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Modelling of the rate of oil spill disappearance from seawater for Kuwaiti crude and its products

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Abstract

In this paper a semi-analytical model has been developed to estimate the amount of oil disappeared from an oil spill floating on seawater surface. The model considers evaporation, dissolution and sedimentation of oil components. Crude oil and wide boiling range fractions are divided into several pseudocomponents using distribution model developed by Riazi (Ind. Eng. Chem. Res., 36 (10) (1997) 4299–4307). Heavy components with densities above density of water, sink to the bottom of sea while light components vaporize or dissolve into water. In the model, oil spill thickness is considered variable versus time. The input data for the model are distillation data (or composition) for oil, API gravity of oil, initial volume of oil spill, initial area of oil spill, air temperature, wind speed and water surface velocity. The only adjustable parameter is a constant in the relation for the mass transfer coefficient for evaporation. The model estimates area, volume and composition of oil spill versus time. It also calculates the amount of oil vaporized, dissolved or sunk into water versus time. Three sets of experiments were conducted for a Kuwaiti export crude oil and four different Kuwaiti petroleum products also used for export to determine the rate of oil disappearance at ambient temperature. Data obtained in these experiments were used to determine the model parameter as well as evaluation of the proposed model.

Keywords: Oil spill; Rate of disappearance; Evaporation; Dissolution; Sedimentation; Crude oil; Petroleum products; Pseudocomponents; Mathematical model

1. Introduction

In the last decade there has been a significant increase in accidental oil spills in aquatic environments especially in the middle east and the Gulf area. Possible sources of spills include oil transportation, offshore oil exploration and storage facilities. Only from 1988 to 1991, 28 oil spills of 500 000 l (3145 barrels) or more occurred [1]. Total volume of oil spilled during this period excluding the Kuwaiti spill of 1991 was 1.84 million barrels. The Kuwaiti oil spill (as a result of the Gulf war) in 1991 was estimated at 900 million barrels [1]. This was the largest oil spill in the human history. Most recently in July 1997 an accident near Sharjah in United Arab Emirates split some 35 000–40 000 barrels of diesel oil. This oil spill had forced the shutdown of a 20 million gallons-a-day desalination plant in Sharjah which supplies drinking water to some 500 000 people in the region [2]. Two more accidents in the same area occurred when tankers carrying illegal Iraqi fuel and gas oils were interrupted due to UN sanctions imposed on Iraq [3].

When a major oil spill occurs it usually involves contamination of coastal or inland shorelines and marshlands which can result in serious environmental and economic damage. With oil spills floating on seawater, the costs are high, beaches are contaminated with black sludge, marine and bird life threatened and local drinking water supplies put in jeopardy. Such damage can be significantly reduced if proper protection and cleanup actions are taken promptly. A good review of damages to coastal and marine resources has been published by US Department of Interior [4]. Problem of oil pollution in the Gulf area became increasingly important after the Gulf war.

There are a number of different methods which might apparently be used to deal with oil floating on the sea. Some of these methods are: burning, to skim it off the surface, to absorb it with something and then remove the absorbent together with the oil, to make it into a gel and then skim it from the surface, to sink it to the bottom and to emulsify or

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disperse it. These methods have been discussed in details by Breuel [5,6] and Zobell [7]. However, it is quite impossible to specify one single method of dealing with an oil slick approaching the coast or even after it has landed onto beach. In selecting an appropriate technique for oil removal some properties of oil such as density, viscosity, pour point, flash point, surface tension, boiling point and oil solubility in seawater are quite important. For example, knowledge of density determines that the oil floats or sinks. Surface tension determines that the oil tends to spread or not. Velocity of an oil spill which depends on the velocities of wind and water affects the rate of dissolution. Surface area of an oil spill depends on its volume and thickness.

The fate of a spill of crude oil or refined product in the marine environment is determined by spreading, evaporation, dissolution, dispersion, emulsification, sedimentation and various degradation processes as discussed by Kuiper and Van den Brink [8]. Therefore, analytical solution to the problems associated with hydrocarbon oil spills are important. An ideal model for oil fate simulates the following processes mathematically:

- evaporation of oil components;
- dissolution of oil components in water;
- sedimentation;
- biodegradation;
- dispersion of oil droplets in water;
- oxidation of oil components (particularly photooxidation);
- advection of slick and water masses;
- emulsification.

All of these processes are time-dependent and must be described by dynamic models. State-of-the-art models include some, but not all of these processes at varying degrees of sophistication, but field or laboratory experiments designed to calibrate or test models usually focus on only one process. For example, Huang and Monastero [9], Spaulding [10], Stiver et al. [11], Villoria et al. [12], Riazi and Edalat [13] and ASCE [1] review and propose some of these models.

Perhaps the cheapest and easiest way to remove an oil spill from seawater is to vaporize and disperse it. Light petroleum fractions such as gasoline or kerosene can be completely vaporized with time. Crude oils which consist some heavy compounds may not be completely vaporized. Heavy compounds and residues tend to disperse into water or to sink into the bottom of sea.

The importance of evaporation in the bulk loss of oil has been noted by many researchers and it is reviewed by Muller [14]. The rate at which a hydrocarbon dissolves in water is generally lower than the rate of evaporation under the same conditions as shown by Wheeler [15]. It is widely considered that, after volatility, the most significant property of oil components, from the point of view of their behavior in aquatic environments, is their solubility in water as discussed by Green and Trett [16]. Riazi and Edalat [13] also showed that the rate of oil dissolution in water is small in comparison with rate of oil evaporation and usually the amount of oil dissolved is less than 1% of original mass of the spill. So the rate of oil dissolution in calculation of the overall rate of oil disappearance may be insignificant and many numerical models developed for oil spill trajectory do not consider this process. But the dissolved concentrations of hydrocarbons in water concern from a toxicological viewpoint and it is important to know the exact amount of oil dissolved in water as a result of an oil spill. The physical process of dissolution is well understood, but the description in the case of oil spills is complicated, due to the complex oil composition with hundreds of components and the necessity of describing the dissolution of a single component with component-specific parameters. The component-specific description may be necessary because toxicity is component-specific as well. The most soluble oil components are usually the most toxic. Even low concentrations of these toxic compounds could lead to serious effects on biological systems. For these reasons we consider dissolution process in our model.

Riazi and Edalat [13] developed simple mathematical relations for rates of oil evaporation and dissolution by introducing two temperature-dependent mass transfer coefficients one for the evaporation and other for the dissolution process with constant slick thickness. The main limitation in that model is to consider the oil as a single pseudocomponent. This assumption may be correct for light and narrow-boiling range petroleum fractions, but certainly it is not true for crude oils or wide-boiling range products. Crude oils contain many different compounds ranging from light compounds such as ethane to heavy compounds which can be lumped into a hydrocarbon-plus fraction such as C_{20+} or C_{30+} fractions. Light compounds quickly vaporize while heavy compounds may sink into the sea. Another limitation of our previous model was lack of sedimentation process in the model. Fingas [17] reviews various models developed for vaporization of oil using pseudocomponent approach for vapor pressure calculations. However, he did not treat dissolution or sedimentation processes.

The main objective of this work was to develop a more general and more accurate model for the fate of oil spills which includes sedimentation in addition to evaporation and dissolution. Crude oils are considered as a mixture of different pseudocompounds, and those compounds whose densities are higher than density of water sink into the sea. Experimental data on a Kuwaiti crude and four Kuwaiti petroleum products used for exports have been used to obtain model parameters as well as evaluation of the proposed model. Results presented in this work can be used for better prediction of the fate of an oil spill (particularly Kuwaiti crude oils and products) on the surface of seawater. Such information will be used in better selection of an appropriate method for the removal of oil spill.

2. Proposed mathematical model

Considering an oil spill floating on the sea surface which its initial number of moles, volume and area are n_o, V_o and A_o, respectively. In our notation, the subscript o indicates an initial value at time zero. The oil can be a crude oil or one of its products. In any case we consider the oil as a mixture of N pseudocomponents or narrow-boiling cuts each designated by i. However, for narrow-boiling range oil products such as naphtha or kerosene we may assume N=1. We develop a mathematical model to calculate the rates of vaporization, dissolution and sedimentation for each pseudocomponent i. Then the total rate of oil disappearance will be equal to sum of the rates of disappearances for all pseudocomponents. We assume the initial mole fraction of each pseudocomponent in the oil mixture is known and it is designated by x_{oi}. The moles of each pseudocomponent shown by n_{oi} is then given by

$$n_{oi} = x_{oi} n_o. \tag{1}$$

At time t, the number of moles of i is n_i. The rate of disappearance of pseudocomponent i is defined as

$$r_i = -\frac{1}{n_{oi}} \frac{dn_i}{dt}. \tag{2}$$

If for a pseudocomponent i, V_{oi} is its initial volume and V_i is its volume at time t, then the volume fraction of pseudocomponent i disappeared (F_{V_i}) is

$$F_{V_i} = \frac{V_{oi} - V_i}{V_{oi}}. \tag{3}$$

In our model we assume that the whole surface area of the spill is divided into N area specified by A_i for each pseudocomponent. Thickness of this oil segment is y_i. Therefore, we have

$$V_{oi} = A_{oi} y_i, \tag{4}$$

$$V_i = A_i y_i, \tag{5}$$

where Eq. (4) applies at the initial time (t=0). Similar relations are valid for the whole oil spill:

$$F_V = \frac{V_o - V}{V_o}, \tag{6}$$

$$V_o = A_o y_o, \tag{7}$$

$$V = Ay, \tag{8}$$

where y is the average slick thickness for the whole spill which varies with time. From the basic definitions we have

$$V = \sum_{i=1}^{N} V_i, \tag{9}$$

$$A = \sum_{i=1}^{N} A_i. \tag{10}$$

Now we define volume fraction of pseudocomponent i, x_{vi} as

$$x_{vi} = \frac{V_i}{V}. \tag{11}$$

By combining Eqs. (3), (6), (9) and (11) one can obtain

$$F_v = \sum_{i=0}^{N} x_{vi} F_{vi}. \tag{12}$$

Therefore, the feature of our model is to calculate x_{vi}, A_i, V_i and y_i for each pseudocomponent at any time t and then using Eqs. (8)–(11) to calculate these parameters for the whole oil spill.

A summary of model description is demonstrated in Fig. 1. In this figure an oil spill is divided into N pseudocomponents (i=1, ..., N). Component 1 is the lightest while component "N" is the heaviest part of the mixture. If initially density of only component "N" is greater than the density of water (S_N>1), then component "N" immediately sinks to the bottom of sea and after a first time step component N no longer exists in the oil spill. If both pseudocomponents "$N-1$" and "N" have specific gravities greater than unity, they both sink and these components do not enter the subsequent calculations for the rates of evaporation and dissolution. As component 1 is the most volatile component in the mixture it vaporizes more rapidly and it becomes thinner than other components after a time step of Δt. Now all components (except those sunk into water) with different thicknesses are mixed with a uniform thickness which is less than the initial thickness of the oil spill. During the time step of Δt, which the oil thickness is assumed to be constant, rates of evaporation and dissolution for each component "i" can be calculated through analytical equations described below. In the next time step similar

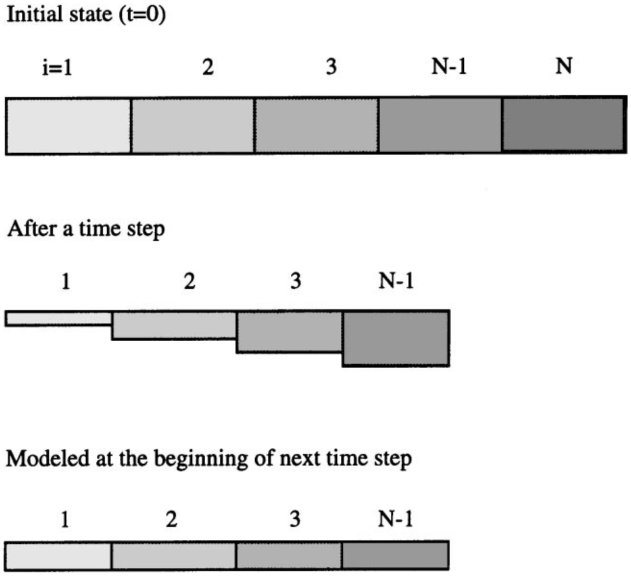

Fig. 1. Proposed model for the rate of disappearance of an oil spill with N components assuming S_N>1.

calculations are repeated with the new oil slick thickness. This is the reason that we call this model a semi-analytical model.

If ρ_i is the absolute density and M_i is the molecular weight of pseudocomponent i, we have

$$n_i = \frac{\rho_i V_i}{M_i}, \tag{13}$$

$$n_{oi} = \frac{\rho_i V_{oi}}{M_i}. \tag{14}$$

Combining Eqs. (3)–(5) and (14) into Eq. (2), one can obtain

$$r_i = -\frac{1}{n_{oi}}\frac{dn_i}{dt} = -\frac{dA_i}{A_{oi}dt} = -\frac{dV_i}{V_{oi}dt} = \frac{dF_{V_i}}{dt}. \tag{15}$$

Eq. (15) is the basic relation for definition of the rate of disappearance of pseudocomponent i in terms of number of moles, surface area, volume or volume fraction disappeared. In the following sections determination of the rate of disappearance (r_i) for three cases of evaporation, dissolution and sedimentation are discussed.

2.1. Rate of evaporation

If the molar flux of oil vaporization for component i is shown by J_i^{vap}, then an evaporation mass transfer coefficient for component i in the air, K_i^{vap}, can be defined:

$$J_i^{\mathrm{vap}} = -\frac{1}{A_i}\frac{dn_i}{dt} = K_i^{\mathrm{vap}}(C_{i,\mathrm{int}}^{\mathrm{vap}} - C_{i,\infty}^{\mathrm{vap}}), \tag{16}$$

where $C_{i,\mathrm{int}}^{\mathrm{vap}}$ is molar concentration of oil vapor in the air at the oil–air interface. $C_{i,\infty}^{\mathrm{vap}}$ is the concentration of oil component in air at infinite altitude which can be assumed zero. Mass transfer coefficient, K_i^{vap} is a function of temperature and oil properties.

If the vapor pressure of oil at the absolute temperature of oil slick (T) is shown by P_i^{sat} then $C_{i,\mathrm{int}}^{\mathrm{vap}}$ may be calculated through the ideal gas law because of low values of vapor pressures. Therefore, as it is also shown by Stiver et al. [11], the rate of evaporation can be expressed in terms of oil vapor pressure:

$$\frac{dn_i}{dt} = -\frac{K_i^{\mathrm{vap}} A_i P_i^{\mathrm{sat}}}{RT}, \tag{17}$$

where R is the gas constant and T is the absolute temperature of the seawater surface. By substituting Eq. (17) into Eq. (15) and integrating the resulting equation for a time period of Δt, one can obtain the following relations for volume fraction vaporized and the surface area:

$$F_{V_i}^{\mathrm{vap}} = 1 - \exp(-Q_i^{\mathrm{vap}}\Delta t), \tag{18}$$

$$A_i = A_{oi}\exp(-Q_i^{\mathrm{vap}}\Delta t), \tag{19}$$

where parameter Q_i^{vap} is defined as

$$Q_i^{\mathrm{vap}} = \frac{K_i^{\mathrm{vap}} Z_{\mathrm{liq},i}^{\mathrm{sat}}}{y_i}, \tag{20}$$

where $Z_{\mathrm{liq},i}^{\mathrm{sat}}$ is the dimensionless saturated liquid compressibility factor of oil fraction and it is defined as

$$Z_{\mathrm{liq},i}^{\mathrm{sat}} = \frac{P_i^{\mathrm{sat}} M_i}{\rho_{\mathrm{liq},i}^{\mathrm{sat}} RT}, \tag{21}$$

where $\rho_{\mathrm{liq},i}^{\mathrm{sat}}$ is the absolute density of saturated liquid at temperature T. Estimation of K_i^{vap} will be discussed later. In derivation of the above relations it is assumed that the slick thickness is constant during the time period of Δt. However, in the present model we assume that only during the short period of Δt the thickness is constant and over the entire time it is a variable parameter. Therefore, Eqs. (18) and (19) are valid only for the chosen time step in which y_i is assumed to be constant. Then after one round of calculations, Eq. (18) will be used to calculate volume fraction vaporized during the second time step and a new value for the slick thickness (y) can be calculated based on the overall volume and area of the spill. So the solution to the problem is semi-analytical and it will be discussed later in full details in the section for calculations. To calculate $Z_{\mathrm{liq},i}^{\mathrm{sat}}$ one need to calculate saturated liquid density, $\rho_{\mathrm{liq},i}^{\mathrm{sat}}$, and the vapor pressure P_i^{sat} at temperature T. Estimation of these physical properties will be discussed in a separate section in details.

Derivation of Eq. (12) from Eq. (10) and derivation of subsequent Eqs. (13)–(21) are valid when the influence of spreading is not considered. Many factors especially gravity and surface tension promote spreading. Green and Trett [16] discussed various models for prediction of the radius of spreading as a function of time based on three models for gravity inertia, gravity viscosity, and surface tension viscosity. None of these models incorporate all factors affecting the radius of spreading. However, as discussed by API Task Force [18] and McAuliffe [19] as a rule of thumb, many spills of widely varying size tend to reach a similar average thickness of about 0.1 mm rather quickly.

2.2. Rate of dissolution

For the rate of dissolution of oil, similar to the rate of evaporation, a mass transfer coefficient for dissolution, K_i^{dis}, can be defined as

$$J_i^{\mathrm{dis}} = -\frac{1}{A_i}\frac{dn_i}{dt} = K_i^{\mathrm{dis}}(C_{si} - C_{wi}) \tag{22}$$

where J_i^{dis} is the molar flux of dissolution, C_{si} is the solubility of pseudocomponent i in water and C_{wi} is the initial concentration of oil in water which can be considered as zero. Combining Eqs. (15) and (22) we can obtain the following relation for the rate of dissolution:

$$r_i^{\mathrm{dis}} = \left(\frac{K_i^{\mathrm{dis}}}{y_i}\right)\left(\frac{A_i}{A_{oi}}\right)\left(\frac{C_{si}}{\rho_{mi}}\right), \tag{23}$$

where ρ_{mi} is the molar density of pseudocomponent i. Based on the Wilke–Chang relation for diffusivity of oil in water, Riazi and Edalat [13] developed the following relation for estimation of K^{dis}:

$$K_i^{\mathrm{dis}} = \frac{4.18 \times 10^{-9}\, T^{0.67}}{V_{Ai}^{0.4} A_i^{0.1}}, \tag{24}$$

where V_{A_i} is the molar volume of oil at its normal boiling point in m^3/mol and can be estimated by the Rackett equation as given by Reid et al. [20]. K_i^{dis} is in m/s and T is in K. A_i is the surface area of pseudocomponent i in m^2.

For calculation of the rate of dissolution, parameter Q_i^{dis} can be defined similar to parameter Q_i^{vap} in the following form:

$$Q_i^{\mathrm{dis}} = \left(\frac{K_i^{\mathrm{dis}}}{y_i}\right)\left(\frac{C_{si}}{\rho_{mi}}\right). \tag{25}$$

Eqs. (18)–(20) can be applied to calculate similar parameters for the case of oil dissolution, by replacing Q_i^{vap} with Q_i^{dis} and $Z_{\mathrm{liq},i}^{\mathrm{sat}}$ with Z_i^{dis} which is defined as

$$Z_i^{\mathrm{dis}} = \frac{C_{si}}{\rho_{mi}}. \tag{26}$$

For example, Eq. (18) for the rate of dissolution for pseudocomponent i after time period of Δt becomes

$$F_{V_i}^{\mathrm{dis}} = 1 - \exp(-Q_i^{\mathrm{dis}} \Delta t). \tag{27}$$

In the above equations solubility of oil in seawater, C_{si}, depends on temperature and salt concentration as well as molecular weight of oil and the method of its estimation will be discussed later. However, as will be seen later the rate of dissolution is quite small in comparison with the rate of evaporation, but as discussed earlier it is important to determine the amount of oil dissolved in water for toxicological consideration.

2.3. Rate of sedimentation

In our model we consider an oil spill as a mixture of different pseudocomponents. These pseudocomponents are treated separately, therefore those components which are heavier than water with specific gravities greater than one would immediately sink into water. Although sedimentation of oil into water is a time-dependent process and is affected by wave conditions, but in our model we consider it as an instant process for the sake of mathematical simplicity. So at the beginning of the calculations if density of component i is greater than water density at the same temperature, then the component sinks into the water and it does not enter the subsequent calculations for the rates of evaporation and dissolution.

Once the volume of each component disappeared by evaporation, dissolution and sedimentation has been determined, total volume disappeared for that component can be calculated by adding these volumes and by subtracting from the initial volume for that component, remaining volume will be determined. Total volume of spill remaining can be calculated from Eq. (9). Area of oil spill remaining at any time can be calculated by a similar approach using Eq. (10).

3. Experiments

In order to evaluate the model for prediction of the rates of evaporation, dissolution and sedimentation for an oil spill floating on the sea surface, actual field data are needed. However, due to lack of complete field data, three sets of experiments were conducted on the open roof of Chemical Engineering Laboratory Building at Kuwait University in different seasons using different oil samples. Solubilities were measured at various temperature and salt concentration conditions.

3.1. Oil and water samples

Five different oil samples were obtained to run the experiments. The Kuwaiti crude for export (API gravity of 31) was obtained from the Marine and Export Operations of Kuwait Oil Company (KOC). General properties of this crude are given in Table 1. In addition to a crude sample, four different samples of petroleum products used for export were obtained from Mina Abdulla Refinery of Kuwait National Petroleum Company (KNPC). These products were naphtha, kerosene, diesel fuel and gas oil. General characteristic and properties of these four petroleum fractions as measured in chemical engineering laboratories are given in Table 2.

Water sample for the experiments was taken from Massela Beach west of Kuwait City. One important property of water in determining the rate of oil dissolution is its salt content which affects oil solubility in water as discussed by Riazi and Edalat [13]. Total salt content of the water was determined in the laboratory by conductivity/TDS meter and it was found to be at 3% by weight (30.8 g/l).

3.2. Experiments on the rate of oil disappearance

To conduct the tests for the crude oil, six cylindrical vessels of exactly the same with large diameter were used. They were filled with water covered by a thin layer of oil. Amounts of water and oil were the same in all vessels. The

Table 1
Composition and general characteristics of Kuwaiti crude oil for export

Component	Mole%
Ethane (C_2)	0.2
Propane (C_3)	2.0
Iso-butane (iC_4)	2.4
n-Butane (nC_4)	4.2
Iso-pentane (iC_5)	2.4
n-Pentane (nC_5)	4.1
Hexanes (C_6)	5.3
Heptane-plus (C_{7+})	79.4
Total	100.0

For the crude: molecular weight=210, API=31, specific gravity=0.8708, sulfur weight % =2.4%.

For C_{7+} fraction: molar weight=266.6, specific gravity=0.8910, weight average boiling point=603.2 K.

Table 2
General characteristics of Kuwaiti petroleum products for export

Property	Sample			
	Naphtha	Kerosene	Diesel fuel	Gas oil
ASTM-D86 distillation (°C) (%)				
0	65.6	147.2	223.9	274.4
5	81.1	162.8	257.8	351.1
10	83.3	167.8	268.9	371.1
30	91.7	180.0	293.3	396.7
50	100.6	195.6	310.0	434.4
70	112.8	214.4	332.2	456.1
90	128.9	235.6	364.4	492.2
95	135.6	243.3	379.4	513.3
100	152.8	257.2	388.9	530.0
Specific gravity (15.5°C)	0.7188	0.7898	0.8589	0.9259
Density (20°C)	0.7136	0.7867	0.8568	0.9225
Refractive index (20°C)	1.4049	1.4410	1.4804	1.5262
Molecular weight	101.3	155.7	243.7	394.3

Samples were obtained from Mina Abdulla Refinery, Kuwait National Oil Company.
Data were obtained from direct laboratory measurements.

inside diameter of each vessel was 0.64 m while the height was 0.25 m. Water height in each vessel was 0.23 m. Amount of oil initially put in each vessel was 0.5 l (0.44 kg). The oil layer covered full water surface area with an initial slick thickness of 1.6 mm. All the vessels were put on the roof of the chemical engineering laboratory at Kuwait University where the wind speed was about 5 m/s. As time elapsed and some of the oil disappeared, area of oil layer was reduced. The area of remaining oil layer was determined by taking photograph of the slick at various times. So vaporization, dissolution and sedimentation in all vessels began at the same time. After one, two, three, four, six and seven days one vessel on each day was taken to the laboratory, its oil was separated from water and volume of oil was measured. Amount of oil sunk to the bottom of the vessel was also measured in each vessel. Since the oil was stuck to the bottom of vessel, toluene was used to dissolve the oil into the solvent and then volume and weight of sedimented oil was measured by measuring the increases in the volume and weight of the solvent used.

Summary of the results is given in Table 3. Average temperature of air was recorded everyday and an average temperature over the entire period of each set of experiments was obtained. Similar experiments were conducted for the four petroleum products. In general three sets of experiments were conducted, two under similar conditions to check accuracy in the measurements. However, we use experimental data at two different temperatures in this work. One set of data were obtained in summer with an average temperature of 42°C and the other set of data were obtained in November of 1997 with an average ambient temperature of 22°C. The last series of experiments were conducted in April 1998 when the average temperature was 32°C.

In general, the experiments show that during a period of one week, vaporization of gas oil sample was almost negligible (F_v=0.002). For kerosene sample, at 32°C about two third (67%) of initial sample was vaporized after 5 h. For naphtha sample at 32°C, the spill was completely vaporized after only 1.5 h.

3.3. Measuring solubilities of oil in water

Solubilities of the five different oil samples in water at different temperatures and salt concentrations were

Table 3
Experimental results for the rate of disappearance of Kuwaiti crude oil for export

Exposed time (h)	Volume of oil disappeared (cm^3)	Area loss A/A_o	Oil Layer thickness (mm)
0	0	1	1.60
10	101	1	1.25
22	175	0.995	1.01
55	218	0.991	0.87
99	250	0.979	0.77
148	267	0.943	0.72
174	275	0.923	0.69

Average air temperature: 42°C; average wind speed: 5 m/s; initial volume of oil slick: 500 cm^3; initial area of oil slick: 3116 cm^2; volume of oil sunk at the end of the experiment: 56 cm^3; volume of oil dissolved in water at the end of the experiment: 0.76 cm^3; experiment began at 11:30 a.m. on 3 August 1997; Experiment ended at 5:30 p.m. on 10 August 1997.

Table 4
Measured solubilities of different oils in water

Oil	Temperature (°C)	Salt concentration (wt%)	C_s (10^5 mol/l)
Crude	20	0	2.5
	20	1.5	1.8
	20	2.9	1.0
	20	3.9	0.7
	50	0	11.9
	50	1.5	6.0
	50	2.9	3.8
	50	3.9	2.9
Naphtha	25	0	3.9
	25	2.9	3.7
	25	3.9	3.5
Kerosene	35	0	6.3
	35	3.9	3.5
	50	0	10
	50	3.9	6.5
Diesel	20	0	2.2
	20	2.9	0.8
	20	3.9	0.5
Gas oil	25	0	1.8
	25	3.9	0.1
	50	0	4.9
	50	3.0	0.2

Other units of solubility: ppm$\simeq C_s \times$Mol. Wt. $\times 1000$; Mole fraction$\simeq C_s/55.5$.

measured. Hydrocarbon concentrations dissolved in water were measured by use of a gas chromatography column (GC) designed specifically to measure concentration of hydrocarbons in water as well as a spectrophotometer for measuring the concentration of heavy hydrocarbons and petroleum fractions. Results are given in Table 4 in terms of molar concentration of dissolved oil (C_s, mol/l). Experimental uncertainty is about ±5%. Molar concentrations can be converted into mole fractions by dividing values of C_s by 55.5. To convert oil solubilities into the unit of ppm, one may multiply values of C_s by 1000 M, where M is the molecular weight of the oil.

For estimation of solubilities under different conditions of temperature and salt concentration and for different oils, the following empirical correlation was derived from data presented in Table 4.

$$C_s = \exp\left[(4.6-0.0036\,\mathrm{M}) + (0.1-0.0018\,\mathrm{M})S_w - \frac{4250}{T}\right]. \tag{28}$$

In the above equation, C_s is the oil solubility in mol/l, T is the absolute temperature of water in K and S_w is salt concentration in water in weight% (1 wt%$=10^4$ ppm). Eq. (28) can reproduce data in Table 4 within an average deviation of about 10%.

4. Estimation of physical properties

To outline the calculation procedure, various properties needed in the model described above must be estimated through the most accurate methods and correlations. Properties needed in our calculations are saturated liquid density, vapor pressure and oil solubility in water. However, before describing methods of calculations for these properties, we must discuss the characterization of crude oil and its products.

4.1. Characterization of crude oils and petroleum products

Characterization method is one the most important steps in accurate estimation of thermophysical properties of crude oils and petroleum products. Usually characterization data for crude oils are given in the form of molar distribution of some compounds as shown in Table 1. For C_{7+} fraction, molecular weight and specific gravity are available. Molar composition of pure compounds up to C_6 are given while all C_6 hydrocarbons are lumped into a single group. Properties of each single hydrocarbon group from C_6 to C_{50} are given by Riazi and Al-Sahhaf [21]. Properties of all pure hydrocarbons from ethane to *n*-pentane can be taken from Reid et al. [20] while for the C_6 group properties given by Riazi and Al-Sahhaf [21] can be used.

To best describe behavior of crude oils and wide-boiling range petroleum mixtures we must split the C_{7+} fraction of a crude into several pseudocomponents. Characterization of wide boiling range fractions has been discussed by Riazi and Daubert [22]. There are several distribution models for C_{7+} characterization, but the distribution model proposed by Riazi [23] well describes behavior of heavy crude oils and residues such as the Kuwaiti crude. The probability density function for a parameter such as molecular weight (M) is given by the following equation:

$$F(M^*) = \frac{B^2}{A} M^{*B-1} \exp\left(-\frac{B}{A} M^{*B}\right) \tag{29}$$

in which M^* is a dimensionless parameter defined as

$$M^* = \frac{M - M_o}{M_o}, \tag{30}$$

where M_o is the molecular weight of lightest component in the mixture. The method of calculation of parameters A, B and M_o are discussed by Riazi [23]. For the C_{7+} fraction of the Kuwaiti crude oil given in Table 1, these parameters are: $A=1.957$, $B=1$ and $M_o=90$. Eq. (29) can also be applied to boiling point and specific gravity. Using these parameters and the method described by Riazi [23], the C_{7+} fraction of the crude was split into eight pseudocomponents. Mole fraction, molecular weight, specific gravity and boiling point of these pseudocomponents are given in Table 5. Molecular weight (M_i), specific gravity (S_i) and the normal boiling point (T_{bi}) for each pseudocomponent are interrelated through the following equation as given by Riazi and

Table 5
Characterization parameters for pseudocomponents of the C_{7+} fraction of Kuwaiti crude oil

Pseudocomponent	Mole%	Weight%	Molecular weight	Specific gravity	T_b (°C)
C_{7+} (1)	16.0	8.2	116.1	0.734	128
C_{7+} (2)	12.0	7.6	142.2	0.773	123
C_{7+} (3)	11.2	9.0	173.9	0.807	221
C_{7+} (4)	9.2	11.8	236.5	0.855	300
C_{7+} (5)	8.9	9.4	331.2	0.907	393
C_{7+} (6)	6.9	18.0	456.3	0.937	482
C_{7+} (7)	3.6	18.2	593.1	0.980	560
C_{7+} (8)	3.6	11.6	727.4	1.049	632
Total C_{7+} fraction	79.4	93.8	266.1	0.891	330

Pseudocomponents and their characterization parameters were determined using the method proposed by Riazi [23].

Daubert [24] which is also included in the API Data Book [25].

$$M_i = 42.9654\exp(2.097\times10^{-4}T_{bi} - 7.78712\,S_i + 2.0848\times10^{-3}\,T_{bi}S)\,T_{bi}^{1.26007}\,S_i^{4.98308}, \tag{31}$$

where T_b is in K. Once the basic characterization parameters (M_i, T_{bi} and S_i) for all the pseudocomponents are known, various physical properties can be calculated from the correlations and methods given in Section 4.2.

The crude sample described in Table 1 is represented by six pure hydrocarbons, one C_6 fraction and the C_{7+} fraction has been split into eight pseudocomponents as given in Table 5. Therefore, the whole crude is described by 15 components/pseudocomponents (N=15).

For narrow-boiling range fractions and petroleum products such as naphtha and kerosene, there is no need for splitting the mixture and the whole sample can be considered as one pseudocomponent with known boiling point and specific gravity. The boiling point is the average boiling point of the fraction, which for the case of narrow-boiling range fractions is very close to the 50% ASTM-D86 distillation point.

4.2. Physical properties of pseudocomponents

As discussed above the properties needed for our model are saturated liquid density ($\rho_{\text{liq}}^{\text{sat}}$), molar volume at normal boiling point (V_A), saturation pressure (P^{sat}) and oil solubility in water (C_s) which can be estimated through Eq. (28). Saturated liquid density can be calculated from the Rackett equation given by Reid et al. [20]:

$$\frac{1}{\rho_{\text{liq},i}^{\text{sat}}} = \left(\frac{RT_{ci}}{P_{ci}}\right) Z_{RA,i}^{[1.0+(1.0-T_{ri})^{2/7}]}, \tag{32}$$

where T_{ci} is the critical temperature in K, P_{ci} is the critical pressure of component i in kPa, T_{ri} is the reduced temperature (T/T_{ci}) and $Z_{RA,i}$ is the Rackett parameter which is dimensionless. In this equation to have $\rho_{\text{liq}}^{\text{sat}}$ in mol/cm^3, one must use the value of 8314 for gas constant R when P_{ci} is in kPa. For pure compounds the Rackett parameter ($Z_{RA,i}$) is given by Reid et al. [20] and for pseudocomponents it can be calculated from the above equation using a known value of density (i.e., specific gravity at 15.5 C). The above equation can also be used to estimate the molar volume at normal boiling point (V_{Ai} needed in Eq. (24)) by replacing $1/\rho_{\text{liq},i}^{\text{sat}}$ with V_{Ai} and substituting reduced temperature with reduced boiling point ($T_{rb} = T_b/T_c$).

To estimate the saturation pressure (P_i^{sat}), we use the relation proposed by Lee and Kesler which is recommended by the API [25] as given below:

$$\ln\left(\frac{P_i^{\text{sat}}}{P_{ci}}\right) = 5.92714 - 6.09648/T_{ri} - 1.28862\ln T_{ri} + 0.169347\,T_{ri}^6 + \omega_i\,(15.2518 - 15.6875/T_{ri} - 13.4721\ln T_{ri} + 0.43577\,T_{ri}^6) \tag{33}$$

in which ω_i is the acentric factor and can be calculated from Lee–Kesler correlation as given by the API [25]:

$$\omega_i = \frac{\ln(101.325/P_{ci}) - 5.92714 + 6.09648/T_{rbi} + 1.28862\ln T_{rbi} - 0.169347\,T_{rbi}^6}{15.2518 - 15.6875/T_{rbi} - 13.4721\ln T_{rbi} + 0.43577\,T_{rbi}^6}. \tag{34}$$

Critical temperature and critical pressure of each pseudocomponent can be estimated from Riazi and Daubert [26] or Riazi and Daubert [24] correlations which are also included in the API [25] and are given as following:

$$T_{ci} = 9.5233\exp(-9.3145\times10^{-4}\,T_{bi} - 0.5444\,S_i + 6.4791\times10^{-4}\,T_{bi}S_i)T_{bi}^{0.81067}S_i^{0.53691}, \tag{35}$$

$$P_{ci} = 31.9497\times10^6\exp(-8.505\times10^{-3}\,T_{bi} - 4.8014\,S_i + 5.7490\times10^{-3}\,T_{bi}S_i)T_{bi}^{-0.4844}S_i^{4.0846}, \tag{36}$$

where T_{bi} is the boiling point of component i in K and S_i is the specific gravity of pseudocomponent i at 15.5 C (60 F). In the above relations T_{ci} is in K and P_{ci} is in kPa. However, one must be careful that as discussed by Riazi and Al-Sahhaf [21], these correlations for estimation of critical properties and acentric factor are accurate only up to C_{20} or approximate molecular weight of 300. For heavier pseudocomponents, analytical equations in terms of molecular weight (M_i) proposed by Riazi and Al-Sahhaf [21] should be used.

Table 6
Estimated properties of pseudocomponents for the Kuwaiti crude oil at 42°C

i	Pseudocomponent	p_i^{sat} (bar)	C_s (10^5 mol/l)	ρ_i (kg/l)
1	C_2	59.5	14.249	0.206
2	C_3	14.4	12.559	0.464
3	iC_4	5.6	11.069	0.529
4	nC_4	4.0	11.069	0.553
5	iC_5	1.6	9.756	0.601
6	nC_5	1.2	9.756	0.604
7	C_6	4.5×10^{-1}	8.929	0.665
8	$C_{7+}(1)$	4.6×10^{-2}	6.569	0.712
9	$C_{7+}(2)$	6.7×10^{-3}	5.194	0.753
10	$C_{7+}(3)$	6.8×10^{-4}	3.905	0.788
11	$C_{7+}(4)$	9.2×10^{-6}	2.222	0.838
12	$C_{7+}(5)$	3.6×10^{-9}	0.948	0.889
13	$C_{7+}(6)$	1.1×10^{-12}	0.308	0.919
14	$C_{7+}(7)$	3.7×10^{-16}	0.090	0.961
15	$C_{7+}(8)$	3.0×10^{-19}	0.027	1.028

P_i^{sat} is the vapor pressure of component i; C_s is the solubility of component i in water; ρ_i is the liquid density of component i.

Three important properties that for each component are needed for calculation of the amounts of vaporization, dissolution and sedimentation are vapor pressure, component solubility in water and liquid density, respectively. For the 15 components which describe the Kuwaiti crude, these properties as calculated through Eqs. (28), (32) and (33) are given in Table 6.

5. Calculation procedure

To use the model proposed in this work, a computer program in Fortran called SPILL.FOR was written which consists of 10 different subroutines. Step-by-step calculations which have been programmed can be summarized as following:

1. Read values of V_o, A_o, T, x_{oi}, M_i, API gravity, U and S_w. For petroleum products average boiling point (T_b) should be given instead of x_{oi}. C_{7+} fraction of the crude must be split into 5–10 pseudocomponents using the method proposed by Riazi [23].
2. Calculate basic characterization parameters for the pseudocomponents as outlined by Riazi [23]. M_i can be calculated from Eq. (31) using T_{bi} and S_i as obtained through distribution model. For a petroleum product M_i can be calculated directly from known values of T_{bi} and S_i through Eq. (31). For a narrow-boiling range petroleum product the number of pseudocomponents is 1.
3. Using T_{bi} and S_i from Step 2, estimate T_{ci}, P_{ci} and ω_i from Eqs. (34)–(36). For pseudocomponents with $M_i>300$, use Riazi and Al-Sahhaf [21] correlations to estimate T_{ci}, P_{ci} and ω_i. Calculate parameter $Z_{RA,i}$ from Eq. (32) using values of S_i at 15.5 C. For pure components take all these properties directly from Reid et al. [20].
4. Calculate P_i^{sat} from Eq. (33).
5. Calculate initial volume fractions (x_{oi}) from x_{oi}, then calculate initial volume, area and thickness for each pseudocomponent ($V_{oi}=x_{voi}V_o$, $A_{oi}=x_{voi}A_o$, $y_{oi}=V_{oi}/A_{oi}$).
6. Calculate ρ_i^{sat} at T from Eq. (32) and then use Eq. (21) to calculate $Z_{\mathrm{liq},i}^{\mathrm{sat}}$.
7. Estimate C_{si} for each compound from Eq. (28).
8. Compounds having $S_i>1.0$ immediately sink into the water. Volume of oil sunk is sum of initial volumes of pseudocomponents with $S_i>1.0$. Mass of oil sunk into water can be estimated through density and volume. For these pseudocomponents set $x_{oi}=0$ so they do not enter subsequent calculations for evaporation and dissolution. Then normalize the composition.
9. Choose a time step for the calculations (i.e., $\Delta t=0.5$ h) and set $t=\Delta t$.
10. Estimate K_i^{vap} from Eq. (37) and K_i^{dis} from Eq. (24) using V_{Ai} estimated from Eq. (32).
11. Calculate Q_i^{vap} and Q_i^{dis} from Eqs. (20) and (25), respectively.
12. Calculate F_{vi}^{vap} and F_{vi}^{dis} from Eqs. (18) and (27), respectively. Using definition of F_{vi} (Eq. (3)), calculate volume of each pseudocomponent vaporized or dissolved. Then using density of each compound mass of component i evaporated or dissolved can be calculated.
13. Estimate total volume and mass of each component disappeared by adding values calculated for sedimentation, evaporation and dissolution from Steps 8 and 12. Also estimate the volume, area and mass of each component remaining in the spill and subsequently calculate the composition of oil spill remaining on the water surface.
14. Calculate total volume, area and mass of oil spill remaining and disappeared by adding the values for these parameters calculated for each component in Step 13 using Eqs. (9), (10) and (12). Also calculate density (or API gravity) of oil spill remaining from the composition determined in Step 13.
15. Calculate slick thickness from Eq. (8) using V and A calculated in Step 14.
16. Using new values for the composition, area, and thickness for the oil spill remaining, the next round of calculations can be started.
17. If the time is less than the desired final time, go back to Step 10 with $t_{\mathrm{new}}=t_{\mathrm{old}}+\Delta t$.
18. Print volume (V), area (A), slick thickness (y), composition and specific gravity (or API) of oil spill remaining at time t. Also print fractional loss (F_v) due to evaporation, dissolution, sedimentation and total disappearance.
19. Stop and end of the program.

In Step 7 for calculation of oil solubility in water, in our model we assume water has the same temperature as the air. This is true because the amount of water sample used for the experiments was limited. But for real cases the water temperature should be used to calculate C_{si} from Eq. (28).

6. Results and discussion

The only parameter yet to be determined is the mass transfer coefficient for vaporization (K_i^{vap}). This temperature-dependent parameter varies from one component to another. For light components, values of K_i^{vap} are higher than those for heavier components. Fingas [17] gives several relations to estimate K_i^{vap}. Usually K_i^{vap} is given in terms of wind speed, temperature and Schmidt number. Based on the rate of oil disappearance for four petroleum fractions studied in this work, the following relation in terms of molecular weight of a fraction was derived to estimate parameter K_i^{vap}.

$$K_i^{\mathrm{vap}} = 1.5 \times 10^{-5}\, U^{0.8} (T/M_i)^2 \qquad (37)$$

in which K_i^{vap} is in m/s, T is in K, U is the wind speed in m/s and M_i is the molecular weight of component i in g/gmol. This is an approximate relation and it is derived based on the Kuwaiti oil samples and it should be used with the method proposed in this work. Fig. 2 shows how this relation predicts the rate of oil evaporation for diesel oil sample. Based on Eq. (37) for estimation of K_i^{vap}, we used the proposed model to predict amount of oil disappeared for the crude oil to evaluate the model. The results are presented in Table 7, and Figs. 3 and 4. As shown in Table 6, only the last component has density of greater than unity and it sinks into water. In Fig. 3, estimated rate of disappearance for the crude at two different temperatures are compared with the measured values. Variation of oil slick thickness versus time for the crude oil at 42°C is presented in Fig. 4. If the model is applied to other crudes or fractions the only parameter needed to be modified in the proposed model is the numerical constant of 1.5×10^{-5} in Eq. (37) which might be

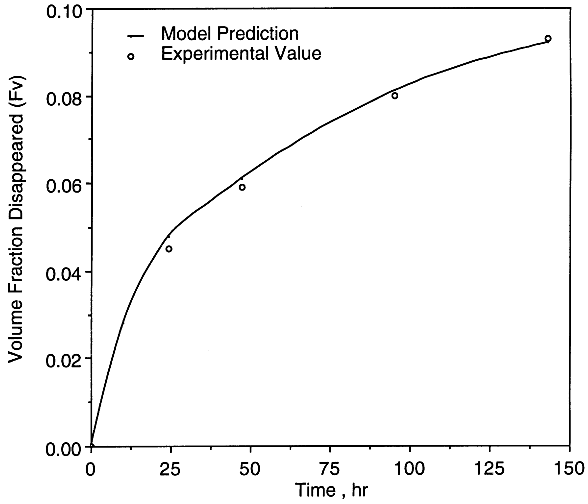

Fig. 2. Rate of disappearance of Kuwaiti diesel fuel at 22°C.

Table 7
Comparison of model predictions with experimental values for the amount of disappearance of Kuwait export crude at 42°C after 174 h

	Experimental	Calculated
Initial volume of oil spill (cm^3)	500	500
Initial oil spill diameter (cm)	63	63
Initial slick thickness (mm)	1.6	1.6
Volume of oil vaporized (cm^3)	218	237
Volume of oil sunk (cm^3)	56	49
Volume of oil dissolved (cm^3)	0.76	0.9
Volume of oil remaining (cm^3)	225.24	213.1
Volume % disappeared (100 Fv)	55.0	57.4
Diameter of oil spill (cm)	60.5	60.2
Slick thickness (mm)	0.78	0.75

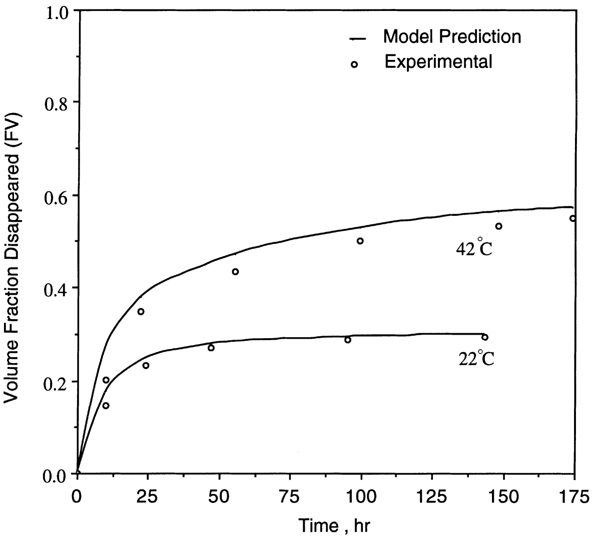

Fig. 3. Rate of disappearance of Kuwaiti crude oil spill at 22°C and 42°C.

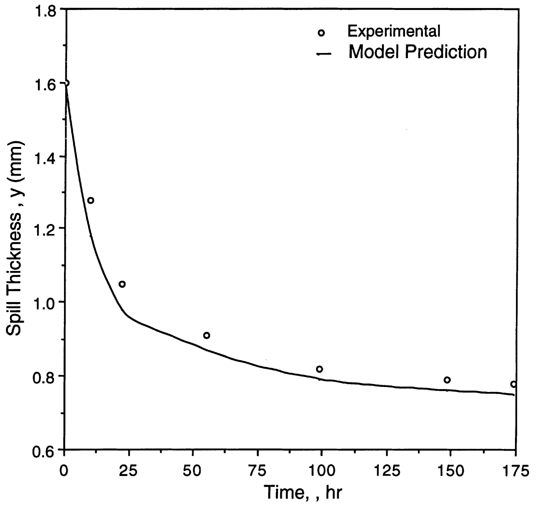

Fig. 4. Rate of change of slick thickness for Kuwaiti crude spill at 42°C.

slightly different for other types of crudes with different composition. This constant is the only adjustable parameter which may vary when applied to other types of crudes.

As it can be seen from the results presented here, the proposed model can accurately predict the rate of oil disappearance for Kuwaiti oil spills. The model performance can be improved by increasing the number of pseudocomponents especially for fractions with specific gravity close to 1. The amount of spill sedimented is quite sensitive to the method used and the number of pseudocomponents defined for the crude. To apply the model to actual field cases, we should include other processes such as degradation, dispersion, spreading, emulsification and wave conditions in the model. Emulsification can greatly affect the rate of vaporization while wave actions can increase the rate of sedimentation. To do this, actual field data are required for development and evaluation of a more comprehensive model. However, the model presented here is one step further toward a general and comprehensive model for the rate of disappearance of an oil spill floating on seawater surface.

7. Conclusions

In this work a semi-analytical model is presented to estimate the rate of disappearance of an oil spill floating on the sea surface from evaporation, dissolution and sedimentation with time-dependent slick thickness. Experiments were conducted to determine the rates of evaporation, dissolution and sinking for one Kuwaiti crude and four petroleum products used for export. Solubilities of these oil samples in water under different temperature and salt concentration were measured and a predictive correlation is presented. Also a characterization scheme is proposed to describe a crude or a product as an oil spill. In this model a crude or wide-boiling range fractions are split into 10–20 pseudocomponents.

The rate constant for evaporation was determined and was correlated to molecular weight, temperature and wind speed. Proposed model well predicts the rate of oil disappearance for the samples tested in this work. It also determines amount of oil sunk into water, evaporated or dissolved, slick volume, area and thickness versus time.

8. Nomenclature

A	oil spill surface area (m^2)
A_o	initial oil spill surface area (m^2)
API	API gravity (=141.5/S−131.5) (dimensionless)
C_{int}^{vap}	oil molar concentration in air at spill interface (gmol/l)
C_s	oil solubility in seawater (gmol/l)
F_v	volume fraction of oil disappeared (dimensionless)
J	molar flux (mol/m^2 s)
K^{dis}	mass transfer coefficient for the rate of dissolution (m/s)
K^{vap}	vaporization mass transfer coefficient (m/s)
M	molecular weight of oil (g/gmol)
n	number of moles of oil sample (gmol)
n_o	initial number of moles of oil sample (gmol)
P^{sat}	vapor pressure of oil at sea surface temperature (Pa)
P_c	critical pressure (Pa)
Q^{vap}	parameter defined in Eq. (13) (1/day or 1/s)
R	gas constant=8.314 (Pa m^3/mol-K)
r	rate of oil disappearance (1/day or 1/s)
S	specific gravity at 15.5°C
S_w	salt concentration in seawater (wt%)
T	temperature (K)
T_b	oil boiling point (K)
T_c	critical temperature (K)
V	oil spill volume (m^3)
V_A	oil molar volume at normal boiling point (m^3/mol)
V_o	initial oil spill volume (m^3)
U	wind speed (m/s)
x_i	mole fraction of pseudocomponent i in oil spill (dimensionless)
y	oil spill thickness (m)
Z^{dis}	reduced solubility concentration, C_s/ρ_m, (dimensionless)
Z_{liq}^{sat}	saturated liquid compressibility factor, $PM/\rho_{liq}^{sat}RT$, (dimensionless)

Greek letters

ρ_m	oil molar density (gmol/m^3)
ρ_{liq}	liquid absolute density (g/m^3)
Δt	time step, day, hour or second

Subscripts

i	pseudocomponent properties
r	reduced parameter
v	a value based on volume
w	a value based on weight (or mass)
o	initial values (variable at t=0)

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