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THE EFFECT OF A NON-VOLATILE SOLUTE ON THE PARTIAL PRESSURES OF LIQUID MIXTURES AT THE BOILING POINT[1]

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The numerous investigations of solutions in mixed solvents recorded in the literature include only two on partial pressures,[3] although from the thermodynamic standpoint vapor pressure is one of the most fundamental and readily treated properties of liquids. The study recorded here deals largely with dilute solutions, of "normal" behavior from the standpoint of the simple laws of dilute solution, but is concerned with selective effects appearing in these systems. The data were obtained in connection with an ebullioscopic study of the same systems.

Apparatus and Materials

The method of Rosanoff, Lamb and Breithut[4] was chosen for the determination of partial pressures. This consists in distillation under conditions such as to avoid reflux condensation, collecting successive measured samples of distillate, analyzing, plotting composition against percentage distilled and extrapolating to zero distillate. The apparatus as described was somewhat modified. The capacity was decreased, vapor was sub-

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[1] Prepared from portions of theses submitted to the Faculty of the Graduate School of the University of Wisconsin by B. H. Carroll and G. K. Rollefson in partial satisfaction of the requirements for the degrees of Doctor of Philosophy and Master of Arts, respectively.

[2] Du Pont Fellow in Chemistry, 1921–1922.

[3] Roloff, *Z. physik. Chem.*, **11,** 7 (1893). Wright, *J. Chem. Soc.*, **121,** 2251 (1922).

[4] Rosanoff, Lamb and Breithut, This Journal, **31,** 448 (1909); *Z. physik. Chem.*, **66,** 349 (1909).

stituted for liquid in the thermostat, and the hand-operated pressure regulator was replaced by a barometric type, as described by Mathews and Faville.[5]

The construction is evident from the diagram (Fig. 1).

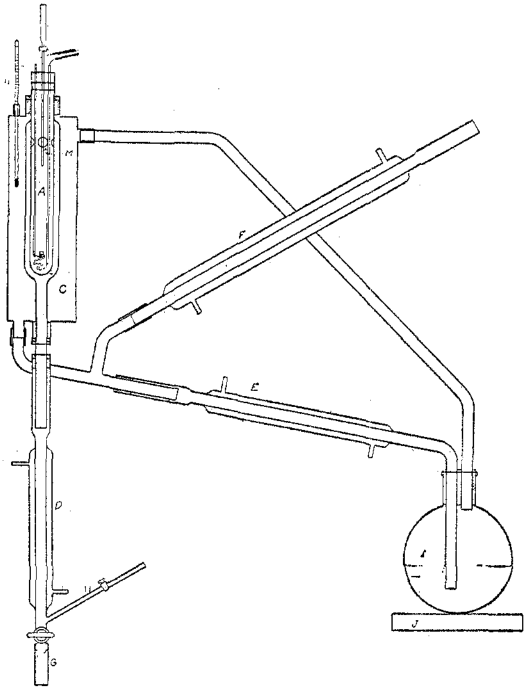

Fig. 1.—Section of partial-pressure apparatus.

The liquid was boiled in the tube A by the electrical heating coil B; the vapor passed out through the holes M into the outer jacket and downward to the condenser D. The metal jacket C was maintained at a temperature 1° to 3° higher than the boiling point of the mixture in A, by boiling a suitable liquid in I. The liquids were introduced into A through L, from a weight pipet.

The solvents were purified by suitable chemical treatment, followed by careful fractionation; purity was tested by boiling point, density and refractive-index measurements. The solutes were standard C. P. chemicals, recrystallized or resublimed.

The mixtures were analyzed by the refractometer, using data obtained from synthetic mixtures. Curves plotted from the data may be read to 0.1% except in the case of ether-acetone mixtures, where the error is ±0.3%.

The vapor-pressure determinations were made rapidly, with only about 25 cc. of liquid; the total time required, including that for analyses, was not over one and one-half hours. Three or four samples of distillate, of 2 to 3 cc. each, were collected, weighed and analyzed.

The results are plotted (Figs. 2–6) in terms of the difference between vapor and liquid composition, in order to present on a sufficiently large scale the changes produced by the solute. Recalculation in terms of vapor pressure does not indicate any new relations, so the data are presented in their original form.

In the first five of the eight systems studied, the solute is highly soluble in both components of the mixture; and its dil. solution, in either component or in mixtures of the two, gives an elevation of the boiling point proportional to the concentration. Benzil, resorcinol and acetanilide in benzene-alcohol mixtures were studied later; each of these three solutes is only slightly soluble in one of the solvents.

[5] Mathews and Faville, *J. Phys. Chem.*, **22**, 1 (1918).

With the one exception of acetanilide in mixtures of benzene and alcohol, the addition of the solute consistently reduced the partial pressure of one component. If the measurements had been made at constant temperature instead of constant pressure, this would have appeared as a greater percentage lowering of one partial pressure. Changes in the total pressure, of the order of those produced by the solute, produced no measurable change in the composition of the vapor.

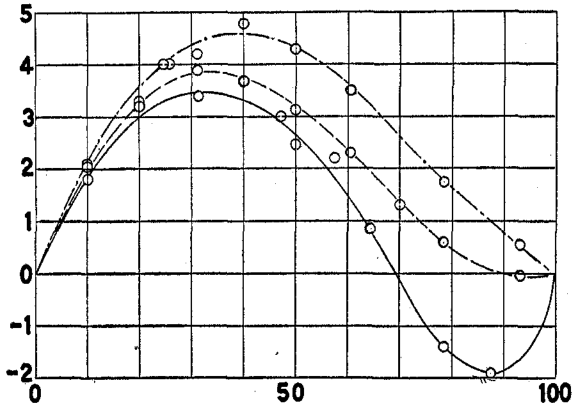

Fig. 2.—Carbon tetrachloride-ethyl acetate. Abscissas, percentages of CCl_4 in liquid phase; ordinates, percentages of CCl_4 in vapor phase minus corresponding abscissas. ——— No solute; — — 5 g. of thymol per 100 g. of solvents; — - — - 10 g. of thymol per 100 g. of solvents.

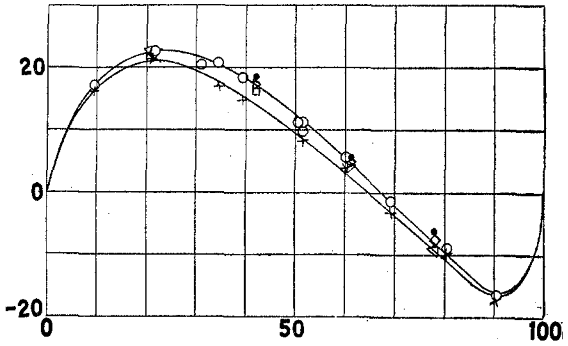

Fig. 3.—Benzene-ethyl alcohol. Abscissas, percentages of benzene in liquid phase; ordinates, percentages of benzene in vapor phase minus corresponding abscissas. Circle, no solute; cross, 10 g. of camphor per 100 g. of solvents; triangle, 10 g. of benzil per 100 g. of solvents; square, 10 g. of acetanilide per 100 g. of solvents; dot, 10 g. of resorcinol per 100 g. of solvents.

The relative effect of the solute on the two components of the mixture seemed most likely to be connected with its relative solubility. The solubility data were available in only a few of the cases and accordingly were determined in the others. The procedure was simple, as relative results only were necessary and time was limited. The solution was nearly saturated at a higher temperature, then allowed to stand for 24 hours at

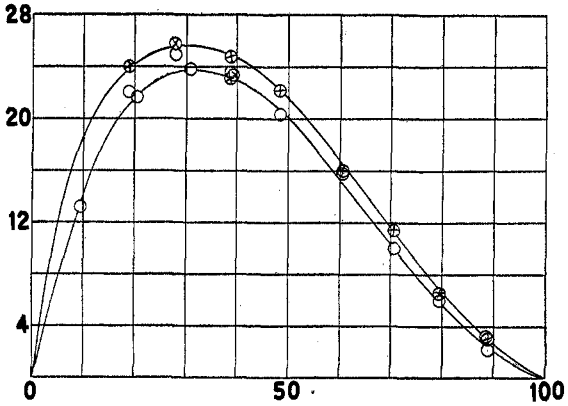

Fig. 4.—Ether-acetone. Abscissas, percentages of ether in liquid phase; ordinates, percentages of ether in vapor phase minus corresponding abscissas. Circle, no solute; cross in circle, 10 g. of benzoic acid per 100 g. of solvents.

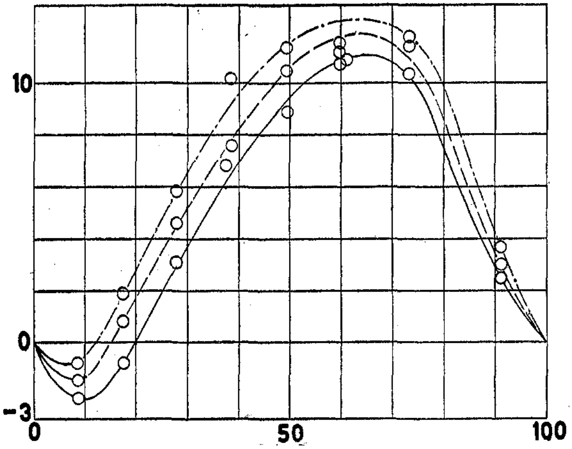

Fig. 5.—Acetone-chloroform. Abscissas, percentages of acetone in liquid phase; ordinates, percentages of acetone in vapor phase minus corresponding abscissas. —— No solute; — — — 5 g. of camphor per 100 g. of solvents; — - — - 10 g. of camphor per 100 g. of solvents.

the final temperature, ± 0.5°, stirred during the last hour, then sampled by the device of Walton and Judd.[6] The solubilities were measured, as nearly as practicable, up to the boiling point of the solvent, or the melting point of the solute. The normal procedure was impossible in certain cases near the boiling point of the solvent, when evaporation was excessive; but as crystallization was going on in these cases, the solution was certainly saturated.

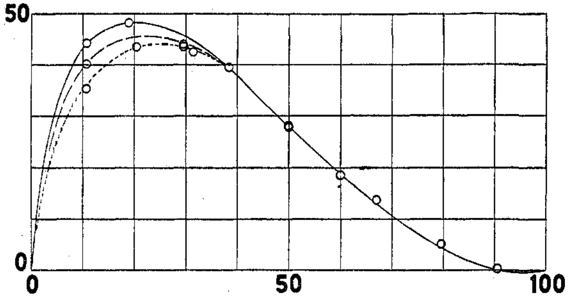

Fig. 6.—Ethyl alcohol-water. Abscissas, percentages of alcohol in liquid phase; ordinates, percentages of alcohol in vapor phase minus corresponding abscissas. ——— No solute; — — 5 g. of acetamide per 100 g. of solvents; - - - - 10 g. of acetamide per 100 g. of solvents.

Analytical Methods

Acetanilide and benzil were determined by evaporation of the solvent at temperatures at which the solute was not measurably volatile and by direct weighing.

Thymol was determined by the refractive index of the solutions, using the Pulfrich refractometer; curves were plotted from known concentrations and the samples diluted to within the range of the curve.

Camphor was determined by the polarimeter, using the green mercury line (5461 Å.). Since the specific rotation changes rapidly with concentration in high concentrations, the rotations of known solutions were determined and plotted; the solubility samples were diluted to values on the curves.

Benzoic acid was titrated with standard sodium hydroxide solution.

Acetamide was hydrolyzed by refluxing with sulfuric acid; after the reaction product had been made alkaline, the ammonia was distilled into standard acid and the excess of acid titrated.

Table I

Data

No.	Solvent	Solute	Temp. °C.	G. of solute per 100 g. of solvent	Mole fraction	"Ideal" mole fraction	Mole fraction by method of Mortimer
1	Carbon tetrachloride	Thymol	0.0	32.0	0.245	0.314	0.294
			25.0	96.3	.500	.596	.584
			38.5	376	.784	.815	.806
2	Ethyl acetate	Thymol	1.0	219	.562	.314	.301
			25.0	412	.709	.596	.589

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[6] Walton and Judd, This Journal, **33**, 1036 (1911).

TABLE I (*Concluded*)

No.	Solvent	Solute	Temp. °C.	G. of solute per 100 g. of solvent	Mole fraction	"Ideal" mole fraction	Mole fraction by method of Mortimer
3	Benzene	Camphor	4.0	224	0.535	0.226	..
			25.0	257	.569	.298	..
			56.0	357	.647	.416	..
4	Ethyl alcohol	Camphor	0.0	104	.240	.214	..
			25.0	181	.353	.298	..
			52.9	311	.485	.405	..
5	Acetone	Camphor	0.0	209	.385	.214	..
			25.0	261	.500	.298	..
			45.0	372	.585	.372	..
6	Chloroform	Camphor	0.4	200	.610	.214	..
			25.0	220	.63	.298	..
			59.2	289	.695	.435	..
7	Acetone	Benzoic acid	0.0	32.5	.134	.0628	0.0525
			25.0	50.8	.195	.132	.1162
8	Ether	Benzoic acid	0.0	23.3	.125	.0628	.0913
			25.0	40.8	.198	.132	.1733
9	Benzene	Benzil	4.5	28.8	.0965	.119	.0721
			25.0	59.0	.179	.216	.150
			64.2	269	.518	.527	.456
10	Ethyl alcohol	Resorcinol	25	242	.508	.158	.525
			50	286	.545	.300	.656
			80	374	.610	.576	.825
11	Ethyl alcohol	Benzil	0.2	1.82	.00398	.1025	.0027
			25.0	4.89	.0106	.216	.0186
			66.4	89.6	.163	.579	.240
12	Benzene	Acetanilide	7.0	0.50	.0028	.0564	.0004
			25.0	1.31	.0075	.106	.0022
			55.2	18.5	.096	.260	.0257
13	Ethyl alcohol	Acetanilide	0	14.7	.0477	.0435	.063
			20	27.0	.0845	.0897	.120
			40	49.0	.1436	.1693	.209
			100	86.5	.228	.735	.782
14	Benzene	Resorcinol	73	3.22	.0228	.500	.089
			82	7.45	.0501	.600	.168
			95.3	59.9	.294	.774	.410
15	Water	Acetamide	0.3	152	.317	.178	.708
			24.5	238	.420	.420	.800
16	Ethyl alcohol	Acetamide	0.0	29.0	.186	.178	.038
			18.6	62.5	.329	.287	.092
			42.5	164	.561	.485	.254
			62.0	478	.789	.685	.486

Numbers 10, 13, 16 determined by Speyers, *Am. J. Sci.*, [4] **14,** 293 (1902).
Number 14 determined by Rothmund, *Z. physik. Chem.*, **26,** 459, 475 (1898).

The observed results are compared with the values calculated by the ideal-solution law, and by the method of Mortimer,[7] using his values of internal pressures. The relative internal pressure of camphor calculated

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[7] Mortimer, THIS JOURNAL, **44,** 1429 (1922); **45,** 633 (1923).

from the solubility data by this method is 0.56 ± 0.05, the internal pressure of naphthalene being taken as 1.00, as is done by Mortimer.

Discussion

With the exception of the highly polar system: water-alcohol-acetamide, the results may be summarized as follows.

When a non-volatile solute is added to a mixture of two volatile solvents, the partial pressure of that solvent in which the solute is more soluble (in terms of mole fractions) is lowered by the greater percentage.

The solute is, in general, more soluble in the solvent with internal pressure nearer its own. It will be noted that the selective action of the solute is as marked in cases where it is highly soluble in both solvents, as in those where the solubility in one of the liquids is low. For example, camphor had a stronger selective action on the partial pressure of benzene than did benzil, although the ratio of the relative solubilities in the two separate liquids was much less in the first case, and the solutions were further from saturation. The effects observed are of the same order as those observed by Wright with solutes chosen for insolubility in one of the liquids. No quantitative relation could be established from the available data.

Summary

1. The change in partial pressures produced by addition of a non-volatile solute to binary liquid mixtures at the boiling point has been measured for eight systems at several compositions.

2. The selective action of a non-volatile solute on the partial pressure of a liquid mixture has been found to be measurable in systems which, as a whole, obey the laws of dilute solution; it is roughly correlated with relative solubility in the separate solvents.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

EBULLIOSCOPIC MEASUREMENTS IN MIXED SOLVENTS[1]

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From the experimental standpoint, the fundamental problems of ebullioscopy are measurement of temperature differences, the attainment of true and therefore permanent and reproducible temperature equilibria, and knowledge of the concentration of the solution. The first may be satisfactorily solved by the differential mercury thermometer of the Beck-

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[1] Prepared from portions of theses submitted to the Faculty of the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degrees of Doctor of Philosophy (B. H. Carroll, 1922) and of Master of Arts (G. K. Rollefson, 1921).

[2] Du Pont Fellow in Chemistry, March-June, 1919 and 1921–22.