	300.4
0.728	52.84	1.077	1.206	277.3
0.836	58.98	1.042	1.335	216.1
0.947	65.10	1.011	1.619	94.9
1.000	68.10	1.000		0.0
x_1 Hexane + x_2 Oleic Acid				
0.000			1.000	0.0
0.027	2.48	2.102	1.002	58.6
0.061	5.39	2.022	1.007	130.8
0.076	6.60	1.986	1.008	157.2
0.104	8.92	1.954	1.015	218.7
0.188	14.96	1.807	1.035	367.6
0.266	19.94	1.698	1.058	480.7
0.359	24.69	1.552	1.103	583.0
0.435	28.04	1.451	1.149	634.6
0.524	31.71	1.359	1.210	664.7
0.606	34.37	1.271	1.317	670.4
0.718	38.25	1.191	1.511	639.3
0.877	42.81	1.089	2.186	451.8
0.939	43.86	1.040	2.994	274.1
1.000	44.92	1.000		0.0
x_1 2-Propanol + x_2 Triolein				
0.000			1.000	0.0
0.069	4.15	3.359	1.023	276.9
0.129	7.26	3.109	1.034	463.6
0.258	10.99	2.364	1.103	778.8
0.359	12.72	1.963	1.203	952.9
0.462	14.04	1.681	1.343	1053.3
0.607	15.41	1.403	1.638	1055.6
0.688	16.04	1.288	1.887	983.9
0.815	16.95	1.148	2.678	778.8
0.917	17.71	1.065	4.201	467.4
1.000	18.13	1.000		0.0
x_1 Acetone + x_2 Triolein				
0.000			1.000	0.0
0.099	6.15	0.948	0.999	−16.4
0.169	10.60	0.955	0.997	−27.2
0.241	15.30	0.964	0.994	−35.4
0.318	20.33	0.968	0.993	−40.0
0.396	25.54	0.974	0.990	−43.6
0.523	34.26	0.983	0.981	−47.9
0.631	41.78	0.989	0.972	−46.1
0.749	50.05	0.993	0.961	−40.3
0.811	54.45	0.995	0.956	−33.2
0.895	60.55	0.998	0.941	−21.6
0.941	63.89	0.999	0.935	−13.0
1.000	68.10	1.000		0.0
x_1 Hexane + x_2 Triolein				
0.000			1.000	0.0
0.089	4.69	1.204	1.002	48.5
0.144	7.46	1.182	1.006	77.2
0.205	10.42	1.157	1.010	99.9
0.284	14.17	1.134	1.018	128.1
0.382	18.62	1.105	1.031	150.6
0.455	21.66	1.077	1.050	159.5
0.613	28.47	1.045	1.089	158.5
0.681	31.35	1.034	1.112	150.4
0.807	36.55	1.014	1.162	106.1
0.904	40.68	1.005	1.191	56.4
0.947	42.57	1.003	1.222	30.3
1.000	44.92	1.000		0.0

chromatographically to be of 96% purity, containing small amounts of other fats of comparable molecular weight and constitution. These impurities would be expected to have similar mixing characteristics with the solvents due to the similarity of intermolecular interactions. The vapor pressures of the solvents were measured at 318.15 K and are compared with published values in Table I. The vapor pressures of oleic acid and triolein were not measurable at this temperature.

Experimental Section

The static apparatus used in this investigation has been described by Sassa Konishi, and Katayama (*4*). The flask and null manometer were enclosed in a thermistor-controlled air bath maintained at 318.15 ± 0.04 K. A vacuum of 6×10^{-4} kPa was applied to the reference limb of the measuring manometer. The manometers were filled with triple-distilled mercury supplied by Belgrave Ltd. which was degassed after every run by heating the limbs with an infrared lamp while the manometers were under vacuum. Bubbles that formed were dislodged by tapping the glass sharply. The degassing procedure for the samples and the operational details are given in ref *4*. A correction was made for the amount of the volatile constituent which assumed the gaseous condition in the apparatus. Vapor pressures were read with a cathetometer accurate to 0.1 mmHg. The temperature was monitored with a calibrated glass thermometer accurate to 0.05 K. A change of 0.04 K produced a maximum pressure variation of 7×10^{-2} kPa. The standard deviation in pressure measurement was 0.05 kPa, and the standard deviation in G^E was 2.0 J mol^{-1}.

Theory

The activity coefficient of a component i in a liquid mixture is given by the relation

$$f_i = Z_i P y_i / (P_i^0 x_i) \tag{1}$$

Z is the vapor-phase nonideality correction factor

$$Z_i = \exp[(P - P_i^0)(V_i - B)/(RT)]$$

Oleic acid and triolein have vapor pressures of less than 10^{-4} kPa at 318.15 K and can be treated as essentially nonvolatile. The oleic acid–solvent and triolein–solvent systems can therefore be regarded as having one-component vapor phases comprising the solvent. Representing the solvent by subscript 1, we have

$$f_1 = Z_1 P / (P_1^0 x_1) \tag{2}$$

f_1 was calculated from total-pressure data. Molar volumes at 318.15 K were determined from density measurements, and second virial coefficients were interpolated from the tables of Dymond and Smith (*2*) where data were available. Values for 2-propanol and methanol were estimated by the method of Tsonopoulos (*5*). Virial coefficients and molar volumes are reported in Table I.

The activity coefficient of the high-molecular-weight compound, f_2, was calculated by integration of the Gibbs–Duhem equation (eq 3) as described by Lewis and Randall (*3*). x_1/x_2

$$\ln f_2 = -\int_0^{x_1'} \frac{x_1}{x_2} \, \mathrm{d} \ln f_1 \tag{3}$$

was represented as a function of $\ln f_1$ by a polynomial, and this equation was integrated from $x_1 = 0$ to $x_1 = x_1'$ to give $-\ln f_2$ at x_1'.

Table III. Constants of the Smoothing Equation $G^E = x_1 x_2 [\Sigma_i A_i (2x_1 - 1)^i]$ J mol^{-1} and Standard Deviation

component 1	A_0	A_1	A_2	A_3	A_4	σ/(J mol^{-1})
Oleic Acid Systems						
methanol	2346.4	315.1	676.4	348.4	552.4	1.7
ethanol	1679.4	344.1	51.3	372.8	296.9	1.2
2-propanol	1046.5	37.8	164.6	354.9	608.9	1.8
acetone	1179.3	340.3	163.1	173.7	239.7	1.2
hexane	2638.4	562.2	876.7	1114.5	369.9	1.3
Triolein Systems						
2-propanol	4275.5	519.8	270.4	877.9	1495.9	1.2
acetone	−187.7	−24.8	−65.8	1.9	50.0	0.6
hexane	654.8	93.9	41.4	−108.4	−127.0	1.3

Results

The experimental results are presented in Table II together with derived activity coefficient and excess Gibbs energy data. G^E was fitted to an equation of the type

$$G^E / x_1 x_2 = \sum_i A_i (2x_1 - 1)^i \tag{4}$$

The constants of the smoothing equation and the standard deviation of experimental G^E from the smoothing equation are given in Table III.

Glossary

A_0, A_1, A_2, ...	constants in eq 4
B	second virial coefficient, cm^3 mol^{-1}
f	activity coefficient
G	Gibbs energy, J mol^{-1}
P	total pressure, kPa
P^0	pure-component vapor pressure, kPa
R	gas constant
T	absolute temperature, K
V	molar volume, cm^3 mol^{-1}
x	liquid-phase mole fraction
y	vapor-phase mole fraction
Z	vapor-phase nonideality correction factor

Subscripts

1, 2, i components 1, 2, and i

Superscripts

E excess property

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