

PROPERTIES OF PARAFFIN/ETHANOL MIXTURES: III. Enthalpies of Mixing in the Paraffin/Ethanol System

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ABSTRACT

Enthalpies of mixing for the paraffin/ethanol system have been determined calorimetrically and used to calculate the relative partial molar enthalpies for ethanol. Calculations of entropies of mixing suggest that little ethanol exists as a monomer in these solutions until the paraffin content is greater than 98% by weight.

INTRODUCTION

This is the third in a series of papers on properties of paraffin/ethanol mixtures (Brown, 1988; Brown and Edwards, 1996) presented as part of a longer term project involving the feasibility of blending ethanol and paraffin for domestic heating and lighting. Measurement of enthalpies of mixing for the paraffin/ethanol system provides data which can be used as a check on earlier measurements (Brown and Edwards, 1996), and also to provide some insight into the nature of molecular interactions in the liquid.

MATERIALS AND METHODS

Absolute ethanol with 0.19% water content by weight, and standard heating/lighting paraffin (average molecular weight 160) were used in this investigation. Details of their characterisation are provided by Brown (1988) and Brown and Edwards (1996).

The enthalpies of mixing were determined by mixing known volumes of ethanol and paraffin (the sum of the volumes being 100 cm³ in each case) in an insulated calorimeter of known thermal capacity (27JK⁻¹) measured using water mixtures. Temperatures were read to $\pm 0.05^\circ\text{C}$ using mercury thermometer calibrated at ice point. Temperature differences after mixing ranged from 1 to 3°C. The heat capacities of the mixtures were taken as the weighted means for ethanol (2.4JK⁻¹ g⁻¹) and paraffin (2.2JK⁻¹ g⁻¹) from the values for C₁₀ - C₁₂ n-alkanes (Lange, 1985).

RESULTS AND DISCUSSION

The experimentally determined enthalpies of mixing in J mol⁻¹ of the mixtures are given in Table 1.

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Table 1. Mean molar enthalpies of mixing in the paraffin/ethanol system.

Wt% paraffin	Mole- fraction paraffin	ΔH_{mix} (J mole ⁻¹)	Wt paraffin	Mole- fraction paraffin	ΔH_{mix} (J mole ⁻¹)
15	0.048	181	90	0.722	701
30	0.110	332	95	0.845	626
50	0.224	512	96	0.874	587
70	0.402	690	97	0.903	548
75	0.463	705	98	0.934	488
80	0.535	730	99	0.966	398
85	0.620	736			

Figure 1 shows the plot of ΔH_{mix} (J mole⁻¹) as a function of the mole-fraction of paraffin in the liquid.

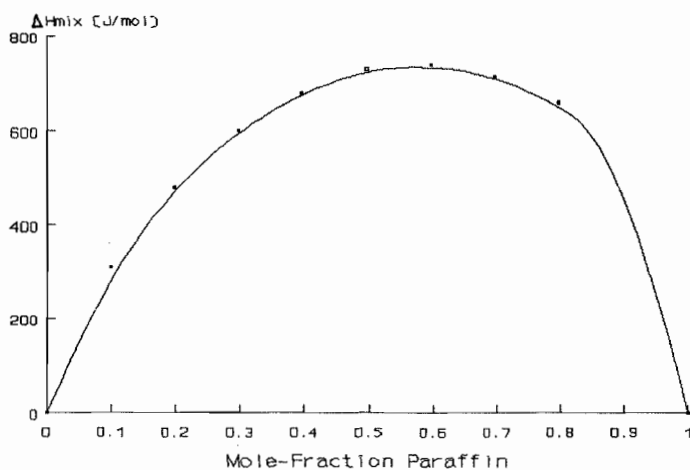


Figure 1 Mean molar enthalpies of mixing for paraffin/ethanol system

Mixing is seen to be endothermic throughout the whole range of composition, due to the mutual repulsion between the ethanol and hydrocarbon molecules (relative to the intermolecular forces in the pure components), and agrees with the positive deviation from Raoult's Law shown by the vapour pressures in the system (Brown and Edwards, 1996).

*Properties of paraffin/ethanol mixtures: III. Enthalpies of mixing
in the paraffin/ethanol system.*

Values for the partial molar enthalpy of ethanol (relative to the molar enthalpy of pure ethanol) can be obtained from Figure 1 by drawing tangents to the curve and finding the intercepts on the enthalpy axis where $x_p = 0$. The procedure treats the paraffin as a pseudo-monocomponent, and is valid because the mole-fraction of each paraffin component is a constant fraction of the overall mole-fraction of paraffin x_p in a paraffin/ethanol mixture. The results are given in Table 2.

Table 2. Relative partial molar enthalpies of ethanol in the paraffin/ethanol system.

Wt% paraffin	Mole- fraction paraffin	ΔH_{mix} (J mole ⁻¹)	Wt paraffin	Mole- fraction paraffin	ΔH_{mix} (J mole ⁻¹)
5	0.015	20	80.0	0.535	650
10	0.031	40	85.0	0.620	800
15	0.048	60	90.0	0.722	1100
20	0.067	80	92.0	0.768	1200
25	0.088	100	94.0	0.819	1300
30	0.110	120	95.0	0.845	1500
35	0.134	140	96.0	0.874	1700
40	0.161	180	97.0	0.903	2100
50	0.224	240	98.0	0.934	2700
60	0.302	320	99.0	0.966	4200
70	0.402	430	99.5	0.983	8600
75	0.463	520			

Free energies of mixing were calculated from the equation:

$$\Delta G_{MIX} = RT \left(x_E \ln \frac{P_E}{P_E^*} + x_P \ln \frac{P_P}{P_P^*} \right) \quad (1)$$

where x_E and x_P are the mole-fractions of ethanol and paraffin in the mixture.

P_E and P_P are the partial vapour pressures of ethanol and paraffin over the mixture.

P_E^* and P_P^* are the vapour pressures of pure ethanol and paraffin.

Values for P_E , P_P , P_E^* and P_P^* at 25°C were taken from Brown and Edwards (1996)

Entropies of mixing are calculated from

$$\Delta S_{mix} = \frac{\Delta H_{mix} - \Delta G_{mix}}{T} \quad (2)$$

and compared with the entropies of mixing for an ideal solution $\Delta S_{mix}(IDEAL)$ by calculating the excess entropy of mixing ΔS_{mix}^E where

$$\Delta S_{mix}^E = \Delta S_{mix} - \Delta S_{mix}(IDEAL) \quad (3)$$

and

$$\Delta S_{mix}(IDEAL) = -R(x_E \ln x_E + x_P \ln x_P) \quad (4)$$

The results of the calculations are given in Table 3.

Table 3. Enthalpies, free energies, and entropies of mixing in the paraffin/ethanol system at 25°C.

Wt% paraffin	Mole- fraction paraffin	ΔH_{mix} (J mol ⁻¹)	$-\Delta G_{mix}$ (J mol ⁻¹)	ΔS_{mix} (JK ⁻¹ mol ⁻¹)	ΔS_{mix}^E (JK ⁻¹ mol ⁻¹)
15.5	0.05	195	124	1.1	-0.55
28.0	0.10	310	178	1.6	-1.10
46.5	0.20	480	231	2.4	-1.76
60.0	0.30	600	251	2.9	-2.18
70.0	0.40	680	273	3.2	-2.40
78.0	0.50	730	263	3.3	-2.46
84.0	0.60	740	265	3.4	-2.20
89.0	0.70	715	245	3.2	-1.88
93.0	0.80	660	245	3.0	-1.16
97.0	0.90	555	195	2.5	-0.20
98.0	0.93	495	132	2.1	-0.01
98.5	0.98	445	123	1.9	+0.25
99.4	0.98	330	104	1.5	+0.68
99.7	0.99	220	93	1.1	+0.63

Properties of paraffin/ethanol mixtures: III. Enthalpies of mixing in the paraffin/ethanol system.

Over most of the composition range (0-98 wt% or 0 - 0.93 mole-fraction paraffin), some degree of intermolecular ordering still remains in the liquid mixture, since ΔS_{mix}^E is negative. However, the bonding is relatively weakened as revealed by the small positive values for the partial molar enthalpies.

At the high paraffin end of the range (98-100 wt% paraffin) there is a sharp increase in the partial molar enthalpies, and the entropies of mixing become greater than those expected for an ideal solution. This suggests that the hydrogen bonds between the ethanol molecules are broken by the paraffin, and confirms an earlier report based on infrared spectroscopic observations (Brown, 1988) that the concentration of ethanol monomers in paraffin/ethanol mixtures containing 1-15% by weight of ethanol is small except at the lowest end of the range.

ACKNOWLEDGMENT

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