that the values of γ obtained from these systems are all influenced more or less by the fields due to these dipoles, which may also affect the results by bringing about molecular orientation. It is apparent that the lack of generality of the principle of independent surface action and the frequent absence of random orientation, as well as the uncertainty in estimating surface areas, prevent the accurate determination of absolute values for the surface energies and limit the applicability of the theory. These results will be further discussed in a subsequent paper, where they will be contrasted with the behavior of systems containing an alcohol as one component.

Summary

An apparatus is described for the measurement of the partial vapor pressures of binary liquid mixtures by a dynamic method. The pressures of eight different combinations of supposedly normal liquids and of several of the pure components are tabulated.

The data are used to examine Langmuir's theory of molecular surface energies, which is found to have an approximate applicability. Deviations from the theoretical behavior are ascribed to the presence of electric doublets in the molecules.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY]

MOLECULAR ORIENTATION AND THE PARTIAL VAPOR PRESSURES OF BINARY LIQUID MIXTURES.
II. SYSTEMS CONTAINING AN ALCOHOL

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The apparatus described in Part I was used to determine the partial pressures of six different binary systems containing an alcohol as one of the components. The purification of the materials and the values of the physical constants used as criteria of their purity have been given in Part I.[1] Because of the somewhat different behavior of these systems containing an alcohol, it has been deemed advisable to treat them in a separate paper and contrast the results with those given by the supposedly normal liquids discussed in Part I. The experimentally determined partial pressures, p_A and p_B, of the components A and B are recorded in Table I, the composition of the mixtures being given in terms of the mole fraction B of the alcohol. The values of the partial pressures are interpolated graphically at intervals of 0.1 in the mole fraction of B and used to calculate the values of p_A/p_AA, p_B/p_BB, φ_A and φ_B, as was done in Part I,[2] the results

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[1] Smyth and Engel, THIS JOURNAL, 51, 2646 (1929).

[2] See Langmuir, "Third Colloid Symposium Monograph," The Chemical Catalog Company, Inc., New York, 1925, p. 3.

being recorded in Table II. In Figs. 1–6 the vapor pressures in millimeters of mercury are plotted as ordinates against the mole fractions B as abscissas. The total pressure curve is uppermost and the partial pressure curve of the alcohol starts at the lower left-hand corner, while that of the other component, A, starts at the lower right-hand corner. The values of φA and φB are plotted as ordinates on the same diagrams against those of **B** as abscissas, the points being indicated by filled circles.

TABLE I

PARTIAL VAPOR PRESSURES OF BINARY MIXTURES (MM. OF HG)

(A) 30° (B)
Heptane–ethyl alcohol

B	p_A	p_B
0	58.2	0
0.0400	56.0	22.0
.0684	56.4	47.2
.1236	56.4	56.1
.2803	54.8	62.9
.3342	54.5	63.5
.5151	54.0	65.9
.5934	51.8	68.1
.7174	49.9	69.7
.7687	47.9	71.0
.8154	43.5	73.5
.8550	40.6	73.9
.8902	32.1	79.2
.9173	18.4	87.9
.9545	10.1	87.0
.9913	4.7	77.8
1.0000	0	78.2

(A) 50° (B)
Heptane–ethyl alcohol

B	p_A	p_B
0	141.1	0
0.0514	132.3	111.9
.1180	133.6	155.8
.3022	130.5	176.9
.4382	130.0	181.3
.5862	126.6	184.7
.6646	121.5	188.0
.7327	120.0	191.3
.7720	114.9	193.9
.8230	106.2	198.6
.8788	71.8	221.8
.9274	47.2	234.5
.9769	21.6	225.8
1.0000	0	220.0

(A) 70° (B)
Heptane–ethyl alcohol

B	p_A	p_B
0	301.4	0
0.0567	265.9	234.4
.1180	274.5	339.8
.1573	272.8	375.2
.2575	275.8	413.8
.3633	274.3	431.6
.4290	269.7	442.4
.5069	269.0	446.7
.5968	267.0	450.7
.6648	259.6	458.1
.7174	252.4	465.3
.8689	251.0	462.8
.8200	245.6	459.3
.8640	227.9	465.5
.8940	183.1	493.4
.9250	129.5	522.3
.9564	83.0	527.0
.9827	44.9	524.5
1.0000	0	539.1

(A) 50° (B)
Heptane–butyl alcohol

0	140.5	0
0.0688	135.6	13.8
.1047	132.5	19.0
.1980	130.0	21.2
.2212	130.1	21.2
.3641	126.6	22.0
.5310	115.9	26.0
.5429	114.9	25.8
.6369	108.5	25.1
.6400	109.0	26.9
.6805	105.5	26.1
.7388	94.2	29.3
.7834	77.5	36.0
1.0000	0	33.3

(A) 50°
Carbon tetrachloride–
(B)
Butyl alcohol

0	308.9	0
0.0245	303.9	5.1
.1128	291.5	13.1
.2236	280.4	15.7
.3286	270.0	15.6
.4164	256.7	18.2
.5051	240.7	19.4
.5241	236.0	18.6
.6153	213.6	19.7
.6839	189.5	20.5
.7408	161.3	20.2
.8234	125.3	21.1
.8648	99.2	22.4
.9218	62.4	23.9
1.0000	0	33.3

(A) 30° (B)
Ethyl bromide–ethyl alcohol

0	567.8	0
0.1175	527.1	40.7
.2810	503.0	49.2
.2997	502.2	47.1
.4166	474.2	51.6
.5431	447.9	53.5
.6210	415.8	59.1
.6784	389.6	60.9
.7547	338.2	64.0
.7562	339.8	63.8
.8086	292.6	65.8
.8553	240.2	68.4
.8663	223.8	67.6
.8956	183.8	69.5
1.0000	0	78.4

TABLE I (*Concluded*)

(A) 50° (B) Butyl bromide–butyl alcohol		
B	p_A	p_B
0	127.0	0
0.1455	116.6	15.8
.2140	113.6	17.3
.2594	111.2	18.4
.2815	109.6	19.0
.3898	104.9	20.9
.5033	97.6	22.4
.5226	97.1	21.9
.5790	92.5	22.7
.6368	86.2	23.3
.7093	78.7	24.3
.7751	67.5	25.3
.8832	43.3	27.2
.9383	26.3	27.9
.9739	16.2	27.5
1.0000	0	33.3

(A) 30° (B) Ethyl iodide–ethyl alcohol		
B	p_A	p_B
0	162.3	0
0.0438	162.4	25.9
.1307	152.9	44.9
.2886	148.2	53.1
.3668	145.3	55.3
.4000	144.4	56.2
.4875	139.8	57.1
.5507	137.3	59.6
.6259	132.1	61.8
.6854	125.8	63.3
.7384	116.7	64.9
.7836	106.5	66.2
.8195	97.4	68.4
.8483	88.2	69.4
.8912	72.1	70.0
.9519	32.1	70.7
1.0000	0	78.2

The partial pressure curve of ethyl alcohol in the heptane–ethyl alcohol system (Fig. 1) shows a small but well-defined rise to a maximum near B = 0.94. The phenomenon was at first attributed to a repeated error in the

TABLE II

VALUES OF p_A/P_AA, p_B/P_BB AND φ

	(A) 30° (B) Heptane–ethyl alcohol P_A = 58.2 P_B = 78.2				(A) 50° (B) Heptane–ethyl alcohol P_A = 141.1 P_B = 220.0			
B	p_A/P_AA	p_B/P_BB	φ_A	φ_B	p_A/P_AA	p_B/P_BB	φ_A	φ_B
0.1	1.069	6.778	55.8	10.7	1.053	6.727	47.4	11.2
.2	1.192	3.900	34.1	8.71	1.178	3.818	32.5	9.02
.3	1.350	2.685	22.8	7.45	1.336	2.667	23.0	7.76
.4	1.561	2.062	17.0	6.67	1.536	2.057	17.3	6.95
.5	1.856	1.688	13.4	6.17	1.814	1.673	13.7	6.39
.6	2.277	1.449	11.0	6.04	2.232	1.409	11.3	5.86
.7	2.921	1.270	9.52	6.04	2.882	1.227	9.58	5.51
.8	3.952	1.151	7.88	6.99	3.969	1.114	8.30	5.59

	(A) 70° (B) Heptane–ethyl alcohol P_A = 301.4 P_B = 539.1				(A) 50° (B) Heptane–butyl alcohol P_A = 140.5 P_B = 33.3			
0.1	1.018	5.832	(15.9)	10.8	1.060	5.560	29.6	8.13
.2	1.145	3.673	28.0	9.14	1.164	3.300	18.3	6.58
.3	1.308	2.542	22.3	7.71	1.303	2.201	13.4	5.37
.4	1.511	2.022	17.3	7.08	1.505	1.726	10.9	4.76
.5	1.778	1.655	13.8	6.50	1.715	1.441	8.19	4.33
.6	2.196	1.391	11.5	5.90	2.023	1.247	7.45	3.84
.7	2.856	1.203	9.90	5.14	2.410	1.157	6.37	4.23
.8	4.114	1.062	8.88	4.88				

TABLE II (*Concluded*)

	(A) 50° (B) Carbon tetrachloride–butyl alcohol $P_A = 308.9$ $P_B = 33.3$				(A) 30° (B) Ethyl bromide–ethyl alcohol $P_A = 567.8$ $P_B = 78.4$			
B	p_A/P_AA	p_B/P_BB	φ_A	φ_B	p_A/P_AA	p_B/P_BA	φ_B	φ_B
0.1	1.054	3.605	21.3	6.18	1.041	4.580	22.8	9.06
.2	1.141	2.250	13.3	4.96	1.130	3.180	16.8	8.49
.3	1.258	1.600	10.2	3.70	1.248	2.125	13.1	6.96
.4	1.398	1.275	8.30	2.62	1.409	1.690	11.1	6.37
.5	1.560	1.081	7.02	1.19	1.609	1.453	9.51	6.35
.6	1.760	0.926	6.15	−1.82	1.875	1.275	8.44	6.22
.7	1.953	.841	5.31	−7.22	2.230	1.146	7.63	6.00
.8	2.170	.754	4.68	−26.4	2.642	1.052	6.85	4.85
.9	2.522	.767	4.44	−98.5	3.170	0.993	6.19	−1.33
	(A) 50° (B) Butyl bromide–butyl alcohol $P_A = 127.0$ $P_B = 33.3$				(A) 30° (B) Ethyl iodide–ethyl alcohol $P_A = 162.3$ $P_B = 78.2$			
0.1	1.042	3.694	17.8	6.22	1.068	5.115	41.1	9.65
.2	1.126	2.628	12.4	5.70	1.163	3.601	22.6	8.36
.3	1.238	1.952	9.77	5.05	1.301	2.293	16.8	7.45
.4	1.382	1.577	8.16	4.58	1.473	1.790	13.4	6.82
.5	1.555	1.321	6.98	3.95	1.716	1.491	11.4	6.48
.6	1.779	1.152	6.20	3.05	2.067	1.300	10.3	6.37
.7	2.073	1.030	5.64	1.10	2.543	1.169	9.24	6.43
.8	2.480	0.946	5.26	−4.70	3.173	1.071	8.35	6.04
.9	2.953	.918	4.85	−30.8	4.190	1.009	7.79	3.09

analysis, but careful checking of the method of analysis eliminated this possibility. The rise is found to decrease with rising temperature, which may be expected to reduce abnormalities arising from molecular association

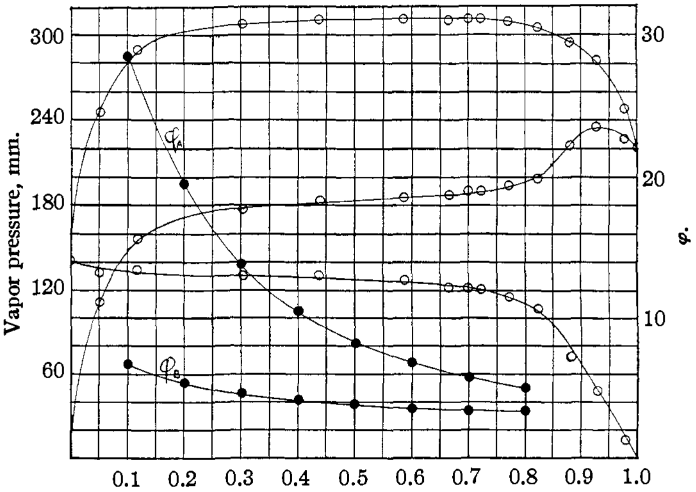

Fig. 1.—Heptane (A)–ethyl alcohol (B) at 50°.

or intermolecular action. No such maximum appears in the curves for the mixtures of ethyl alcohol with other substances than heptane, but in the heptane–butyl alcohol system (Fig. 2), the beginning of a rise is indicated from $B = 0.7$ to $B = 0.8$ which might lead to a maximum in the neighborhood of $B = 0.9$. Unfortunately, however, this region could not be investigated as the butyl alcohol mixtures containing a little heptane bumped so violently, apparently because of an abnormally high surface tension, that the vapor pressures could not be measured. It appears that some complex formation may occur in this region of the heptane–alcohol mixtures, but the dielectric behavior of the mixtures shows no irregularity in this region and an attempt at explanation is unwise until more definite knowledge is obtained.

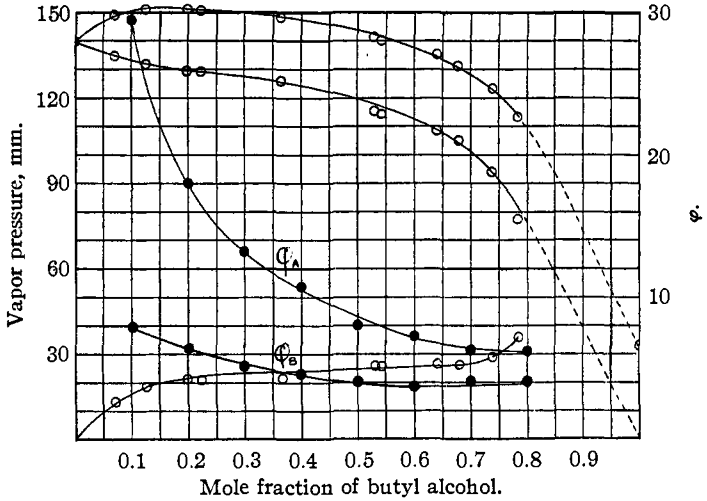

Fig. 2.—Heptane (A)-butyl alcohol (B) at 50°.

Table II shows that these systems deviate much more from Raoult's law than do the normal liquids considered in Part I, the value of p_B/P_BB for $B = 0.1$ in the heptane (A)–ethyl alcohol (B) system at 30° being 6.778 as compared to the theoretical 1 of Raoult's law. The deviation of the partial pressure of a component from Raoult's law increases with decreasing concentration of the component. The values of φ are larger and vary more widely than those for the mixtures in Part I. Indeed, the variation of φ is so great that it is impossible to select a value from those in Table II for a system with any expectation of reproducing the partial pressures from it.

As an illustration of the manner in which a single value of φ fails to reproduce the experimentally observed vapor pressures, Fig. 4 shows as partly filled circles the pressures for the ethyl bromide–ethyl alcohol system, calculated by means of the Langmuir equation, the value of φ being taken from Table III as 5.88. A similar failure in the calculation of the pressures has been found to occur in the other systems. The calculated points are, however, omitted from the other figures in order to avoid too great complication of the diagrams.

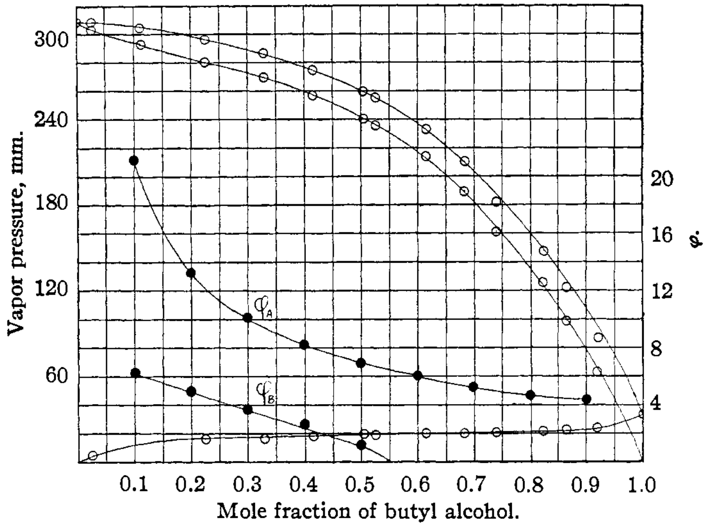

Fig. 3.—Carbon tetrachloride (A)–butyl alcohol (B) at 50°.

If log p_A/P_AA is plotted against β^2 and log p_B/P_BB against α^2, straight lines are not obtained, as should be the case if φ were constant. When log

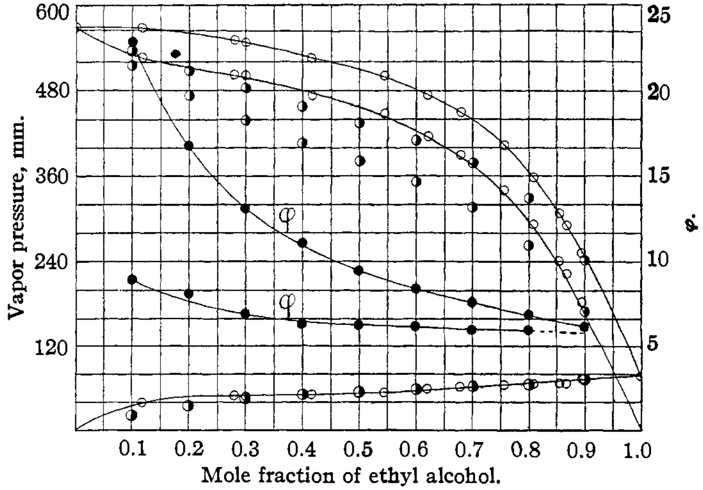

Fig. 4.—Ethyl bromide (A)–ethyl alcohol (B) at 30°.

(log (p_A/P_AA)) is plotted against 2 log β and log (log (p_B/P_BB)) against 2 log α, portions of the curves obtained are linear and average values of φ

are calculated from these portions. The curves for the two components give somewhat different values of φ, but the values from the curves for the non-alcoholic components which are constant over a wider concentration range will be used in discussion.

For the sake of comparison, all the values are given in Table III together with the values of the surface energy calculated from them, the values of γ from Part I being used when necessary in the calculation. The first column gives the interface for which γ is calculated, the second column the temperature at which the vapor pressures were determined, the third under A gives the component from the partial pressures of which the values of φ in the fourth column are obtained and the values of γ calculated from them are in the fifth column. The sixth column under B gives the alcohol from the partial pressures of which the values of φ and γ in the remaining columns are calculated. At the foot of the table are given the values of γ used in calculating the surface energies for the halogen–hydroxyl interfaces, together with the surface areas (in square Ångströms) not previously used in Part I.

TABLE III

VALUES OF φ AND γ FOR SYSTEMS CONTAINING AN ALCOHOL

Interface	t, °C.	A	φ	γ	B	φ	γ
R–OH	30	C_7H_{16}	5.77	68.2	C_2H_5OH	7.05	83.3
R–OH	50	C_7H_{16}	6.1	72.4	C_2H_5OH	7.6	89.9
R–OH	70	C_7H_{16}	6.78	80.2	C_2H_5OH	8.67	102.5
R–OH	50	C_7H_{16}	4.7	97.7	C_4H_9OH	6.4	133.1
Cl–OH	50	CCl_4	4.0	101.6 (80.8)	C_4H_9OH	7.25	95.7
Br–OH	30	C_2H_5Br	5.88	64.9	C_2H_5OH	8.34	81.8
Br–OH	50	C_4H_9Br	4.47	108.9 (92.4)	C_4H_9OH	6.65	134.6 (118.2)
I–OH	30	C_2H_5I	6.85	70.0	C_2H_5OH	6.67	68.9

Areas: OH = 24.7; C_2H_5OH = 84.9; C_4H_9OH = 112.5. Values of γ used in calculations: R–OH = 73.7 for C_2H_5OH; 97.7 for C_4H_9OH (but values in parentheses are calculated from R–OH = 73.7); R–Cl = 0.6; R–Br = 6.8 for C_2H_5Br, 9.2 for C_4H_9Br; R–I = 7.9.

Possessed of the same uncertainties as the values obtained in Part I, these results are rendered more difficult of interpretation by the greater effect of molecular orientation in the mixtures. The energy at an interface where an hydroxyl group is involved is evidently so large in comparison with the energies at the other interfaces that the orientation of the alcohol molecules relative to one another must be more important in determining the behavior of the system than their orientation relative to the molecules of the other component or the orientation of the molecules of the other components relative to one another. For example, in an ethyl bromide–ethyl alcohol mixture at 30°, if an hydroxyl surface is in contact with bromine, γ is 64.9, if in contact with hydrocarbon, γ is 68.2, but, if in contact with another hydroxyl, γ is 0, while, if a bromine surface is in contact with hydrocarbon, γ is 6.8 as compared to 0 when the bromine is in contact with another bromine.

It is evident that when a butyl compound is used to obtain γ, the resulting value is higher than when an ethyl compound is used. Thus, the value of $\gamma_{\text{R-OH}}$ at 50° is 72.4 when ethyl alcohol is used and 97.7 when butyl is employed and $\gamma_{\text{Br-OH}}$ is 64.9 when the ethyl compounds are used and 108.9 in the butyl mixtures. Similarly, in Part I, it was found that the value obtained from the heptane–butyl bromide mixtures was higher than that from the heptane–ethyl bromide system. This difference could be largely eliminated by adjustment of the values of the surface areas, but, as these are derived by a consistent procedure from experimental data, their treatment as adjustable constants is not justifiable. The mean value $\gamma_{\text{R-OH}} = 73.7$ is used in calculation where ethyl alcohol is concerned and the value 97.7 for the mixtures containing butyl alcohol, but, for the sake of comparison, the value 73.7 is also used with the latter and the results thus obtained are shown in parentheses. It is safer to compare molecules with the same hydrocarbon chain. One may thus conclude from the values for the ethyl compounds that $\gamma_{\text{R-OH}}$, $\gamma_{\text{Br-OH}}$ and $\gamma_{\text{I-OH}}$ are not very different from one another and, similarly, from those for the butyl compounds, that $\gamma_{\text{R-OH}}$, $\gamma_{\text{Cl-OH}}$ and $\gamma_{\text{I-OH}}$ differ little from one another, and that all are much larger than those for the interfaces considered which do not contain hydroxyl. The values in Table III are not sufficiently accurate to warrant their arrangement in a definite order, but it may be concluded that $\gamma_{\text{R-OH}}$, $\gamma_{\text{Cl-OH}}$ and $\gamma_{\text{I-OH}}$ are of the same order of magnitude and are much larger than the values for the hydro-

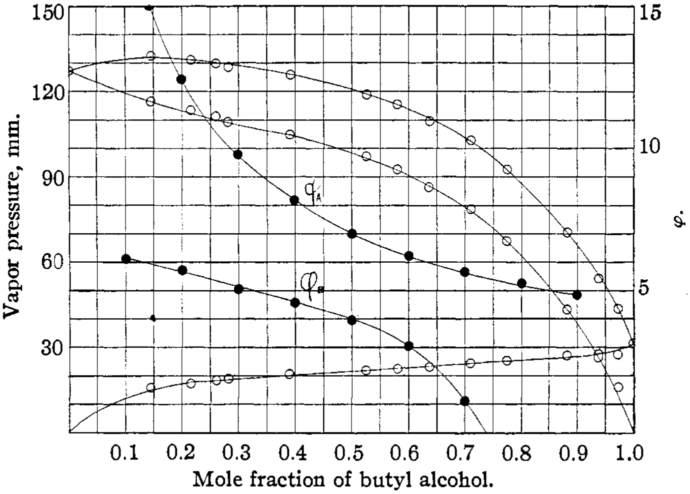

Fig. 5.—Butyl bromide (A)–butyl alcohol (B) at 50°.

carbon–halogen and halogen–halogen interfaces. The values of $\gamma_{R\text{-}OH}$ and $\gamma_{R\text{-}OH}$ are quite different from those of Langmuir, 33.7 and 49.6, respectively, but when Langmuir's value 33.7 is used for $\gamma_{R\text{-}OH}$ instead of 73.7 in calculating $\gamma_{Br\text{-}OH}$ from the data for the ethyl bromide–ethyl alcohol system, the value 49.5 is obtained, which shows how dependent these results are upon one another as well as upon the uncertain surface fractions.

Langmuir examined the effect of molecular orientation in a hexane–ethyl alcohol mixture by means of a necessarily approximate method and was misled by a numerical error to the belief that the effect was very slight, but concluded that it might be important in some liquids, particularly in those whose molecules act as dipoles. Consequently, a second term was introduced into the exponent of the original equation to take care of the energy of orientation in such liquids. When this equation is applied to these systems, a straight line is sometimes found but the frequent failure to obtain linearity shows that the equation is not generally applicable, although, of course, the mere presence of an additional adjustable constant renders it more capable of reproducing experimental data.

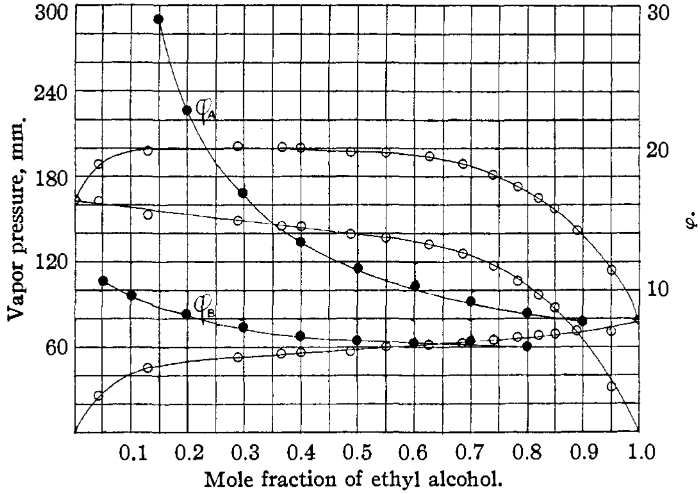

Fig. 6.—Ethyl iodide (A)–ethyl alcohol (B) at 30°.

A general explanation of the deviations of the mixtures from normal behavior may be given in qualitative terms. The field of force around a molecule due to a doublet in its interior depends not merely upon the electric moment of the doublet, but also upon its location in the molecule. Thus the diethyl ether molecule has an electric moment of 1.14×10^{-18} e.s.u.,[3] the resultant, presumably, of two dipoles located in the regions of

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[3] Stuart, *Z. Physik*, **51**, 1490 (1928).

attachment of the ethyl groups to the oxygen atom. The ethyl groups serve as a shield for the dipoles and thus prevent the molecule from being surrounded by a strong field of force. Ether, consequently, behaves as a normal unassociated liquid, even measurements of dielectric polarization at room temperature failing to give evidence of interference of the molecular force fields with one another. The ethyl alcohol molecule has two somewhat similar doublets located in the regions where the ethyl group and the hydrogen are attached to the oxygen atom, the resultant moment[4] being 1.74×10^{-18}. The ethyl group may be pictured as partially screening one side of the molecule from the action of the doublets, but the doublets are close to the surface on the hydroxyl side of the molecule and a strong molecular field results. Alcohol, consequently, shows properties which cause it to be termed a highly associated liquid, and its dielectric behavior is abnormal in the extreme. The water molecule, of electric moment[3,5] 1.8×10^{-18}, possesses two doublets similar to those in the alcohol molecule, but has no ethyl group to serve as a screen. The resultant powerful molecular field renders water a strongly associated and very abnormal liquid. If the higher alcohols are considered, it is evident that with increasing size of the hydrocarbon chain, which contains no appreciable doublets, the doublets at the hydroxyl group will be more and more screened from those in neighboring molecules and the effects of their fields thereby reduced. Consequently, the alcohols become less abnormal with increasing molecular weight.

Ethyl bromide, in spite of the moment, 1.86×10^{-18}, possessed by its molecule, is ordinarily termed a normal liquid.[6] Its doublet should lie in the region of attachment of the ethyl group to the bromine atom and should thus be screened not only by the ethyl group but also by the large bromine atom, which should greatly reduce the molecular field as compared to that of the ethyl alcohol molecule. In ethyl iodide the screening effect of the large iodine atom should be greater than that of the bromine atom, and this, taken in conjunction with the slightly smaller moment of the molecule,[7] 1.67×10^{-18}, should give a smaller molecular field. In conformity with this the dielectric behavior of the two substances shows that the ethyl bromide molecules affect one another more strongly than do those of ethyl iodide. This effect is also apparent in the vapor pressures given in Part I, for the heptane–ethyl bromide system shows a somewhat greater variation in the values of φ, presumably as the result of orienting forces, than is found in the heptane–ethyl iodide system. Butyl bromide, in which the longer hydrocarbon chain should reduce the effect of the mo-

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[4] Stranathan, *Phys. Rev.*, **31**, 653 (1928).

[5] Williams, *Physik. Z.*, **29**, 204 (1928).

[6] Smyth and Morgan, THIS JOURNAL, **50**, 1547 (1928).

[7] Value recently obtained in this Laboratory by Mr. W. N. Stoops.

lecular dipoles upon one another, shows but slight variation in the value of φ, and the heptane–butyl chloride mixtures behave similarly.

It appears that the deviations of liquids from the behavior required by the Langmuir equation may be qualitatively explained in terms of the forces acting between the molecular dipoles. Forces which greatly restrict the freedom of orientation of the dipoles in an externally applied electric field may yet be insufficient to impair seriously the validity of the Langmuir equation. As the effects of the dipoles upon one another depend not only upon their electric moments but also upon their location in the molecules and upon the sizes and shapes of these molecules and probably upon the electronic constraints in them, it appears impossible to formulate any generally valid expression for the exact quantitative representation of the interaction of molecular dipoles. Evidently the assumptions upon which the Langmuir equation is derived are too simple to permit of its general and exact application, but the approximate agreement between the calculated and the observed results for the less polar liquids and the general trend of the surface energies calculated indicate that the theory bears a relation to fact beyond a mere resemblance of the equation to the Duhem thermodynamic equation, and the idea of molecular surface energies may lead to most interesting results in spite of the difficulties in its exact quantitative application.

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Summary

The partial vapor pressures of six binary liquid systems containing an alcohol as one component are measured. The results are found to deviate considerably from the behavior required by Langmuir's theory of molecular surface energies. The deviations are explained in terms of the interaction of the electric doublets contained in the molecules. It is concluded that, as this interaction is dependent upon not only the electric moments of the doublets but also their locations in the molecules and the sizes and shapes of these molecules and, probably, the constraints upon the electrons in them, no generally valid quantitative formulation of the effect is possible at present.

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