Surface Properties of Pure Liquids and Binary Liquid Mixtures of Ethylene Glycol + Methylcyclohexanols

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Surface tension, $\sigma(t)$, for binary mixtures of ethylene glycol + 2-methylcyclohexanol, +3-methylcyclohexanol, and +4-methylcyclohexanol was measured over the whole composition range. Measurements were made under atmospheric pressure in the temperature range between 293.15 K and 323.15 K. The experimental values were correlated with mol fraction and temperature and also have been used to calculate the excess surface tensions. The thermodynamics properties of the mixture, the surface entropy, and surface enthalpy have been calculated.

Introduction

Experimental data of physical properties in mixtures of liquids are required for a full understanding of their thermodynamic properties as well as for use in the chemical engineering industry. The surface tension of liquid mixtures is an important property that reveals information on the structure and energetics of the surface region between two phases and exerts a considerable influence on the transfer of mass and energy across the interface. An estimate of this surface property is required in many fields including separation processes, gas absorption, and environmental engineering. Further, the surface tension is often very sensitive to small changes in the composition of the mixture. The surface tension of a liquid mixture is not a simple function of the surface tensions of the pure components because, in a mixture, the composition of the surface is not the same as that of the bulk. In a typical situation, we know the bulk composition but not the surface composition.

The surface tension of a mixture is usually less than that calculated from a mol fraction average of the surface tensions of the pure components.[1−4] As a result, it is essential to have a knowledge of the surface tension of mixtures over the entire composition range. Surface tension measurements provide the basis for the thermodynamic treatment of the surface. Recently, surface tension of binary mixtures of ethylene glycol with linear alkanols were investigated by us (ethylene glycol + ethanol)[4] and Jimenez et al. (ethylene glycol + 1-propanol or 1-butanol).[5] In this paper, we describe the composition dependence of the surface tension of binary ethylene glycol + cyclic alkanol (2-methylcyclohexanol, 3-ethylcyclohexanol, and 4-methylcyclohexanol) mixtures at various temperatures. Then by employing the measured surface tensions, the thermodynamic properties of the surface have been obtained.

Experimental Section

Ethylene glycol with a purity of >99.5% mass, 2-methylcyclohexanol with a purity of >98% mass, 3-methylcyclohexanol with a purity of >98% mass, and 4-methylcyclohexanol with a purity of >98% mass were supplied by Merck and were used as received. Mixtures were prepared in all the cases by mass using a Mettler Toledo AB 204-M balance with the precision of $\pm 1 \times 10^{-4}$ g, but the uncertainty of the mol fraction is estimated to be about 1×10^{-3}. Surface tension was determined at 5 °C intervals between (20 and 50) °C, using a Sigma 70 automated tensiometer, which employs a platinum ring. The platinum ring was thoroughly cleaned and flame dried before each measurement. The tensiometer was calibrated with ethanol. The system was thermostated with a precision of ±0.1 K, using a Multi Temp III thermostat and the temperature measured by sensor probe. Each value reported was an average of 8−10 measurements, where the maximum deviation from the average value were always less than 0.4%. The uncertainty of the measurements was ±0.02 $mN \cdot m^{-1}$. Table 1 shows the measured surface tension compared with literature data for pure components.

Table 1. Comparison of Experimental Surface Tension Values of Pure Liquids with Literature Values

t/°C	σ(exp)/$mN \cdot m^{-1}$	σ(ref)/$mN \cdot m^{-1}$
	Ethylene Glycol	
20	48.55	48.44[a]
		48.40[b]
		49.15[c]
		48.9[d]
		47.46[e]
35	47.14	47.09[a]
		47.5[d]
		46.49[e]
		47.5[f]
	2-Methylcyclohexanol	
20	31.01	30.91[b]
		29.57[h]
45	28.98	28.99[b]
		29.43[g]
	3-Methylcyclohexanol	
20	27.82	27.82[b]
		27.97[h]
45	26.06	26.25[b]
		27.13[g]
	4-Methylcyclohexanol	
20	27.63	27.69[b]
		27.94[h]
45	25.96	25.97[b]
		27.94[g]

[a] Reference 6. [b] Reference 7. [c] Reference 8. [d] Reference 4. [e] Reference 5. [f] Reference 9. [g] Reference 10. [h] Reference 11.

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Table 2. Surface Tension, σ, of 2-Methylcyclohexanol (2) + Ethylene Glycol (1) at Various Temperatures

	σ/mN·m^{-1}						
x_2	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C
0.000	48.55	48.11	47.58	47.14	46.79	46.29	45.99
0.040	40.61	40.30	39.94	39.67	39.40	39.13	38.89
0.105	36.13	35.89	35.62	35.32	35.07	34.81	34.56
0.200	34.46	34.17	33.85	33.55	32.26	32.98	36.68
0.307	33.49	32.20	32.88	32.58	32.22	31.94	31.63
0.399	32.94	32.61	32.26	31.96	31.62	31.31	30.97
0.514	32.38	32.03	31.68	31.33	30.98	30.69	30.36
0.553	32.22	31.87	31.54	31.19	30.81	30.49	30.13
0.760	31.72	31.36	30.97	30.61	30.29	29.91	29.52
0.791	31.51	31.10	30.73	30.38	30.00	29.59	29.24
0.892	31.2	30.78	30.39	30.05	29.67	29.27	28.87
1	31.01	30.57	30.19	29.81	29.37	28.98	28.57

Table 3. Surface Tension, σ, of 3-Methylcyclohexanol (2) + Ethylene Glycol (1) at Various Temperatures

	σ/mN·m^{-1}						
x_2	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C
0.000	48.55	48.11	47.58	47.14	46.79	46.29	45.99
0.050	36.72	36.51	36.29	36.07	35.88	35.66	35.44
0.097	34.08	33.87	33.67	33.46	33.26	33.08	32.89
0.258	31.57	31.25	30.97	30.70	30.42	30.15	29.91
0.329	30.94	30.60	30.32	30.01	29.75	29.48	29.17
0.389	30.57	30.23	29.98	29.65	29.38	29.09	28.76
0.535	29.84	29.51	29.19	28.86	28.57	28.28	27.96
0.623	29.39	29.05	28.75	28.43	28.14	27.82	27.42
0.768	28.85	28.47	28.16	27.80	27.46	27.18	26.84
0.864	28.43	28.02	27.68	27.34	27.03	26.69	26.33
0.899	28.24	27.90	27.56	27.24	26.85	26.50	26.18
1	27.82	27.48	27.12	26.76	26.4	26.06	25.7

Table 4. Surface Tension, σ, of 4-Methylcyclohexanol (2) + Ethylene Glycol (1) at Various Temperatures

	σ/mN·m^{-1}						
x_2	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C
0.000	48.55	48.11	47.58	47.14	46.79	46.29	45.99
0.050	38.10	37.85	37.64	37.39	37.15	36.90	36.69
0.109	34.38	34.18	33.98	33.78	33.60	33.40	33.21
0.208	32.47	32.24	32.03	31.79	31.57	31.34	31.10
0.303	31.48	31.24	30.99	30.74	30.48	30.26	30.01
0.419	30.64	30.37	30.08	29.81	29.55	29.32	29.04
0.491	30.35	30.05	29.77	29.48	29.23	28.96	28.68
0.604	29.63	29.34	29.02	28.74	28.48	28.18	27.88
0.684	29.21	28.92	28.60	28.29	28.02	27.73	27.40
0.804	28.71	28.41	28.07	27.76	27.47	27.18	26.84
0.910	28.07	27.75	27.43	27.11	26.77	26.45	26.15
1	27.63	27.30	26.98	26.61	26.31	25.96	25.63

Results and Discussion

The measured surface tensions of (ethylene glycol + 2-methylcyclohexanol), (ethylene glycol + 3-methylcyclohexanol), and (ethylene glycol + 4-ethylcyclohexanol) at various concentrations at each temperatures are listed in Tables 2, 3, and 4, respectively. The variation of surface tension, $\sigma(t)$, with temperature is linear for each composition and decreases with increasing temperature for all mixtures.

The surface tension of binary mixtures was correlated with temperature by following linear expression proposed by Jasper[6]

$$\sigma(t)/\mathrm{mN{\cdot}m^{-1}} = K_1 - K_2(t/°\mathrm{C}) \qquad (1)$$

where $\sigma(t)$ is surface tension, t is temperature, and K_1 and K_2 are constants of equation. Equation 1 was fitted to the data of Tables 2−4 for each concentration, with an average deviation of less than 1%. The fitted values of K_1 and K_2 for all systems are given in Table 5. For most of mixtures, K_1 values decrease with increasing mol fractions of methylcyclohexanols while K_2 values increase.

For a given temperature, the surface tensions of all binary mixtures investigated here decreased with an increase of the methylcyclohexanols mol fractions. Figure 1 represents this behavior for the binary mixture of ethylene glycol + 2-methylcyclohexanol. As shown in this figure, this trend is nonlinear, with the change in surface tension caused by a given change in 2-methylcyclohexanol mol fraction being larger at low mol fractions than at high

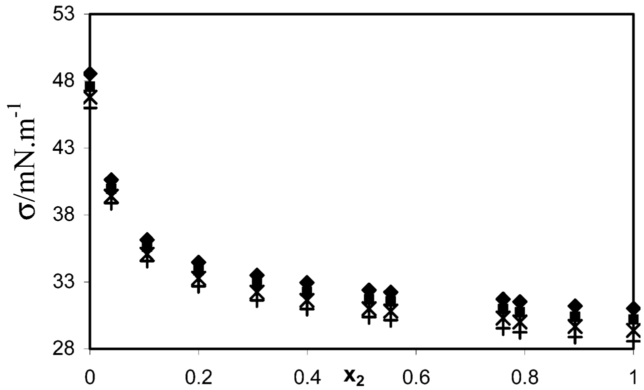

Figure 1. Plot of surface tension vs mol fraction of 2-methylcyclohexanol (x_2) at various temperatures. ◆, t = 20 °C; ■, t = 30 °C; *, t = 40 °C; +, t = 50 °C.

Table 5. Surface Tension Parameters K_1 and K_2 (Equation 1) for 4-Methylcyclohexanol, 3-Methylcyclohexanol, and 2-Methylcyclohexanol + Ethylene Glycol

x_2	K_2	K_1
	4-Methylcyclohexanol	
0.000	0.0865	50.24
0.050	0.0473	39.04
0.109	0.0389	35.15
0.207	0.0455	33.38
0.301	0.0491	32.46
0.419	0.0531	31.69
0.491	0.0553	31.44
0.604	0.0579	30.78
0.684	0.0599	30.41
0.804	0.0619	29.95
0.910	0.0644	29.36
1	0.0668	28.97
	2-Methylcyclohexanol	
0.000	0.0865	50.24
0.040	0.0574	41.72
0.105	0.0530	37.20
0.200	0.0594	35.64
0.031	0.0626	34.75
0.399	0.0654	34.24
0.514	0.0674	33.71
0.553	0.0697	33.62
0.760	0.0727	33.17
0.791	0.0754	33.00
0.892	0.0766	32.72
1	0.0809	32.62
	3-Methylcyclohexanol	
0.000	0.0865	50.24
0.050	0.0425	37.57
0.097	0.0397	34.86
0.258	0.0552	32.64
0.329	0.0580	32.07
0.389	0.0594	31.74
0.535	0.0623	31.07
0.623	0.0641	30.67
0.768	0.0665	30.15
0.864	0.0686	29.76
0.899	0.0692	29.63
1	0.0709	29.24

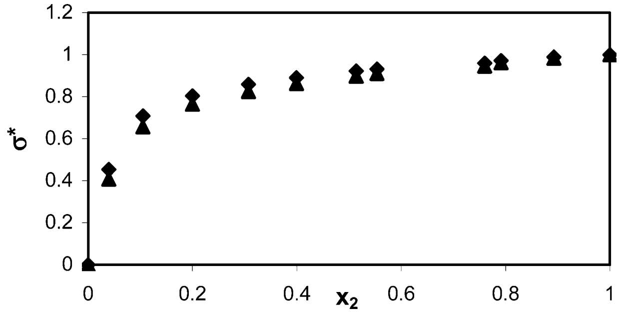

Figure 2. Dimensionless surface tension, σ^*, vs the mol fraction of 2-methylcyclohexanol (x_2) at various temperatures. ◆, $t = 20$ °C; ▲, $t = 50$ °C.

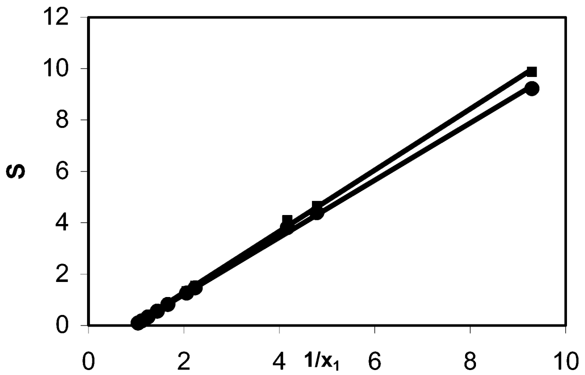

Figure 3. Plot of $S = x_2/(\sigma^* - x_2)$ vs $1/x_1$ for 2-methylcyclohexanol + ethylene glycol. ●, $t = 20$ °C; ■, $t = 50$ °C.

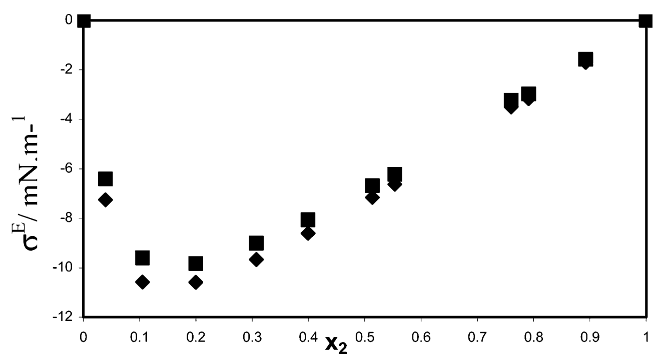

Figure 4. Plot of the excess surface tension, σ^E, vs mol fraction of 2-methylcyclohexanol, x_2, at 20 and 50 °C. ◆, $t = 20$ °C; ■, $t = 50$ °C.

mol fractions. The surface tensions variation of binary mixtures of ethylene glycol with 3-methylcyclohexanol and 4-methylcyclohexanol are similar to those represented in the figure. This behavior was also observed for binary mixtures of ethylene glycol with linear chain alcohols.[4,5] Connors and Wright[13] have developed a model for the dependence of surface tension on the composition of binary solutions. They found the following equation that relates the surface tension of binary mixture, $\sigma(t)$, to the mol fraction of components 1 and 2 at constant temperature

$$\sigma(t) = \sigma_1(t) - \left(1 + \frac{bx_1}{1 - ax_1}\right)x_2[\sigma_1(t) - \sigma_2(t)] \qquad (2)$$

where $\sigma_1(t)$ and $\sigma_2(t)$ are the surface tensions of pure components 1 and 2, x_1 and x_2 are the mol fractions of these components, and a and b are the fitting coefficients. This equation has been used previously.[1−4,14,15] The reduced surface tension (σ^*), which is dimensionless, is defined as below

$$\sigma^* = \frac{\sigma_1(t) - \sigma(t)}{\sigma_1(t) - \sigma_2(t)} \qquad (3)$$

This quantity (σ^*) is a weak function of temperature over most of the concentration range. The σ^*−x_2 curve for binary mixtures of ethylene glycol and 2-methylcyclohexanol is shown in Figure 2 for temperatures of 20 °C and 50 °C, which indicates the very low dependence of σ^* to temperature. The similar curve was observed for mixtures of ethylene glycol with other isomers. By combination of eqs 2 and 3 and then rearrangement, one obtains

$$\frac{x_2}{\sigma^* - x_2} = \frac{1}{bx_1} - \frac{a}{b} \qquad (4)$$

The plot of $x_2/(\sigma^* - x_2)$ vs $1/x_1$ gives a straight line with a slope equal to $1/b$ and an intercept equal to $-a/b$. So fitted parameters b and a were determined at each temperature from the slope and intercept, respectively.

These plots for ethylene glycol + 2-methylcyclohexanol at 20 °C and 50 °C are represented in Figure 3. For all mixtures of ethylene glycol and methylcyclohexanols, the a and b values were obtained at each temperature from plots such as Figure 3 and were listed in Table 6.

The deviation of surface tension from ideal behavior can be quantified by excess surface tension, $\sigma^E(t)$, defined by

$$\sigma^E(t) = \sigma(t) - [\sigma_1(t)x_1 + \sigma_2(t)x_2] \qquad (5)$$

Plotting $\sigma^E(t)$ against x_2 (Figure 4 shows typical plots for

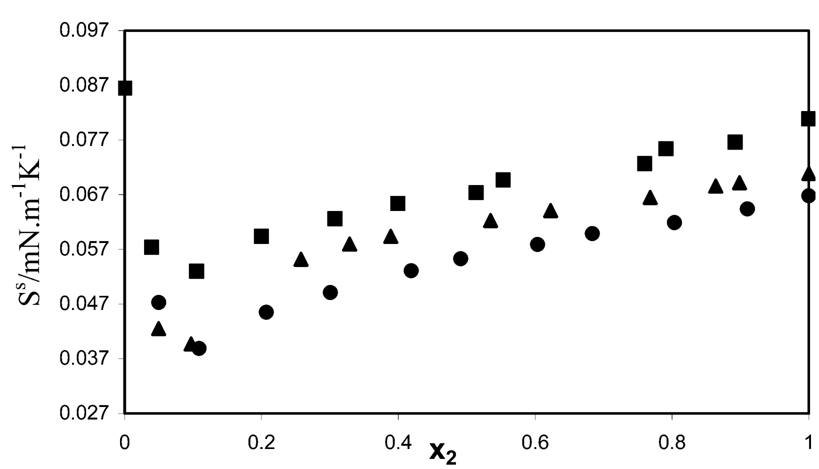

Figure 5. Plot of surface entropy vs mol fraction of ●, 4-methylcyclohexanol; ■, 2- methylcyclohexanol; ▲, 3-methylcyclohexanol.

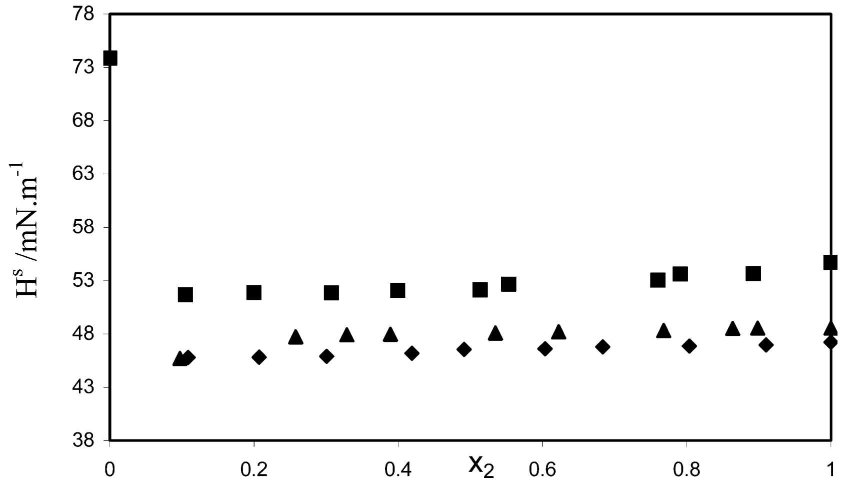

Figure 6. Plot of surface enthalpy vs mol fraction of ◆, 4-methylcyclohexanol; ■, 2- methylcyclohexanol; ▲, 3-methylcyclohexanol.

Table 6. Surface Tension Parameters *a* and *b* (Equations 2 and 4) for 2-Methylcyclohexanol, 3-Methylcyclohexanol, and 4-Methylcyclohexanol + Ethylene Glycol

t/°C	20	25	30	35	40	45	50
			2-Methylcyclohexanol				
a	1.4111	1.1675	1.14404	1.2164	1.3325	1.2944	0.9088
b	0.8981	0.8867	0.8908	0.8710	0.8399	0.8450	0.8440
			3-Methylcyclohexanol				
a	1.5492	1.6161	1.5643	1.6786	1.6041	1.5616	1.6653
b	0.7962	0.7985	0.7928	0.7748	0.7813	0.7842	0.7694
			4-Methylcyclohexanol				
a	1.6551	1.6843	1.6890	1.5766	1.6983	1.8035	1.9161
b	0.7653	0.7584	0.7568	0.7672	0.7487	0.7302	0.7159

2-methylcyclohexanol) at various temperatures shows that maximum deviation from ideality is about $x_2 = 0.1$. It is obvious that by increasing temperature the deviation from ideal behavior slightly decreases.

Thermodynamic properties of the surface could be obtained by measuring the surface tension at various temperatures. The temperature derivative of surface tension corresponds to excess surface entropy per unit area[16]

$$S^s = -(\partial\sigma/\partial T) \tag{6}$$

and surface enthalpy per unit area is

$$H^s = \sigma(t) - T(\partial\sigma/\partial T) \tag{7}$$

These equation were employed for the investigation of the thermodynamic properties of surfaces recently.[15,17−21] We have calculated the surface entropies and enthalpies for mixtures of ethylene glycol with isomers of methylcyclohexanols. The obtained data were plotted in Figures 5 and 6. As it was shown in this figures, the patterns of both H^s and S^s are nearly identical for all mixtures of ethylene glycol with isomers of methylcyclohexanols. The obtained surface entropy (Figure 5) exhibited a rapid decrease at dilute concentration of methylcyclalkanols (until $x_2 \approx 0.1$) and then increased linearly with an increase in the concentration of methylcyclohexanols. As shown in Figure 6, surface enthalpy decreases rapidly with the addition of methylcyclohexanol to the ethylene glycol until $x_2 \approx 0.1$ and then increases very slowly and linearly with the addition of methylcyclohexanol. It is interesting to note that where the H^s and S^s are at a minimum ($x_2 \approx 0.1$) the surface tension of the mixtures shows maximum deviation from ideality (σ^E is maximum). At $x_2 \approx 0.1$ where all systems show maximum deviation from ideality, the values of σ^E for isomers change in the order 2-methylcyclohexanol < 4-methycyclohexanol < 3-methylcyclohexanol. Variation of H^s and S^s at the same mol fraction ($x_2 \approx 0.1$) is in the order 3-methylcyclohexanol ≤ 4-methylcyclohexanol < 2-methylcyclohexanol.

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