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IMPURITY EFFECTS ON THE SOLUBILITY OF HIGH MOLECULAR WEIGHT NORMAL ALKANES IN ETHYLBENZENE

P.M. GHOGOMU, J. DELLACHERIE and D. BALESDENT

Laboratoire de Thermodynamique Chimique et Appliquée, Ecole Nationale Supérieure des Industries Chimiques, 1, Rue Grandville, BP451 – 54001 Nancy Cedex (France)

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ABSTRACT

The solubility of three even-numbered normal alkanes ($C_{20}H_{42}$, $C_{22}H_{46}$ and $C_{24}H_{50}$) in ethylbenzene has been measured by simple thermal analysis. Different quality grades of both solvent and solutes were used. The presence of impurities, even in small amounts, increases the solubility of the aliphatic compounds in ethylbenzene. *n*-Alkanes of similar grade obtained from different suppliers may show different solubilities in the same solvent.

INTRODUCTION

The crystallization of normal paraffin hydrocarbons in middle distillate fuels has been shown to be the origin of the nightmare of refiners and diesel-fuel consumers in very cold regions [1,2]. Many solutions have been adopted in an attempt to stop, or at least retard, this undesirable crystallization, which leads, for example, to the plugging of filters in diesel cars. The most attractive of these solutions has been the use of flow improvers, the effectiveness of which depends on the fuel *n*-paraffin concentration and distribution [3].

A phenomenological approach is being carried out in this laboratory. The determination of the structural and thermodynamic properties of the pure normal alkanes and their mixtures may lead to the prediction of the temperatures at which wax crystals start forming in fuels, thus providing for a proper understanding of the phenomenon of wax crystallization, and an opportunity for a more rigorous solution.

Most of the earlier studies on normal alkanes were bedevilled by the presence of small amounts of impurities, which at times led to the wrong classification of some solid phases [4,5]. This prompted us to carry out an investigation of the effects of impurities in the *n*-alkanes on their solubilities in ethylbenzene. The effects of impurities in the solvent are also studied.

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EXPERIMENTAL DETAILS

Simple thermal analysis consists of the slow cooling of a solution of known concentration. The temperature at which the first crystals appear is noted. This is the point at which the saturated liquid solution is in equilibrium with the solid solute. On the cooling curves, a change of slope is observed at this point.

Apparatus

This comprised a refrigerator from Froid et Machines, a circulating piston pump, two Dewar vessels, a K4 potentiometer with a d.c. null detector from Leeds and Northrup, a Sefram Servotrace recorder and a platinum resistance thermometer from Comptoir Lyon–Allemand.

Ethylene glycol, used as refrigerating fluid, was obtained from Prolabo.

Chemicals

The *n*-alkanes and ethylbenzene were purchased from Fluka, Aldrich Chemie or Prolabo and used without further purification. The quality grades of these substances are given in Table 1.

RESULTS AND DISCUSSION

The experimental set-up and the calculation of the equilibrium temperatures from cooling curves have been described in detail by Belaadi [6]. Our

TABLE 1

Quality grades of materials used

Name	Formula	Symbol [a]	Quality grade (%)	Supplier
Eicosane	$C_{20}H_{42}$	EF 97	> 97	Fluka
Eicosane	$C_{20}H_{42}$	EA 99	99	Aldrich Chemie
Docosane	$C_{22}H_{46}$	DF 98	⩾ 98	Fluka
Docosane	$C_{22}H_{46}$	DA 99	99	Aldrich Chemie
Tetracosane	$C_{24}H_{50}$	TF 99	≈ 99	Fluka
Tetracosane	$C_{24}H_{50}$	TA 99	99	Aldrich Chemie
Ethylbenzene	$C_6H_5-C_2H_5$	EB-T [b]	–	Prolabo
Ethylbenzene	$C_6H_5-C_2H_5$	EB-P	99	Aldrich Chemie
Ethylbenzene	$C_6H_5-C_2H_5$	EB-UP	⩾ 99.8	Prolabo

[a] Refers to the nomenclature used in this text.

[b] The quality grade indicated by the suppliers was 'technical'. This product was analysed by NMR and found to be not more than 97% pure.

results are qualitatively given here as T–X diagrams, where T is the equilibrium temperature (in K) and X is the mole fraction of the paraffin in solution. A quantitative discussion of the results is given in the following section.

We consider first the effects of impurities in the *n*-alkanes when the same quality of solvent is used, then the influence of impurities in the solvent when the same solute is used.

Impurities in the solute

For each quality grade of solvent we have drawn the solubility curves of the two batches of each paraffin (Figs. 1–3). At low alkane concentrations (mole fractions less than 0.01), no significant difference is found between the two solubility curves of the solute. At higher concentrations a difference appears between the two curves. For a given temperature, the solubility of the purer paraffin is less than that of the less-pure product. This means that the presence of impurities in the *n*-alkane increases its solubility in the organic solvent.

The quality grades mentioned by the manufacturers seem to vary from one supplier to another. This is the case for *n*-tetracosane ($C_{24}H_{50}$), where a temperature difference of 3.5° is registered for a mole fraction of 0.135 in

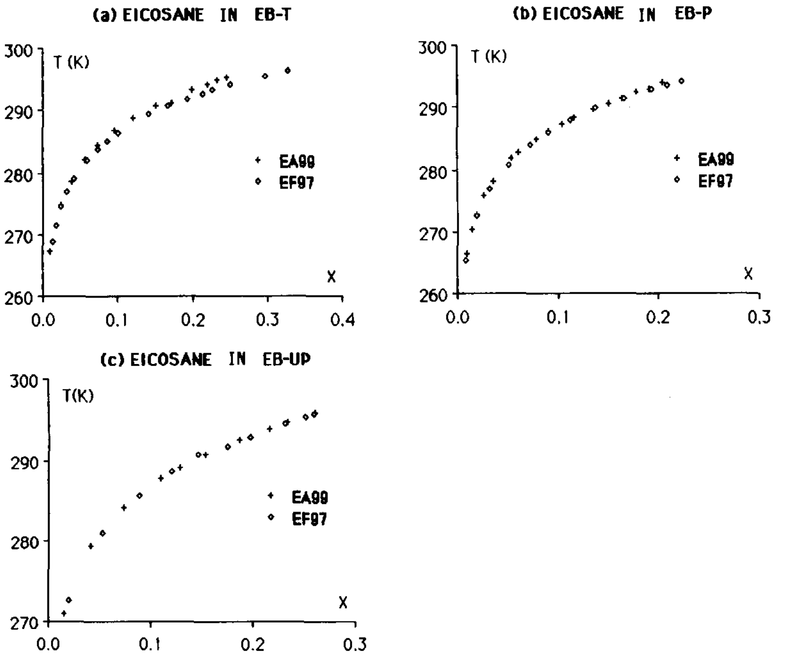

Fig. 1. Solubilities of different grades of eicosane in the same solvent.

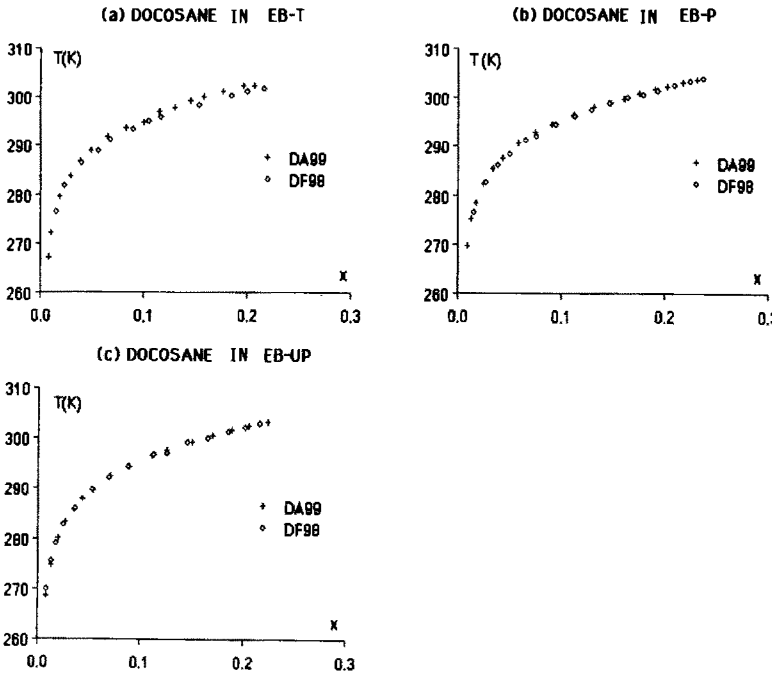

Fig. 2. Solubilities of different grades of docosane in the same solvent.

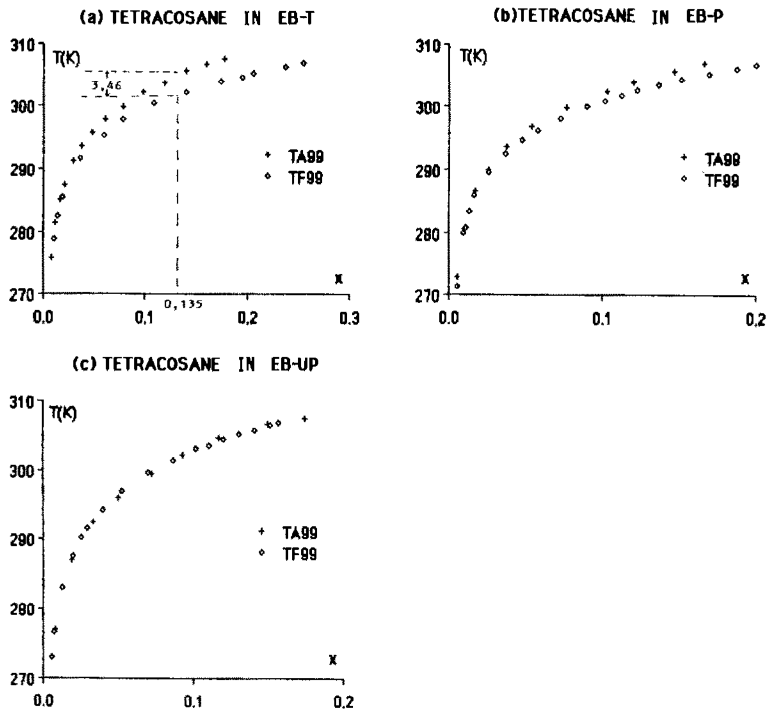

Fig. 3. Solubilities of different grades of tetracosane in the same solvent.

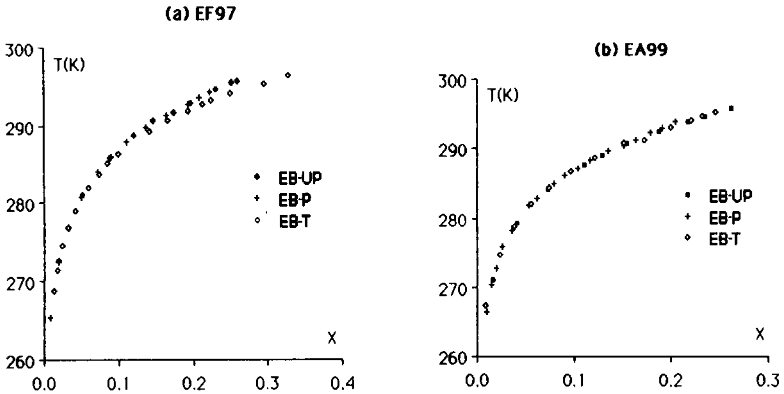

Fig. 4. Solubility of eicosane in different grades of ethylbenzene.

EB-T (Fig. 3a), the two paraffin compounds TF 99 and TA 99 having a purity of 99%.

Impurities in the solvent

We have measured the solubility of each *n*-alkane in a more or less pure solvent. The solubility curves are given in Figs. 4–6. Here again, the nature of the solvent does not influence the solubility of the solute at very low solute concentrations. At higher concentrations, the purity of the solvent plays an important role. The solubility of an *n*-alkane increases when the solvent contains impurities. In Fig. 6b we have shown the case of tetracosane TF 99 in a solution of molar fraction 0.135, where the crystallization temperature differs by 3.5° between EB-T and EB-UP, and by 2° between EB-P and EB-UP.

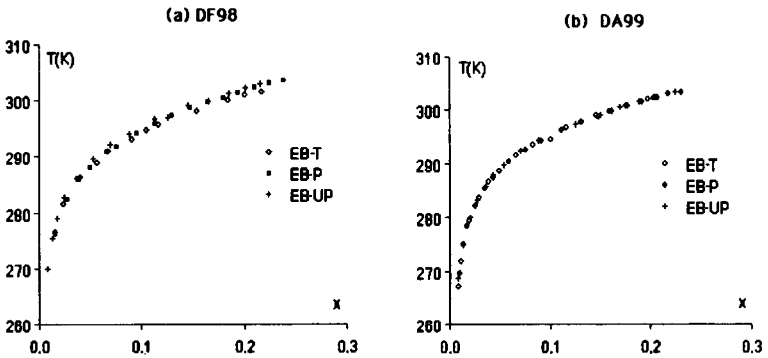

Fig. 5. Solubility of docosane in different grades of ethylbenzene.

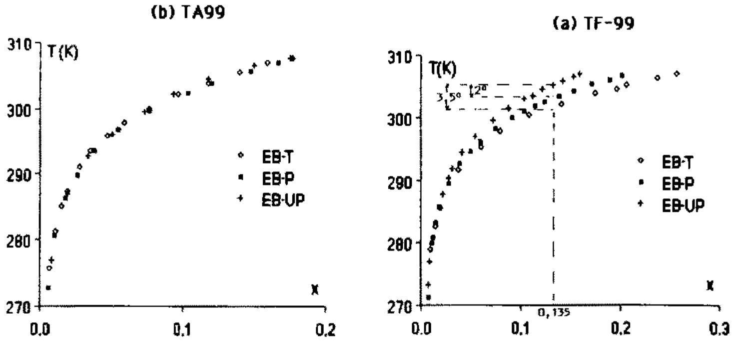

Fig. 6. Solubility of tetracosane in different grades of ethylbenzene.

CONCLUSION

The qualitative description of our results given above clearly shows that impurities in the solute or solvent have a very significant influence on the solubility of the solute in the solvent. In order to give a semi-quantitative analysis of these results, we have defined a scalar quantity

$$\delta_i(20\,^\circ\mathrm{C}) = \frac{\text{solubility of paraffin } i \text{ in solvent } j}{\text{solubility of purest } i \text{ in purest } j}$$

which is the relative solubility of each paraffin sample i in different quality solvents at 20 °C. The values of δ_i are given in Table 2.

Table 2 shows clearly that the presence of impurities simultaneously in solvent and solute leads to a rather large increase in solubility. Such an increase (up to 1.4 times) may lead to false conclusions on the wax properties and composition at the fuel cloud-point. It is therefore essential to use the same batches of chemicals of very high purity, obtained preferably from the same manufacturer, if further purification cannot be carried out.

TABLE 2

Relative solubility δ_i values for the paraffin samples

Ethylbenzene	*n*-Eicosane		*n*-Docosane		*n*-Tetracosane	
	EF 97	EA 99	DF 98	DA 99	TF 99	TA 99
Technical EB-T	1.1202	1.0128	1.1795	1.0513	1.3871	1.0968
Pure EB-P	1.0179	1.0026	1.1282	1.0156	1.2581	1.0166
Ultrapure EB-UP	1.0077	1	1.0128	1	1.0645	1

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