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Design rules for reversible thermochromic mixtures

D. C. MACLAREN, M. A. WHITE
Department of Chemistry and Institute for Research in Materials, Dalhousie University, Halifax, NS B3H 4J3, Canada
E-mail: mary.anne.white@dal.ca

The results of a systematic study of the influence of the color developer and the solvent on thermochromic properties of a reversible thermochromic system—crystal violet lactone as dye; propyl gallate, octyl gallate or lauryl gallate as developer; 1-tetradecanol, 1-hexadecanol or 1-octadecanol as solvent—are presented. Thermodynamic analysis of the developer-solvent phase diagrams is used to determine and compare the developer-solvent interactions in the systems, and observed variations in thermochromic properties are correlated with these interactions. The relationship between thermochromic behavior and competing dye-developer and developer-solvent interactions leads us to the first design rules for reversible thermochromic mixtures based on intermolecular interactions.

1. Introduction

Thermochromism can arise from mechanisms as diverse as thermally induced changes in crystal field, thermal expansion of nematic liquid crystals, melt-induced interactions in mixtures [1], and tautomerism [2]. Thermochromic organic mixtures are part of the larger family of functional dyes, which are smart materials with optical properties that can change with chemical, electrical and/or thermal stimuli [3]. These systems are potentially especially useful for reversible thermal printing via production of a metastable, but long-lived, color-developed state that can be erased by heating the system to a decolorization temperature where it converts to the non-colored equilibrium state [4]. Reversible thermochromic systems of this type generally consist of three organic molecular components: a thermochromic dye, a color developer, and a solvent [1, 5].

In thermal and spectroscopic investigations of an archetypal thermochromic dye/developer/solvent system of the general composition crystal violet lactone (CVL, dye)/alkyl gallate (developer) and n-alcohol (solvent), we found that the interaction between CVL dye and lauryl gallate (LG) color developer led to colored complexes of the form $(LG)_3{\cdot}CVL$ at equilibrium conditions after cooling from the melt, with metastable complexes of stoichiometry up to $(LG)_9{\cdot}CVL$ [6]. We also found that binary lauryl gallate/1-octadecanol (LG/OD) mixtures displayed strong attractive interactions between the components, leading to formation of a congruently melting compound of the form $(LG)_2{\cdot}OD$ [7]. Concurrent destruction of colored $(LG)_x{\cdot}CVL$ and formation of $(LG)_2{\cdot}OD$ were observed as the ternary systems changed from their metastable colored states to equilibrium non-colored states [6]. The presence of CVL significantly slowed the rate of formation of $(LG)_2{\cdot}OD$ in the ternary CVL/LG/OD mixture, relative to the binary LG/OD mixture: the metastability of the colored dye-developer complex is attributed to a competition between dye-developer and solvent-developer interactions [7]. Interaction between LG and OD is weak in the melt, as evidenced by the flat liquidus curve at the congruently melting $(LG)_2{\cdot}OD$ compound [7] indicating complete dissociation [8], and the stronger interaction between LG and CVL produces a colored complex, $(LG)_x{\cdot}CVL$. Upon quenching the melt, the colored complex was found to be metastable with respect to the formation of $(LG)_2{\cdot}OD$, leading to decolorization [7].

Understanding the detailed relationship between metastable and equilibrium compositions in reversible thermochromic mixtures is critical to overcome the present barriers to their application, namely good color contrast, rapid decolorization rates and equilibrium color stability [4, 9]. Their properties could be better optimized if all the interactions between the components were well understood [1, 5, 9].

An important, but unanswered, question has been: How do the compositions of the developer and the solvent influence the competitive binary interactions, and, hence, affect color contrast and decolorization rate? In the present study we systematically changed alkyl chain lengths in both the developer and the solvent, in otherwise similar ternary thermochromic mixtures. Through thermal and spectroscopic means, we quantify the developer-solvent interactions for a range of systems, and correlate these with the observed thermochromic properties. On the basis of these results we are able, for the first time, to propose design rules for optimization of reversible thermochromism based on intermolecular interactions.

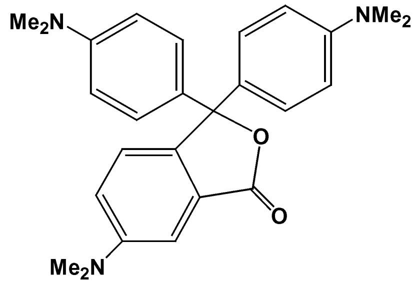


Figure 1 The molecular structure of crystal violet lactone, CVL.

2. Experimental methods

2.1. Materials

Crystal violet lactone (3,3-bis(p-N,N-dimethylaminophenyl)-6-N,N-dimethyl-aminophthalide, CVL, 97%, see Fig. 1), octyl gallate (octyl(3,4,5-trihydroxy) benzoate; OG, 97%), lauryl gallate (dodecyl(3,4,5-trihydroxy)benzoate, LG, 97%), 1-tetradecanol (TD, 96%), and 1-octadecanol (OD, 99%) were obtained from Aldrich. Propyl gallate (propyl(3,4,5-trihydroxy) benzoate; PG, 97%) and 1-hexadecanol (HD, 96%) were obtained from Eastman Kodak. All were used without further purification. The melting point of each was characterized by differential scanning calorimetry: 453 ± 2 K for CVL (quoted as 453–456 K by Aldrich), 421 ± 1 K for PG (literature value 423 K) [10], 375 ± 2 for OG (literature value 373 ± 1) [11], 370 ± 1 K for LG (literature value 369.7–370.2 K) [12], 311 ± 1 for TD (literature value 311–313 K) [13–15], 322 ± 1 K for HD (literature value 321–323 K) [12–14], and 331 ± 2 K for OD (literature value 331 ± 1 K) [16].

2.2. Differential scanning calorimetry (DSC)

DSC data were obtained using a Perkin Elmer Pyris 1 DSC calibrated using the melting temperature and enthalpy of fusion for indium (Aldrich 99.99%) under an atmosphere of ultra-dry nitrogen (20 mL min^{-1}). Phase diagram data were obtained at a scan rate of 5 K min^{-1}.

2.3. Raman spectroscopy

Raman data were obtained with a Bruker RFS 100 Raman spectrometer using the 1064.5 nm line of an Nd:YAG laser with an incident power of 447 mW. A Ge diode detector collected scattered light. For most measurements, the material was melted onto circular aluminium discs for measurement and 200 scans were obtained with a resolution of 2.0 cm^{-1}. For time-dependent measurements, samples were melted onto circular aluminium discs, quenched in liquid nitrogen, and placed into the Raman spectrometer. For rapid measurement, scans of 30 s (average of 15 scans) at 4.0 cm^{-1} resolution were obtained at 30 s intervals.

2.4. Diffuse reflectance spectrophotometry

Diffuse reflectance spectra were obtained using an Ocean Optics PC2000 reflectance spectrophotometer with a hand-held probe. A white Spectralon Teflon reference was used to calibrate for 100% reflectance. Samples were prepared on glass microscope slides and measured with the probe held at 45° to the sample surface. Single scans were carried out every 10 s with a 5-pixel boxcar smoothing routine.

3. Results and discussion

3.1. Influence of the solvent on CVL/LG/solvent systems

3.1.1. CVL/LG/TD, CVL/LG/HD and CVL/LG/OD thermochromism

Melting a CVL/LG/TD mixture resulted in the development of color that can be maintained in a metastable, but long-lived, state, if the mixture is rapidly cooled ($dT/dt > 300$ K min^{-1}). Mixtures maintained high color density below 10°C, but above 10°C, the mixture rapidly lost color and achieved the original low color density in 30–60 s.

As the solvent's alkyl chain is lengthened from TD to HD to OD, the color contrast between the metastable and equilibrated CVL/LG/alcohol solid was found to decrease. This can be seen quantitatively in diffuse reflectance results for CVL/LG/TD, CVL/LG/HD, and CVL/LG/OD in three states: the melt, the metastable solid state, and the equilibrated solid. The % reflectance at 620 nm (the wavelength of the absorption maximum), in the three respective states, is: (a) CVL/LG/TD, 1:6:50 (all composition ratios are mole ratios): 70 ± 10, 15 ± 3, 85 ± 5; (b) CVL/LG/HD, 1:6:44: 25 ± 5, 10 ± 3, 30 ± 5; (c) CVL/LG/OD, 1:6:40: 30 ± 5, 7 ± 3, 30 ± 5.

The rate of decolorization of the quenched metastable solids also changes with solvent chain length (Fig. 2). Whereas the CVL/LG/TD mixture reached its equilibrium color density (maximum reflectance) in about 500 s, the CVL/LG/HD mixture required over 1800 s to reach an equilibrium color density, and the CVL/LG/OD mixture showed negligible change in color density after 1800 s (although a 3-fold increase in reflectance was noted after 24 h).

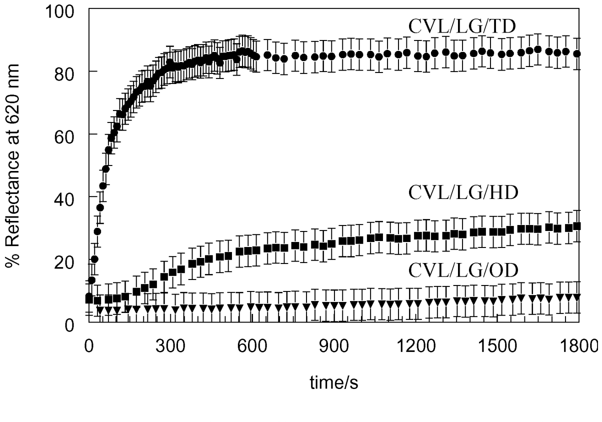
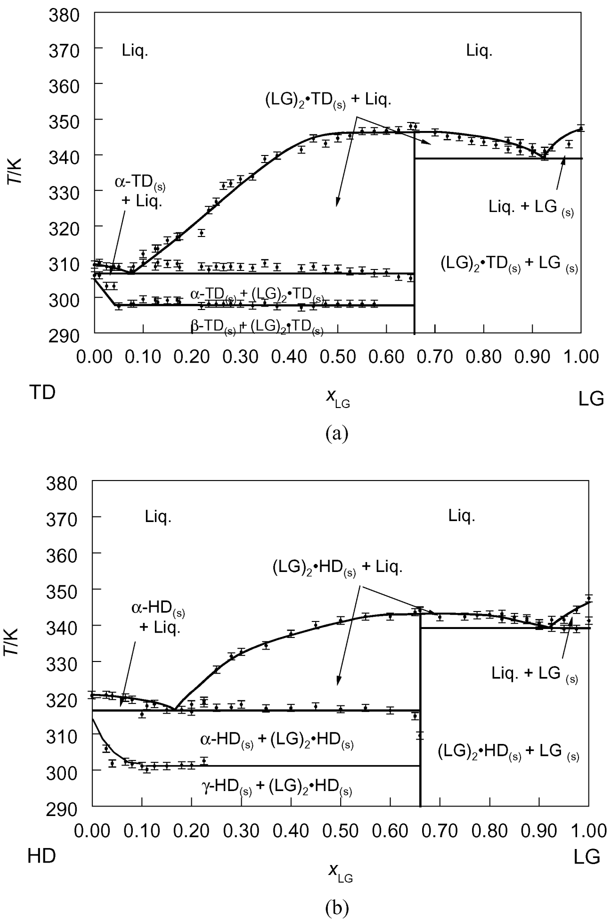


Figure 2 Comparison of the diffuse reflectance intensity at 620 nm at mole ratios of 1:6:40 at room temperature during decolorization of the metastable solids after quench cooling for (●) crystal violet lactone/lauryl gallate/1-tetradecanol (CVL/LG/TD), (■) crystal violet lactone/lauryl gallate/1-hexadecanol (CVL/LG/HD), and (▼) crystal violet lactone/lauryl gallate/1-octadecanol (CVL/LG/OD).



(a)

(b)

Figure 3 Binary phase diagrams of alcohol/lauryl gallate mixtures on cooling. (a) 1-tetradecanol/lauryl gallate (TD/LG); (b) 1-hexadecanol/lauryl gallate (HD/LG). The points with error bars represent measured DSC transition (onset) temperatures and uncertainties. The phase boundaries are added to aid the eye.

3.1.2. Complexes with LG

The phase diagrams of the LG/TD and LG/HD developer-solvent systems, as determined by DSC on cooling, are shown in Fig. 3. The features observed are analogous to the LG/OD phase diagram [7], i.e. formation of a congruently melting compound of the form, $(LG)_2$·alcohol, which melts to give dissociated LG and alcohol. The Raman spectra of $(LG)_2$·TD and $(LG)_2$·HD are virtually identical to that of $(LG)_2$·OD [7]. The most prominent feature is the asymmetric carbonyl vibration at 1683 cm^{-1}, assigned to the carbonyl group of LG within the complex $(LG)_2$·alcohol, shifted by ~25 cm^{-1} relative to pure LG [7].

When CVL dye is added, a developer-dye complex forms in the melt. Raman spectra of CVL/LG/TD taken at room temperature after quenching the melt in liquid nitrogen show the prominent peaks previously reported [6] for $(LG)_x$·CVL in the binary CVL/LG mixture, corresponding to $C{=}N^+$ (1584 and 940 cm^{-1}) [17–19] and COO^- (1359 and 720 cm^{-1}) [17–19] functionalities, only present as small shoulders 1 min after quenching. This is consistent with the rapid destruction of the $(LG)_x$·CVL complex and corresponding color loss in the ternary mixture.

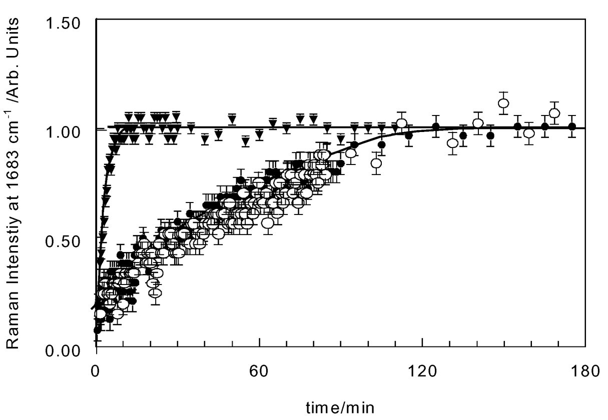


Figure 4 Time evolution of the intensity of the carbonyl peak at 1683 cm^{-1} of lauryl gallate in $(LG)_2$·alcohol for: (▼) crystal violet lactone/lauryl gallate/1-tetradecanol (CVL/LG/TD, 1:6:40), (○) crystal violet lactone/lauryl gallate/1-hexadecanol (CVL/LG/HD, 1:6:40), and (●) crystal violet lactone/lauryl gallate/1-octadecanol (CVL/LG/OD, 1:6:40), all quenched from the melt in liquid nitrogen and equilibrated at 25°C. Error bars represent averages over three experiments.

Raman spectra of CVL/LG/HD taken at room temperature after quenching the melt in liquid nitrogen show features similar to those observed for CVL/LG/TD except for the time required for the observed change. As for the CVL/LG/OD mixtures examined previously [7], the CVL/LG/TD and CVL/LG/HD mixtures show a Raman peak at 1683 cm^{-1}, representative of the formation of $(LG)_2$·alcohol in the mixtures as they equilibrate. Equilibration to produce $(LG)_2$·alcohol also is observed in the Raman spectra of binary LG/TD and LG/HD mixtures. The intensities of the peak at 1683 cm^{-1} observed in the equilibration of CVL/LG/TD, CVL/LG/HD (1:6:40), and LG/TD and LG/HD (6:40) show that the presence of CVL dye slows the rate of $(LG)_2$·alcohol formation, as for CVL/LG/OD [7]. Fig. 4 shows the growth of the intensity of the 1683 cm^{-1} ($(LG)_2$·alcohol) peak of CVL/LG/TD, CVL/LG/HD, and CVL/LG/OD mixtures, indicating that the rate of $(LG)_2$·alcohol formation is in the order: $(LG)_2\cdot TD > (LG)_2\cdot HD \sim (LG)_2\cdot OD$.

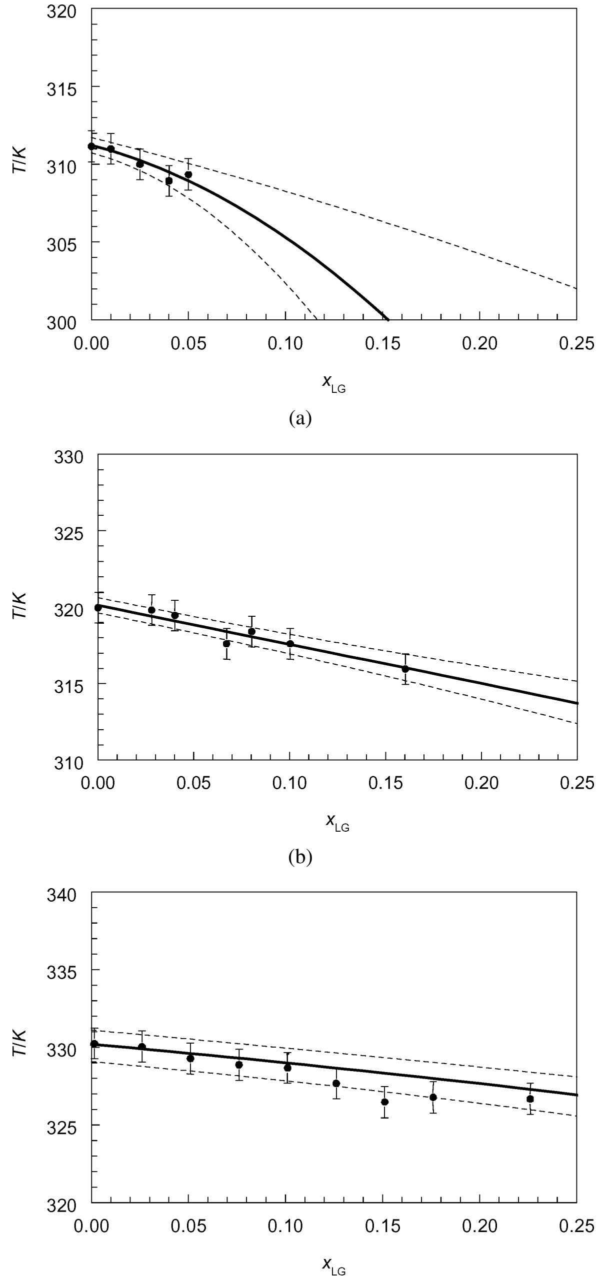
3.1.3. Thermodynamic analysis of LG-solvent interactions

As established above, changing the alkyl-chain length of the solvent component has a dramatic influence on the thermochromic properties of the dye/developer/solvent mixture. The binary phase diagrams for LG/TD, LG/HD, and LG/OD can be used to quantify and rank the interactions between the components. The method used here is based on melting points, expressed as [20–22]:

$$T_{\mathrm{fus,A}} = \left(\Delta_{\mathrm{fus}} H^{\circ}_{\mathrm{A}} / R + W^{\mathrm{H}}_{\mathrm{A}} (1 - x_{\mathrm{A}})^2 / R\right) \Big/ \left(\Delta_{\mathrm{fus}} H^{\circ}_{\mathrm{A}} / R T^{\circ}_{\mathrm{fus,A}} - \ln(x_{\mathrm{A}})\right). \quad (1)$$

This equation was fit to experimental liquidus data using W^H (<0 for attractive A-B interactions) as a fitting parameter.

The experimental and least-squares-fit liquidus curves for the alcohol (TD, HD and OD) in LG/TD, LG/HD and LG/OD mixtures are shown in Fig. 5. The W^{H} values, $W^{\mathrm{H}}_{\mathrm{TD}} = -20 \pm 10$ kJ mol^{-1}, $W^{\mathrm{H}}_{\mathrm{HD}} = +1 \pm 4$ kJ mol^{-1}, and $W^{\mathrm{H}}_{\mathrm{OD}} = -2 \pm 2$ kJ mol^{-1}, show a significant attractive interaction for TD with LG, while



(a)

(b)

(c)

Figure 5 The alcohol liquidus of (a) the lauryl gallate/1-tetradecanol (LG/TD) binary phase diagram, (b) the lauryl gallate/1-hexadecanol (LG/HD) binary phase diagram, and (c) the lauryl gallate/1-octadecanol (LG/OD) binary phase diagram. The calculated liquidus (solid line) is compared with the experimental data, shown as data points with error bars. Dashed lines represent the range of uncertainty in the fit of W^H, including uncertainties associated with T_{fus} and $\Delta_{fus}H$ for the alcohol in Equation 1.

HD/LG and OD/LG show much weaker, nearly ideal, interactions. Similar results have been obtained from the analysis of the melting point near the $(LG)_2$·alcohol compound in these systems [23]. The magnitude and direction of this interaction is important in determining the viability of these systems as reversible thermochromic materials (*vide infra*).

3.2. Influence of the developer on CVL/developer/alcohol systems

3.2.1. CVL-Alkyl gallate complexes

From our earlier thermal and spectroscopic studies, we found that LG and CVL form a colored complex with an equilibrium stoichiometry of $(LG)_3$·CVL [6]. The other developers investigated, propyl gallate (PG) and octyl gallate (OG), share the same functional groups as LG, and we found that they, too, form colored complexes with CVL dye. The stoichiometries of the PG/CVL and OG/CVL colored complexes were determined by annealing mixtures using DSC; exothermic and endothermic events consistent with the crystallization and fusion of excess alkyl gallate were observed in mixtures that had been slowly cooled from the melt. For PG/CVL, exotherms were observed between 80 and 120°C for mixtures with $x_{CVL} < 0.33$ [23], corresponding to a stoichiometry of $(PG)_2$·CVL for its equilibrium colored complex. For OG/CVL mixtures, exotherms were observed [23] between 60 and 80°C for mixtures with $x_{CVL} < 0.20$ corresponding to a colored complex of equilibrium stoichiometry $(OG)_4$·CVL. These stoichiometries were both confirmed by vibrational spectroscopy [23]. Without annealing, metastable complexes with stoichiometries of up to (alkyl gallate)$_9$·CVL have been observed [6, 23]. (Complexes of approximately 2:1 stoichiometry have recently been found for the BPA-DDSIX developer-dye system [24].)

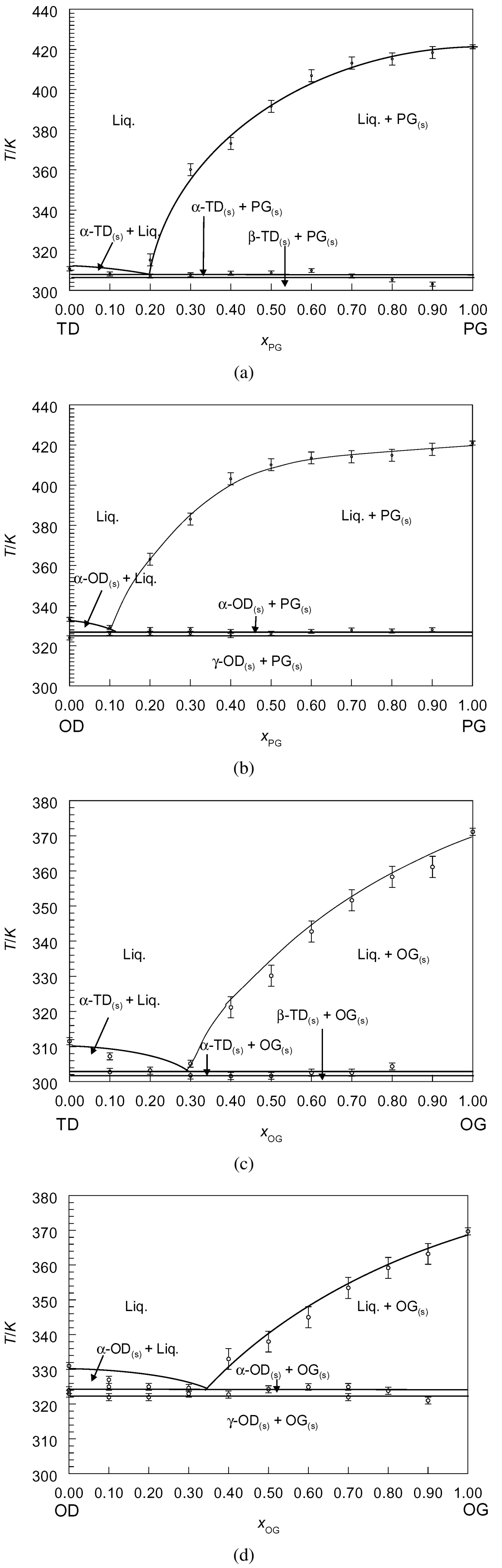
Raman spectra of $(PG)_2$·CVL, $(OG)_4$·CVL, and $(LG)_3$·CVL show nearly identical features. The most significant assignments are attributed to the ring-open form of crystal violet lactone, 1584 cm^{-1} (υ(C=N)) and 920 cm^{-1} (β(C=NR$_2$)), with the asymmetric and symmetric bending modes (β(N$^+$C$_4$)) appearing as weak peaks at 940 and 790 cm^{-1}. Peaks assigned to the carboxylate moiety of ring-open CVL were observed at 1359 cm^{-1} (υ(CO—)$_{sym}$). and 730 cm^{-1} (γ(CO—)$_{sym}$) [15–17]. Although there is some variation in equilibrium complex stoichiometry, alkyl gallate—CVL interactions did not show significant variation as the alkyl-chain length of the alkyl gallate developer was changed, and the structural features attributed to color development by formation of developer-CVL complexes are essentially the same.

3.2.2. Alkyl gallate/alcohol binary mixtures

The alkyl gallate/alcohol binary phase diagrams provide useful data for the examination of developer-solvent interactions. The PG/TD, PG/OD, OG/TD and OG/OD phase diagrams, as derived from DSC on heating, are shown in Fig. 6. All show simple eutectic mixtures, as also was observed for PG/HD and OG/HD [23] and for long-chain ketones with long-chain alkanes [25]. This is in striking contrast to the LG/alcohol phase diagrams, *vide supra*, which all showed the formation of congruently melting compounds of the form $(LG)_2$·alcohol. The lack of compound formation in the similar PG/alcohol and OG/alcohol systems shows that their developer-solvent interactions are significantly less attractive than those observed in the LG/alcohol systems, as we now quantify through thermodynamic analysis.

3.2.3. Thermodynamic analysis

Here W^H was determined by fitting a first-order Margules equation to the alcohol fusion enthalpy data as



(a)

(b)

(c)

(d)

Figure 6 Alkyl gallate/alcohol binary phase diagrams, as determined on heating. (a) propyl gallate/1-tetradecanol (PG/TD); (b) propyl gallate/1-octadecanol (PG/OD); (c) octyl gallate/1-tetradecanol (OG/TD); (d) octyl gallate/1-octadecanol (OG/OD). The points with error bars represent measured DSC transition (onset) temperatures and uncertainties. The phase boundaries are added to aid the eye.

alkyl gallate is added [21, 22]:

$$\Delta_{\mathrm{fus}}H^{\mathrm{obs}} = \Delta_{\mathrm{fus}}H^{\mathrm{ideal}} + W^{\mathrm{H}}x_{\mathrm{A}}x_{\mathrm{B}}, \qquad (2)$$

where W^{H} is the fit parameter, given in Table I for PG/alcohol and OG/alcohol mixtures. W^{H} values show two trends within these data. First, more negative W^{H} values are observed in OG/alcohol mixtures relative to PG/alcohol mixtures. This indicates that, for a given alkyl gallate/alcohol combination in this series, the alcohol is more attracted to OG than to PG. Although OG is more strongly attracted to the alcohols than is PG, the attraction is not strong enough for compound formation, as seen in LG-alcohol systems. Second, for a given alkyl gallate, W^{H} values show that increasing the alkyl-chain length of the alcohol beyond 14 carbons decreases the attractive interaction between the alkyl gallate and the alcohol.

3.2.4. Thermochromism in CVL/PG/alcohol mixtures

The melted then quenched CVL/PG/alcohol mixtures were highly colored solids regardless of cooling rate (slow and rapid cooling produced indistinguishable color density) and showed little change of color over extended periods of time (see Fig. 7). With little or no solid-state color contrast, combined with negligible decolorization rates, none of these mixtures displayed rewritable thermochromic properties. However, some of these compositions can be used to produce conventional reversible thermochromic behaviour. PG is considered an “ideal developer” for conventional (non-hysteretic) reversible thermochromic applications [26–28]. If a mixture is prepared with low proportions of PG relative to alcohol solvent (PG:alcohol <1:10 mole ratio), the resulting liquid has reduced color density relative to the solid. This provides a mechanism for reversible thermochromism that has been addressed by Burkinshaw *et al.* [29] and Luthern and Peredes [30], based on a mixture with a highly stable colored solid state, and a solvent able to dissolve a significant portion of the developer in the molten state. However, if developer is used in amounts in excess of its solubility in the solvent, the excess developer interacts with the dye, the liquid state develops high color density, and the thermochromic effect is lost.

3.2.5. Thermochromism in CVL/OG/alcohol mixtures

Cooling rate did not appear to make a significant difference in the initial color density of CVL/OG/alcohol mixtures (see Fig. 8). However, the color stability was not as high as that observed in CVL/PG/alcohol mixtures and noticeable color density was lost as the mixtures equilibrated. Mixtures with low concentrations of developer relative to solvent (OG:alcohol < 1:10 mole ratio) again displayed low color density in the liquid state and are, as for CVL/PG/alcohol, amenable to applications as conventional reversible thermochromic materials.

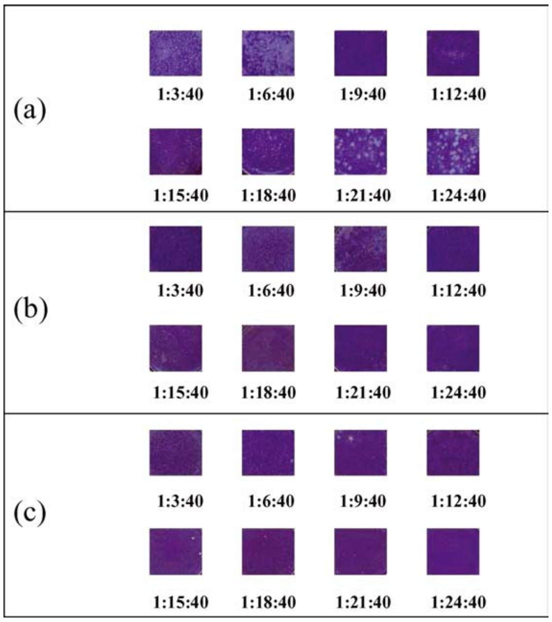


Figure 7 Images of selected (a) crystal violet lactone/propyl gallate/1-tetradecanol (CVL/PG/TD), (b) CVL/propyl gallate/1-hexadecanol (CVL/PG/HD) and (c) crystal violet lactone/propyl gallate/1-octadecanol (CVL/PG/OD) mixtures obtained after one week of equilibration at 25°C following slow cooling from the melt.

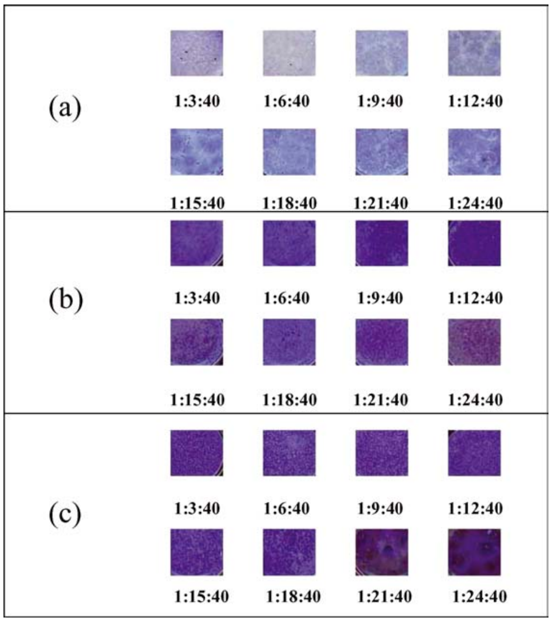


Figure 8 Images of selected (a) crystal violet lactone/octyl gallate/1-tetradecanol (CVL/OG/TD) (b) crystal violet lactone/octyl gallate/1-hexadecanol (CVL/OG/HD) and (c) crystal violet lactone/octyl gallate/1-octadecanol (CVL/OG/OD) mixtures obtained after one week of equilibration at 25°C following slow cooling from the melt.

3.3. Thermochromism and design rules

3.3.1. Comparison of thermochromic properties

We have found that PG and OG developers produce mixtures with poor reversible thermochromic properties when mixed with CVL dye and alcohol solvents. On the other hand, LG developer produces reversible thermochromic properties with varying quality, from poor to good, depending on the developer-solvent interaction. The primary problem associated with reduced developer-solvent interactions is an increase in equilibrium color density, and concomitant low color contrast. Equilibrium Raman spectra of CVL/alkyl gallate/TD, and CVL/alkyl gallate/OD show that the intensity of the peak at 1584 cm^{-1} (corresponding to $\upsilon(\mathrm{C{=}N})$ of ring-open CVL) is strongly correlated to color density. The ratios of the 1584 cm^{-1} peak intensity to the 1616 cm^{-1} peak intensity (an aromatic $\upsilon(\mathrm{C{=}C})$ mode common to all three alkyl gallates) after quenching and room-temperature equilibration are presented in Table II. These results show that equilibrium color density (which correlates with concentration of ring-open CVL) increases as the developer-solvent interaction becomes less attractive.

3.3.2. Design rules

A general summary of the contrast and decolorization rates of the nine systems examined in this study is given in Table III. CVL/PG/alcohol mixtures display poor contrast and slow decolorization rates. CVL/OG/TD (1:6:40) shows good contrast but requires very long periods of time (days) for equilibration. CVL/LG/TD

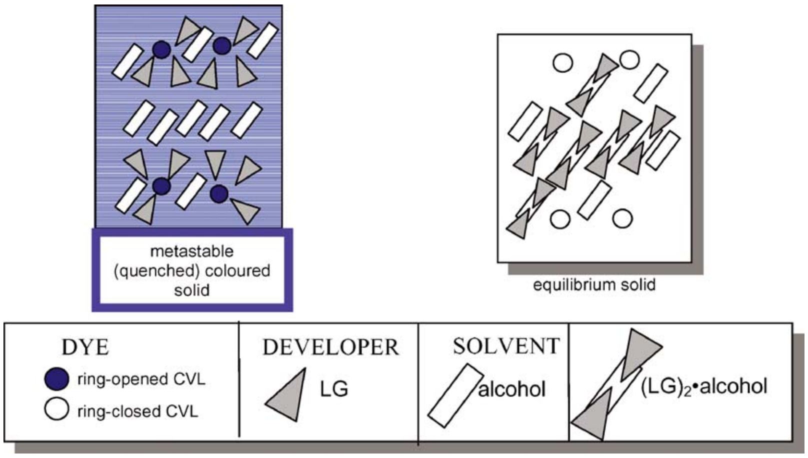


Figure 9 A schematic view of the optimal reversible thermochromic mechanism based on the CVL/LG/alcohol mixture. The metastable solid mixture is colored and characterized by attractive dye-developer interactions. Stronger developer-solvent attractive interactions result in the formation and phase separation of $(\mathrm{LG})_2{\cdot}$alcohol in the equilibrium, non-colored solid.

TABLE I Summary of the interaction parameters determined for the alcohol component, $W^{\mathrm{H}}_{\mathrm{alcohol}}$, of alkyl gallate/alcohol (developer/solvent) binary mixtures

	1-tetradecanol (TD) $W^{\mathrm{H}}_{\mathrm{TD}}/(\mathrm{kJ\ mol^{-1}})$	1-hexadecanol (HD) $W^{\mathrm{H}}_{\mathrm{HD}}/(\mathrm{kJ\ mol^{-1}})$	1-octadecanol (OD) $W^{\mathrm{H}}_{\mathrm{OD}}/(\mathrm{kJ\ mol^{-1}})$
Propyl gallate (PG)	−18 ± 6	13 ± 8	+2 ± 2
Octyl gallate (OG)	−46 ± 2	−20 ± 4	−5 ± 5
Lauryl gallate (LG)	NC*	NC*	NC*

*NC = not comparable, since the solid in coexistence with the alcohol is not the alkyl gallate, but rather the solid compound $(\mathrm{LG})_2\cdot$alcohol.

TABLE II The ratios of the Raman intensities of the υ(C=N) mode in ring-open crystal violet lactone (at 1584 $\mathrm{cm^{-1}}$) to the aromatic υ(C=C) mode of propyl gallate, octyl gallate, and lauryl gallate at (1616 $\mathrm{cm^{-1}}$) in crystal violet lactone/alkyl gallate/1-alcohol mixtures (1:6:40 mole ratio) obtained after quenching in liquid nitrogen and equilibrating at 25°C for 24 h

	1-tetradecanol (TD)	1-hexadecanol (HD)	1-octadecanol (OD)
Propyl gallate (PG)	0.4 ± 0.2	0.8 ± 0.2	0.7 ± 0.2
Octyl gallate (OG)	0.3 ± 0.2	0.5 ± 0.2	0.4 ± 0.2
Lauryl gallate (LG)	0	0	0.1 ± 0.2

TABLE III Comparison of the reversible thermochromic properties, based on quality of color contrast and decolorization rates, for the nine crystal violet lactone/alkyl gallate/alcohol (dye/developer/solvent) thermochromic systems examined. A system is considered good only if it displays high color contrast and rapid decolorization

	1-tetradecanol (TD)	1-hexadecanol (HD)	1-octadecanol (OD)
Propyl gallate (PG)	Very poor	Very poor	Very poor
Octyl gallate (OG)	Poor	Very poor	Very poor
Lauryl gallate (LG)	Good	Poor	Poor

(1:6:40) has good color contrast and decolorizes in 30–60 s at room temperature while CVL/LG/HD and CVL/LG/OD (1:6:40) have poor color contrast and require hours to equilibrate.

Our studies have shown that the competition between the developer-dye and developer-solvent interaction plays a pivotal role in optimizing reversible thermochromic properties. In the systems examined, those that have sufficiently strong developer-solvent interactions to form developer-solvent compounds show the best color contrast and fastest decolorization rates. This is shown schematically in Fig. 9. Systems that do not form developer-solvent compounds tend to form highly stable colored solids and are better suited for conventional thermochromic applications. Within the system studied, mixtures containing PG show high color stability and little to no color contrast between equilibrium and metastable mixtures. Mixtures with OG developer have more attractive developer-solvent interactions and show better color contrast than CVL/PG/alcohol mixtures. Systems containing PG and OG color developers show the same trend in attractive developer-solvent interaction as observed for systems containing LG color developer: the attractive interaction increases as the alcohol chain length is decreased within the range explored. Quite likely, for each developer there is an alcohol alkyl chain length which would optimize the developer-solvent attraction, and, hence, increase the probability of reversible thermochromic properties.

Desirable reversible thermochromic properties of similar mixtures could be optimized by using strongly attractive developer-solvent combinations that can compete with attractive dye-developer interactions in the solid state. Therefore, the following design rules are proposed for the optimization of reversible thermochromic properties: high color contrast, low equilibrium color density, and rapid decolorization rates could be optimized by selecting developer-solvent combinations that show strongly attractive interactions, preferably displaying binary compound formation in the solid state.

Acknowledgement

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