

874. *Solutions of Alcohols in Non-polar Solvents. Part IV.* Some Thermodynamic Properties of Glycols in Benzene, Heptane, and cyclo-Hexane.*

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Measurements have been made by the synthetic method, over a range of temperature, of the solubilities of five glycols in benzene, heptane, and *cyclo*-hexane. The heats of solution ΔH and the standard entropies of solution ΔS° have been evaluated; in any one solvent there is a linear relation between ΔH and ΔS° .

Specificity in the relation between solute and solvent molecules is shown by there being no uniform trend in solubility with increasing molecular weight of the glycol in any solvent. Moreover, the dependence of both ΔH and ΔS° on the number of carbon atoms in the glycol molecule "alternates," *i.e.*, a large increment in ΔH or ΔS° on passing from one glycol to the next is followed by a smaller one, and *vice versa*. The steps which give the larger increments in heptane solutions produce the smaller increments in benzene and *cyclo*hexane. A possible explanation of the effect for the heptane solutions is advanced.

PREVIOUS papers of this Series concerned dilute solutions of primary alcohols in non-polar solvents. Certain properties of these solutions reveal specificity in the solute-solvent relation. Thus measurements of their viscosity¹ and the heat of solution of water in them² indicated that the molecules of alcohols from butanol or pentanol onwards, when dissolved in benzene, tend to adopt a cyclic configuration with partial screening of the hydroxyl group, while the values of the partial molar volumes of the alcohols at infinite dilution "alternate" in benzene and *cyclo*hexane, but not in heptane,³ as the homologous series is ascended. We have now investigated solutions where the solute molecules have polar groups at each end, interaction between which will influence the relative stabilities of different molecular configurations. The solutes chosen have been the first five polymethylene glycols $\text{HO} \cdot [\text{CH}_2]_n \cdot \text{OH}$, whose solubility we measured in benzene, heptane, and *cyclo*hexane as a function of temperature. These solubilities are so small that the solutions can be regarded as ideal, allowing values of the heat and entropy of solution to be derived.

* Part III, Staveley and Taylor, *J.*, 1956, 200.

¹ Staveley and Taylor, *J.*, 1956, 200.

² Staveley, Johns, and Moore, *J.*, 1951, 2516.

³ Staveley and Spice, *J.*, 1952, 406.

EXPERIMENTAL

Solubilities were determined by the synthetic method.^{2,4} Known masses of solute (from a weight pipette) and solvent were introduced into a glass tube (capacity *ca.* 25 ml. in experiments with benzene, and *ca.* 60 ml. with heptane and *cyclohexane*) which was then sealed and heated until the contents became homogeneous. As it cooled slowly the temperature at which the two phases separated (the "cloud-point") was determined. Care was taken to exclude moisture during filling. Numerous determinations were made of the cloud-point with each tube, and an average taken. Deviations of individual values from the mean seldom exceeded $\pm 0.2^\circ$ for benzene solutions and $\pm 0.4^\circ$ for heptane and *cyclohexane*.

Doubts about the reliability of the synthetic method were expressed by Joris and Taylor,⁵ who, using tritium as tracer, obtained a markedly lower value for the solubility of water in benzene. Recently, however, Wing and Johnson,⁶ also radiochemically, have obtained a value in good agreement with that found by the synthetic method, so there seems no reason to distrust its reliability for the determination of the solubility of one liquid in another even when the solubility is small.

Ethylene, trimethylene, and pentamethylene glycols were dried (Na_2SO_4) and then fractionated at atmospheric pressure. Tetramethylene and hexamethylene glycols were fractionally crystallized, the former then being distilled *in vacuo*. B. p.s (corr. to 760 mm.) or f. p.s of the glycols were as follows: ethylene, b. p. 196.8° ; trimethylene, b. p. 214.0 — 214.4° ; tetramethylene, f. p. 18.7° ; pentamethylene, b. p. 240.2 — 241.8° ; hexamethylene, f. p. 41.6° . The three solvents were as pure as those used earlier,³ and were all finally dried by distillation from phosphoric oxide.

TABLE 1. Solubility of glycols (N = mole fraction in benzene, cyclohexane, and heptane).

Benzene									
Ethylene		Trimethylene		Tetramethylene		Pentamethylene		Hexamethylene	
10^3N	t	10^3N	t	10^3N	t	10^3N	t	10^3N	t
2.51	29.0	2.92	26.2	3.01	27.0	3.33	31.5	7.00	43.8
4.79	47.1	5.23	42.1	4.49	36.4	4.36	37.6	9.81	51.9
6.71	56.8	7.16	51.0	6.97	47.3	6.49	47.5	12.97	58.5
9.43	67.4	10.09	60.7	10.75	58.7	8.20	52.8	14.72	61.4
		11.73	66.2						
$a = 6.5108$		6.6347		7.2734		7.4774		8.0476	
$b = 1.5452$		1.5482		1.7396		1.8142		1.9669	
cycloHexane									
0.380	46.1	0.283	39.3	0.192	33.2	0.292	40.9	0.359	41.1
0.490	51.8	0.635	54.4	0.348	44.1	0.788	59.2	0.675	53.1
0.816	62.9	0.9645	63.9	0.651	56.7	1.074	65.6	1.186	64.1
1.065	67.7	1.219	68.3	1.179	68.4	1.486	74.2	1.414	67.3
1.418	75.2	1.297	69.4						
$a = 7.5223$		7.6851		7.9097		7.9224		8.2208	
$b = 2.2181$		2.2568		2.3369		2.3386		2.4092	
Heptane									
0.344	42.7	0.244	39.5	0.2785	39.3	0.401	46.2	0.476	45.6
0.408	47.0	0.500	50.1	0.3795	44.8	0.491	49.9	0.501	46.7
0.448	49.7	0.771	58.6	0.385	45.0	0.754	58.0	0.664	51.2
0.672	56.6	1.027	64.6	0.5645	52.7	1.095	65.6	1.152	62.6
0.864	63.4			0.927	62.9			1.522	68.0
1.029	67.9								
$a = 7.1772$		7.8840		7.8327		8.2368		8.3308	
$b = 2.1001$		2.3212		2.3067		2.4372		2.4386	

Results are recorded in Table 1. N is the mole fraction of the glycol in a saturated solution at the "cloud-point," t° C. For every solution, $\log_{10}N$ was linear with $1/T$, where $T = t + 273.1^\circ$. Values of a and b in the equation $\log_{10}(10^4N) = a - 10^3b/T$ were evaluated for each system by the method of least squares, and are given in Table 1.

⁴ Staveley, Jeffes, and Moy, *Trans. Faraday Soc.*, 1943, **39**, 5.

⁵ Joris and Taylor, *J. Chem. Phys.*, 1948, **16**, 45.

⁶ Wing and Johnson, *J. Amer. Chem. Soc.*, 1957, **79**, 86

Some rough measurements were also made of the solubility of the three hydrocarbons in ethylene glycol, and of benzene and *cyclohexane* in pentamethylene glycol. Values of x , the mole fraction of the hydrocarbon, were: (1) in ethylene glycol, for benzene $x = 0.04$ at 53° , for *cyclohexane* $x < 0.014$ at 100° , for heptane $x < 0.003$ at 100° ; (2) in pentamethylene glycol, for benzene $x = 0.38$ at 87° and 0.30 at 57° , for *cyclohexane* $x = 0.10$ at 70° .

DISCUSSION

The existence of marked specificity in the relations between glycol and hydrocarbon molecules is apparent on comparing plots of $\log N$ against $1/T$ for the several glycols in a given solvent, or on considering the solubilities of the glycols in the same solvent at a given temperature. In Table 2 the solubilities are given at 39.4° ($10^3/T = 3.2$). In no solvent is there a steady increase in solubility with increasing length of the hydrocarbon chain in the glycol. For the first four glycols in *cyclohexane* and heptane there is little change in the solubility.

TABLE 2. *Interpolated solubilities of glycols in benzene, heptane, and cyclohexane at 39.4° C expressed as the mole fraction of glycol $\times 10^4$.*

	Benzene	Heptane	<i>cycloHexane</i>
Ethylene glycol	36.8	2.86	2.66
Trimethylene glycol	47.9	2.86	2.91
Tetramethylene glycol	50.9	2.83	2.70
Pentamethylene glycol	47.0	2.74	2.75
Hexamethylene glycol	56.9	3.37	3.25

Before the results in Table 1 can be used to give heats and entropies of solution, we must consider whether these dilute solutions of glycols in non-polar solvents can be regarded as ideal. Glycol molecules are in a sense intermediate between primary alcohol molecules and water molecules. Wolf⁷ has shown that at room temperature primary alcohols are effectively unassociated in benzene up to a mole fraction of *ca.* 10^{-2} , and in hexane and *cyclohexane* up to *ca.* 3×10^{-3} and *ca.* 1.5×10^{-3} respectively. These concentrations are considerably higher than the solubilities of the glycols. Water in benzene has a normal molecular weight⁸ up to its solubility limit at 5.4° , and at 20° accurately obeys Henry's law to the limit of saturation,⁹ when the mole fraction of water is 2.5×10^{-3} . This is roughly the same as the solubility of the glycols in benzene at the same temperature. Therefore it is reasonable to suppose that in the present solutions the glycols behave as unassociated, ideal solutes. If it is further supposed that the glycol-rich phase which separates from a saturated solution is pure glycol, the heat of solution ΔH and the entropy of solution ΔS can be readily evaluated from the slope and intercept respectively of the plot of $\log N$ against $1/T$. For the evaluation of the entropy of solution we shall take as the standard solution an ideal supersaturated solution of unit molality, when the entropy increase ΔS° per mole of glycol on passing from the pure liquid to the standard solution is given by $\Delta S^\circ = 4.573 [a - 4 + \log_{10} (1 + 1000/M)]$, where M is the molecular weight of the solvent and a , as defined above, determines the intercept of $\log_{10} 10^4 N$ with $10^3/T$. The heat of solution (to give the ideal dilute solution) is given by $\Delta H = 4.573b$, where b is the slope of the same plot. Values of ΔH and ΔS° are given in Table 3. Since the glycol-rich phase can never be quite pure, a correction involving the temperature variation of the composition of the glycol-rich phase should be applied, but the solubilities of the *cyclohexane* and heptane in the glycol are so small that this must be negligible, and the ΔH and ΔS° values of Table 3 should be good approximations to those of pure glycols. For benzene the correction will be more important and, from the results for pentamethylene glycol, the change in ΔH on applying it might be *ca.* 1 kcal./mole. It should be less for the lower

⁷ Wolf, *Trans. Faraday Soc.*, 1937, **33**, 179.

⁸ Peterson and Rodebush, *J. Phys. Chem.*, 1928, **32**, 709.

⁹ Greer, *J. Amer. Chem. Soc.*, 1930, **52**, 4191.

glycols. Unfortunately, only ethylene glycol was available in sufficient amount to permit the solubility of the hydrocarbon in it to be measured accurately. However, while ΔH and ΔS° of Table 3 for benzene solutions would be slightly altered if the correction could be applied, they are still useful for comparison.

TABLE 3. *Heats of solution (ΔH , kcal./mole) and entropies of solution [ΔS° , cal./(mole deg.)].*

	Benzene		Heptane		<i>cyclo</i> Hexane	
	ΔH	ΔS°	ΔH	ΔS°	ΔH	ΔS°
Ethylene glycol	7.07	16.70	9.60	19.29	10.14	21.18
Trimethylene glycol	7.08	17.26	10.62	22.52	10.32	21.93
Tetramethylene glycol	7.96	20.18	10.55	22.29	10.69	22.96
Pentamethylene glycol	8.30	21.12	11.15	24.14	10.69	23.01
Hexamethylene glycol	9.00	23.72	11.15	24.57	11.02	24.38

The values of ΔH for the glycols with even numbers of carbon atoms are approximately double those for the primary alcohols with half the number of carbon atoms (ΔH for alcohols has been determined calorimetrically by Wolf and his co-workers¹⁰), as shown in Table 4. The lower heats of solution (both of the glycols and of the alcohols) in benzene

TABLE 4. *Comparison of the molar heats of solution (ΔH , kcal./mole) of primary alcohols and glycols. The values for the alcohols refer to infinitely dilute solution.*

	Benzene	<i>cyclo</i> Hexane	Alcohol in hexane, glycol in heptane
$2\Delta H$ for $\text{CH}_3\cdot\text{OH}$	7.0	12.4	11.4
ΔH for $(\text{CH}_2\cdot\text{OH})_2$	7.1	10.1	9.6
$2\Delta H$ for $\text{C}_2\text{H}_5\cdot\text{OH}$	7.4	11.6	11.4
ΔH for $(\text{C}_2\text{H}_4\cdot\text{OH})_2$	8.0	10.7	10.6
$2\Delta H$ for $\text{C}_3\text{H}_7\cdot\text{OH}$	7.7	—	11.3
ΔH for $(\text{C}_3\text{H}_6\cdot\text{OH})_2$	9.0	11.0	11.2

than in heptane and *cyclo*hexane are evidence of the stronger interaction of the hydroxyl groups with benzene molecules than with the other hydrocarbon molecules. This stronger interaction leads to more pronounced solvation with its accompanying entropy loss and hence accounts for the smaller ΔS° values in benzene. But in their effect on the solubility, the smaller ΔH values in benzene have a larger influence than the smaller ΔS° values, so that the solubilities of the glycols in benzene are considerably larger than in the other solvents.

While Wolf's figures show a decrease in ΔH for the primary alcohols with increasing chain length in hexane, and an increase in benzene, for the glycols ΔH increases with increasing chain length in all three solvents. And whereas the trend in ΔH with the primary alcohols is irregular, for the glycols it shows an interesting alternation (Fig. 1). The same effect is shown by ΔS° (Fig. 2). A large increment in ΔH or ΔS° is followed by a smaller one, and *vice versa*, and small though some of these increments are, this is true for all twenty-four increments involved. The origin of this alternation could reside, *a priori*, in the nature of the pure liquid glycols, or in that of the solutions, or both. The m. p.s of the solids show an alternation, so that if the liquids are considered at a fixed temperature then there is an alternation in the separation of this temperature from the m. p. However, the physical properties (even molar volumes) of the glycols have not been sufficiently studied to provide evidence of any alternation. That the steps which produce the *larger* increments in ΔH and ΔS° in benzene and *cyclo*hexane solutions (such as that from trimethylene to tetramethylene glycol) give the *smaller* ones in heptane strongly suggests that the observed alternations in ΔH and ΔS° depend partly on the nature of the solute-solvent interactions.

These interactions may be simplest when heptane is the solvent, since then the solute

¹⁰ Wolfe, Pahlke, and Wehage, *Z. phys. Chem.*, 1935, **B**, 28, 1.

FIG. 1.

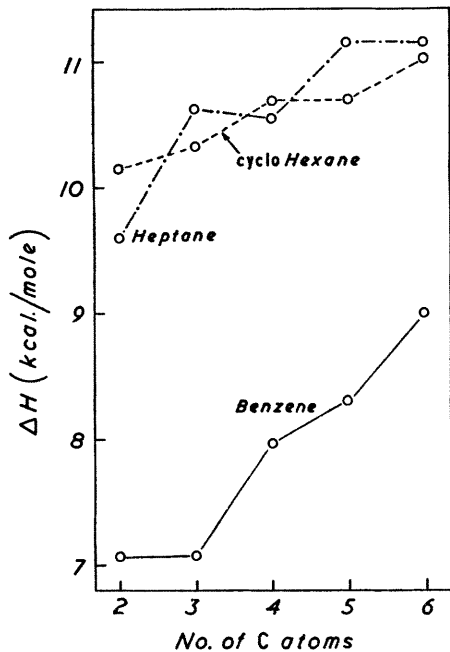


FIG. 2.

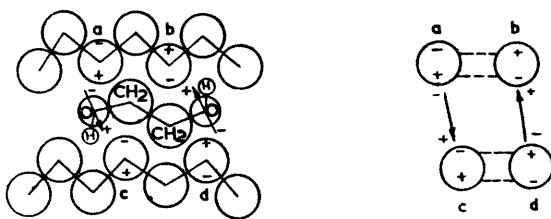
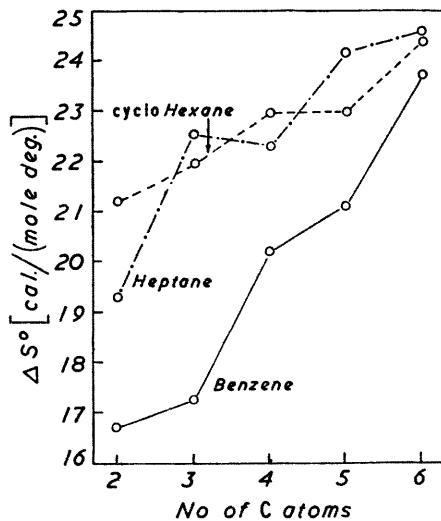
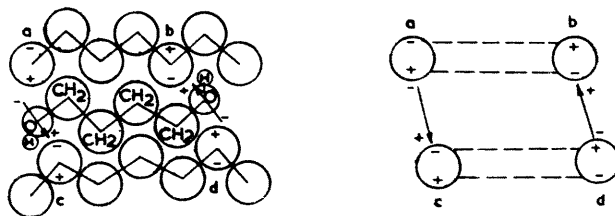
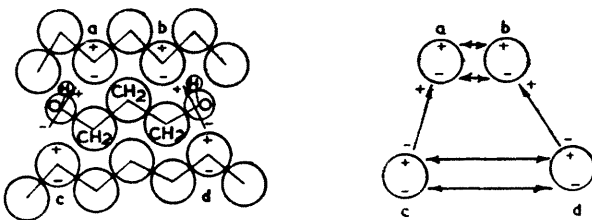


FIG. 3. Possible idealized arrangements of the molecules of (from top to bottom) ethylene, trimethylene, and tetramethylene glycol in solution in heptane.



and solvent alike have flexible zig-zag chains, and it seems probable that (owing to dispersion forces and short-range repulsion forces) glycol molecules will tend to pack as economically as possible into the surrounding heptane molecules. Parallel alignment of hydrocarbon chains is preferred, and Fig. 3 shows idealized arrangements in which two parallel heptane molecules with stretched chains have a glycol molecule between them. Close-packing is assisted if the ethylene and tetramethylene glycols have *trans*-configurations while the trimethylene glycol is *cis*. This has some support in the dipole moments of polymethylene dibromides in heptane, which for ethylene, trimethylene, tetramethylene, and pentamethylene dibromide also show an alternation, being respectively 1.02, 2.02, 1.96, and 2.44 D at 25°.¹¹ Each polar $-\text{CH}_2\cdot\text{OH}$ group will induce dipoles in segments of the adjacent surrounding heptane molecules. The direction of the resultant moment of this group makes an angle of between 61° and 67° with the C-O bond,¹² so that the induced dipoles lettered a, b, c, and d will have approximately the directions shown. Fig. 3 shows that there is attraction between the pairs of dipoles a-b and c-d for ethylene and tetramethylene glycols, but repulsion for trimethylene glycol. The potential energy of the

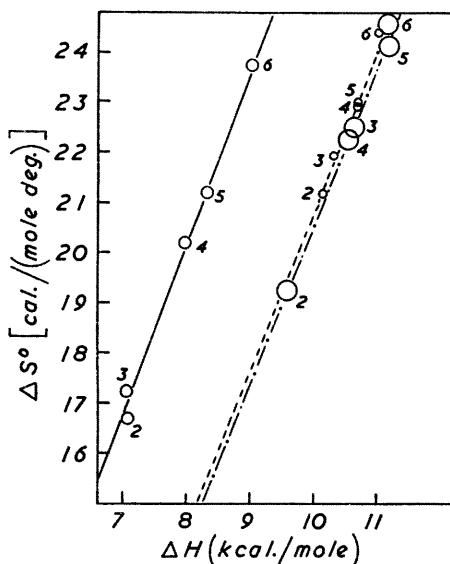


FIG. 4.

Large circles, heptane; medium circles, benzene; small circles, cyclohexane. Numerals refer to the number of carbon atoms in the glycol molecules.

solute-solvent system will be higher for the last glycol, both because of this and because of the repulsion between the *cis*-dipoles within the glycol molecule. The heat of solution, being the heat absorbed when the glycol passes from pure liquid to solution, will be smaller the greater the attraction between solute and solvent molecules and the lower their potential energy. This could account, therefore, for ΔH for trimethylene glycol in heptane being higher than for ethylene and tetramethylene glycol. The alternation would then be expected to die out as the series is ascended, but it is noteworthy that the dipole moments of polymethylene dibromides and dicyanides do not reach a steady value below the hexamethylene compounds.

It is more difficult to visualise the sort of intermolecular relation which may be preferred in benzene and cyclohexane, where the alternation effects in ΔH and ΔS° are the reverse of those in heptane, but it is noteworthy that in benzene the moment of ethylene dibromide (1.50 D) is considerably greater than it is in heptane, whereas those of trimethyl (1.97), tetramethyl (2.00), and pentamethyl dibromide (2.25 D) are respectively less, greater, and less than those in heptane at the same temperature (25°).¹¹ Thus benzene may favour

¹¹ Smyth and Walls, *J. Chem. Phys.*, 1933, **1**, 200.

¹² Smyth, "Dielectric Behaviour and Structure," McGraw-Hill Book Co., Inc., New York, 1955, p. 302.

somewhat the adoption of *cis* (or skew) polar configurations of the glycol molecules with an even number of carbon atoms. Since the geometry of the benzene molecules has less affinity with that of glycol molecules than that of either heptane or *cyclohexane* molecules, it might be expected that as the glycol chain lengthens and its polar ends (and the effects that they induce) become more independent, any particular configuration of the solute molecules should be less preferred and consequently the entropy of solution should be correspondingly increased. In fact, ΔS° increases more rapidly with increasing chain length of the glycol in benzene than it does in either heptane or *cyclohexane*. If ΔS° were corrected to allow for the impurity of the glycol phase (p. 4371), then the approximate results for the composition of the glycol-rich phase obtained for ethylene and pentamethylene glycol indicate that the corrected ΔS° values for benzene solutions would show an even more rapid increase with increasing glycol chain length.

Finally, Fig. 4 shows that these solutions provide further examples of systems in which the relation between the heat and entropy of solution for a series of solutes in a given solvent is linear. All three lines have approximately the same slope, but that for benzene is displaced very considerably from the other two, which fall very close together.

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