Dielectric Constants and Clausius-Mossotti Functions for Simple Liquid Mixtures: Systems Containing Nitrogen, Argon and Light Hydrocarbons

Dielectric constants and Clausius-Mossotti functions (CM) have been determined for selected pure components, binary mixtures, and ternary mixtures at temperatures between 91 and 115 K and pressures near saturation. Excess Clausius-Mossotti functions (CM^E) have been calculated from the pure fluid and mixture values.

Mixture CM^E values are found to be generally less than 0.1% of the mixture CM values for systems containing only nonpolar species. Thus, dielectric constant measurements can be conveniently used as substitute density measurements for simple liquid mixtures. Methods have been developed to utilize dielectric constant measurements to accurately determine densities and heating values per unit liquid volume for liquefied natural gas mixtures.

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SCOPE

Volumetric measurements for simple liquids and their mixtures have proven difficult at low temperatures (near 100 K). Careful determinations of pure component saturated liquid molar volumes by ordinary volumetric techniques in different laboratories have often disagreed by more than 0.2%. To provide for equitable custody transfer of liquefied natural gas it would be desirable to have accurate knowledge of the molar volume for a reasonably wide range of typically encountered mixtures. It may now be possible to predict molar volumes for typical liquefied natural gases within ±0.2% from accurate measurements of composition, temperature, and pressure (Klosek and McKinley, 1968; Boyle and Reece, 1971; Albright, 1973; Rodosevich and Miller, 1973, 1974; Mollerup and Rowlinson, 1974). However, compositions and temperatures are difficult to measure within the required tolerances. It would often be highly desirable to determine quickly or monitor continuously liquid mixture molar volumes by use of some relatively simple device.

Dielectric constant measurements can be used to indirectly determine molar volumes. A particular combination of the dielectric constant and the molar volume, termed the *Clausius-Mossotti* function (CM), is found to undergo changes of only a few percent as a simple fluid is taken from the ideal gas at high temperatures to the saturated liquid near the triple point. For an ideal gas mixture the CM function is rigorously given by the mole fraction average of the pure component values. If this same relationship is sufficiently accurate for liquid mixtures, that is, if CM^E is very nearly zero, then measurements of composition and dielectric constant can be readily used to obtain molar volumes. In addition, if pure component CM values are proportional to heating values for the components of a liquefied natural gas, it will be possible to use dielectric constant measurements alone to convert a total volume measurement directly into total heating value, the basis for sale of such commodities.

To test the above conjectures, the present investigation was designed to provide a consistent set of low temperature dielectric constants and Clausius-Mossotti functions for some relatively simple liquids and liquid mixtures, including components and mixtures of interest relative to liquefied natural gas. Previous results are available in the same temperature range for some of the pure components (Ar, N_2, and CH_4). No previous results appear to be available for the mixtures.

CONCLUSIONS AND SIGNIFICANCE

The mixture results indicate that the excess Clausius-Mossotti function (CM^E) is less than 0.1% of the mixture CM value for saturated liquid mixtures composed of simple nonpolar species. For such mixtures a dielectric constant measurement may be used as a substitute for a density measurement, if the composition and pure component CM values are known. This experimental approach could reduce the effort required to determine the PVT surface for a fluid mixture.

Pure component results for propane and isobutane indicate that their small permanent dipole moments are of sufficient magnitude to effect their liquid dielectric properties at low temperatures. This is also confirmed by the larger CM^E values for mixtures containing these species. For typical liquefied natural gases, where concentrations of these components are not too large, mixture CM values can be accurately estimated by a mole fraction average

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calculation using infinite dilution CM values for these species in methane rather than their pure-component CM values.

Deviations from a direct proportionality between the light hydrocarbon liquid CM values and heating values were found to be as large as 3%. Thus, such a proportionality should not be assumed in calculations where highly accurate heating values are desired.

Based upon the experimental results discussed above, calculational schemes have been developed: (1) to allow accurate liquefied natural gas densities to be determined from accurately measured dielectric constants and compositions; and (2) to allow accurate liquefied natural gas heating values per unit liquid volume to be determined from accurately measured dielectric constants, with only approximate knowledge required for the compositions of all components except nitrogen. These simple calculational methods should provide a basis for using capacitance measurements in the custody transfer of liquefied natural gas.

EXPERIMENTAL METHOD

An apparatus was used in this study with which simultaneous molar volume and dielectric constant measurements can be made. The molar volume experiment is by the gas expansion method and has been described previously (Liu and Miller, 1972; Rodosevich and Miller, 1973). Most of the molar volumes used in the present work were not remeasured but rather taken directly or estimated closely from previous studies.

Dielectric constants ϵ were determined from capacitance measurements using a capacitor located in the volumetric cell:

$$\epsilon = \frac{C - C_S}{C_0 - C_S} \tag{1}$$

In this equation C and C_0 are the capacitances with the fluid as medium and under vacuum, and C_S is the stray capacitance.

The cell capacitor configuration which was chosen is similar to that described by Younglove and Straty (1970). The capacitor consists of two concentric cylindrical plates which are held in position by a central mandrel (compare Figure 1). There are two essential differences between the capacitor design and that of Younglove and Straty. The solid cylindrical plates have been replaced with plates constructed from spaced round bars connected at the ends by solid rings (slotted plates). Also, the liquid filling capillary passes through the mandrel head and empties into the space between the capacitor plates. These two modifications provide for improved performance in mixture work.

Both the capacitor and its confining cell are constructed of stainless steel. There are holes provided in the cell wall for a dummy filling line and a platinum resistance thermometer. Two rigid shielded electrical leads and a filling line pass through the cell plug, the bottom portion of which is one end of the mandrel. Cell closure is made by tightening a nut which compresses a softened copper gasket between the plug and cell body. The shielding on the leads, the cell body, and the central mandrel form a common ground which is the third lead to the capacitance bridge.

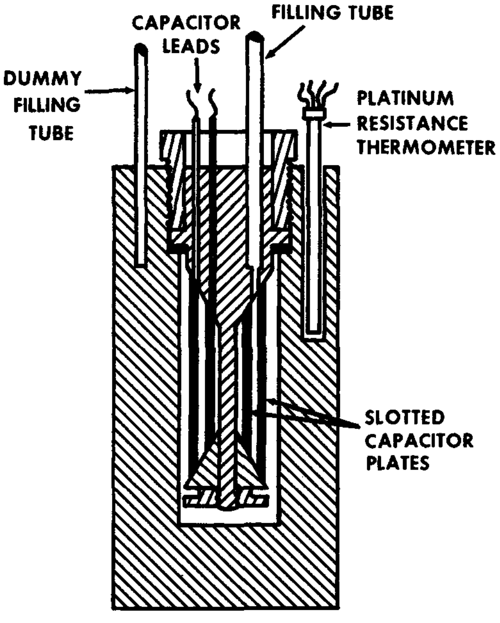

Fig. 1. Combination volumetric-capacitance cell.

Each capacitor plate has 10 round bars between the solid end rings, spaced evenly around the circumference. The mandrel supports the cylindrical plates on conical support surfaces at each end designed for three-point support. Films of a polymeric material are attached to the mandrel contact surfaces to electrically separate the plates from the supporting mandrel. The electrical leads are soldered to brass screws threaded into each plate. The vacuum capacitance of the assembled unit is about 6 pF and the internal free volume about 6 cm^3.

Capacitance measurements were made with a three-lead capacitance measuring assembly, which was operated at 1 kHz oscillator frequency and had an accuracy of ±0.01% + 0.00003 pF in the capacitance. The resolution was better than 1 ppm for capacitances above 1 pF. Since both C and C_0 were measured on the same instrument, at nearly the same time, expected uncertainties in the dielectric constant due to bridge inaccuracies should be considerably less than 0.01%.

From preliminary tests it was found that the vacuum capacitance had a slightly different value at a given temperature each time the volumetric cell was cooled from room temperature to near 100 K. However, the change in vacuum capacitance with temperature from 91 to 115 K was found to be quite reproducible. Thus, a vacuum capacitance was always measured at some convenient temperature after cooling the cell from room temperature.

A nominal 50 Ω platinum resistance thermometer was used for temperature measurement. It was calibrated from 91 to 115 K by using a calibrated gas-operated piston gauge to measure argon vapor pressures. Corresponding temperatures were taken from the compilation of Gosman, McCarty, and Hust (1969). Temperature was fit as a quadratic function of the resistance. Standard deviation of the fit was 0.02 K, yielding 90% confidence limits of about ±0.03 K. New argon vapor pressure data by Wagner (1973) are somewhat in disagreement with the Gosman et al. compilation and would yield temperature discrepancies of 0.02 to 0.05 K in the temperature range of this study. Even if these discrepancies are real, they will have negligible effect on the results of the present study because of the density and dielectric constant calibration techniques described below.

Both the molar volume and dielectric constant experiments were calibrated using recent pure methane data. Six calibration runs were made on pure methane. The resulting molar volumes were forced to agree with the saturated liquid data of Goodwin and Prydz (1972) by least squares determination of two equipment constants as described previously (Liu and Miller, 1972). Similarly, the methane saturated liquid dielectric constants of Straty and Goodwin (1973) were used to evaluate the stray capacitance (C_S) in Equation (1). In this work C_S was quite small and was assumed to be independent of temperature.

Pressure was fixed at about 0.2 atm* above the saturation pressure for all experiments, making compressibility corrections negligible. Standard deviation from the reference data was 0.01 $cm^3 mol^{-1}$ for the molar volumes and 0.0001 for the dielectric

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* Throughout this paper atm = 101325 $N\ m^{-2}$.

constants, which are indicative of the precision levels for these measurements. Absolute accuracies depend also on uncertainties in the reference data and systematic experimental errors. Straty and Goodwin place the uncertainty in the methane molar volumes at ±0.1%, while their uncertainties in $\epsilon - 1$ probably do not greatly exceed ±0.01%. Based on the above figures, combined with reasonable systematic experimental error estimates, it is expected that the CM values reported herein are accurate within ±0.15% for pure methane and methane-rich mixtures and accurate within ±0.25% for the other pure components and mixtures. Since the precision of the CM values is better than ±0.1%, the CM^E values should be accurate within about ±0.1% of the mixture CM values.

Component purities and the mixture preparation method were the same as reported by Liu and Miller (1972) and Rodosevich and Miller (1973). Methane impurities were determined to have negligible effect on both the molar volume and dielectric constant by limited experimentation with a 99.997 mole % minimum purity methane sample. Mole fraction compositions are believed accurate to four decimal places as reported. Further details of the equipment and results of the present study are available in other sources, (Pan, 1974; Miller, 1974).

TABLE 1. PURE LIQUID SATURATION DIELECTRIC CONSTANTS AND CLAUSIUS-MOSSOTTI FUNCTIONS

Species	T/K	$v/\mathrm{cm^3mol^{-1}}$	ϵ	CM/ $\mathrm{cm^3mol^{-1}}$
Ar	91.00	29.12	1.4937	4.115
	100.00	30.41	1.4698	4.117
	108.00	31.76	1.4473	4.121
	115.00	33.16	1.4261	4.124
N_2	91.00	(37.87)[a]	1.3932	4.388
	100.00	(40.63)	1.3634	4.390
	108.00	(44.00)	1.3328	4.394
	115.00	(48.34)	1.3001	4.397
CH_4	91.00	35.56	1.6762	6.541
	100.00	36.55	1.6544	6.545
	108.00	37.50	1.6347	6.548
	115.00	38.41	1.6169	6.551
C_2H_6	91.00	(46.21)	1.9438	11.059
	100.00	(46.92)	1.9260	11.067
	108.00	(47.56)	1.9103	11.072
	115.00	(48.14)	1.8966	11.077
C_3H_8	91.00	(60.63)	2.0997	16.263
	100.00	(61.38)	2.0777	16.222
	108.00	(62.08)	2.0589	16.196
	115.00	(62.70)	2.0427	16.172
iC_4H_{10}	114.00	(78.41)	2.1084	21.154
	116.00	(78.59)	2.1039	21.140
	118.00	(78.78)	2.0994	21.127
	120.00	(78.96)	2.0950	21.114

[a] The molar volumes in parentheses were taken from Rodosevich and Miller (1973).

TABLE 2. COMPARISON OF SATURATED LIQUID CLAUSIUS-MOSSOTTI FUNCTIONS WITH RESULTS FROM PREVIOUS INVESTIGATORS

Species	T/K	Literature $\mathrm{CM/cm^3mol^{-1}}$	This work $\mathrm{CM/cm^3mol^{-1}}$
Ar	87.15	4.118[a]	4.113
	87.27	4.106[b]	4.113
	100.00	4.125[a]	4.117
N_2	91.00	4.388[c]	4.388
	100.00	4.394	4.390
	108.00	4.400	4.394
	115.00	4.404	4.397

[a] Cops, Caubergh, and Van Dael (1970).
[b] Amey and Cole (1964).
[c] Straty and Ely (1974).

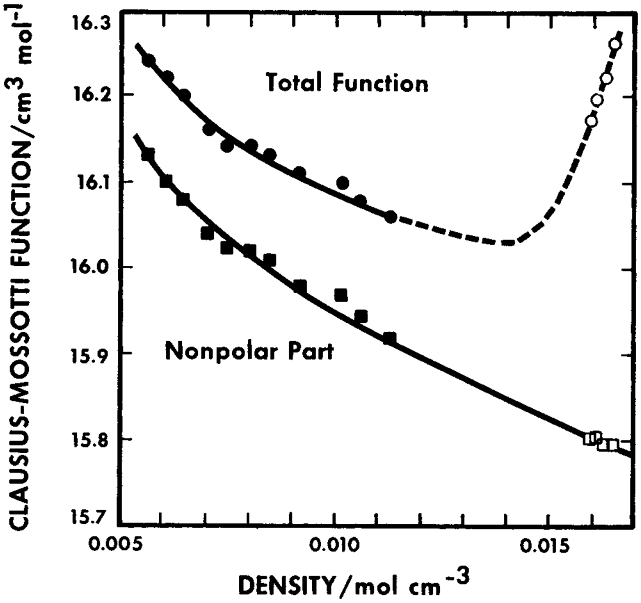

Fig. 2. Total and nonpolar Clausius-Mossotti functions as a function of density for saturated liquid propane [○ and □—this work; ● and ■—Sliwinski (1969)].

PURE FLUID RESULTS

The experimental results for pure components are summarized in Table 1. All of the saturated liquid molar volumes are from Rodosevich and Miller (1973) except those for argon. New argon molar volumes are reported as measured on the current methane calibration. Many of the dielectric constants in Table 1 represent duplicate or triplicate determinations. The Clausius-Mossotti functions were calculated from the defining equation:

$$CM = v\left(\frac{\epsilon - 1}{\epsilon + 2}\right) \tag{2}$$

The CM results are compared with those from previous workers in Table 2. Argon and nitrogen are the only species, except methane, which have been studied previously in the present temperature range. The small discrepancies in CM can almost all be traced to differences in molar volumes, that is, the dielectric constant measurements are generally in good agreement.

The propane and isobutane CM values are found to decrease with increasing temperature, while the opposite trend holds for all of the simpler species. The propane dielectric constants in Table 1 represent triplicate determinations, with a maximum scatter of 0.04% in $\epsilon - 1$. In addition, new simultaneous molar volume-dielectric constant runs were made for propane late in the experimental program. Although the molar volumes from these new measurements were about 0.04 $\mathrm{cm^3mol^{-1}}$ higher than from our previous work, the temperature dependence of the CM values was virtually unchanged.

Rather conclusive evidence that the experimental CM behavior of propane and isobutane is reasonable can be obtained by the following considerations. Microwave absorption methods have shown that propane and isobutane have permanent dipole moments (μ) of 0.083 D and 0.132 D, respectively (McClellan, 1963). Although not rigorous for dense polar fluids, the CM function is given approximately for polar fluids by

$$CM = \frac{4}{3}\pi N_A\left(\alpha + \frac{\mu^2}{3kT}\right) \tag{3}$$

TABLE 3. COMPARISON OF EXCESS VOLUMES FROM CURRENT EQUIPMENT WITH PREVIOUS WORK

Composition[a]	T/K	$v^E/\text{cm}^3\text{mol}^{-1}$	Previous $v^E/\text{cm}^3\text{mol}^{-1}$	References
50.105% Ar	91.00	+0.19	+0.19	Liu and Miller (1972)
50.40% Ar	91.00	+0.19	+0.19	Liu and Miller (1972)
	91.00	+0.17	+0.19	Liu and Miller (1972)
30.34% C_2H_6	100.00	−0.45	−0.45	Rodosevich and Miller (1973)
49.21% C_2H_6	108.00	−0.58	−0.57	Rodosevich and Miller (1974)
10.21% C_3H_8	108.00	−0.47	−0.46	Rodosevich and Miller (1973)
16.96% C_3H_8	100.00	−0.55	−0.54	Rodosevich and Miller (1974)
	108.00	−0.67	−0.66	Rodosevich and Miller (1974)
8.63% iC_4H_{10}	91.00	−0.33	−0.33	Rodosevich and Miller (1973)
	108.00	−0.50	−0.48	Rodosevich and Miller (1973)

[a] Compositions are in mole percent with methane the second component in each mixture.

where α is the polarizability. From the behavior of nonpolar liquids methane and ethane, the effective polarizability α must increase with increasing temperature along the saturated liquid line. The first term in Equation (3) will be referred to as the nonpolar CM function, and it may be estimated by subtracting the polar term from the experimental CM values. The present nonpolar CM function results for propane and isobutane do increase with increasing temperature. The total and nonpolar CM functions for saturated liquid propane are plotted versus density in Figure 2. Both the present low-temperature data and the high-temperature data of Sliwinski (1969) are shown. The nonpolar CM values from these investigations yield a smooth monotonically decreasing dependence on density. Thus, it is most likely the polar term in Equation (3) which is highly significant only at low temperatures and causes the CM versus density curve for saturated liquid propane (and isobutane) to pass through a weak minimum somewhere between the present low temperature data and previous data near room temperature.

MIXTURE RESULTS

The procedure employed in making all mixture runs was to rapidly condense the mixture into the volumetric cell at a pressure greater than the vapor pressure of the most volatile component. After the cell was full of liquid and the temperature stabilized, the pressure above the sample was reduced to about 0.2 atm above the mixture bubble point. This procedure was intended to minimize separation of the components during condensation, which would result in concentration gradients within the cell. There was no stirring mechanism in the volumetric cell.

To test the above procedure, several combination molar volume-dielectric constant runs were made on mixtures where excess volumes could be closely estimated from previous work. The excess volumes resulting from these experiments are compared with values extracted from previous work in Table 3. These comparisons demonstrate that the excess volumes from the previous stirred volumetric cells can be duplicated in the present apparatus.

There would still be the possibility that liquid of undesired composition could be trapped during condensation in the region between the capacitor plates. If this liquid is not mixed with the bulk liquid in the cell, then spurious dielectric constant measurements should result. Such an effect should be a strong function of the rate at which the mixture is condensed. In the present experiment this rate of condensation is controlled by regulating the pressure of the sample gas being forced into the cell.

A series of runs were made at 108 K for a nearly equimolar Ar + N_2 mixture to determine the effect of condensation pressure on the dielectric constant. The results indicate that the measured dielectric constant is nearly independent of the condensation pressures at pressures higher than the vapor pressure of N_2, the most volatile component.

Eleven binary mixtures have been studied. Two of these were equimolar mixtures of argon and methane, one an equimolar mixture of nitrogen and argon, two about 30% and 49% ethane in methane, two about 10% and 17% propane in methane, one about 9% isobutane in methane, two about 14% and 50% nitrogen in methane, and one about 5% normal butane in methane. Five ternary mixtures were also studied.

Dielectric constants were measured for all mixtures at temperatures between 91 and 115 K. Molar volumes were measured in some cases (compare Table 3) but most were estimated from previous work. Pure component molar volumes from Table 1 were corrected to the experimental mixture pressures and combined with excess volumes from Liu and Miller (1972), Massengill and Miller (1973), Rodosevich and Miller (1973), or Miller (1973) to yield most of these mixture molar volumes. Excess volumes for the nearly equimolar methane + ethane mixture and the 17% propane in methane mixture were calculated by the method of Rodosevich and Miller (1974).

The molar volumes, dielectric constants, and mixture CM values are summarized in Table 4. The excess Clausius-Mossotti functions (CM^E) are also listed, as calculated from the equation

$$CM^E(P,T) = CM(P,T) - \Sigma x_i CM_i(P,T) \qquad (4)$$

The pressure effect on the pure component CM values was neglected, and the values from Table 1 were used directly in Equation (4). The compressed liquid methane and nitrogen results of Straty and Goodwin (1973) and Straty and Ely (1974) confirm that this approximation has negligible effect on the calculated CM^E values. For many of the mixtures reported in Table 4, duplicate runs were made for confirmation. Only selected values are reported here, more complete sets of run data are available elsewhere (Pan, 1974). In nearly all cases, the reproducibility of the results was better than ±0.1% in the mixture CM values.

For the binary mixtures containing only nonpolar species, the CM^E values are generally less than 0.1% of the mixture CM values. A reasonable conclusion would be that CM^E is quite small for such liquid mixtures at all compositions. Within the scatter in the data, no significant temperature trends can be deduced for these small CM^E values.

In the cases of the relatively dilute CH_4 + C_3H_8 and CH_4 + iC_4H_{10} mixtures, the CM^E values are considerably

TABLE 4. MIXTURE DIELECTRIC CONSTANTS, CLAUSIUS-MOSSOTTI FUNCTIONS AND EXCESS CLAUSIUS-MOSSOTTI FUNCTIONS

Mixture	Composition in mole percentages
1	50.50% N_2 + 49.50% Ar
2	50.40% Ar + 49.60% CH_4
3	50.10% Ar + 49.90% CH_4
4	13.63% N_2 + 86.37% CH_4
5	50.19% N_2 + 49.81% CH_4
6	69.66% CH_4 + 30.34% C_2H_6
7	50.79% CH_4 + 49.21% C_2H_6
8	89.79% CH_4 + 10.21% C_3H_8
9	83.04% CH_4 + 16.96% C_3H_8
10	91.37% CH_4 + 8.63% iC_4H_{10}
11	94.99% CH_4 + 5.01% nC_4H_{10}
12	18.16% N_2 + 22.89% Ar + 58.95% CH_4
13	21.99% N_2 + 55.85% Ar + 22.16% CH_4
14	30.75% N_2 + 37.18% Ar + 32.07% CH_4
15	4.16% N_2 + 86.75% CH_4 + 9.09% C_2H_6
16	84.80% CH_4 + 10.08% C_2H_6 + 5.12% C_3H_8

Mixture	T/K	P/ atm	v/ cm^{3}mol^{-1}	ϵ	CM/ cm^{3}mol^{-1}	CM^E/ cm^{3}mol^{-1}
1	91.00	2.90	33.29	1.4393	4.252	−0.001
	100.00	5.74	35.14	1.4134	4.256	0.001
	108.00	9.46	37.14	1.3882	4.256	−0.003
	115.00	14.01	39.42	1.3640	4.266	0.004
2	91.00	1.04	32.50	1.5866	5.315	−0.003
3	91.00	1.03	32.52	1.5870	5.322	−0.003
	100.00	2.01	33.64	1.5643	5.326	−0.002
	108.00	3.40	34.76	1.5432	5.329	−0.003
	115.00	5.37	35.87	1.5240	5.334	−0.001
4	91.00	1.20	35.72	1.6358	6.246	−0.002
	100.00	2.09	36.81	1.6135	6.250	−0.001
	108.00	3.47	37.87	1.5932	6.252	−0.002
5	91.00	2.54	36.37	1.5301	5.462	0.001
	100.00	4.58	37.85	1.5056	5.459	−0.005
	108.00	7.48	39.39	1.4827	5.459	−0.008
	115.00	10.58	40.96	1.4619	5.465	−0.005
6	91.00	0.29	38.42	1.7783	7.914	0.002
	100.00	0.43	39.24	1.7585	7.919	0.003
	108.00	0.77	40.03	1.7405	7.925	0.004
	115.00	1.18	40.74	1.7250	7.929	0.005
7	91.00	0.24	40.40	1.8316	8.768	0.004
	100.00	0.35	41.18	1.8125	8.776	0.006
	108.00	0.56	41.88	1.7953	8.776	0.002
	115.00	0.84	42.53	1.7803	8.779	0.001
8	91.00	0.31	37.81	1.7495	7.558	0.024
	100.00	0.57	38.70	1.7286	7.563	0.030
	108.00	0.89	39.55	1.7096	7.566	0.032
	115.00	1.35	40.33	1.6927	7.566	0.032
9	91.00	0.31	39.40	1.7920	8.229	0.035
	100.00	0.51	40.22	1.7705	8.219	0.030
	108.00	0.83	41.02	1.7516	8.218	0.030
	115.00	1.30	41.77	1.7350	8.220	0.033
10	91.00	0.32	38.75	1.7622	7.850	0.035
	100.00	0.54	39.64	1.7409	7.851	0.039
	108.00	0.90	40.50	1.7217	7.854	0.042
	115.00	1.38	41.31	1.7043	7.854	0.043
11	108.00	1.06	39.08	1.6807	7.227	—
	115.00	1.56	39.90	1.6639	7.230	—
12	91.00	1.86	34.45	1.5824	5.601	0.006
	100.00	3.27	35.63	1.5594	5.599	0.001
	108.00	4.90	36.87	1.5380	5.606	0.005
	115.00	6.97	38.02	1.5184	5.602	−0.002
13	91.00	1.97	32.35	1.5111	4.709	−0.004
	100.00	3.83	33.79	1.4869	4.718	0.003
	108.00	6.46	35.22	1.4640	4.717	−0.001
	115.00	9.62	36.84	1.4427	4.737	0.015
14	91.00	2.07	33.74	1.5189	4.975	−0.002
	100.00	4.15	35.20	1.4946	4.982	0.002
	108.00	6.70	36.71	1.4718	4.989	0.006
	115.00	9.93	38.22	1.4508	4.993	0.006
15	91.00	0.48	36.38	1.6975	6.863	0.001
	100.00	0.87	37.32	1.6762	6.865	−0.001
	108.00	1.44	38.22	1.6572	6.868	−0.001
	115.00	2.18	38.96	1.6424	6.871	−0.001
16	91.00	0.30	37.61	1.7475	7.502	0.008
	100.00	0.48	38.48	1.7269	7.505	0.011
	108.00	0.87	39.33	1.7081	7.510	0.012
	115.00	1.35	40.11	1.6913	7.512	0.012

larger. They can exceed 0.1% of the mixture values if there is more than about 4% propane or 2% isobutane present in the mixtures. Based on the composition behavior of other excess properties, reasonable guesses for the maximum in the CM^E/CM versus composition curves at 115 K would be about 0.6% for CH_4 + C_3H_8 and over 1% for CH_4 + iC_4H_{10}.

Since the triple point temperature for normal butane is 135 K, no pure component CM values can be obtained in the current temperature range. Thus, excess Clausius-Mossotti functions cannot be calculated for the CH_4 + nC_4H_{10} mixture.

The ternary mixture results basically confirm the observations from the binary data. The nonpolar mixtures have small CM^E values, while the values for the mixture with 5% C_3H_8 are positive and are larger than 0.1% of the mixture CM values.

TABLE 5. TEMPERATURE-INDEPENDENT CM VALUES AND OTHER COMPONENT PROPERTIES FOR LNG MIXTURE CALCULATIONS

Component	CM_i/ cm^{3}mol^{-1}	HV_i/ kcal mol^{-1}	α_i/ kcal cm^{-3}	A_i/ kcal mol^{-1}
CH_4	6.548	212.8[a]	32.50	0
C_2H_6	11.072	372.8	33.67	13.0
C_3H_8	16.406[b]	530.6	32.34	−2.6
iC_4H_{10}	21.66[b]	685.6	31.65	−18.4
nC_4H_{10}	20.1[b]	687.6	34.2	34
N_2	4.394	0	0	−142.8

[a] Standard heats of combustion at 25°C in thermochemical kcal (1 kcal = 4184 J) from Zwolinski et al. (1973).

[b] Infinite dilution values CM_i^∞ in pure methane solvent.

CORRELATIONS FOR LIQUEFIED NATURAL GAS

The Clausius-Mossotti functions for the pure components vary only weakly with temperature. In particular, values for methane and ethane change by less than 0.1% between 100 and 115 K. These components typically form the major part of liquefied natural gas (LNG). Thus, it seems reasonable to ignore this temperature dependence in developing correlations for which the uncertainty will be on the order of ±0.1% or larger.

Methane, ethane, and nitrogen mix with negligibly small excess in the Clausius-Mossotti function. The higher hydrocarbons are usually present in LNG in rather low concentrations. They can be accurately incorporated into a simple mixture calculation by using infinite dilution CM values (CM_i^∞) instead of pure component values in a mole fraction average:

$$\mathrm{CM} = \Sigma x_i \mathrm{CM}_i + \Sigma x_i \mathrm{CM}_i^{\infty} \tag{5}$$

methane propane
ethane i-butane
nitrogen n-butane

For LNG calculations in the range 100 to 115 K the CM_i^{∞} values will be taken as the infinite dilution values in pure methane and considered to be independent of temperature. Values obtained from the binary mixture data (Table 4) are given in Table 5, along with the 108 K pure fluid CM_i values for methane, ethane, and nitrogen. Use of these temperature-independent values in Equation (5) reproduces the mixture CM values of Table 4 within ±0.15%.

Accurate LNG molar densities can be obtained from measured composition and dielectric constant by use of Equations (2) and (5):

$$\rho = \frac{1}{\mathrm{CM}}\left(\frac{\epsilon - 1}{\epsilon + 2}\right) \tag{6}$$

To obtain densities from Equation (6) with accuracies approaching ±0.1%, the dielectric constant must be measured within ±0.04% and all mole fractions known to ±0.001. This level of accuracy in composition measurements for LNG may not be easy to achieve in practice.

Also listed in Table 5 are the pure component heating values (HV_i) and ratios of HV_i to CM_i, termed α_i. These ratios are not sufficiently constant to allow consistently accurate heating values per unit liquid volume to be obtained directly from measured dielectric constants. However, the reasonably close proportionality between CM_i and HV_i for the hydrocarbon components can still be used to advantage in obtaining LNG heating values. The heating value per unit volume of liquid is given rigorously by

$$\rho HV = \rho \Sigma x_i HV_i \tag{7}$$

If a deviation factor (A_i) is defined for each component by

$$A_i = HV_i - \alpha_{\mathrm{CH_4}} \mathrm{CM}_i \tag{8}$$

then Equation (7) becomes

$$\rho HV = \rho \alpha_{\mathrm{CH_4}} \Sigma x_i \mathrm{CM}_i + \rho \Sigma x_i A_i \tag{9}$$

Using Table 5 values for CM_i's, the summation in the first term becomes the mixture CM value, and

$$\rho HV = \alpha_{\mathrm{CH_4}}\left(\frac{\epsilon - 1}{\epsilon + 2}\right) + \rho \Sigma x_i A_i \tag{10}$$

The first term in Equation (10) can be obtained from a measurement of dielectric constant alone. For typical LNG's the second term will be a small correction, usually about 1% or less. Thus, the density in the second term can be handled by the approximate relationship

$$\rho = \frac{1}{v} \cong \frac{1}{\Sigma x_i v_i} \tag{11}$$

giving a final form for Equation (10) as

$$\rho HV = \alpha_{\mathrm{CH_4}}\left(\frac{\epsilon - 1}{\epsilon + 2}\right) + \frac{\Sigma x_i A_i}{\Sigma x_i v_i} \tag{12}$$

For use in this equation, $\alpha_{\mathrm{CH_4}} = 32.50$ from Table 5, A_i values are listed in Table 5, and v_i values can be taken from Table 1. The A_i deviation factors are not large, except for nitrogen, and the compositions of ethane and higher hydrocarbons do not have to be known with great accuracy. Approximate accuracies in the mole fractions which are required to yield heating values with an accuracy approaching ±0.1% are as follows: ±0.01 for C_2H_6, ±0.05 for C_3H_8, ±0.01 for iC_4H_{10}, ± 0.003 for nC_4H_{10} and ±0.001 for N_2.

Equation (12) should give typical LNG heating values per unit liquid volume with accuracies better than ±0.2% for temperatures from 100 to 115K and pressures near atmospheric (less than about 3 atm). The dielectric constant must be obtained within ±0.04% and the mole fractions of the minor components known within the limits specified above. If a less accurate heating value is sufficient, then these restrictions may be relaxed accordingly.

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NOTATION

A = deviation factor defined by Equation (8)
C = capacitance with liquid medium
C_0 = vacuum capacitance
C_s = stray capacitance
CM = molar Clausius-Mossotti function
HV = molar gross heating value
k = Boltzmann's constant
N_A = Avogadro's number
P = pressure
T = absolute temperature
v = molar volume
x = mole fraction
α = polarizability in Equation (3); ratio of HV to CM elsewhere
ϵ = dielectric constant
μ = permanent dipole moment
ρ = molar density

Subscripts

$\mathrm{CH_4}$ = pure methane
i = component i

Superscripts

E = excess property
∞ = infinite dilution property

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Diffusion and Partitioning of Macromolecules Within Finely Porous Glass

Measurements of diffusion and partitioning of nearly monodisperse polystyrene, having molecular weights of from 600 to 670,000, in chloroform and dichloroethane and of two proteins in aqueous solution were made with leached borosilicate glass cubes having a narrow pore size distribution and pore radi of from 2.5 to 47.6 nm. With increasing ratio of molecular to pore size, the partition coefficient for all solutes decreased; the ratio of effective to bulk diffusivity decreased for the proteins but remained constant for polystyrene. This suggests that polystyrene behaved like a free-draining macromolecule under the conditions of this study.

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SCOPE

Two independent phenomena may lead to a reduced rate of solute diffusion in a pore which is of a size comparable to that of the solute molecule. Both arise as a result of the proximity of the pore wall. First, the solute is effectively excluded from a fraction of the pore volume. This leads to equilibrium partitioning wherein the solute concentration inside the pore is less than the bulk concentration outside the pore. Second, the additional hydrodynamic resistance (above that in free solution) hinders the movement of solute molecules through the pore. Equilibrium partitioning and/or restricted diffusion can play an important role in determining the rate of mass transport through finely porous media, such as catalyst pellets, membranes, and gel chromatography supports.

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