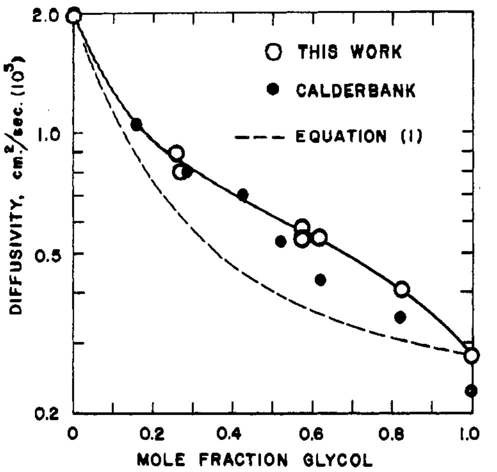

Figure 4. Diffusivity of carbon dioxide in aqueous ethylene glycol solutions at 25° C

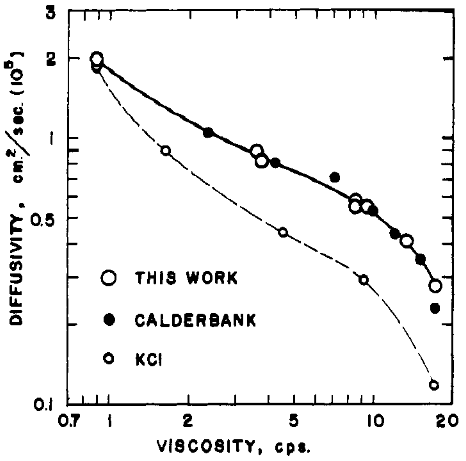

Figure 5. Carbon dioxide diffusivity in aqueous ethylene glycol solutions as a function of solvent viscosity

vent. The diffusivity data of Perkins and Geankoplis (*8*) for KCl in aqueous glycol at 25° C are shown for comparison to indicate the similarity in the viscosity–diffusivity relationship.

NOMENCLATURE

D = diffusivity in binary solvent solution, cm^2/sec
D^0_{12}, D^0_{13} = diffusivities of solute in pure solvents, 2 and 3, cm^2/sec
L = diffusion path length, cm
n_1 = mass flux of solute, g/cm^2 sec
x_2, x_3 = mole fraction of components 2 and 3 in solute-free solvent solution

Greek Letters

ρ = solution density, g/cm^3
ω_{10} = mass concentration solute at (saturated) solvent interface, g/cm^3
ω_{1L} = mass concentration of solute in capillary cell, g/cm^3
η = solvent solution viscosity
η_2, η_3 = viscosities of pure solvent components

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Vapor-Liquid Equilibria for Carbon Dioxide–Difluoromethane System

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Published data on the phase equilibria of systems containing carbon dioxide as one of the components are abundant, but those containing a fluorocarbon as the second component are rare. Also scarce are studies of fluorocarbon solutions containing difluoromethane. Thus, the combination of carbon dioxide and difluoromethane in this study provides an interesting addition to the available phase equilibrium data on the fluorocarbons.

The flammability of difluoromethane removes it from consideration as a commercial refrigerant. However, in combination with a second refrigerant which is nonflammable, such as carbon dioxide, the fire hazard may be overcome. At the same time, the mixture might produce a refrigerant whose physical-property range would be desirable. Establishment of such properties requires, among other things, accurate data describing the vapor-liquid equilibria of the mixture.

EXPERIMENTAL

An apparatus of the vapor-recirculation type (*9*) was used in this investigation. With this technique vapor was continuously removed from the top of the vapor-liquid equilibrium cell and reintroduced at the bottom of the

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Experimental vapor-liquid equilibrium data for the carbon dioxide–difluoromethane binary were determined at −60, −20, 20, and 50° F using the vapor-recirculation technique. Liquid-phase activity coefficients, which were computed from the data with the assumption that the Redlich-Kwong equation of state adequately described the nonidealities of the vapor phase, were correlated as a function of composition and temperature with the Wilson equation. A correlation was developed from which the vapor-liquid equilibria for this system can be computed at any temperature between −60° and 50° F.

cell where it bubbled up through the liquid, establishing the vapor-liquid contact needed to reach equilibrium. Between removal from the top of the cell and reintroduction at the bottom the vapor passed through a vapor-sampling coil, a pump, a variable-volume device, which permitted removal of samples from the system without reduction in system pressure, and a conditioning coil, which ensured that the vapor reintroduced at the bottom of the cell was at the temperature of the run. Details of the construction of the apparatus (*6*) and of the experimental technique used (*1*) have been described elsewhere.

The pressure of the system was measured with an accuracy of ±0.1 psia by means of Heise Bourdon-tube gages, which had been previously calibrated against a precision deadweight gage manufactured by the Ruska Instrument Corp. The weights of the deadweight gage were calibrated by Ruska against class S standards. The piston area was certified by Ruska, based on light-wave micrometer readings accurate to 5×10^{-6} in. The temperature was measured with a three-junction copper-constantan thermopile to within ±0.05° F; the temperature scale was established by calibration against a platinum resistance thermometer which had been previously calibrated by the U. S. National Bureau of Standards.

The phase samples were analyzed with a Beckman Instruments, Inc. GC-2A gas chromatograph using a di-*n*-butyl maleate column for separation and thermal conductivity for detection. An electronic integrator was used to determine the peak areas. The composition of each phase sample was determined by direct ratio of the peak area of the unknown sample to the peak area of a known standard sample of similar composition. The standard and the unknown were always run in immediate succession. Most pairs were run in duplicate. The standard samples, representing the composition range studied, were prepared at a total pressure of two atmospheres. The composition of each standard was determined from partial pressure measurements coupled with second-virial-coefficient corrections, which were quite small for the two-atmosphere-and-less pressure range involved. The calibration procedure for these standard samples and the analytical apparatus and technique are reported elsewhere (*1*). The estimated error in each reported CO_2 and CH_2F_2 composition is less than 2% of the lesser mole fraction.

Carbon dioxide of purity 99.8% was used as received. The purity of the difluoromethane, as received, was 99.0%. The major impurity was trifluoromethane. By successively liquefying and evacuating the material, this purity was increased to 99.8%.

EXPERIMENTAL RESULTS

Experimental vapor-liquid equilibrium data were determined at −60, −20, 20, and 50° F. These data are presented in Table I. The liquid phase was observed to behave nearly ideally at each temperature level. The pressure-composition diagram for 50° F is shown in Figure 1.

The pure-component vapor pressures were measured at each temperature level studied. These results are presented in Table II. The carbon dioxide data show an average deviation of 0.20% from the published data (*2*), with a maximum deviation of 0.37% at −20° F. The difluoromethane data show an average deviation of 0.34% from the published data (*4*), with a maximum deviation of 0.55% at 20° F.

CORRELATION OF EXPERIMENTAL DATA

Thermodynamic equilibrium between a liquid phase and a vapor phase is established when the temperature and pressure of both phases are equal and when the fugacity of each molecular species present is the same in both phases. In terms of two auxiliary functions, the fugacity coefficient and the activity coefficient, the equality of fugacity at equilibrium for any component, *i*, can be written.

$$\phi_i y_i P = \gamma_i x_i f_i^{oL} \tag{1}$$

The correlation presented follows closely a method demonstrated in several places by Prausnitz (*7*). Consequently, only a brief description featuring the numerical values and equations required to use the correlation is given.

Table I. Vapor-Liquid Equilibrium Data for CO_2–CH_2F_2

Temp = 50.00° F			Temp = −20° F		
Press, psia	Liquid mole fraction, CO_2	Vapor mole fraction, CO_2	Press, psia	Liquid mole fraction, CO_2	Vapor mole fraction, CO_2
161.0	0.0	0.0	41.6	0.0	0.0
171.0	0.0200	0.062	44.7	0.0190	0.079
198.0	0.081	0.215	49.5	0.0480	0.183
217.1	0.120	0.294	54.4	0.073	0.275
244.6	0.186	0.414	64.9	0.135	0.424
290.3	0.286	0.543	75.9	0.197	0.540
348.5	0.418	0.656	95.6	0.313	0.676
387.6	0.483	0.721	115.1	0.429	0.771
438.4	0.583	0.789	138.8	0.560	0.847
503.9	0.719	0.863	161.1	0.689	0.904
553.0	0.814	0.910	180.4	0.798	0.942
592.2	0.893	0.948	193.8	0.883	0.9651
624.4	0.949	0.9751	204.0	0.944	0.9819
651.6	1.0	1.0	214.2	1.0	1.0
Temp = 20.00° F			Temp = −60.00° F		
95.2	0.0	0.0	15.2	0.0	0.0
99.7	0.0138	0.051	16.6	0.0199	0.101
107.1	0.0370	0.120	18.8	0.044	0.213
127.7	0.103	0.296	24.7	0.124	0.447
149.4	0.173	0.442	30.2	0.199	0.587
175.2	0.252	0.556	40.6	0.324	0.737
197.0	0.320	0.628	51.1	0.458	0.825
227.7	0.427	0.712	60.3	0.564	0.882
273.4	0.567	0.804	70.0	0.688	0.924
297.7	0.633	0.847	80.8	0.822	0.9609
333.9	0.747	0.895	83.9	0.864	0.9694
363.5	0.831	0.932	89.1	0.927	0.9822
386.5	0.898	0.9590	94.6	1.0	1.0
408.5	0.9605	0.9810			
422.4	1.0	1.0			

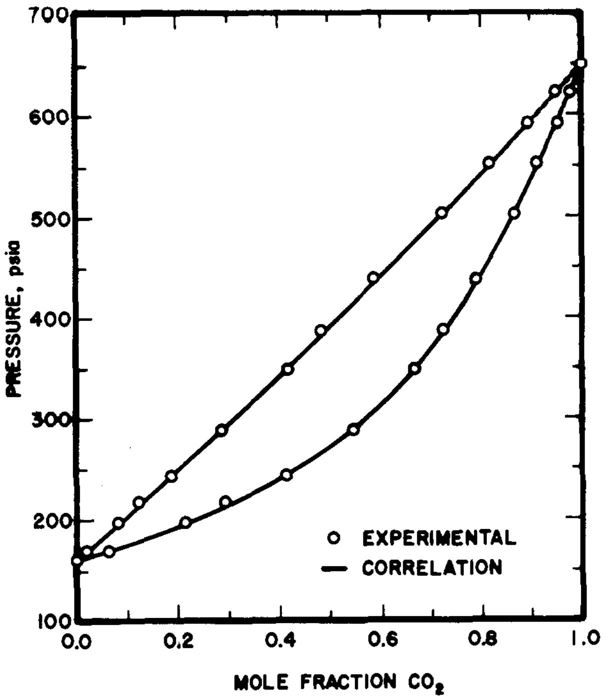

Figure 1. Pressure-composition diagram for CO_2–CH_2F_2 at 50° F

The pressure-volume-temperature properties of the vapor phase were described by the Redlich-Kwong equation of state (*8*). For this equation of state, the fugacity coefficient of component, *i*, can be written as follows:

$$\ln \phi_i = \ln \frac{v}{v-b} + \frac{b_i}{v-b} - \frac{2\sum_{j=1}^{N} y_j a_{ij}}{RT^{3/2}b} \ln \frac{v+b}{v} + \frac{ab_i}{RT^{3/2}b^2}\left(\ln \frac{v+b}{v} - \frac{b}{v+b}\right) - \ln \frac{Pv}{RT} \qquad (2)$$

The Redlich-Kwong constants, *a* and *b*, for the mixture were calculated from the mixing rules proposed by Chueh (*3*). The dimensionless constants, Ω_a and Ω_b, required in the calculation of a_{ij}, b_i, *a*, and *b* were evaluated by fitting the Redlich-Kwong equation to the volumetric data of the saturated vapor for each component. For carbon dioxide Chueh (*3*) reported values of 0.4470 and 0.0911 for Ω_a and Ω_b, respectively; for difluoromethane, Adams (*1*) obtained 0.4550 and 0.0927, respectively, after getting saturated vapor volumes by the application of the equation of state given by Malbrunot (*4*) to vapor pressure points. The binary interaction constant k_{ij}, which is used in the mixing rules cited, was taken to be zero. The critical-point values required in the calculations were taken from the literature (*4, 5*).

The liquid-phase standard-state fugacity, f_i^{oL}, for each component was taken to be the pure liquid component at the system temperature and at zero pressure. Both components in this study were subcritical. Thus, it was assumed that the partial molar volume, which is needed in the small corrective term applied to the liquid-phase activity coefficients in order to bring them to a common reference pressure, could be equated to the molar volume. The molar volume of these liquids (*2, 4*) was taken to be independent of pressure over the range involved. Thus, the activity coefficients, corrected to a zero reference pressure, were calculated as follows:

$$\gamma_i = \frac{\phi_i y_i P}{x_i P_i^s \phi_i^s \exp\left[\frac{(P - P_i^s)\, v_i^L}{RT}\right]} \qquad (3)$$

Equation 3 is a rearrangement of Equation 1 in which the liquid-phase-fugacity term has been written in an expanded form showing the terms required to account for pressure effects.

The activity coefficients calculated from Equation 3, which inherently contain the assumption that the nonidealities of the vapor phase were adequately described by the Redlich-Kwong equation of state, were correlated by the Wilson equation (*10*):

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

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

where subscript 1 refers to CO_2 and subscript 2 to CH_2F_2.

The parameters Λ_{21} and Λ_{12} were arbitrarily adjusted such that the root-mean-square percentage difference between calculated and experimental values of the activity coefficients was a minimum. These parameters, with the corresponding root-mean-square percentage difference, appear in Table III for each temperature level.

The Wilson-equation parameters are related to an energy term, $(\lambda_{ij} - \lambda_{ii})$, as follows:

$$\Lambda_{ij} = \frac{v_j^L}{v_i^L} \exp - \left[\frac{\lambda_{ij} - \lambda_{ii}}{1.987T}\right] \qquad (6)$$

The energy terms were calculated from Equation 6 for each isotherm and were correlated with temperature as follows:

$$(\lambda_{12} - \lambda_{11}) = -364.5 - 0.612t \qquad (7)$$

$$(\lambda_{12} - \lambda_{22}) = 696.6 + 1.150t \qquad (8)$$

These correlations for the fugacity coefficient and the activity coefficient allow accurate calculation of the vapor-liquid equilibria for this system at any temperature between

Table II. Comparison of Experimental and Literature Vapor Pressures

Temp, ° F	Experimental vapor press, psia	Literature vapor press, psia	% Deviation
	Carbon Dioxide (*2*)		
−60.00	94.6	94.7	0.11
−20.00	214.2	215.0	0.37
20.00	422.4	421.8	0.14
50.00	651.6	652.7	0.17
	Difluoromethane (*4*)		
−60.00	15.18	15.13	0.29
−20.00	41.6	41.5	0.16
20.00	95.2	94.7	0.55
50.00	161.0	160.4	0.36

Table III. Wilson Equation Parameters

Temp, ° F	Λ_{21}	Λ_{12}	Root-mean-square percentage difference between experimental and Wilson eq γ's
−60.00	0.48	1.49	1.5
−20.00	0.45	1.54	1.1
20.00	0.40	1.68	2.2
50.00	0.41	1.70	1.6

-60 and 50° F. For each experimental liquid composition and temperature, the corresponding pressure and vapor composition were back calculated using the correlation as given in Equations 1, 2, and 4–8. (Equations 7 and 8, which represent the temperature correlation of the Λ's, are considered to be the correlation rather than the Λ values from Table III, which are the best Λ's for each isotherm independent of the others.) The results of this calculation for 50° F are superimposed on the experimental data in Figure 1.

The overall average absolute difference between experimental and calculated pressures was 0.6%. Calculated vapor compositions had a root-mean-square difference of 0.005 mole fraction from the experimental compositions. The correlation fits the isotherms of 50, 20, and -20° F equally well with an average absolute difference between experimental and calculated pressures of 0.4%; the maximum deviation was about 1% on each of these isotherms. (At these maximums, the deviations in terms of pressure differences were 3.2, 2.7, and 0.8 psia, respectively.) The poorest fit was for -60° F where the average deviation was 1.1% with a maximum difference of 3.3% which corresponded to 1.0 psia. With respect to calculated vapor compositions for a given liquid composition and temperature, the best fit was for -20° F where the root-mean-square difference between calculated and experimental composition was 0.004; the poorest fit was for -60° F where the root-mean-square difference was 0.007.

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The donation of a sample of CH_2F_2 by E. I. du Pont de Nemours and Co is sincerely appreciated.

NOMENCLATURE

a, b = constants in the Redlich-Kwong equation of state
f_i^{oL} = liquid-phase standard-state fugacity, psia
k_{ij} = binary interaction constant
P = system pressure, psia
P^s = vapor (saturation) pressure, psia
R = gas constant, 10.73 psia cu ft/lb mole ° R
t = temperature, ° F
T = temperature, ° R
v = molar volume of vapor phase, cu ft/lb mole
v^L = molar volume of liquid phase, cu ft/lb mole
x = liquid-phase mole fraction
y = vapor-phase mole fraction

Greek Letters

$\Lambda_{ij}, \Lambda_{ji}$ = parameters in the Wilson equation
$(\lambda_{ij} - \lambda_{ii})$ = energy-difference term in the Wilson equation, Btu/lb mole
ϕ = vapor-phase fugacity coefficient
ϕ^s = fugacity coefficient of pure saturated vapor
Ω_a, Ω_b = dimensionless constants in the Redlich-Kwong equation of state

Subscripts

i = component i
j = component j
k = component k

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Vapor-Liquid Equilibria in Binary Aromatic–Olefin Systems

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The thermodynamic properties of mixtures of normal and branched paraffins with aromatics have been discussed recently (*4, 5*).

For mixtures of olefins with aromatics there are very few experimental results. Only data for three systems have been previously reported: benzene–cyclohexene (*2*) (25°, 50°, and 75° C); ethylbenzene–octene-1 (*28*) (760 mm Hg); and naphthalene–hexadecene-1 (*27*) (200 mm Hg).

For rational design of distillation equipment and for fundamental understanding of the effect of molecular structure on thermodynamic properties, we require additional vapor-liquid equilibrium data for aromatic–olefin systems.

In this work, isothermal, low-pressure vapor-liquid equilibrium data are reported in the temperature range 10° to 50° C for five binary systems: benzene–hexene-1; benzene–2-methylpentene-1; benzene–4-methylpentene-1; benzene–octene-1; and toluene–hexene-1.

The new data and those previously published are reduced to yield thermodynamic excess functions.

EXPERIMENTAL

Total vapor pressures for the five systems studied were measured as a function of composition at constant temperature. The static method was used. A detailed discussion of the advantages and disadvantages of this method has been given previously by Scatchard (*23*).

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