

NIPER-707
September 1993

NIPER
Commitment to Excellence

STATUS REPORT

**PHASE BEHAVIOR AND INTERFACIAL TENSION
FOR CO₂-WATER-OIL SYSTEMS**

By Ting-Hong Chung

Work Performed for
U. S. Department of Energy
Under Cooperative Agreement DE-FC22-83FE60149

National Institute for Petroleum and Energy Research
IIT Research Institute • P. O. Box 2128
Bartlesville, Oklahoma 74005-2128 • (918) 336 - 2400

Status Report

**PHASE BEHAVIOR AND INTERFACIAL TENSION
FOR CO₂-WATER-OIL SYSTEMS**

Project BE5A, Milestone 6, FY93

By Ting-Horng Chung

Work performed for
U.S. Department of Energy
Under Cooperative Agreement
DE-FC22-83FE60149

Jerry F. Casteel, Program Manager
U.S. Department of Energy
Bartlesville Project Office

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

IIT Research Institute
NATIONAL INSTITUTE FOR PETROLEUM AND ENERGY RESEARCH
P.O. Box 2128
Bartlesville, Oklahoma 74005
(918) 336-2400

TABLE OF CONTENTS

	<u>Page</u>
Abstract.....	1
Introduction	1
Results and Discussion	4
Literature Survey	4
Construction of IFT Measurement Apparatus.....	4
IFT Measurement Procedure	4
Method for IFT Determination	6
Calibration and Testing of the IFT Measurement Method	8
Prediction of CO ₂ -Solubilities in Hydrocarbon and Water/Brine Phases.....	11
Summary	17
Nomenclature	18
References.....	19
Appendix—Literature Survey for Surface and Interfacial Tension Data.....	21
Surface Tension.....	22
Interfacial Tension-Binary System	23
Interfacial Tension-Ternary System	25
Interfacial Tension-Ternary System (CO ₂ as one of the components)	27
Interfacial Tension-Hydrocarbon System.....	28
Benzlic-Systems	29
Interfacial Tension-Alcohol System	31
Alcohol-Alcohol System.....	32
Keton-Systems.....	33
References.....	34

ILLUSTRATIONS

1. Fluid system in gas displacement processes.....	2
2. IFT measurement apparatus	5
3. A digitized pendant drop shape	6
4. Testing the symmetry of the digitized drop shape	9
5. Surface tension of water	10
6. Interfacial tension of n-pentane with water	10
7. Interfacial tension of n-heptane with water	11

ILLUSTRATIONS—Continued

	<u>Page</u>
8. Measured and predicted CO ₂ solubility in water phase (experimental data from Ref. 21).....	12
9. Measured and predicted CO ₂ solubility in water and brine	13
10. Measured and predicted CO ₂ solubility in water and brine (experimental data from Ref. 23)	14
11. Vapor pressure of CO ₂ from Triple-point (T.P.) to Critical-point (C.P.)	15
12. Vapor pressure of water (experimental data from Ref. 24).....	15
13. Calculated CO ₂ solubility in water by modified P-R EOS (experimental data from Ref. 23)	16
14. Calculated CO ₂ solubility in water by modified P-R EOS (experimental data from Ref. 21)	17

PHASE BEHAVIOR AND INTERFACIAL TENSION FOR CO₂-WATER-OIL SYSTEMS

By Ting-Horng Chung

ABSTRACT

The objective of this research project is to improve prediction techniques for gas miscible displacement through fundamental research on displacement mechanisms. The project was designed to investigate the partitioning of CO₂ in oil and water phases and the effects of CO₂-dissolution on interfacial tension (IFT) and relative permeability of oil-water systems. The scope of work includes both laboratory measurements and theoretical studies. To perform this research, an apparatus was designed and constructed to measure high-pressure IFT for CO₂-water-oil systems. An image analysis technique was applied to determine the pendant-drop size and shape profile. A computer program for matching the contour of the pendant-drop and determining IFT was developed. Measurements have been conducted for water surface tension and the IFTs of water-hydrocarbon systems.

To measure the IFT for CO₂-saturated water/brine and hydrocarbon/oil systems, an accurate prediction technique for CO₂ solubility in aqueous and nonaqueous phases is required. Conventional equations of state (EOS) such as the Peng-Robinson (P-R) EOS and the Redlich-Kwong (R-K) EOS cannot adequately predict the phase behavior of CO₂ aqueous systems. The P-R equation of state has been modified to improve the accuracy for CO₂ and water systems. The attractive term of the P-R EOS was changed with a new temperature-dependence function for CO₂ and water, but its original function for hydrocarbon systems was retained. Thus, this modification will not destroy the applications of original P-R EOS in phase behavior predictions for hydrocarbons and in reservoir simulations. This modification significantly improves the accuracy of CO₂-solubility prediction. Other modifications published in the literature were tested, but results were unsatisfactory.

INTRODUCTION

Gas displacement processes involves three-phase flow in reservoir formations. The three major phases are gas, oil, and water. As illustrated in Fig. 1, there are three interfaces among these fluids. The interfacial tensions (IFT) between two fluids and the wettability of formation rock to these three fluids determine the flow of these three fluids in reservoir formations. Thus, gas displacement processes are more complicated than other oil recovery processes. In gas enhanced oil recovery (EOR) research, efforts are usually concentrated on the development of

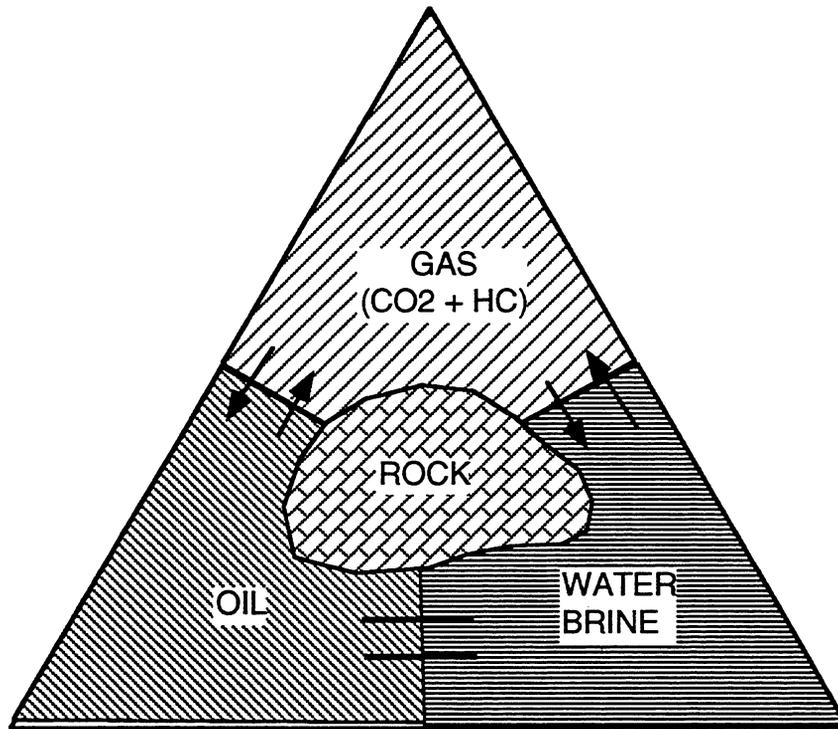


FIGURE 1. - Fluid system in gas displacement processes.

techniques for achieving miscibility so that the IFT between injection gas and reservoir oil can be reduced to zero. Without the capillary force, gas miscible displacement can achieve 100% oil recovery if the flooding is conducted in a homogeneous porous media and under gas stable conditions like laboratory slim-tube and core flooding experiments. To obtain such high displacement efficiency, the displaced oil has to form a continuous oil bank. Unfortunately, in most cases, gas EOR is applied after waterflooding. After waterflooding, the residual oil is usually surrounded by a water phase and separated into discontinuous parts. To mobilize the residual oil, the capillary force created by the interfacial tension between oil and water phases still has to be overcome even though the interfacial tension between gas and oil phases can be reduced to zero by injecting miscible gas. Besides, with water phase blocking, the injected gas may have to pass through the water phase before dissolving into the residual oil phase. This will affect gas performance and reduce the displacement efficiency. The presence of a water-oil interface can significantly affect oil flow and therefore cannot be ignored. Carbon dioxide has higher solubilities in both water and oil phases than nitrogen and hydrocarbon gases. The solubility of CO_2 in aqueous phases cannot be ignored at reservoir conditions. In a recent simulation study, it was found that ignoring CO_2 solubility in an aqueous phase will result in overprediction of CO_2 flooding performance.¹ The dissolution of CO_2 in both oil and water phases will have some effects on water and oil properties and their IFT. Since IFT is one of the important factors which

determine relative permeability curves,² the effect of CO₂ on oil-water IFT will affect oil displacement efficiency. This problem has not been thoroughly studied. So far no measurement has been conducted on the IFTs of CO₂-water and oil-water saturated with CO₂. Although some simulators have taken into account the effect of IFT on two-phase gas and oil relative permeability, the effect of CO₂ on oil-water relative permeability was neglected. The relationships between IFT and relative permeabilities used in simulators are totally empirical and lack support from either theoretical study or experimental data. Some parameters were introduced to the IFT-relative permeability correlations for tuning to match field performance.

Experimental difficulty hinders IFT studies for gas EOR. First, the system is at high-pressure condition. Secondly, oil and water properties will change with CO₂ dissolution. Thirdly, due to CO₂ supercritical extraction, consistent crude oil composition is difficult to maintain during experiments when it co-exists with the CO₂ phase. Therefore, it is difficult to obtain consistent results. Systematic studies from simple systems to complicated crude oil are being conducted in this project. This research started with pure hydrocarbon-water systems and will advance to more complicated systems. Construction and testing of a high-pressure IFT measurement apparatus is the major task of the FY93 research plan. For high-pressure systems, pendant drop method is the only method that has been used. A new method of applying image analysis techniques to improve the accuracy of the pendant drop method was developed in this work. This new IFT measurement method can be applied to investigate the IFT change with time for chemical EOR and MEOR studies. Associated with the IFT measurements, a theoretical study on the modeling of IFT property for multicomponent systems has been conducted. Available theories and modeling techniques are being reviewed. An attempt to develop a practical prediction technique for petroleum industry applications will be made.

To determine the IFT for CO₂-saturated water/brine and hydrocarbon/oil systems, an accurate prediction technique for CO₂ solubility in aqueous and nonaqueous phases is required. This project also attempts to develop a more accurate compositional prediction method for CO₂-water-hydrocarbon systems. Conventional equations of state (EOS) such as the Peng-Robinson (P-R) EOS and the Redlich-Kwong (R-K) EOS cannot adequately predict the phase behavior of CO₂ aqueous systems. Predicted aqueous phase gas solubilities may be in error by orders of magnitude.³ Several modifications to cubic EOS have been proposed to achieve better predictions for the phase behavior of mixtures including water.³⁻⁶ Available methods for the prediction of CO₂ solubilities in water and brines have been reviewed. Since the Peng-Robinson (P-R) equation of state (EOS) is commonly used in the petroleum industry, an attempt to modify the P-R EOS to improve its accuracy for CO₂ and water systems has been made. This modification still maintains its integrity and thermodynamic consistency of the original equation of state. Therefore, the

equation is still the same for hydrocarbons and oils. Preliminary results have shown success in improving the prediction of CO₂ solubility in water.

RESULTS AND DISCUSSION

Literature Survey

A literature survey for IFT measurements has been conducted. The data sources for hydrocarbon-water systems and for CO₂-hydrocarbon systems are listed in the Appendix. Methods including pendant drop, sessile drop, and spinning drop have been used for IFT measurements. Most of the water-hydrocarbon IFTs were measured at 1 atm. No IFT measurement for hydrocarbon-water systems with dissolved CO₂ at reservoir pressure and temperature ranges have been found from the literature survey. However, CO₂-oil systems have been studied.²⁵

Construction of IFT Measurement Apparatus

Current developments in personal computers with the ability to capture and digitize video images provide an improved method to determine IFT. A simple and fast system for measuring IFT using the pendant-drop method coupled with an image analysis technique has been developed in this work. A schematic diagram of the apparatus for pendant drop IFT measurements is shown in Fig. 2. The major parts are: high-pressure IFT cell (Temco Co.), optical system, and computer image processing system. For applications to high-pressure CO₂ systems, the IFT cell was designed and tested at high temperatures (up to 177° C) and high pressures (up to 69 MPa). A chemical injection pump with adjustable injection rate was used to inject liquid into the cell and to generate a pendant drop. The optical system consists of an illuminator, a light diffuser, a heat filter filled with water, and a high-resolution stereo-microscope (Nikon Inc.). The small pendant drop is magnified by the stereo-microscope, and the image is converted to electrical signals by a color CCTV camera (Sony). The RGB signals from the camera are fed to a frame grabber (Truevision TARGA-Plus) inside the personal computer. The frame grabber card is connected with the computer monitor and an additional S-VHS video monitor. The PC computer is a 486DX/66MHz model with 32-MB RAM and 200-MB hard disk drive, which provides speed for image processing.

IFT Measurement Procedure

The IFT cell was first filled with fluid-1 (lighter one), and the temperature was controlled at the setting point. The second fluid (heavier one) was then injected into the cell through the pendant drop tip with a chemical pump which has a finely adjustable injection rate. To generate a good

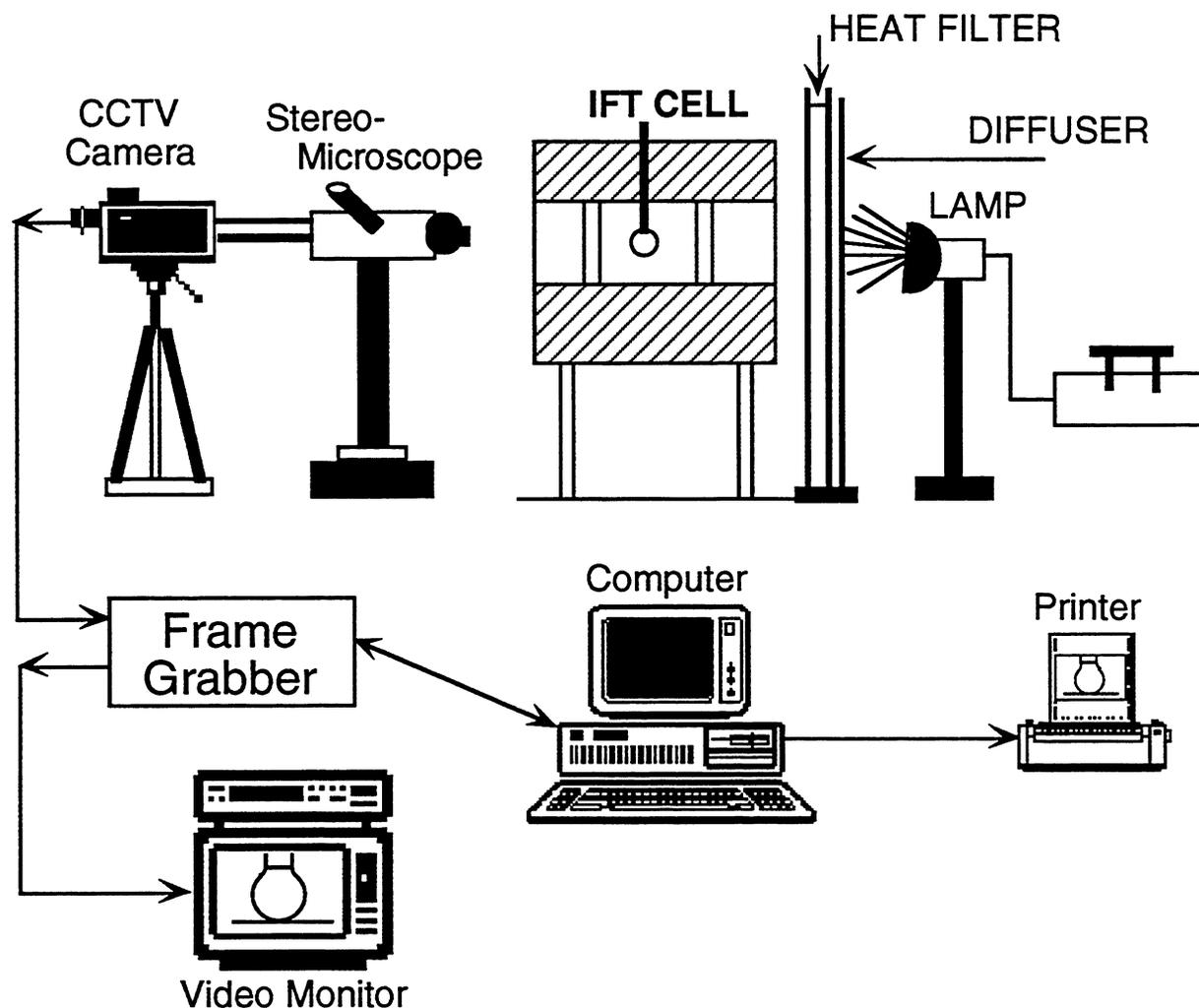


FIGURE 2. - IFT measurement apparatus.

drop shape, an adequate tip size must be used. The effect of tip radius on the pendant drop shape has been discussed.⁷ The generated pendant drop image can be viewed from the video monitor. After reaching the largest size, the injection pump is shut down and the drop is allowed to reach equilibrium for about ten minutes before the computer captures the image. The captured drop images are stored in the computer as digital information and printed out. An image analysis software (Image-Pro Plus) is used to determine the drop size and to digitize the edge of the drop image, which gives the X and Z coordinates of the points at the edge of the drop profile, as shown in Fig. 3. The coordinates of a pendant drop are then matched with theory by tuning the interfacial tension and the radius of curvature at the apex point. The principle and method of data matching are described in the following section.

Method for IFT Determination

The drop profile is described by the classical Young-Laplace equation:

$$\gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \Delta P \quad (1)$$

where γ is the interfacial tension, R_1 and R_2 represent the two principal radii of curvature, and ΔP is the pressure difference across the interface.

Mathematically, the curve of the drop profile (shown in Fig. 3) can be described in a parametric form

$$X = X(S) \text{ and } Z = Z(S) \quad (2)$$

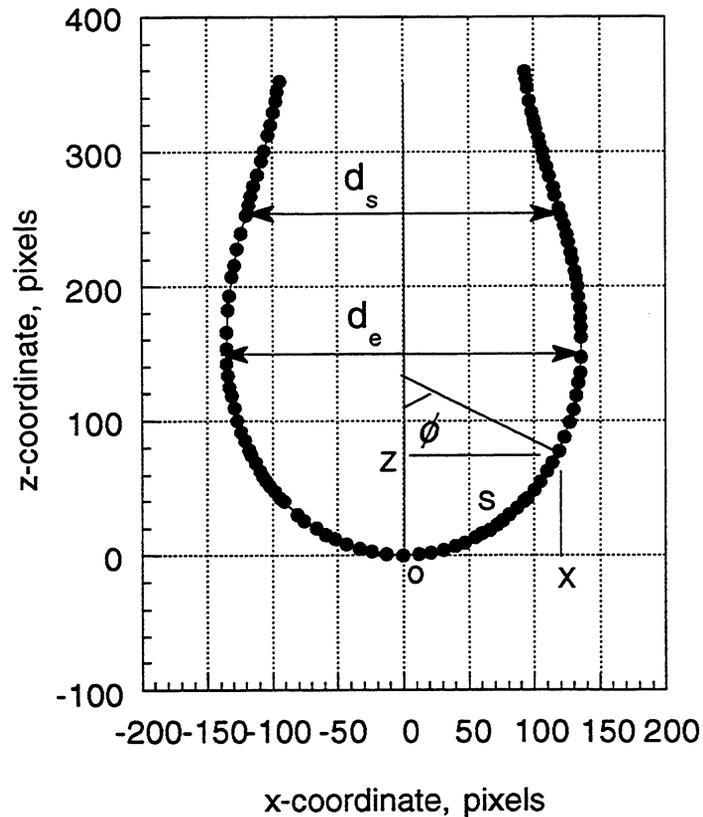


FIGURE 3. - A digitized pendant drop shape.

S being the arc length measured from the origin, o. Following previous development,⁸ the equation of Young and Laplace can be expressed as a set of three differential equations:

$$\frac{dx}{ds} = \cos \phi \quad (3)$$

$$\frac{dz}{ds} = \sin \phi \quad (4)$$

$$\frac{d\phi}{ds} = 2 - \beta z - \frac{\sin \phi}{x} \quad (5)$$

At the apex point (S=0), the radius of curvature is R_o , and

$$x(0) = z(0) = s(0) = \phi(0) = 0 \quad (6)$$

The dimensionless coordinates, x , z , and s are defined as

$$x = X/R_o, \quad z = Z/R_o, \quad s = S/R_o \quad (7)$$

and

$$\beta = \frac{(\Delta\rho) \cdot g \cdot R_o^2}{\gamma} \quad (8)$$

For given R_o and β (or $(\Delta\rho)g/\gamma$), the complete shape of the curve can be obtained by integrating simultaneously Eqs. 3 to 5. Equations 3 to 5 with the initial condition 6 can be solved using a fourth-order Runge-Kutta numerical method. The optimal values of R_o and β are determined by minimizing the objective function⁹

$$E = \sum_{i=1}^N \{ [X_i - X(z_i, \beta, R_o)] \sin \phi \}^2 \quad (9)$$

where X_i , $i=1, N$ are the X-coordinates of the selected points at the edge of the drop image, and X is the calculated value of the corresponding point (at the same Z-coordinate). At any step in the regression, values of R_o and β are updated from the previous step. Good initial estimates of R_o and β are obtained from the ratio $\sigma = D_s / D_e$ and the following correlations.¹⁰

$$\beta = 0.12836 - 0.7577\sigma + 1.7713\sigma^2 - 0.5426\sigma^3 \quad (10)$$

$$\frac{D_e}{2R_o} = 0.9987 + 0.1971\beta - 0.0734\beta^2 + 0.34708\beta^3 \quad (11)$$

A regression package to match the captured drop profile with the Young-Laplace equation (Eqs. 3-5) and determine the interfacial tension, γ , has been developed. This IFT determination

method was tested to be more accurate than the conventional method of Bashforth and Adams' treatment.¹¹

Calibration and Testing of the IFT Measurement Method

Methods used for calibration are described as follows:

1. **Magnification of drop image:** The small liquid drop hung at the tip was magnified by a high-resolution stereo-microscope (Nikon SMZ-2T). To obtain the magnification factor, several calibration objects which includes a spherical ball and a cylindrical bar of known diameters comparable to that expected for the test drop were installed at the position of the drop in the test cell. Illumination light was adjusted to give a sharp image of the calibration object on the monitor. The magnification was determined from the actual object diameter and the horizontal pixel number of the image diameter. The obtained magnification factor is within $\pm 0.5\%$ accuracy. This value is used to determine the real liquid drop size and shape from the digitized image.
2. **Horizontal vs. vertical coordinates:** The video camera and the monitor give an image composed of 400 lines, each having a resolution of 512 pixels. The digitized coordinate readings from the video monitor are based on the pixel number (x-coordinate) and the horizontal line number (z-coordinate). Therefore, the horizontal and vertical readings are different. To calibrate this, two methods were used. One uses a low reflection chrome contact reticle (Edmund Scientific Co.), which has scales in 0.1-mm increments on both horizontal and vertical cross hair line, to convert the digitized coordinate readings (pixels) to the unit of length (in cm). Another method uses a steel ball of uniform diameter. The measured image diameters (horizontal and vertical) of the ball from video monitor were compared with actual ball diameter and the factors for conversion can be determined.
3. **Justification of the digitized drop image:** The drop image shape was plotted based on the calibrated coordinate-readings for the digitized edge points (as shown in Fig. 3). Because of the axisymmetric nature of the drop, the plotted drop shape should be symmetric with respect to the z-coordinate. With this criterion, we can check the accuracy of digitization and the located apex point by superimposing the left-hand half on the right-hand half (Fig. 4). In our approach for IFT determination through drop shape matching, only the half-part points were used. Therefore, we have to ensure that the two half parts match each other.

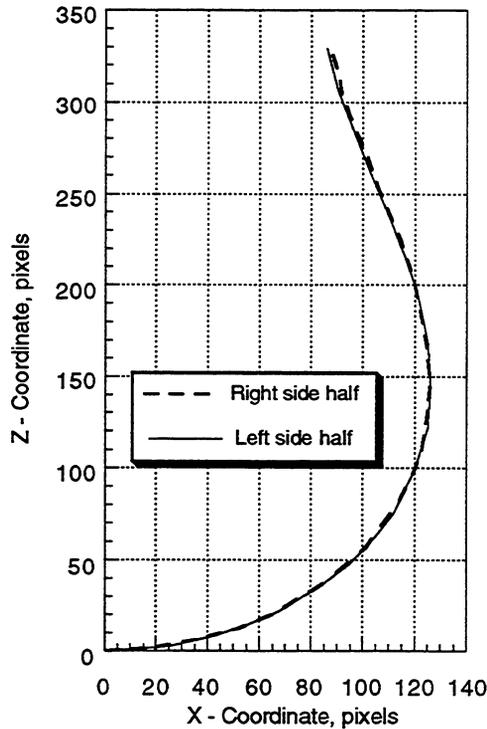


FIGURE 4. - Testing the symmetry of the digitized drop shape.

The three calibration steps are very critical to the accuracy of the IFT measurement. Preliminary IFT measurements have been conducted for water and n-heptane. The measured surface tensions for deionized water and n-heptane at 25° C compared with Du Nouy ring method are

	<u>This method</u>	<u>Du Nouy method</u>
Water	70.62 dyne/cm	70.58
n-Heptane	20.40	20.49

Measurements for the surface tension of distilled water were conducted at various temperature levels. The water used in this experiment was purified by distilling deionized water twice with potassium permanganate. The results are shown in Fig. 5. Our measured data agree well with the literature data. In the IFT measurements, we have completed n-pentane-water and n-heptane-water systems. Results are given in Figs. 6 and 7, respectively. Our measurements are reasonably accurate as compared with that of others. These tests demonstrate that our IFT measurement is accurate and comparable with others. The IFT measurements for high-pressure water-hydrocarbon and CO₂-water systems are in progress.

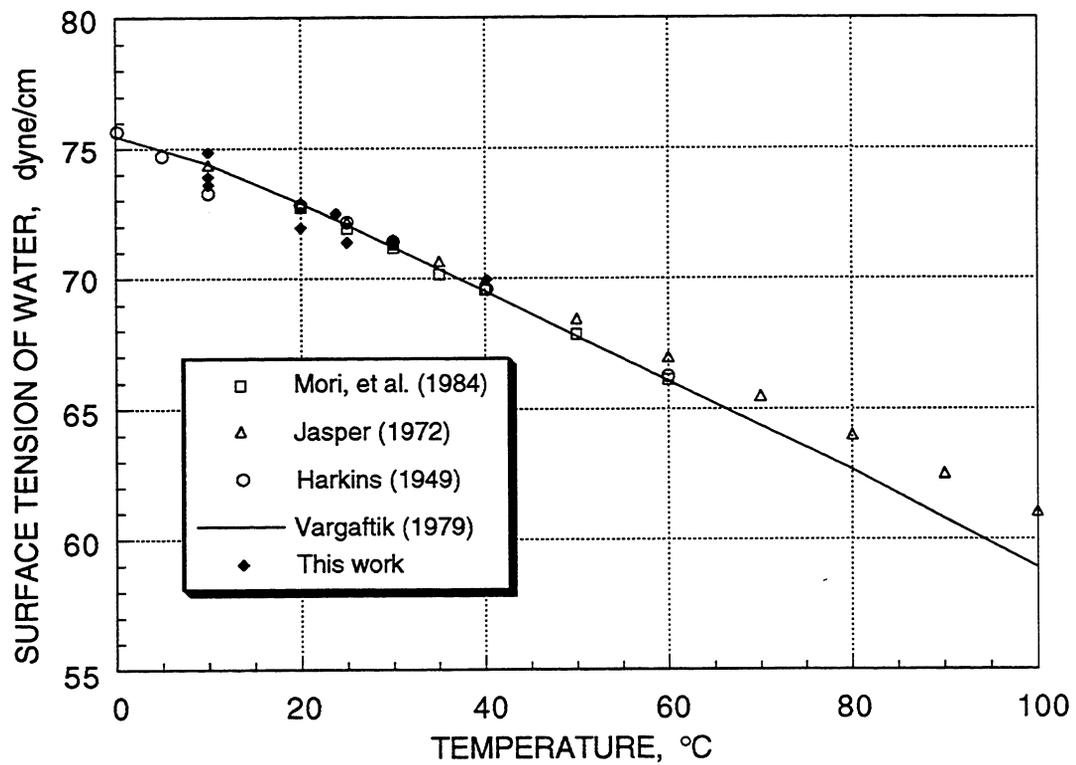


FIGURE 5. - Surface tension of water.

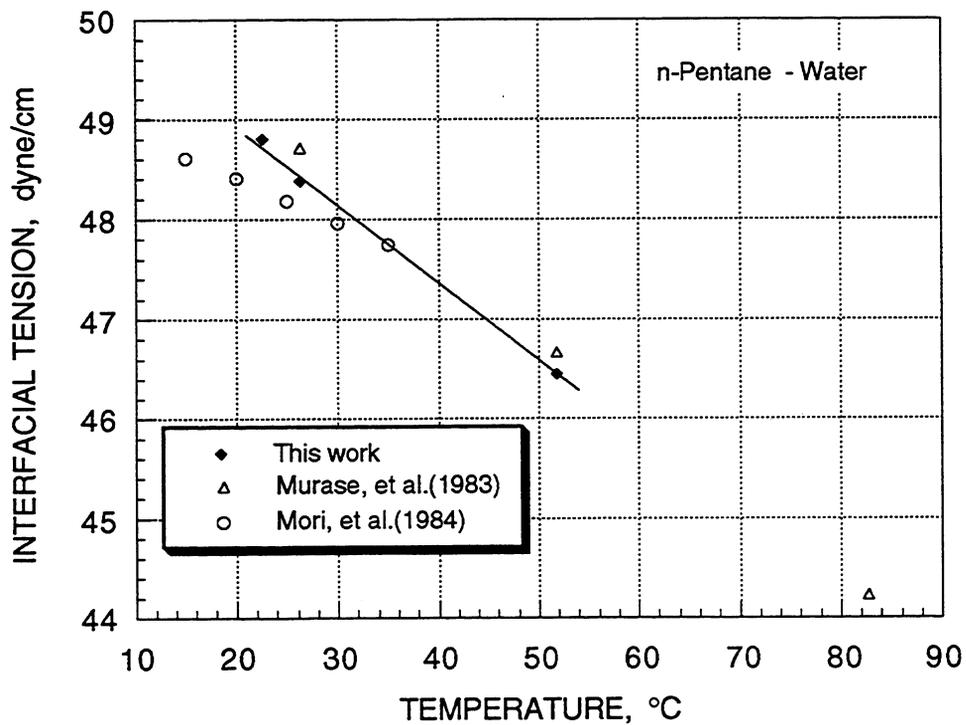


FIGURE 6. - Interfacial tension of n-pentane with water.

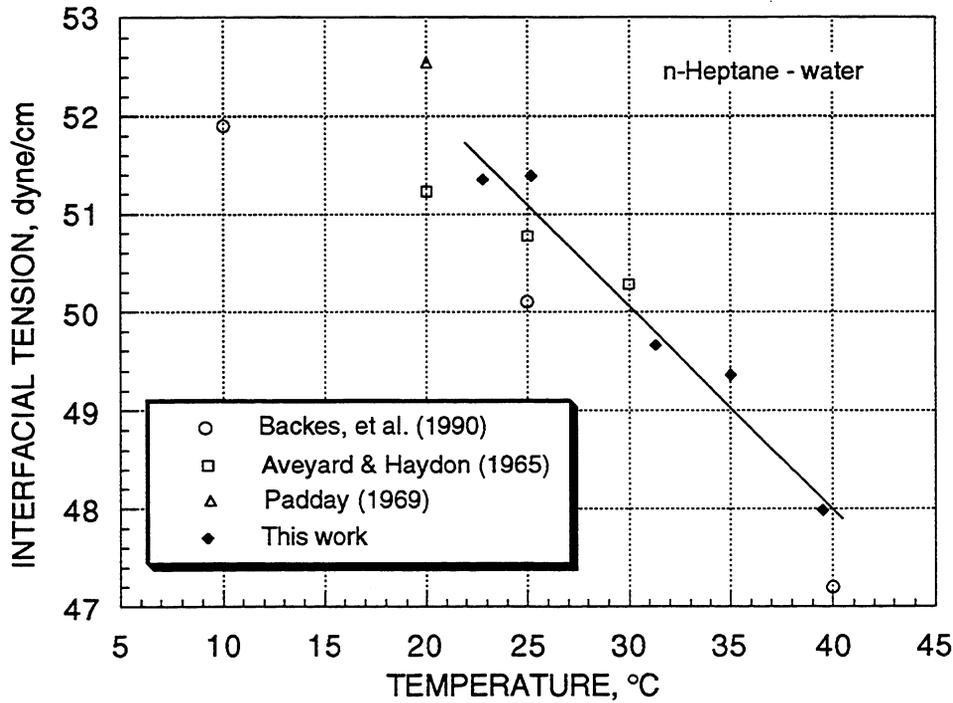


FIGURE 7. - Interfacial tension of n-heptane with water.

Prediction of CO₂-Solubilities in Hydrocarbon and Water/Brine Phases

To measure the IFT for CO₂-saturated water/brine and hydrocarbon/oil systems, an accurate prediction technique for CO₂ solubility in aqueous and nonaqueous phases is required. Conventional cubic equations of state (EOS) such as the Peng-Robinson (P-R) EOS and the Redlich-Kwong (R-K) EOS can not adequately predict the phase behavior of CO₂-aqueous systems. The predicted aqueous phase gas solubility may be in error orders by magnitude of error.³ Several modifications to cubic EOS have been proposed to achieve a better prediction for the phase behavior of mixtures including water.³⁻⁶ Recently, a modified P-R EOS was published³ for CO₂ with pure water and NaCl brine. The α -term of the P-R EOS for water/brine was modified as functions of reduced temperature, T_r , and salinity (molal), C_{sw} :

$$\alpha^{1/2} = 1 + 0.453[1 - T_r(1 - 0.0103C_{sw}^{1.1})] + 0.0034(T_r^{-3} - 1) \quad (12)$$

For a mixture including aqueous phase, two different EOS constants a_{ij} are used, one for aqueous phase (AQ) and the other for nonaqueous phase (NA):

$$a_{ij}^{AQ} = \sum \sum x_i x_j (a_i a_j)^{1/2} (1 - k_{ij}^{AQ}) \quad (13)$$

$$a_{ij}^{NA} = \sum \sum x_i x_j (a_i a_j)^{1/2} (1 - k_{ij}^{NA}) \quad (14)$$

where k_{ij}^{AQ} and k_{ij}^{NA} are binary interaction parameters (BIPs) for aqueous and non-aqueous phases, respectively. The BIPs are determined by data regression. This modified P-R EOS was tested with experimental data for CO₂ solubility in pure water and NaCl brine. Results are shown in Figs. 8 and 9. It can be seen that this modified P-R EOS is not accurate enough to predict CO₂ solubility in water and brine. In addition, the modified P-R EOS is only applicable for NaCl brine. This new modified P-R EOS suffers some shortcomings: (1) it is thermodynamically inconsistent using two different values of the attractive term "a," and (2) it is not good for extrapolation.

Recently, Twu et al.⁶ also presented a new α -function for the attractive term "a" of the Redlich-Kwong (R-K) EOS,

$$a(T) = a(T_c)\alpha(T) \quad (15)$$

where

$$a(T_c) = 0.427481R^2T_c^2/P_c \quad (16)$$

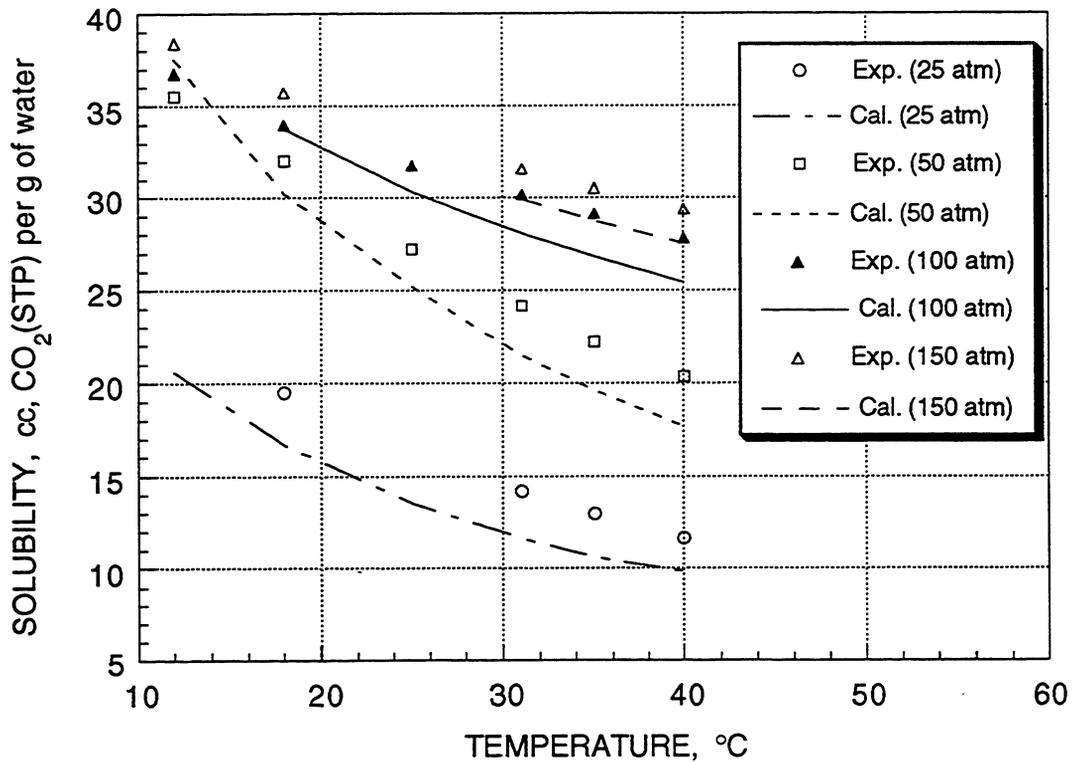


FIGURE 8. - Measured and predicted CO₂ solubility in water phase (experimental data from Ref. 21).

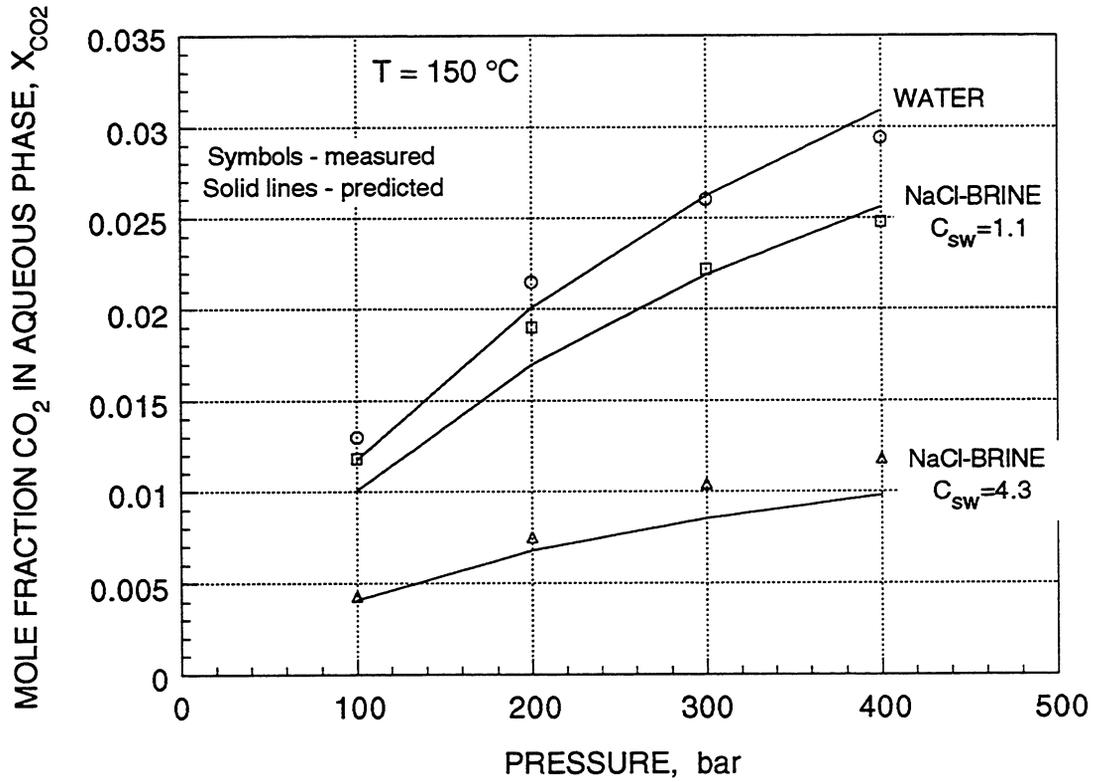


FIGURE 9. - Measured and predicted CO₂ solubility in water and brine.

and the new α -function

$$\alpha(T) = T_r^{2(m-1)} e^{l(1-T_r^{2m})} \quad (17)$$

where $T_r = T/T_c$; l and m are parameters for each compound which were determined from vapor pressure data regression. With the new α -function, the modified R-K EOS can model vapor pressures of water and CO₂ from the triple point to the critical point within 1% accuracy. For binary mixtures, Twu et al.⁶ proposed a new mixing rule as

$$a_m = \sum \sum x_i x_j a_{ij} \quad (18)$$

$$b_m = \sum x_i b_i \quad (19)$$

$$a_{ij} = (a_i a_j)^{1/2} \left[(1 - k_{ij}) + (k_{ji} - k_{ij}) x_j^2 \right] \quad (20)$$

For a binary system, there are two binary interaction parameters, k_{12} and k_{21} . They are temperature-dependent. This modified R-K EOS was tested with experimental data for CO₂ solubility in pure water. Results are shown in Fig. 10. It can be seen that this modified R-K EOS is able to predict CO₂ solubility in water accurately up to extremely high-pressure conditions. The results were calculated with $k_{water-CO_2} = 0$ and $k_{CO_2-water} = 0.277365 - 123.38/T(k)$.

The approach presented by Twu et al.⁶ does not have the inconsistency problem as that of Soreide and Whitson,³ but does have the capability for extrapolation. In the petroleum industry, the P-R EOS is the most commonly used equation. In this research, we have tried to apply the new α -function for the P-R EOS and redetermine the parameters: l and m for CO₂ and water. The modified P-R EOS is

$$P = \frac{RT}{v-b} - \frac{a\alpha(T_r)}{v^2 + 2bv - b^2} \quad (21)$$

where a and b are estimated from the same formulas as original P-R EOS. The original α -function was still used for all substances except CO₂ and water. For CO₂ and water, Eq. 17 was used and the two parameters: l and m were determined from regression of vapor pressure data. The results are shown in Figs. 11 and 12 for CO₂ and water, respectively.

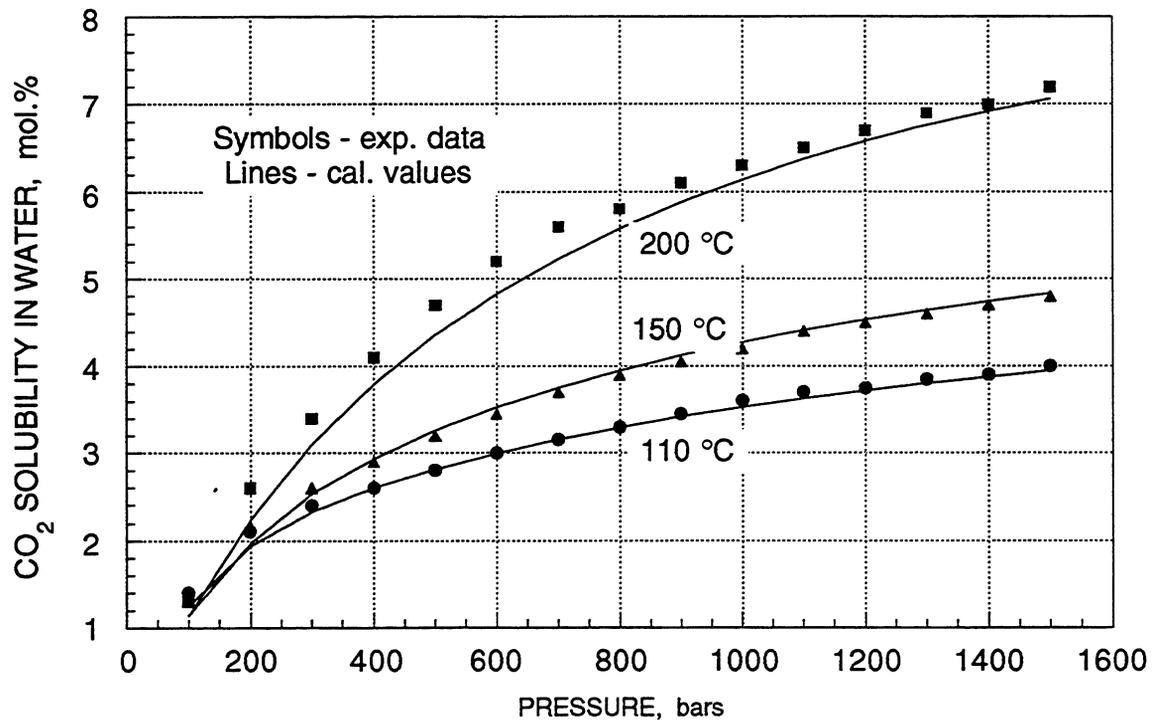


FIGURE 10. - Measured and predicted CO₂ solubility in water and brine (experimental data from Ref. 23).

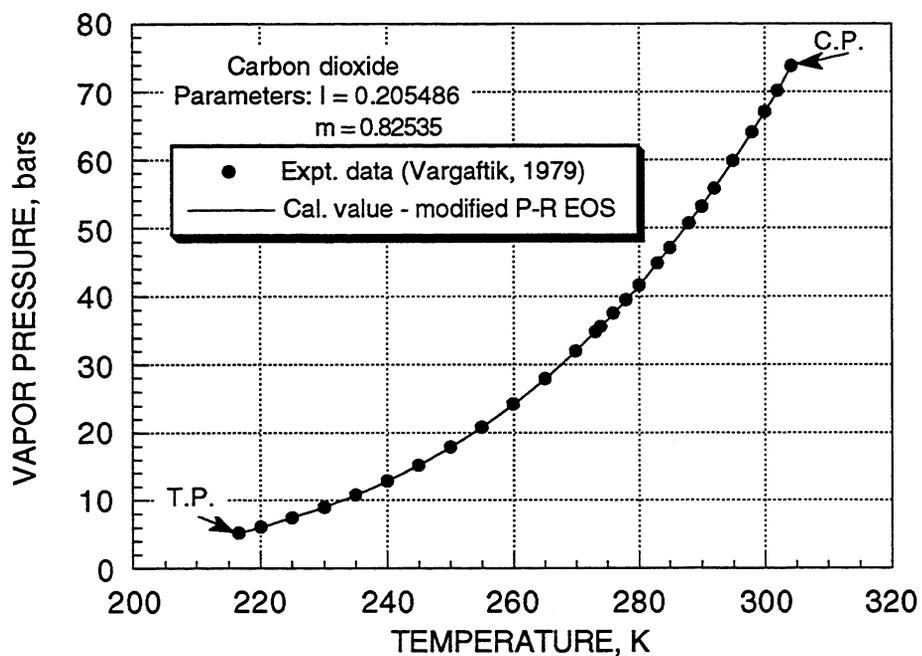


FIGURE 11. - Vapor pressure of CO₂ from Triple-point (T.P.) to Critical-point (C.P.).

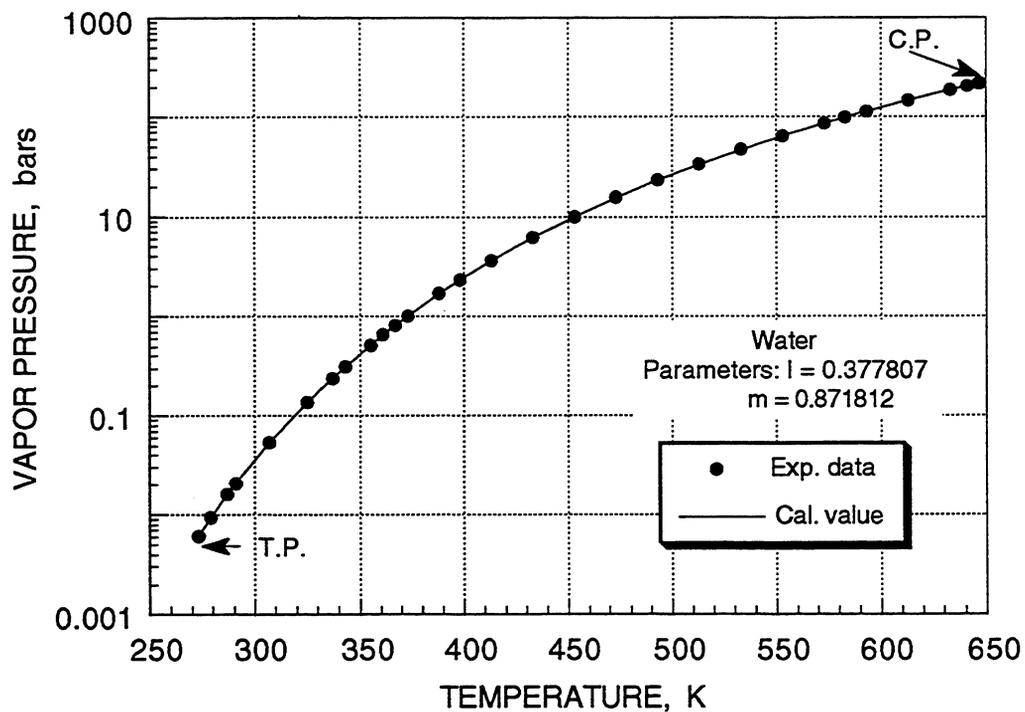


FIGURE 12. - Vapor pressure of water (experimental data from Ref. 24).

For mixtures, a more accurate mixing rule was suggested by Twu et al.,¹² as

$$a_m = \sum \sum x_i x_j (a_i a_j)^{1/2} \left(1 - \frac{k_{ij}}{T} \right) + \sum_i x_i \left[\sum_j x_j H_{ij}^{1/3} (a_i a_j)^{1/6} \right]^3 \quad (22)$$

where

$$H_{ij} = (k_{ji} - k_{ij})/T \quad (23)$$

Unlike the conventional mixing rule, which can be obtained by setting $k_{ij} = k_{ji}$ at a fixed temperature for Eqs. 22 and 23, the asymmetric definition of k_{ij} in this new mixing rule provides a more accurate representation of polar systems. The two binary interaction parameters: k_{12} and k_{21} for CO₂ (1) and water (2) can be explained in terms of the infinite dilution activity coefficients of CO₂ and water or can be obtained from regressing PTxy data. In this work, we determined the binary interaction parameters from regression of CO₂-solubility data. The obtained BIPs are: $k_{12} = 0.318642 - 136.042/T(K)$, $k_{21} = 0.380952$. The calculated results are shown in Fig. 13 for high temperatures and Fig. 14 for low temperatures. It can be seen that the modified P-R EOS has the capability to predict CO₂-solubility in water over a wide temperature and pressure

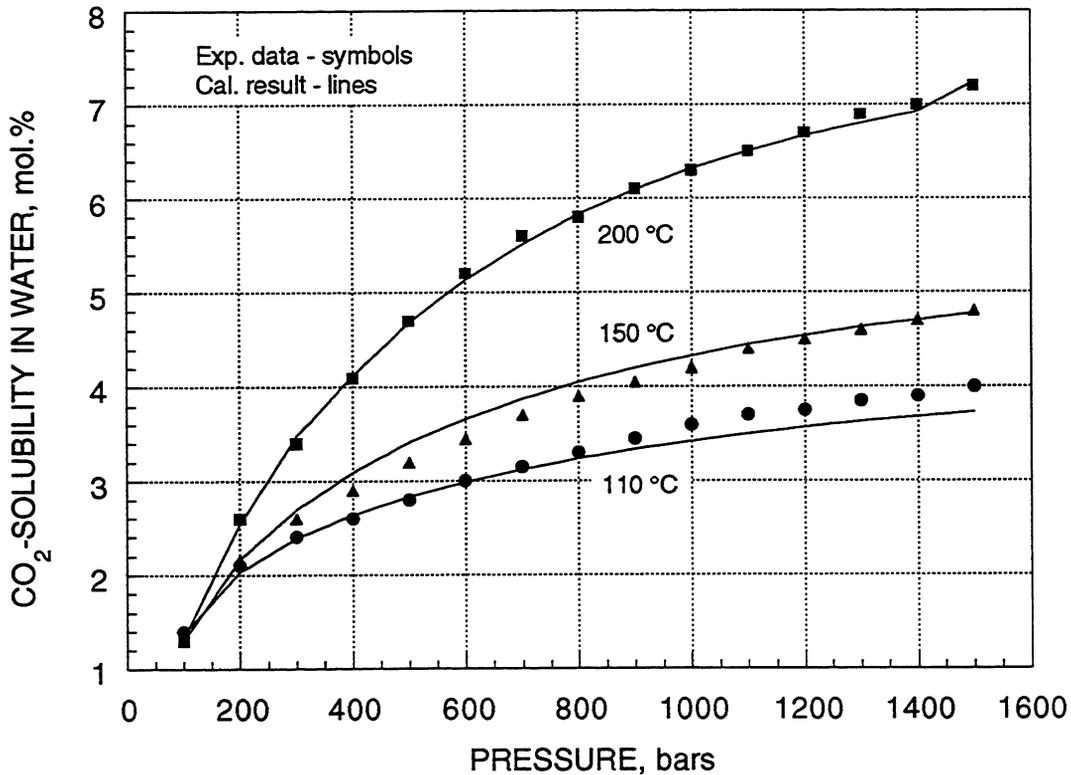


FIGURE 13. - Calculated CO₂ solubility in water by modified P-R EOS (experimental data from Ref. 23).

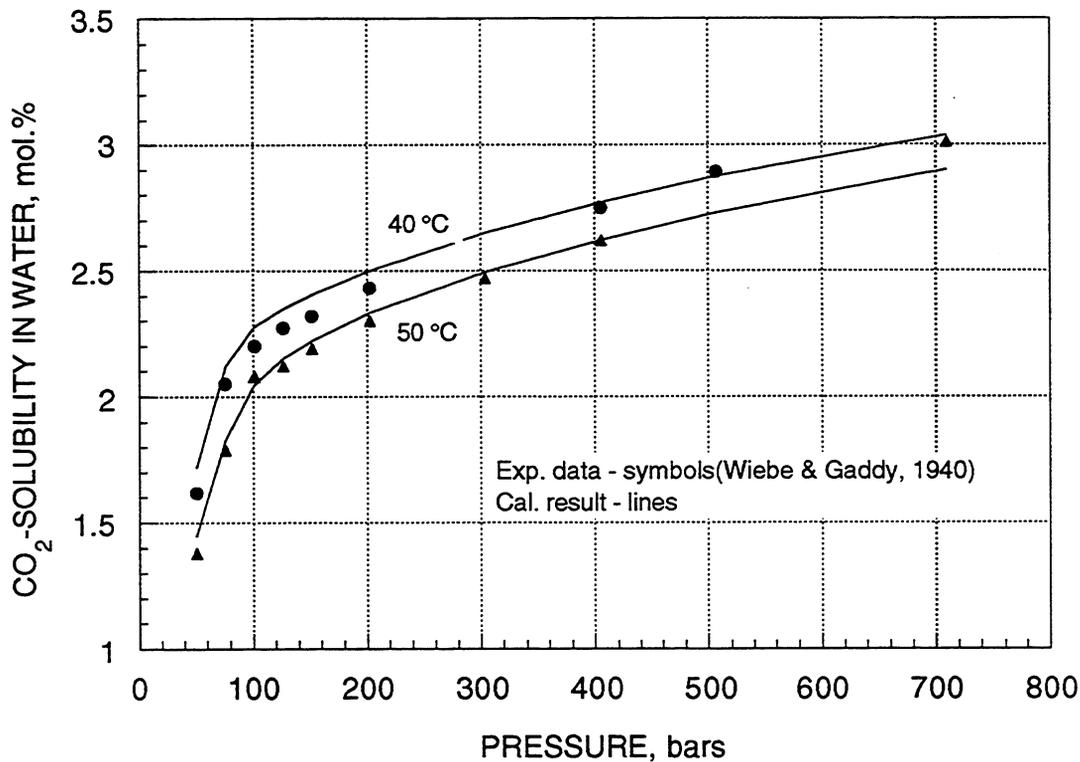


FIGURE 14. - Calculated CO₂ solubility in water by modified P-R EOS (experimental data from Ref. 21).

range. Testing of the modified P-R EOS for the three phase system of CO₂-water-oil are on-going.

SUMMARY

1. A high-pressure IFT measurement apparatus was set up, and a new technique of employing image analysis for IFT determination was developed. The apparatus and experimental procedure HAVE been calibrated and tested. Results show that the measured surface tension and IFT for water and hydrocarbon systems are reasonably accurate. The IFT measurements are still in progress and will be continued next year. Theoretical studies on the modeling of IFT and on the development of a prediction technique have also been initiated.

2. A new technique to improve the accuracy of equation-of-state for the prediction of CO₂ solubility in water has been developed. The approach is to modify the P-R equation of state for CO₂ and water to improve its accuracy for vapor pressure prediction and to apply a new mixing rule for CO₂-water systems. For hydrocarbons and oil, the original equation of state and mixing rule are still valid. Therefore, this modification will create no inconvenience for applications of the

P-R EOS in the petroleum industry. Further effort will be to extend the modification to CO₂-brine systems and to complete the prediction package for CO₂-oil-water (brine) phase behavior.

NOMENCLATURE

a	=	attraction parameter
b	=	van der Waals co-volume
C_{sw}	=	salinity of aqueous solution
D_e	=	largest diameter of the pendant-drop
g	=	gravitational constant
H_{ij}	=	defined by Eq. 23
k_{ij}	=	binary interaction parameter between component i and component j
l, m	=	parameters in Eq. 17
P	=	pressure
P_c	=	critical pressure
R	=	Universal gas constant
R_i	=	principal radius of curvature
R_o	=	radius of curvature at the apex point
S	=	arc length of the contour of the pendant-drop image
s	=	defined by Eq. 7
T	=	temperature
T_c	=	critical temperature
T_r	=	T/T_c
v	=	molar volume
$X(S)$	=	horizontal coordinate
$x(s)$	=	defined by Eq. 7
x_i	=	composition of i -component
$Z(S)$	=	vertical coordinate

Greek Letters

$\alpha(T)$	=	temperature-dependent function in the cubic type equations
β	=	defined by Eq. 8
γ	=	surface or interfacial tension
ϕ	=	angle on the X-Z plane, shown in Fig. 3

REFERENCES

1. Agarwal, R., Y-K Li and L. Nghiem. An Efficient method for Modeling Gas Solubility in the Aqueous Phase for Compositional Simulators, pres. at the Int. Tech. Meeting of CIM/SPE, Calgary, Canada, June 10-13, 1990. Paper No. CIM/SPE 90-123.
2. Asar, H. and L. L. Handy. Influence of Interfacial tension on Gas/Oil Relative Permeability in a Gas-Condensate System, *SPEJ Reservoir Eng*, February 1988, pp. 257-264.
3. Soreide, I. and C. H. Whitson. Peng-Robinson Predictions for Hydrocarbons, CO₂, N₂, and H₂S with Pure Water and NaCl Brine, *Fluid Phase Equil.*, v.77, 1992, pp. 217-240.
4. Peng, D.-Y. and D. B. Robinson. Two- and Three-phase Equilibrium Calculations for Coal Gasification and Related Processes. In: S.A. Newman (Ed.), *Thermodynamics of Aqueous Systems With Industrial Applications*. ACS Symp. Ser., 393, 1980, pp. 393-414.
5. Chu, J.-Z., Y.-X. Zuo and T.-M. Guo. Modification of the Kumar-Starling Five-Parameter Cubic Equation of State and Extension to Mixtures, *Fluid Phase Equil.*, v.77, 1992, pp. 181-216.
6. Twu, C.-H. A Modified Redlich-Kwong Equation of State for Highly Polar, Supercritical Systems, Inter. Symp. on Thermo. in Chem. Eng. and Industry, May 30-June 2, 1988, pp. 148-169.
7. Hartland, S. and R. W. Hartley. *Axisymmetric Fluid-Liquid Interfaces*, Elsevier Scientific Publishing Co., Amsterdam, 1976.
8. Rotenberg, Y., L. Boruvka and A. W. Neumann. Determination of Surface Tension and Contact Angle from the Shapes of Axisymmetric Fluid Interfaces, *J. Colloid and Interf. Sci.*, v. 93, No. 1, May 1983, pp. 169-183.
9. Huh, C. and R. L. Reed. A Method for Estimating Interfacial Tensions and Contact Angles from Sessile and Pendant Drop Shapes, *J. Colloid Interf. Sci.*, v. 91, No. 2, February 1983, pp. 472-484.
10. Hansen, F. K. and G. Rodsrud. Surface Tension by Pendant Drop: 1. A Fast Standard Instrument using Computer Image Analysis, *J. Colloid Interf. Sci.*, v.141, No. 1, January 1991, pp. 1-9.
11. Adamson, A. W. *Physical Chemistry of Surfaces*, John Wiley & Sons, New York, NY, 1982.
12. Twu, C.-H., D. Bluck, J. R. Cunningham and J. E. Coon. A Cubic Equation of State with a New Alpha Function and A New Mixing Rule, *Fluid Phase Equil.*, v. 69, 1991, pp. 33-50.
13. Mori, Y. H., N. Tsul and M. Klyomlya. Surface and Interfacial Tensions and Their Combined Properties in Seven Binary, Immiscible Liquid-Liquid-Vapor Systems, *J. Chem. Eng. Data*, v. 29, 1984, pp. 407-412.
14. Murase, M., Y. H. Mori and A. Nagashima. Interfacial Tension Measurements by the Pendant Drop Method: Development of Apparatus and Measurements in N-Pentane-Water System. The 4th Japan Symp. on Thermophysical Properties, 1983, pp. 153-156.

15. Jasper, J. J. The Surface Tension of Pure Liquid Compounds, *J. Phys. Chem. Ref. Data*, v. 1, No. 4, 1972, pp. 841-980.
16. Harkins, W. D. *Physical Methods of Organic Chemistry*, v. 1, pt. I, A. Weissberger, Ed. Interscience, New York, 1949, p. 369.
17. Vargaftik, N. B. *Handbook of Physical Properties of Liquids and Gases*, 2nd edit., Hemisphere Publishing Corp., Washington, 1975.
18. Padday, J. F., Surface Tension. Part I. The Theory of Surface Tension. *Surface and Colloid Science*, v. 1. Edit. by E. Matijevic, Wiley-Interscience, New York, 1969, pp. 39-99.
19. Backes, H. M., J. J. Ma, E. Bender and G. Maurer. Interfacial Tensions in Binary and Ternary Liquid-Liquid Systems. *Chem. Eng. Sci.*, v. 45, No. 1, 1990, pp. 275-286.
20. Aveyard, R. and D. A. Haydon. Thermodynamic Properties of Aliphatic Hydrocarbon/Water Interfaces. *Trans. Faraday Soc.*, v.61, 1965, pp. 2255-2261.
21. R. Wiebe and V. L. Gaddy. The Solubility of Carbon Dioxide in Water at Various Temperatures from 12 to 40° C and at Pressures to 700 Atmospheres, *J. Am. Chem. Soc.*, v. 62, 1940, pp. 815-817.
22. S. Takenouchi and G. Kennedy. The Solubility of Carbon Dioxide in NaCl Solutions at High Temperatures and Pressures, *Am. J. Sci.*, v. 263, 1965, pp. 445-454.
23. Takenouchi, S. and G. E. Kennedy. The Binary System H₂O-CO₂ at High Temperatures and Pressures, *Am. J. Sci.*, v. 262, November 1964, pp. 1055-1074.
24. Haar, L., J. S. Gallagher and G. S. Kell. *Steam Tables, NSRDS*, Hemisphere Publishing Co., Washington, D.C., 1984.
25. Gasem, K. A. M., K. B. Dickson, R. D. Shaver and R. L. Robinson Jr. Experimental Phase Densities and Interfacial Tensions for a CO₂/Synthetic-oil and a CO₂/Reservoir-oil System. *SPE Reservoir Engineering*, August 1993, pp. 170-174.

APPENDIX

Literature Survey for Surface and Interfacial Tension Data

INTERFACIAL TENSION-BINARY SYSTEM

Acetic acid	Acetone	4	298K	1atm	53
Acetic acid	1,4 Dioxane	10	298-313K	1atm	53
Acetic acid	Methanol	9	308K	1atm	49
Acetic acid	Water	48	291-313K	1atm	53
Acetone	Methanol	6	308K	1atm	49
Acetonitrile	Water	21	293K	1atm	53
Aniline	Water	4	10-40C	1atm	1,9,15,23
Benzaldehyde	Water	1	20C	1atm	74
Biocyclohexyl	Water	6	20C	1atm	39
Bromoethane	Water	1	25C	1atm	15,23
Butane	Carbon dioxide	42	115-220F	80-7965MPa	20
Butyl acetate	Water	2	25C	1atm	9,15,23
Butyl alcohol	Water	1	20C	1atm	9
Butyl bromide	Water	1	298K	0.1MPa	33
Carbon disulfide	Perfluorohexane	1	25C	1atm	23,43
Carbon disulfide	Water	2	25C	1atm	1,9,15,17,23
Carbontetrachloride	Cyclopentane	1	25C	1atm	58,63
Carbontetrachloride	Water	2	20-25C	1atm	9,75
Chlorobenzene	Water	1	25C	1atm	1,17
Chloroform	Water	2	25C	1atm	1,15,23,26
Cis-decalin	Cyclohexane	1	25C	1atm	58,63
Cyclohexane	Benzene	1	20C	1atm	58,63
Cyclohexane	Cis-decalin	1	25C	1atm	58,63
Cyclohexane	i-Octane	1	30C	1atm	10,58
Cyclohexane	Tetra-chloroethylene	1	25C	1atm	58,63
Cyclohexane	Trans-decalin	1	25C	1atm	58,63
Cyclohexane	Toluene	1	25C	1atm	58,63
Cyclohexane	Water	2	298K	0.1MPa	15,23,33
Cyclopentane	Benzene	1	25C	1atm	58,63
Cyclopentane	Carbontetrachloride	1	25C	1atm	58,63
Cyclopentane	Tetrachloroethylene	1	25C	1atm	58,63
Cyclopentane	Toluene	1	25C	1atm	58,63
1,2-Dichloroethane	Water	1	25C	1atm	1
Dichloromethane	Water	2	25C	1atm	1,9,15,17,23
Diethylether	Water	2	25C	1atm	1,9,15,23
Diisoproylether	Water	2	25C	1atm	1,9,15,23
2,2 Dimethylbutane	Water	1	25C	1atm	16,23
2,4 Dimethylpentane	Water	1	25C	1atm	16,23
2,3 Dimethylbutane	Water	1	25C	1atm	16,23
1,4 Dioxane	Acetic acid	10	298-313K	1atm	53
1,4 Dioxane	Benzene	12	293-303K	1atm	52
1,4 Dioxane	Toluene	5	303K	1atm	8
1,4 Dioxane	Water	36	293-351K	1atm	53
Dodecane	Hexane	1	30C	1atm	46,58
Dodecane	i-Octane	1	30C	1atm	10,58
Ethanol	Benzene	1	25C	1atm	31,58
Ethylacetate	Water	4	10-40C	1atm	1,9,15,23
Ethylbromide	Water	1	25C	1atm	9
Ethylether	Water	1	25C	1atm	9
2-Ethylhexanol	Water	1	25C	1atm	1
Ethylbutyrate	Water	1	25C	1atm	9
Furan	Glycerol	12	15-30C	1atm	32
Furfural	Water	1	25C	1atm	15,23
Glycerol	Furan	12	15-30C	1atm	32
Glycerol	Pentane	15	15-35C	1atm	32
Heptanoic acid	Water	1	20C	1atm	75
Hexane	Dodecane	1	30C	1atm	46,58
Hexane	Methanol	5	293K	1atm	53
Hexane	Propanol	30	293-333K	1atm	30
Hexyl bromide	Water	1	298K	0.1MPa	33
Methane	Propane	47	5-194F	42-1239psi	56

INTERFACIAL TENSION-BINARY SYSTEM—Continued

Methanol	Acetic acid	9	308K	1atm	49
Methanol	Acetone	6	308K	1atm	49
Methanol	Benzene	1	30C	1atm	31,58
Methanol	Hexane	5	293K	1atm	53
Methanol	Tetradecane	1	25C	1atm	15,23
Methanol	Toluene	9	308K	1atm	49
Methylacetate	Water	1	25C	1atm	1
Methylcyclohexane	Water	1	25C	1atm	1
3-Methylhexane	Water	1	25C	1atm	16,23
3-Methylpentane	Water	1	25C	1atm	16,23
4-Methyl-2-pentanone	Water	3	10-40C	1atm	1,34
MIBK	Water	4	21C	1atm	2,57
Nitromethane	Water	2	25C	1atm	1,9,15,17,23,34
i-Octane	Benzene	1	30C	1atm	10,58
i-Octane	Cyclohexane	1	30C	1atm	10,58
i-Octane	Dodecane	1	30C	1atm	10,58
Pentane	Glycerol	15	15-35C	1atm	32
Perfluorohexane	Benzene	1	25C	1atm	23,43
Perfluorohexane	Carbon disulfide	1	25C	1atm	23,43
Perfluorohexane	Tetradecane	2	25C	1atm	16,23,43
Propane	Methane	47	5-194F	1atm	56
Propanol	Hexane	30	293-333K	1atm	30
i-Propyl ether	Water	1	25C	1atm	9
R113	Water	27	20-151.8C	?	29,32
Silicone oil KF54	Water	14	20-90C	1atm	32
Tetrachloromethane	Water	3	20-25C	1atm	1,9,15,17,23
Tetrachloroethylene	Cyclohexane	1	25C	1atm	58,63
Tetrachloroethylene	Cyclopentane	1	25C	1atm	58,63
Tetradecane	Methanol	1	25C	1atm	15,23
Tetradecane	Perfluorohexane	2	25C	1atm	16,23,43
Trans-decalin	Cyclohexane	1	25C	1atm	58,63
1,1,1-Trichloroethane	Water	3	10-40C	1atm	1
1,1,2-Trichloroethane	Water	4	10-40C	1atm	1,15,23
Trichloromethane	Water	3	10-40C	1atm	1,9
2,2,4 Trimethylpentane	Water	1	25C	1atm	16,23
Vinylacetate	Water	1	25C	1atm	1

INTERFACIAL TENSION-TERNARY SYSTEM

COMP 1	SYSTEM COMP 2	COMP 3	DATA PTS	T RANGE	P RANGE	REFERENCE
Acetic acid	Acetic acid ethylene ester	Water	5	25C	1atm	1
Acetic acid	Acetic acid i-propylester	Water	5	24.6C	1atm	1
Acetic acid	Butylester	Water	1	25C	1atm	1,9
Acetic acid	i-Butylester	Water	1	25C	1atm	1
Acetic acid	Cyclohexylester	Water	1	25C	1atm	1
Acetic acid	2-Ethylhexanol	Water	5	24.6C	1atm	1
Acetic acid	Hexane	Water	22	25C	1atm	34
Acetic acid	i-Propylester	Water	1	25C	1atm	1
Acetic acid ethylene ester	Acetic acid	Water	5	25C	1atm	1
Acetic acid i-propylester	Acetic acid	Water	5	24.6C	1atm	1
Acetonitrile	Ethanol	Hexane	6	25C	1atm	1
Acetonitrile	Hexane	Methanol	5	25C	1atm	1
Butylester	Acetic acid	Water	1	25C	1atm	1,9
i-Butylester	Acetic acid	Water	1	25C	1atm	1
Carbondisulfide	Hexane	Perfluorohexane	4	25C	1atm	43
Carbontetrachloride	Propanol	Water	7	20C	1atm	43
Carbontetrachloride	Propionic acid	Water	9	25C	1atm	26
Chloroform	Propionic acid	Water	6	25C	1atm	26
Cyclohexane	Ethanol	Water	?	25C	1atm	6
Cyclohexane	Propanol	Water	6	25C	1atm	26
Cyclohexane	i-Propanol	Water	13	25C	1atm	26,45
Cyclohexylester	Acetic acid	Water	1	25C	1atm	1
Ethanol	Acetonitrile	Hexane	6	25C	1atm	1
Ethanol	Cyclohexane	Water	?	25C	1atm	6
Ethanol	Ethylacetate	Water	?	20C	1atm	6
Ethanol	Hexane	Water	18	20C	1atm	11,44
Ethylacetate	Ethanol	Water	?	20C	1atm	6
Ethylacetate	Methanol	Water	?	20C	1atm	6
Ethylacetate	Propanol	Water	?	20C	1atm	6
2-Ethylhexanol	Acetic acid	Water	5	24.6C	1atm	1
Heptane	Propionic acid	Water	6	25C	1atm	26
Heptane	Propanol	Water	5	25C	1atm	1
Hexane	Acetic acid	Water	22	25C	1atm	34
Hexane	Acetone	Water	32	20-25C	1atm	34,42
Hexane	Acetonitrile	Ethanol	6	25C	1atm	1
Hexane	Acetonitrile	Methanol	5	25C	1atm	1
Hexane	Carbondisulfide	Perfluorohexane	4	25C	1atm	43
Hexane	Ethanol	Water	18	20C	1atm	11,44
Hexane	Methylethyl ketone	Water	13	25C	1atm	42
Hexane	Propanol	Water	5	25C	1atm	1
Hexane	i-Propanol	Water	13	25C	1atm	42
Methanol	Ethylacetate	Water	?	20C	1atm	6
Perfluorohexane	Benzene	Hexane	5	30C	1atm	28
Perfluorohexane	Carbondisulfide	Hexane	4	25C	1atm	43
Propanol	Carbontetrachloride	Water	7	20C	1atm	43
Propanol	Cyclohexane	Water	6	25C	1atm	26
i-Propanol	Cyclohexane	Water	13	25C	1atm	26,45
Propanol	Ethylacetate	Water	?	20C	1atm	6
Propanol	Heptane	Water	5	25C	1atm	1
Propanol	Hexane	Water	5	25C	1atm	1
i-Propanol	Hexane	Water	13	25C	1atm	42
Propionic acid	Carbontetrachloride	Water	9	25C	1atm	26

INTERFACIAL TENSION-TERNARY SYSTEM—Continued

Propionic acid	Chloroform	Water	6	25C	1atm	26
Propionic acid	Heptane	Water	6	25C	1atm	26
i-Propylester	Acetic acid	Water	1	25C	1atm	1
Trichloromethane	Acetone	Water	5	25C	1atm	1
1,1,2 Trichloroethane	Acetone	Water	34	25C	1atm	1,28,34,43
1,1,2 Trichloroethane	2-Butanone	Water	6	25C	1atm	28
1,1,2 Trichloroethane	Methylethylketone	Water	?	25C	1atm	43

**INTERFACIAL TENSION-TERNARY SYSTEM
(CO₂ as one of the components)**

	SYSTEM		DATA PTS	T RANGE	P RANGE	REFERENCE
COMP 1	COMP 2	COMP 3				
Benzene	Carbon Dioxide		16	160F	1000-1589psia	37
Butane	Carbon Dioxide		42	115-220F	2180-7965psia	20
Butane	Decane	Carbon Dioxide	12	160F	9.31-11.45Mpa	35
Decane	Carbon Dioxide		41	344-378K	926-2386psia	36
Decane	Butane	Carbon Dioxide	12	160F	9.31-11.45MPa	35
Tetradecane	Carbon Dioxide		18	160F	1000-2360psia	14
Cyclohexane	Carbon Dioxide		14	160F	997-1586psia	37

INTERFACIAL TENSION-HYDROCARBON SYSTEM

SYSTEM		DATA PTS	TEMP RANGE	PRESS RANGE	REFERENCE
COMP 1	COMP 2				
Methane		3	minus180 to -160	1atm	86,87
Ethane		7	33-81F	1atm	24
Ethane		8	minus160 to-90	1atm	78
Propane		10	minus130 to -40C	1atm	86
Propane		12	34-103F	1atm	24
Butane		14	36-114F	1atm	24
Butane		3	115-220F	VP 65-241psia	20,50
Butane		8	minus100to-30	1atm	81
i-Butane		8	minus100to-30C	1atm	81
Pentane		8	minus20 to+40C	1atm	81
Pentane		5	78F	1atm	56
Pentane	Water	1	25C	1atm	15,23
Pentane	Water	18	20.2-149.6C	?	29
Pentane	Water	15	15-35C	1 atm	32
Cyclopentane		1	13.5C	1 atm	79
i-Pentane		7	minus20to+30C	1 atm	81
Hexane		6	30C	1atm	43
Hexane		26	0-220C	1 atm	21,44,51,78
Hexane	Water	2	20-25C	1atm	15,23
Hexane	Water	1	25C	1atm	15,23
Hexane	Water	16	20-60C	1atm	32
Hexane	Water	3	10-40C	1atm	1,9,12,34,41,58
Hexane	Water	1	298.15K	0.1MPa	33
Cyclohexane		8	10-75C	1atm	21,79
Cyclohexane	Water	1	298.15K	0.1Mpa	33
Cyclohexane	Water	3	25C	1 atm	1,9,15,23,26,41
i-Hexane		1	25C	1 atm	16,23
Heptane		3	78F	1 atm	56
Heptane		25	20-240C	1 atm	2,21,78
Heptane	Water	1	25C	1 atm	15,23
Heptane	Water	4	10-40C	1 atm	1,4,9,75
Heptane	Water	1	25C	1 atm	1,26
Octane		30	minus40 to 240C	1atm	21,78
Octane	Water	1	25C	1 atm	15,23
Octane	Water	1	298.15K	0.1MPa	33
Nonane		1	20C	1atm	21
Decane		1	21C	1 atm	27
Decane		2	160-220F	1-2psia	21,36
Decane	Water	1	25C	1 atm	16,23
Decane	Water	1	298.15K	0.1MPa	33
Dodecane		1	25C	1 atm	27
Dodecane	Water	1	25C	1 atm	16,23
Dodecane	Water	1	298.15K	0.1MPa	33
Tetradecane		1	21C	1 atm	27
Hexadecane		1	21C	1 atm	27
Hexadecane	Water	1	25C	1 atm	16,23

BENZYLIC-SYSTEMS

SYSTEM			DATA PTS	T RANGE	P RANGE	REFERENCE
COMP 1	COMP 2	COMP 3				
Aniline			19	0-180C	1atm	78
Benzaldehyde	Water		1	20C	1atm	74
Benzene			13	76F	1atm	56
Benzene			12	10-80C	1atm	21,44,51,79
Biphenyl			7	100-250C	1atm	80
Benzene	Acetone		17	291.15-298.15K	1atm	48,53
Benzene	Carbon dioxide		16	160F	1000-1589psia	37
Benzene	Cyclohexane		1	20C	1atm	58,63
Benzene	Cyclopentane		1	25C	1atm	58,63
Benzene	1,4 Dioxane		12	293.15-303.15K	1atm	52
Benzene	Ethanol		1	25C	1atm	31,58
Benzene	Ethylene glycol		1	27C	1atm	57
Benzene	Methanol		1	30C	1atm	31,58
Benzene	i-Octane		1	30C	1atm	10,58
Benzene	Perfluoro-hexane		1	25C	1atm	23,43
Benzene	Water		1	25C	1atm	1,4,9,17,34,41,47
Benzene	Water		1	298.15K	0.1MPa	33
Benzene	Water		9	20-30C	1atm	1,2,9,15,23,26,62
Benzene	Water		15	20-25C	1atm	3,7,18,32,40,75
Benzene	o-Xylene		1	25C	1atm	58,63
Benzene	Acetic acid	Water	5	25C	1atm	1,6
Benzene	Acetone	Water	19	30C	1atm	43
Benzene	Butanol	Water	?	25C	1atm	6
Benzene	t-Butanol	Water	7	25C	1atm	45
Benzene	1,4 Dioxane	Water	5	25C	1atm	1
Benzene	Ethanol	Water	6+?	25C	1atm	6,44,45
Benzene	Ethanol	Water	18	20C	1atm	11,44
Benzene	Hexane	perfluoro-hexane	12	30C	1atm	23,43
Benzene	Methanol	Water	4+?	25C	1atm	42,43
Benzene	Perfluoro-hexane	Hexane	12	30C	1atm	43,44
Benzene	Propanol	Water	8+?	20-30C	1atm	6,23
Benzene	i-Propanol	Water	19	25C	1atm	42,45
Benzene	Propionic acid	Water	6	25C	1atm	26
Toluene	Bromobenzene		1	25C	1atm	58,61
Water	Bromobenzene		2	25C	1atm	9,15,23
Bromonaphthalene			1	21C	1atm	27
Butylbenzene	Water		1	25C	1atm	16,23
Chlorobenzene			34	0-330C	1atm	78
Chlorobenzene	Toluene		1	20C	1atm	58,61
Chlorobenzene	Water		2	20-25C	1atm	1,15,17,23
Ethylbenzene	Water		3	20-25C	1atm	1,9,15,17,23,47
Nitrobenzene			21	0-200C	1atm	78
Nitrobenzene	Water		3	20-25C	1atm	9,15,23,75
i-Propylbenzene			13	20-90C	1atm	81,83
Pyridine			1	20C	1atm	51
Toluene			17	0-100C	1atm	2,21,51,55,81
Toluene	Bromobenzene		1	25C	1atm	58,61
Toluene	Chlorobenzene		1	20C	1atm	58,61
Toluene	Cyclohexane		1	25C	1atm	58,63
Toluene	Cyclopentane		1	25C	1atm	58,63
Toluene	Methanol		9	308.15K	1atm	49
Toluene	Water		2	25C	1atm	1,15,23,26

BENZYLIC-SYSTEMS—Continued

Toluene	Water		3	10-40C	1atm	1,9,17,34,47
Toluene	Acetic acid	Water	22	25C	1atm	34
Toluene	Acetone	Water	18	25C	1atm	34
Toluene	Ethanol	Water	7	25C	1atm	45
Toluene	Propanol	Water	21	22-25C	1atm	22,45
Toluene	Propionic acid	Water	6	25C	1atm	26
Toluene	i-Propanol	Water	6	25C	1atm	45
m-Xylene			12	0-100C	1atm	79
m-Xylene	Water		2	25C	1atm	1,16,17,23
o-Xylene			12	0-100C	1atm	81
o-Xylene	Benzene		1	25C	1atm	58,63
o-Xylene	Water		1	25C	1atm	1,17
p-Xylene			10	20-100C	1atm	81
p-Xylene	Water		1	25C	1atm	1

INTERFACIAL TENSION-ALCOHOL SYSTEM

SYSTEM		DATA PTS	T RANGE	P RANGE	REFERENCE
COMP 1	COMP 2				
Methanol		31	0-235C	1atm	2,21,51,55,78
Methanol	Water	1	30C	1atm	28,58
Methanol	Water	132	263-325K	1atm	53
Ethanol		32	0-240C	1atm	2,21,44,51,55,78
Ethanol	Water	6	24-30C	1atm	2,27,55,58
Ethanol	Water	318	268-369K	1atm	53
Propanol		1	20C	1atm	51
2-Propanol		13	minus10to+100C	1atm	51,78
i-Propanol		1	24C	1atm	2,21
Propanol	Water	123	268-323K	1atm	53,60
Butanol		15	0-140C	1atm	78
Butanol	Water	6	21-25C	1atm	1,2,9,15,23,57
2-Butanol	Water	1	25C	1atm	1,9,54
i-Butanol	Water	1	25C	1atm	15,23
Pentanol	Water	2	10-40C	1atm	1,9,15,23
i-Pentanol	Water	1	25C	1atm	15,23
Hexanol	Water	1	25C	1atm	1,9
Cyclohexanol	Water	2	25C	1atm	1,9,15,23,34
Heptanol	Water	2	25C	1atm	1,9,15,23
Octanol	Water	1	25C	1atm	16,23
2-Ethyl hexanol	Water	1	25C	1atm	1
n-Butyl alcohol	Water	3	25C	1atm	9,13
i-Butyl alcohol	Water	3	25C	1atm	9,13
Amyl alcohol	Water	2	25C	1atm	9
i-Amyl alcohol	Water	5	21C	1atm	2,62
t-Amyl alcohol	Water	2	18-24C	1atm	2,55,62
Hexyl alcohol		2	25C	1atm	9
Heptyl alcohol		3	25C	1atm	9,13
1,2-Propanediol		1	20C	1atm	51
1,2-Propanediol	Water	16	303K	1atm	38
1,3-Propanediol		1	20C	1atm	51
1,3-Propanediol	Water	16	303K	1atm	38
1,3- Butanediol		1	20C	1atm	51
1,3- Butanediol	Water	16	303K	1atm	38
1,4- Butanediol		1	20C	1atm	51
1,4- Butanediol	Water	16	303K	1atm	38
Ethylene glycol		3	20-24C	1atm	21,27,51
Ethylene glycol	Water	19	298-303K	1atm	38,60
Diethylene glycol		1	21C	1atm	27
Thiodiglycol		1	21C	1atm	27
Glycerol		19	15-150C	1atm	32,51,85
Glycerol	Water	14	291-298K	1atm	53
2-Ethyl hexanol	Water	1	25C	1atm	1

ALCOHOL-ALCOHOL SYSTEM

SYSTEM		DATA PTS	T RANGE	P RANGE	REFERENCE
COMP 1	COMP 2				
Butanol	Decanol	1	25C	1atm	5,58
Butanol	Methanol	1	25C	1atm	5,58
i-Butanol	Methanol	1	25C	1atm	5,58
s-Butanol	Methanol	1	25C	1atm	5,58
t-Butanol	Methanol	1	25C	1atm	5,58
Decanol	Ethanol	1	25C	1atm	5,58
Decanol	Hexanol	1	25C	1atm	5,58
Decanol	Methanol	1	25C	1atm	5,58
Decanol	Propanol	1	25C	1atm	5,58
Decanol	i-Propanol	1	25C	1atm	5,58
Ethanol	Phenol	1	35C	1atm	31,58
Methanol	Propanol	15	298K	1atm	53

KETONE-SYSTEMS

COMP 1	SYSTEM		DATA PTS	T RANGE	P RANGE	REFERENCE
	COMP 2	COMP 3				
Acetone			11	0-80C	1atm	51,55,78
Acetone	Acetic acid		4	298K	1atm	53
Acetone	Benzene		17	291-298K	1atm	48,53
Acetone	Benzene	Water	19	30C	1atm	43
Acetone	Hexane	Water	32	25C	1atm	34,42
Acetone	Methyl i-butyl ketone	Water	11	25C	1atm	42
Acetone	4-Methyl-2-pentanone	Water	5	25C	1atm	1
Acetone	1,1,2-Trichloroethane	Water	22	25C	1atm	1,43
Acetone	1,1,2-Trichloromethane	Water	5	25C	1atm	1
Acetone	Water		137	273-343K	1atm	19,53
Acetophenone	Water		1	25C	1atm	1
Cyclohexanone	Water		1	25C	1atm	1
2-Heptanone	Water		1	25C	1atm	15,23
2-Hexanone	Water		1	25C	1atm	15,23
Methyl i-butyl ketone	Water		1	25C	1atm	23,42
Methyl i-butyl ketone	Acetone	Water	11	25C	1atm	42
Methyl ethyl ketone			2	20-23.5C	1atm	21,51
Methyl ethyl ketone	Hexane	Water	13	25C	1atm	42
Methyl ethyl ketone	1,1,2-Trichloroethane	Water	?	25C	1atm	43
Methyl ethyl ketone	Water		82	273-318K	1atm	53
4-Methyl-2-pentanone	Acetone	Water	1	25C	1atm	1
4-Methyl-2-Pentanone	Water		3	10-40C	1atm	1,34
2-Pentanone	Water		1	25C	1atm	15,23
1,1,2-Trichloroethane	Acetone	Water	22	25C	1atm	1,43
1,1,2-Trichloroethane	Methyl ethyl ketone	Water	?	25C	1atm	43
1,1,2-Trichloromethane	Acetone	Water	5	25	1atm	1

REFERENCES

1	Backes,H.M., J.J.Ma, E.Bender & G.Maurer, Chem. Eng. Sci., 45, 1990, pp 275-286
2	Baird,M.H.I. & I.Nirdoosh, Canadian J. Chem. Eng., 59, 1981, pp 369-376
3	Bartell,F.E., L.O.Case & H.J.Brown, Am. Chem. Soc., 55, 1933, p 2769
4	Bartell,F.E. & J.K.Brown, Am. Chem. Soc., 55, 1933, p 2769
5	Benson,G.C. & V.T. Lam, J.C.I.S., 38, 1972 P 296
6	Buqiang,L., M.S. Thesis,Beijing Institute of Chemical Technology, 1984
7	Carter,E.G. & D.C.Jones, Trans. Faradau Soc., 30, 1934 p 1027
8	Chand,K., V.Ramaakrishma, Indian J. Chem., 7, 1969, p698
9	Donahue,D.J. & F.E.Bartell, J. Phys. Chem., 56, 1952, pp 480-484
10	Evans,H.B.,Jr. & H.L. Clever, J. Phys. Chem., 68, 1964, p 3433
11	Fleming, P.D.,III & J.E.Vinatieri, J. Chem. Eng. Data, 26, 1961, pp 172-174
12	Franks,F. & D.F.G.Ives, Nature, 163, 1959, pp 287-296
13	Fuchs,V.N., Kolloid Z., 52, 1930, p 262
14	Gasam,K.A.M., K.B.Dickson, P.B.Dulcamara, N.Nagarajan & R.L.Robinson Jr., J. Chem. Eng. Data, 34, 1989, pp 191-195
15	Gerhard,H., Chem. Tech., 31, 1979, p 143
16	Good,R.J., Interfacial Tension in Systems Having Appreciable Mutual Solubilitu, Symposium on Chemisstry and Physics of Interface, Washington, D.C., 1968, pp 72-96
17	Good,R.J. & E.Elbing, Ind. Eng. Chem., 62, 1970, pp 54-78
18	Harkins,W.D., J. Chem. Phys., 9, 1941, p552
19	Howard,K.S. & R.A.McAllister, AIChE J., 3, 1957, p 325
20	Jack,J., C.Hsu, N.Nagarajan & R.L.Robinson,Jr., J. Chem. Eng. Data, 30, 1985 pp 485-491
21	Jasper,J.J., J. Phys. Chem. Ref. Data, 1, 1972, pp 841-1009
22	Jon,D.I., H.I.Rosano & H.Z.Cummins, J. Colloid Interface Sci., 114, 1986, pp330-341
23	Jufu,F.,L.Buquing & W. Zihao, Chem. Eng. Sci., 41, 1986, pp 2673-2679
24	Katz,D.L. & W.Saltman, Ind. & Eng. Chem., 31, 1939, p 91
25	Kharin,S.E. & G.E. Sorokina, Ferment. Sprit. Prom., 36 (5), 1970, p7
26	Li,B. & J.Fu, J. Chem. Eng. Data, 37, 1992, pp 172-174
27	Li,D & A.W.Neumann, J. Colloid Interface Sci., 148, 1992, pp 190-200
28	Pliskin,I. & R.E.Trebal, J. Chem. Eng. Data, 11, 1966, pp 49-51
29	Matsubara,H., M.Murase, Y.H.Mori & A.Nagashima, Internat. J. Thermo Phys., 9, 1988, pp 409-424
30	McLure,I.A., J.T.Sipowsha & I.L.Pegg, J. Chem. Thermo., 14, 1982, p 733
31	Morgan,J.R.L. & A.J.Scarlett, Jr., J. Am. Chem. Soc. ,39, 1917, p 2280
32	Mori, Y.H., N.Tsul & M.Kiyomlya, J. Chem. Eng. Data, 29, 1984, pp 407-412
33	Motomura,K., H.Iyota, M.Yamanaka & R.Matuura, J. Colloid Interface Sci., 93, 1983, pp 264-269
34	Murphy,N.F., J.E.Lastovica & J.G.Fallis, Ind. Eng. Chem., 49,1957, pp 1035-1042
35	Nagarajan,N.,K.A.M.Gasam & R.L.Robinson,Jr., J. Chem. Eng. Data, 35, 1990, pp 228-231
36	Nagarajan,N. & R.L.Robinson Jr., J. Chem. Eng. Data, 31, 1986, pp 168-171
37	Nagarajan,N. & R.L.Robinson Jr., J. Chem. Eng. Data, 32, 1987, pp 369-371
38	Nakanishi,K., T.Matsumoto & M.Hayatsu, J. Chem. Eng. Data, 16, 1971, p 44
39	Owens,D.K., J. Phys. Chem., 74, 1970, pp 3305-3306
40	Patterson, R.E. & S.Ross, Surf. Sci., 81, 1979, p451
41	Paul,G.W. & M. deChazel, J. Chem. Eng. Data, 11, 1966, pp 105-106
42	Paul,G.W. & M. deChazel, J. Chem. Eng. Data, 12, 1967, pp 105-106
43	Pliskin,I. & R.E. Trebal, J. Chem. Eng. Data, 11, 1966, pp 49-51
44	Ross,S. & R.E. Patterson, J. Chem. Eng. Data, 24, 1979, pp 111-114
45	Sada, E., S.Kilo & M.Yamashita, J. Chem. Eng. Data, 20, 1975, p 376
46	Schmidt,R.L. & H.L.Clever, J.C.I.S., 26, 1968, p 19
47	Shewmaker,J.E., C.E. Vogler & E.R. Washburn, J. Chem. Phys., 58, 1966, pp 945-948

REFERENCES—Continued

48	Shipp, W.E., J. Chem. Eng. Data, 15, 1970, p 308
49	Singh, S., B.S.Lark & S.K.Aggarwal, Indian J. Chem., 21, 1982, p 1116
50	Stegmeier, G.L., Ph.D. Dissertation, University of Texas Austin, Tx, 1959
51	Suarez, J.T., C.Torres-Marchal & P.Rasmussen, Chem. Eng. Sci., 44, 1989, pp 782- pp 786
52	Suri, S.R. & V.Ramakrishna, J. Phys. Chem., 72, 1968, p 3073
53	Timmermans, J., Physico-Chemical Constants of Pure Organic Substances, 2nd Ed., Elsevier, New York, 1965
54	Timmons, C.O. & W.A.Zisman, J. Colloid Interface Sci., 28, 196, pp 106-117
55	Weast, R.C.(ed), "Handbook of Chemistry and Physics", 54 edn., CRC Press, 1973
56	Weinaug, C.F. & D.L.Katz, Ind. Eng. Chem., 35, 1943, p239
57	Wellek, R.M., A.K.Agrawal & A.H.Skelland, AIChE J., 12, 1966, p 854
58	Winterfield, P.H., L.E.Scriven & H.T.Davis, AIChE J., 24, 1978, pp 1010-1014
59	Wolf, K.L., Physik und Chemie' der Grenzflächen. Springer Verlag, Berlin, 1957
60	Won, Y.S., D.K.Chung & A.F.Mills, J. Chem. Eng. Data, 26, 1981, p 140
61	Yajnik, N.A., R.K.Sharma & M.C. Bharadway, J. Indian Chem. Soc., 3, 1926, p 63
62	Young, T.F. & W.D.Harkins, "International Critical Tables", 4, 1930, p 436
63	_____, Can. J. Chem., 48, 1970, p 3773
64	Harkins, W. & F.E.Brown, J. Amer. Chem. Soc., 41, 1919, p 499
65	Weast, R.C. & S.M.Selbey (Eds.), "Handbook of Chemistry & Physics," pp F-25, F-27 Chemical Rubber Co., Cleveland, Ohio, 1966
66	Johansson, K. & J.C.Eriksson, J. Colloid Interface Sci., 40, 1972, p 398
67	Harkins, W.D. & A.E.Alexander, "Physical Methods of Organic Chemistry"(A.Weissberg, Ed) 3rd ed., Vol 1, Part 1, Interscience, New York, 1959
68	Grzeskowiak, R., G.H.Jeffery & A.I.Vogel, J. Chem. Soc., 1960, p 4728
69	Fredrickson, J.E., J. Colloid Interface Sci., 48, 1974, p 506
70	Clever, H.L. & C.C.Snead, J. Phys. Chem., 67, 1963, p 918
71	Bernett, M.K., N.L.Jarvis & W.A.Zisman, J. Phys. Chem., 66, 1962, p328
72	Richards, T.W. & E.K.Carver, J. Am. Chem. Soc., 43, 1921, p 827
73	Snead, C.C. & H.L. Clever, J. Chem. Eng. Data, 7, 1962, p 393
74	Addison, C.C. & J.M. Coldrey, J. Chem. Soc., 1961 p 468
75	Girifalco, L.A. & R.J.Good, J. Phys. Chem., 61, 1957, p 904
76	Griffin, J.B. & H.L.Clever, J. Chem. Eng. Data, 5, 1960, p 390
77	Herrick, C.S. & G.L.Gaines, Jr., J. Phys. Chem., 77, 1973, p 2703
78	Volyak, L.D., Teploenergetika, 7, 1958
79	Tatevskiy, V.M.(ed) Physico-Chemical Properties of Individual Hydrocarbons, Gostoptech Press, 1960
80	Vukalovich, M.P.et al. Thermophysical Properties of Organic Coolants, Atoms Press, 1969
81	Rossini, F.D. ety al., Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, NBS, Pittsburg, 1953
82	Badylkes, I.S., Kholodilinaya tekhnika, Encyclopedia Dictionary, Vol 1, Gosenergo Press, 1960
83	Kurbatov, V.Y., Zhurnal Obshchey Khimii, 18(11), 1947, p 1999
84	Elverum, G. & Doescher, R., J Chem. Phys. 20(12), 1952, p 1834
85	Kagan, S.E. & A.V.Chechetkin, "Organic High-Temperature Coolants", Goschem Press, 1951
86	Vargaftik, N.B.(ed) Thermophysical Properties of Substances. A Handbook, Gosenergo Press, 1956
87	Naziev, Ya.M. & A.A.Abasov, Transaction of the Third All-Union Conference on Thermophysics, Thermophysical Properties of Gases, Nauka Press, Moscow, 1970, Izvestiya MVO SSSR, Series Petroleum and Gas 13(3), 1968, Khimiya i tekhnologiya topliv i masel, No. 3, 22, 1970
88	Vargaftik, N.B., L.D.Volyak & B.N.Volkov, Transactions of the VII International Conference on the Properties of Water and Steam, Tokyo, 1968, Transactions of

REFERENCES—Continued

	All-Union Conference on Thermodynamics, Thermophysical Properties of Substances, Leningrad, 1970
89	Harkins, W.D., in "Physical Methods of Organic Chemistry", Vol 1, Pt 1, A. Weissberger, Ed., Interscience, New York, 1949, p 369
90	Li, B. & J. Fu, J. Chem. Ind. and Eng., China, No. 3, 1989, pp 355-364

