

A Thermodynamic Study of the Ternary System, Triethylamine, Water and Heavy Water, with Special Reference to Isotope Separation Problems

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1. An experimental isotope separation and solubility study in the two-phase region of the system, water ($D_2O + H_2O$) — triethylamine (TEA) has been carried out.

Concentrations of D_2O and H_2O in TEA have been determined by their absorption at 4.0μ and 6.1μ , respectively.

2. Diethylamine and ethylamine as impurities in the triethylamine used, have been determined by quantitative paper chromatography using a modified Levy-procedure.

3. Fundamental thermodynamic equations pertinent to the calculation of hydrogen isotope separation effects in the system at equilibrium are developed.

4. The total water concentration, x_w , of a phase and the isotopic composition, y_D , of this water (both in mole fractions) are chosen as independent variables. It is presumed that changes in activity coefficients, f , when y_D is varied at constant x_w are small compared to changes when x_w is varied at constant y_D .

On this basis it is postulated that reasonable first-order or second-order approximate relations are obtained when it is assumed that $(\partial \ln f / \partial y_D)_{x_w, T} = 0$ or $(\partial \ln f / \partial y_D)_{x_w, T} = \text{a constant}$ (*i.e.* independent of y_D), respectively.

5. These relations are introduced into the fundamental equations and it is shown that in both cases a numerical calculation of the isotope separation effect can be carried through with reasonable accuracy, using available enthalpy data and/or vapour pressure data for pure H_2O -TEA together with two-phase equilibrium data for the binary systems, H_2O -TEA and D_2O -TEA.

The numerical calculation indicates that $\partial \ln f / \partial y_D$ is less than $0.01 \times (\partial \ln f / \partial x_w)$.

6. The relative solubility change of water in TEA, when H_2O is replaced by D_2O at constant temperature, $(d \ln x'_w / dy'_D)_{eq, T}$ multiplied by a factor, $Q = 1 + x'_w (\partial \ln f'_w / \partial x_w)$, expressing the degree of ideality in the triethylamine phase, is found to be a simple and convenient measure of the isotope separation effect.

It is shown that the large $d \ln x'_w / dy'_D$ found in this system and in other similar systems must be compensated to a great extent by a small Q , so the absence of any high isotope separation effect is easily understood.

The remarkably high difference between the solubility of ordinary water (H_2O) and heavy water (D_2O) in triethylamine (TEA) may seem at first glance to promise a high isotope separation effect when H_2O and D_2O are mixed. However, Carlson¹, using water enriched with a few percent D_2O , found hardly any effect, (for instance, at 35°C the separation factor was 1.004 ± 0.004) and Hahn and Street² working with 98 % D_2O found no effect at $15-25^\circ\text{C}$.

The high expectation probably is based on the often applicable assumption that the solubility of one component in another to a first approximation is independent of the addition of a third component, a condition which, however, is far from being fulfilled when the third component (*e.g.* heavy water), as is the case here, is soluble in both phases.

In order to corroborate these results an experimental study has been undertaken and the system has been given a theoretical treatment. The discussion below is based on elementary thermodynamic principles which, however, do not seem to have been applied to this particular problem before; therefore the solution may have some general interest.

Approximate chemical potential functions are developed and a numerical calculation of the separation effects based on available thermodynamic data is attempted. The resulting figures may furnish only the order of magnitude of the terms involved, however, this appears sufficient to illustrate their relative importance.

EXPERIMENTAL PART

The triethylamine was a Fluka p.a. quality dried for a short time with sodium and decanted.

The heavy water was a 99.8 % quality from which a 20 % D_2O standard solution was prepared.

Procedure. In equilibration tubes shaped as shown on Fig. 1, 3 ml of triethylamine were placed in the horizontal part together with varying amounts (from 0.2 to 1 ml) of H_2O , pure D_2O , or the 20 % mixture. The tubes were shaken in a thermostat (regulating to within 0.01°C). A mercury seal was placed on top of the ground joints.

The shaking was fairly slow and it was extended over night as a convenient routine step though of course much shorter periods would have been sufficient. In order to detect any slow exchange with TEA or impurities in it, even longer periods were used.

After equilibration the mixture, while in the thermostat, was transferred to the vertical section of the tube and the mercury poured off.

A 2 ml sample of the TEA phase was taken and, if necessary for the subsequent determination, diluted with dry TEA.

Then a sample (either $50 \mu\text{l}$ or $100 \mu\text{l}$) of the water phase was drawn with a constriction pipette (Carlsberg). It was noticed that even a few bubbles of expired air through the TEA phase, when passing it with the pipette were enough to produce a turbidity — undoubtedly a carbon dioxide effect. No measures were taken in order to reduce the amount of CO_2 present but as the equilibration procedure was always the same, the relative solubility was probably not affected, nor was the change of solubility with temperature.

The water phase samples were diluted with dry TEA (2–3 ml). In this way the D/H ratio in the two phases became directly comparable.

The concentrations were determined with a "Perkin Elmer 221" infrared spectrophotometer, " H_2O " at 6.1μ and " D_2O " at 4.0μ , in 0.125 mm CaF_2 -cells. 20 % D_2O for the equilibration was chosen because in this concentration region the ratio of the optical densities at the two wavelengths was near unity (approx. 1.2). An appropriate number of standards was always run simultaneously with the unknowns. It was found impossible to store standards in a satisfactory way, so fresh ones were always made up for each experiment.

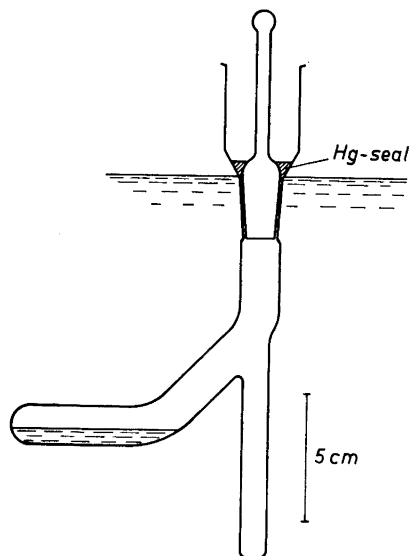


Fig. 1. Equilibration tube.

The varying amount of water phase revealed to what extent disturbing impurities accumulated in the water. The only other source of error that seemed likely to have any importance was a rapid exchange with an impurity in the TEA.

The supplier gave the information that it might contain some diethylamine (DEA) and ethanol. The actual amounts of DEA and, as it turned out, monoethylamine (MEA) present were determined by using a modified Levy procedure¹⁰, *i.e.* reaction with dinitrofluorobenzene and identification and estimation by chromatography on paper. A somewhat higher pH than Levy's was used in order to make the reaction conveniently fast. The DNP derivatives were extracted with ether after neutralizing the reaction mixture to pH 5–6. Dinitrophenol was removed from the ether phase with aqueous sodium hydroxide. A 0.1 M phosphate buffer in 50 % ethanol was used as solvent for the chromatographic development; however it is not claimed that the choice is ideal. Otherwise Levy's procedure was followed. The values obtained are believed to be accurate to within 10 % (see Table 1).

Alcohol in TEA was estimated by oxidation for two days with 0.1 N potassium dichromate in 4 N sulphuric acid at 40°C and determination of the excess of dichromate by reaction with iodide and titration of the iodine formed with thiosulphate. The value obtained is believed to be accurate to within 10 % (see Table 1).

TEA, dried for a short time, *i.e.* until bubbles ceased to be evolved, with sodium showed no decrease in alcohol content (tested at different alcohol concentrations) nor was there any detectable residue after evaporation in vacuum.

EXPERIMENTAL RESULTS

There is a slow chemical exchange between 20 % D₂O and TEA which leads to a small decrease in D₂O concentration. It amounts to about 1–2 % (relative) per day. It may be assumed therefore that, if the total amount of water present in an equilibration experiment is 3/2 times the water dissolved in the TEA phase the expected recovery will be approx. 99 %. In most experiments, however, the amount of water is much larger and therefore the correc-

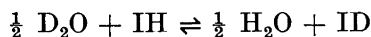
Table 1. Hydrogen exchanging impurities in the triethylamine used, as found by the analytical procedures described in the text.

	mequiv./mole TEA
Diethylamine	1.8
Ethylamine	1.5 (= 0.75 mmole/mole TEA)
Ethanol	1.3
Total	4.6 mequiv. exchangeable hydrogen per mole TEA.

tion much smaller. In agreement with this, the simple recovery average of 21 experiments, corrected for rapid exchange (see below) was 99.6 % (S.D. of the distribution 1 %). Equilibrium is probably attained in much less than one day, so in no case has a correction to the distribution ratio to be made.

Variation of the ratio of water phase to TEA phase had no effect on the optical density ratio of the water phase; therefore, no impurities affecting the spectrophotometric determination appear to accumulate in the water phase.

If a rapidly exchanging impurity is present it may react in the following manner



the equilibrium constant being

$$E = \frac{[\text{ID}] [\text{H}_2\text{O}]^{\frac{1}{2}}}{[\text{IH}] [\text{D}_2\text{O}]^{\frac{1}{2}}} \simeq 1$$

If $\text{ID} \equiv 2\varepsilon$ (in moles per mole TEA-phase) and $y_{\text{D}}/(1-y_{\text{D}}) \equiv r$, where y_{D} is mole fraction of D_2O , *i.e.* $y_{\text{D}} \simeq 0.20$ (see eqn. 8), then

$$\Delta r = \frac{W y_{\text{D}} - \varepsilon}{W(1-y_{\text{D}}) + \varepsilon} - \frac{W y_{\text{D}}}{W(1-y_{\text{D}})} \simeq - \frac{\varepsilon}{(1-y_{\text{D}})^2 W}$$

Here $(1-y_{\text{D}}) = \frac{4}{5}$ so $\Delta r = - \frac{25}{16} \frac{\varepsilon}{W}$. W is the number of moles of water (20 % D_2O) in equilibrium with, and contained in, one mole of TEA phase (and therefore approx. one mole of TEA). ε is independent of W as long as the amount of impurity is small compared to the amount of D_2O .

The r -values of the water phase samples need no correction for rapidly exchanging impurity, because the standards run simultaneously are treated in exactly the same manner — provided, as already mentioned, the impurities do not accumulate in the water phase and there interfere with the measurements.

The TEA phase r -values will be too high when compared to ordinary standards in which the D_2O concentration (y_{D}) has been somewhat reduced by the impurities. Relevant standards, which were prepared from TEA "deuterated" with 20 % D_2O and then dried, gave lower TEA phase r -values in agreement with the above; however, a comparison of the different standard curves obtained gave only fair agreement with theory even when this was elaborated to take into account corrections based on: (1) distribution factors

Table 2. Experimental results. 3 ml triethylamine were equilibrated with varying amounts of 20 % D_2O (i.e., $y_D = 0.20$). The isotopic composition of samples drawn from the water phase (and diluted with TEA) and from the TEA phase was determined spectrophotometrically at 6.1μ (${}^{\prime\prime}H_2O$) and 4.0μ (${}^{\prime\prime}D_2O$). For details see text.

T °C	Vol. of Water phase μl	Water in TEA phase μl	Isotope separation effect, $\frac{y_D'' - y_D'}{y_D''(1 - y_D')}$	
			uncorrected	corrected for rapid exchange (see Table 1)
27	100	200	+ 0.060	
	100	200	0.000	
	300	200	0.000	
	300	200	- 0.005	
	300	200	+ 0.005	
	800	200	+ 0.005	
	800	200	- 0.005	
	800	200	0.000	
		Average	+ 0.008	0.014
35	140	110	+ 0.025	
	140	110	- 0.005	
	390	110	- 0.003	
	390	110	- 0.010	
	890	110	- 0.007	
	890	110	+ 0.005	
			Average	+ 0.001
45	175	75	+ 0.010	
	175	75	- 0.010	
	425	75	- 0.005	
	425	75	- 0.010	
	925	75	- 0.020	
	925	75	- 0.020	
			Average	- 0.009

of the impurities, and (2) their absorptions at the two wavelengths. Deviations from Lambert-Beer's law, caused by shifts, with changing water concentration, in the peak wave-length at 6μ , were a further complication.

In addition the reduction in TEA r -values was greater than accounted for by chemical analysis and though the explanation may be a trace of water present, it was felt safer to base the TEA phase r -values on a correction calculated from known available exchangeable hydrogen (see Table 1).

Table 2 shows the results of the analytical determinations. The isotope effect, $[y_D'' - y_D']/[y_D'(1 - y_D'')]$, (see eqn. 9) has been calculated from the r -values of the TEA phase and the water phase, r' and r'' , respectively. One has $[y_D'' - y_D']/[y_D'(1 - y_D'')] = (r'' - r')/r$ where r with sufficient accuracy is $0.2/0.8 = 1/4$.

The correction for rapid exchange has been calculated as $-\frac{\Delta r}{r} =$
 $= 4 \cdot \frac{25}{16} \cdot \frac{1}{5} \cdot \frac{4.6}{2} \cdot \frac{10^{-3}}{W}$, where W (in moles per mole TEA) now is the

amount of water in the TEA phase sample (or rather in the corresponding standard).

The standard deviation of $[y_D'' - y_D']/[y_D'(1 - y_D'')]$ is estimated to be *ca.* 1–1.5 % (absolute) so the averaged values should be accurate to about 0.5 %. However, the presence of a small amount of water in the TEA employed, a possibility that cannot be excluded, may have introduced a systematic error of about the same magnitude. The solubility determinations are of course less accurate, the estimated standard deviation being 3 % (relative), and, as mentioned earlier, include a systematic error due to the presence of CO₂. The relative position of the two curves is thought to be relevant to the isotope effects found. The calculation is straight forward.

THEORETICAL PART

1. Equilibrium conditions, fundamental equations.

If μ_D' , μ_H' and μ_A' are the chemical potentials of D₂O, H₂O, and TEA in the TEA-rich phase and μ_D'' , μ_H'' and μ_A'' are the corresponding potentials in the water-rich phase, then

$$\begin{aligned}\mu_D' &= \mu_D'' \\ \mu_H' &= \mu_H'' \\ \mu_A' &= \mu_A''\end{aligned}\quad (1)$$

at equilibrium (denoted below by "eq"), or for any change in composition and temperature (and pressure)

$$d\mu' = d\mu'' \quad (2)$$

for any of the components. The three equations represented by eqn. 2 may be combined in the following way

$$x_D'' d\mu_D'' + x_H'' d\mu_H'' + x_A'' d\mu_A'' = x_D'' d\mu_D' + x_H'' d\mu_H' + x_A'' d\mu_A', \quad (3)$$

where x_D , x_H and x_A are mole fractions, *i.e.* the number of moles of *pure* component, D₂O, H₂O, and TEA, to be added in order to produce one mole of mixture: $x_D + x_H + x_A = 1$.

Changes in chemical potential may be written (at constant pressure)

$$d\mu = \left(\frac{\partial\mu}{\partial z_1}\right)_{T, z_2} dz_1 + \left(\frac{\partial\mu}{\partial T}\right)_{z_1, z_2} dT; \quad (dz_2 = 0) \quad (4)$$

where z_1 and z_2 are any two concentrations, sufficient for describing the composition of the system.

Gibbs-Duhem's equation,

$$x_D \left(\frac{\partial\mu_D}{\partial z_1}\right)_{T, z_2} + x_H \left(\frac{\partial\mu_H}{\partial z_1}\right)_{T, z_2} + x_A \left(\frac{\partial\mu_A}{\partial z_1}\right)_{T, z_2} = 0 \quad (5)$$

and eqn. 4 combined with eqn. 3 gives

$$\begin{aligned} & \left(x_D'' \frac{\partial \mu_D''}{\partial T} + x_H'' \frac{\partial \mu_H''}{\partial T} + x_A'' \frac{\partial \mu_A''}{\partial T} \right) dT = \\ & \left(x_D'' \frac{\partial \mu_D'}{\partial T} + x_H'' \frac{\partial \mu_H'}{\partial T} + x_A'' \frac{\partial \mu_A'}{\partial T} \right) dT + \left(x_D'' \frac{\partial \mu_D'}{\partial z_1} + x_H'' \frac{\partial \mu_H'}{\partial z_1} + x_A'' \frac{\partial \mu_A'}{\partial z_1} \right) dz_1 \end{aligned} \quad (6)$$

Eliminating $\partial \mu_A' / \partial z_1$ (Gibbs-Duhem, eqn. 5) * and introducing $\partial \mu / \partial T = -S$ (the partial molar entropy) give

$$\begin{aligned} & \left[\left(x_D'' - x_D' \frac{x_A''}{x_A'} \right) \frac{\partial \mu_D'}{\partial z_1} + \left(x_H'' - x_H' \frac{x_A''}{x_A'} \right) \frac{\partial \mu_H'}{\partial z_1} \right] \left(\frac{dz_1}{dT} \right)_{\text{eq}, z_1} = \\ & x_D'' (S_D' - S_D'') + x_H'' (S_H' - S_H'') + x_A'' (S_A' - S_A'') \end{aligned} \quad (7)$$

Two new variables, y_D and x_W , are now introduced, defined in the following way

$$\begin{aligned} y_D \cdot x_W & \equiv x_D \\ (1 - y_D) \cdot x_W & \equiv x_H \\ \text{i.e., } x_W + x_A & = 1 \end{aligned} \quad (8)$$

Thus the isotope separation factor, α , may be written

$$\alpha = \frac{y_D''}{1 - y_D''} \bigg/ \frac{y_D'}{1 - y_D'} = 1 + \frac{y_D'' - y_D'}{y_D' (1 - y_D'')} \quad (9)$$

The following two relations (cf. eqn. 7) may now be obtained

$$x_D'' - x_D' \frac{x_A''}{x_A'} = (y_D'' - y_D') x_W'' + y_D' \frac{x_W'' - x_W'}{1 - x_W'} \quad (10)$$

and

$$x_H'' - x_H' \frac{x_A''}{x_A'} = - (y_D'' - y_D') x_W'' + (1 - y_D') \frac{x_W'' - x_W'}{1 - x_W'} \quad (11)$$

The variables, z_1 and z_2 in eqn. 6 or 7 may represent y_D and x_W ; correspondingly eqn. 7 yields two equations

$$\begin{aligned} & \left[\frac{x_W'' - x_W'}{1 - x_W'} (y_D' (\partial \mu_D' / \partial x_W)_{T, y_D} + (1 - y_D') (\partial \mu_H' / \partial x_W)_{T, y_D}) + x_W'' (y_D'' - y_D') ((\partial \mu_D' / \partial x_W)_{T, y_D} \right. \\ & \left. - (\partial \mu_H' / \partial x_W)_{T, y_D}) \right] \\ & = (dT / dx_W')_{\text{eq}, y_D} [x_W'' (y_D'' (S_D' - S_D'') + (1 - y_D'') (S_H' - S_H'')) + (1 - x_W'') (S_A' - S_A'')] \end{aligned} \quad (12)$$

* When partial derivatives, as here, are supplied with dash, e.g. $\partial \mu' / \partial x_W$, it means $(\partial \mu / \partial x_W)_{T, y_D}$ at $x_W = x_W'$, $y_D = y_D'$ and $T = T_{\text{eq}}$ where $(x_W', y_D', T_{\text{eq}})$ is a point on the solubility surface.

and

$$\left[\frac{x''_w - x'_w}{1 - x'_w} (y'_D (\partial \mu'_D / \partial y_D)_{T, x_w} + (1 - y'_D) (\partial \mu'_H / \partial y_D)_{T, x_w}) + x''_w (y''_D - y'_D) ((\partial \mu'_D / \partial y_D)_{T, x_w} - (\partial \mu'_H / \partial y_D)_{T, x_w}) \right]$$

$$= (dT/dy'_D)_{\text{eq}, x_w} [x''_w (y''_D (S'_D - S''_D) + (1 - y''_D) (S'_H - S''_H)) + (1 - x''_w) (S'_A - S''_A)] \quad (13)$$

Introducing

$$(dT/dy'_D)_{\text{eq}, x_w} = -(dT/dx'_w)_{\text{eq}, y_D} (dx'_w/dy'_D)_{\text{eq}, T} \quad (14)$$

a third equation involving $(dx'_w/dy'_D)_{\text{eq}, T}$ is obtained by combining eqns. 12 and 13:

$$-\left[\frac{x''_w - x'_w}{1 - x'_w} (y'_D (\partial \mu'_D / \partial x_w)_{T, y_D} + (1 - y'_D) (\partial \mu'_H / \partial x_w)_{T, y_D}) + x''_w (y''_D - y'_D) ((\partial \mu'_D / \partial x_w)_{T, y_D} - (\partial \mu'_H / \partial x_w)_{T, y_D}) \right] (dx'_w/dy'_D)$$

$$= \left[\frac{x''_w - x'_w}{1 - x'_w} (y'_D (\partial \mu'_D / \partial y_D)_{T, x_w} + (1 - y'_D) (\partial \mu'_H / \partial y_D)_{T, x_w}) + x''_w (y''_D - y'_D) ((\partial \mu'_D / \partial y_D)_{T, x_w} - (\partial \mu'_H / \partial y_D)_{T, x_w}) \right] \quad (15)$$

ΔH , the partial molar enthalpy of mixing, may be substituted for S , the partial molar entropy, in the following way:

$$\Delta H - T(S - S_0) = \mu - \mu_0 \text{ and } \mu' - \mu_0 = \mu'' - \mu_0 \text{ so}$$

$$S'_D - S''_D = S'_D - S_{D0} - (S''_D - S_{D0}) = (\Delta H'_D - \Delta H''_D)/T, \text{ etc.} \quad (16)$$

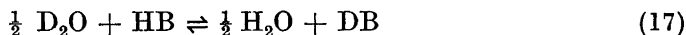
where subscript 0 refers to the pure state.

Eqn. 13 or 15 may form the basis for a calculation of $y''_D - y'_D$ and thereby the isotope separation effect, $[y''_D - y'_D]/[y'_D(1 - y''_D)]$ (while the term in eqn. 12 containing $(y''_D - y'_D)$ is of second order only).

2. Approximations

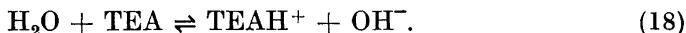
2. 1. *Basic considerations.* Eqns. 12, 13 and 15 are valid regardless of the number of chemical species, due to reactions between the three components, that may be present in the two phases as long, as full equilibrium has been reached. It should be noted, however, that the formulation of approximate chemical potential functions is simplified when information about the presence or non-presence of chemical species, can be introduced. In general three types of reactions leading to the formation of new chemical species should be considered:

1) Equilibrium isotope exchange with the organic component according to the following reaction scheme

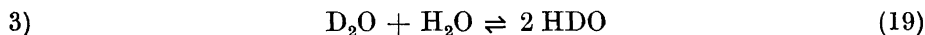


where HB is added organic component and DB is the same deuterated. TEA exchanges slowly, if at all, with D_2O . The following theoretical considerations are valid only when this kind of reaction can be neglected.

2) Reaction with the organic component of the following type:



Such reaction products may be present in the $\text{D}_2\text{O}-\text{H}_2\text{O}-\text{TEA}$ system. No accurate information is available and is, in fact, thought to be unnecessary for the following description of the system (where the parameters $[\text{D}_2\text{O}]$ and $[\text{H}_2\text{O}]$ include both ions and neutral molecules, and any isotope effects in the reactions are disregarded.) See below (p. 1742) for further comments.



This reaction takes place to a degree determined by

$$\frac{f_{\text{HDO}}^2 [\text{HDO}]^2}{f_{\text{H}} f_{\text{D}} [\text{H}_2\text{O}] [\text{D}_2\text{O}]} = K^* \text{ where } K^* \simeq 4 \quad (20)$$

and f_{D} , f_{H} and f_{HDO} are the activity coefficients of D_2O , H_2O , and HDO , respectively.

By taking into account that $K \equiv \frac{1}{4} \cdot \frac{f_{\text{H}} f_{\text{D}}}{f_{\text{HDO}}} K^*$ is near one (see below) and introducing the two conditions that

$$[\text{D}_2\text{O}] + [\text{H}_2\text{O}] + [\text{HDO}] = x_{\text{W}} \quad (21a)$$

$$\text{and} \quad [\text{D}_2\text{O}] + \frac{1}{2} [\text{HDO}] = y_{\text{D}} x_{\text{W}} \quad (21b)$$

one obtains the following three equations

$$\begin{aligned} [\text{D}_2\text{O}] &= (1 + a) y_{\text{D}}^2 x_{\text{W}} \\ [\text{H}_2\text{O}] &= (1 + b) (1 - y_{\text{D}})^2 x_{\text{W}} \\ [\text{HDO}] &= 2(1 + c) y_{\text{D}} (1 - y_{\text{D}}) x_{\text{W}} \end{aligned} \quad (22)$$

Here a , b and c are small compared to one, so the approximation may be made that

$$K = \frac{(1 + c)^2}{(1 + a)(1 + b)} \simeq 1 + 2c - a - b$$

then a , b , and c can be expressed in the following way

$$\begin{aligned} a &= - (K - 1) (1 - y_{\text{D}})^2 \\ b &= - (K - 1) y_{\text{D}}^2 \\ c &= (K - 1) y_{\text{D}} (1 - y_{\text{D}}) \end{aligned} \quad (23)$$

In pure $\text{D}_2\text{O}-\text{H}_2\text{O}$ mixtures $K = 0.83$ (Ref.³) and the same must be approximately the case in the TEA-water mixture, since f_{DHO} must be near $\sqrt{f_{\text{D}} f_{\text{H}}}$.

2.2. *First approximation.* The change in chemical potential with composition may be written

$$\left(\frac{\partial\mu_D}{\partial z_1}\right)_{T,z_2} = RT\left(\frac{\partial\ln[D_2O]}{\partial z_1}\right)_{T,z_2} + RT\left(\frac{\partial\ln f_D}{\partial z_1}\right)_{T,z_2} \quad (24)$$

and similarly for μ_H and μ_A . The three partial derivatives, $(\partial\ln f/\partial y_D)_{T,x_W}$, result from changes in the medium (triethylamine phase) when D_2O is substituted for H_2O at constant water content (x_W); while the three partial derivatives, $(\partial\ln f/\partial x_W)_{T,y_D}$ result from changes in the medium when the water content is increased at constant y_D , the isotopic composition. $|\partial\ln f/\partial y_D|$ must obviously be considerably smaller than the corresponding $|\partial\ln f/\partial x_W|$, so it would seem to be a justifiable first approximation to assume that

$$\partial\ln f/\partial y_D = 0 \quad (25)$$

This has the following implications:

1) K (eqn. 23) will be independent of y_D .

$$2) \text{ (eqn. 22): } \left(\frac{\partial\mu_D}{\partial y_D}\right)_{T,x_W} = RT\left(\frac{\partial\ln[D_2O]}{\partial y_D}\right)_{T,x_W} = \frac{2RT}{y_D} + RT\left(\frac{\partial\ln(1+a)}{\partial y_D}\right)_{T,x_W}$$

$$\left(\frac{\partial\mu_H}{\partial y_D}\right)_{T,x_W} = RT\left(\frac{\partial\ln[H_2O]}{\partial y_D}\right)_{T,x_W} = -\frac{2RT}{1-y_D} + RT\left(\frac{\partial\ln(1+b)}{\partial y_D}\right)_{T,x_W} \quad (26)$$

$$\text{Here } \frac{\partial\ln(1+a)}{\partial y_D} = (K-1)2(1-y_D) \text{ and } \frac{\partial\ln(1+b)}{\partial y_D} = -(K-1)2 y_D \quad (27)$$

These two derivatives are fairly small correction terms, so

$$y_D \frac{\partial\mu_D}{\partial y_D} + (1-y_D) \frac{\partial\mu_D}{\partial y_D} = 0 \text{ and} \quad (28)$$

$$\frac{\partial\mu_D}{\partial y_D} - \frac{\partial\mu_H}{\partial y_D} = \frac{2RT}{y_D} + \frac{2RT}{1-y_D} + 2RT(K-1) \simeq \frac{2RT}{y_D(1-y_D)} \quad (29)$$

Neglecting $K-1$ probably causes only a 5 % error at maximum, at $y_D = \frac{1}{2}$.

3) From $\partial\ln f_A/\partial y_D = 0$ at any x_W and the Gibbs-Duhem equation applied to pure H_2O -TEA and D_2O -TEA mixtures as follows:

$$x_W \frac{\partial\ln f_{Hh}}{\partial x_W} + (1-x_W) \frac{\partial\ln f_{Ah}}{\partial x_W} = 0$$

and (30)

$$x_W \frac{\partial\ln f_{Dd}}{\partial x_W} + (1-x_W) \frac{\partial\ln f_{Ad}}{\partial x_W} = 0$$

it follows that

$$\frac{\partial\mu_D}{\partial x_W} = \frac{\partial\mu_H}{\partial x_W} \equiv \frac{\partial\mu_W}{\partial x_W} \text{ at any } y_D \quad (31)$$

and

$$y_D \frac{\partial\mu_D}{\partial x_W} + (1-y_D) \frac{\partial\mu_H}{\partial x_W} = \frac{\partial\mu_W}{\partial x_W} \quad (32)$$

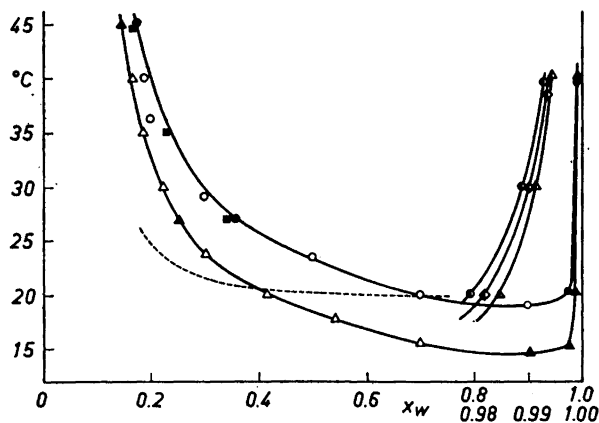


Fig. 2. Solubility curves for mixtures of triethylamine, water and heavy water. x_w is mole fraction of water ($D_2O + H_2O$). The water phase data have been determined by titration.

y_D	Own data main x_w -scale	enlarged x_w -scale	Hahn and Street's data ² (main x_w -scale)
0	●	◐	○
0.20	■	◑	
0.50	◆	◒	
1.00	▲	◓	△

The dashed curve corresponds to the data of Rothmund⁹ ($y_D = 0$).

4) With sufficient accuracy it may be assumed that

$$\Delta H_D = \Delta H_H \equiv \Delta H_W \quad (33)$$

These approximations do not imply that there is no difference between f_D and f_H — the activity coefficients of D_2O and H_2O compared at equal x_w — but do imply that the activities or vapour pressures of D_2O and H_2O at any x_w are proportional to $[D_2O]$ and $[H_2O]$, respectively, and that the activity or vapour pressure of TEA at any x_w is independent of y_D . If the latter statement is true for the triethylamine phase it cannot be simultaneously true for the water phase, since the solubility curves (Fig. 2) do not intersect.

2.3. *Second approximations.* The approximate potential functions developed above give simple and useful equations when applied to the fundamental equilibrium conditions (eqns. 12, 13 and 15); it is, however, of interest to estimate the magnitude of the error introduced by neglecting the derivatives $\partial \ln f / \partial y_D$. The data available make in fact this possible if the assumption is made that all three derivatives are constants in the interval $0 \leq y_D \leq 1$. This immediately necessitates (the Gibbs-Duhem eqn. 5) that

$$\frac{\partial \ln f_D}{\partial y_D} = \frac{\partial \ln f_H}{\partial y_D} \left(= - \frac{1-x_w}{x_w} \frac{\partial \ln f_A}{\partial y_D} \right) \equiv M \quad (34)$$

Therefore

$$\ln f_D - \ln f_{Dd} = -M(1 - y_D)$$

and $\ln f_H - \ln f_{Hh} = My_D$ (35)

so $\left(\frac{\partial \ln f_D}{\partial x_W}\right)_{T, y_D} = \left(\frac{\partial \ln f_{Dd}}{\partial x_W}\right)_T - (1 - y_D) \left(\frac{\partial M}{\partial x_W}\right)_T$ (36)

and $\left(\frac{\partial \ln f_H}{\partial x_W}\right)_{T, y_D} = \left(\frac{\partial \ln f_{Hh}}{\partial x_W}\right)_T + y_D \left(\frac{\partial M}{\partial x_W}\right)_T$

where d and h refers to pure D₂O- and H₂O-triethylamine systems, respectively. Differentiating eqn. 34 gives

$$\frac{\partial M}{\partial x_W} = -\frac{1 - x_W}{x_W} \frac{\partial}{\partial x_W} \left(\frac{\partial \ln f_A}{\partial y_D}\right) + \frac{1}{x_W^2} \frac{\partial \ln f_A}{\partial y_D}$$
 (37)

The following relations may now be derived:

1) Eqn. 34, with the reasonable assumption that also $\partial \ln f_{DHO} / \partial y_D = M$, shows that K of eqn. 23 under these conditions also becomes independent of y_D .

2) From eqns. 34 (cf. eqns. 28 and 29) the following results are obtained:

$$\begin{aligned} y_D \frac{\partial \mu_D}{\partial y_D} + (1 - y_D) \frac{\partial \mu_H}{\partial y_D} &= RTM = -RT \frac{1 - x_W}{x_W} \frac{\partial \ln f_A}{\partial y_D} \\ &= -RT \frac{1 - x_W}{x_W} \left(\ln \frac{f_{Ad}}{f_{Ah}}\right)_{x_W} \end{aligned}$$
 (38)

and $\frac{\partial \mu_D}{\partial y_D} - \frac{\partial \mu_H}{\partial y_D} \simeq \frac{2RT}{y_D(1 - y_D)}$ (39)

3) From eqns. 36 and 37 it follows that

$$\frac{\partial \ln f_D}{\partial x_W} - \frac{\partial \ln f_H}{\partial x_W} = \frac{\partial \ln(f_{Dd}/f_{Hh})}{\partial x_W} + \frac{1 - x_W}{x_W} \frac{\partial}{\partial x_W} \left(\frac{\partial \ln f_A}{\partial y_D}\right) - \frac{1}{x_W^2} \frac{\partial \ln f_A}{\partial y_D}$$

and introducing eqn. 30 gives

$$\frac{\partial \mu_D}{\partial x_W} - \frac{\partial \mu_H}{\partial x_W} = -\frac{RT}{x_W^2} \left(\ln \frac{f_{Ad}}{f_{Ah}}\right)_{x_W}$$
 (40)

Eqn. 36 yields

$$y_D \frac{\partial \mu_D}{\partial x_W} + (1 - y_D) \frac{\partial \mu_H}{\partial x_W} = y_D \frac{\partial \mu_{Dd}}{\partial x_W} + (1 - y_D) \frac{\partial \mu_{Hh}}{\partial x_W}$$
 (41)

4) Differentiation of eqn. 34 with respect to temperature and introduction of

$$\frac{\partial \ln f}{\partial T} = -\frac{\Delta H}{RT^2}$$
 (42)

(where ΔH is the partial molar enthalpy of mixing) gives

$$-\frac{\partial \Delta H_D}{\partial y_D} = -\frac{\partial \Delta H_H}{\partial y_D} = \frac{1-x_w}{x_w} \frac{\partial \Delta H_A}{\partial y_D} = RT^2 \frac{\partial M}{\partial T} \quad (43)$$

$$\text{So } -\Delta H_D + \Delta H_{Dd} = -RT^2 \frac{\partial M}{\partial T} (1-y_D) \quad (44)$$

$$\text{and } -\Delta H_H + H_{Hh} = RT^2 \frac{\partial M}{\partial T} y_D$$

$$\text{By subtraction } (\Delta H_D - \Delta H_H) - (\Delta H_{Dd} - \Delta H_{Hh}) = RT^2 \frac{\partial M}{\partial T} \quad (45)$$

$$\text{while } y_D \Delta H_D + (1-y_D) \Delta H_H = y_D \Delta H_{Dd} + (1-y_D) \Delta H_{Hh} \quad (46)$$

The preceding systems of equations are based on the assumption that ideal conditions or conditions approaching the ideal are maintained when, in TEA-water mixtures, D_2O is interchanged with H_2O , the total amount of water (x_w) being held constant. It is, however, possible, as mentioned earlier, that reactions of the following type take place: $TEA + H_2O \rightleftharpoons TEAH^+ + OH^-$. The extent to which TEA reacts with H_2O is probably not exactly the same as with D_2O . The ratio of the amounts of the two types of chemical species could have marked influence on the medium, so one could expect that a different parameter in place of x_w might be required. Infrared tests for the presence of NH^+ — and ND^+ —bonds showed that not more and probably much less than 10 % of the water in the TEA-phase is in the ionized form. An approximate calculation shows that the presence of ions in that concentration probably has so little effect that it is taken into account in a satisfactory manner by the introduction of the second set of approximations (eqn. 34). A comparatively successful determination of $\ln(f_{Ad}/f_{Ah})$ which is discussed below points in the same direction.

3. Application of the approximations to the equilibrium equations.

3.1. *First approximations.* Introducing the simple first approximations represented by eqns. 28, 29, 31, and 32 into eqns. 12, 13, and 15 gives

$$\left(\frac{\partial \mu'_w}{\partial x_w}\right)_{T, y_D} \left(\frac{dx'_w}{dT}\right)_{\text{eq}, y'_D} = \frac{\Delta H'_w}{T} \quad (47)$$

$$2RT \frac{y''_D - y'_D}{y'_D(1-y'_D)} \left(\frac{dy'_D}{dT}\right)_{\text{eq}, x'_w} = \frac{\Delta H'_w}{T} \quad (48)$$

$$\left(\frac{\partial \mu'_w}{\partial x_w}\right)_{T, y_D} \left(\frac{dx'_w}{dy'_D}\right)_{\text{eq}, T} = -2RT \frac{y''_D - y'_D}{y'_D(1-y'_D)} \quad (49)$$

where x''_w has been set equal to one, $\Delta H''_w$ equal to zero and where $(1-x''_w)(\Delta H'_A - \Delta H''_A) \ll \Delta H'_w$ is neglected (see Fig. 2).

The isotope separation effect, $[y''_D(1-y'_D)/y'_D(1-y''_D)] - 1$, for all practical purposes equal to $(y''_D - y'_D)/y'_D(1-y'_D)$, may now be calculated from either eqn. 48 or 49 using available data for the partial vapour pressure of H_2O in

TEA—H₂O mixtures and available determinations of the heat of mixing of TEA and H₂O, together with the solubility curves.

Eqn. 49 is analogous to the Duhem-Margules equation (in one of its forms) for a binary liquid mixture (e.g. D₂O and H₂O) in equilibrium with its vapour: in fact, substituting in eqns. 3 to 5 $x_A d\mu_A$ for $v \cdot dp$ (where v is the molar volume of the gaseous mixture and p the total pressure) and choosing as independent variables y_D (the composition of the vapour) (or x_D , since $x_W = 1$) and p , one arrives at three equations analogous to eqns. 47 to 49.

$$RT \left(\frac{d \ln p}{dT} \right)_{\text{eq}, y} = y_D'' (S_D' - S_D'') + (1 - y_D'') (S_H' - S_H'') \quad (50)$$

$$2RT \frac{y_D'' - y_D'}{y_D' (1 - y_D')} \left(\frac{dy_D'}{dT} \right)_{\text{eq}, p} = y_D'' (S_D' - S_D'') + (1 - y_D'') (S_H' - S_H'') \quad (51)$$

and the Duhem-Margules equation:

$$RT \left(\frac{d \ln p}{dy_D'} \right)_{\text{eq}, T} = - 2RT \frac{y_D'' - y_D'}{y_D' (1 - y_D')} \quad (52)$$

Eqn. 50 is the equation for the vapour pressure curve.

From eqn. 51 the separation effect may be calculated when the heat of evaporation (and, if necessary, of solution) and the boiling point as a function of vapour composition are known.

Eqn. 52 relates the relative volatility of the pure components to the separation effects. If, in eqn. 49, $\partial \mu_W' / \partial x_W$ is set equal to RT/x_W' , eqns. 49 and 52 become identical in form. It will be shown below that this assumption is not at all permissible; however, eqn. 49, simplified in this manner, is of interest because it may have formed the basis for optimistic estimations of the isotope separation potentialities of this system and other similar systems.

3.2. *Second approximations.* Introducing the second approximation represented by eqns. 38, 39, 40, and 41 into eqns. 12, 13, and 15 gives: (eqn. 12)

$$\frac{x_W'' - x_W'}{1 - x_W'} \left(y_D' \frac{\partial \mu_{Dd}}{\partial x_W} + (1 - y_D') \frac{\partial \mu_{Hh}}{\partial x_W} \right) - x_W'' \frac{(y_D'' - y_D')}{x_W'^2} RT \left(\ln \frac{f_{Ad}}{f_{Ah}} \right)_{x_W'} = \quad (53)$$

$$\left(\frac{dT}{dx_W'} \right)_{\text{eq}, y_D'} \left[x_W \left(y_D'' \frac{\Delta H_{D'}' - \Delta H_{D}''}{T} + (1 - y_D'') \frac{\Delta H_{H'}' - \Delta H_{H}''}{T} \right) + (1 - x_W'') \frac{\Delta H_{A'}' - \Delta H_{A}''}{T} \right]$$

(eqn. 13)

$$- \frac{x_W'' - x_W'}{x_W'} \left(\ln \frac{f_{Ad}}{f_{Ah}} \right)_{x_W'} RT + 2RT \frac{x_W'' (y_D'' - y_D')}{y_D' (1 - y_D')} = \quad (54)$$

$$\left(\frac{dT}{dy_D'} \right)_{\text{eq}, x_W'} \left[x_W'' \left(y_D'' \frac{\Delta H_{D'}' - \Delta H_{D}''}{T} + (1 - y_D'') \frac{\Delta H_{H'}' - \Delta H_{H}''}{T} \right) + (1 - x_W'') \frac{\Delta H_{A'}' - \Delta H_{A}''}{T} \right]$$

(eqn. 15)

$$\left[\frac{x''_w - x'_w}{1 - x'_w} \left(y'_D \frac{\partial \mu_{Dd}}{\partial x_w} + (1 - y'_D) \frac{\partial \mu_{Hh}}{\partial x_w} \right) - \frac{x''_w (y''_D - y'_D)}{x'^2_w} RT \left(\ln \frac{f_{Ad}}{f_{Ah}} \right)_{x'_w} \right] \times$$

$$\times \left(\frac{dx'_w}{dy'_D} \right)_{\text{eq}, T} = \frac{x''_w - x'_w}{x'_w} \left(\ln \frac{f_{Ad}}{f_{Ah}} \right)_{x_w} RT - 2RT \frac{x''_w (y''_D - y'_D)}{y'_D (1 - y'_D)} \quad (55)$$

(It should be noted that $(\partial \mu_{Dd} / \partial x_w)_{x_w = x'_w}$ and $(\ln f_{Ad})_{x'_w}$ apply to the unstable region, because $x'_w > x'_{w,d}$ (the solubility of D_2O .)

The terms that distinguish eqns. 53–55 from eqns. 47–49 contain $\ln(f_{Ad}/f_{Ah})$. When therefore an estimate of this quantity has been made, it will be possible to calculate the separation effect by eqn. 54 or 55. The difference between $\partial \mu_{Dd} / \partial x_w$ and $\partial \mu_{Hh} / \partial x_w$ and between ΔH_D and ΔH_H may be neglected, at least at low y_D .

3.3. $\ln(f_{Ad}/f_{Ah})$ could be easily calculated, if the vapour pressure curve of pure D_2O –TEA mixtures were known. Failing this the same information may in principle be obtained from the solubility curves (Kohler⁴); however the accuracy of this approach is limited so that the following treatment may furnish only the order of magnitude of $\ln(f_{Ad}/f_{Ah})$.

3.3.1. First an expression for $(\ln(f_{Dd}/f_{Hh}))_{x_w}$ is to be found:

Corresponding to eqn. 1 the following two equations may be written, inserting eqn. 22,

$$\text{for } \mu_D \quad \text{at } T = T_D, x_w = x'_w \text{ and } y'_D = 1:$$

$$\ln x'_w + \ln f'_{Dd} = \ln x''_{w,D} + \ln f''_{Dd} \quad (56)$$

$$\text{for } \mu_H \quad \text{at } T = T_H, x_w = x'_w \text{ and } y'_D = 0:$$

$$\ln x'_w + \ln f'_{Hh} = \ln x''_{w,H} + \ln f''_{Hh} \quad (57)$$

where x'_{w,T_D} and x''_{w,D,T_D} are corresponding points on the D_2O –TEA solubility curve and x'_{w,T_H} and x''_{w,H,T_H} are corresponding points on the H_2O –TEA curve.

By subtraction and introduction of eqn. 42 (integrated)

$$\left(\ln \frac{f'_{Dd}}{f'_{Hh}} \right)_{T=T_D} = \frac{T_D - T_H}{RT_D T_H} \Delta H'_{Hh} + \ln \frac{x''_{w,D}}{x''_{w,H}} + (\ln f''_{Dd})_{T=T_D} - (\ln f''_{Hh})_{T=T_H} \quad (58)$$

The vapour pressure data available show that $\ln f''_{Hh} \simeq 0.01$ and it is unlikely that $\ln f''_{Dd}$ is very much different.

Solubility experiments (see Fig. 2) show that

$$\ln \frac{x''_{w,D}}{x''_{w,H}} \simeq \ln 0.999 = -10^{-3}.$$

Enthalpy data and solubility data (see Table 3 and Fig. 2) show that

$$\frac{T_D - T_H}{RT_D T_H} \Delta H'_{Hh} \simeq 0.03$$

so eqn. 58 may be reduced to

$$\left(\ln \frac{f'_{Dd}}{f'_{Hh}} \right)_{T=T_D} = \frac{T_D - T_H}{RT_D T_H} \Delta H'_{Hh} \quad (59)$$

From eqn. 42 it follows that at any temperature, at constant x_w

$$\left(\ln \frac{f_{Dd}}{f_{Hh}} \right)_{x_w, T} = - \frac{T - T_D}{RT_D T_D} \left[\Delta H_{Dd} - \Delta H_{Hh} \right] + \frac{T_D - T_H}{RT_D T_H} \Delta H_{Hh} \quad (60)$$

which is reduced to eqn. 59 as long as

$$|(T - T_D)(\Delta H_{Dd} - \Delta H_{Hh})| \ll |(T_D - T_H)\Delta H_{Hh}| \quad (61)$$

This is probably valid in the interval covered by the known parts of the solubility curves. ΔH has been assumed independent of T .

From the reduced form of eqn. 60 it is seen that

$$\frac{\partial \ln(f_{Dd}/f_{Hh})}{\partial x_w} = \frac{d}{dx_w} \left(\frac{T_D - T_H}{RT_D T_H} \Delta H_{Hh} \right) \quad (62)$$

This relationship probably holds even near the critical compositions ($x_{cr, D}$ may be somewhat different from $x_{cr, H}$) as may be seen in the following way:

$\left(\frac{dT_D}{dx'_w} \right)_{eq, y'_D=1}$ and $\left(\frac{dT_H}{dx'_w} \right)_{eq, y'_D=0}$ (subscripts D and H refers to the solubility curves for pure D_2O and H_2O , respectively) are zero at, and very small in an interval around, the critical points. In eqn. 53 the enthalpy terms are proportional to $(x'_w - x_w)^2$ near the critical composition as expansion of these terms by Taylor's Series will show so, at $x_w \simeq x_{cr}$,

$$\left(\frac{\partial \mu'_{Dd}}{\partial x_w} \right)_{T_D} \simeq \left(\frac{\partial \mu'_{Hh}}{\partial x_w} \right)_{T_H} \simeq 0 \quad (63)$$

this leads to eqn. 62 (cf. eqn. 42) noting that

$$\frac{d}{dx_w} \left(\frac{T_D - T_H}{RT_D T_H} \right) \simeq \frac{1}{RT_D T_H} \left(\frac{dT_D}{dx_w} - \frac{dT_H}{dx_w} \right) \simeq 0 \quad (64)$$

Incidentally, a comparison of eqns. 63 and 31 shows the limited applicability of the simple approximations, represented by eqn. 25 near the critical points.

3.3.2. Since $f_{Ad} = f_{Ah} = 1$ for $x_w = 0$ (as has been tacitly assumed above) an integration of eqn. 30 at temp. T between 0 and x'_w yields

$$\left(\ln \frac{f_{Ad}}{f_{Ah}} \right)_{x'_w} = - \int_0^{x'_w} \frac{x_w}{1 - x_w} \frac{\partial \ln(f_{Dd}/f_{Hh})}{\partial x_w} dx_w \quad (65)$$

$\lim_{x_w \rightarrow 0} \frac{x_w}{1 - x_w} \frac{\partial \ln(f_{Dd}/f_{Hh})}{\partial x_w} = 0$, so extrapolating eqn. 62 to $x_w = 0$ and inserting it into eqn. 65 probably results in only a relatively small error:

$$\left(\ln \frac{f_{Ad}}{f_{Ah}} \right)_{x'_w} \simeq - \int_0^{x'_w} \frac{x_w}{1 - x_w} \frac{d}{dx_w} \left(\frac{T_D - T_H}{RT_D T_H} \Delta H_{Hh} \right) dx_w \quad (66)$$

Integrating by parts

$$\begin{aligned} \left(\ln \frac{f_{Ad}}{f_{Ah}} \right)_{x'_w} &\simeq - \left[\frac{x'_w}{1 - x'_w} \frac{T_D - T_H}{RT_D T_H} \Delta H'_{Hh} - \int_0^{1/(1-x'_w)} \frac{T_D - T_H}{RT_D T_H} \Delta H_{Hh} d \frac{1}{1 - x_w} \right] \\ &\equiv - \frac{x'_w}{1 - x'_w} \left[\frac{T_D - T_H}{RT_D T_H} \Delta H'_{Hh} - \frac{T_D - T_H}{RT_D T_H} \Delta H_{Hh} \right] \end{aligned} \quad (67)$$

where $\frac{T_D - T_H}{RT_D T_H} \Delta H_{Hh}$ is the average of $\frac{T_D - T_H}{RT_D T_H} \Delta H_{Hh}$ as a function of $1/(1-x_w)$ in the interval from 1 to $1/(1-x'_w)$.

NUMERICAL CALCULATION

The simplification that the enthalpy of mixing, ΔH , is independent of temperature is not necessary for the development of the system of equations presented above (though a large temperature coefficient would make the step from eqn. 60 to 59 more uncertain). In the numerical calculation, on the other hand, any appreciable change with temperature should be taken into account. Only enthalpy data below 18°C are available but it is possible to obtain some idea of the temperature dependence of ΔH in the range considered from a comparison between results obtained in different ways (see below). The conclusion reached is that ΔH , with sufficient accuracy, may be considered independent of temperature.

First approximations. The simple eqns. 48 or 49 may be used for the calculation of $(y'_D - y_D)/y'_D(1 - y'_D)$, when $(dT/dy'_D)_{eq, x'_w}$ or $(dx'_w dy'_D)_{eq, T}$, respectively, are assumed to be constant. These conditions are incompatible and it is seen that $(dx'_w/dy'_D)_{eq, T}$ cannot be independent of y'_D (at constant T) near the critical temperature while this is quite possible for $(dT/dy'_D)_{eq, x'_w}$ (at constant x'_w). Eqn. 48 is therefore the more correct. This is, however, of only small importance when the solubility curves are sufficiently close to being straight parallel lines.

Eqn. 49 may be written

$$\frac{y''_D - y'_D}{y'_D(1 - y'_D)} = - \frac{x'_{w,d} - x'_{w,h}}{2x'_w} Q \quad (68)$$

where

$$Q = \frac{\partial \mu'_w / \partial x_w}{RT(\partial \ln x'_w / \partial x_w)} = 1 + x'_w \frac{\partial \ln f'_w}{\partial x_w} = x'_w \frac{\partial \ln(P'_w/P_{w0})}{\partial \ln x_w} \quad (69)$$

and $x'_{w,h}$ and $x'_{w,d}$ are the solubilities of pure D₂O and H₂O at temperature T . For the present calculation, Q has been found by extrapolating the vapour pressure data of Kohler⁵ at 18°C with the help of the enthalpy data from Copp and Everett⁶ at 15°C (see Table 3 and Fig. 3).

Eqn. 48 may be written

$$\frac{y''_D - y'_D}{y'_D(1 - y'_D)} = \frac{T_D - T_H}{2RT^2} \Delta H'_w \quad (70)$$

where T_D and T_H are the temperatures at which the solubilities of pure D₂O and H₂O are x'_w . Again the ΔH data from Copp and Everett⁶ have been employed, without any temperature corrections (see Table 3 and Fig. 3).

For both sets of calculations the solubility curves shown in Fig. 2 has been used. These are drawn through the experimental points obtained in this labora-

Table 3. Numerical results obtained with the vapour pressure data of Kohler⁵, the enthalpy data of Copp and Everett⁶ and with the solubility data shown in Fig. 2. $y_D = 0.20$. For further explanation see text.

T °C	$-\frac{x'_{W,d}-x'_{W,h}}{2x'_W} Q$ (eqn. 68)	$\frac{T_D-T_H}{2RT^2} \Delta H'_W$ (eqn. 70)	$\frac{T_D-T_H}{2RT_D T_H} \Delta H_{Hh}$ (eqn. 72)
22	0.008	0.009	0.018
27	0.017	0.013	0.025
35	0.025	0.021	0.029
45	0.022	0.025	0.030

tory but supported by curves from the paper of Hahn and Street². The absolute position of these curves is not very accurate because small amounts of carbon dioxide may reduce the solubility noticeably (Krichevskii⁷).

The agreement at 35° and 45°C between the separation effects based on eqn. 68 and those based on eqn. 70 may be taken to support the assumption used for their calculation that ΔH varies only little with temperature.

It should be added that such an agreement is not consistent with Kohlers assumption in a later paper⁸ according to which ΔH should become zero at 70°C. His conclusion, however, is based on a solubility curve (in a paper by Rothmund⁹) which disagrees with others (*cf.* Fig. 2); in addition, the temperature in question could be anything between 25°C and 145°C, so the disagreement may not be so pronounced as could be expected at first glance.

Second approximations. When $\ln(f_{Ad}/f_{Ah})$ is taken into account in the calculation of the separation effect eqn. 54 should form the basis. It may be simplified

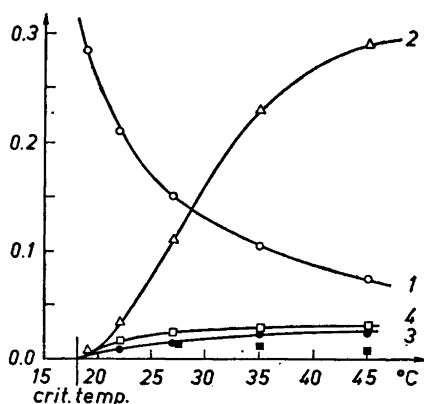


Fig. 3. Calculated (●, eqns. 68 and 70; □, eqn. 72; see Table 3), and experimental (■) isotope separation effects, $(y''_D - y'_D)/y'_D(1 - y'_D)$, as compared to a hypothetic separation between ideal mixtures, $\frac{1}{2}(x'_{W,h} - x'_{W,d})/x'_W$ (○, eqn. 52) and the factor $Q = (\partial\mu'_W/\partial x_W)/RT(\partial\ln x'_W/\partial x_W)$ (△, eqn. 69), expressing deviation from ideality.

since

- 1) $RT^2(\partial M'/\partial T)$ (eqn. 43) is probably small compared to $\Delta H'_{Dd}$ or $\Delta H'_{Hh}$
- 2) $\Delta H'_{Dd} \approx \Delta H'_{Hh}$
- 3) $RT^2(\partial M''/\partial T) \ll \Delta H''_{Hh}$ and $\Delta H''_{Dd} \approx \Delta H''_{Hh} \ll \Delta H'_{Hh}$
- 4) $(1-x''_w)(\Delta H'_A - \Delta H''_A) \ll \Delta H'_{Hh}$
- 5) $x''_w \approx 1$.

In addition the approximation is again made that $dT/dy'_D = T_D - T_H$. So eqn. 54 becomes

$$\frac{y''_D - y'_D}{y'_D(1-y'_D)} = \frac{T_D - T_H}{2RT^2} \Delta H_{Hh} + \frac{1-x'_w}{2x'_w} \left(\ln \frac{f_{Ad}}{f_{Ah}} \right)_{x'_w} \quad (71)$$

which when eqn. 67 is introduced gives

$$\frac{y''_D - y'_D}{y'_D(1-y'_D)} = \frac{1}{2} \frac{T_D - T_H}{RT_D T_H} \Delta H_{Hh} \quad (72)$$

(see Table 3 and Fig. 3).

$\frac{T_D - T_H}{RT_D T_H} \Delta H_{Hh}$ has been obtained by graphical integration of

$\frac{T_D - T_H}{RT_D T_H} \Delta H_{Hh}$ as a function of $\frac{1}{1-x_w}$.

Instead of eqn. 54 it may, however, be more instructive to modify eqn. 55 though the resulting equation will be less accurate near the critical point, where $(dx_w/dy_D)_{eq,T} \rightarrow \infty$ (while $[y''_D - y'_D]/[y'_D(1-y'_D)] \rightarrow 0$):

If the second-order term

$$\frac{x''_w(y''_D - y'_D)}{x'^2_w} RT \left(\ln \frac{f_{Ad}}{f_{Ah}} \right)_{x'_w} \left(\frac{dx'_w}{dy'_D} \right)_{eq,T}$$

is neglected and eqn. 34 is introduced, eqn. 55 may be written

$$\left[\frac{1}{x'_w} + y'_D \frac{\partial \ln f'_D}{\partial x_w} + (1-y'_D) \frac{\partial \ln f'_H}{\partial x_w} \right] \left(\frac{dx'_w}{dy'_D} \right)_{eq,T} = - \frac{\partial \ln f'_H}{\partial y_D} - 2 \frac{y''_D - y'_D}{y'_D(1-y'_D)} \quad (73)$$

or, approximately,

$$\frac{y''_D - y'_D}{y'_D(1-y'_D)} \approx - \frac{x'_{w,d} - x'_{w,h}}{2x'_w} - \frac{x'_{w,d} - x'_{w,h}}{2} \frac{\partial \ln f'_H}{\partial x_w} - \frac{1}{2} \frac{\partial \ln f'_H}{\partial y_D} \quad (74)$$

(cf. eqns. 68 and 69). The significance of the different terms in eqn. 74 is illustrated in Fig. 3.

CONCLUSION

The approximate chemical potential functions and other relations developed above rest on the assumption that the numerical value of $\partial \ln f / \partial y_D$ is small compared to $\partial \ln f / \partial x_w$; this has been verified by calculation, the actual result being

$$\frac{1}{500} \frac{\partial \ln f_H}{\partial x_w} < \frac{\partial \ln f_H}{\partial y_D} < \frac{1}{100} \frac{\partial \ln f_H}{\partial x_w} \text{ in the interval } 0.1 < x_w < 0.5$$

In Fig. 3 it is illustrated by the difference between curve 1 and 3 (see Fig. 2 for the numerical value of $x'_{w,d} - x'_{w,h}$) compared to the difference between curve 3 and 4; see eqn. 74 for further explanation. Curve 1, the relative solubility change divided by the statistical factor, 2, would be the isotope separation effect to be expected if the simplified version of eqn. 49, analogous to eqn. 52, were applicable — as it would be in an ideal system. The agreement between experimental (also shown in Fig. 3) and theoretical separation effects is satisfactory if the purpose is to verify that this simplification is not permissible.

When the absolute values of $[y''_D - y'_D] / [y'_D(1 - y'_D)]$ are considered, the discrepancy appears somewhat more important (Note that the experimental values include one or two border line cases).

It may be caused by an erroneous $x'_{w,d} - x'_{w,h}$ (eqn. 68); this in fact is the most probable explanation because the effect of introducing $\partial \ln f / \partial y_D \neq 0$, almost certainly must cause an increase in $[y''_D - y'_D] / [y'_D(1 - y'_D)]$, due to the less ideal appearance of the D_2O -TEA system in comparison to the corresponding H_2O system.

Expressed in another way: It is probable that $T_H - T_D$ (eqn. 70) is too large as the sign of

$$- \frac{T_D - T_H}{RT_D T_H} \Delta H'_{Hh} + \frac{T_D - T_H}{RT_D T_H} \Delta H_{Hh}$$

or any modification of this term, representing a better approximation to the non-ideality of the systems, almost certainly, is positive (eqn. 72).

The discrepancy may, however, be caused by impurities not accounted for by chemical analysis. A doubling of the amount found would be sufficient to make the discrepancy disappear. It may be shown, as mentioned earlier, that a trace of water would have the same effect.

From the point of view of deuterium oxide separation it may, in general, be said that the difference between the solubilities of D_2O and H_2O in an organic medium ($x'_{w,d} - x'_{w,h}$) furnishes a very poor measure of the degree of separation obtainable because large $x'_{w,d} - x'_{w,h}$ almost invariably must mean that the solubility curve is very flat ($(dx'_w/dT)_{eq,y_D}$ large); this again necessitates values of $(\partial \mu'_w / \partial x_w)_{T,y_D}$ very near zero, *i.e.* very far from the ideal RT/x'_w , unless the absolute values of ΔH or/and $T_D - T_H$ are very large. An equation like 68 or 70 is therefore a simple and better basis for comparison.

A general conclusion would seem to be that it is quite unlikely that large D_2O - H_2O separation effects in liquid-liquid mixtures are possible, at any rate, in the absence of extensive chemical isotope exchange.

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