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Abstract: The presence of volatile iodine in containment buildings is one of the major safety concerns in the potential event of nuclear reactor accidents. Organic impurities in containment water, originating from various painted structural surfaces and organic materials, could have a significant impact on iodine volatility following an accident. To determine the source and magnitude of organic impurities and their effects on time-dependent iodine volatility, the dissolution for organic constituents from paints used in reactor buildings has been studied under postulated accident conditions. The studies of the organic dissolution from carbon steel coupons coated with zinc-primed vinyl, epoxy-primed polyurethane or epoxy paints over the temperature range 25–90°C are reported. Relatively large activation energies were measured for the release of the principal organic compounds from painted surfaces, suggesting it is the release of the solvents from the paint matrix rather than their diffusion through the solution that is the rate determining step for the dissolution mechanism. The similarities in the values of activation energies for the dissolution of different organic compounds from the paints suggest the release rate is independent of the nature of the painted surface or the type of organic being released from the surface. These two observations indicate that it may be possible to write a generalized rate expression for the release of organic compounds from painted surfaces in containment following an accident. The possible implications of these results for predicting iodine volatility in containment are also discussed.

Key words: dissolution kinetics, organic solvents, painted surfaces, reactor accidents.

Résumé : La présence d'iode volatil dans les enceintes de confinement est une des préoccupations majeures en matière de sécurité dans les cas d'accidents de réacteurs nucléaires. Les impuretés organiques présentes dans l'eau de confinement, qui pourraient provenir de divers matériaux organiques et de surfaces structurales peintes, pourraient avoir des répercussions significatives sur la volatilité de l'iode après un accident. Dans le but de déterminer la source et l'amplitude des impuretés organiques ainsi que leurs effets sur la volatilité de l'iode en fonction du temps, on a étudié la dissolution des constituants organiques des peintures utilisées dans les édifices des réacteurs dans les conditions prévues en cas d'accident. On rapporte les résultats d'études, effectuées à des températures allant de 25 à 90°C, sur la dissolution des produits organiques provenant d'échantillons d'acier au carbone recouverts peintures époxy, au vinyle avec couche d'apprêt au zinc ou au polyuréthane avec couche d'apprêt époxy. On a déterminé que les énergies d'activation sont relativement élevées pour la libération des principaux produits organiques des surfaces peintes; cette observation suggère que l'étape déterminante du mécanisme de dissolution est probablement la libération des solvants à partir de la matrice de peinture plutôt que leur diffusion à travers la solution. Les similarités dans les valeurs des énergies d'activation pour la dissolution de différents composés organiques à partir des peintures suggèrent que la vitesse de libération est indépendante de la nature de la surface peinte ou du type de composé organique libéré de la surface. Ces deux observations indiquent qu'il serait vraisemblablement possible de définir une expression de vitesse généralisée permettant de décrire la libération des composés organiques, à partir de surfaces peintes sur les enceintes de confinement, à la suite d'un accident. On discute aussi des implications possibles de ces résultats pour prédire la volatilité de l'iode dans les enceintes de confinement.

Mots clés : cinétique de dissolution, solvants organiques, surfaces peintes, accidents dans des réacteurs.

[Traduit par la Rédaction]

I. Introduction

The time-dependent airborne concentration of iodine in the reactor containment building is one of the most important parameters used to evaluate the potential radiological consequences of a nuclear reactor accident. The parameter is important because of the large inventory of iodine in irradiated nuclear fuel, and the radiological impact to public dose from an airborne emission of volatile ^{131}I species which could be released to the outside atmosphere through contain-

ment leakage or controlled venting. The behaviour of iodine under containment accident conditions has thus been a subject of extensive studies for the nuclear industry world-wide including Atomic Energy of Canada Limited (AECL) for many years. Recent critical reviews on iodine behaviour (1–3) and references therein provide a comprehensive technical background on this subject.

The results of these studies have established that iodine behaviour in containment would depend strongly on the pH and the steady-state concentration of water radiolysis products such as $\cdot OH$, O_2^-:, and H_2O_2 in the containment sump water, both of which influence the rate of conversion of non-volatile I^- to volatile I_2 (1, 2, 4–7). Under accident conditions, organic impurities in containment water (or the sump), could significantly affect the pH and the concentrations of the water radiolysis products via the following reactions (1, 2, 4–7):

[1] $\quad R + \cdot OH \rightarrow R\cdot + H_2O$

[2] $\quad R\cdot + O_2 \rightarrow RO_2\cdot \rightarrow \rightarrow R'\cdot$, alcohols, aldehydes,

$$\text{acids and } CO_2$$
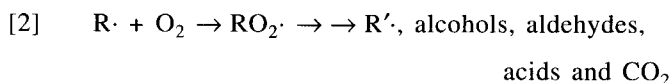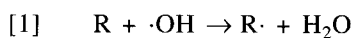
where R and R· represent an organic compound and corresponding organic radical dissolved in water. Organic iodides would also be formed thermally and radiolytically through aqueous phase reactions of I_2 with the organic impurities:

[3] $\quad R\cdot + I_2/HOI \rightarrow RI + I\cdot$
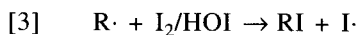
The formation and decomposition of organic iodides will influence iodine volatility by changing the steady-state concentration of volatile I_2. Some organic iodides are also volatile, and would contribute directly to the volatile iodine component in containment.

Although there are many different organic surfaces and impurities in containment, those that are dissolved in aqueous solutions and undergoing reactions [1] to [3] would have the largest effect on iodine volatility (1, 2). Consequently, the relative rates for the release of organic impurities from painted surfaces to the aqueous phase, and their subsequent degradation to organic acids and organic iodides, are important parameters required to describe iodine behaviour following an accident. The objective of the current study is to establish one of these parameters; the release rate of organic impurities into the sump water. The dissolution kinetics of organic solvents from paints have been studied using carbon steel coupons coated with zinc-primed vinyl, epoxy-primed polyurethane, or epoxy paint in a temperature range of 25–90°C. The studied temperature range is that expected in containment following an accident, and the vinyl, polyurethane, and epoxy paints have been used to coat the containment surfaces of CANDU®[3] nuclear generating stations. The results of the dissolution study are presented in this paper.

II. Experimental

The studies were performed under controlled temperature conditions in glass cells containing water at 25, 40, 60, 70, and 90°C. The temperature of the cell was controlled by either a circulating-water bath or heating tape. The solution

pH was held constant at either pH = 5 or pH = 10 using a 0.1 mol dm^{-3} H_3BO_3–NaOH buffer. All solutions were made using filtered water from a Millipore Filtration System.

II.A Coatings and coupons

Release of organic compounds into both the aqueous and gas phases from painted surfaces immersed in water was studied using cylindrical carbon steel coupons coated with zinc-primed vinyl, epoxy-primed polyurethane, or epoxy coatings. The constituents of these paints as supplied by the manufacturer are listed in Table 1.

The coupons (geometric surface area = 5.7 cm^2) were sandblasted and within two hours spray-coated with the appropriate coating(s). For the zinc primer, a layer of approximately 0.015 cm was applied while for the other coatings, a thickness of approximately 0.025 cm was used. The epoxy-coated coupons and epoxy-primed-polyurethane-coated coupons were stored for 9 and 60 months, respectively, while the zinc-primed-vinyl-coated coupons were stored for various periods (15 days to 36 months). The coupons were stored in a ventilated area at room temperature (i.e., under conditions that did not inhibit solvent release by evaporation). The thinners used in applying the paints contained toluene, xylenes, methyl isobutyl ketone (MIBK), or 1,1,1-trichloroethane.

At the end of many of the dissolution experiments performed at 90°C there was evidence for blistering of the paint. The vinyl paint was particularly susceptible, with immersion resulting in the whole coupon surface being covered with blisters, 1 to 2 mm in diameter, and in some cases, exposure of the carbon steel on the edges of the coupon. A layer of the vinyl polymer was peeled, revealing yellow discoloration underneath, and ethanol and 2-propanol, the major solvent constituents of the zinc primer base undercoating, were observed in solution. Blistering was not observed at lower temperatures.

II.B Reaction vessel apparatus

Glass vessels were prepared from 500 cm^3 beakers, with final total volumes of 375 cm^3. These beakers were modified to accommodate a thermowell in the liquid phase for thermocouple readings, and a screw-on Teflon Mininert septum valve for sampling. The Mininert valve consisted of a push-type Teflon valve and a replaceable septum. The Teflon valve provided a seal when not sampling whereas the septum provided the only other seal when taking samples and allowed multiple punctures during the study. For studies at 60, 70, and 90°C the glass vessels were inserted into insulated machined-out aluminum cylinders, wrapped with heating tape. The temperature difference between the aluminum wall and the liquid phase was approximately 1 to 2°C. At 25 and 40°C, the glass vessels were kept in a circulating water bath.

The glass vessels, containing 60-cm^3 of air-sparged and buffered solutions, were heated to temperature at which point a single painted coupon was added to each vessel. Blank runs, for which no coupon was added to a vessel, were also conducted. There was no intentional mixing of the gas or liquid phase during the runs except when 1.0-cm^3 gas and aqueous samples were removed using a Hamilton gas-tight syringe.

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[3]CANDU is a registered trademark of Atomic Energy of Canada Limited.

Table 1. Constituents of the zinc primer, vinyl, epoxy, and polyurethane paints.[a]

Paint	Ingredients[b]	wt %
INTERVINUX VM HB (Vinyl paint)		
	Methyl ethyl ketone	15–40
	Ethyl 3-ethoxy propionate	10–30
	Tricresyl phosphate	3–7
	Xylene	1–5
	Methyl isobutyl ketone	1–5
	Silica amorphous	1–5
	Ferric/ferrous oxide	1–5
Thinner		
	Methyl isobutyl ketone	30–60
	Toluene	30–60
CARBOLINE CARBOZINC 11 (Zinc primer)		
Part A (base)[c]		
	Ethanol	30
	2-Propanol	20
	Silica	15
	2-Butoxy ethanol	10
	Aluminum silicate	10
	Ethyl silicate	10
	Methanol	10
	Pigment	5
	Methyl silicate	5
	Mica	5
	Water	4.4
Part B (zinc filler)[c]		
	Zinc dust	97
	Zinc oxide dust	3
Thinner #21		
	2-Propanol	100
Thinner #26		
	1-Methoxy-2-propanol	>1
	2-Ethoxy butanol	>1
AMERCOAT 66 (Epoxy paint)		
Part A (cure)[d]		
	Polyamide resin	<75
	Xylene	<30
	Triethylene tetramine	<5
Part B (resin)[d]		
	Epoxy resin	<25
	Methyl isobutyl ketone	<10
	Xylene	<10
	Methyl n-amyl ketone	<10
	2-Butoxyethanol	<5
	Talc	<40
	Titanium dioxide	<10
	Iron oxide	<10
	Amercoat 7 (thinner)	No Data provided
NORMAC NR-5S (Polyurethane paint)		
Part A[e]		
	Polyether polyol	42–60
	Methylene bis-(4-cyclohexylisocyanate)	2.1–3.6
	1,1,1-Trichloroethane	35–55
Part B[e]		
	Dihydro-2(3H)-furanone	35–60
	4-4'-Methylene dianiline	42–50

Table 1 (*concluded*).

Paint	Ingredients[b]	wt %
Thinner		
	1,1,1-Trichloroethane	96.5
	Diethylene ether	2.5
	1,2-Butylene oxide	0.5
	Nitromethane	0.3

[a]Paint compositions provided by manufacturers.

[b]Only hazardous materials are listed. Paint is up to 30% solids (vinyl-chloride, vinyl-acetate co-polymer) by volume.

[c]One gallon part A (base) mixed with 8 kg (zinc filler). Thinner added as required.

[d]One part A (hardener) mixed with 4 parts B (resin). Thinner added as required.

[e]One part A mixed with 0.15 parts B. Thinner added as required.

II.C Analyses

The gas-phase concentrations of the organic compounds were determined using a Model 3700 Varian Gas Chromatograph (GC) equipped with a HNU Model PI-52 photoionization detector. The GC was routinely calibrated using gas mixtures of known composition. Gas-phase constituents were identified using a Hewlett Packard (HP) Model 5890 GC fitted with a HP Series 5972 mass selective detector. The detection limit of the GC for the organic molecules was 0.05 × 10^{-6} mol dm^{-3}.

The concentrations of the aqueous-phase carbonyl species were determined using a Waters' HPLC (High Performance Liquid Chromatography) system, following derivatization by 2,4-dinitrophenylhydrazine (DNPH) (8). The aqueous organic species detected by this method were formaldehyde, acetaldehyde, acetone, methyl ethyl ketone, n-heptan-2-one, and MIBK. The detection limits of the HPLC/derivatization method ranged from 0.5 × 10^{-6} to 1 × 10^{-6} mol dm^{-3} for aldehydes and ketones and from 4 × 10^{-6} to 10 × 10^{-6} mol dm^{-3} for organic acids. The concentrations of aromatic compounds were too low to be detected by direct injections. At the end of each test, the pH was measured and the liquid sent for chloride analyses by ion chromatography. The statistical measurement uncertainties (±1 σ with 95% confidence limits) of the gas and aqueous phase analysis were 12 and 5%, respectively, except for low concentrations near the detection limits.

During a typical experiment, one of the coupons was placed in the reaction flask containing the solution and the flask was sealed with a screwed septum cap. This arrangement provided a surface area to volume ratio in the aqueous phase (A_{surf}/V_{aq}) of ~0.095 cm^{-1} and a gas to aqueous volume ratio (V_g/V_{aq}) of approximately 5.25.

Both gas and aqueous samples were taken periodically using micro-syringes and analyzed for organic content; from every half an hour to an hour at 90°C to every 24 h at 25°C. Because of the small sampling volumes, the total reduction in the aqueous volumes due to sampling was no more than 8% by the end of the test. A test lasted until a steady-state was reached or up to 20 days.

III. Results

III.A Dissolution and partitioning of organic compounds between gas and aqueous phases

A number of organic compounds were found in the gas and aqueous phases in the presence of the three coatings.

MIBK is common to all coatings as it was present in either the paint, the undercoating (e.g., it is not present in the polyurethane paint, but was present in the epoxy undercoating), or the thinner. One organic compound that appears in the epoxy and vinyl tests but is absent from the list of the manufacturer's ingredients is acetone. This component must have been present as either an impurity (present in the MIBK) or as a product of hydrolysis or oxidation of one of the other components. A number of other lower-weight aliphatic aldehydes and ketones which may be by-products of reactions or impurities were also identified. Components of the thinners, such as aromatic (toluene and m-xylene) and chlorinated (1,1,1-trichloroethane) hydrocarbons were also observed. For the organic compounds detected in the aqueous phase, the following sequence was observed for their concentrations in the presence of the three surfaces:

Epoxy: acetone > MIBK > n-heptan-2-one > m-xylene

Vinyl: acetone ≅ MIBK ≅ MEK ≅ acetaldehyde > formaldehyde

Polyurethane: MIBK > formaldehyde

while in the gas phase:

Epoxy: m-xylene > MIBK ≅ n-heptan-2-one > acetone

Vinyl: MIBK > m-xylene > toluene

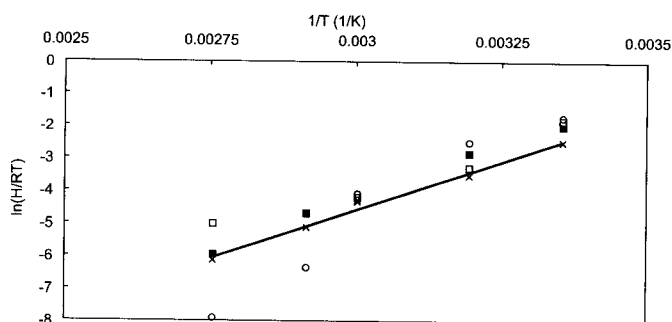Polyurethane: MIBK > m-xylene >> 1,1,1-trichloroethane

The different order of abundance in the gas and aqueous phases is due to different partition coefficients of these compounds, where the partition coefficient (H) is defined as the ratio of the *aqueous* to the *gas*-phase concentration at equilibrium, and is related to the equilibrium constant K (Henry's law constant) obtained from the free energy, by the relationship $H = K(RT)$.

The equilibration of these organic compounds between the gas and aqueous phases in a shallow pool should be quite rapid and thus the concentrations of organic compounds in the gas phase should reflect those in the aqueous phase. This was confirmed experimentally by injecting MIBK at the bottom of an aqueous solution and then analyzing the gas phase for MIBK as a function of time. Equilibrium was obtained within 10 min, much faster than the time scale of these

Table 2. Values for the partition coefficient (H) for MIBK at 25, 40, 60, 70, and 90°C.

Temperature (°C)	H			
	Vinyl	Epoxy	Polyurethane	Water
25	330	204	440	400
40	150	76	210	97
50	—	—	—	83
60	38	36	46	41
70	26	17	4.9	26
90	7.8	6.5	1.1	20

Table 3. Values of $\Delta H°$ and $\Delta S°$ for the gas–liquid phase partitioning of various organics in water.

Organic	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J K^{-1} mol^{-1})	Reference
MIBK	–(59 ± 6)	–(214 ± 16)	This study
	–1.4[a]		(9)
acetone	–(69 ± 13)	–(245 ± 13)	This study
	–46		(9)
n-heptan-2-one	–(57 ± 18)	–(210 ± 5)	This study
	–37		(9)
methanol	–46	–107	(10)
ethanol	–54	–134	(10)

[a]Both the reported partition coefficient and the reported activation energy are very low in comparison to those for similar compounds.

Fig. 1. Plot of ln (H) versus $1/T(K)$ for the distribution of MIBK between the gas and aqueous phases in the absence of any surface (□) and in the presence of the epoxy (×), vinyl (■), and polyurethane (○) surfaces.

Fig. 2. Aqueous-phase concentrations of MIBK in the presence of the epoxy surface (pH = 10) at 25 (○), 40 (■), 60 (▲), 70 (●), and 90°C (□). The lines drawn through the data are those calculated using eq. [14].

thermal dissolution studies. The fast equilibrium between the gas and aqueous phases enabled us to use both the aqueous- and gas-phase data to determine the dissolution rates.

The partition coefficient of MIBK as a function of temperature, measured in water in the absence of a painted surface, is listed in Table 2. Similar values, generally within a factor of two (which is within experimental uncertainties) were obtained using painted coupons as the source of MIBK. These values are also listed in Table 2. Note that the uncertainties are greater for lower partition coefficients (i.e., at higher temperatures).

A least-squares fit of ln (H/RT) versus $1/T(K)$ (Fig. 1) using all of the data in Table 2 yields a $\Delta H° = -(59 \pm 6)$ kJ mol^{-1} and $\Delta S° = -(214 \pm 16)$ J mol^{-1} K^{-1} for the transfer of MIBK from the gas phase to the aqueous phase using the slope and intercept, respectively (MIBK(g) = MIBK(aq)).

[4] $\Delta G° = -RT \ln (H/RT) = \Delta H° - T\Delta S°$
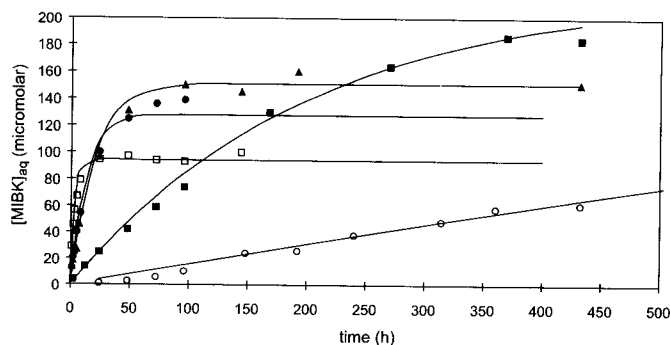
[5] $\ln (H) - \ln (RT) = -(\Delta H°/R)(1/T) + \Delta S°/R$

A similar analysis of the data obtained for n-heptan-2-one and acetone during the epoxy test gives the results in Table 3. The values for $\Delta H°$ are compared to literature values for the same compounds obtained from Ref. 9. $\Delta S°$ values for the ketones were not readily available from the literature, therefore $\Delta S°$ values for organic compounds having similar heats of vapourization e.g., ethanol and methanol are provided for comparison in Table 3 (10).

III.B Dissolution of MIBK from coatings

To assess the release of organic compounds from the coatings under containment conditions, it is best to study the release of one representative compound common to all coatings. Since MIBK is present in varying degrees in all of the coatings (it is not present in the polyurethane coating per se., but is present in the epoxy undercoating), the MIBK data have been used to obtain the dissolution kinetics. The dissolution kinetics of MIBK from vinyl, epoxy, and polyurethane surfaces were studied at 25, 40, 60, 70, and 90°C. Some of the results are shown in Figs. 2 to 6. For each coating, additional analysis included several other organic compounds, ranging from other ketones (acetone, n-heptan-2-one), to aromatic compounds (m-xylene, toluene) and halogenated hydrocarbons (trichloroethylene, chloroform). All of these species showed dissolution kinetics very similar to MIBK.

Comparing the time dependent concentration profiles for the various surfaces, it appears that the final steady-state MIBK concentrations, which were far below the solubility limit of MIBK in water, depend on both coating type and paint aging. MIBK dissolution also follows the rate laws derived from the simple mechanism:
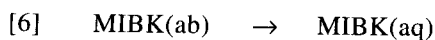
[6]   MIBK(ab)   →   MIBK(aq)

Fig. 3. Gas-phase concentrations of MIBK in the presence of the epoxy surface (pH = 10) at 25 (○), 40 (■), 60 (▲), 70 (●), and 90°C (□). The lines drawn through the data are those calculated using eq. [14].
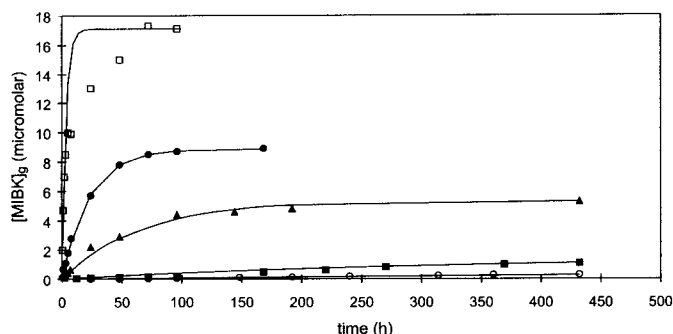

Fig. 5. Normalized concentrations of MIBK in the presence of the polyurethane surface (pH = 5) at 25 (○), 40 (■), 60 (▲), 70 (●), and 90°C (□). The lines drawn through the data are those calculated using eq. [14] normalized to the steady-state concentration.

Fig. 4. Normalized concentrations of MIBK in the presence of the epoxy surface (pH = 10) at 25 (○), 40 (■), 60 (▲), 70 (●), and 90°C (□). The lines drawn through the data are those calculated using eq. [14] normalized to the steady-state concentration.
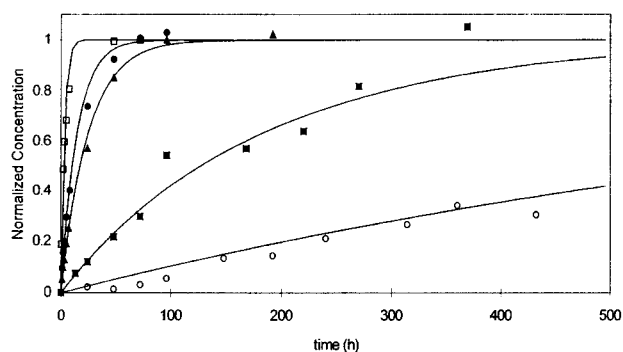

Fig. 6. Normalized concentrations of MIBK in the presence of the vinyl surface (pH = 10) at 25 (○), 40 (■), 60 (▲), 70 (●), and 90°C (□). The lines drawn through the data are those calculated using eq. [14] normalized to the steady-state concentration.
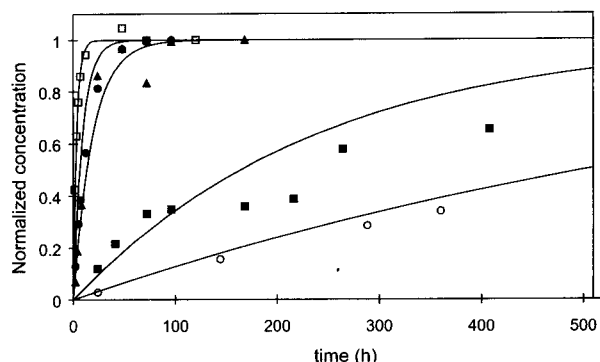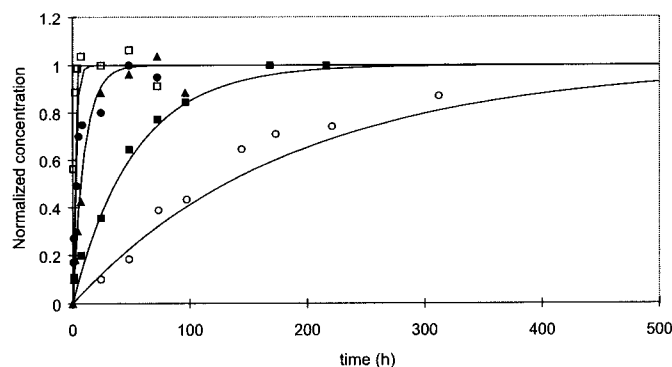

[7] $MIBK(aq) \leftrightarrow MIBK(g)$
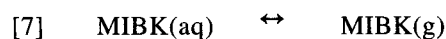
where aq, ab, and g in the brackets represent aqueous, absorbed, and gas phase, respectively. Assuming a fast equilibrium for eq. [7] leads to the following equation for the concentration of MIBK in solution, $[MIBK(aq)]_t$ (μmol dm^{-3}):

[8] $[MIBK(aq)]_t = [MIBK(aq)]_\infty \cdot (1 - \exp(-kt))$

[9] $= \alpha(1 - \exp(kt))$

and for the gas-phase concentration of MIBK, $[MIBK(g)]_t$ (μmol dm^{-3}):

[10] $[MIBK(g)]_t = \dfrac{1}{H}[MIBK(aq)]_\infty (1 - \exp(-kt))$

[11] $= \beta(1 - \exp(kt))$

where k is the dissolution rate constant (s^{-1}), α and β are proportional constants, H is the partition coefficient, and $[MIBK(aq)]_\infty$ (μmol dm^{-3}) is the final MIBK concentration present in the water at the end of dissolution, and is related to the amount of MIBK present in the paint polymer initially, $[MIBK(ab)]_0$.

Table 4 shows the values of k and $[MIBK(aq)]_\infty$ that result from fitting eq. [8] to the observed time-dependent aqueous-phase concentrations for the epoxy, vinyl, and polyurethane surfaces. The amount of MIBK originally on the surface $[MIBK(ab)]_0$ is also shown in the table. $[MIBK(ab)]_0$ was calculated using the measured partition coefficient of MIBK in water at the appropriate temperature, (see Table 2), the surface area of the coupon, and the appropriate liquid and gas volumes. The aqueous-phase data for the test in the presence of the epoxy surface at pH = 10 is shown graphically in Fig. 2 while the gas-phase data for the same test is shown in Fig. 3. The lines drawn through the data are those predicted by eqs. [9] and [11] using the k and $[MIBK(aq)]_\infty$ values given in Table 4. In general, the calculated lines reproduce the data extremely well, indicating the simple mechanism represented by reactions [6] and [7] adequately describes the dissolution process.

From Table 4 (Fig. 2), it can be seen that the final steady-state concentration for MIBK, $[MIBK(aq)]_\infty$, in the presence of a painted surface varies from one test to another. The range of the final concentration is more than expected from the variations in paint thickness which were kept small. This variance is considered to be mainly due to the difference in

Table 4. Values for the parameters resulting from the fit of eq. [14] to the time-dependent aqueous-phase MIBK concentration data.

Surface	pH	T (°C)	k (h^{-1})	[MIBK(ab)]$_o$ (nmol cm^{-2})	[MIBK(aq)]$_\infty$ (μmol dm^{-3})
Epoxy	5	25	0	1770	160
		40	0	3100	270
		60	0.051	1850	150
		70	0.074	1710	130
		90	0.3	1300	94
	10	25	0	1440	130
		40	0.01	3450	300
		60	0.041	1600	130
		70	0.074	1710	130
		90	0.33	830	60
Polyurethane	5	25	0	460	42
		40	0.01	760	66
		60	0.052	1230	100
		70	0.11	1580	120
		90	0.28	1530	110
	10	25	0	660	60
		40	0	1500	130
		60	0.028	1720	140
		70	0.069	1840	140
		90	0.33	1800	130
Vinyl	5	25	0	3650	330
		40	0.01	1500	130
		60	0.084	2300	200
		70	0.14	1640	130
		90	0.77	1480	80
	10	25	0.01	3650	330
		40	0.019	1380	120
		60	0.1	3080	250
		70	0.41	2100	160
		90	1.7	1080	78

Fig. 7. The final steady-state concentration of MIBK released from vinyl-painted coupons as a function of the aging of paint.
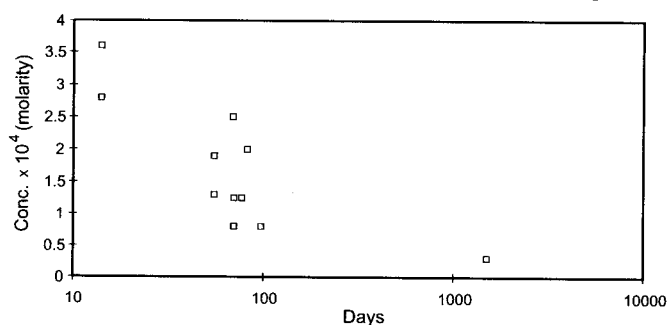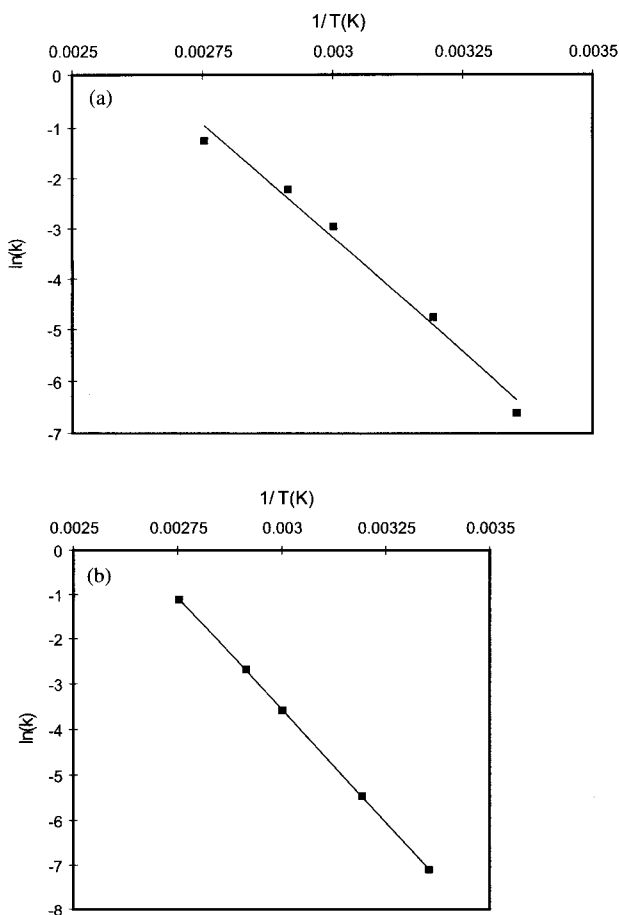

the amount of solvent initially in the paint polymer, and related to the degree of aging of the paint. The maximum concentration of MIBK released into the aqueous phase from the vinyl painted coupons is shown as a function of paint aging in Fig. 7. Data obtained at different pH values and temperatures are all included in the figure. (We do not have enough data to establish the effect of aging for the other paints.) Although the data show large scatter, the effect of aging on the final concentration can be seen clearly. Therefore, it is assumed that the initial MIBK concentration

within the coating surface controls the maximum MIBK concentration in solution and that the MIBK content in the coating decreases with aging due to evaporative losses.

To compensate for this aging effect in the graphical presentation, the concentrations of MIBK were normalized by dividing by final steady-state concentration. A plot of the normalized data for the epoxy, polyurethane, and vinyl surfaces can be found in Figs. 4–6, respectively. Only the initial data are shown for low temperature tests due to the variable time frame over which the tests were conducted, i.e., tests at 25°C take much longer to reach steady-state than tests performed at 90°C. The lines drawn through the data are those calculated using eq. [9] normalized to the final steady-state concentration.

The solution pH appears to have only a minor effect on the dissolution of MIBK. For most of the data, the dissolution behaviour of MIBK at pH 5 is not that much different than that at pH 10. For the most part, the time-dependent dissolution curves at the two pHs parallel each other for the three surfaces at the various temperatures; although generally, the dissolution curves at pH = 10 yield slightly higher final concentrations. This is unlikely to be a consequence of small variations in the painted samples, because the higher of the two final concentrations would be expected to be dis-

Fig. 8. Arrhenius plot of the dissolution rate constants observed for MIBK from polyurethane painted coupons, using (*a*) gas-phase data and (*b*) aqueous-phase data.

Fig. 9. Arrhenius plot of the dissolution rate constants observed for MIBK from epoxy-painted coupons, using aqueous-phase data.

the E_a values are within experimental error of each other, yielding an average of $E_a = 82 \pm 11$ kJ mol^{-1}.

We have also analyzed the data for acetone and *m*-xylene and obtained the activation energies for the dissolution of these compounds; $E_a = 83 \pm 3$ and 65 ± 4 kJ mol^{-1} respectively, similar to those observed for MIBK.

IV. Discussion

Unlike the dissolution of a pure solid, the release of MIBK from the painted surface does not involve the rupture or hydrolysis of chemical bonds within the structure of the solid, but rather occurs through the diffusion of the organic compound out of the paint matrix. A typical final concentration for MIBK in the experiments is ~100 μmol dm^{-3}. For the 60 cm^3 of water, this indicates an overall release of ~6 μmoles or 4×10^{18} molecules of MIBK per coupon (surface area = 5.7 cm^2). Typical BET (Brunauer, Emmett and Teller) surface area measurements have shown that small organic molecules like pyridine usually occupy an adsorbed surface area of 26×10^{-16} cm^2 (11); therefore, it would have required a surface with an area of ~1 $\times$ 10^4 cm^2 to have released this amount of MIBK as an adsorbed monolayer. This is ~2000 times more than the surface area of the coupon; therefore, MIBK must be diffusing out of the paint matrix.

Except for one of the results obtained in the presence of the polyurethane surface, the E_a values are within experimental error of each other yielding an average of 82 ± 11 kJ mol^{-1}. The similar values of E_a obtained for the three surfaces imply that the diffusion of the organic solvents through the matrix is relatively independent of the chemical composition of the matrix of the paint. Furthermore, the absolute dissolution rate constants are very similar for the three surfaces, indicating that, for a given substrate (in this case sandblasted carbon steel), the painted surface area does not vary significantly with the type of paint. This is important, for if this assumption is valid, it is possible that a general expression can be used to predict the release rate and time dependent concentrations for MIBK from a painted surface, provided the surface concentration and temperature are known. This assumption can be extended one step further. Fits of the Arrhenius equation to the data obtained for acetone and *m*-xylene yield $E_a = 83 \pm 3$ and 65 ± 4 kJ mol^{-1}, respectively. These values are similar to that obtained for

tributed randomly between the two pH values, which is not the case. It may be possible that the results obtained from the DNPH derivatization are pH dependent.
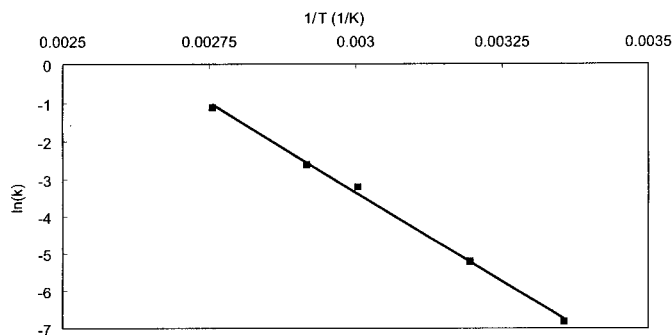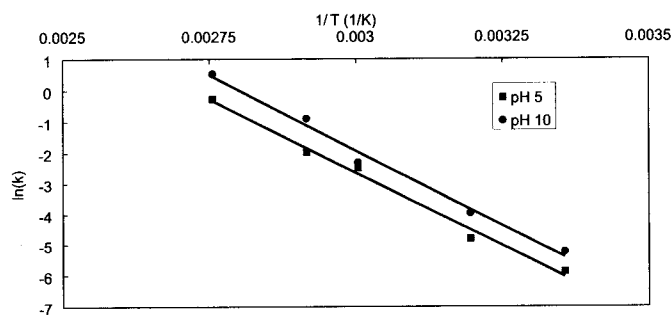
As can be seen in Figs. 4–6, the effect of temperature on dissolution is as expected, increasing the dissolution rate for MIBK sharply as the temperature increases. The dissolution rate constant for MIBK from polyurethane measured as a function of temperature is shown in an Arrhenius plot, i.e., ln *k* versus (1/*T*), in Fig. 8, where the slope of the plot provides the activation energy (E_a) of the dissolution process:

[12] $k = A \exp (-E_a/RT)$

The rate constants obtained using the gas-phase data are nearly identical with those obtained from the aqueous-phase data for all paints studied. Arrhenius plots of the dissolution constants from epoxy and vinyl paints are shown in Figs. 9 and 10, respectively.

The activation energies determined from Arrhenius plots for the dissolution of MIBK are listed in Table 5. Table 5 includes data from all three surfaces at pH = 5 and 10 using both the aqueous and gas-phase measurements. The errors on E_a listed in Table 5 are those associated with the slopes based on a least-squares (Arrhenius) fit of the ln (*k*) and 1/*T*(*K*) values listed in Table 4. Except for some of the results obtained in the presence of the polyurethane surface,

Fig. 10. Arrhenius plot of the dissolution rate constants observed for MIBK from vinyl-painted coupons, using aqueous-phase data.

Table 5. Activation energies for the dissolution of MIBK from different painted surfaces.

Surface	Phase	pH	E_a (kJ mol^{-1})
Epoxy[a]	Aqueous	5	79 ± 5
	Aqueous	10	78 ± 3
	Gas	10	75 ± 7
Polyurethane	Aqueous	5	75 ± 5
	Aqueous	10	83 ± 0.3
	Gas	5	85 ± 5
	Gas	10	108 ± 10 (91 ± 3)[b]
Vinyl	Aqueous	5	82 ± 5
	Aqueous	10	73 ± 6
	Gas	5	72 ± 4
	Gas	10	72 ± 8

[a]Gas phase data was not obtained for pH 5.

[b]This number was obtained from 40, 60, 70, and 90°C data only.

MIBK, which suggests that the dissolution rate is also independent of the type of organic compound.

The mechanism for the release of organic compounds from paint surfaces exposed to water is believed to be assisted by, and dependent upon, the rate of diffusion of water through the paint matrix.[4] This is supported by the fact that coupons aged several years (cf. the polyurethane coupons used in this study) retain significant quantities of solvents, but readily lose these solvents upon exposure to water. It is also supported by the observation that the dissolution rate appears to be independent of chemical nature of the organic compound. Finally, the water assisted dissolution is suggested by the measured activation energies. Diffusion of water through a layer of paint should have a large activation energy (E_a), typically between 50 and 100 kJ mol^{-1} (12), whereas the diffusion of a molecule away from the surface should be smaller, typically 10–20 kJ mol^{-1} (13, 14). The relationship between the adsorption of water by a polymer coating, and the release of solvents is discussed in detail elsewhere (See footnote 4). Briefly however, the apparent first order kinetic behaviour observed for the release of solvents from painted surfaces exposed to water is analogous to that observed for surface evaporation of a solvent from a solid to a final equilibrium concentration in the gas phase. The initial boundary conditions and physical processes assumed in deriving the solvent evaporation model in Ref. 15 (i.e., concentration of the diffusing species constantly decreasing in the solid and increasing outside of the solid) were consistent with our experimental conditions, and result in the first-order kinetics behaviour observed in our experiments.

The effect of radiation on the rate of dissolution of the organic compounds was negligible, although radiation rapidly decomposed the organic compounds once they had been released into the aqueous phase. This is consistent with studies described in Refs. 1 and 2. Release of MIBK from coupons in which dissolution followed a period of irradiation appeared to have the same rate constant, although the final concentrations of MIBK in solution were smaller. Solutions in contact with painted coupons that were irradiated subsequent to a dissolution period were found to yield increased

gas-phase concentrations of acetaldehyde, acetone, and MEK; and reduced concentrations of MIBK. The former three compounds were found to arise as a result of decomposition of dissolved MIBK. Toluene and xylene were not observed, because the small amounts present decomposed to phenol derivatives (and to some extent to organic acids), which are non-volatile and difficult to detect in the gas phase by conventional GC techniques.

From these observations, we concluded that irradiation at the total absorbed doses and dose rates (0.13 Gy s^{-1}) used here does *not* have a significant impact on the chemistry of the paint coating per se, although it decomposes the organic solvents that have been released to solution, affecting their concentrations observed in the aqueous and gas phases. A factor not considered in this study but which should be investigated further, is the impact of the thickness of the coating on the release rate. Presumably, as with aging time, there should be some dependence of the release rate on thickness, because it should affect the amount of MIBK originally in the coating for the surface. Also, a thicker coating may increase the length of the pathway that the organic solvent takes through the paint matrix before reaching the surface. Therefore, a study of the activation energy as function of paint thickness for one of the coatings is required to determine the effect of coating thickness on the E_a for the dissolution process (See footnote 4).

The studies on the radiolysis of organic compounds presented in Refs. 4–6 have shown that, compared to the dissolution rate, the rate of the radiolytic decomposition of organic solvents in the aqueous phase would be very fast under postulated accident containment conditions in which the radiation dose rate is expected to be in the range of 1–10 kGy h^{-1} immediately following an accident but fall off exponentially with time. These relative rates of organic dissolution and organic radiolysis have been observed in integral tests performed in the intermediate-scale Radioiodine Test Facility[5] (1, 2, 7, 16). These studies show that, (*i*) the

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[4] J.M Ball, J.C. Wren, and J.R. Mitchell. Manuscript in preparation.

[5] The Radioiodine Test Facility is an intermediate scale (350 dm^{-3}) facility which provides a combination of potential reaction media (gas phase, aqueous phase and variety of surfaces) and conditions (pH, temperature, radiation, initial concentrations and speciation of iodine), simulating a reactor containment building following an accident. The RTF is equipped with various on-line sensors to follow various chemical and physical properties as a function of time. A description of the RTF and test procedures can be found in refs. (1), (2), (7), and (16).

radiolysis of organic compounds from paint coatings will occur primarily in the aqueous phase and not on the surface, and (ii) under reactor accident containment conditions, the rates of radiolytic decomposition of organic compounds and formation of organic iodides are much faster than the rate of organic dissolution. The slower rate for organic dissolution is the principal parameter determining the pH reduction rate. Differences in the composition of the surfaces result in small variations in the rate of pH change because of the differences in the overall radiolysis production rate of organic acids and CO_2 from the different paint constituents.

The implication of these studies on modelling the effects of organic impurities on the time dependent iodine volatility in containment following an accident is that the dissolution process appears to be the rate-determining step for the changes in pH, dissolved oxygen concentration and organic iodide concentration observed when aqueous solutions containing CsI are irradiated in the presence of painted surfaces. Consequently, detailed kinetic mechanisms for the radiolytic decomposition of organic compounds and organic iodide formation may not be necessary.

V. Conclusions

The release of organic solvents from a variety of painted coupons exhibits pseudo-first order behaviour. Values of k, the pseudo-first order rate constant for solvent release, are relatively insensitive to solvent type, the effect of radiation, and water pH, and are similar in magnitude for various surfaces at a given temperature. Relatively large activation energies were measured for the release of organic compounds from painted surfaces. This suggests that it is the release from the paint-matrix rather than diffusion through the solution that is the rate determining step for the dissolution mechanism. The similarities in the values of activation energies for the dissolution of different organic compounds from the paint further suggests the release rate is relatively independent of the nature of the painted surface or the type of organic compound being released from the surface. Based on these two observations, it may be possible to write a generalized rate expression for the release of organic compounds from painted surfaces in containment during an accident.

Thermodynamic values have been obtained for the partitioning of the major constituents found in paints used to coat the containment surfaces of several CANDU® nuclear generating stations. Under the conditions of these experiments, the distribution of organic compounds between the gas and aqueous phases is rapid relative to the dissolution of these organic compounds from the paint matrix. All of these constituents have large negative ΔS values (Table 3) for the distribution equilibrium, suggesting the reverse process (i.e., partitioning of the organic compound from the aqueous to the gas phase) is entropy driven.

This work, in combination with the study on the radiolysis of organic compounds (4–6) and various integral effects test results from the intermediate scale Radioiodine Test Facility (1, 2, 7, 16), has established that dissolution of organic compounds from a painted surface into water is a key rate controlling step for any changes in the iodine volatility due to

organic reactions, i.e., pH change and organic iodide formation. Since the release rate appears to be largely independent of the nature of the paint for a given surface substrate, it may be possible that a generalized expression for the dissolution rate for compounds will be sufficient to describe the kinetics of pH change and organic iodide information in containment.

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