

Calorimetric Method for the Direct Evaluation of the Thermodynamic Functions for the Transfer of Non-ionic Solutes between Immiscible Liquid Phases

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Summary A simple method is proposed which allows a straight-forward evaluation of the thermodynamic functions of transfer by using the results of calorimetric mixing experiments

WHILE the standard free-energy change for the transfer process (ΔG_t^0) of a solute between two slightly soluble liquid phases can be obtained by many different techniques,^{1,2} the enthalpy change (ΔH_t^0) is usually derived indirectly either from the temperature dependence of ΔG_t^0 or from the difference between the solution enthalpies of the solute in the two solvents.³ Although new calorimeters have been developed recently for measuring enthalpies of solution with more accuracy,^{4,5} there is still a large uncertainty in the relatively small enthalpies of transfer which are obtained from the difference between large numbers.⁶

We have tested the possibility of a direct evaluation of the thermodynamic functions (ΔG_t^0 , ΔH_t^0 , and ΔS_t^0), of the transfer process of a non-ionic solute between two liquid phases with a very low mutual solubility, using the results of microcalorimetric mixing experiments, and have applied the method to the distribution of phenol between water saturated with octane and octane saturated with water at 298.15 K.

The partition constant of a non-ionic solute between two immiscible liquid phases 1 and 2 is defined, if the solute follows Henry's law in each solvent, as in equation (1),

$$K_r^c = c_1^c/c_2^c \quad (1)$$

where c_1^c and c_2^c are the solute molar concentrations when the equilibrium distribution is reached

If c_w and c_{org} are the initial solute concentrations in the aqueous and in the organic phase respectively, V_w and V_{org} the volume of the solutions used for the mixing

process, and x the number of moles of solute transferred from one phase to the other, the equilibrium concentrations will be given by equations (2) and (3), assuming that the volume change of both solutions after the transfer process is negligible. Combination of equations (1), (2), and (3)

$$c_1^c = (c_w V_w + x)/V_w \quad (2)$$

$$c_2^c = (c_{org} V_{org} - x)/V_{org} \quad (3)$$

leads to equation (4) which can be rewritten as equation (5)

$$K_r^c = V_{org}/V_w [(C_w V_w + x)/c_{org} V_{org} - x] \quad (4)$$

$$c_w/c_{org} = K_r^c - \{[1 + K_r^c(V_w/V_{org})]/c_{org}\}x/V_w \quad (5)$$

If Q is the experimental thermal effect arising from the transfer of x moles of solute and ΔH_t is the corresponding molar enthalpy change it follows that for dilute solutions $x = Q/\Delta H_t^0$ and the relationship shown in equation (6) holds. Equation (6) indicates that if the experimental

$$c_w/c_{org} = K_r^c - \{[1 + K_r^c(V_w/V_{org})]/c_{org}\}Q/\Delta H_t^0/V_w \quad (6)$$

measurements are carried out at constant c_{org} and at constant ratio V_w/V_{org} the partition constant K_r^c and the standard enthalpy of transfer ΔH_t^0 can be evaluated from a linear plot of c_w/c_{org} against Q/V_w . This expression will be a straight line relationship only if K_r^c is independent of solute concentration and if the mutual solubility between the water and the organic solvent is not significantly affected by the presence of the solute, i.e. if the salting-in or salting-out effect is negligible. It is well known that in dilute solutions of non-ionic solutes both conditions apply.⁷ When the solutions are made up by weight, as in this work, equation (6) can be then converted into equation (7) where

$$m_w/m_{org} = K_r^c(d_w^0/d_{org}^0) - \{[1 + K_r^c(d_w^0/d_{org}^0)]/m_{org}\}Q/\Delta H_t^0/w_w \quad (7)$$

TABLE 1. Transfer of phenol between the aqueous (*i.e.* water pre-saturated with octane) and the organic (*i.e.* octane pre-saturated with water) phase at 298.15 K.

w_w/g	w_{org}/g	$m_w/mol\ kg^{-1}$	$m_{org}/mol\ kg^{-1}$	$10^3 Q^a/J$
1.8957	2.1207	0.01006	0.01408	-334.7
1.8951	2.0965	0.01883	0.01408	-295.0
1.8654	2.0853	0.02837	0.01408	-217.6
1.8323	2.1032	0.03870	0.01408	-162.8
1.9168	2.1065	0.04668	0.01408	-129.3
1.8807	2.1147	0.05692	0.01408	-71.5
1.8854	2.1104	0.06343	0.01408	-27.9
1.8902	2.1105	0.07196	0.01408	19.3
1.9065	2.0999	0.07529	0.01408	45.2

^a Q denotes the corrected heat effect connected with the transfer process.

d_w and d_{org} are the densities of the aqueous and the organic solutions, m_w and m_{org} the corresponding solute concentrations expressed as the number of moles of solute per kg of solution, and w_w and w_{org} are the weights of the solutions used for the mixing process. Since the solutions are dilute and the mutual solubility of water and octane is very low, we may assume that the ratio of the solution densities is the same as that of the pure solvents, *i.e.* $d_w/d_{org} = d_w^0/d_{org}^0$; equation (8) then follows from equation (7).

$$m_w/m_{org} = K_r^c(d_w^0/d_{org}^0) - \{[1 + K_r^c(d_w^0/d_{org}^0)]m_{org}\Delta H_t^0\}Q/w_w \quad (8)$$

Experimental data for the transfer of phenol at 298.15 K from the organic phase (*i.e.* octane pre-saturated with water) to the aqueous phase (water pre-saturated with octane) are

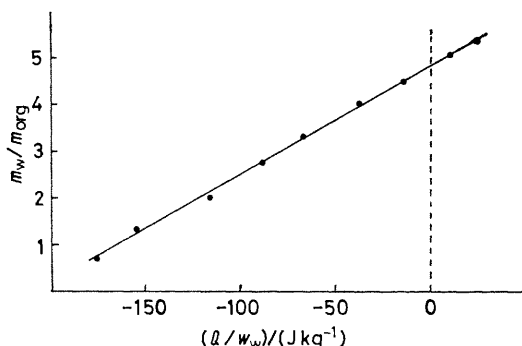


FIGURE. Fit of equation (8) for the transfer process.

reported in Table 1, and the plot of m_w/m_{org} against Q/w_w is shown in the Figure. A straight line was obtained with intercept (4.85 ± 0.04) and the slope (0.0232 ± 0.0004) estimated by least-squares analysis. Given that the densities of the pure solvents (d_w^0 0.99704 g cm⁻³; d_{org}^0 0.69849 g cm⁻³)⁸ and the mean value of the w_w/w_{org} ratios (0.896 ± 0.004) were known, K_r^c and ΔH_t^0 could be calculated from equation (8).

TABLE 2. Derived standard thermodynamic functions for the transfer of phenol between the aqueous and organic phase at 298.15 K.

	This work	Ref. 7
ΔG_t^0 (kJ mol ⁻¹)	-4.79 ± 0.02	-4.77
ΔH_t^0 (kJ mol ⁻¹)	-16.3 ± 0.3	-16.4 ± 0.5
ΔS_t^0 (J mol ⁻¹ K ⁻¹)	-38.6 ± 1.1	-38.5

The thermodynamic functions (ΔG_t^0 , ΔH_t^0 , and ΔS_t^0) for this transfer process are summarized in Table 2, where, for comparison, literature data are also reported. It appears that the values obtained by the above method are in excellent agreement with the data of K. J. Breslauer *et al.*;⁷ the only difference being that the literature values have been obtained by a much more complicated experimental analysis than the present one.

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