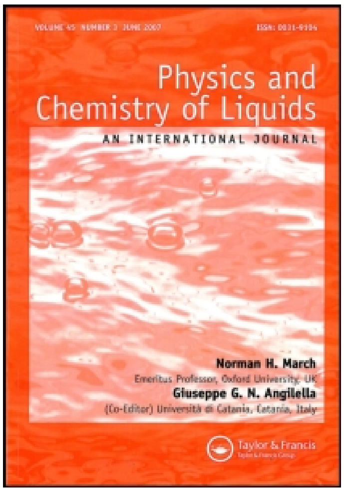

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Thermodynamic investigation of the surface tension of liquid mixtures of *cis*-decaline with either methyl–acetate or *n*-pentyl–acetate in the temperature range from 283.15 to 303.15 K

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Surface tensions (σ) and densities (ρ) of binary liquid mixtures of *cis*-decaline with either methyl–acetate (MAC) or *n*-pentyl–acetate (PAC) were measured over the entire composition range at the temperatures 283.15, 288.15, 298.15 and 303.15 K. The excess surface tensions (σ^E) and the excess molar volumes (V^E) were calculated. The σ^E and V^E values were fitted by the Redlich–Kister polynomial equation and the A_k coeffients as well as the standard deviations (d) between the calculated and the experimental excess parameters were derived. The σ values were further used for the calculation of the surface entropy (S^S) and the surface enthalpy (H^S) per unit surface area. The lyophobicity (β) and the surface mole fraction (x_2^S) of the surfactant component (either MAC or PAC) were also derived using the extended Langmuir model. The results were used for the characterisation of the molecular interactions at the surface and the bulk-phase region.

Keywords: *cis*-Decaline; excess molar volume; excess surface tension; Langmuir model; lyophobicity; methyl–acetate; *n*-pentyl–acetate; surface entropy; surface mole fraction

1. Introduction

The thermodynamic properties of liquids and liquid mixtures have been extensively used during the last years for the characterisation of the molecular interactions between the components of the liquid [1–3]. Among the experimental methods for the investigation of the molecular interactions in liquid mixtures, the surface tension can be distinguished because of its simplicity and its precision. The surface tension represents the Gibbs free energy per unit surface area required for the formation of the liquid–air interface. It can be considered to be the result of the specific molecular interactions that occur not only at the surface but also in the bulk-phase of the liquid. The variation in surface tension depends on the variation in molecular forces as well as on the variation of the density of the molecular packing [4–6].

Continuing previous investigations of the surfaces of binary liquid systems [7–9], here we report the surface tensions (σ) and densities (ρ) of binary mixtures of *cis*-decaline

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(DCL) with either methyl–acetate (MAC) or *n*-pentyl–acetate (PAC) at four different temperatures, 283.15, 288.15, 298.15 and 303.15 K. From the experimental σ and ρ values, the excess molar volumes (V^E) and the excess surface tensions (σ^E) were calculated and fitted by the Redlich–Kister polynomial equation. The surface entropies (S^S) and the surface enthalpies per unit surface area (H^S) were obtained. Furthermore, the surface mole fractions (x_2^S) and the lyophobicity (β) of the surfactant component (either MAC or PAC) relative to DCL were derived using the extended Langmuir model. The aim of the present article is the investigation of the molecular interactions that occur at the surface and the bulk-phase region.

Surface tension data for pure liquids and liquid mixtures are widely used for chemical engineering applications [10–12] because surface properties play an important role in mass transfer processes such as liquid–liquid extraction, gas absorption, distillation, and condensation. A critical review of the available literature reveals that even if there is a large database on surface properties of a number of binary liquid mixtures over wide temperature and concentration ranges [13–19], experimental σ values for the DCL binary mixtures are still not available. Consequently, another scope of the present article is to provide accurate experimental σ values for binary mixtures of DCL with either MAC or PAC in a large composition and temperature range.

2. Experimental section

2.1. *Materials*

cis-Decaline, (mass fraction purity 0.99), MAC (mass fraction purity 0.99), and PAC (mass fraction purity 0.99) were Merck products and were used without further purification. The solvents were dried over 0.4 nm molecular sieves before use. The purity of the liquids was assessed by comparing the experimental surface tensions of the pure liquids with the available literature values at 298.15 K. The experimental values of $\sigma = 32.1\,\mathrm{mN\,m^{-1}}$ (DCL), $\sigma = 25.4\,\mathrm{mN\,m^{-1}}$ (MAC), and $\sigma = 25.8\,\mathrm{mN\,m^{-1}}$ (PAC), were found to agree satisfactorily with the available literature values of $\sigma = 32.2\,\mathrm{mN\,m^{-1}}$ (DCL) [20], $\sigma = 24.7\,\mathrm{mN\,m^{-1}}$ (MAC) [21], and $\sigma = 25.2\,\mathrm{mN\,m^{-1}}$ (PAC) [22].

2.2. *Solutions*

The binary mixtures were prepared by mass using an analytical balance (Mettler, A210P) with a precision of ±0.0001 g. The mole fraction of each mixture was obtained from the measured masses of the components with an accuracy of ±0.0001. All molar quantities are based on the relative atomic mass table of 1985 issued by IUPAC.

2.3. *Apparatus and procedures*

The densities were measured with an Anton Paar digital precision densimeter (model DMA 58, Austria) with a built-in solid state thermostat. The cell was calibrated with dry air and doubly distilled water in the temperature range from 283.15 to 303.15 K. The thermostat temperature was constant to ±0.01 K. The estimated uncertainty of the measured density values was $\pm 0.00005\,\mathrm{g\,cm^{-3}}$.

The surface tensions were measured using a Du Nouy tensiometer A. Krüss (Model K8600, Germany) equipped with a platinum–iridium ring having a wire diameter of

0.37 mm. The platinum–iridium ring was cleaned with chromosulfuric acid and boiling distilled water. The tensiometer was calibrated with distilled water in the temperature range from 283.15 to 303.15 K and a correction factor was employed in all cases. The surface tensions of the water at different temperatures were selected from the literature [23]. The samples were introduced into a double-walled glass cell connected to a water-bath thermostat. A precision digital thermometer was used to read the cell temperature with an accuracy of ±0.01 K. The error of the surface tension values was found to be less than $\pm 0.1\,\mathrm{mN\,m^{-1}}$.

3. Results and discussion

The experimental values of density and surface tension for the DCL/MAC and DCL/PAC binary mixtures at 283.15, 288.15, 298.15 and 303.15 K are listed in Tables 1 and 2. The values of σ are presented graphically *versus* the mole fraction of DCL (x_1) in Figures 1 and 2. There is a systematic non-linear decrease of σ with the increase of the mole fraction of either MAC or PAC. Furthermore, the variation of σ with the temperature was found to be linear with a negative temperature coefficient, $(\partial\sigma/\partial T)_P < 0$, which is in perfect agreement with the reports of Jasper and others [24–26].

A comparison of the values of the surface tension of the pure components indicates that the σ value of DCL is about 20% larger than that of either MAC or PAC. Since the surface tension is the energy per unit area required to bring the molecules from the bulk-phase region to the surface, the difference between the σ values demonstrates that the interactions between the ester molecules (either MAC or PAC) in the bulk-phase region are weaker compared to the interactions among the DCL molecules.

The thermodynamic properties, excess molar volumes and excess surface tensions were determined in order to get information about the type and the strength of the molecular interactions in the binary systems. The calculations of V^E and σ^E were carried out from the well known general equation [27,28]:

$$\Delta Y = Y_m - \sum_{i=1}^{2} c_i Y_i, \tag{1}$$

where ΔY is the V^E or σ^E, Y_m and Y_i the property of the mixture and the respective property of the ith pure component, respectively, and c_i the mixture composition expressed in mole fraction (x_i). The uncertainties of the derived V^E and σ^E values are $\pm 0.006\,\mathrm{cm^3\,mol^{-1}}$ and $\pm\,0.1\,\mathrm{mN\,m^{-1}}$, respectively. The calculated V^E and σ^E values are listed in Tables 3 and 4 and presented graphically *versus* the mole fraction of DNP (x_1) in Figures 3–6.

Each set of the calculated values ΔY (V^E and σ^E) was fitted by the Redlich–Kister [29] polynomial equation in order to derive the binary coefficients A_k:

$$\Delta Y = x_1 x_2 \sum_{k=0}^{n} A_k (2x_1 - 1)^k. \tag{2}$$

A non-linear least-squares method was used to estimate the parameters A_k of the polynomials. In each case, the optimum number m of the A_k coefficients ($m = n + 1$) was

Table 1. Mole fractions of DCL (x_1), densities (ρ) and surface tensions (σ) of binary mixtures of DCL with PAC in the temperature range from 283.15 to 303.15 K.

x_1	$\rho/\mathrm{g\,cm^{-3}}$	$\sigma/\mathrm{mN\,m^{-1}}$	x_1	$\rho/\mathrm{g\,cm^{-3}}$	$\sigma/\mathrm{mN\,m^{-1}}$
DCL/PAC					
	$T = 283.15$ K			$T = 288.15$ K	
0.0000	0.88794	27.2	0.0000	0.88380	26.7
0.1100	0.88783	27.8	0.1100	0.88355	27.3
0.2377	0.88787	28.4	0.2377	0.88355	28.0
0.3010	0.88798	28.8	0.3010	0.88366	28.3
0.3512	0.88812	29.1	0.3512	0.88380	28.6
0.4078	0.88832	29.4	0.4078	0.88402	28.9
0.5012	0.88876	29.9	0.5012	0.88451	29.5
0.6096	0.88944	30.6	0.6096	0.88528	30.1
0.7121	0.89025	31.2	0.7121	0.88622	30.8
0.7724	0.89080	31.6	0.7724	0.88686	31.2
0.8210	0.89129	31.9	0.8210	0.88743	31.5
0.9100	0.89228	32.5	0.9100	0.88858	32.2
1.0000	0.89341	33.1	1.0000	0.88990	32.8
	$T = 298.15$ K			$T = 303.15$ K	
0.0000	0.87380	25.8	0.0000	0.87030	25.4
0.1100	0.87375	26.3	0.1100	0.87005	25.8
0.2377	0.87401	27.0	0.2377	0.87015	26.5
0.3010	0.87427	27.3	0.3010	0.87036	26.8
0.3512	0.87453	27.6	0.3512	0.87059	27.1
0.4078	0.87489	28.0	0.4078	0.87094	27.5
0.5012	0.87564	28.5	0.5012	0.87169	28.1
0.6096	0.87673	29.3	0.6096	0.87284	28.8
0.7121	0.87799	30.0	0.7121	0.87421	29.6
0.7724	0.87883	30.4	0.7724	0.87514	30.1
0.8210	0.87956	30.8	0.8210	0.87596	30.5
0.9100	0.88104	31.5	0.9100	0.87762	31.1
1.0000	0.88270	32.1	1.0000	0.87950	31.8

determined through an examination of the variation of the standard deviation (d) according to the equation:

$$d = \left[\sum \frac{\left(\Delta Y_{\mathrm{Calc}} - \Delta Y_{\mathrm{Exp}}\right)^2}{(P - m)} \right]^{1/2}, \tag{3}$$

where P represents the number of the experimental data and m represents the number of the coefficients used for fitting the experimental values in Equation (2). The estimated values of A_k and d for the V^E and σ^E properties are presented in Table 5. A graphical comparison between the experimental and the theoretical V^E and σ^E values is shown in Figures 3–6. The agreement between the experimental excess quantities and those calculated from the Redlich–Kister relation was found to be satisfactory.

Table 2. Mole fractions of DCL (x_1), densities (ρ) and surface tensions (σ) of binary mixtures of DCL with MAC in the temperature range from 283.15 to 303.15 K.

x_1	$\rho/\mathrm{g\,cm^{-3}}$	$\sigma/\mathrm{mN\,m^{-1}}$	x_1	$\rho/\mathrm{g\,cm^{-3}}$	$\sigma/\mathrm{mN\,m^{-1}}$
DCL/MAC					
	$T = 283.15\,\mathrm{K}$			$T = 288.15\,\mathrm{K}$	
0.0000	0.94680	26.6	0.0000	0.94020	26.3
0.0502	0.93827	26.8	0.0502	0.93270	26.4
0.1322	0.92706	27.0	0.1322	0.92080	26.7
0.2658	0.91311	27.7	0.2658	0.90810	27.3
0.3322	0.90832	28.1	0.3322	0.90430	27.7
0.4312	0.90215	28.7	0.4312	0.89800	28.3
0.5021	0.89857	29.1	0.5021	0.89410	28.7
0.6032	0.89439	29.9	0.6032	0.89090	29.5
0.6906	0.89239	30.6	0.6906	0.88850	30.2
0.7521	0.89136	31.0	0.7521	0.88720	30.7
0.8533	0.89144	31.9	0.8533	0.88700	31.6
0.9011	0.89185	32.4	0.9011	0.88860	32.0
1.0000	0.89341	33.1	1.0000	0.88990	32.8
	$T = 298.15\,\mathrm{K}$			$T = 303.15\,\mathrm{K}$	
0.0000	0.92743	25.4	0.0000	0.92070	25.0
0.0502	0.91960	25.5	0.0502	0.91470	25.1
0.1322	0.90940	25.7	0.1322	0.90305	25.2
0.2658	0.89820	26.1	0.2658	0.89310	25.6
0.3322	0.89415	26.4	0.3322	0.88850	25.8
0.4312	0.88820	26.9	0.4312	0.88398	26.3
0.5021	0.88504	27.4	0.5021	0.88095	26.8
0.6032	0.88166	28.3	0.6032	0.87830	27.7
0.6906	0.88023	29.0	0.6906	0.87650	28.4
0.7521	0.87959	29.6	0.7521	0.87560	29.0
0.8533	0.88015	30.6	0.8533	0.87555	30.1
0.9011	0.88097	31.1	0.9011	0.87810	30.6
1.0000	0.88270	32.1	1.0000	0.87950	31.8

The dependence of the V^E on the mole fraction of DCL (x_1) for the DCL/PAC and DCL/MAC binary mixtures is illustrated in Figures 3 and 4, respectively. The V^E values of the DCL/PAC binary mixtures are positive over the entire range of the composition, display a maximum at the equimolar composition ($x_1 \approx 0.5$), and become more positive with the rise of the temperature (Figure 3). Similar trends can be derived from the V^E values of the DCL/MAC binary mixtures (Figure 4) with the exception that the variation of V^E with the temperature is almost insignificant. The positive V^E values indicate volume expansion upon mixing. It is obvious that the association between like molecules in the pure liquids (the self-association) is thermodynamically more favourable than the association between unlike molecules in the binary mixtures (the hetero-association). Anyhow, the positive deviations of V^E follow the sequence: PAC $<$ MAC, indicating that in binary mixtures which contain MAC the hetero-association is weaker.

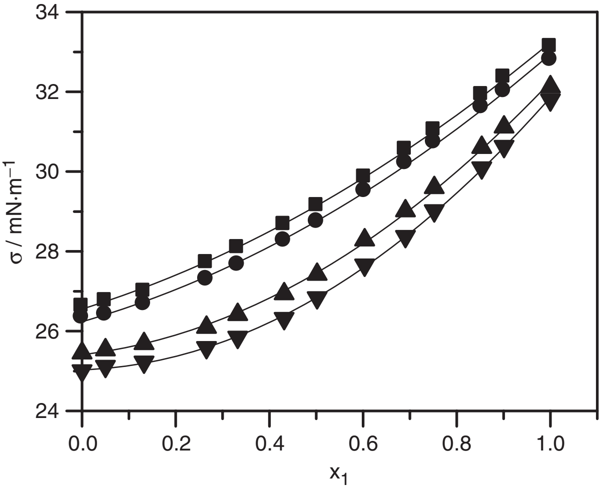

Figure 1. Surface tension (σ) *vs.* the mole fraction of DCL (x_1) for DCL/MAC binary mixtures at various temperatures: $T = 283.15$ K (■), $T = 288.15$ K (●), $T = 298.15$ K (▲), and $T = 303.15$ K (▼).

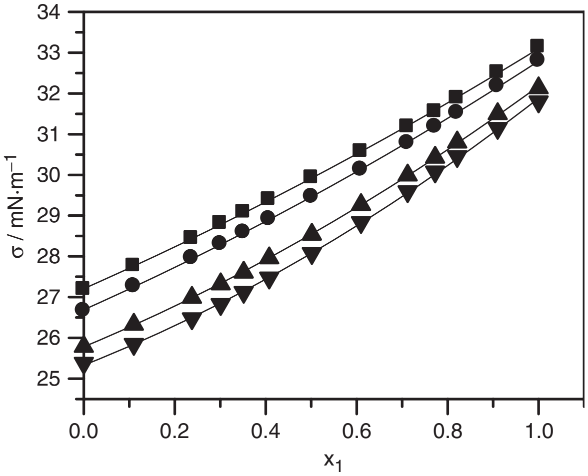

Figure 2. Surface tension (σ) *vs.* the mole fraction of DCL (x_1) for DCL/PAC binary mixtures at various temperatures: $T = 283.15$ K (■), $T = 288.15$ K (●), $T = 298.15$ K (▲), and $T = 303.15$ K (▼).

The σ^E values of the binary mixtures investigated are plotted *versus* the mole fraction of DCL (x_1) in Figures 5 and 6. The σ^E values are negative in the whole range of composition, pass through a minimum at $x_1 \approx 0.5$, and tend to become more negative with the rise of the temperature. The negative σ^E values indicate a different molecular distribution between the surface and the bulk-phase region. Most likely the surface concentration of the surfactant component (either MAC or PAC) is higher than its bulk-phase concentration (see below x_2^S values, Table 8). The affinity of MAC for the surface seems to be larger than that of PAC as the deviations of σ^E follow the sequence: PAC < MAC (see below β values, Table 7). According to the reports in the

Table 3. Mole fractions of DCL (x_1), excess molar volumes (V^E) and excess surface tensions (σ^E) of binary mixtures of DCL with PAC in the temperature range from 283.15 to 303.15 K.

x_1	$V^E/\mathrm{cm^3\,mol^{-1}}$	$\sigma^E/\mathrm{mN\,m^{-1}}$	x_1	$V^E/\mathrm{cm^3\,mol^{-1}}$	$\sigma^E/\mathrm{mN\,m^{-1}}$
		DCL/PAC			
	$T = 283.15$ K			$T = 288.15$ K	
0.0000	0.000	0.00	0.0000	0.000	0.00
0.1100	0.123	−0.09	0.1100	0.160	−0.07
0.2377	0.238	−0.16	0.2377	0.297	−0.16
0.3010	0.280	−0.17	0.3010	0.347	−0.21
0.3512	0.304	−0.20	0.3512	0.377	−0.23
0.4078	0.324	−0.22	0.4078	0.400	−0.25
0.5012	0.338	−0.24	0.5012	0.415	−0.27
0.6096	0.325	−0.25	0.6096	0.398	−0.27
0.7121	0.282	−0.24	0.7121	0.344	−0.25
0.7724	0.243	−0.22	0.7724	0.296	−0.22
0.8210	0.204	−0.19	0.8210	0.247	−0.18
0.9100	0.114	−0.09	0.9100	0.139	−0.07
1.0000	0.000	0.00	1.0000	0.000	0.00
	$T = 298.15$ K			$T = 303.15$ K	
0.0000	0.000	0.00	0.0000	0.000	0.00
0.1100	0.184	−0.15	0.1100	0.226	−0.24
0.2377	0.343	−0.31	0.2377	0.421	−0.44
0.3010	0.399	−0.38	0.3010	0.490	−0.49
0.3512	0.433	−0.40	0.3512	0.533	−0.51
0.4078	0.460	−0.42	0.4078	0.565	−0.53
0.5012	0.477	−0.43	0.5012	0.587	−0.52
0.6096	0.456	−0.39	0.6096	0.561	−0.46
0.7121	0.394	−0.31	0.7121	0.485	−0.36
0.7724	0.339	−0.26	0.7724	0.417	−0.26
0.8210	0.284	−0.19	0.8210	0.349	−0.19
0.9100	0.158	−0.06	0.9100	0.194	−0.08
1.0000	0.000	0.00	1.0000	0.000	0.00

literature [30,31], negative σ^E values appear for binary liquid mixtures in which the formation of hetero-aggregated adducts in the bulk-phase region is insignificant. Taking into account this explanation, the negative deviations of σ^E can be attributed to the preference of the surfactant molecules for the surface given that the hetero-association in the bulk-phase is somehow reduced. The last conclusion is fully consistent with the V^E values (Tables 3 and 4).

The thermodynamic investigation of the surface was performed through the determination of the entropy of the surface formation per unit surface area according to the thermodynamic equation of Clapeyron [32,33] modified for liquid surfaces:

$$S^S = -\left(\frac{\partial \sigma}{\partial T}\right)_P, \tag{4}$$

Table 4. Mole fractions of DCL (x_1), excess molar volumes (V^E) and excess surface tensions (σ^E) of binary mixtures of DCL with MAC in the temperature range from 283.15 to 303.15 K.

x_1	$V^E/\mathrm{cm^3\,mol^{-1}}$	$\sigma^E/\mathrm{mN\,m^{-1}}$	x_1	$V^E/\mathrm{cm^3\,mol^{-1}}$	$\sigma^E/\mathrm{mN\,m^{-1}}$
DCL/MAC					
$T = 283.15$ K			$T = 288.15$ K		
0.0000	0.000	0.00	0.0000	0.000	0.00
0.0502	0.304	−0.19	0.0502	0.244	−0.25
0.1322	0.703	−0.48	0.1322	0.751	−0.52
0.2658	1.232	−0.63	0.2658	1.217	−0.76
0.3322	1.370	−0.69	0.3322	1.267	−0.82
0.4312	1.556	−0.75	0.4312	1.502	−0.86
0.5021	1.645	−0.75	0.5021	1.656	−0.84
0.6032	1.717	−0.69	0.6032	1.625	−0.72
0.6906	1.598	−0.56	0.6906	1.587	−0.59
0.7521	1.474	−0.47	0.7521	1.522	−0.47
0.8533	1.005	−0.25	0.8533	1.127	−0.24
0.9011	0.721	−0.12	0.9011	0.657	−0.14
1.0000	0.000	0.00	1.0000	0.000	0.00
$T = 298.15$ K			$T = 303.15$ K		
0.0000	0.000	0.00	0.0000	0.000	0.00
0.0502	0.330	−0.25	0.0502	0.198	−0.22
0.1322	0.766	−0.65	0.1322	0.823	−0.68
0.2658	1.190	−1.13	0.2658	1.189	−1.22
0.3322	1.319	−1.25	0.3322	1.418	−1.41
0.4312	1.588	−1.39	0.4312	1.557	−1.62
0.5021	1.697	−1.38	0.5021	1.678	−1.58
0.6032	1.757	−1.19	0.6032	1.671	−1.44
0.6906	1.629	−1.05	0.6906	1.627	−1.32
0.7521	1.493	−0.88	0.7521	1.554	−1.09
0.8533	1.017	−0.54	0.8533	1.214	−0.71
0.9011	0.694	−0.35	0.9011	0.612	−0.49
1.0000	0.000	0.00	1.0000	0.000	0.00

where S^S represents the variation of the entropy per unit surface area due to interface formation. Considering that the surface enthalpy is the sum of the surface free energy required to extend the surface (e.g. the surface tension, σ) and the latent heat (q) required to maintain isothermal conditions: $H^S = \sigma + q$, the surface enthalpies per unit surface area were calculated according to the following equation [34]:

$$H^S = \sigma - T\left(\frac{\partial \sigma}{\partial T}\right)_P = \sigma + TS^S. \tag{5}$$

The calculated values of S^S and H^S for the investigated binary liquid mixtures in the temperature range from 283.15 to 303.15 K are listed in Table 6.

The H^S values are positive in the whole composition range and independent of the temperature in the range from 283.15 to 303.15 K [35].

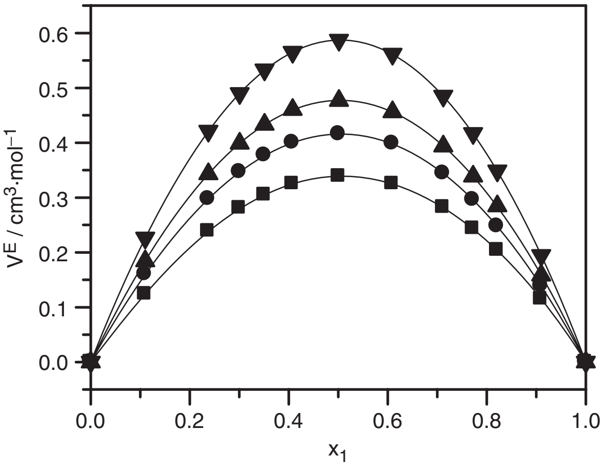

Figure 3. Excess molar volume (V^E) *vs.* the mole fraction of DCL (x_1) for DCL/PAC binary mixtures at various temperatures: $T = 283.15$ K (■), $T = 288.15$ K (●), $T = 298.15$ K (▲), and $T = 303.15$ K (▼). The symbols represent the experimental V^E values and the lines represent the V^E values calculated from the Redlich–Kister equation.

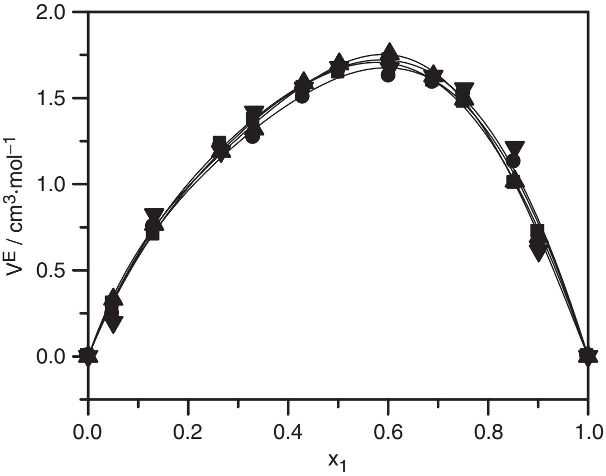

Figure 4. Excess molar volume (V^E) *vs.* the mole fraction of DCL (x_1) for DCL/MAC binary mixtures at various temperatures: $T = 283.15$ K (■), $T = 288.15$ K (●), $T = 298.15$ K (▲), and $T = 303.15$ K (▼). The symbols represent the experimental V^E values and the lines represent the V^E values calculated from the Redlich–Kister equation.

The S^S values of the DCL/MAC and DCL/PAC binary mixtures are plotted *versus* the mole fraction of DCL (x_1) in Figure 7. The S^S values are positive in the whole composition range and display a wide maximum in the concentration range $x_1 \approx 0.2$–0.4. The positive S^S values demonstrate that upon mixing the surface becomes more disordered than the surface of the pure liquids. The results indicate that the weakening of the hetero-association, which occurs in the bulk-phase region, plays probably the main role for the enrichment of the surface with the surfactant component and thus the increase of the

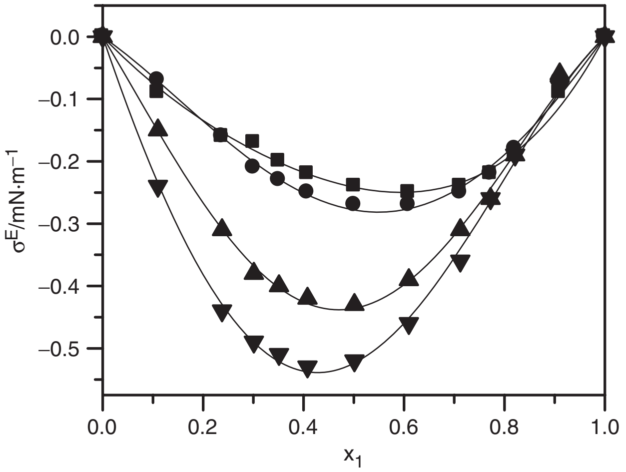

Figure 5. Excess surface tension (σ^E) *vs.* the mole fraction of DCL (x_1) for DCL/PAC binary mixtures at various temperatures: $T = 283.15$ K (■), $T = 288.15$ K (●), $T = 298.15$ K (▲), and $T = 303.15$ K (▼). The symbols represent the experimental σ^E values and the lines represent the σ^E values calculated from the Redlich–Kister equation.

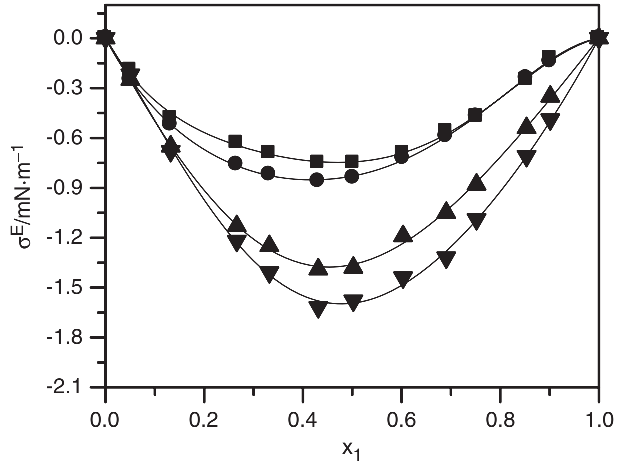

Figure 6. Excess surface tension (σ^E) *vs.* the mole fraction of DCL (x_1) for DCL/MAC binary mixtures at various temperatures: $T = 283.15$ K (■), $T = 288.15$ K (●), $T = 298.15$ K (▲), and $T = 303.15$ K (▼). The symbols represent the experimental σ^E values and the lines represent the σ^E values calculated from the Redlich–Kister equation.

disordering of the surface. However, the surface of the MAC solutions appears to be more disordered indicating once more the greater affinity of MAC for the surface. The results of S^S are in absolute accordance with the σ^E results (Tables 3 and 4), the β values (Table 7) as well as the x_2^S values (Table 8).

In order to investigate the influence of the bulk composition on the surface tension of the binary mixtures the extended Langmuir model was applied [36–38]. According to this model, the surface of the liquid mixture is considered to be a thin layer of finite depth.

Table 5. Parameters A_k of the Redlich–Kister equation (Equation (2)) and standard deviations (d) (Equation (3)) of binary mixtures of DCL with either PAC or MAC in the temperature range from 283.15 to 303.15 K.

Function	A_0	A_1	A_2	A_3	d
			DCL/PAC		
			$T = 283.15$ K		
V^E/cm^3 mol^{-1}	1.3552	0.0439	−0.0378	0.0670	0.0007
σ^E/mN m^{-1}	−0.9695	−0.4745	−0.2178	0.4730	0.0080
			$T = 288.15$ K		
V^E/cm^3 mol^{-1}	1.6627	0.0374	−0.0053	−0.0019	0.0004
σ^E/mN m^{-1}	−1.1133	−0.3489	0.2648	0.2272	0.0117
			$T = 298.15$ K		
V^E/cm^3 mol^{-1}	1.9086	0.0273	0.0001	0.0161	0.0005
σ^E/mN m^{-1}	−1.7460	0.2034	0.6841	0.2860	0.0123
			$T = 303.15$ K		
V^E/cm^3 mol^{-1}	2.3486	0.0444	−0.0112	−0.0069	0.0004
σ^E/mN m^{-1}	−2.1009	0.6512	0.5181	0.5010	0.0084
			DCL/MAC		
			$T = 283.15$ K		
V^E/cm^3 mol^{-1}	6.6711	1.9715	1.0110	−1.2936	0.0253
σ^E/mN m^{-1}	−2.9771	0.3420	0.2357	2.0658	0.0198
			$T = 288.15$ K		
V^E/cm^3 mol^{-1}	6.4686	2.2965	1.6814	−1.5056	0.0755
σ^E/mN m^{-1}	−3.3190	1.1404	0.2741	1.3109	0.0084
			$T = 298.15$ K		
V^E/cm^3 mol^{-1}	6.7562	2.6505	0.9497	−3.0554	0.0212
σ^E/mN m^{-1}	−5.4466	1.2441	0.9792	−0.5371	0.0232
			$T = 303.15$ K		
V^E/cm^3 mol^{-1}	6.6957	2.0815	1.6410	−1.0714	0.1086
σ^E/mN m^{-1}	−6.3756	0.6863	1.2643	−1.1608	0.0305

At equilibrium the relation between the surface volume fraction (φ_2^S) and the bulk volume fraction (φ_2) of the surfactant component (either MAC or PAC) is given by the following equation:

$$\varphi_2^S = \frac{\beta\varphi_2}{[1 + (\beta - 1)\varphi_2]}, \tag{6}$$

where β is a measure of the lyophobicity of the surfactant component (either MAC or PAC) relative to that of DCL and represents its tendency to be adsorbed by the surface. A value of β close to unity shows the same affinity of the surfactant component for both the bulk-phase region and the surface, whereas $\beta > 1$ demonstrates the greater affinity of the surfactant component for the surface. The bulk volume fraction of either MAC or PAC (φ_2) is obtained from the following equation:

$$\varphi_2 = \frac{x_2 V_2}{(x_1 V_1 + x_2 V_2)}, \tag{7}$$

where V_1 and V_2 are the molar volumes of DCL and either MAC or PAC, respectively.

Table 6. Mole fractions of DCL (x_1), surface entropies (S^S) and surface enthalpies per unit area (H^S) of binary mixtures of DCL with either PAC or MAC in the temperature range from 283.15 to 303.15 K.

x_1	S^S/mJ m^{-2} K^{-1}	H^S/mJ m^{-2}	x_1	S^S/mJ m^{-2} K^{-1}	H^S/mJ m^{-2}
	DCL/PAC			DCL/MAC	
0.0000	0.090	52.6	0.0000	0.083	50.1
0.1100	0.096	54.8	0.0502	0.083	50.4
0.2377	0.098	56.2	0.1322	0.091	52.7
0.3010	0.099	56.9	0.2658	0.109	58.7
0.3512	0.098	56.8	0.3322	0.115	60.6
0.4078	0.096	56.5	0.4312	0.121	63.0
0.5012	0.093	56.2	0.5021	0.119	62.8
0.6096	0.087	55.1	0.6032	0.113	61.8
0.7121	0.079	53.7	0.6906	0.111	62.1
0.7724	0.074	52.6	0.7521	0.104	60.4
0.8210	0.072	52.1	0.8533	0.094	58.5
0.9100	0.068	51.9	0.9011	0.088	57.2
1.0000	0.067	52.1	1.0000	0.067	52.1

Table 7. Values of lyophobicity (β) for PAC and MAC relative to DCL in the temperature range from 283.15 to 303.15 K.

T/K	β	
	PAC	MAC
283.15	1.20 ± 0.05	3.2 ± 0.1
288.15	1.20 ± 0.05	3.5 ± 0.1
298.15	1.40 ± 0.05	4.8 ± 0.1
303.15	1.67 ± 0.05	5.5 ± 0.2

According to this model, the surface tensions of the binary mixtures are related with the corresponding surface volume fractions of the components by the following equation:

$$\sigma = \varphi_1^S \sigma_1 + \varphi_2^S \sigma_2 - \lambda \varphi_1^S \varphi_2^S (\sigma_1 - \sigma_2), \tag{8}$$

where σ is the surface tension of the binary mixture, σ_1, φ_1^S the surface tension and surface volume fraction of DCL, respectively, and σ_2, φ_2^S the surface tension and surface volume fraction of either MAC or PAC, respectively. The factor λ represents the effect of the unlike-pair interactions on the surface tension of the mixture which is related to structural changes. If we assume that the structural changes upon mixing are insignificant (consequently λ becomes 0), the Equation (8) simplifies to:

$$\sigma = \varphi_1^S \sigma_1 + \varphi_2^S \sigma_2. \tag{9}$$

Table 8. Bulk mole fractions (x_2) and surface mole fractions (x_2^S) of either PAC or MAC in binary mixtures with DCL in the bulk composition range $0.05 < x_2 < 0.70$ and the temperature range from 283.15 to 303.15 K.

x_2	x_2^S			
	$T = 283.15$	$T = 288.15$	$T = 298.15$	$T = 303.15$
		DCL/PAC		
0.6488	0.6936	0.6971	0.7227	0.7377
0.5922	0.6420	0.6455	0.6696	0.6853
0.4988	0.5519	0.5566	0.5788	0.5924
0.3904	0.4450	0.4481	0.4642	0.4743
0.2879	0.3404	0.3402	0.3482	0.3548
0.2276	0.2760	0.2744	0.2780	0.2787
0.1790	0.2202	0.2170	0.2174	0.2172
0.0900	0.1094	0.1063	0.1037	0.1064
		DCL/MAC		
0.6678	0.8718	0.8847	0.9205	0.9324
0.5688	0.8116	0.8229	0.8725	0.8910
0.4979	0.7584	0.7690	0.8235	0.8411
0.3968	0.6670	0.6714	0.7261	0.7530
0.3094	0.5648	0.5689	0.6309	0.6649
0.2479	0.4833	0.4818	0.5442	0.5747
0.1467	0.3103	0.3072	0.3660	0.3958
0.0989	0.2096	0.2131	0.2587	0.2880

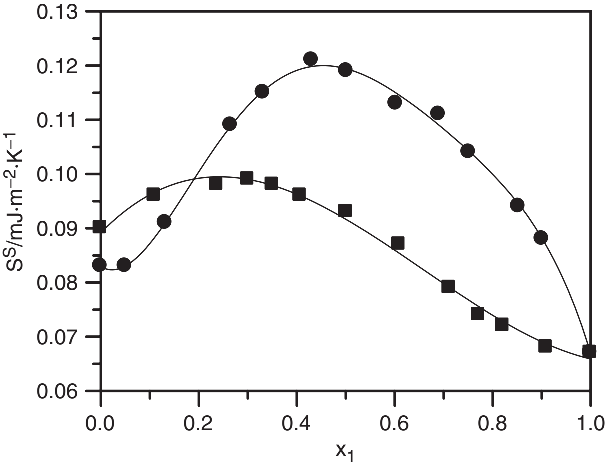

Figure 7. Surface entropy (S^S) *versus* the mole fraction of DCL (x_1) for DCL/MAC (●) and DCL/PAC (■) binary mixtures in the temperature range from 283.15 to 303.15 K.

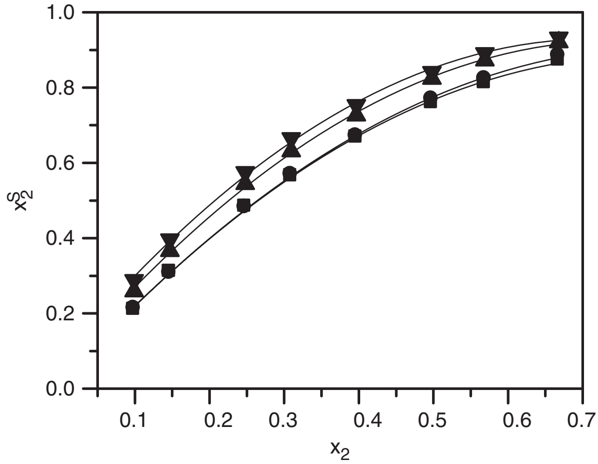

Figure 8. Surface mole fraction (x_2^S) *versus* bulk mole fraction of MAC (x_2) in DCL/MAC binary mixtures in the bulk composition range, $0.05 < x_2 < 0.70$, at various temperatures: $T = 283.15$ K (■), $T = 288.15$ K (●), $T = 298.15$ K (▲), and $T = 303.15$ K (▼).

The Equation (9) offers the opportunity to calculate the surface volume fraction of the surfactant component in the binary liquid mixtures. The combination of Equations (6) and (9) results to the following relation:

$$\frac{(\sigma - \sigma_1)}{(\sigma_2 - \sigma)} = \beta\left(\frac{\varphi_2}{\varphi_1}\right). \tag{10}$$

For the binary mixtures investigated in the present work, the plot of $(\sigma - \sigma_1)/(\sigma_2 - \sigma)$ *versus* φ_2/φ_1 was found to be linear (in the composition range: $0.05 < x_2 < 0.70$) suggesting that the effect of the unlike–pair interactions on the surface tension of the mixture is negligible (consequently $\lambda = 0$) in this composition region. The slope of $(\sigma - \sigma_1)/(\sigma_2 - \sigma)$ *versus* φ_2/φ_1 is equal to the value of lyophobicity of the surfactant component (either MAC or PAC) relative to that of DCL. The obtained β values in the temperature range from 283.15 to 303.15 K are listed in Table 7. The experimental error for the determination of β was 3%. The observed β values confirm the greater affinity of MAC for the surface ($\beta > 1$). Furthermore, the β values tend to increase, and consequently, the affinity of MAC for the surface increases, with rising temperature. In contrast, the affinity of PAC for the surface appears to be weaker than that of MAC ($\beta \approx 1$) and almost unaffected from the temperature. The β values are in absolute accordance with the values of σ^E (Tables 3 and 4), the S^S values (Table 6) as well as the x_2^S values (Table 8).

The surface volume fractions (φ_2^S) of MAC and PAC in the composition range $0.05 < x_2 < 0.70$ were calculated from the following equation:

$$\varphi_2^S = \frac{(\sigma - \sigma_1)}{(\sigma_2 - \sigma_1)}. \tag{11}$$

Which results from Equation (9) after rearrangement and considering that $\varphi_1^S + \varphi_2^S = 1$. The surface volume fractions (φ_2^S) have been converted to the surface mole fractions (x_2^S) using the following equation:

$$\varphi_2^S = \frac{x_2^S V_2}{\left(x_1^S V_1 + x_2^S V_2\right)}, \tag{12}$$

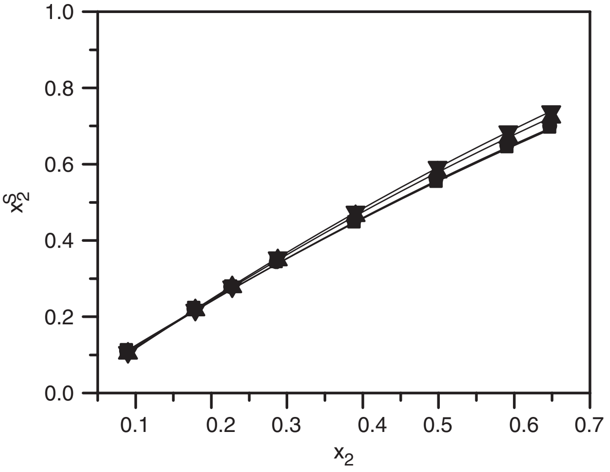

Figure 9. Surface mole fraction (x_2^S) *versus* bulk mole fraction of PAC (x_2) in DCL/PAC binary mixtures in the bulk composition range, $0.05 < x_2 < 0.70$, at various temperatures: $T = 283.15$ K (■), $T = 288.15$ K (●), $T = 298.15$ K (▲), and $T = 303.15$ K (▼).

where x_1^S is the surface mole fraction of DCL and x_2^S is the surface mole fraction of either MAC or PAC. The values of x_2^S for both surfactant components are given in Table 8 and presented graphically *versus* the bulk mole fractions (x_2) in Figures 8 and 9.

The x_2^S data imply that the surface concentration of MAC in DCL/MAC binary mixtures is two times higher from its bulk-phase concentration ($x_2^S \approx 2x_2$) and consequently the surface can be considered to be enriched with MAC. The results confirm the preference of the MAC molecules being present at the surface. In contrast, the surface concentration of PAC in DCL/PAC binary mixtures seems to be slightly higher from its bulk-phase concentration (almost $x_2^S \approx x_2$) indicating a weaker preference of PAC for the surface. The x_2^S results are in full accordance with the σ^E values (Tables 3 and 4), the S^S values (Table 6), as well as the β values (Table 7).

4. Conclusions

The present article presents the thermodynamic investigation of the binary liquid mixtures of DCL with either (MAC) or (PAC) in the temperature range from 283.15 to 303.15 K. The excess surface tensions and the excess molar volumes were obtained by using surface tension and density data, respectively. The surface entropies and surface enthalpies per unit surface area were determined. Furthermore, the lyophobicities as well as the surface mole fractions (x_2^S) of the surfactant components (either MAC or PAC) were determined using the extended Langmuir model. The V^E results indicate that the degree of the hetero-association in the bulk-phase region is insignificant in both liquid mixtures. However, the last incident appears to be more noticeable in MAC solutions explaining, therefore, the greater affinity of MAC for the surface compared to that of PAC, which was illustrated initially through the σ^E and S^S results and confirmed, afterwards, with the β values. The surface composition of MAC was found to be two times larger its bulk composition ($x_2^S \approx 2x_2$), while the surface composition of PAC was almost equal with its bulk composition ($x_2^S \approx x_2$).

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