T = temperature, °K
V = molar volume of liquid at normal boiling point, cm^3 per gram mole
β = cell constant, cm^{-2}
Δc = difference in concentration between cell compartments, grams/liter
η = viscosity of solution, centipoises
χ = association parameter of solvent

Subscripts

a = solute
b = solvent
o = initial
f = final

LITERATURE CITED

(1) Anderson, D. K., Hall, J. R., Babb, A. L., *J. Phys. Chem.*, **62**, 404 (1958).
(2) Byers, C. H., King, C. J., *ibid.*, **70**, 2499 (1966).
(3) Dullien, F. A. L., Shemilt, L. W., *Can. J. Chem. Eng.*, **39**, 242 (1961).
(4) Emanuel, A., Olander, D. R., *J. Chem. Eng. Data*, **8**, 31 (1963).
(5) Gainer, J. L., Metzner, A. B., A.I.Ch.E.-I. Chem. E. Symposium Series No. 6., "Transport Phenomena," pp 6, 74, Institution of Chemical Engineers, London, 1965.
(6) Garner, F. H., Marchant, P. J., *Trans. Inst. Chem. Eng. (London)*, **39**, 397 (1961).
(7) Gross, F., *Z. Angew. Phys.*, **9**, 606 (1957).
(8) Hammond, B. R., Stokes, R. H., *Trans. Faraday Soc.*, **49**, 890 (1953).
(9) Jones, J. R., Rowlands, D. L. G., Monk, C. B., *Ibid.*, **61**, 1384 (1965).
(10) Lemonde, H., *Ann. Phys.*, **9**, 539 (1938).
(11) Lewis, J. B., *J. Appl. Chem.*, **5**, 228 (1955).
(12) Merliss, F. E., Colver, C. P., *J. Chem. Eng. Data*, **14**, 149 (1969).
(13) Olander, D. R., *A.I.Ch.E. J.*, **7**, 175 (1961).
(14) Randall, M., Longtin, B., Weber, H., *J. Phys. Chem.*, **45**, 343 (1941).
(15) Sarram, P., M.Sc. thesis, Loughborough University of Technology, England, 1970.
(16) Schatzberg, P., *J. Polym. Sci.*, Part C, No. 10, 87 (1965).
(17) Sitaraman, R., Ibrahim, S. H., Kuloor, N. R., *J. Chem. Eng. Data*, **8**, 198 (1963).
(18) Smith, I. E., Storrow, J. A., *J. Appl. Chem.*, **2**, 225 (1952).
(19) Stokes, R. H., *J. Amer. Chem. Soc.*, **72**, 763 (1950).
(20) *Ibid.*, p. 2243.
(21) Valiev, K. A., Emelyanov, M. I., *J. Struct. Chem. (USSR)*, **5** (1), 7 (1964).
(22) Wilke, C. R., Chang, Pin, *A.I.Ch.E. J.*, **1**, 264 (1955).

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Surface Tension of Aqueous Solutions of Some Glycols

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The surface tensions of aqueous solutions of ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,3-butanediol, and 1,4-butanediol were measured at 30° C. A correlation between the surface tension of pure glycols and the volume contraction in an aqueous solution is presented.

As part of a thermodynamic study on aqueous solutions of alcohols and glycols (*4, 5*), the surface tensions of aqueous solutions of five glycols were measured at 30.00° C and are reported. This paper also calls attention to the fact that the surface tension of a pure glycol parallels the volume contraction of the same glycol in aqueous solution reported previously (*5*).

EXPERIMENTAL

The samples used were of G. R. grade JIS (Japan Industrial Standard) guaranteed reagent and were purified further by dehydrating over anhydrous salts such as Na_2SO_4 and distilling repeatedly with a fractionating column until their gas chromatogram (polyethylene glycol as column and H_2 as carrier gas) showed minimum impurities (probably isomeric glycols). Estimated purity was 99.8%. The densities of the final purified liquids were practically the same as those given in our previous report (*4, 5*).

The capillary height method (*2*) was used throughout the surface tension measurements. The uniformity in the inner diameter of capillaries was checked by measuring the length of a known amount of mercury in the capillary. Since by the conventional single capillary method it is difficult to determine the position of meniscus of free surface accurately, we adopted the two-capillary method, a modification credited to Sugden (*7*) and Richards *et al.* (*6*). The diameters of capillaries were 0.50 and 0.27 mm. The height of capillary rise was determined with a traveling microscope. All the measurements were made in a thermostat controlled to ±0.01° C. The accuracy of surface tension determination was estimated to be ±0.3 dyn/cm.

RESULTS AND DISCUSSION

In Table I are given the data for the surface tension of aqueous solutions of five glycols: ethylene glycol (12ED), 1,2-propanediol (12PD), 1,3-propanediol (13PD), 1,3-butanediol (13BD), and 1,4-butanediol (14BD).

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Table I. Surface Tension of Glycol–Water Solutions at 30.00° C

Ethylene glycol + H_2O			1,2-Propanediol + H_2O		
w[a]	x[b]	γ[c]	w	x	γ
0	0	71.15	0	0	71.15
0.0283	0.0084	69.33	0.0179	0.0043	68.43
0.0482	0.0145	68.58	0.0496	0.0122	65.00
0.0798	0.0246	67.54	0.0679	0.0170	63.32
0.0990	0.0309	66.84	0.0803	0.0203	61.92
0.1440	0.0466	65.04	0.1146	0.0297	59.41
0.1672	0.0550	64.19	0.1489	0.0398	57.75
0.1987	0.0671	63.37	0.1808	0.0497	55.88
0.2595	0.0923	61.58	0.2178	0.0619	53.92
0.3025	0.1118	60.25	0.3033	0.0934	50.56
0.3500	0.1351	59.54	0.3703	0.1222	48.13
0.4004	0.1624	58.28	0.5016	0.1924	44.46
0.5046	0.2282	56.02	0.5995	0.2617	41.53
0.6046	0.3074	54.13	0.6403	0.2965	40.28
0.6999	0.4037	52.08	0.6990	0.3547	38.64
0.7977	0.5337	49.99	0.8069	0.4973	37.56
0.8989	0.7206	48.28	0.9012	0.6834	36.26
1	1	46.24	1	1	35.46

1,3-Propanediol + H_2O			1,3-Butanediol + H_2O		
w	x	γ	w	x	γ
0	0	71.15	0	0	71.15
0.0287	0.0070	68.18	0.0317	0.0065	64.27
0.0362	0.0088	67.38	0.0679	0.0144	60.10
0.0619	0.0154	65.23	0.1028	0.0224	57.85
0.0979	0.0250	62.72	0.1486	0.0337	54.56
0.1246	0.0326	61.74	0.1704	0.0395	52.87
0.1613	0.0435	60.25	0.2208	0.0536	50.91
0.2274	0.0651	57.75	0.2451	0.0610	49.79
0.2544	0.0747	57.10	0.3094	0.0822	48.49
0.3021	0.0929	55.60	0.3516	0.0978	47.04
0.3410	0.1091	54.97	0.4150	0.1242	45.51
0.3783	0.1259	54.11	0.4980	0.1655	43.94
0.5003	0.1916	52.82	0.6791	0.2972	41.41
0.6371	0.2936	51.29	0.7862	0.4236	40.21
0.7438	0.4073	50.39	0.8592	0.5494	39.32
0.8320	0.5396	49.14	0.9261	0.7146	38.73
0.9478	0.8112	47.64	0.9584	0.8217	37.38
1	1	46.95	1	1	37.04

1,4-Butanediol + H_2O		
w	x	γ
0	0	71.15
0.0295	0.0060	66.69
0.0556	0.0116	64.47
0.0802	0.0172	62.49
0.0981	0.0213	61.31
0.1298	0.0290	59.64
0.1522	0.0346	58.30
0.2026	0.0483	56.82
0.2559	0.0643	55.05
0.3031	0.0800	54.15
0.4029	0.1189	51.96
0.5007	0.1670	50.73
0.5516	0.1974	50.21
0.5988	0.2298	49.51
0.6996	0.3177	47.95
0.8008	0.4455	46.63
0.9002	0.6432	45.23
1	1	43.79

[a] Weight fraction of glycol. [b] Mole fraction of glycol. [c] Surface tension in dyn/cm.

Table II. Correlation between Surface Tension of Pure Glycols and Partial Molar Volume Data

Glycols	γ, dyn/cm	$(\overline{v}_1)_{\min} - v_1^{0a}$, cc/mole
Ethylene glycol	46.2	−1.7 (0.060)[b]
1,2-Propanediol	35.5	−3.8 (0.060)
1,3-Propanediol	47.0	−1.9 (0.090)
1,3-Butanediol	37.0	−3.6 (0.045)
1,4-Butanediol	43.8	−2.6 (0.085)

[a] Taken from Figure 3 of Ref (5). [b] The number in parentheses indicates the mole fraction of glycol.

No activity data are reported for aqueous glycol solutions so that it is impossible to make a detailed thermodynamic analysis of the present data. Recently, there has been an increasing interest in studies of the structures of water and aqueous solutions (*1*, *3*). Therefore, we call attention to the following two evidences which might be of use for those studies.

First, we have shown (5) that the partial molar volume of glycol $\overline{v}$ is always lower than the molar volume v^0 and that the difference $\overline{v} - v^0$ is strongly affected by the presence of the methyl group in the glycol molecule. It is interesting to compare the γ values of pure glycol with the minimum values of $\overline{v} - v^0$—i.e., those at the minimum point in the $\overline{v}$ vs. x curve. The correlation is striking. As seen in Table II, a large volume contraction is associated with a low surface tension of the pure glycol. This fact is consistent with the interpretation that the filling of the void in volume of water is the cause of the larger $\overline{v}_{\min} - v^0$ observed with 12PD and 13BD (5).

Second, it appears that, when two glycols have almost the same γ values, a large decrease in the surface tension of dilute aqueous solutions is associated with the glycols having two hydroxyl groups separated by methylene groups (compare 12ED with 13PD and 13BD with 12PD). This may be due to strong intramolecular hydrogen bonding between two neighboring hydroxyl groups.

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LITERATURE CITED

(1) Franks, F., Ives, D. J. G., *Quart. Rev. Chem. Soc.*, **20**, 1 (1966).

(2) Harkins, W. D., Alexander, A. E., "Technique of Organic Chemistry," Vol. I, Part 1, p 757, Chap XIV, A. Weissberger Ed, Interscience, New York, N. Y., 1959.

(3) Kavanau, J. L., "Water and Solute-Water Interactions," Holden-Day, Inc, San Francisco, Calif., 1964.

(4) Nakanishi, K., *Bull. Chem. Soc. Jap.*, **33**, 793 (1960).

(5) Nakanishi, K., Kato, N., Maruyama, M., *J. Phys. Chem.*, **71**, 814 (1967).

(6) Richards, T. W., Speyers, C. L., Carver, E. K., *J. Amer. Chem. Soc.*, **46**, 1196 (1924).

(7) Sugden, S., *J. Chem. Soc.*, **119**, 1438 (1921).

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