Cycloalkane solubility determination through differential scanning calorimetry

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Abstract

Solid–liquid equilibrium data for hydrocarbons are necessary in modeling of paraffin deposition in crude oil production. A multi-cell differential scanning calorimeter (DSC) has been used to measure solubility of pentadecylcyclohexane and nonadecyclohexane in pentane, octane and toluene. The equilibrium solubility temperature of solutions of known composition was determined by a simple linear extrapolation of the characteristic solubility temperature to an infinitely slow heating rate. The thermodynamic properties necessary for solubility prediction (enthalpy of fusion and melting point temperature) were obtained for the pure solutes. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Crude oil is composed of a wide range of hydrocarbon compounds, typically consisting of a distribution of normal and isoalkanes, cycloalkanes, and aromatics. The high molecular weight components of crude oil can crystallize or precipitate out of the solution as the crude oil is cooled from reservoir conditions during transport, resulting in buildup of solids on the pipeline wall leading to pressure losses and blockage of the pipeline at extreme conditions. This phenomenon is often referred to as paraffin deposition.

The distribution of components in crude oil depends in part on the origin and geological age of the oil reservoir with oil originating from marine and mixed organic matter containing relatively high fractions of cyclic components [1]. Precipitated paraffin is expected to often contain significant quantities of cycloalkanes, also known as napthenes. Much of the research in paraffin deposition has focused on deposition of long chain normal alkanes with little information available on napthenes and other crude oil components. In our calorimetric studies, we measured the solubility of two napthenes, pentadecylcyclohexane and nonadecylcyclohexane, in pentane, octane and toluene using differential scanning calorimetry. The enthalpy of fusion and melting temperature of pure pentadecylcyclohexane and nonadecylcyclohexane was also measured.

Solute solubility is often determined by sampling saturated solutions and analyzing samples by spectroscopy or gas or liquid chromatography. Sample detection often requires a separation step and the presence of chromophores for detection. Errors can occur in

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sampling, particularly in systems with finely dispersed solute particles with little density difference between solid and liquid phases.

Optical methods of solubility measurement have also been used to provide accurate solubility data. The simplest of the optical methods is the visual inspection of solubility points. In this method, a sample of known composition is heated to dissolve and disperse solute. The sample is then cooled until solids form, then reheated slowly until all solids redissolve. The temperature at which all solids disappear is recorded as the solubility temperature. The use of visual inspection in solubility determination is not very accurate in regions of low solute concentration because of the limitations of human vision.

Solution turbidity or light scattering can be used to detect the appearance or disappearance of particulates in solution. Temperature programmed heating and cooling cycles can be coupled to turbidity or light scattering measurement, bracketing closely the equilibrium solubility. However, crystallization events occurring outside the vicinity and light path of the sensor are not detected, thus leading to errors in the measured solubility.

Calorimetry provides an almost universal signal for solid phase formation or dissolution. Castronuovo et al. [2] used titration calorimetry to study the solubility of organic substances in aqueous solution, obtaining, solubility, heat of dissolution and heat of mixing data for samples of known composition.

In our research, we measured the solubility of pentadecylcyclohexane and nonadecylcyclohexane in organic solvents using differential scanning calorimetry (DSC). DSC can be used to determine the equilibrium solubility temperature, T_E, by measuring the heat signal generated as solute crystals dissolve. A large endothermic peak is normally associated with this transition. Heat signals are recorded as a function of temperature upon heating, with the endothermic heat of dissolution signal returning to baseline upon complete dissolution of solids. The advantages of using DSC to measure solubility include, low detection limit, computerized data recording and analysis, and the ability to control the heating rates. While the idea of using DSC to determine solubility is not new [3–5], our research is unique in that the DSC we use is capable of analyzing binary solutions with fairly volatile solvents such as pentane, octane, and toluene

at fairly dilute concentrations. In addition, we take into account the variation of measured solubility temperature (dissolution of solute upon heating) with respect to heating rate.

To validate our solubility measurement method, solubility of a well characterized binary system, octacosane in heptane [6,7], was determined at four compositions and compared to literature data.

2. Experimental

2.1. Equipment

The calorimetry experiments were performed on a Calorimetry Science Corporation CSC 4100 multi-cell differential scanning calorimeter equipped with three Hasteloy sample cells and a common reference cell, each with a capacity of 1 ml. The CSC 4100 is a heat flux DSC. The sensitivity of the DSC detectors (piezoelectric devices), as specified by the manufacturer, is approximately 40 μJ/°C. The temperature range of the DSC is −40 to 200°C with scan rates (heating or cooling) of 0.1–2°C/min. During the scanning operation, Argon was purged through the DSC chamber at 4.0 ml/min.

2.2. Materials

Alkylcycloalkanes, pentadecylcyclohexane (CAS No.: 6006-95-7) and nonadecylcyclohexane (CAS No.: 22349-0307) were obtained from TCI America. A Shimadzu gas chromatograph (GC) equipped with a Restek RTX-1® 30 m × 0.53 mm ID capillary column and a flame ionization detector was used to verify the purity of the two alkylcyclohexanes. The purity measured by GC was 99.7 and 99.1% (by weight) for pentadecylcyclohexane and nonadecylcyclohexane, respectively. It was assumed that the mass fraction of all species was directly proportional to the integrated areas under the chromatographic peaks. All other chemicals were purchased from Sigma–Aldrich. The solvents used in the solubility experiments included pentane, octane, and toluene with specified purity of no less than 99%. Octacosane and heptane were used for solubility method verification and had specified purity of no less than 99%. Hexadecane, triacontane, (purity ≥ 99.9%)

and cyclohexane (purity $\geq 99.9\%$) were used for temperature and enthalpy calibration.

2.3. Sample preparation

Binary solutions of alkylcyclohexanes in organic solvents were prepared by weight in the DSC sample cell using a Denver Instrument Model M-120 microbalance with accuracy of ± 0.5 mg. The solutes were weighed in the sample cell first. Solvents were then added into the cell, weighed, and sealed hermetically. The resulting concentration of the binary solution was then calculated by weight. After DSC analysis, sample cells were again weighed and no measurable weight loss was detected. The DSC cells could be opened after analysis and additional solvents added to lower the concentration of the binary solutions inside the cells. The cells could then be resealed and analyzed again.

2.4. Solubility measurement

The samples were placed in the DSC, scanned up to $75°C$ and held for 5 min to melt the sample. The samples were then cooled at $2°C/min$ to $-20°C$ and held for 5 min to allow for crystallization of solute. The cycle was repeated four times at four different heating rates of 2.0, 1.5, 1, and $0.5°C/min$. The cooling rate for each cycle was $2.0°C/min$. Extrapolated peak completion (or characteristic) temperature, T_c, the temperature at which the heat of dissolution peak returns to baseline, was obtained from the heating scan. T_c can be determined from the DSC thermograms by calculating the intersection between the auxiliary line through the descending peak slope and the baseline (Fig. 1). The equilibrium solubility temperature for each binary composition was then determined by extrapolating the peak completion temperatures to zero heating rate. This solubility measurement method was verified by comparing our results to published solubility data for octacosane in heptane [6,7].

2.5. Alkylcyclohexane thermophysical properties

The enthalpy of fusion and melting point temperature of the alkylcyclohexanes were measured using DSC. Temperature calibration of the DSC
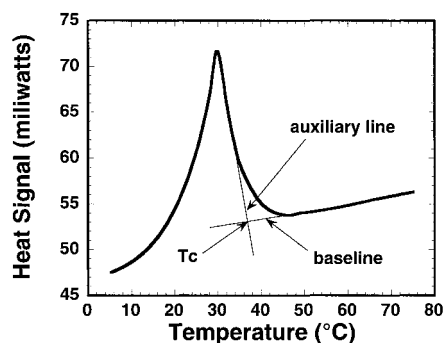

Fig. 1. Determining the characteristic temperature: The figure shows the dissolution thermogram of octacosane in heptane on heating. Endothermic events appear as peaks above the baseline. The auxiliary line is drawn by fitting a straight line through the linear section of the descending section of the endothermic peak. The baseline is the linear extrapolation of the baseline following the peak. The characteristic temperature, T_c, is the intersection point between the auxiliary line and the baseline.

was performed by analyzing the crystal I to liquid transition temperature of cyclohexane ($6.69°C$) [8] and triacontane crystal II to crystal I transition temperature ($62.1°C$) [9]. The standards were cooled to $-20°C$, held at temperature for 5 min, and then heated to $75°C$ at $0.1°C/min$. The scans were repeated four times. The average of the measured melting point temperatures for each cell was compared to the standard temperatures and a linear correction was applied for each cell. Melting points of pentadecylcycloalkane and octadecylohexane were determined using the calibration scan rates.

The heat signal calibration of the DSC was performed by measuring the heat of fusion of hexadecane at a scan rate of $0.5°C/min$. A correction factor for the heat signal at $0.5°C/min$ was calculated for each sample cell. The measured heat signals of the alkylcyclohexanes were then corrected using the calculated correction factor. Enthalpy of fusion of the alkylcyclohexanes was measured at a heating rate of $0.5°C/min$ and an average value was calculated for four thermograms.

3. Results

3.1. Solubility method verification

The measured characteristic temperature varies with the DSC heating rate (Fig. 2). This is the result
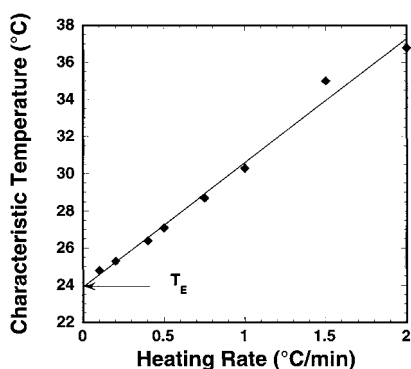
Fig. 2. Characteristic temperature versus heating rate: The characteristic temperature, measured as described in Fig. 1, for a binary mixture of octacosane in heptane (mole fraction of octacosane is 0.0162) at various heating rates. The equilibrium temperature, T_c, is determined by linear extrapolation of T_c to zero heating rate.
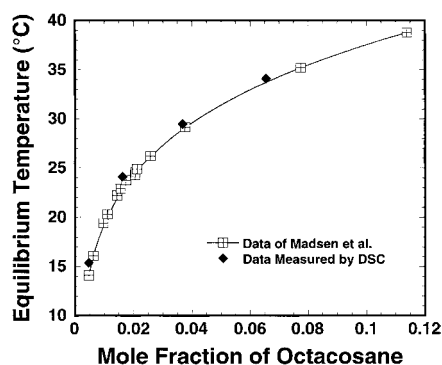

Fig. 3. Solubility method validation: The hatched squares represent solubility data of octacosane in heptane published by Madsen and Boistelle [7]. The solid diamonds represent solubility data measured by DSC.

of thermal lag and kinetics of dissolution. The change in characteristic temperature, T_c, with heating rate is a kinetic phenomenon that can be corrected by extrapolation of T_c to an infinitely slow heating rate ($0°C$/min). If we could measure heat signals at infinitely slow heating rates, we could then obtain the equilibrium solubility temperature directly. An example of variation of characteristic temperature with heating rate is provided in Fig. 2. As can be seen, T_c varies linearly with scan rate. Thus, equilibrium solubility was determined by simple linear extrapolation of T_c to a zero heating rate.

Verification of the DSC solubility method was performed using four binary solutions of octacosane dissolved in heptane with octacosane mole fractions of 0.0048, 0.0162, 0.0367, and 0.0656. The characteristic temperatures were determined at heating rates of 2.0, 1.5, 1, and $0.5°C$/min with linear extrapolation to zero heating rate. The agreement between our equilibrium solubility temperatures determined by DSC and the values published by Madsen and Boistelle [6] was good (Fig. 3). The equilibrium solubility data measured by DSC are only slightly higher, by 0.1 and $0.3°C$, than the Madsen data, at octacosane mole fractions of 0.0367 and 0.0656. The largest deviations, 1.0 and $1.6°C$, occurred at mole fractions of 0.0162 and 0.0048. The solubility data of Madsen and Boistelle was determined using a visual technique.

Samples were slowly heated until solids completely disappeared as detected by visual observation. The difference in solubility determined by DSC compared to Madsen's technique is probably due to limitations of visual detection of solid phases, especially at low concentration.

3.2. Thermodynamic properties of pentadecylcyclohexane and nonadecylcyclohexane

The enthalpy of fusion of pentadecylcyclohexane and nonadecylcyclohexane as determined by DSC (average and one standard deviation for four replicates) was 199.2 ± 2.5 and $227.8 \pm 0.5\,J/g$, respectively. The melting temperature for pentadecylcyclohexane and nonadecylcyclohexane was found to be $25.0 \pm 0.05°C$ and $42.5 \pm 0.03°C$. These melting point temperatures differed from values of 29.0 and $45.2°C$ previously published by the American Petroleum Institute [10]. Our values of the melting temperatures were used in solubility modeling.

3.3. Solubility data for alkylcyclohexanes in pentane, octane and toluene

The equilibrium solubility temperatures for varying mole fractions of pentadecylcyclohexane and nonadecylcyclohexane in pentane, octane, and toluene are listed in Tables 1 and 2 and shown graphically in Figs. 4 and 5.

Table 1
The solubility temperature of pentadecylcyclohexane in pentane, octane, and toluene at various concentrations is listed below

Solvent	Mole fraction pentadecylcyclohexane	Temperature (°C)
Pentane	0.07506	−3.4
	0.1181	0.0
	0.2203	6.7
	0.2857	9.7
	0.3469	12.3
	0.5161	18.2
	0.5573	18.6
Octane	0.0730	−5.8
	0.1093	−1.3
	0.1764	4.2
	0.2555	8.4
	0.2905	9.9
	0.4093	14.2
Toluene	0.07419	−1.2
	0.09675	−2.7
	0.1329	2.8
	0.1388	3.8
	0.1439	2.0
	0.1872	6.3
	0.3115	11.6

Table 2
The solubility temperature of nonadecylcyclohexane in pentane, octane, and toluene at various concentrations is listed below

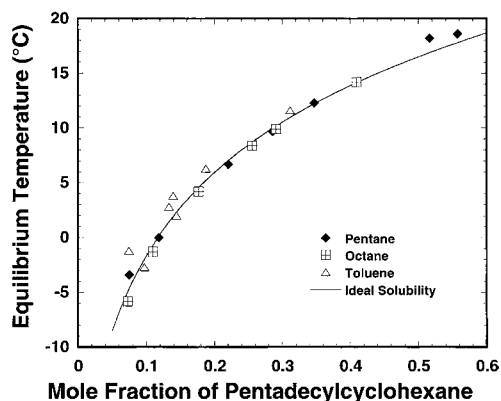| Solvent	Mole fraction nonadecylcyclohexane	Temperature (°C)
Pentane	0.0734	15.4
	0.1334	21.5
	0.1609	24.3
	0.1952	27.0
	0.2049	25.5
	0.2290	27.6
	0.2855	29.1
Octane	0.05735	14.6
	0.1072	20.4
	0.1104	20.4
	0.1705	24.9
	0.2918	30.0
Toluene	0.07215	16.2
	0.1040	19.0
	0.1280	20.6
	0.1383	22.2
	0.1504	23.4
	0.2070	26.3
	0.2201	27.4
	0.2537	28.9
	0.3228	31.6

Fig. 4. Pentadecylcyclohexane solubility in organic solvents: Experimental solubility data is compared to predicted solubility using the ideal solution model and the enthalpy of fusion and melting point data of pure solute.
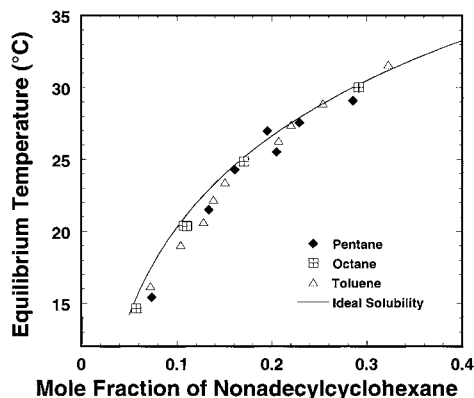

Fig. 5. Nonadecylcyclohexane solubility in organic solvents: Experimental solubility data is compared to predicted solubility using the ideal solution model and the enthalpy of fusion and melting point data of pure solute.

4. Discussion

The solubility of solids in solution can often be predicted using the ideal solution equation:

$$\ln x_2 = \frac{\Delta H_{\text{fus}}}{RT_{\text{m}}}\left(1 - \frac{T_{\text{m}}}{T}\right)$$

where x_2 is the mole fraction of solute in solution; ΔH_{fus} the molar enthalpy of fusion of solute; T_{m} the absolute melting point temperature of pure solute; R the universal gas constant; T the solution temperature.

In the above equation, solutions are assumed to be ideal (the activity coefficient has a value of one) and the difference in solute heat capacity between solid and liquid phases is assumed to be small. The predicted solubility of pentadecylcyclohexane and non-adecylcyclohexane in pentane, octane, and toluene using the ideal solubility model (with our measured values of enthalpy of fusion and melting temperature) is shown in Figs. 4 and 5 along with our experimental solubility results. The alkylcyclohexane solubility in pentane and octane is fairly well predicted with the ideal solution equation. Deviations from this model are evident in solubility data in toluene. This is not unexpected due to the structural dissimilarity between the napthenes and toluene.

5. Conclusions

DSC was used to obtain solubility data of pentadecylcyclohexane and nonadecyclohexane in pentane, octane and toluene. The equilibrium solubility temperature of solutions of known composition was determined by a simple linear extrapolation of the characteristic solubility temperature to an infinitely slow heating rate.

While the ideal solubility model provides an estimate of the solubility of pentadecylcyclohexane and nonadecyclohexane in pentane, octane and toluene, there is still some disagreement between the experimental data and this model. Incorporating heat capacity changes and activity coefficient models into the solubility prediction algorithms may provide better solubility prediction and will be incorporated in future work.

Acknowledgements

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