The Adsorption of Organic Acids from Single and Mixed Solvents

By *N. Yermolenko* and *S. Levina*

The problem of the dependence of the adsorption of substances upon the polarity of the medium has for some time past been subjected to close investigation. Thus, Heymann and Boye[1] found an inverse depend nce between the adsorption of benzoic and picric acids from alcohols of the same homologous series and the molar polarization, P_{em}, of the latter. A similar relation was established by us[2] in a study of the adsorption of picric acid from alcoholic solutions on mineral adsorbents and animal charcoal. The process of the adsorption of this acid from solvents of a diverse chemical nature passed in a more complex way.

Starting with the conception that the distribution of a substance at the boundary of two phases is dependent upon its polarity, it would seem that the simplest dependence should be observed between the solubility of the substance in a solvent and its capacity for adsorption from the media used.

Indeed, in many cases an inverse relation is observed between the solubility and adsorption of substances[3].

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[1] Heymann a. Boye, Z. physik. Chem., **A 150,** 219 (1930).
[2] N. F. Yermolenko a. E. N. Novikova, Coll. J. (Russ.), **2,** 179 (1936).
[3] Herz a. Levi, Koll. Z., **50,** 21 (1930); N. Sata, Koll. Z., **49,** 275 (1929); N. Sata a. S. Watanabe, Koll. Z., **70,** 159 (1935); N. Sata a. Kurano, Koll. Z., **65,** 283 (1933); N. F. Yermolenko a. D. Z. Ginsburg, Coll. J. (Russ.), **3,** 837 (1937); E. F. Lundelius, Koll. Z., **26,** 145 (1920).

Studies of this dependence, carried out with a great number of substances, particularly in investigations concerned with mixed solvents, have shown that it is far from being always satisfied [4].

In general, in media consisting of substances belonging to one homologous series, a regularity is usually observed in the change of the processes of adsorption, swelling etc., as one passes from one solvent of a given series to the next one. But in the case of solvents of a different chemical nature, it is not always possible to establish a regular dependence between some definite property of the medium and the change in some process or other occurring in it.

This particularly applies to the adsorption of either one substance or a mixture of substances from single or mixed solvents. Wishing to avoid secondary effects, V. S. Molodensky [5] investigated the adsorption of formic and valeric acids on blood charcoal from aqueous solutions. Thus, using acids belonging to the same homologous series, he was able to establish certain regularities in he adsorption process; in particular he confirmed Masius' conjectures [6] of the mutual displacement of acids during their adsorption from solutions.

However, such a regularity in the course of the adsorption process apparently cannot be expected to occur in more complex systems.

Thus, Shilov and Lepin [7], in studying the adsorption of a mixture of acids differing in their chemical nature, *viz.*, an organic acid — acetic acid, and an inorganic one — HCl, on the contrary came to the conclusion that in this case there occurs independent adsorption of each acid from their mixture. The same independence in the manner of adsorption from solutions was noted by Dubinin [8] for the process of adsorption of HCl and HNO_3 on charcoal from their mixture.

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[4] N. Shilov a. S. Pewsner, Z. physik. Chem., **118**, 361 (1925); Russ. Phys. Chem. Soc., **59**, 125 (1927).

[5] V. S. Molodensky, J. Phys. Chem. (Russ.), **2**, 125 (1931).

[6] Masius, Diss., Leipzig, 1908, S. 48; Freundlich a. Masius, V. Bemmelen, Z. Festschrift, 1910, S. 88.

[7] N. Shilov a. L. Lepin, Bull. of the Lomonosov Phys. Chem. Soc., (Russ.), **1**, (1919).

[8] M. Dubinin, Z. physik. Chem., **135**, 24 (1928).

The data available being so contradictory, it was interesting to study the adsorption on charcoal of a mixture of organic acids differing in their chemical nature — one of an aliphatic series (butyric) and the other of an aromatic series (salicylic). Both single and, to a greater extent, mixed media were chosen as solvents.

The latter are important because the adsorption of salicylic acid alone from a number of mixed media had been studied previously[9]. During this investigation it was established that, with a change in the percentage composition of the components of a mixed solvent and with the resulting change in the molecular polarization, P_{sm}, of the solution, the isothermal adsorption of salicylic acid is not always a linear function of P_{sm} of the medium, but either passes through a minimum or has the shape of a broken line.

In introducing butyric acid together with salicylic into the system we intended to establish the mutual influence of the acids during their adsorption from complex, mixed media.

Active animal charcoal (Kahlbaum) was used as an adsorbent. The following mixtures of substances were used as solvents:

Group 1. Both components non-polar: $CCl_4 — C_6H_6$.

" 2. One component non-polar and the other polar, not affecting the polarity of the first: $CCl_4 — C_6H_5CH_3$, $C_6H_6 — C_6H_5CH_3$ and $C_6H_6 — CHCl_3$.

" 3. One component non-polar and the other polar, affecting the polarity of the first: $C_6H_6 — C_2H_5OH$, $CCl_4 — C_2H_5OH$ and $CCl_4 — (CH_3)_2CO$.

" 4. Both components polar: $H_2O — C_2H_5OH$, $(CH_3)_2CO — C_2H_5OH$ $CHCl_3 — (CH_3)_2CO$ and $CHCl_3 — C_2H_5OH$.

The initial concentrations of the acids in the solvents were as follows: salicylic acid — 0,69 mgr./cm.^{3}, butyric acid — 0,44 mgr./cm.^{3}; *i. e.*, the total concentration was 0,01*N*. The amount of charcoal used for 20 cm^3. of solution was 0,2 gr. In the separate adsorption of these acids, the initial concentration was 0,05 *N* per 0,1 gr. of charcoal.

The approximate proportion of the solvents in the mixtures is given in the following Table:

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[9] W. Hetz a. Levi, Koll. Z., l. c. N. F. Yermolenko a. D. Ginsburg, l. c.

Number of cm.³ of the solution of acids in CCl_4	Number of cm³. of CCl_4 added	Volume percentage content of CCl_4	Number of cm.³ of the solution of acids in C_6H_6	Number of cm.³ of C_6H_6 added	Volume percentage content of C_6H_6
2	18	100	0	0	0
2	13	75	0	5	25
2	8	50	0	10	50
0	5	25	2	13	75
0	0	0	2	18	100

The solution of the acids in each solvent had the following composition:

$$\left.\begin{array}{l}\text{Salicylic acid} - 0{,}05\ N \\ \text{Butyric acid} - 0{,}05\ N\end{array}\right\} 0{,}1\ N$$

The initial solution was diluted 10 times, so that the total concentration of the acids, before the beginning of adsorption, was equal to 0,01 *N*.

Adsorption of the acids by charcoal was carried out by shaking the mixture of charcoal and the solution for 30 min. The charcoal was then removed by centrifuging. The total acid concentration in the solution was determined by titration with barium hydroxide; the concentration of salicylic acid was determined colorimetrically and the concentration of butyric acid was found from the difference.

The adsorption of salicylic and butyric acids from mixtures of the non-polar solvents C_6H_6 and CCl_4

The data on the adsorption of the acids from a mixture of two non-polar solvents are presented in Table 1 and Fig. 1; the data on the separate adsorption of each acid from the same media are given in Table 2 and Fig. 2. The adsorption curves for salicylic and butyric acids are marked with *S* and *M* respectively.

If the complete adsorption of both salicylic and butyric acids from a given solution is taken as 200%, the following figures given in Table 3 will represent the data (in $\%\%$) on: (a) the total adsorption of the acids on charcoal from a $CCl_4 - C_6H_6$ solution when both acids are present, and (b) the total adsorption calculated from the data on the separate adsorption of each acid from the same media.

It follows that the separate adsorption of each acid (Table 2) from a mixture of two non-polar solvents is decreased with a decrease in P_{sm} of the medium. For butyric acid, when passing from a mixed solvent to pure C_6H_6, the adsorption somewhat increases.

Upon simultaneous adsorption of these acids (Table 1), the trend of the isotherm for each acid does not change while there is an excess of CCl_4 in solution. In pure C_6H_6, adsorption of pure

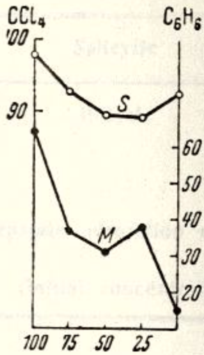


Fig. 1.

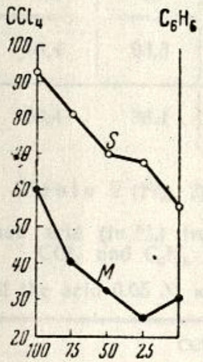


Fig. 2.

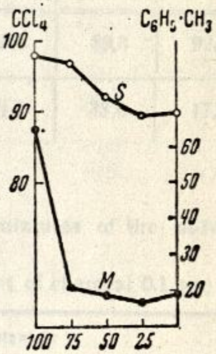


Fig. 3.

salicylic acid increases, and this simultaneously suppresses the adsorption of butyric acid.

The system considered confirms Masius's rule that the same component is preferentially adsorbed from the mixture which is adsorbed to a greater extent separately (salicylic acid).

The adsorption of salicylic and butyric acids from a mixture of a polar and a non-polar solvent

In all the cases of the adsorption of a mixture of the acids from mixed media consisting of polar and non-polar components (Tables 4—10), there is a decrease in the isothermal adsorption as one proceeds from a non-polar to a polar medium. It is only in the case of the adsorption of butyric acid from the media C_6H_6—$C_6H_5CH_3$ and CCl_4—$(CH_3)_2CO$ that a small maximum is observed in the isotherms.

An analogous trend in the isotherms was observed by Sata and Watanabe[10] in a study of the adsorption of salicylic acid alone from the same media.

Table 1 (Fig. 1)

Adsorption of the acids (in %) from mixtures of the solvents CCl_4 and C_6H_6

Acid	CCl_4 content in %				
	100	75	50	25	0
Salicylic	98,4	93,3	89,3	89,3	92,4
Butyric	64,4	36,1	31,1	38,0	17,1

Table 2 (Fig. 2)

Separate adsorption of each acid (in %) from mixtures of the solvent CCl_4 and C_6H_6

(Initial concentration of the acid 0,05 N; weight of charcoal 0,1 gr.)

Acid	CCl_4 content in %				
	100	75	50	25	0
Salicylic	92,8	82,1	69,4	68,1	56,0
Butyric	63,4	40,2	34,0	24,3	31,1

Table 3

	CCl_4 content in %				
	100	75	50	25	0
(a)	162,8	129,4	120.4	127,3	109,5
(b)	156	122,3	103,4	92,4	87,1

[10] N. Sata a. Watanabe, Koll. Z., **70**, 163 (1935).

Our determination of the separate adsorption of each acid from the mixed media CCl_4 and $C_6H_5CH_3$ (Table 5), showed that the shape of the adsorption isotherms obtained does not fundamentally differ from the isotherms obtained in carrying out adsorption of these acids from their mixture (Table 4).

Table 4 (Fig. 3)

Adsorption of the acids (in %) from mixtures $CCl_4 - C_6H_5CH_3$

Acid	CCl_4 content in %				100% $C_6H_5CH_3$
	100	75	50	25	
Salicylic	98,4	97,1	93,4	89,8	89,4
Butyric	64,4	21,2	19,0	16,5	18,0

Table 5 (Fig. 4)

Adsorption (in %) from mixtures $CCl_4 - CH_3C_6H_5$

Acid	CCl_4 content in %				100% $C_6H_5CH_3$
	100	75	50	25	
Salicylic	92,8	79,9	72,1	68,2	60,8
Butyric	63,4	42,4	41,9	28,9	21,4

Table 6

(a) Total adsorption of the acids (in %) on charcoal from the $CCl_4 - C_6H_5CH_3$ mixtures when both acids are present.

(b) Total adsorption (in %) using the data on separate adsorption of each acid from the same media

	CCl_4 content in %				
	100	75	50	25	0
(a)	162	118,3	112,4	106,4	107,4
(b)	156,2	122,3	114,0	97,1	82,2

Table 7 (Fig. 5)

Adsorption (in %) from mixtures $C_6H_6 - C_6H_5CH_3$

Acid	C_6H_6 content in %				100% $C_6H_5CH_3$
	100	75	50	25	
Salicylic	92,2	90,6	90,2	89,7	87,1
Butyric	17,1	13,1	14,3	14,9	17,4
Total adsorption of the two acids	109,3	103,7	104,5	104,6	104,5

Table 8 (Fig. 6)

Adsorption (in %) from mixture $C_6H_6 - CHCl_3$

Acid	C_6H_6 content in %				100% $CHCl_3$
	100	75	50	25	
Salicylic	92,2	87,6	87,0	85,2	84,3
Butyric	17,1	14,1	13,8	9,0	10,4
Total adsorption of the two acids	109,3	101,7	100,8	94,2	95,3

Table 9 (Fig. 7)

Adsorption (in %) from mixtures $CCl_4 - C_2H_5OH$

Acid	CCl_4 content in %				100% C_2H_5OH
	100	75	50	25	
Salicylic	97,7	63,3	59,1	55,9	44,3
Butyric	64,2	26,8	26,8	26,6	24,3
Total adsorption of the two acids	161,9	90,1	85,9	82,5	68,6

Table 10 (Fig. 8)
Adsorption (in %) from mixtures $CCl_4 - (CH_3)_2CO$

Acid	CCl_4 content in %				100% $(CH_3)_2CO$
	100	75	50	25	
Salicylic	98,4	77,6	71,8	70,4	54,8
Butyric	60,2	10,5	17,0	17,3	19,7
Total adsorption of the two acids	158,6	88,1	88,8	87,7	74,5

The percentage adsorption of each acid somewhat changes in both cases, which points to the mutual displacement of the acids from the adsorbent surface during adsorption of the acids from heir mixture.

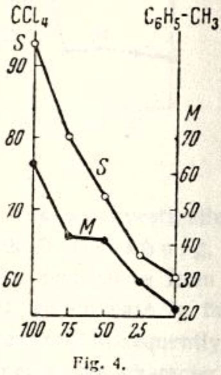


Fig. 4.

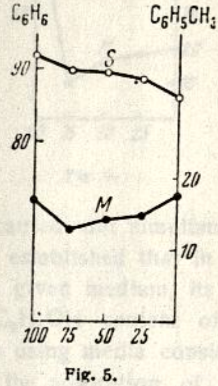


Fig. 5.

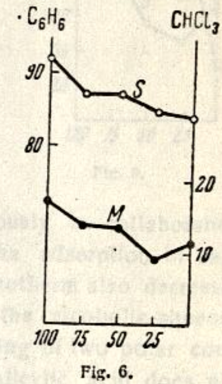


Fig. 6.

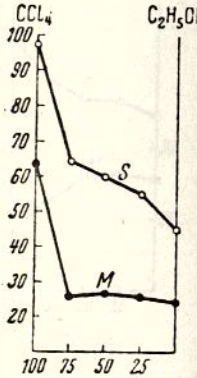
The total percentage adsorption of both acids from their mixture always falls with a decrease in the amount of the non-polar component in the medium.

When both components — polar and non-polar — do not differ much in composition and polarity, *e. g.*, $C_6H_6 - C_6H_5CH_3$ (Table 7), the total adsorption of salicylic and butyric acids from the mixture remains practically constant with a change in the proportion of the components in the medium.

The adsorption of salicylic and butyric acids on charcoal from mixtures of two polar solvents in the presence of both acids

The most characteristic of these series of mixed media is a mixture of the most polar medium, H_2O, and the least polar medium, C_2H_5OH (Table 11).

Adsorption of salicylic acid markedly decreases with an increase in C_2H_5OH content in the mixed solvent, passing through a small minimum at a 25% alcohol content.



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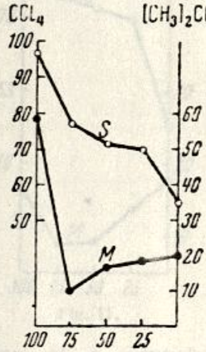

Fig. 8.

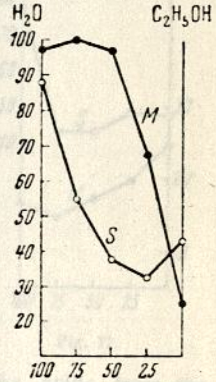

Fig. 9.

In an investigation carried out simultaneously in collaboration with D. Ginsburg, we established that in the adsorption of salicylic acid alone from the given medium, its isotherm also decreases with an increase in the C_2H_5OH content of the alcoholic-aqueous medium. Consequently, in using media consisting of two polar components, the character of the adsorption of salicylic acid does not change, irrespective of whether it is alone in the solution or mixed with another acid, *e. g.*, butyric acid. The adsorption isotherm of butyric acid for a mixture of the latter with salicylic acid also markedly decreases with an increase in the percentage of alcohol in the mixture, from 50% and higher.

The total adsorption of the ácids decreases regularly with an increase in the percentage of the less polar component (C_2H_5OH) in the mixed solvent.

The adsorption of the acids from mixed solvents $(CH_3)_2CO$ — C_2H_5OH (Table 12) having almost equal polarity constants follows the rule of mutual displacement most completely. While the isothermal adsorption of salicylic acid falls with an increase in the C_2H_5OH content in the medium, the adsorption of butyric acid correspondingly increases. The total adsorption of the acids from their mixture remains almost constant, irrespective of the ratio of C_2H_5OH to $(CH_3)_2CO$ in the solvent.

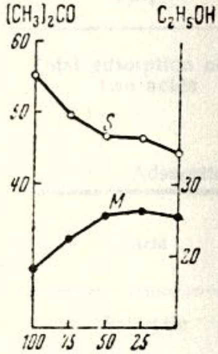

Fig. 10.

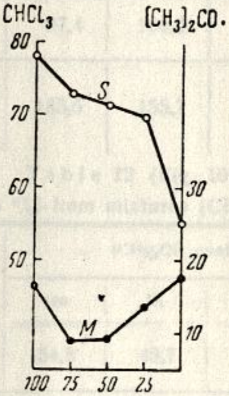

Fig. 11.

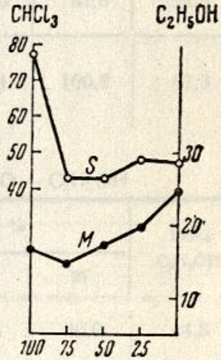

Fig. 12.

During the adsorption of a mixture of the acids from the solvents $CHCl_3$ — $(CH_3)_2CO$, the isotherm for butyric acid passes through a minimum while the solvent composition changes from pure $CHCl_3$ to pure $(CH_3)_2CO$ or C_2H_5OH. The adsorption of salicylic acid from the first pair of solvents falls and the adsorption from the second pair passes through a minimum. Such a behaviour of salicylic acid may be due to a different degree of association in the chloroform medium with the admixture of a second polar component.

Sata and Kurano[3] also observed that the adsorption isotherm passes through a minimum when picric and benzoic acids are adsorbed from the same media.

The dependence of the adsorption of salicylic and butyric acids on the polarity of the solvents

The adsorption of salicylic and butyric acids from pure solvents (Table 15) exhibits a regular dependence on the polar properties of the medium.

Table 11 (Fig. 9)

Adsorption (in %) from mixtures H_2O — C_2H_5OH

Acid	H_2O content in %				100% C_2H_5OH
	100	75	50	25	
Salicylic	88,2	55,7	37,6	33,2	43,0
Butyric	97,4	100,0	97,5	67,6	24,3
Total adsorption of the two acids	185,6	155,7	135,1	100,8	67,3

Table 12 (Fig. 10)

Adsorption (in %) from mixtures $(CH_3)_2CO$ — C_2H_5OH

Acid	$(CH_3)_2CO$ content in %				100% C_2H_5OH
	100	75	50	25	
Salicylic	54,8	48,7	46,6	46,0	44,3
Butyric	18,2	22,4	24,8	25,4	24,8
Total adsorption of the two acids	73,0	71,7	71,4	71,4	69,3

Table 13 (Fig. 11)

Adsorption (in %) from mixtures $CHCl_3$ — $(CH_3)_2CO$

Acid	$CHCl_3$ content in %				100% $(CH_3)_2CO$
	100	75	50	25	
Salicylic	78,2	72,6	71,5	69,5	54,8
Butyric	17,1	9,2	9,2	13,4	18,2
Total adsorption of the two acids	95,3	81,8	80,7	82,9	73,0

Table 14 (Fig. 12)

Adsorption (in %) from mixtures $CHCl_3 - C_2H_5OH$

Acid	$CHCl_3$ content in %				100% C_2H_5OH
	100	75	50	25	
Salicylic	78,2	42,0	43,2	47,7	44,3
Butyric	17,1	14,7	17,3	19,3	24,3
Total adsorption of the two acids	95,3	56,7	60,5	64,0	68,6

Table 15

Adsorption (in %) of salicylic and butyric acids from pure media

No.	Medium	% adsorption		ε	$\mu \cdot 10^{18}$	$P_{\varepsilon m}$
		salicylic	butyric			
1	CCl_4	98,0	62,1	2,56	0,0	28,1
2	C_6H_6	92,2	17,1	2,26	0,0	26,3
3	$C_6H_5CH_3$	88,2	17,4	2,38	0,5	32,7
4	$CHCl_3$	81,5	14,5	4,95	1,05	46,8
5	$(C_2H_5)_2O$	63,4	10,7	4,33	1,14	54,9
6	$(CH_3)_2CO$	54,8	19,7	21,5	2,6	63,7
7	$C_6H_5NO_2$	44,9	19,1	34,0	3,9	93,9
8	H_2O	88,2	97,4	81	1,85	
9	CH_3OH	46,8	29,1	32	1,68	36,8
10	C_2H_5OH	44,3	24,3	25	1,7	52,1
11	C_3H_7OH	42,0	15,5	26	1,78	65,1
12	C_4H_9OH	28,9	11,1	18	1,7 (1,53)	78,4
13	$C_5H_{11}OH$	23,5	10,2	16	1,77	90,6

The adsorption of the acids from solvents of one homologous series (alcohols) steadily falls with a fall in ε or with an increase in $P_{\varepsilon m}$ of the media. In this case, with an increase in the length of the alcohol radical, the polarity of the medium approaches that of the molecules of the adsorbed acid, and this naturally reduces their capability for being adsorbed on charcoal.

During adsorption of the acids from pure solvents of a different chemical nature, a similar relation is to be observed between the percentage adsorption of the acids and the polar constants of the media. In individual cases, deviations associated with various secondary effects are observed.

Summary

The adsorption of salicylic and butyric acids in their mixture from single and mixed solvents was studied. It was established that:

1) The character of the adsorption isotherm of either of the acids is not fundamentally altered by the presence of the second acid in the mixed medium.

2) For the case of complex systems studied by us, Masius' rule is confirmed: from an acid mixture that acid is adsorbed more which is adsorbed more when taken separately.

3) The total adsorption of acids from media which approach each other in their polarity [$(CH_3)_2CO$ — C_2H_5OH] or, at the same time, also in their chemical nature (C_6H_6 — $C_6H_5CH_3$) was found to be almost constant with a change in the proportion of the components in the medium.

4) The adsorption of salicylic acid (in the presence of butyric acid) from mixed media consisting of a polar and a non-polar component, steadily falls with a fall in the amount of the non-polar component in the solvent.

5) The adsorption of salicylic and butyric acids in their mixture from pure solvents of the same homologous series steadily falls with a fall in the dielectric constant and with an increase in the molecular polarization of the medium.

Dniepropetrovsk.

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