International Journal of Thermophysics, Vol. 14, No. 2, 1993

Equation-of-State Measurements for Crude Oils at Pressures up to 1 GPa

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Received October 28, 1992

Equation-of-state measurements of two crude oils with different compositions and viscosity were performed at room temperature in the pressure range $0 < P < 1.0$ GPa. We found large compressibilities and a strong dependence of the compressibility on oil content and viscosity. The bulk modulus changed with pressure from 2.0 to 12.1 GPa for one oil and from 1.3 to 9.5 GPa for the other. We discuss the possibility of detecting phase transitions in the region under investigation. The Tait and Murnaghan equations of state were fitted to the data, and residuals are presented.

KEY WORDS: bulk modulus; compressibility; crude oil; equation of state; high pressure.

1. INTRODUCTION

The investigation of crude-oil properties at high pressures is of great interest to the oil industry, especially in view of the problem of oil recovery from deep wells. Until now, the equation of state of different crude oils has been studied for pressures up to only 10–20 MPa. However, the oil pressure in very deep wells may be much higher. A knowledge of the high-pressure properties of oils may also be useful in attempts to understand the nature of oil-forming processes at high depths. Furthermore, because oils are complex multicomponent liquid mixtures having a probably colloidal (microheterogeneous) structure, it could be quite informative to test the applicability of some well-known equations of state in the high-pressure range, usually used for solids, on these substances.

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2. EXPERIMENTAL DETAILS AND RESULTS

The volume measurements were performed in a piston-cylinder device with an internal diameter of 15 mm. The piston displacement was measured with two calibrated differential transformers. The force was measured by a load cell and pressure was calculated as force over cylinder area. All measurements were corrected for piston compression (by calibration) and mean-area expansion. The mean-area expansion was calculated from theory [1]. The oils were enclosed in an indium capsule 30 mm high and with a wall thickness of 0.5 mm, to prevent leakage and ensure low friction. All volume data were calculated as the average of values taken under increasing and decreasing pressure, and the friction was about $\pm 2.5\%$ of the load. The equipment has so far been tested against indium, and comparison with literature data [2] shows that the accuracy in V/V_0 is better than 0.1 %. A detailed description of the equipment, which also will include facilities for measuring V/V_0 over a wide range of temperatures, will be presented in a future publication.

As a first step, we have undertaken PV measurements for two crude oils from the Usinsk and Kumkolsk oil fields in Russia. Properties of the oils investigated are shown in Table I. Usinsk oil is much more viscous than Kumkolsk oil and contains practically no paraffins. The oils were degassed and dried before the investigations. We have measured the relative volume of the oil samples at room temperature, $T = 294$ K, in the pressure range $0 < P < 1$ GPa. The experimental results for $V(P)/V(0)$ are presented in Table II and in Figure 1.

Table I. Properties of Crude Oils

Properties	Usinsk oil	Kumkolsk oil
Density ($kg \cdot m^{-3}$)	962	813
Average molecular weight	415	225
Initial boiling point (K)	404	298
Viscosity ($10^6\ m^2 \cdot s^{-1}$)		
$T = 293$ K	4820	—
$T = 303$ K	—	7.1
$T = 323$ K	513	3.7
Content (%)		
Silica-gel pitches	22	10
Asphaltens	11	<0.1
Paraffins	0.25	15

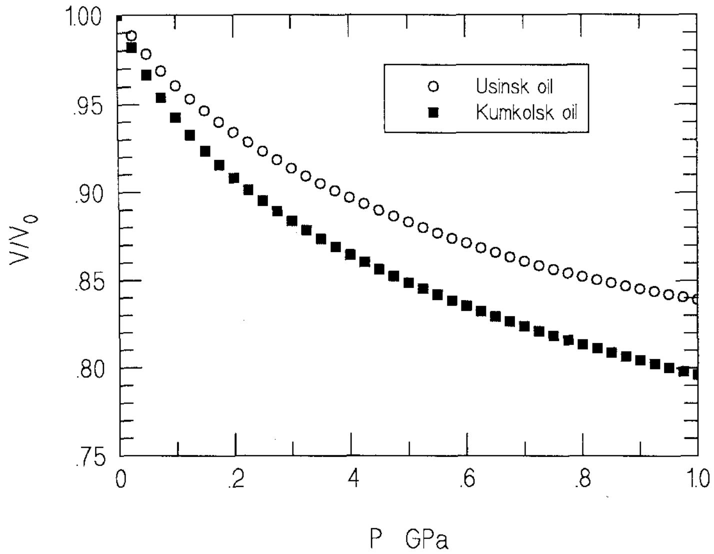

Fig. 1. Experimental data for Usinsk and Kumkolsk oils at $T = 294$ K.

Table II. Experimental PV Data for Usinsk and Kumkolsk Oils: $T = 294$ K

	V/V_0	
Pressure (GPa)	Usinsk oil	Kumkolsk oil
0.050	0.9781	0.9667
0.100	0.9607	0.9427
0.150	0.9465	0.9237
0.200	0.9342	0.9082
0.250	0.9234	0.8952
0.300	0.9138	0.8838
0.350	0.9051	0.8737
0.400	0.8972	0.8645
0.450	0.8900	0.8563
0.500	0.8832	0.8486
0.550	0.8770	0.8418
0.600	0.8711	0.8353
0.650	0.8658	0.8293
0.700	0.8608	0.8236
0.750	0.8562	0.8183
0.800	0.8522	0.8133
0.850	0.8486	0.8087
0.900	0.8452	0.8043
0.950	0.8421	0.8000
1.000	0.8390	0.7960

3. DISCUSSION

The first striking feature of the results presented is the great compressibility of the oils. This may possibly be explained by their colloidal, dispersed nature. The second interesting feature is the large difference between the compressibilities of the two oils under investigation. As the main difference between these two oils is the anomalously small amount of paraffins in Usinsk oil and its much greater viscosity, the results suggest a strong correlation between these characteristics and their compressibilities.

It is interesting to test how the isothermal equations of state, usually used for solids, fit to our experimental data. We chose two widely known isothermal equations of state: the Tait equation [3],

$$\frac{V(P, T)}{V(0, T)} = 1 - A \ln\left(1 + \frac{P}{C}\right) \tag{1}$$

where $A(T)$ and $C(T)$ are the pressure-independent parameters to be identified, and the Murnaghan [4] equation of state,

$$\frac{V(P, T)}{V(0, T)} = \left(1 + \frac{\eta P}{B_0}\right)^{-1/\eta} \tag{2}$$

The last equation may be deduced from the assumption that the bulk modulus $B_T = -V(\partial P/\partial V)_T$ is a linear function of P at constant T: $B_T = B_0 + \eta P$, B_0 being the bulk modulus at zero pressure and η its first derivative with respect to P (assumed to be independent of P). The Tait equation [Eq. (1)], on the other hand, corresponds to the assumption that $-(\partial P/\partial V)_T$ is a linear function of P. The Murnaghan equation is usually considered to be more appropriate to use in the GPa pressure range [5]. In any case it is very convenient that the fitted parameters B_0 and η have a clear physical meaning. However, the Tait equation is the one widely used for the description of PVT data of polymer liquids in general [6] and for oils at pressures up to 20 MPa.

Another point of interest is the visible smoothness of the curves. At first sight this indicates that there are no phase transitions in the oils in the pressure range under investigation. However, it has previously been detected in transient hot-wire measurements [7] that viscous Usinsk oil undergoes a smooth liquid-to-glass transition in a small pressure interval near 0.4 GPa at a temperature $T = 295$ K. The visible smoothness of the $V(P)/V(0)$ plot in the transition region indicates that derivatives of thermodynamic parameters change very little at this transition. As far as Kumkolsk oil is concerned, the paraffin crystallization in this oil occurs at a pressure of some MPa. As we could not make the first pressure step smaller than 0.02 GPa, it was not possible to investigate the pressure region of the paraffin crystallization. However, the presence of this trans-

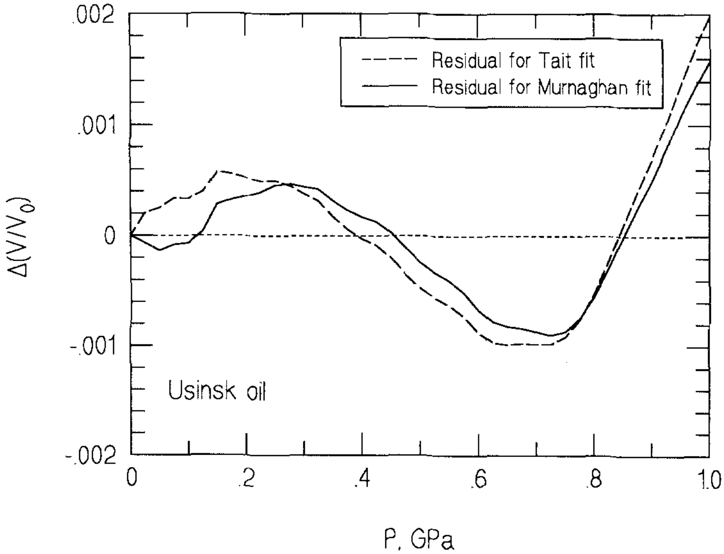

Fig. 2. Residuals of two fits for Usinsk oil. The constants are as follows: for the Murnaghan equation [Eq. (2)], $B_0 = 2.03$ GPa and $\eta = 10.06$; and for the Tait equation [Eq. (1)], $A = 8.33 \times 10^{-2}$ and $C = 0.163$ GPa.

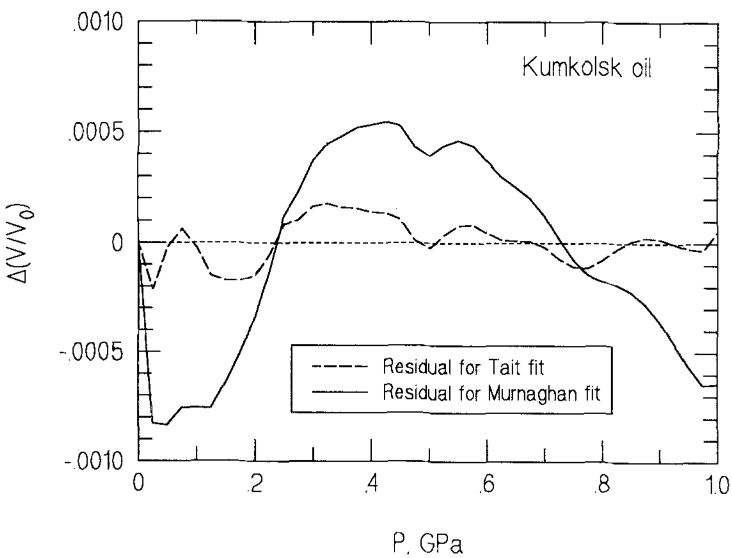

Fig. 3. Residuals of two fits for Kumkolsk oil. The constants are as follows: for the Murnaghan equation [Eq. (2)], $B_0 = 1.30$ GPa and $\eta = 9.19$; and for the Tait equation [Eq. (1)], $A = 8.79 \times 10^{-2}$ and $C = 0.109$ GPa.

ition can be detected by comparing the values of bulk modulus obtained from our high-pressure experimental data and from data [8, 9] for Kumkolsk oil with paraffin before crystallization. The difference between these two values is greater than 40%.

The fitting of Eqs. (1) and (2) to our data revealed that, despite rather large compressibilities, both equations yield comparatively good fits of data (Figs. 2 and 3). Using Murnaghan's equation, we find that the bulk modulus of Usinsk oil changes from 2.03 GPa for zero pressure to 12.9 GPa for the pressure 1 GPa; the corresponding values for Kumkolsk oil are 1.30 and 10.49 GPa. The value of the bulk modulus at zero pressure calculated from the Tait equation [$B(0) = C/A$; see Eq. (1)] is equal to 1.96 GPa for Usinsk oil and 1.24 GPa for Kumkolsk oil. The residuals of these fits may be informative in the light of the presence of a glass transition (in Usinsk oil; Fig. 2) in the pressure range investigated.

4. CONCLUSION

We have investigated the compressibility of crude oils at $T = 294$ K for pressures up to 1 GPa. The results show large values of compressibility for crude oils and a strong dependence of compressibility on oil content and viscosity. The Tait and Murnaghan equations of state yield comparable representations of the experimental data.

ACKNOWLEDGMENTS

One of us (V. K.) would like to express his gratitude to the Physics Department, University of Umeå, Sweden, for hospitality and good research facilities. The authors thank Prof. G. Bäckström, Prof. M. Anisimov, and Dr. A. Chernoutsan for helpful discussions.

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