

DEUTERIUM ISOTOPE EFFECTS IN TWO-PHASE LIQUID SYSTEMS CONTAINING WATER

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INTRODUCTION

The solubility of heavy and light water in certain organic solvents is quite different. This isotope solubility effect is related to the isotope separation effect encountered in a two-phase system containing a mixture of light and heavy water in equilibrium with an organic compound. It has not been possible, however, to make immediate predictions about the one effect in terms of the other. In this paper an equation is developed which permits such a prediction. By applying this equation to different systems it is shown what order of magnitude of isotope separation effects is, in general, to be expected. It should be noted that these effects are distinguishable from those that may result from chemical exchange between the organic component and the water.

The following treatment is a generalization and revision of a previous study¹ of the ternary system, triethylamine, water and heavy water.

1. BASIC THEORY

At equilibrium the chemical potential, μ_j , of any chemical species present in the system is the same in the two phases, distinguished by a single prime and a double prime, *i.e.*

$$\mu_j' = \mu_j'' \quad \text{and} \quad d\mu_j' = d\mu_j'' \quad (1)$$

Additional relations applicable to any one of the phases are (a) the Gibbs–Duhem equation:

$$SdT + \sum x_j d\mu_j = 0 \quad (2)$$

where x_j represents the mole fraction, and where the pressure is kept constant, and (b) equations referring to chemical equilibria between the species, represented by

$$\sum \frac{1}{\nu_k} d\mu_k = \sum \frac{1}{\nu_l} d\mu_l \quad (3)$$

where $1/\nu_k$ and $1/\nu_l$ are stoichiometric factors.

The ternary system is determined (at constant pressure) by fixing the temperature and two composition variables. The relations represented by equation (3) may thus be used to eliminate all but three chemical potentials in equation (1) or (2). It is more convenient, however, when rapid chemical exchange takes place in the system, to retain at this stage the fully deuterated

organic component (D_vA) as a separate species. Equations (2) and (3) may then be re-written as follows:

$$SdT + x_D d\mu_D + x_H d\mu_H + x_{DA} d\mu_{DA} + x_{HA} d\mu_{HA} \equiv \sum x_i S_i dT + \sum x_i d\mu_i = 0 \quad (4)$$

and

$$\frac{1}{2}d\mu_D + \frac{1}{v}d\mu_{HA} = \frac{1}{2}d\mu_H + \frac{1}{v}d\mu_{DA} \quad (5)$$

Here μ_D , μ_H , μ_{DA} and μ_{HA} are taken to refer to D_2O , H_2O , fully deuterated (DA) and ordinary (HA) organic component; S_i represents the partial molar entropies of the same species; x_D , x_H , x_{DA} and x_{HA} are the numbers of moles of pure component to be added in order to produce one mole of mixture, *i.e.*

$$x_D + x_H + x_{DA} + x_{HA} = 1 \quad (6)$$

without effecting chemical exchange according to (5).

As independent variables it is most convenient to choose the isotopic composition of the water, y , and the total water concentration, x (both mole fractions), so that:

$$yx \equiv x_D \quad \text{and} \quad (1 - y)x \equiv x_H \quad (7)$$

For systems at equilibrium, y' and x' are arbitrarily chosen as independent variables.

Changes in chemical potential, as occurring in equations (1), (4) and (5), may be written

$$d\mu_i = \left(\frac{\partial\mu_i}{\partial x}\right)_{y, T} dx + \left(\frac{\partial\mu_i}{\partial y}\right)_{x, T} dy - S_i dT \quad (8)$$

Thus, equation (1) becomes

$$\frac{\partial\mu_1'}{\partial x} dx' - \frac{\partial\mu_1''}{\partial x} dx'' + \frac{\partial\mu_1'}{\partial y} dy' - \frac{\partial\mu_1''}{\partial y} dy'' = (S_1' - S_1'')dT \quad (9)$$

It is possible to eliminate all potentials of one phase by writing equation (1) in the form:

$$\sum x_i'' d\mu_i' = \sum x_i' d\mu_i'' \quad (10)$$

and introducing equation (4). Substitution according to (8) then leads to the expression:

$$\sum x_i'' \frac{\partial\mu_i'}{\partial x} dx' + \sum x_i'' \frac{\partial\mu_i'}{\partial y} dy' = \sum x_i' (S_1' - S_1'') dT \quad (11)$$

Equations (9) and (11) in fact, each represent three equations, describing changes through equilibrium states, in which y' , x' or T , respectively, are kept constant. When $dy' = 0$ these relationships represent equations for the solubility curves. When $dx' = 0$ or $dT = 0$, they may be used, as will be shown later, for the calculation of isotope effects.

2. APPROXIMATIONS

2.1

The chemical potential, μ , may be split into a concentration term and an activity coefficient term. When chemical exchange between the organic component and the water is included as in equations (4)–(6), it is possible and convenient to take into account in the concentration terms, the existence of only three water species, H_2O , D_2O and DHO , and of only ν organic component species (analogous to the water species), while any other interaction is included in a simple way in the activity coefficient terms. It can be shown¹, on the basis of equation (3) that for the water species the concentrations in question are given approximately by:

$$[\text{D}_2\text{O}] = y^2x, \quad [\text{H}_2\text{O}] = (1 - y)^2x \quad \text{and} \quad [\text{HDO}] = 2y(1 - y)x \quad (12)$$

Thus (if $dT = 0$),

$$d\mu_{\text{D}} = RTd \ln y^2x f_{\text{D}} \quad (13)$$

$$d\mu_{\text{H}} = RTd \ln (1 - y)^2x f_{\text{H}}$$

One may define for the organic species (*cf.* equation (7))

$$x_{\text{DA}} \equiv y_a x_a \quad \text{and} \quad x_{\text{HA}} \equiv (1 - y_a) x_a \quad (14)$$

and it may be shown that (for $dT = 0$)

$$d\mu_{\text{DA}} = RTd \ln y_a^\nu (1 - x) f_{\text{DA}} \quad (15)$$

$$d\mu_{\text{HA}} = RTd \ln (1 - y_a)^\nu (1 - x) f_{\text{HA}}$$

2.2

The partial derivatives in equations (9) and (11) may be written in terms of (13) and (15). Thus, for the deuterated components

$$\frac{1}{RT} \frac{\partial \mu_{\text{D}}}{\partial x} = \frac{\partial \ln x f_{\text{D}}}{\partial x} \quad (16)$$

and

$$\frac{1}{RT} \frac{\partial \mu_{\text{D}}}{\partial y} = \frac{2}{y} + \frac{\partial \ln f_{\text{D}}}{\partial y} \quad (17)$$

and, if $(\partial \ln y_a / \partial x)_y$ is neglected, whereby second-order errors only are introduced,

$$\frac{1}{RT} \frac{\partial \mu_{\text{DA}}}{\partial x} = \frac{\partial \ln (1 - x) f_{\text{DA}}}{\partial x} \quad (18)$$

and

$$\frac{1}{RT} \frac{\partial \mu_{\text{DA}}}{\partial y} = \left(\frac{\nu}{y_a} + \frac{\partial \ln f_{\text{DA}}}{\partial y_a} \right) \frac{dy_a}{dy} \quad (19)$$

The derivatives of the non-deuterated components are similar.

Expressions for the isotope separation effects

$$\beta_{\text{w}'} = \frac{y'' - y'}{y(1 - y)} \quad \text{and} \quad \beta_{\text{a}'} = \frac{y_a'' - y_a'}{y_a(1 - y_a)} \quad (20)$$

may now conveniently be obtained by combining the four equations represented by equation (9) as follows (written in terms of (1))

$$y''(d\mu_D' - d\mu_D'') + (1 - y'')(d\mu_H' - d\mu_H'') = 0 \quad (21)$$

and

$$y_a''(d\mu_{DA}' - d\mu_{DA}'') + (1 - y_a'')(d\mu_{HA}' - d\mu_{HA}'') = 0 \quad (22)$$

and introducing the relations obtained in equations (16)–(19).

The final expressions obtained may be written in the form:

$$\begin{aligned} \frac{\partial \ln x'f_W'}{\partial x} \left(\frac{dx'}{dy} \right)_{\text{eq.}} - \frac{\partial \ln x''f_W''}{\partial x} \left(\frac{dx''}{dy} \right)_{\text{eq.}} + 2\beta_w' + \frac{\partial \ln f_W'/f_W''}{\partial y} \\ = \left(\frac{dT}{dy} \right)_{\text{eq.}} \frac{\Delta H_W' - \Delta H_W''}{RT^2} \end{aligned} \quad (23)$$

and

$$\begin{aligned} \frac{\partial \ln (1 - x')f_A'}{\partial x} \left(\frac{dx'}{dy_a} \right)_{\text{eq.}} - \frac{\partial \ln (1 - x'')f_A''}{\partial x} \left(\frac{dx''}{dy_a} \right)_{\text{eq.}} + \nu\beta_a' + \frac{\partial \ln f_A'/f_A''}{\partial y_a} \\ = \left(\frac{dT}{dy_a} \right)_{\text{eq.}} \frac{\Delta H_A' - \Delta H_A''}{RT^2} \end{aligned} \quad (24)$$

where subscript W and A denote averages of the type

$$\frac{\partial \ln xf_W}{\partial z} = y \frac{\partial \ln xf_D}{\partial z} + (1 - y) \frac{\partial \ln xf_H}{\partial z}, \quad (z = y \text{ or } x) \quad (25)$$

$$\begin{aligned} \frac{\partial \ln (1 - x)f_A}{\partial z} = y_a \frac{\partial \ln (1 - x)f_{DA}}{\partial z} + (1 - y_a) \frac{\partial \ln (1 - x)f_{HA}}{\partial z} \\ (z = y_a \text{ or } x) \end{aligned} \quad (26)$$

assuming the isotope separation effects to be so small that differences between y' and y'' (or y_a' and y_a'') may be neglected when these expressions are inserted into equations (23) and (24). Superscripts over dy and dy_a may, for the same reason, be omitted. ΔH_W and ΔH_A are partial molar enthalpies of mixing.

2.3

In the numerical calculation of β_w and β_a either x' or T is kept constant. The similarity between solubility curves corresponding to differing isotope compositions, in the sense that any curve may be obtained simply by a vertical displacement of any other (see *Figures 1–3*), serves to show that

$$dx'' = 0 \text{ for } dx' = 0 \text{ and that } \left(\frac{dT}{dy} \right)_{\text{eq.}, x'} = \left(\frac{dT}{dy} \right)_{\text{eq.}, x''} \quad (27)$$

The linearity between displacement and isotope composition, as found by Patterson for the phenol² and n-butyric acid³ systems (see also ref. 1) shows in addition that

$$\frac{dT}{dy} \simeq \frac{dT}{dy_a} \simeq T_a - T_h \quad (28)$$

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where $T_d - T_h$ is the vertical distance between the solubility curves of the two binary systems, containing pure heavy and light water.

For the calculation of the enthalpy terms in equations (23) and (24,) data for the binary system without heavy water, which in many cases are available, are sufficiently accurate. In the same way the derivatives with

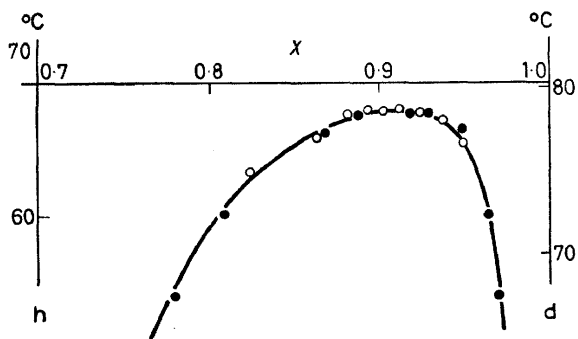


Figure 1. Mutual solubility of phenol and light water (●, left ordinate), and of deutero-phenol (C_6H_5OD) and heavy water (○, right ordinate) as function of temperature; $T_d - T_h = 12^\circ C$; x is mole fraction of water; data from ref. 2, corrected for chemical exchange

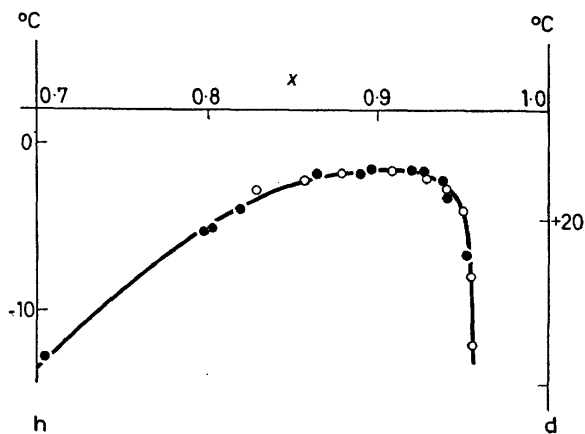


Figure 2. Mutual solubility of n-butyric acid and light water (●, left ordinate) and of deuterated n-butyric acid (C_3H_7COOD) and heavy water (○, right ordinate) as function of temperature; $T_d - T_h = 24\frac{1}{2}^\circ C$; x is mole fraction of water; data from ref. 3, corrected for chemical exchange

respect to water content, x , may be obtained from available vapour pressure data for the pure light water-organic component system, neglecting small differences due to the presence of deuterium compounds.

A determination of the contribution of the derivatives with respect to isotope composition still has to be made; great accuracy in this determination is not possible but a rough estimate may be obtained as will be shown in the following treatment.

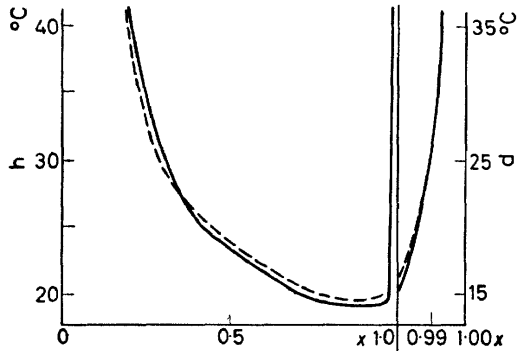


Figure 3. Mutual solubility, as function of temperature, of triethylamine and light water (full line, left ordinate) and of triethylamine and heavy water (broken line, right ordinate); $T_d - T_h = 5^\circ\text{C}$; x is mole fraction of water; data from refs. 1 and 4

2.4

The mixing of a solution of x moles of D_2O and $(1 - x)$ moles of deuterated organic component with a solution of x moles of H_2O and $(1 - x)$ moles of ordinary organic component in any proportion is a process which may be assumed to be ideal, that is to say (neglecting differences between y and y_a)

$$\frac{\partial}{\partial y} (x \ln f_D + (1 - x) \ln f_{DA}) = 0 \text{ and}$$

$$\frac{\partial}{\partial y} (x \ln f_H + (1 - x) \ln f_{HA}) = 0 \quad (29)$$

Each term within the parentheses may vary with y and this variation must be known or at least its order of magnitude estimated.

In systems without chemical exchange f_{DA} and f_{HA} refer to the same species and the following relation is obtained directly:

$$\frac{\partial \ln f_D}{\partial y} = \frac{\partial \ln f_H}{\partial y} = - \frac{1 - x}{x} \frac{\partial \ln f_A}{\partial y} \quad (30)$$

where $\partial \ln f_A / \partial y$ to a first approximation may be taken as $\ln(f_{Ad}/f_{Ah})$ i.e. the difference between $\ln f_A$ for the two binary systems containing pure heavy and pure light water, respectively; this difference manifests itself in the relative shape of the two corresponding solubility curves, as will be shown later (equation 37).

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In systems with chemical exchange there is no possibility of calculating the derivatives in question, they may be on the other hand considerably less important in this case, since for symmetry reasons it is probable that

$$y \frac{\partial \ln f_D}{\partial y} + (1 - y) \frac{\partial \ln f_H}{\partial y} \simeq 0 \text{ and}$$

$$y_a \frac{\partial \ln f_{DA}}{\partial y_a} + (1 - y_a) \frac{\partial \ln f_{HA}}{\partial y_a} \simeq 0 \quad (31)$$

or, to be more precise, the sums of the two terms (which also appear in equations 25 and 26) are small compared with $\ln f_{Da}/f_{Hh}$ and $\ln f_{DAa}/f_{HAh}$, respectively, where d and h, as above, refer to the binary systems. Since the order of magnitude of the latter terms, as mentioned above, may be estimated, the maximum contribution of $\partial \ln f/\partial y$ to the isotope separation effect may also be estimated.

The approximation introduced by (31) is justified only in cases where the interaction of one organic component molecule with another is determined to a large extent by the exchangeable hydrogen atom(s) but this will generally be the case since easily exchangeable hydrogen atoms are likely to exhibit extensive hydrogen-bonding.

2.5. An estimate of $\ln f_{Da}/f_{Hh}$; and $\ln f_{DAa}/f_{HAh}$

It has been pointed out by Kohler⁵ that the free energy of mixing, ΔG , of the binary systems (or for that matter of any of the intermediate systems in which y is kept constant) may be obtained from solubility curves and enthalpy data on the basis of equation (11) ($dy = 0$). In other words, for the present purpose, a comparison between data for the two binary systems may in principle lead to an estimate of the values of the terms in question.

Equation (11) may be written, when equations (25) and (26) and the Gibbs–Duhem equation are introduced, in the following form:

$$-\frac{x'' - x'}{x'} \frac{\partial \ln (1 - x')f_A'}{\partial x}$$

$$= \left(\frac{dT}{dx'}\right)_{e.q., y'} \frac{x''(\Delta H_{W'} - \Delta H_{W''}) + (1 - x'')(\Delta H_{A'} - \Delta H_{A''})}{RT^2} \quad (32)$$

where y may have any value but which in the present case is either zero or one. Introducing total instead of partial derivatives leads to

$$\left(\frac{d \ln (1 - x')f_A'}{dx'}\right)_{e.q., y'} = \frac{1}{RT^2} \left(\frac{dT}{dx'}\right)_{e.q., y'} \frac{x''\Delta H' - x'\Delta H''}{-(x'' - x')} \quad (33)$$

where ΔH is the integral enthalpy of mixing.

The critical composition of the two systems is not very different and according to equation (33) $d \ln (1 - x')f_A'/dx' = 0$ at the critical point. Hence at the same temperature

$$\frac{d}{dx'} \left(\ln \frac{f_{DAa}}{f_{HAh}} \right) = \frac{d}{dx'} \left(\frac{T_d - T_h}{RT^2} \Delta H_A \right) \quad (34)$$

where the following equation has been used: $\partial \ln f_A / \partial T = -\Delta H_A / RT^2$ and where $T_d - T_h$ is the temperature difference between corresponding points on the two solubility curves.

Away from the critical point, at smaller values of x' (assigning superscript ', for the moment, to the organic phase) where $|dT/dx'|$ increases, this expression is modified to:

$$\frac{d}{dx'} \left(\ln \frac{f_{DA d}}{f_{HA h}} \right) = \frac{d}{dx'} \left(\frac{T_d - T_h}{RT^2} \Delta H_A \right) + N \quad (36)$$

here, N is the difference between the right-hand side of equation (33) for the pure heavy water system and that for the pure light water system. There is no way of judging the relative importance of the terms in equation (36) at temperatures considerably removed from the critical temperature, because the difference $\Delta H_d - \Delta H_h$ (where d and h refer to the above two systems) which cannot be neglected here, is not known and $d(T_d - T_h)/dx'$ must be known with great accuracy in order that the contribution of N may be estimated. x'' and x' which also appear in (33), seem to be sufficiently independent of y' (see equation 27). It is, however, to be expected that $\ln f_{DA d}/f_{HA h}$, which is zero at $x = 0$ is steadily increasing with x , so that extrapolation of the term in equation (34) to $x = 0$ (where it should be zero) followed by integration should give:

$$\ln \frac{f_{DA d}}{f_{HA h}} \simeq \frac{T_d - T_h}{RT^2} \Delta H_A \quad (37)$$

near the solubility curve. Due to the generally low solubility of organic components in water, $\ln f_{D d}/f_{H h}$ in the organic phase may be obtained directly from equation (1) and, as is readily seen, the result

$$\ln \frac{f_{D d}}{f_{H h}} = \frac{T_d - T_h}{RT^2} \Delta H_W \quad (38)$$

is similar to equation (37), so that by analogy one might expect that this relation also has some experimental foundation.

The two relations together are, however, seen to imply that $\Delta G_d/T_d$ at T_d is identical to $\Delta G_h/T_h$ at T_h for which there appears to be no theoretical basis. Nevertheless, the above relation is thought to give some idea about the probable magnitude of the term in question.

3. FINAL EQUATIONS

On the basis of the foregoing discussion it is now possible to write down final equations which can be used directly for the calculation of the isotope separation effects.

3.1. x' (and x'') constant

Equations (23) and (24) read (on insertion of equations (27) and (28))

$$2\beta_w' + \frac{\partial \ln f_w' / f_w''}{\partial y} = \frac{T_d - T_h}{RT^2} (\Delta H_w' - \Delta H_w'') \quad (39)$$

and

$$v\beta_a' + \frac{\partial \ln f_a' / f_a''}{\partial y_a} = \frac{T_d - T_h}{RT^2} (\Delta H_a' - \Delta H_a'') \quad (40)$$

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3.1.1—In systems without chemical exchange $v\beta_{a'} = 0$. This condition in equation (40) gives a relationship between $\partial \ln f_{A'}/\partial y$ and $\partial \ln f_{A''}/\partial y$ which is seen not to be contradictory to equation (37) (see also equation 30).

It may be shown that combination of equations (40) and (39) (when $v\beta_{a'} = 0$) and introduction of the Gibbs–Duhem equation lead to

$$\beta_{w'} = \frac{y'' - y'}{y(1-y)} = \frac{T_d - T_h}{2RT^2} \left(\frac{\Delta H'}{x'} - \frac{\Delta H''}{x''} \right) \quad (41)$$

where ΔH is the integral enthalpy of mixing. This is a relation which may also be obtained directly from equation (11) (see ref. 1). A reasonable value for the probable error is thought to be ± 100 per cent of the postulated value of $(\partial \ln f_{w'}/f_{w''})/\partial y$ (as shown in Figure 4).

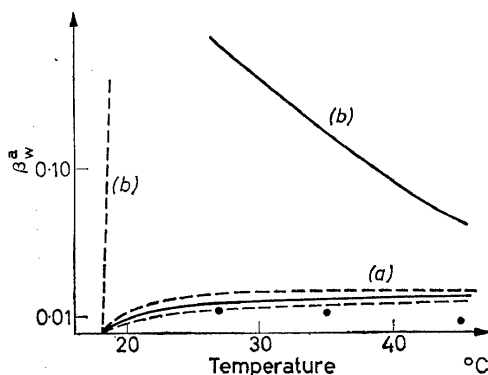


Figure 4 Curve (a): calculated isotope separation effect, β_w^a , in triethylamine/water system as function of temperature (see equations 41, 39, 45, 42); ● experimental β_w^a from ref. 1 Curve (b): ideal isotope effect according to equation (48); curves calculated on the basis of Figure 3 and enthalpy data from ref. 6 (checked by vapour pressure data from ref. 7)

3.1.2—For systems with chemical exchange, the two terms containing derivatives in equations (39) and (40) may be neglected in accordance with equation (31), so that the terms on the right side of the equations express directly the isotope effects times the statistical factor 2 or v .

The error introduced by neglecting $\partial \ln f_w/\partial y$ and $\partial \ln f_A/\partial y$ in equations (39) and (40) may be estimated by considering two limiting cases: (i) $\partial \ln f_A/\partial y = (T_d - T_h)\Delta H_A/RT^2$; hence, from equation (40) $\beta_a = 0$ and $\beta_{w'}$ is calculated according to equation (41). (ii) $\partial \ln f_w/\partial y = (T_d - T_h)\Delta H_w/RT^2$; hence, from equation (39) $\beta_w = 0$ and $\beta_{a'}$ is calculated according to an equation equivalent to equation (41). In Figures 5 and 6, 20 per cent of these deviations are (arbitrarily) shown as probable errors.

3.1.3—The results, as shown in Figures 4–6, indicate that the uncertainty is probably of about the same order of magnitude as the calculated effect, so that the expressions developed are useful in so far as they provide upper limits to the isotope separation effects to be expected. The experimental

evidence in the case of the triethylamine system (*Figure 4*) is in agreement with this conclusion; the agreement may be even better than shown since the discrepancy at higher temperature may well arise from experimental errors.

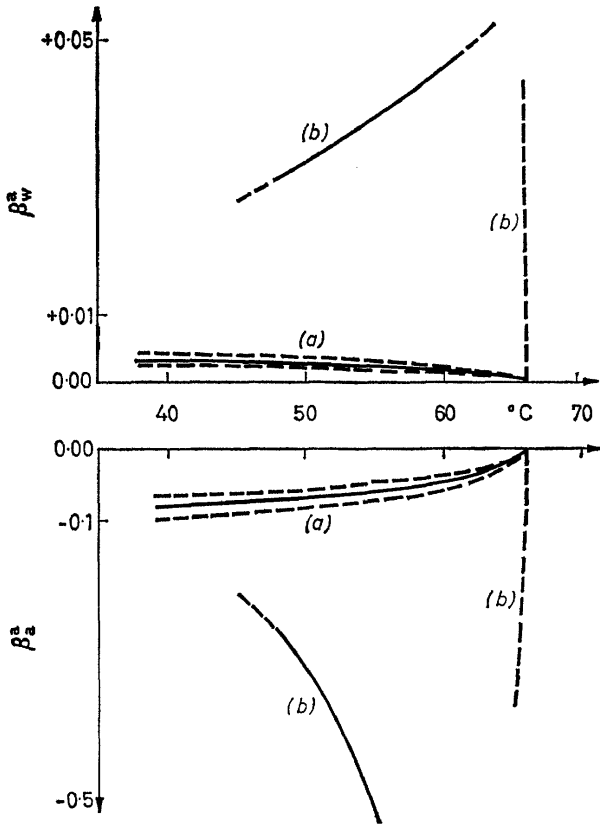


Figure 5 Curve (a): calculated isotope separation effect of water species (β_w^a) and phenol species (β_a^a) in phenol/water system as function of temperature (see equations 39, 40; 42, 43) Curve (b): ideal isotope effect according to equation (48); curves calculated on the basis of *Figure 1* and enthalpy data from ref. 8

3.2. *T* constant

Equations (23) and (24) read

$$2\beta_w' = -\left(\frac{d \ln x'f_w'}{dy}\right)_{\text{eq., } T} + \left(\frac{d \ln x''f_w''}{dy}\right)_{\text{eq., } T} \quad (42)$$

and

$$v\beta_a' = -\left(\frac{d \ln (1 - x')f_A'}{dy_a}\right)_{\text{eq., } T} + \left(\frac{d \ln (1 - x'')f_A''}{dy_a}\right)_{\text{eq., } T} \quad (43)$$

where *e.g.*

$$\frac{d \ln xf_w}{dy} = \frac{\partial \ln xf_w}{\partial x} \frac{dx}{dy} + \frac{\partial \ln f_w}{\partial y} \quad (44)$$

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3.2.1—In systems without chemical exchange $\beta_a = 0$. It may be shown (by introduction of the Gibbs–Duhem equation) that this condition leads to

$$\beta_{w'} = -\frac{x'' - x'}{2x''(1 - x')} \left(\frac{d \ln x' f_{w'}}{dy} \right)_{\text{eq., } T} \quad (45)$$

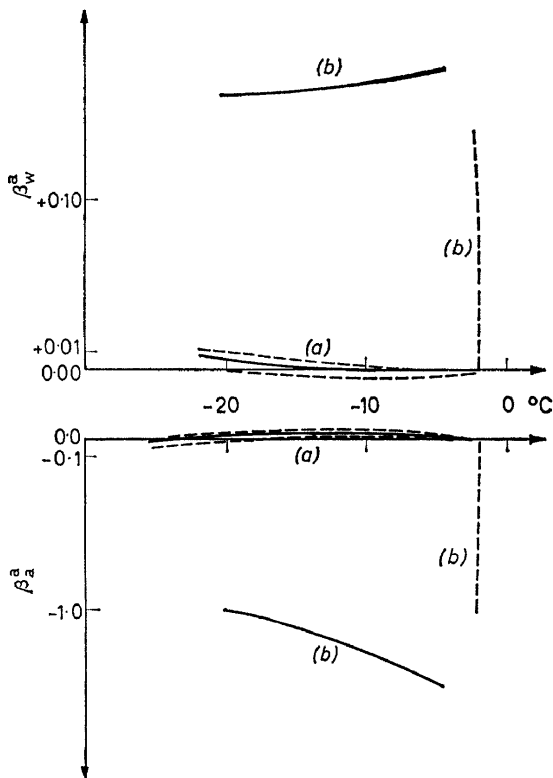


Figure 6 Curve (a): calculated isotope separation effect of water species (β_w^a) and n-butyric acid species (β_a^a) in n-butyric acid/water system as function of temperature (see equations 39, 40; 42, 43)

Curve (b): ideal isotope effect according to equation (48); curves calculated on the basis of Figure 2 and enthalpy data from ref. 9

It should be noted that these derivatives represent averages of derivatives and not derivatives of averages. This is important since the latter would be close to $\ln x_d' f_{Dd}' - \ln x_h' f_{Hh}'$ (where x_d/x_h is the solubility ratio) which is almost zero, while the former has an additional term, $-\ln f_D'/f_H'$.

In equation (45) the superscript ' should be taken to refer to the organic phase; the opposite choice would make the result emerge as a small difference between two rather large figures, since the value of $\ln f_{Ad}/f_{Ah}$ increases with x . In this connection, it should be noted, that when $\beta_a = 0$, both derivatives in equation (42) are negative although dx'/dy and dx''/dy are of opposite sign.

3.2.2—For systems with chemical exchange, equations (42) and (43) are directly applicable. $\partial \ln f/\partial y$ may be neglected in the calculation (see equation 44).

In this case, the two derivatives in *e.g.* equation (42) must be of opposite sign so that, in both systems studied, $\beta_w^a > 0$ at all temperatures. The *n*-butyric acid data (*Figure 6*) are not in agreement with this conclusion, because, as may be shown, the enthalpy data are inaccurate. A small displacement of a point of inflexion on the enthalpy curve towards greater values of x will rectify the error and at the same time give rise to isotope effects of about the same order of magnitude as that shown but of opposite sign.

4. COMPARISON WITH OTHER TWO-PHASE SYSTEMS

Far removed from the critical temperature the solubility of the organic component, $(1 - x^w)$ is usually small, so that from equations (45) and (42)

$$\beta_w^a = \frac{y^w - y^a}{y(1 - y)} = -\frac{1}{2} \left(\frac{d \ln f_w^a x^a}{dy^a} \right)_{\text{eq.}, T} \quad (46)$$

which is seen to be analogous to the Duhem–Margules equation relating the total vapour pressure of a binary solution of D_2O and H_2O to the difference in composition of the vapour and liquid phase.

Equation (39) (applied to systems with chemical exchange) is also simpler when $x^w \simeq 1$:

$$\beta_w^a = \frac{y^w - y^a}{y(1 - y)} = \frac{T_d - T_h}{2RT^2} \Delta H_w^a \quad (47)$$

The same result is obtained from equation (41) when x^a becomes so small that ΔH_w^a is the principal component of ΔH^a .

Equation (47), where ΔH_w^a corresponds to the heat of evaporation, is similar to the equation relating the boiling point difference of a binary mixture of D_2O and H_2O to the difference between vapour and liquid compositions.

5. DISCUSSION

Equation (47) represents the largest isotope effect that may be encountered in the system. As the critical solution temperature is approached the effect becomes proportional to the enthalpy difference between the two phases, so that it decreases and becomes zero at the critical temperature.

The behaviour of the different factors in equation (45) is not so simple, since dx'/dy is a function of y' . Neglecting $\partial \ln f_w'/\partial y$ in equation (45), the connection between the three factors of the remaining term may be elucidated by the use of equation (32). At the critical point, $x'' - x' = 0$ and $\partial \ln x'f_w'/\partial x = 0$, while $dx'/dy = \infty$; the product of these terms is zero. As one passes along the solubility curve, $|dT/dx'|$ increases so that $(x'' - x')\partial \ln x'f_w'/\partial x$ also shows an increase, amplified by changes in ΔH . At the same time dx'/dy rapidly decreases and the product, therefore, never

becomes very large. In other words, a solution near its critical solution temperature is very far from being ideal, so that on the one hand $\partial \ln x'f_w'/\partial x$ is considerably smaller than the ideal value, $1/x'$, and on the other hand a small difference between ΔG for the ordinary water and heavy water systems, although their general trend is very similar, will tend to produce a noticeable gap between otherwise similar solubility curves, which will again lead to large values of dx'/dy . It is also clear that a very flat solubility curve is an indication of a straight ΔG -curve, *i.e.* $\partial \ln f_w'x'/\partial x$ is very small in a large x -interval; this, on the other hand, will give rise to relatively large values of dx'/dy . In order to illustrate the importance of the deviation from ideality, curves are shown in *Figures 4-6* which are calculated from equations (42) and (43) on the assumption that all derivatives of activity coefficients are zero; hence

$${}^{''}2\beta_w = \ln \frac{x_d'x_h''}{x_h'x_d''} \quad \text{and} \quad {}^{''}\nu\beta_a = \ln \frac{(1-x_d')(1-x_h'')}{(1-x_h')(1-x_d'')} \quad (48)$$

It is clear from the figures that such effects bear little or no relation to experimental behaviour.

It will be noted that there may be a difference in the order of magnitude between the two isotope effects observed in a given system. The relationship between β_w and β_a may also be obtained directly from equations (13) and (15).

6. CONCLUSION

The three examples used here for calculation are typical of systems with critical solution temperatures: The triethylamine system has a lower critical solution temperature, so that $\Delta S < 0$ and $\Delta H = \Delta G + T\Delta S < 0$ has a large negative value. The phenol system has an upper critical solution temperature, so that $\Delta S > 0$. ΔS is greater than the statistical value and ΔH is fairly large and positive. The n-butyric acid system also has an upper critical solution temperature. ΔS is not much greater than the statistical value; the maximum value of ΔH is about the same as in the previous case.

All three systems show comparatively large displacements of the solubility curves with changing isotope composition, a fact which is undoubtedly a result of the important rôle played by hydrogen-bonding in all three mixtures. Since this type of interaction is more specific than ordinary van der Waals' forces, isotope substitution in such cases has a relatively large effect on the solution properties.

More $T_d - T_h$ data are available¹⁰, and heats of solution which may be used to calculate maximum effects according to equation (47) are tabulated for many systems. On the basis of such experimental evidence, it is possible to draw the conclusion that deuterium solution separation effects of the type treated here are often smaller than, and probably never exceed, the value of effects encountered in vapour-liquid systems. This also seems to be a very reasonable result since it is difficult to explain how the interaction between molecules in a liquid which is weak in comparison with a true chemical bond can be specific enough to create a large isotope separation effect.

List of special symbols*Subscripts*

- D and H: Refer to chemical species D₂O and H₂O
 DA and HA: Refer to chemical species D_vA and H_vA, *i.e.* deut. and ord. organic component
 i: Is any of the four
 W and A: Refer to averages with respect to D₂O–H₂O and D_vA–H_vA (equations 25 and 26)
 d and h: Refer to the two binary systems containing deuterocompounds and ordinary compounds
 eq. Denotes equilibrium

Superscripts

- ' and '': Distinguish the two phases at equilibrium
 a and w: Refer to organic phase and water phase
 v: Is number of rapidly exchanging hydrogen atoms in organic component
 x_D, x_H, x_{DA}, x_{HA}: Are mole fractions of components as "added" (6) *i.e.* with due regard to the equilibrium condition between them
 x: Is mole fraction of total water in a phase
 y: Is mole fraction of heavy water in total water
 y_a: Is mole fraction of deuterocompound in total organic component

$$\beta_w' = \frac{y'' - y'}{y(1 - y)} \quad \text{and} \quad \beta_w^a = \frac{y^w - y^a}{y(1 - y)}$$

: Are isotope separation effects
 (see equation 20)

$$\beta_a' = \frac{y_a'' - y_a'}{y_a(1 - y_a)} \quad \text{and} \quad \beta_a^a = \frac{y_a^w - y_a^a}{y_a(1 - y_a)}$$

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