PROPERTIES OF PARAFFIN/ETHANOL MIXTURES:
II Vapour pressures in the Paraffin/Ethanol system

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ABSTRACT

Total vapour pressures at 25°C were determined over a range of compositions in a paraffin/ethanol system and ethanol partial pressures were measured using infrared spectroscopy at 18°C, 25°C, and 33°C. Partial enthalpies of vaporisation for ethanol were calculated from the vapour pressure data compared with results based on a calorimetric determination. Implications are drawn for the possible use of such mixtures as domestic fuels.

INTRODUCTION

In an earlier paper Brown (1988) presented data on the solubility of water in the paraffin/ethanol system as part of a longer-term project investigating the feasibility of blending ethanol and paraffin for domestic heating and lighting. Another important factor to be considered is the vapour pressure of the system, since this affects the flash-point and has therefore implications for the safety of these blends.

MATERIALS AND METHODS

Absolute ethanol was obtained from The Ethanol Company of Malawi and standard heating/lighting paraffin from Oilcom (Malawi). The ethanol was tested for such impurities as water using analytical methods already described by Brown (1988), benzene using UV spectroscopy, and other straight chain hydrocarbons by GLC on a 15.0% silicone grease 2m x 3.5mm i.d. column at 200°C. The benzene content was determined using the characteristic vibrational fine structure of the absorbance band around 253 nm and the method of standard addition.

Standard hydrocarbons were used to identify the $n-C_6H_{14}$, $n-C_8H_{18}$, $n-C_{10}H_{22}$, and $n-C_{12}H_{26}$ peaks. By extrapolation and interpolation of expected elution times, assuming that the Flame Ionisation Detector response on a mass basis is the same for all these hydrocarbons at the smallest $(0.1\mu l)$ practical injection of paraffin, mass percentages of paraffin eluting from the column at a time equivalent to various chain lengths of hydrocarbons were determined.

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Total Vapour Pressures

Total vapour pressures were determined by injecting 3.0 cm^3 of liquid into a water-jacketed (at 25.0 ± 0.1°C) 310 cm^3 side-arm flask connected to a mercury manometer. The air in the flask was dried over silica gel in a desiccator. A small amount of air interchange with the atmosphere occurred on connection to the manometer.

Ethanol Partial Vapour Pressures

The ethanol partial vapour pressures were obtained by measuring the infrared absorbance of the vapour at 3 660 cm^{-1}. A sample of 4.5 cm^3 contained in a small glass boat was placed inside a 9 cm long gas cell fitted with KBr windows. Experiments had shown that maximum absorbance was reached in less than ten minutes at all temperatures. Readings were therefore taken after 13 minutes in every case. During equilibration the liquid was shaken gently from time to time to avoid surface depletion of ethanol. This would give low partial pressures. Longer equilibration times were avoided since the cell leaked slightly.

Measurements were made at 18°C, 25°C and 33°C. Room temperature was controlled to avoid condensation problems on the cell windows. The temperature was measured to ±0.2°C using a chromel alumel thermocouple fitted tightly through a port in the cell and dipped into the sample. The thermocouple was continually checked against a mercury thermometer which had been calibrated at the ice point. It could be withdrawn out of line with the infrared beam just before the absorbance was measured. The vapour was scanned from 3 800 to 3 500 cm^{-1}, for 45 seconds. There was a negligible rise in temperature of the sample due to the heating effect of the beam during this time interval.

The possibility was considered of the correction due to absorption at 3 650 cm^{-1} by the symmetric stretching vibration of water contained in the approximately 70.0% relative humidity laboratory air. Although the reference beam should compensate, the water might be absorbed by the sample leading to slightly lower measured absorbances. However, for several samples, when a cell containing dry air was placed in the reference beam, there was no significant change in absorbance at 3 660 cm^{-1} compared to the room air reference, and so no corrections necessary.

The ethanol partial vapour pressure of a sample was calculated from Equation 1

$$P_E = \frac{A}{A^*} \times P_E^* \tag{1}$$

where P_E =   ethanol partial vapour pressure in mmHg
  P_E^* =   vapour pressure of pure ethanol in mmHg at the same temperature
  A =   absorbance of sample vapour at 3 660 cm^{-1}
  A^* =   absorbance of vapour at 3 660 cm^{-1} over pure ethanol at the same temperature

The vapour pressure of pure ethanol was calculated using Equation 2 (Lange, 1973).

$$\log_{10}P_E^* = 8.04494 - \frac{1554.3}{222.65 + TC} \tag{2}$$

where TC = temperature in °C

The variation of the absorbance of the pure ethanol vapour with temperature (Equation 3) was obtained experimentally over the range 18 to 33°C.

$$A^* = 1.722 \times \frac{P_E^*}{T} + 0.031 \tag{3}$$

where T = absolute temperature. The linearity of Equation 3 follows from Beer's Law and the ideal gas law. When extrapolated it should pass through the origin. The small positive intercept on A^* is probably due to the experimental method in which the temperature of the whole room, including the spectrometer, was varied. At the constant gain setting, this would cause the spectrometer slit width to decrease at higher temperatures, thus reducing the absorbance and accounting for the intercept.

Equation 1 also assumes Beer's Law and the ideal gas law for the unsaturated ethanol vapour. These assumptions were verified by injecting known volumes (0 to 15 μl) of ethanol at 25°C into the infrared gas cell and measuring the absorbance when all the liquid had evaporated. The volumes were insufficient to saturate the cell volume (104 cm³). The ethanol partial vapour pressures could be calculated from the ideal gas law. The observed absorbances were always less than expected using equation 1, and were also observed to decrease with time due to leakage from the cell and absorption of vapour onto the walls of the cell. A correction for cell leakage could be made by measuring the absorbance as a function of time, and when extrapolated back to zero time the absorbance was found to be directly proportional to ethanol pressure up to about 50.0% saturation. The probable explanation for the low absorbances nearer to saturation is that the extrapolation was inaccurate for these higher pressures and also the surface absorption was more important. It is unlikely to be a real departure from Beer's Law or the ideal gas law, since the observed absorbances for saturated ethanol/paraffin vapours would then lead to higher ethanol partial pressures, whereas those calculated from equation 1 are already slightly greater than the total pressures over the range 0 to 75.0% paraffin.

Corrections were applied to the made-up sample compositions to allow for ethanol loss; these are small but important for the high paraffin content samples. For example a nominal 95.0% paraffin sample at 25°C becomes 95.31% after correcting for evaporation into the 104 cm³ gas cell, and 95.48% after further allowing for vapour loss during the 13 minute equilibration discussed above; at 18°C and 33°C the final corrected compositions are 95.27% and 95.96% respectively.

Because the actual sample temperatures varied slightly ($\pm 0.5°C$) from the nominal 18°C, 25°C or 33°C room temperatures, the following calculation procedure was adopted:

(1)   A plot of log P_E vs 1/T(K) was made for each nominal composition and, assuming linearity, P_E was interpolated for 18.0°C, 25.0°C and 33.0°C.

(2)   The interpolated values of P_E were then plotted against the actual wt% paraffin for each temperature (Figure 1), and values of P_E for 99.5, 99, 98, etc., wt% paraffin were read off and listed (Table 2).

(3)   The values of P_E were used to plot graphs of log P_E vs 1/T(K), and the linear slopes used to compute the partial molar enthalpy of vaporisation of ethanol, ΔH_v, from the relationship $\Delta H_v = -8.314 \times 10^{-3} \times$ slope (kJ mol^{-1}). The interpolated values of P_E for 18.0°C, 25.0°C and 33.0°C, obtained from these graphs, agreed (± 0.5 mmHg) with those from (2).

RESULTS AND DISCUSSION

The ethanol contained 0.19% water by weight. Examination by GLC showed over 20 different peaks. Other peaks were observed between those of the consecutive straight chain hydrocarbons, implying that branched chain hydrocarbons were also present. For calculation of mass percentages, each branched chain hydrocarbon peak area was included with the straight chain hydrocarbon peak area nearest to it. Since branching decreases the boiling point, a branched hydrocarbon would be expected to elute from the column at a time corresponding to a straight chain hydrocarbon of lower molecular weight. The obtained mass percentages of paraffin eluting from the column at a time equivalent to various chain lengths of hydrocarbons are given in Table 1. From these results the molecular weight of paraffin was estimated to be 160.

Table 1.   Hydrocarbon content of paraffin.

Hydrocarbon Equivalent	Mass Percentage	Hydrocarbon Equivalent	Mass Percentage
C_6H_{14}	0.1	$C_{12}H_{26}$	25.5
C_7H_{16}	0.4	$C_{13}H_{28}$	14.1
C_8H_{18}	1.7	$C_{14}H_{30}$	7.4
C_9H_{20}	6.6	$C_{15}H_{32}$	3.0
$C_{10}H_{22}$	17.6	$C_{16}H_{34}$	0.5
$C_{11}H_{24}$	23.1	-	-

The UV spectroscopy revealed traces (0.015 wt%) of benzene impurity and other aromatic hydrocarbons. These have boiling points higher than straight chain hydrocarbons with the same number of carbon atoms. The effects of branched chain hydrocarbons and aromatic hydrocarbons on the calculated molecular weight are opposing and assumed to approximately cancel.

Vapour Pressures

Pure water vapour pressure ranged from 19.0 mm and 22.2 mm depending on the room relative humidity and time in the desiccator. Since the vapour pressure of pure water at 25.0°C is 23.8 mmHg, about 1.6 mm to 4.8 mm of water vapour remained in the dry flasks. Injection of 2.0 μl of water into the flasks after equilibrium between liquid and vapour had been established, indicated that ethanol absorbed all of the water vapour, whereas paraffin absorbed about 50.0%.

Corrections for change in pressure due to loss of water vapour were made, on the assumption that the percentage absorbed is a linear function of the mole-fraction of ethanol. Corrections were also made for the air displaced by the liquid and for the slight increase in gas volume due to mercury displacement in the manometer.

It was necessary to correct the nominal percentage composition of each sample for preferential loss of ethanol to the vapour by plotting pressure against injection volume (0 to 90 μl) of liquid ethanol. As saturation was approached, the ethanol vapour pressure was less than that calculated by the ideal gas law, probably due to adsorption on the glass walls. However, from the graph it was possible to determine the amount of ethanol required to give any pressure.

For example, the injection of 3.0 cm^3 of a 99.0% paraffin sample into the 310 cm3 flask increased the mercury height by 27.0 mm. After correcting for volume changes due to liquid injection, mercury movement (-6.0 mm), and water absorption (+ 1.3 mm), the corrected pressure change was 22.3 mm. Initially, assuming the nominal paraffin percentage, an approximation of the amount of ethanol lost to the vapour can be calculated using the experimental spectroscopic ethanol pressure and the pressure-injection volume graph for unsaturated ethanol vapour. This gives an improved paraffin percentage. The process is repeated until consistency is reached, which for this example was at 99.62% paraffin, for which the ethanol vapour pressure was 18.3 mmHg.

Interpolation between pairs of experimental points was carried out in a stepwise fashion on the assumption that the curves fit rectangular hyperbolas of the form $P_T - 4.3 = P_{MAX}x_E/(x_E + C)$ where P_T is the total vapour pressure, x_E is the mole fraction of ethanol and P_{MAX} and C are constants calculated from the experimental pressures for each pair of points. The 99.5% paraffin point was calculated from the nominal 98.0% and 99.0% points extrapolated through the 100%, $P_T = 4.3$ mm point.
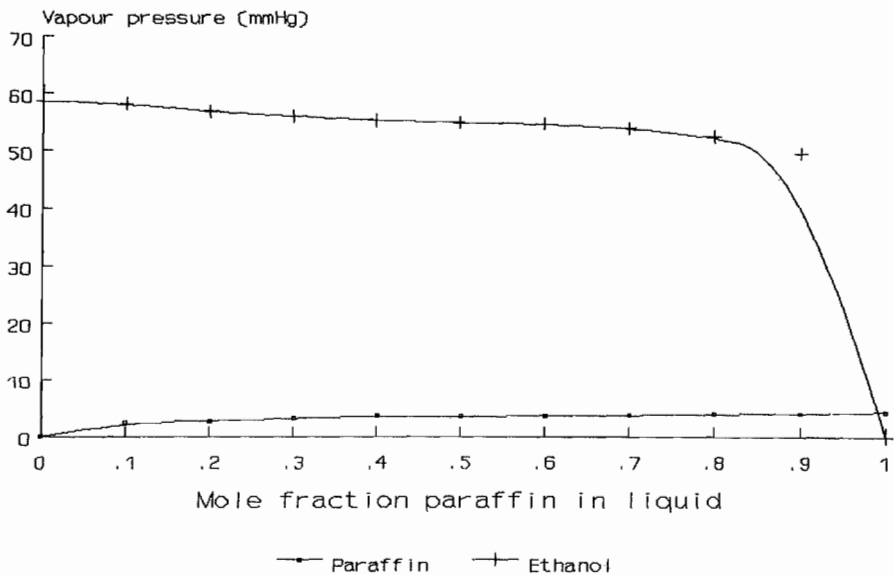
Figure 1   Partial vapour pressures of ethanol and paraffin at 25°C plotted against the mole-fraction of paraffin in liquid.

The absorbances of high paraffin content samples fell gradually as the ethanol content of the liquid and therefore its partial pressure fell. The absorbance of a 99.0% paraffin sample at 25°C fell by about 10.0% over a period of one hour.

Table 2 shows the partial vapour pressures of ethanol at 18°C, 25°C and 33°C and the total vapour pressures at 25°C, over the whole range of composition.

The ethanol partial vapour pressures remained close to the value for pure ethanol as paraffin is added, and did not fall substantially until the mixture contains more than 95.0% by wt of paraffin. This means that the flash-points of these mixtures will be close to that for pure ethanol, which is 13°C (Timmermans, 1965). This raises serious questions safety of these systems for domestic use.

The partial vapour pressures of paraffin at 25°C can be determined by subtracting the partial vapour pressures of ethanol at 25°C from the corresponding total vapour pressures. The values obtained this way are not accurate and there is a systematic error in the data leading to some negative paraffin pressures for mixtures below 75.0% paraffin.

Table 2.   Vapour pressures (v.p.) and partial molar enthalpies of vaporisation of ethanol in paraffin/ethanol systems.

Wt% paraffin	Vapour Pressure of Ethanol (mmHg)			ΔH_v Ethanol	Total v.p. at 25°C	Paraffin v.p. at 25°C
	18°C	25°C	33°C	kJ mol^{-1}	(mmHg)	(mmHg)
100					4.3	4.3
99.5	16.7	22.2	33.3	34.1	26.1	4.2
99	21.1	30.0	46.3	38.8	34.4	4.2
98	25.3	36.8	57.2	40.3	42.1	4.2
97	27.8	40.8	63.8	41.1	45.5	4.1
96	29.8	43.8	68.7	41.2	47.2	4.1
95	30.7	46.0	71.6	41.8	48.2	4.0
94	31.5	47.1	73.1	41.5	49.1	4.0
92	32.5	48.3	74.7	41.1	50.4	4.0
90	33.5	49.8	76.3	40.6	51.2	4.0
85	34.6	51.5	80.0	41.4	52.3	3.9
80	35.5	52.7	82.3	41.5	53.0	3.9
75	35.8	53.4	83.7	41.9	-	3.8
70	36.0	54.1	84.5	42.1	53.6	3.7
60	36.1	54.8	85.0	42.2	54.0	3.6
50	36.2	55.0	85.6	42.5	54.3	3.5
40	36.3	55.3	86.6	42.9	54.8	3.5
35	36.5	55.6	87.8	43.3	-	3.4
30	36.5	56.0	88.8	43.9	55.1	3.2
25	36.7	56.2	89.4	43.9	-	3.1
20	36.9	56.8	90.3	44.2	55.9	2.7
15	37.4	57.2	91.2	44.0	-	2.5
10	38.2	58.3	91.9	43.3	57.1	1.6
5	38.6	58.6	92.0	42.9	-	1.1
0	38.6	58.7	92.3	43.1	58.6	0

A better estimate can be obtained by treating the paraffin as a pseudo-mono-component, assuming that the contributions of each of the paraffin components to its total vapour pressure are affected proportionally in the same way by the change in ethanol mole-fraction. Thus $\{(\delta\log p_i/\delta x_E)_T\}$ is the same for all i components of the paraffin, applying the Gibbs-Duhem relation to the resulting binary mixture.

The calculation was carried out by plotting x_E/x_P against $\log \gamma_E$ where

x_E = mole fraction of ethanol
x_p = mole fraction of paraffin
γ_E = activity coefficient of ethanol = $\dfrac{P_E}{P*_E x_E}$

and finding γ_p, the activity coefficient of paraffin from the equation

$$\log\gamma_P = \int_{x_p=1}^{} \frac{x_E}{x_P} d\log\gamma_E \tag{4}$$

The paraffin vapour pressure can then be found from

$$P_P = 4.3\gamma_P x_P \tag{5}$$

where 4.3 mmHg is the experimental vapour pressure of the paraffin at 25°C.

The results are given in Table 2. There is a gradual decrease in the paraffin partial pressure as the paraffin content of the mixture decreases until it reaches about 25.0%, when the pressure falls more steeply. A comparison between the calculated paraffin partial pressures and the experimental pressures obtained by difference shows that the latter are close to the calculated values for samples from 100 to 95.0%, but are systematically lower by about 2 mmHg from 95.0 to 90.0% paraffin, 3 mm from 90.0 to 80.0% paraffin, and 4 mm over most of the remainder of the range. The agreement at the beginning of the range suggests that 4.3 mmHg is a reasonable value for the 100% paraffin vapour pressure.

Two possible explanations for the discrepancies are 1) the total pressures are too low (perhaps due to an under-correction for water absorption), and 2) the ethanol partial pressures are too high. On the latter point, no correction was made to the calibrating vapour pressure of pure ethanol (taken as 58.7 mmHg at 25°C from equation 2) for any impurities in the ethanol. Assuming Raoult's Law holds for the solvent, correcting for the major observed impurity (0.19 wt% water) lowers the ethanol pressures by about 0.3 mm.

The partial molar enthalpies of vaporisation of ethanol determined spectroscopically also show small systematic differences compared to the preferred calorimetric values, but the pattern of discrepancies with respect to sample composition does not correspond to that found for the paraffin pressures. It is thought unlikely that the assumption of ideality for the paraffin/ethanol vapour mixture made in Equation 1 would significantly affect the results in view of the low pressures involved and the small fraction of the total contributed by the paraffin (less than 10.0% over the region of greatest discrepancy). It is, therefore, not possible at present to give a satisfactory account of the reasons for the observed systematic discrepancies between the two sets of vapour pressure data.

The ethanol and paraffin partial pressures were plotted against the mole-fraction of paraffin (Figure 2) in the mixture at constant temperature (25°C).
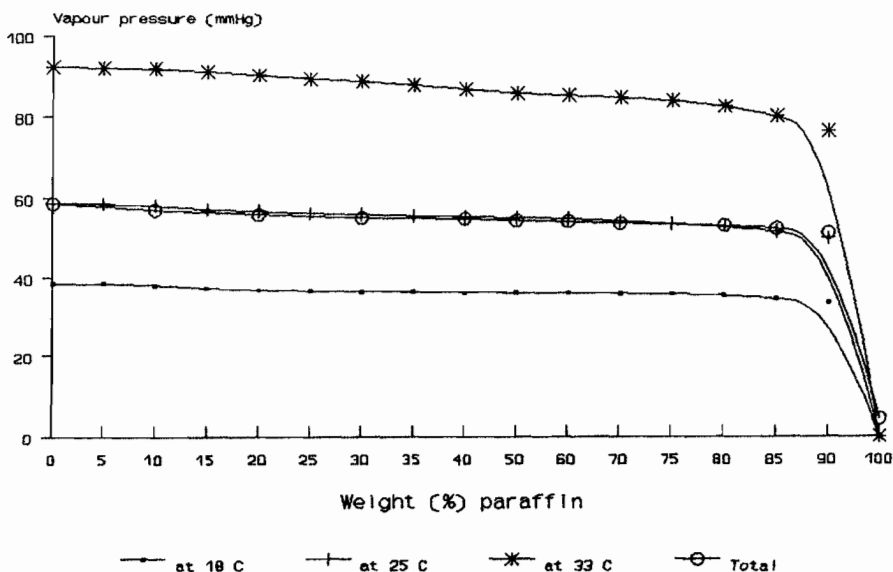
Figure 2   Ethanol vapour pressures at 18, 25, and 33°C in paraffin/ethanol systems.

Positive deviations from Raoult's Law were observed over the whole composition range due to mutual repulsion between the ethanol and hydrocarbon molecules. This behaviour is paralleled by a positive enthalpy of mixing for the system (Brown, 1996). Using calculated partial molar enthalpies for ethanol H_E, the partial molar enthalpies of vaporisation of ethanol from the paraffin/ethanol mixtures, ΔH_v, can be obtained, since

$$\Delta H_v = 43.1 - H_E \text{ kJ mol}^{-1}$$

where the enthalpy of vaporisation of pure ethanol = 43.1 kJ mol^{-1} (Equation 2). The results are given in Table 3.

Table 3:   Partial Molar Enthalpies and Partial Molar Enthalpies of Vaporisation for Ethanol in the Paraffin/Ethanol System

Wt% Paraffin	H_E kJ mol^{-1}	ΔH_v(ethanol) kJ mol^{-1}	Wt% Paraffin	H_E kJ mol^{-1}	ΔH_v(ethanol) kJ mol^{-1}
99.5	8.6	34.5	70	0.43	42.7
99	4.2	38.9	60	0.32	42.8
98	2.7	40.4	50	0.24	42.9
97	2.1	41.0	40	0.18	42.9
96	1.7	41.4	35	0.14	43.0
95	1.5	41.6	30	0.12	43.0
94	1.3	41.8	25	0.10	43.0
92	1.2	41.9	20	0.08	43.0
90	1.1	42.0	15	0.06	43.0
85	0.8	42.3	10	0.04	43.1
80	0.65	42.4	5	0.02	43.1
75	0.52	42.6	0	0	43.1

Since the values of ΔH_v are calculated by subtracting the relatively small H_E from published enthalpy of vaporisation of pure ethanol, they should be more accurate than those calculated from the variation in ethanol vapour pressure over the narrow temperature range 18 to 33°C (Table 2), and can therefore be used as a check on the latter. Generally, there is good agreement with a mean and maximum deviation between the two sets of data of 0.5 and 1.4 kJ mol^{-1} respectively. Closer inspection shows agreement for samples containing 100 to 94.0% paraffin, calorimetric values (Table 3) up to 1.2 kJ mol^{-1} greater than the vapour pressure values (Table 2) from 92.0 to 50.0% paraffin, agreement at 40.0%, and Table 3 values up to 1.2 kJ mol^{-1} less than Table 2 values for high ethanol contents. In view of the assumptions made in the calculation, particularly in treating the paraffin as a mono-component with a molecular weight of 160, it is probably not profitable to analyze these discrepancies in any further detail.

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