salts capable of complexing with the solvent show heat effects of the order of heats of reaction (10.0 kcal. or better). The ΔH_S of KNO_3 is negative, as it is in water and anhydrous liquid ammonia at −33.5° C. It should be pointed out that the ΔH_S for water in anhydrous ethylenediamine is of the same order of magnitude as it is in liquid NH_3 at 25° C. (*1*) and is independent of the concentration as shown in Table I.

If the concentration of both silver nitrate and lead II nitrate was greater than solvent-solute ratio of 6000 to 1, oxidation of the solvent took place, and the results were meaningless.

Unfortunately the alkali metals themselves are not soluble without reaction in this solvent, so no comparison could be made of ΔH_S for the metals in the simple amine solvents.

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Surface Thermodynamic Properties of Alcohols and Related Compounds

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Surface thermodynamic properties of a series of alcohols (C_6 to C_{18}), cellosolves, and carbitols have been derived from surface-tension measurements for various temperatures in the liquid or molten-solid states. A systematic variation of thermodynamic properties with respect to chain length and change in temperature was observed in the case of the series of alcohols and cellosolves. The carbitols showed an irregular behavior with respect to the chain length.

SURFACE thermodynamic properties of pure liquids or molten solids at various temperatures have been measured to understand the nature and behavior of their surface region. The contraction of the surface area of a liquid is a naturally occurring phenomenon whose final effect is to decrease the free surface energy. The free surface energy is a property of the liquid-surface region (5) and plays an important role in the interpretation of liquid-surface phenomena. Since the free surface energy of a unit area of a surface is dependent on surface tension, the surface tensions of a series of alcohols (C_6 to C_{18}, even carbon chain) and alkoxy ethanols (cellosolves and carbitols) were measured at various temperatures, and the relevant thermodynamic quantities were derived.

SURFACE TENSION MEASUREMENTS

Cellosolves, carbitols, and alcohols from C_6 to C_{18} carbon chain, obtained from the British Drug Houses in fairly pure state, were further subjected to purification processes for the required purity. Alcohols from C_6 to C_{12}, cellosolves, and carbitols were purified by repeated fractional distillation in a 65-cm. long fractionating column having a diameter of 2 cm. and packed with concentric borosilicate glass helices. The C_{14}, C_{16}, and C_{18} alcohols were first subjected to a triangular method of fractional recrystallization, with dry acetone as the solvent, followed by a process of acetylation and deacetylation. Later, the alcohols were fractionally distilled through the same column under vacuum. Purity was checked by vapor-phase chromatography using an Aerograph (A-350-B), and samples showing purity over +99% were used for measurements. The boiling point and density values available in the literature were compared with those measured in the present work (Table I).

Table I. Tabulation of Boiling Point and Density Values

Compounds	Boiling Points		Density	
	Obsd.	Lit.	Obsd.	Lit.
C_6H_{13}—OH	156° C./710 mm.	157.5° C./761 mm.[a]	0.8121/30° C.	0.81201/30° C.[a]
C_8H_{17}—OH	192.5° C./710 mm.	194.4° C./760 mm.[a]	0.8220/30° C.	0.82192/30° C.[a]
$C_{10}H_{21}$—OH	228.9° C./708 mm.	231° C./759 mm.[a]	...	...
$C_{12}H_{25}$—OH	113.5° C./20 mm.	114° C./20 mm.[a]	...	...
$C_{14}H_{29}$—OH	169.2° C./20 mm.	170° C./20 mm.[a]	...	...
$C_{16}H_{33}$—OH	130° C./1 mm.	190° C./20 mm.[a]	0.8149/55° C.	0.81521/55° C.[a]
$C_{18}H_{37}$—OH	150° C./1 mm.	217° C./17 mm.[a]	...	...
$CH_3O—C_2H_4OH$	...	...	0.9612/25° C.	0.96024/25° C.[b]
$C_2H_5O—C_2H_4OH$	...	...	0.9281/25° C.	0.92520/25° C.[b]
$C_4H_9O—C_2H_4OH$	...	...	0.8960/25° C.	0.89664/25° C.[b]
$CH_3(O—CH_2CH_2)_2—OH$	...	...	1.0160/25° C.	1.0167/25° C.[c]
$C_2H_5(O—CH_2CH_2)_2—OH$	...	...	0.9833/25° C.	0.9841/25° C.[c]
$C_4H_9(O—CH_2—CH_2)_2—OH$	...	...	0.9477/25° C.	0.9484/25° C.[c]

[a] Reference No. 6. [b] Reference No. 2. [c] Reference No. 7

Surface tensions of pure liquids were measured by the ring detachment (*8*) method using a Chainomatic balance sensitive to ±0.05 mg. A platinum ring, 1.3 cm. in diameter, was attached to one arm of the beam balance. The liquid was tested in stoppered, clean, dry conical flasks and allowed to attain the temperature of the bath. Exposure of the surface to the air through the narrow neck of the flask was allowed only for the time required to bring the ring in contact with the surface and pull it out. The chances of such a surface getting contaminated are negligible. The temperature of the bath was maintained within ±0.05° C. The ring was allowed to touch the surface of the liquid and dipped a little, ensuring complete wetting. As the ring rested on the surface of the liquid, weights were added slowly to the other arm of the balance to determine the weight required to raise the ring from the surface of the liquid. The surface tension was calculated with the help of the following equation (*4*) where the density and the diameter of the ring were known.

$$\gamma = p \times f = (Mg/4\pi R) \times f$$

where f = Harkin's correction factor, M = mass required to pull out the ring, g = force due to gravity = 978.59 cm. per sec.,^{2} R = radius of the ring. Corrections (*3*) involving the densities of the liquid and the diameters of the ring and wire were applied. The maximum overall error in the measurement of γ at higher temperature was ±0.05 dyne per cm. However, at lower temperatures, values accurate within ±0.025 dyne per cm. were obtained. Densities of these liquids were measured by pycnometer following a standard procedure (*1*) at required temperatures.

RESULTS AND DISCUSSION

The two-dimensional form of the Clapeyron equation for the liquid surface region may be expressed as

$$-d\gamma/dT = L^s/T = \Delta S^s \qquad (1)$$

where γ is the surface tension, L^s is the latent heat of surface formation, and ΔS^s is the entropy of surface formation. Equation 1 may be rearranged as

$$-T(d\gamma/dT) = L^s \qquad (2)$$

The enthalpy of surface formation (ΔH^s) was calculated from the following equation (*4*).

$$\Delta H^s = \gamma - T(d\gamma/dT)_{p,x} = \gamma + L^s \qquad (3)$$

γ, L^s, and ΔH^s can all be presented in terms of erg per cm.^{2}.

The total surface energy is nothing but the enthalpy of surface formation, which involves both the free surface energy and the latent heat of surface formation. Surface tension obtained for the series of the alcohols and the alkoxy ethanols at different temperatures are given in Tables II to IV, along with corresponding thermodynamic quantities calculated from the above equations. The comparison of the surface tension values of hexanol and octanol with those available in the literature at 30° C. may not be irrelevant to check the accuracy of the present measurements.

	Surface Tension at 30° C.	
	Obsd.	Lit. (*6*)
Hexanol	23.64	23.68
Octanol	25.16	25.21

The surface tension decreased linearly, and the latent heat of surface formation increased linearly with an increase in the temperature. The slopes of these two linear curves (not shown) were equal in magnitude but opposite in sign (Table II).

Table II. Surface Tension and Related Thermodynamic Properties of C_6 to C_{18} Alcohols

Temp., °C.	γ	L^s	ΔH^s	γ	L^s	ΔH^s	γ	L^s	ΔH^s	γ	L^s	ΔH^s
		Hexanol			Octanol			Decanol			Dodecanol	
25	24.08	26.79	50.87	25.56	24.48	50.04	27.02	22.93	49.96	27.37	22.49	49.86
30	23.64	27.24	50.88	25.16	24.89	50.05	26.64	23.30	49.97	27.09	22.87	49.96
35	23.23	27.68	50.91	24.75	25.28	50.03	26.25	23.68	49.93	26.66	23.25	49.91
40	22.78	28.14	50.92	24.33	25.71	50.04	25.89	24.07	49.82	26.31	23.63	49.93
45	22.35	28.58	50.93	23.92	26.10	50.02	25.50	24.45	49.95	25.97	24.00	49.97
50	21.90	29.04	50.94	23.51	26.53	50.04	25.10	24.83	49.92	25.59	24.38	49.97
55	21.47	29.48	50.95	23.07	26.92	49.99	24.73	25.22	49.95	25.25	24.75	50.01
60	21.05	29.93	50.98	22.65	27.34	49.99	24.35	25.60	49.95	24.90	25.14	49.94
65	20.60	30.38	50.98	22.25	27.75	50.00	23.97	25.99	49.96	24.55	25.51	50.06
70	20.16	30.83	50.99	21.82	28.16	49.98	23.60	26.37	49.97	24.20	25.89	50.09
75	19.73	31.28	51.01	21.40	28.57	49.97	23.23	26.76	49.96	23.85	26.27	50.12
$\Delta S^s = d\gamma/dt$		0.0899			0.0821			0.0769			0.0755	
ΔH^s from Equation 6		50.79			50.11			50.14			50.15	
		Tetradecanol			Hexadecanol			Octadecanol				
25	23.39	20.47	43.86	24.97	20.23	45.10	25.97	19.66	45.63			
30	23.05	20.81	43.86	24.65	20.57	45.22	25.65	19.99	45.64			
35	22.71	21.15	43.86	24.30	20.91	45.21	25.30	20.32	45.62			
40	22.37	21.50	43.87	23.95	21.25	45.20	24.96	20.65	45.61			
45	22.02	21.85	43.87	23.61	21.59	45.20	24.62	20.98	45.60			
50	21.67	22.19	43.86	23.27	21.93	45.20	24.30	21.31	45.61			
55	21.35	22.53	43.88	22.95	22.27	45.76	23.97	21.64	45.61			
60	21.02	22.88	43.89	22.64	22.61	45.25	23.64	21.98	45.62			
65	20.65	23.22	43.89	22.24	22.95	45.19	23.31	22.31	45.61			
70	20.32	23.56	43.88	21.90	23.29	45.19	22.98	22.64	45.61			
75	19.99	23.90	43.89	21.57	23.63	45.20	22.64	22.97	45.61			
$\Delta S^s = d\gamma/dt$		0.0687			0.0679			0.0660				
ΔH^s from Equation 6		43.85			45.25			45.79				

Table III. Specific Constants Obtained from Equations 4 and 5

Compounds	a	b	c	d
Hexanol	26.24	0.0899	24.55	0.08988
Octanol	27.66	0.0821	22.45	0.08215
Decanol	29.04	0.0769	21.10	0.0796
Dodecanol	29.55	0.0755	20.60	0.0755
Tetradecanol	25.00	0.0687	18.85	0.0685
Hexadecanol	26.75	0.0679	18.50	0.0679
Octadecanol	27.79	0.066	18.00	0.0669

Table IV. Surface Tension and Related Thermodynamic Quantities of Cellosolves and Carbitols

Temp., °C.	γ	L^s	ΔH^s	γ	L^s	ΔH^s	γ	L^s	ΔH^s
		Methyl Cellosolve			Ethyl Cellosolve			Butyl Cellosolve	
30	30.02	30.91	60.93	27.67	27.72	55.39	26.98	23.63	50.61
35	29.50	31.42	60.92	27.20	28.18	55.38	26.57	24.02	50.59
40	28.97	31.93	60.90	26.75	28.64	55.39	26.23	24.41	50.64
45	28.48	32.44	60.92	26.27	29.09	55.36	25.82	24.80	50.62
50	27.98	32.95	60.93	25.84	29.55	55.39	25.42	25.19	50.61
$\Delta S^s = d\gamma/dt$		0.1020			0.0915			0.0780	
ΔH^s from Equation 6		60.95			55.40			50.63	
		Methyl Carbitol			Ethyl Carbitol			Butyl Carbitol	
25	28.49	13.37	41.86	29.53	21.09	50.63	25.01	16.93	41.94
30	28.23	13.59	41.82	29.17	21.45	50.62	24.72	17.21	41.93
35	28.03	13.82	41.85	28.83	21.81	50.64	24.45	17.49	41.94
40	27.81	14.05	41.86	28.46	22.16	50.62	24.16	17.78	41.96
45	27.57	14.27	41.84	28.10	22.52	50.61	24.03	18.06	42.06
50	27.35	14.49	41.84	27.76	22.87	50.63	23.59	18.35	41.94
$\Delta S^s = d\gamma/dt$		0.0448			0.0708			0.0568	
ΔH^s = from Equation 6		41.81			50.65			41.92	

The enthalpy of surface formation ΔH^s was independent of temperature but decreased slowly as the chain length increased from C_6 to C_{12} alcohol. From C_{12} to C_{14}, there was a large drop in ΔH^s, which increased slowly thereafter up to the C_{18} alcohol. On the other hand, the latent heat of surface formation values continuously decreased as the chain length increased from C_6 to C_{18} alcohols.

The entropy of surface formation ΔS^s was independent of temperature but decreased slowly as the chain length was increased. The values of γ, L^s, and ΔH^s for C_{14}, C_{16}, and C_{18} alcohols at temperatures below their melting points were obtained from extrapolated values of γ to these temperatures. The sudden change in the surface property—i.e., from C_{12} to C_{14} alcohol—may be due to the fact that the alcohols below C_{12} are liquids at room temperature, whereas C_{14} and above are solids. This change in the physical state may affect the packing of the molecules, which in turn alters the surface energy.

The linear variation of γ and L^s can be expressed by Equations 4 and 5.

$$\gamma = a - bt \tag{4}$$

$$L^s = c + dt \tag{5}$$

where t is the temperature. The specific constants a, b, c, and d for the alcohol series are given in Table III. According to Equation 3, the enthalpy of surface formation at any temperature can be calculated by combining Equations 4 and 5 according to Jasper (5).

$$\Delta H^s = a + c + t\,(d - b) \tag{6}$$

ΔH^s values obtained by substituting constants a, b, c, and d in Equation 6 agree well with those obtained from Equation 3; comparative values are shown in Tables II and IV.

Although the entropy of surface formation is independent of temperature for different alcohols, column d of Table III indicates that entropy decreases with increasing molecular weight. This seems to indicate that the degree of orderliness in the liquid surface region increases with the increase in chain length.

The results of the surface tension and the related thermodynamic quantities for the cellosolves—i.e., ethylene glycol monomethyl and ethyl and butyl ethers—and carbitols—i.e., diethyleneglycol monomethyl and ethyl and butyl ethers—have been given in Table IV. The behavior of the cellosolves is similar to those of alcohols. Surface tension and latent heat of surface formation change linearly with the temperature, with equal but opposite slopes. The enthalpy of the surface-formation constant for a particular compound is independent of temperature. At any particular temperature, L^s decreases as the chain length increases from methyl to butyl as was observed in the case of alcohols. The entropy of surface formation ΔS^s also follows the same trend as found for the alcohols. Carbitols, unlike the cellosolves and the alcohols, do not show any systematic variation as the chain length is increased. For individual compounds, both the surface tension and the latent heat of surface formation exhibit the same behavior as in the case of the alcohols and cellosolves. ΔH^s values are also constant for each homolog.

Ethyl carbitol showed higher values of γ than methyl or butyl carbitol at all temperatures. Therefore, other properties of ethyl carbitol obtained from γ—i.e., ΔH^s, ΔS^s, and L^s—were comparatively higher than those of methyl and butyl carbitol. This behavior was not observed in the other series of compounds.

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Physical and Spectral Properties of 2-Aryl-1,3-Dioxolanes and Heteroatomic Analogs

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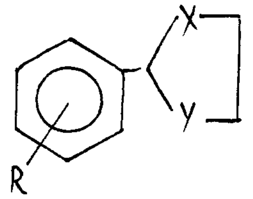
Physical properties of 2-aryl-1,3-dioxolanes, 1,3-dithiolanes, 1,3-oxathiolines, and 1,3-N,N-dimethyl imidazolidines are reported. A very convenient pair of bands of medium to strong intensity is invariably found in the IR between 10.0 and 11.1 microns (1000 to 901 cm.$^{-1}$) characteristic of the heterocyclic five-membered ring and useful for analysis in the presence of the usual starting materials for the preparation of these compounds. The benzylic hydrogens of the four different heterocyclic systems show markedly different chemical shifts in their NMR spectra. Substituents on the phenyl rings have almost no effect on the chemical shift.

FOR THE PURPOSES of careful kinetic investigations (autoxidations, hydrolyses, hydrogen abstraction reactions), the authors desired pure samples of compounds of the form



I $X = Y =$ oxygen
II $X = Y =$ sulfur
III $X =$ oxygen, $Y =$ sulfur
IV $X = Y = {>}NCH_3$

These compounds were obtained by standard procedures described in the experimental section.

Table I shows densities, refractive indexes, melting and boiling points, and infrared spectra bands between 10.0 and 11.1 microns (1000 to 901 cm.$^{-1}$), which were invariably found in the compounds studied. Spectra of alkyl analogs (Nos. 8, 15, and 20) also gave these bands, indicating that these absorptions do not arise from the aromatic moiety. All starting materials showed complete absence of absorptions in these regions. Assignments have been made in an earlier work for compounds related to the types reported here.

Bergman and Pinchas (*4*) have assigned bands to noncyclic acetals in the 8.7- to 10.0-micron (1200 to 1000 cm.$^{-1}$) region as characteristic of the C—O—C—O—C grouping. The bands reported do not invariably appear in IR spectra of cyclic acetals (*4, 17*), such as compounds of Type I. Other workers (*2, 23*) have studied cyclic acetals and ketals in detail and report bands at or near those reported here. These absorptions are attributed to ring breathing and ring stretching.

Compounds of Type II have been studied in detail (*11*). Bands in the far infrared region (900 to 300 cm.$^{-1}$) from 11.1 to 33.3 microns have been assigned to the ring system. All compounds reported were cyclic dithioacetals or ketals in the aliphatic series. Bands at 970 to 975 cm.$^{-1}$ (10.30 to 10.25 microns) were attributed to —CH_2— twisting. Absorption at 955 cm.$^{-1}$ (10.48 microns) was not reported.

Compounds of Type III have been studied in somewhat less detail. 2-Alkyl-1,3-oxathiolanes are reported to have a strong absorption at $\sim$9.3 microns (*3, 6*). This absorption is also found in spectra of aromatic aldehydes. Therefore, the choice for characterizing the heterocyclic system would avoid that absorption.

The imidazolidine system, IV, has been studied for *N,N*-dibenzyl analogs (*5*). Absorption at 9.1 and 9.8 microns (1099 to 1020 cm.$^{-1}$) have been attributed to the heterocyclic ring. 2-Phenyl-1,3-*N,N*-dimethyl imidazolidine gave no absorption at 9.1 microns and a medium band at 9.73 microns (1028 cm.$^{-1}$). Other members of our series absorbed at or near 9.1 and 9.8 microns. The bands observed at 10.24 and 11.06 microns (977, 904 cm.$^{-1}$) are considered more reliable in this system for the purposes of analysis, since starting materials show absorption between 9.1 and 9.8 microns.

Table I also describes the NMR spectra of the systems. Midpoints of the chemical shifts for the indicated groupings are tabulated. Integration of the spectra gave excellent agreement with indicated structures. Compounds of Type I, II, and IV gave A_2B_2 patterns for the ethylene hydrogen resonances. Compounds of Type III gave complex patterns for the ethylene hydrogens consisting of three groups of multiplets in the ratio 1:1:2. The phenyl absorptions were all normal for the substituents involved. The benzylic hydrogens were observed as a sharp singlet characteristic for the heterocyclic system but insensitive to substituents on the phenyl ring.

Detailed analysis of NMR spectra for systems of Type I (*1*) and III (*19*) have been carried out for the sake of describing conformation of the cyclic systems. Our chemi-