

# Adsorption of n-Octanol at the n-Dodecane/Water Interface

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*Received 4th February, 1970*

The adsorption of n-octanol from dilute solutions in n-dodecane to the dodecane/water interface has been studied in the temperature range 15–35°C. Standard free energies of adsorption have been calculated as a function of temperature and a mean standard heat of adsorption for the temperature range has been computed. The Volmer equation represents the data adequately, with a molecular "co-area" of  $0.24 (\pm 0.02) \text{ nm}^2 \text{ molecule}^{-1}$ . The present results are compared with previously reported data for 20°C.

Adsorption at liquid/liquid interfaces has received relatively little attention in the past. Surface concentrations of an adsorbed solute at liquid/liquid interfaces can be obtained from the variation of interfacial tension with solute concentration. The calculation requires a knowledge of the activity coefficients of the solute in the phase from which the adsorption is being studied, and of the distribution ratio of the solute between the two phases. It is also necessary to know the mutual solubilities of the solvents.<sup>1</sup>

The present work is part of a comprehensive study of the adsorption of n-alkanols at alkane/water interfaces. Alkane+water systems have been chosen because of the particularly low mutual solubilities.<sup>2, 3</sup> In addition, using the values for the distribution ratios of alkanols between water and alkanes<sup>4</sup> it has been possible to choose solutes which are effectively confined to the alkane phase. Further, activity coefficients of some alkanols in alkanes have been determined<sup>5</sup> so that in the present study it has been possible to choose solute concentrations which result in ideal dilute solutions.

Data are presented here for the adsorption of n-octanol at the n-dodecane/water interface at nine temperatures in the range 15–35°C. Standard free energies of adsorption have been calculated and a mean standard heat of adsorption in this temperature range computed. The data have been fitted to the Volmer equation and compared with some previous results obtained by Ross and Chen<sup>6</sup> at 20°C.

## EXPERIMENTAL

### MATERIALS

Fluka *puriss* grade n-octanol was further purified by preparative g.l.c. and contained no impurities which were detectable by g.l.c. The n-dodecane was supplied by Newton-Maine as 99 % pure and had a purity, as estimated by g.l.c., of 99.5 %. It was passed through alumina prior to use. Water was three times distilled from glass apparatus.

### PROCEDURE

Interfacial tensions were determined by the drop-volume technique<sup>7</sup> and were reproducible to  $\pm 0.02 \text{ mN m}^{-1}$ . A steel tip of radius  $r = 2.728 \text{ mm}$  was used and values of  $r/V^{1/3}$  of between 0.4 and 0.6 were obtained, where  $V$  is the volume of the drop. The correction factors  $f$  corresponding to the various values of  $r/V^{1/3}$  were interpolated graphically

TABLE 1.—INTERFACIAL TENSION  $\gamma$  AS A FUNCTION OF MOL FRACTION  $x$  OF n-OCTANOL IN n-DODECANE

$10^4x$ $T = 288.15 \text{ K}$	$\gamma/\text{mN m}^{-1}$	$10^4x$ $T = 290.65 \text{ K}$	$\gamma/\text{mN m}^{-1}$	$10^4x$ $T = 293.15 \text{ K}$	$\gamma/\text{mN m}^{-1}$
0.000	53.22	0.000	52.96	0.000	52.90
0.227	52.85	0.292	52.47	0.227	52.50
0.415	52.48	0.437	52.23	0.415	52.21
0.629	52.07	0.843	51.60	0.629	51.94
0.876	51.66	1.015	51.32	0.876	51.57
1.097	51.27	1.31	50.90	1.097	51.25
2.19	49.71	2.61	49.22	2.19	49.85
5.44	45.80	6.54	45.32	3.62	48.29
8.41	43.40	11.15	42.09	7.65	44.87
17.1	38.27	16.2	39.39	13.37	41.35
17.4	38.21			17.4	39.44
20.6	36.77				
$T = 295.65 \text{ K}$		$T = 298.15 \text{ K}$		$T = 300.65 \text{ K}$	
0.000	52.74	0.000	52.50	0.000	52.28
0.232	52.41	0.226	52.20	0.232	52.01
0.489	52.03	0.454	51.88	0.489	51.71
0.719	51.75	0.684	51.66	0.719	51.50
0.962	51.46	0.890	51.40	0.962	51.24
1.203	51.15	1.134	51.13	1.203	51.01
2.38	49.78	2.26	49.81	2.38	49.78
4.68	47.64	4.70	47.76	4.68	48.00
14.95	41.31	8.29	45.25	9.05	45.22
19.0	39.56	13.03	42.65	14.95	42.27
		17.7	40.57	19.0	40.69
		21.9	39.02	23.5	39.17
$T = 303.15 \text{ K}$		$T = 305.65 \text{ K}$		$T = 308.15 \text{ K}$	
0.000	52.07	0.000	51.82	0.000	51.61
0.226	51.84	0.279	51.54	0.279	51.38
0.454	51.55	0.515	51.34	0.515	51.17
0.684	51.37	0.810	51.14	0.810	50.96
0.890	51.17	1.004	50.98	1.004	50.84
1.134	50.93	1.305	50.71	1.305	50.59
2.26	49.93	2.61	49.69	2.61	49.66
4.70	48.09	6.54	47.12	5.44	47.81*
8.29	45.86	11.15	44.70	8.41	46.24
13.03	43.52	16.2	42.56	17.1	42.60
17.7	41.59	21.0	40.91	17.4	42.47
22.2	40.13	25.7	39.44	20.6	41.51
26.2	38.82	29.5	38.42	24.6	40.31
				29.8	38.93

from the “smoothed” values listed by Harkins and Brown.<sup>8</sup> These values were used in preference to those given by Lando and Oakley.<sup>9</sup> The latter workers point out that Harkins and Brown used only a limited amount of the experimental data in order to obtain the “smoothed” values. Nonetheless, in the region of  $r/V^{\frac{1}{3}}$  used in the present work, the Harkins and Brown “smoothed” values represent all the experimental values (5 points) better than the values given by Lando and Oakley. The difference in interfacial tensions calculated from the two sets of interpolated  $f$  values can be as much as  $0.3 \text{ mN m}^{-1}$  (in about  $50 \text{ mN m}^{-1}$ ) but the difference in surface pressures obtained is much less and lies within the experimental error of the measurements.

For alkane+water systems, interfacial tensions obtained by the drop-volume method using the Harkins and Brown correction tables are in good agreement with values determined by the Wilhelmy plate method.<sup>10</sup>

The apparatus was maintained at the required temperature to within 0.01° by a water thermostat. Stock solutions of n-octanol in n-dodecane were made up and diluted by weight to the required concentrations. It can be inferred from work on the distribution of alkanols between water and alkanes<sup>4</sup> that the maximum error in concentration in the dodecane, due to extraction of the solute by the water during the experiments, is *ca.* 0.5 %. For alkanols lower than n-octanol, account would have to be taken of this distribution effect if precise results were required.

## RESULTS AND DISCUSSION

The interfacial tensions between water and dilute solutions of n-octanol in n-dodecane, of mol fraction  $x$  ranging from zero to approximately  $3 \times 10^{-3}$ , are given in table 1. Measurements have been made at 2.5° intervals from 15 to 35°C. At the lower values of  $x$  the surface pressure,  $\Pi$  is a linear function of  $x$ , within the reproducibility of the results, but at higher values of  $x$  the  $(\Pi, x)$  relationship becomes curved.  $\Pi$  is defined as the lowering of the interfacial tension of the clean interface, resulting from adsorption.

The initial slope  $(\Pi/x)_0$  of the (surface pressure, mol fraction) curve, is related to a standard free energy of adsorption  $\Delta\mu^\ominus$  by<sup>11</sup>

$$\Delta\mu^\ominus = -RT \ln \left( \frac{\Pi}{x} \right)_0 \frac{x_s}{\Pi_s}, \quad (1)$$

where  $\Pi_s$  is a standard surface pressure and is independent of the temperature  $T$ .  $x_s$  is a standard mol fraction for the bulk. A hypothetical bulk standard state of  $x_s = 1$ , where the solute behaves in the same way as in ideal dilute solution, is normally employed. Some of the present data lie in the linear  $(\Pi, x)$  region and values of  $(\Pi/x)_0$  have been obtained from these data by the method of least squares. The six lowest concentration points (including the origin) were used for all temperatures except for 15 and 17.5°C, where the five lowest concentration points were taken. Values of  $\Delta\mu^\ominus$  using  $x_s = 1$  and  $\Pi_s = 1 \text{ mN m}^{-1}$  are listed in table 2.

TABLE 2.—STANDARD FREE ENERGIES  $\Delta\mu^\ominus$  OF ADSORPTION OF n-OCTANOL FROM DODECANE TO THE DODECANE/WATER INTERFACE

$T/\text{K}$	$-\Delta\mu^\ominus/\text{kJ mol}^{-1}$	$T/\text{K}$	$-\Delta\mu^\ominus/\text{kJ mol}^{-1}$
288.15	23.48	300.65	23.15
290.65	23.39	303.15	23.20
293.15	23.40	305.65	22.93
295.65	23.31	308.15	22.94
298.15	23.28		

Standard heats of adsorption  $\Delta H^\ominus$  may be obtained from the temperature variation of  $\Delta\mu^\ominus$  at constant pressure, from the relationship

$$\Delta H^\ominus = \frac{d(\Delta\mu^\ominus/T)}{d(1/T)}. \quad (2)$$

$\Delta H^\ominus$  is the limiting value, at low surface pressures, of the “equilibrium” heat of adsorption. The plot of  $\Delta\mu^\ominus/T$  against  $1/T$  shown in fig. 1, is linear within experimental error and  $\Delta H^\ominus$  may be considered approximately constant in this temperature range. The mean value obtained by least squares is  $-31.4 \text{ kJ mol}^{-1}$ . The heat of

transfer of the n-alkanols butanol to hexanol from dilute solution in alkanes to dilute solution in water is about  $-30 \text{ kJ mol}^{-1}$ , determined calorimetrically.<sup>4</sup> The larger part of this heat is supposed to result from the transfer of the  $-\text{OH}$  group. The adsorption process also involves the transfer of the  $-\text{OH}$  group from alkane to water at the interface and so  $\Delta H^\ominus$  is of the expected magnitude.

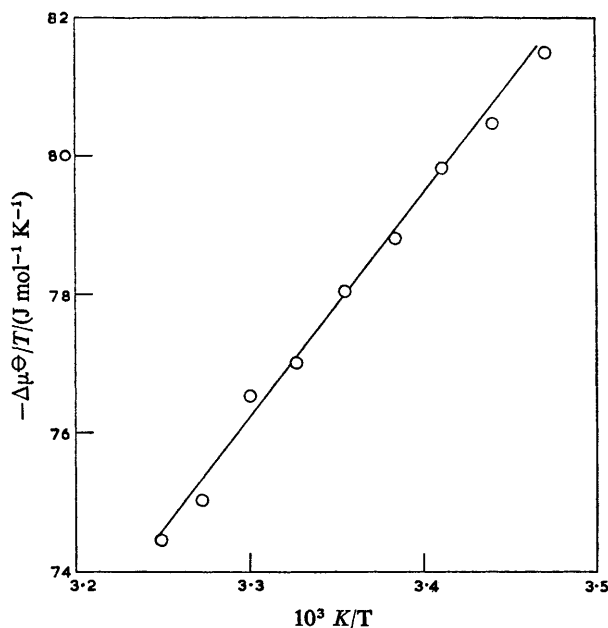


FIG. 1.—Temperature dependence of the standard free energy  $\Delta\mu^\ominus$  of adsorption

In previous studies it has been common to describe data for adsorption at liquid surfaces in terms of empirical surface equations of state. The Schofield-Rideal equation<sup>12</sup>

$$\Pi(a-a_0) = ikT \quad (3)$$

is useful in this respect.  $a$  is the area per molecule at the interface,  $a_0$  the molecular “co-area”, and  $i$  a constant. When  $i = 1$  eqn (3) is the Volmer equation. Values of  $a$  can be calculated from interfacial tensions obtained at a single temperature by the use of an appropriate form of the Gibbs adsorption equation. For two immiscible liquids, 1 and 2, and a solute, 3, which is distributed between them, the Gibbs equation is

$$-\partial\gamma = [\Gamma_3 - \Gamma_2 x_3^\beta/x_2^\beta - \Gamma_1 x_3^\alpha/x_1^\alpha] \partial\mu_3. \quad (4)$$

$\alpha$  denotes the phase consisting mainly of component 1 and  $\beta$  that of mainly component 2. The  $x$  are mol-fractions and the  $\Gamma$  are surface concentrations. For the present system, with water component 1 and dodecane component 2,  $x_3^\beta$  is very small ( $\sim 3 \times 10^{-3}$  at most) and  $x_3^\alpha$  is effectively zero;<sup>4</sup>  $x_2^\beta$  and  $x_1^\alpha$  are both effectively equal to unity.<sup>2, 3</sup> Thus, to a good approximation, eqn (4) becomes

$$1/\Gamma_3 = a = -(kT/fx)(\partial fx/\partial\gamma) \quad (5)$$

where  $x_3^\beta$  has been written as  $x$ .  $f$  is the activity coefficient which  $\rightarrow 1$  as  $x \rightarrow 1$ . In ideal dilute solutions  $f$  attains the constant value of  $f^0$  and may therefore be omitted from (5). For solutions of n-alkanols in n-alkanes preliminary work<sup>5</sup>

has shown that  $f$  may deviate significantly from  $f^0$  even in dilute solution, due probably to the auto-association of the alkanols. As an example, for n-dodecanol in n-octane at 25°C and  $x = 2 \times 10^{-3}$ ,  $f/f_0 \approx 0.9$ . In the present analysis only values of  $a$  for  $x < 0.9 \times 10^{-3}$  have been calculated so as to minimize errors arising from neglect of bulk non-idealities.

The  $(\gamma, x)$  data have been fitted to the third-order polynomial,

$$x = c_1\gamma^3 + c_2\gamma^2 + c_3\gamma + c_4, \quad (6)$$

and the constants  $c_1$ ,  $c_2$ ,  $c_3$  and  $c_4$  are given in table 3. The constants were obtained by the method of least squares<sup>13, 14</sup> with the aid of a computer using a simplex method.<sup>15</sup> Values of  $(\partial x/\partial \gamma)$  necessary for the calculation of  $a$  using eqn (5) were then obtained by the differentiation of eqn (6).

TABLE 3.—CONSTANTS FROM (6) FOR THE SYSTEM  $\text{H}_2\text{O} + \text{DODECANE} + \text{OCTANOL}$

$T/\text{K}$	$-c_1 \times 10^7$	$c_2 \times 10^5$	$-c_3 \times 10^3$	$c_4 \times 10^2$
288.15	1.562 70	2.684 33	1.580 88	3.166 25
290.65	1.609 43	2.787 12	1.656 61	3.346 78
293.15	1.651 57	2.897 02	1.740 94	3.547 33
295.65	1.669 67	2.988 13	1.828 20	3.779 73
298.15	1.749 92	3.165 50	1.951 93	4.054 85
300.65	1.810 08	3.315 17	2.066 78	4.330 66
303.15	1.853 77	3.443 94	2.171 15	4.584 79
305.65	3.301 74	5.463 15	3.119 00	6.086 50
308.15	3.940 47	6.474 86	3.659 03	7.054 62

Eqn (3) may be rearranged to the linear form

$$\Pi a = \Pi a_0 + i k T. \quad (7)$$

Values of  $a_0$  and  $i$  for each of the temperatures studied have been calculated from eqn (7) by the method of least squares (table 4). Values of  $i$  do not differ from unity by more than 3 % for any of the temperatures except 15°C when  $i = 0.94$ . The mean value of  $a_0$  in the temperature range is 0.24 ( $\pm 0.02$ )  $\text{nm}^2 \text{ molecule}^{-1}$ . We therefore consider that the present results (up to  $x \sim 0.9 \times 10^{-3}$ ) can be adequately represented by the Volmer equation.

In systems where the Volmer equation is applicable, some workers<sup>16, 17</sup> have used the corresponding adsorption isotherm

$$x = K \frac{a_0}{a - a_0} \exp \frac{a_0}{a - a_0} \quad (8)$$

to obtain standard free energies of adsorption since the constant  $K$  is related to a standard free energy  $\Delta\mu_v^\ominus$ . Haydon and Taylor,<sup>16</sup> for example, used the expression

$$\Delta\mu_v^\ominus = RT \ln K \quad (9)$$

which implies a standard surface coverage ( $a_0/a$ ) of 0.362. Possibly a more convenient standard state for the surface is half-coverage (i.e.,  $a_s = 2a_0$ ) when

$$\Delta\mu_v^\ominus = RT(\ln K + 1). \quad (10)$$

The  $\Delta\mu_v^\ominus$  obtained from eqn (10) is related to  $\Delta\mu^\ominus$  (for  $\Pi_s = 1 \text{ mN m}^{-1}$ ) by

$$\Delta\mu^\ominus = \Delta\mu_v^\ominus + RT\{\ln(a_0/kT) - 1\}. \quad (11)$$

The standard heat of adsorption obtained from the temperature variation of  $\Delta\mu_v^\ominus$  is the limiting low  $\Pi$  value of the "isosteric" heat of adsorption and differs from  $\Delta H^\ominus$  by an amount  $RT$ .

Ross and Chen<sup>6</sup> have studied the same system as that reported here, at 20°C, but using higher concentrations (up to  $x = 1.2 \times 10^{-2}$ ). They report values of  $i$  and  $a_0$  (eqn (3)) of 0.712 and 0.313 nm<sup>2</sup> molecule<sup>-1</sup> respectively which differ considerably from our values (0.97 and 0.25 nm<sup>2</sup> molecule<sup>-1</sup> respectively). To fit their data they found it necessary to replace the exponential term in eqn (8) by  $\exp [a_0/(a - a_0) - 2\alpha/kTa_0]$ , where  $\alpha$  is a molecular interaction constant. The value of  $K$  obtained was  $1.95 \times 10^{-3}$ , which, using eqn (10) and (11) yields a value for  $\Delta\mu^\ominus$  of  $-21.4$  kJ mol<sup>-1</sup>. Our values of  $K$  and  $\Delta\mu^\ominus$  are  $0.99 \times 10^{-3}$  and  $-23.4$  kJ mol<sup>-1</sup> respectively.

TABLE 4.—VALUES OF  $a_0$  AND  $i$  (eqn (3))

$T/K$	$i$	$a_0/\text{nm}^2 \text{ molecule}^{-1}$
288.15	0.94	0.25
290.65	0.98	0.23
293.15	0.97	0.25
295.65	1.00	0.23
298.15	1.00	0.24
300.65	0.99	0.25
303.15	1.00	0.24
305.65	0.99	0.23
308.15	1.02	0.26

For solutions of n-octanol in n-octane we have found from infra-red measurements that there are considerable deviations from ideal dilute solution behaviour in the region of  $x = 1 \times 10^{-2}$ . It appears likely that this will also be the case for solutions of n-octanol in n-dodecane. In their analysis, Ross and Chen neglected non-idealities and it seems probable that the lack of agreement between their values of  $a_0$ ,  $i$  and  $K$  and ours is due, at least in part, to this. It is also known that the auto-association of alkanols in alkanes is strongly temperature dependent.<sup>18</sup> Thus, if heats of adsorption are to be obtained from the constants associated with the Volmer model in systems similar to the present one, it is particularly important to work with very dilute solutions or to have a knowledge of the appropriate activity coefficients as a function of temperature.

One of the authors (B. J. B.) is indebted to the Science Research Council for a maintenance grant.

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