

CCXXVII.—*Cryoscopic Irregularities with Phenols.*

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IN spite of extensive investigation, the forces causing deviation from Raoult's law are still but poorly understood, especially where solvents and solutes possess such ill-defined electrochemical character as is found with organic compounds. Early attempts to account for such cryoscopic irregularities were based variously on theories of solute ionisation or association, of solvate formation, and of separation of solid solutions, yet their inadequacy has now necessitated the introduction of thermodynamic concepts. The consequent emphasis on intermolecular forces suggests the possibility of correlating cryoscopic irregularities with those physical properties (*e.g.*, molecular volume, viscosity, vapour or osmotic pressure) which are governed by such forces. In this paper, which continues previous investigations of typical organic liquids in phenol solution (Robertson, J., 1903, **83**, 1425; 1904, **85**, 1617; 1905, **87**, 1574; 1906, **89**, 567), cryoscopic measurements have been accompanied in typical cases by simultaneous determination of the alteration in molecular volume of the liquid solutes upon addition to the solvent.

Cryoscopic Deviations.

Calculation of Results.—The molecular depression constant $K = \Delta Mb/100a$ for Raoult's equation was calculated after successive additions of solute in amount sufficient to cause a depression increasing from 0.5° to 5.0° . These depression "constants" were then plotted against the depressions, and the values of K at depressions of 1° (K_1) and of 3.5° ($K_{3.5}$) were read off from the curves. A simple qualitative expression for the deviation was then obtained

by expressing the difference between these constants ($K_{3.5} - K_1$) as a percentage of the depression constant at 1° (K_1). The "percentage deviations," $100(K_{3.5} - K_1)/K_1$, so obtained are numerically equal to approximately one-third of Robertson's "rate" of association.

Table I contains the values obtained for K_1 , $K_{3.5}$, and the percentage deviation for alcohols, phenols, anilines, anilides, and amides, also pyridine and quinoline, in phenol solution.

TABLE I.

<i>Alcohols.</i>	K_1 .	$K_{3.5}$.	% Dev.	<i>Phenols.</i>	K_1 .	$K_{3.5}$.	% Dev.
Methyl	67.4	67.4	0	<i>m</i> -Cresol	43.4	41.6	- 4.1
Ethyl	68.1	69.2	+ 1.6	Resorcinol	55.0	53.0	- 3.6
Propyl	65.2	68.2	+ 4.6	<i>o</i> -Cresol	53.4	52.0	- 2.6
<i>iso</i> Propyl	66.5	68.6	+ 3.2	Pyrocatechol	54.7	53.4	- 2.4
Allyl	67.0	67.4	+ 0.6	<i>o</i> -Chlorophenol	57.1	55.7	- 2.5
<i>n</i> -Butyl	68.1	68.9	+ 1.2	<i>p</i> -Cresol	65.5	64.4	- 1.7
<i>n</i> -Octyl	68.2	68.7	+ 0.7	Quinol	60.3	58.1	- 3.6
Cetyl	62.6	55.2	-12.0	<i>p</i> -Chlorophenol	66.3	65.2	- 1.7
Benzyl	68.1	68.2	+ 0.1	<i>s</i> -Tribromophenol	68.8	66.9	- 2.9
<i>Anilines.</i>				<i>Anilides.</i>			
Aniline	69.1	70.5	+ 2.0	Acetanilide	69.5	72.9	+ 4.9
<i>o</i> -Toluidine	68.0	71.2	+ 4.7	Phenylacetanilide	70.9	74.5	+ 5.1
<i>m</i> -Toluidine	68.3	71.7	+ 5.0	Chloroacetanilide	69.6	70.8	+ 2.0
<i>p</i> -Toluidine	68.6	71.9	+ 4.8	Propionanilide	68.5	72.0	+ 5.2
<i>p</i> -Bromoaniline	68.5	69.4	+ 1.3	<i>n</i> -Butyranilide	70.5	73.4	+ 4.1
<i>s</i> -Tribromoaniline	68.0	63.9*	- 7.5	<i>iso</i> Butyranilide	70.5	72.8	+ 3.3
<i>Substituted Anilides.</i>				<i>n</i> -Octoanilide	71.5	73.6	+ 2.9
Aceto- <i>p</i> -toluidide	71.7	75.9	+ 5.9	Palmitanilide	68.8	66.2	- 3.8
Chloroaceto- <i>p</i> -toluidide	70.6	74.0	+ 4.8	Succinanilide	74.1	83.5	+12.7
Propiono- <i>p</i> -toluidide	70.0	73.7	+ 5.3	Azellanilide	79.6		
Aceto- <i>p</i> -bromoanilide	71.1	72.5	+ 2.0	Sebacanilide	75.1		
Phenylaceto- <i>p</i> -bromoanilide	69.5	70.9	+ 2.3	<i>Amides.</i>			
Glutaro- <i>p</i> -bromoanilide	77.4			Acetamide	69.5	74.6	+ 7.3
Dinono- <i>p</i> -phenylenediamide	75.4			Phenylacetamide	70.3	74.2	+ 5.5
Dihepto- <i>p</i> -phenylenediamide	75.8			Chloroacetamide	68.3	70.8	+ 3.7
				Pyridine	68.8	74.7	+ 8.6
				Quinoline	65.1	69.0	+ 6.0

* Owing to the limited solubility of tribromoaniline this figure is for a depression of 3°. For the percentage deviation a correction has been made.

A general perusal of these deviations reveals two main tendencies : (1) As an homologous series is ascended, deviations of K increase at first in a positive direction, but at the fourth carbon atom a reversal occurs until in the long-chain carbon compounds deviations finally become negative (compare alcohols and anilides); (2) substitution by a phenyl group produces no regular change of deviation, but substitution by a halogen atom tends to produce negative deviation (compare aniline with *p*-bromo- and *s*-tribromo-aniline; anilides with *p*-bromoanilides; chloroacetanilide and chloroacetamide with the unsubstituted compounds).

These tendencies, noted already by Robertson in his investigations on acids and esters, would seem to be general in all homologous series, and to point to a differentiation of the effect on percentage deviation of the hydrocarbon chain and of the attached polar group. In the view of Hildebrand (*J. Amer. Chem. Soc.* 1916, **38**, 1452), osmotic phenomena are considered to be the,

observable expression of intermolecular forces induced (*a*) by the internal pressure and (*b*) by the polarities of the interdiffused liquids. Since relative internal pressure among homologues presumably varies as the size of the molecule, whereas polarity is largely dependent on the attached group, this view may be regarded as receiving confirmation in these results.

Another feature of the table not so readily explained is observed with the cresols, where, although noticeable parallelism is shown by the depression curves, the molecular depression constants are markedly dissimilar whatever the concentration. Bruni's explanation involving the separation of solid solutions is not applicable here even if we accept his analytical technique (see Robertson, *loc. cit.*, 1906); for, first, van Bijlert (*Z. physikal. Chem.*, 1891, **8**, 352), using this technique, found no separation of solid solution whatever with *m*-cresol, whereas in its depression constant this is the most irregular phenol; secondly, crystallographic data reveal marked divergence in crystal structure among compounds found to exhibit very similar molecular depressions; and finally, while morphotropic considerations indicate that *p*-substitution, in affecting least the symmetry of the molecule, favours similarity of crystal structure between the simple and substituted compounds, in this investigation the greatest deviation is found with *o*- and *m*-substituted compounds. A theory of active molecules propounded by Brown and Bury (*J. Physical Chem.*, 1926, **30**, 694) provides no better explanation, since it involves regularity at infinite dilution and has no explanation for parallel depression curves.

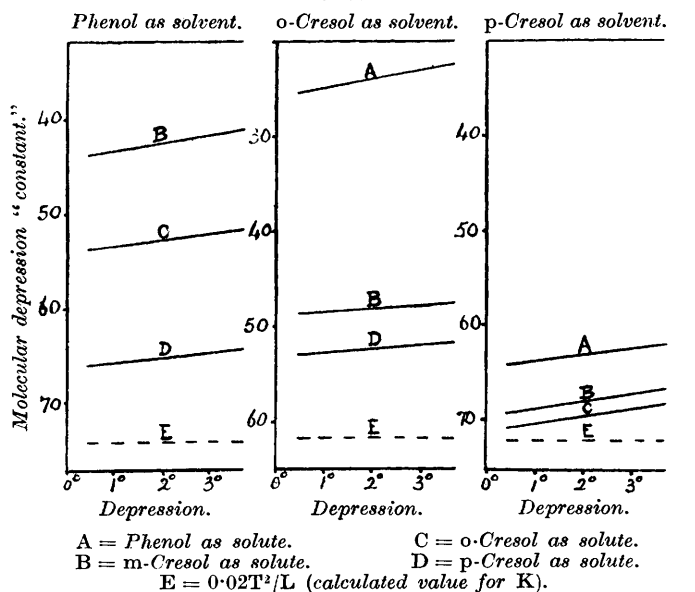
Further light was sought by investigating *o*- and *p*-cresol as solvents for simple phenols; the curves shown in Fig. 1 were obtained. The remarkable parallelism of curves would seem to indicate the formation of solid solutions, as would also the fact that phenol-*o*-cresol and phenol-*p*-cresol mixtures show abnormalities of like extent whichever component be in excess. However, the characteristically greater abnormality of *m*-cresol, as compared with *o*- or *p*-cresol, in each of the structurally different solvents is incompatible with this conclusion, and the previous criticisms have been in no wise invalidated.

The smaller abnormalities disappear almost completely if a mean depression constant (69) for the homologous series investigated is used for comparison in preference to the van 't Hoff theoretical constant ($K = 0.02T^2/L = 74$). Hence the explanation of abnormality may be that in phenolic solutions the van 't Hoff equation requires considerable modification to include some theory of active molecules, though the theory of Brown and Bury cannot be accepted in its present form.

Variations of Molecular Volume.

Calculation of Results.—The alteration of molecular volume of the solute is expressed as the ratio (Molecular solution volume)/(Molecular volume), where the molecular volume is derived from the density of the pure liquid at 40°, and the molecular solution volume is calculated on the simple mixture law from the solution density at 40° of that solution which produces a depression of 4.5° in the freezing point of phenol. Thus the solutions are of approximately the same molecular concentration, but the assumption is made that the

FIG. 1.



whole change of volume upon solution takes place in the molecules of the smaller component.

The molecular volume changes in the various binary liquid mixtures are tabulated in Tables IIa and b, where p is the percentage composition required to produce a depression of 4.5°. Direct determinations of density at 40° were made except for the molecular volumes of the pure simple alcohols, which were obtained by extrapolation of their known densities at other temperatures. Figures for a hydrocarbon, an ester, and an acid are also included, since each of these types shows a characteristic deviation curve.

It is noted from Table II (a) that the alcohols show a typically low ratio of M.S.V./M.V., whereas the phenols (omitting the not unexpected exceptional values for halogen derivatives) show little volume

TABLE II.

(a) Phenol as solvent.		K (experimental mean) = 69.0.					Devi- ation, %
Solute.	p .	M.S.V.	M.V.	M.S.V.	$K_{4.5}$.		
Methyl alcohol	2.2	40.0	41.6	0.96 ₁	67.5	0	
Ethyl alcohol	3.1	57.2	59.6	0.96 ₀	69.5	+ 1.6	
Propyl alcohol	4.0	73.1	76.3	0.95 ₈	68.3	+ 4.6	
<i>iso</i> Propyl alcohol	3.8	74.4	78.0	0.95 ₄	69.2	+ 3.2	
Allyl alcohol	3.8	69.1	71.1	0.97 ₂	67.4	+ 0.6	
<i>iso</i> Butyl alcohol	5.1	90.2	94.5	0.95 ₁	69.3	+ 1.2	
<i>n</i> -Octyl alcohol	7.5	157.0	159.8	0.98 ₂	68.8	+ 0.7	
Cetyl alcohol	21.0	282.9	294.0	0.96 ₂	52.5	- 12.0	
Benzyl alcohol	7.2	104.5	104.9	0.99 ₇	68.5	+ 0.1	
<i>m</i> -Cresol	11.7	105.9	106.1	0.99 ₇	40.7	- 4.1	
<i>o</i> -Cresol	9.1	104.8	105.0	0.99 ₈	50.6	- 2.6	
<i>o</i> -Chlorophenol	10.6	104.8	103.6	1.01 ₂	55.0	- 2.5	
<i>p</i> -Cresol	7.9	106.0	106.1	0.99 ₈	63.9	- 1.7	
<i>p</i> -Chlorophenol	9.0	104.2	101.6	1.02 ₈	64.8	- 1.7	
Toluene	6.6	104.6	108.4	0.96 ₁	61.3	- 5.4	
Ethyl malonate	9.5	153.4	154.8	0.99 ₀	80.0	+ 11.0	
Acetic acid	4.4	58.3	58.3	1.00 ₀	—	—	

(b) *o*-Cresol and *p*-cresol as solvents.

Solute.	<i>o</i> -Cresol, K (mean) = 56.0.				<i>p</i> -Cresol, K (mean) = 70.0.			
	p .	M.S.V.	$K_{4.5}$.	Dev., %.	p .	M.S.V.	$K_{4.5}$.	Dev., %.
Toluene	8.3	0.97 ₅	48.9	- 8.0	6.4	0.97 ₂	62.3	- 6.2
Ethyl malonate	11.4	0.99 ₁	64.8	+ 10.0	9.0	0.98 ₈	79.8	+ 5.3
<i>iso</i> Propyl alcohol	5.0	0.96 ₁	53.6	+ 0.6	3.9	0.95 ₇	68.5	+ 0.2
Acetic acid	4.3	0.97 ₅	—	—	4.4	0.99 ₂	—	—
<i>p</i> -Cresol	9.0	0.99 ₈	51.1	- 2.1	—	—	—	—
<i>o</i> -Cresol	—	—	—	—	6.7	0.99 ₁	67.9	- 2.7
<i>m</i> -Cresol	9.6	0.99 ₉	47.1	- 2.3	7.6	0.99 ₇	65.8	- 2.8
Phenol	16.6	1.00 ₅	20.9	- 9.6	6.4	1.00 ₁	60.6	- 2.5

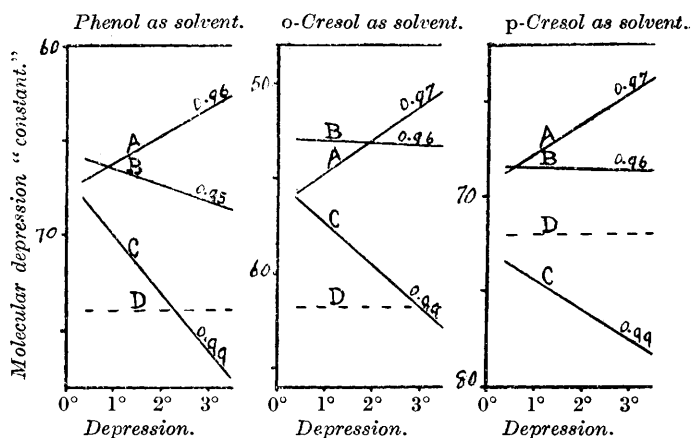
change. Benzyl alcohol, though alcoholic in cryoscopical behaviour, behaves in volume change as a benzene derivative. The absence of volume change in mixtures of phenols is confirmed in Table II (b), so that, whatever the nature of the molecular environment producing such divergent magnitudes for K , it has no effect on molecular volumes. It is therefore not surprising that the depression curves of these phenolic mixtures are found to be parallel.

TABLE III.

Solute.	Toluene.	<i>m</i> - Xylene.	<i>iso</i> Amyl acetate.	<i>o</i> - Cresol.	Phenol.	<i>p</i> - Cresol.
Toluene	—	1.00 ₆	1.00 ₃	0.97 ₅	0.96 ₄	0.97 ₂
Ethyl malonate	1.02 ₄	1.02 ₆	1.02 ₃	0.99 ₄	0.99 ₀	0.98 ₈
<i>o</i> -Cresol	1.02 ₅	1.01 ₈	0.98 ₈	—	0.99 ₈	0.99 ₁
<i>m</i> -Cresol	1.02 ₂	1.01 ₂	0.98 ₅	0.99 ₉	0.99 ₇	0.99 ₇
Phenol	1.03 ₀	1.01 ₄	0.98 ₂	1.00 ₅	—	1.00 ₄
<i>p</i> -Cresol	1.01 ₅	1.01 ₆	0.98 ₅	0.99 ₈	0.99 ₃	—
<i>iso</i> Propyl alcohol	1.04 ₃	1.02 ₃	1.02 ₄	0.96 ₁	0.95 ₄	0.95 ₇
Acetic acid	1.07 ₆	1.03 ₆	0.89 ₄	0.97 ₅	1.00 ₀	0.99 ₂
Mean (excluding acetic acid)	1.02 ₇	1.01 ₅	0.99 ₉	0.99 ₀	0.98 ₅	0.98 ₅

To strengthen any conclusions based on volume changes, molecular volume changes were determined with the unassociated toluene, *m*-xylene, and *iso*amyl acetate as solvents. These figures, together with those for the phenols, are in Table III, where both solutes and solvents are arranged in order of their "degree of association" in the liquid state. It would appear that unassociated solvents have the effect of increasing the molecular volume of solutes in solution. Yet generalisations based on concepts of molecular association require solutes in normal solvents to be associated, and to have, almost certainly, smaller molecular volumes, so that these figures enlarge the increasing mass of evidence which

FIG. 2.



A = Toluene as solute.

C = Ethyl malonate as solute.

B = *iso*Propyl alcohol as solute.D = $0.02T^2/L$ (calculated value for K).

discredits the widespread use of "association" concepts to explain irregular behaviour in intermolecular phenomena (see Brown and Bury, *loc. cit.*, p. 702). It is significant that *isopropyl* alcohol and acetic acid, which would commonly be regarded as the most "associated" of the solutes, show this contrary result in molecular volume change to the greatest extent.

General Discussion.

Results for solutes of the three types, alcohol, ester, and hydrocarbon, in the three phenolic solvents are compared in Fig. 2. (Type phenols have already been discussed, and comparison with type acids is invalidated by large polar effects.) The figures placed on each curve represent the ratio M.S.V./M.V., and it seems obvious that each typical deviation is accompanied by an equally typical

alteration of the molecular volume. Hence it becomes significant to enquire whether the intermolecular forces causing this volume change are also capable of governing the cryoscopic deviations.

Referring first to volume changes and to Table III, we find that the anomaly there remarked vanishes if we explain the results in terms of internal pressures, since a solute of internal pressure similar to that of its solvent will be dissolved without volume change, whereas a solute of smaller internal pressure would be compressed on solution, or *vice versa*. By forming a general estimate of internal pressures in this way, we find that their descending order for our compounds is: acetic acid, *isopropyl* alcohol, the phenols and ethyl malonate, the hydrocarbons and amyl acetate—a good agreement with generalisations from Mortimer's internal-pressure data (*J. Amer. Chem. Soc.*, 1923, **45**, 633). The marked irregularity of phenols and acetic acid when dissolved in amyl acetate is a good illustration of specific disturbing influences which may arise out of polar groups.

Referring now particularly to the solutes of Fig. 2, we find that in toluene and xylene solutions, ethyl malonate and *isopropyl* alcohol are expanded and toluene is normal, whereas in phenolic solutions, the ester is normal and toluene and *isopropyl* alcohol are compressed. This anomalous behaviour with alcohol-phenol mixtures is satisfactorily attributed to the tendency towards chemical combination of the molecules resulting in a closer binding and a smaller molecular volume.

Correlation between the deviation of the cryoscopic constant and these demonstrated internal-pressure differences is now sought. Hildebrand (*J. Amer. Chem. Soc.*, 1916, **38**, 1473; 1919, **41**, 1078) finds that in mixed liquids difference of internal pressure produces positive deviation from Raoult's law, since such a mixture results in smaller molecular attractions and increased vapour pressure, thereby reducing the "lowering of vapour pressure" and the amount of change in boiling point or freezing point. This diminution results in that increase of molecular weight (or decrease of K) so commonly stated to be due to "association." Inequality of polarity produces a like effect, but with two highly polar liquids deviation is found to be negative.

Toluene and phenol show differences in both internal pressure and polarities (as estimated qualitatively from dielectric constants); they reveal a marked decrease of K with concentration. Ethyl malonate and phenol possess similar internal pressures and are both highly polar; K increases markedly with concentration. *iso*-Propyl alcohol and phenol possess different internal pressures and polarities, but show a tendency to unite; the expected decrease

in K is balanced by the increase due to a tendency to solvate formation. The cresols have internal pressures similar to that of phenol, but lower polarities; for each solute, the cresols show deviations of a slightly less positive character than phenol.

Thus a very interesting relation between deviations from cryoscopic normality and changes in molecular volume seems to have been established, and to be correlated with a difference of internal pressures and polarity of the intermixed liquids; but until further data have accumulated it is impossible to formulate more trustworthy conclusions. Since throughout the investigation great care was taken to eliminate as far as possible any error due to the hygroscopic nature of the solvents or other experimental sources of irregularity, it is considered that the deviations observed were conditioned by the forces governing interaction of solvent and solute.

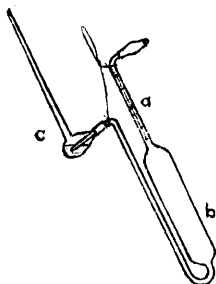
Finally, we append a table of densities (d_{40}^{40}) of various liquids :

Acetic acid ...	1.0291	Phenol	1.0586	<i>o</i> -Chlorophenol	1.2416
<i>iso</i> Amyl acetate	0.8524	<i>o</i> -Cresol	1.0290	<i>p</i> -Chlorophenol	1.2651
Ethyl malonate	1.0349	<i>m</i> -Cresol	1.0184	Toluene	0.8498
Allyl alcohol ...	0.8166	<i>p</i> -Cresol	1.0186	<i>m</i> -Xylene	0.8487
Benzyl alcohol	1.0303				

EXPERIMENTAL.

The Beckmann apparatus with magnetic stirring device was employed in the cryoscopic work. Determinations were made with considerable care, and by adopting special precautions—notably a cooling bath insulated with cotton-wool and maintained at 35° over a steam boiler—highly comparable results were obtained.

FIG. 3.



Density determinations of pure liquids in amounts of about 3 c.c. were made in a specially constructed pyknometer of volume known at 40° (Fig. 3). With the trap c turned downwards, the liquid was aspirated into the weighed pyknometer b until it reached the scale on the arm a , which was next closed with a rubber cap. Then the pyknometer, inserted in its containing vessel in the position shown in the figure, was immersed in the thermostat at 40°; when equilibrium was reached, the vessel was tilted to displace the liquid in the trap from the mouth of the pyknometer, the volume was read to 1/10,000 c.c. from the scale, and cooling was allowed in this position. Then the trap was removed and the second weighing made.

Solution densities were determined in a special long-necked

specific-gravity bottle, graduated at 40° to read to 0.001 c.c. over the range 13.5—14.0 c.c. The final solution from the Beckmann apparatus was transferred directly to the bottle by means of a long-pointed pipette of the same capacity, the volume was read off after equilibrium was attained in the thermostat, and weighings were made. It is believed that through the use of these methods, the experimental error in the final ratio M.S.V./M.V. is no greater than 0.5%.

The best materials obtainable commercially were used. Liquids were further purified by drying and repeated fractionation until the b. p. of the accepted sample varied by no more than $\pm 0.1^\circ$. Solids were successively recrystallised, generally from aqueous alcohol, until the correct m. p.'s were obtained. The amido- and anilido-compounds were prepared from pure constituents by treating the base directly with the acid chloride of the appropriate acid (prepared by use of thionyl chloride). In certain instances this method was not applicable, and the methods indicated in the literature were adopted. The phenol, *o*-cresol, and *p*-cresol used as solvents were twice fractionated and twice recrystallised with the rejection of one-third during each operation, and gave final freezing points in good agreement with the literature. Suitable methods for successive deliveries of about 15 g. of solvent to the Beckmann tube without contact with the atmosphere were adopted.

Summary.

(1) The van 't Hoff equation ($K = 0.02T^2/L$) does not hold for the solutes investigated, even at low concentrations.

(2) The observed deviations seem to depend on internal pressure and polarity in accordance with the theory of Hildebrand.

(3) Derived phenols have been found to show in their binary mixtures marked divergences not traceable to these causes. The theories of solid solutions and of activity (as formulated by Brown and Bury) have been shown to be unsatisfactory as explanations, but some theory of activity seems to be required.

(4) A general relation is shown between changes in molecular volume upon solution and cryoscopic behaviour, and this relation is in agreement with deductions drawn from internal-pressure data.

(5) Densities of various phenols and other compounds have been determined at 40°.