

appears not to have been rigorously established. Thus, the authors plan in the future to measure, with the wedge microinterferometer, the diffusion coefficients of several systems for which the diffusivities are already known—i.e., determined by a well-established method, such as that which uses the Gouy interferometer.

NOMENCLATURE

- a, b, c = constants in Gompertz equation
 A = constant in the linear solution density vs. concentration function
 D_{ij}^n = pseudo-binary (differential or concentration dependent) molecular diffusion coefficient of solute i in solution j using method n , cm.²/sec.
 \bar{D}_{ij}^n = integral (concentration-averaged) value of D_{ij}^n , cm.² per second =

$$\int_{y_1^*}^{y_2^*} y^* D_{ij}^n dy^* / (y_2^* - y_1^*)$$

- $G(x)$ = a scaled distance coordinate, dimensionless
 p = location of the original interface on the x axis, cm.
 t = time measured from the beginning of mass transfer, sec.
 W = weight fraction of the solute in the solution
 x = distance coordinate, cm.
 X_{cp} = volume fraction of the continuous phase portion of the polymer solution
 y = concentration of solute, grams per 100 cm.³
 y^* = reduced solute concentration = W_A / W_{A1}
 yp = value of y^* at x equal to p

Subscripts

- A = solute A
 B = solution B , polymer plus solvent, as indicated in Table I
 $A1$ = initial weight fraction of solute
 $A0$ = solute-free weight fraction
 NN = diffusivity of a non-Newtonian fluid
 N = diffusivity of a Newtonian fluid

- 1 = zero value of reduced concentration
 2 = the largest value of reduced concentration
 cp = parameter of the continuous phase portion of the non-Newtonian fluid

Greek Letters

- μ = viscosity of the fluid, centipoise
 ζ = number neighbors of the diffusing molecule which are sheared during its advancing a distance equal to one lattice parameter
 η = Boltzmann transformation = $x/2t^{1/2}$, cm. per second^{1/2}
 ρ = total solution density, gram per cm.³
 ρ_s = solute-free solution density, gram per cm.³

LITERATURE CITED

- (1) Ambrose, E.J., *J. Sci. Instr.* **25**, 134 (1948).
- (2) Berg, W.F., *Proc. Roy. Soc. (London)* **164A**, 79 (1938).
- (3) Clough, S.G., Read, H.E., Metzner, A.B., Behn, V.C., *A.I.Ch.E. J.* **8**, 346 (1962).
- (4) Crank, J., Robinson, C., *Proc. Roy. Soc. (London)* **204A**, 549 (1950).
- (5) David, D.S., "Nomography and Empirical Equations," 2nd ed., p. 74-89, Reinhold, New York, 1962.
- (6) Duda, J.L., Vrentas, J.S., *Ind. Eng. Chem. Fundamentals* **4**, 301 (1965).
- (7) *Ibid.*, **5**, 69 (1966).
- (8) *Ibid.*, **6**, 217 (1967).
- (9) Huang, A.L., M.S. thesis, University of Missouri-Rolla, Rolla, Mo., 1968.
- (10) Kegeles, G., Gosting, L.J., *J. Am. Chem. Soc.* **69**, 2516 (1947).
- (11) Longworth, L.G., *J. Am. Chem. Soc.* **69**, 2410 (1947).
- (12) Nishijima, Y., Oster, G., *J. Chem. Educ.* **38**, 114 (1961).
- (13) *Ibid.*, *J. Polymer Sci.* **19**, 337 (1956).
- (14) Paul, D.R., *Ind. Eng. Chem. Fundamentals* **6**, 217 (1967).
- (15) Ree, T., Eyring, H., "Rheology," Vol. 2, F. R. Eirich, Ed., p. 137, Academic Press, New York, 1958.
- (16) Robinson, C., *Proc. Roy. Soc. (London)* **204A**, 339 (1950).
- (17) Searle, G.F.C., *Phil. Mag.* **37**, 361 (1946).
- (18) Secor, R.H., *A.I.Ch.E. J.* **11**, 452 (1965).
- (19) Wilke, C.R., Chang, P., *A.I.Ch.E. J.* **1**, 264 (1955).

RECEIVED for review August 5, 1968. Accepted March 7, 1969

Surface Thermodynamic Properties of n -Long-Chain Alcohols, Alkoxy Ethanols, Propanols, and Butanols

SAMIR PATHAK and S. S. KATTI

National Chemical Laboratory, Poona, India

The surface thermodynamic properties of even-membered straight-chain alcohols (C_{20} and C_{22}), alkoxy ethanols (C_{16} to C_{22}), alkoxy propanols (C_{16} to C_{22}), and alkoxy butanols (C_{16} and C_{18}) have been derived from surface tension measurements at different temperatures. There is no significant variation in the thermodynamic properties with the introduction of different extended polar groups to the hydrophobic chain.

TO ELUCIDATE the nature of interaction of monolayers of fatty alcohols and alkoxy ethanols, a recent communication (4) from this laboratory reported the results of surface tension studies on a number of alcohols (C_6 to C_{18}), lower homologs of alkoxy ethanols, and carbitols, and derived the surface thermodynamic quantities. In this communication, the results of a similar study on the long-chain alcohols (C_{20} and C_{22}), alkoxy ethanols (C_{16} to C_{22}), propanols (C_{16} to C_{22}), and butanols (C_{16} and C_{18}) are reported.

EXPERIMENTAL

Materials. Alcohols commercially obtained (from B.D.H. or Fluka) were first subjected to the triangular method of fractional recrystallization, with dry acetone as the solvent, followed by a process of acetylation and deacetylation of the corresponding fractions of the acetates. Thereafter, they were fractionally distilled through a 65-cm. column packed with borosilicate glass helices. Alkoxy ethanols, pro-

Table I. Densities and Refractive Indices (*n*)

	Alcohols		Alkoxy Ethanols		Alkoxy Propanols		Alkoxy Butanols				
	Temp., ° C.	Density, G./Cc.	Temp., ° C.	Density, G./Cc.	Temp., ° C.	Density, G./Cc.	Temp., ° C.	Density, G./Cc.			
C ₂₀	75	0.8059	C ₁₆	45	0.8491	C ₁₆	45	0.8506	C ₁₆	50	0.8469
	85	0.7987		50	0.8447		50	0.8475		55	0.8436
	95	0.7919		55	0.8418		55	0.8445		65	0.8371
C ₂₂	75	0.8063	C ₁₈	55	0.8473	C ₁₈	55	0.8423	C ₁₈	55	0.8443
	85	0.7986		60	0.8432		60	0.8395		60	0.8412
	95	0.7911		65	0.8392		65	0.8362		65	0.8374
			C ₂₀	75	0.8059	C ₂₂	75	0.8297			
				85	0.7987		85	0.8208			
				95	0.7919		95	0.8134			
			C ₂₂	75	0.8255						
				85	0.8186						
				95	0.8119						
	Temp., ° C.	Refractive Index (<i>n</i>) ^a	Temp., ° C.	Refractive Index (<i>n</i>) ^a	Temp., ° C.	Refractive Index (<i>n</i>) ^a	Temp., ° C.	Refractive Index (<i>n</i>) ^a	Temp., ° C.	Refractive Index (<i>n</i>) ^a	
C ₂₀	75	1.4341	C ₁₆	55	1.4380	C ₁₆	55	1.4395	C ₁₆	55	1.4404
C ₂₂	75	1.4360	C ₁₈	55	1.4405	C ₁₈	55	1.4417	C ₁₈	55	1.4427
			C ₂₀	75	1.4356						
			C ₂₂	75	1.4356	C ₂₂	75	1.4365			

^a Unpublished data from this laboratory.

Table II. Surface Tension and Related Thermodynamic Quantities

Temp., ° C.	C ₁₆			C ₁₈			C ₂₀			C ₂₂		
	γ	L ^s	ΔH ^s	γ	L ^s	ΔH ^s	γ	L ^s	ΔH ^s	γ	L ^s	ΔH ^s
Alcohols												
55	22.95	22.27	45.22									
65	22.24	22.95	45.19	23.31	22.31	45.62						
75	21.57	23.63	45.20	22.64	22.97	45.61	21.15	22.79	43.94	21.82	22.45	44.27
85	20.88	24.31	45.19	21.98	23.63	45.61	20.49	23.43	43.92	21.17	23.12	44.29
95	20.18	24.99	45.17	21.32	24.29	45.61	19.84	24.09	43.93	20.53	23.75	44.28
		ΔS ^s = 0.067			ΔS ^s = 0.066			ΔS ^s = 0.065			ΔS ^s = 0.064	
Alkoxy Ethanols												
45	26.86	22.42	49.28									
55	26.15	23.12	49.27	21.42	21.98	43.40						
65	25.45	23.83	49.28	20.74	22.65	43.39						
75	24.76	24.53	49.29	20.08	23.32	43.40	27.57	22.97	50.54	21.01	22.45	43.46
85	24.05	25.24	49.29	19.41	23.99	43.40	26.91	23.63	50.54	20.36	23.09	43.45
95	23.35	25.94	49.29	18.74	24.66	43.40	26.25	24.29	50.54	19.72	23.74	43.46
		ΔS ^s = 0.070			ΔS ^s = 0.067			ΔS ^s = 0.066			ΔS ^s = 0.064	
Alkoxy Propanols												
45	21.53	24.64	46.17									
55	20.76	25.42	46.18	21.99	24.76	46.75						
65	19.98	26.19	46.17	21.24	25.52	46.76						
75	19.20	26.97	46.17	20.48	26.27	46.75				27.26	23.66	50.92
85	18.43	27.74	46.17	19.72	27.03	46.75				26.59	24.34	50.93
95	17.65	28.52	46.17	18.97	27.78	46.75				25.90	25.02	50.92
		ΔS ^s = 0.077			ΔS ^s = 0.075						ΔS ^s = 0.068	
Alkoxy Butanols												
50	22.31	20.99	43.40									
55	22.00	21.32	43.32	21.91	19.68	41.59						
60	21.68	21.64	43.32	21.61	19.98	41.59						
65	21.35	21.97	43.32	21.31	20.28	41.59						
75	20.69	22.65	43.34	20.70	20.88	41.58						
85	20.02	23.31	43.33	20.10	21.47	41.57						
95	19.40	23.92	43.32	19.52	22.08	41.60						
		ΔS ^s = 0.065			ΔS ^s = 0.060							

panols, and butanols were synthesized by Williamson's method (5), which consists of converting alkyl bromides of the long-chain alcohol to the corresponding ethers by condensing them with monosodium salts of ethane diol, 1,3-propane diol, and 1,4-butane diol, respectively. The products were vacuum-distilled and then fractionally recrystallized until a constant melting point was obtained. The purities of the compounds were finally checked by vapor phase chromatography, using an aerograph (A-350-B). Samples showing purity over 99.8% were used for measurements.

The boiling point and density values available in the literature of the lower homologs of the alcohols, alkoxy ethanols, and carbitols were compared with the authors' values in a table in an earlier communication (4) to establish the purities. Such values, however, are not available in the literature for the present set of long-chain compounds.

The values of the density measurements—by pycnometer, following a standard procedure (1)—and the refractive indices are reported in Table I for the long-chain alcohols, alkoxy ethanols, propanols, and butanols.

Surface Tension Measurements. Surface tensions of pure molten solids were measured by the ring method (6) with the aid of a chainomatic balance sensitive to ± 0.05 mg. The ring used had a diameter of 1.3 cm. and was made of a platinum-iridium alloy. The liquid under test was taken in a stoppered, clean, dry conical flask, and was allowed to attain the temperature of a thermostatic bath capable of maintaining the temperature within $\pm 0.05^\circ\text{C}$., in the stoppered condition. The chances of the surface of the test sample in the conical flask getting contaminated were negligible. The ring was scrupulously cleaned by dipping it in cleaning solution (hot chromic acid) for about 15 minutes and then washing it with distilled water. It was dried over a flame by heating it to red heat. The whole cleaning process was repeated before each measurement.

The weight required to detach the ring from the surface of the test liquid after complete wetting was determined. Using the density (at the temperature of measurement) and the diameter of the ring, the surface tension was calculated by the equation (2, 3)

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

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, and R = the radius of the ring. The maximum over-all error in the measurement of γ in the temperature range of 50° to 95°C . was ± 0.05 dyne per cm.

RESULTS AND DISCUSSION

Surface tension measurements along with the thermodynamic quantities derived therefrom have been presented in Tables I and II for different alcohols, alkoxy ethanols, alkoxy propanols, and alkoxy butanols. The surface tension

(γ) decreased with an increase in temperature for all the compounds (C_{16} to C_{22}) studied (Table II), whereas the latent heat of surface formation (L^s) increased with an increase in the temperature. Enthalpy of surface formation (ΔH^s) remained nearly constant at all temperatures and for all the compounds studied. No systematic variation of increase in chain length was observed. Values of ΔH^s showed a slight increase at C_{18} and then a decrease for C_{20} . It remained nearly the same for C_{22} alcohol. The entropy of surface formation (ΔS^s) was independent of temperature. However, it decreased slowly as the chain length increased.

Alkoxy ethanols, alkoxy propanols, and alkoxy butanols showed trends similar to the alcohols (Table II). The surface tension and the latent heat of surface formation changed linearly with temperature, with equal but opposite slopes. The ΔH^s values were independent of temperature. Values of L^s increased with an increase of temperature and decreased as the chain length was increased.

The introduction of $-\text{OC}_2\text{H}_4\text{OH}$, $-\text{OC}_3\text{H}_6\text{OH}$, and $-\text{OC}_4\text{H}_8\text{OH}$ groups to the hydrocarbon chain does not seem to show any systematic trends in the values of the various thermodynamic quantities, though the actual values of γ , ΔH^s , and L^s were different for compounds having different functional groups.

ACKNOWLEDGMENT

Thanks are due to H. B. Mathur for his keen interest and helpful discussions during the course of this work and to M. V. Natekar for supplying pure alkoxy ethanols, propanols, and butanols.

NOMENCLATURE

- γ = surface tension, dynes/cm. or erg/cm.² (MT^{-2})
 L^s = latent heat of surface formation, erg/cm.² (MT^{-2})
 ΔH^s = enthalpy of surface formation, erg/cm.² (MT^{-2})
 ΔS^s = entropy of surface formation, erg/cm.² degree

LITERATURE CITED

- (1) American Society for Testing and Materials, Standards Suppl., Part III, p. 164, 1945.
- (2) Harkins, W.D., Yong, T.F., Cheng, Lan, *Science* **64**, 333 (1926).
- (3) Harkins, W.D., Jardan, H.F., *J. Am. Chem. Soc.* **52**, 1751 (1930).
- (4) Katti, S.S., Pathak, Samir, *J. Chem. Eng. Data* **14**, 73 (1969).
- (5) Wringley, A.N., Striton, A.J., Howard E. Jr., *J. Org. Chem.* **25**, 439 (1960).
- (6) Weissberger, A., "Physical Methods of Organic Chemistry," Part I, p. 382, Interscience, New York, 1950.

RECEIVED for review September 18, 1968. Accepted February 26, 1969. Communication No. 1274 from the National Chemical Laboratory, Poona-8, India. This research has been financed in part by a grant made by the United States Department of Agriculture, Agricultural Research Service under P.L.-480.