Thermodynamics of Liquid-Liquid Distribution Reactions
II. Lithium Bromide-Water-2-Ethylhexan-1-ol System

Yizhak Marcus
Institut für Heisse Chemie, Kernforschungszentrum Karlsruhe, 75 Karlsruhe, Germany

The standard molar enthalpy of transfer of lithium bromide between aqueous solutions and 2-ethylhexanol solutions is obtained directly by two-phase calorimetry. Heats of dilution are also obtained to give the corrected $\Delta H_{tr}°/(\text{kJ mol}^{-1}) = -7.69 \pm 0.21$. The corresponding unitary Gibbs energy change and entropy change are $\Delta G_{tr}°/(\text{kJ mol}^{-1}) = 15.21$ and $\Delta S_{tr}°/(\text{JK}^{-1}\ \text{mol}^{-1}) = -77.3$. The entropy effect which dominates the transfer at infinite dilution is due to loss of water structure breaking by the bromide ion on transfer. The transfer in concentrated solutions, however, is dominated by the exothermic ion-pairing enthalpy.

The thermodynamics of the transfer of a solute from one solvent to another has received increasing attention in recent years. Standard enthalpies of transfer have often been obtained from the difference in the heats of solution of a solid electrolyte in water and an organic solvent. Because the difference is usually small compared with the heats of solution, serious uncertainties result, which may be avoided in the case of mutually insoluble phases by measuring directly enthalpies of solute distribution reactions (*11*). Gibbs energies of transfer are readily obtainable from equilibrium concentration measurements in the two-phase system.

The solubility of lithium halides in alcohols is well known and is the basis for their analytical separation from heavier alkali metal halides. Their extraction has also been studied, and the bromide found more extractable than the chloride (*14*). A preliminary estimate of the heat of transfer of lithium chloride from an aqueous solution to water-saturated isopentanol, $\Delta H_{tr}° = 0$, has been made (*9*) on the basis of the temperature coefficient of the distribution constant between 298 and 323K. The nonvalidity of this procedure has already been commented on (*11*). Alcohols with longer alkyl chains have lower water contents at saturation and should show more clearly the difference between the alcoholic environment and an aqueous environment than the lower alcohols such as isopentanol (*9*). The solvent 2-ethylhexan-1-ol (2-EtHx-OH) has been used for the recovery of lithium from concentrated brines (*10*) and is readily available in pure form. The thermodynamics of such a distribution reaction is relatively simple to study and has been investigated. Some insight into the interactions of the ions with the solvents and among themselves is gained from such a study.

Experimental

The experimental setup used has been described elsewhere (*11*). It has been improved by using a smaller Dewar vessel of 200-cm³ capacity, reducing the heat capacity of the system to 400 J K^{-1}. This permits precisions of ±0.1 J to be attained. A ground glass plug, actuated from outside, has been added to the internal bulb to prevent diffusion.

The 2-ethylhexan-1-ol used (Fluka) was of "pure" grade, as was the anhydrous lithium bromide (Merck). The salt was determined in the organic phase by addition of water and titration with Titrisol silver nitrate with chromate indicator. Duplicate analysis showed ±0.2% agreement. Aqueous-phase concentrations were obtained by difference (usually about 2% of the salt was extracted) and checked by density determination.

The mutual solubility of water and 2-ethylhexan-1-ol was obtained from the literature. The solubility of 2-ethylhexan-1-ol in water at 20–25°C is 0.06–0.10 wt %, i.e., a mole fraction of 8×10^{-5}, which is negligible. The solubility of water in the alcohol, however, is considerable at 20–25°C: 2.48–2.6 wt %, i.e., a mole fraction of 0.16 or a ratio of 1:5.3 water to alcohol (*3, 5, 15*). The concentration of water in 2-ethylhexan-1-ol into which lithium bromide had been extracted was determined by standard Karl-Fischer titration. All data for the present study were obtained at 23.0 ± 0.5°C.

Calculations

The following cycle has been used to obtain the standard state (infinite dilution of salt in the mutually saturated solvents) enthalpy of transfer $\Delta H_{tr}°$ from experimental data at appreciable salt concentrations m ($\geq 10m$ in the aqueous phase) and $\bar{m}$, the bar designating the organic phase:

$$\begin{tikzcd}
\text{Li}^+(\text{aq}, m) + \text{Br}^-(\text{aq}, m) \arrow[rr, "q_{obs}/\Delta\bar{n}_{LiBr}"] \arrow[d, "\Delta H_{dil}(m \to 10)"] & & \text{LiBr}(\text{org}, \bar{m}) \\
\text{Li}^+(\text{aq}, 10) + \text{Br}^-(\text{aq}, 10) \arrow[d, "\Delta H_{dil}(10 \to 0)"] & & \\
\text{Li}^+(\text{aq}, m = 0) + \text{Br}^-(\text{aq}, m = 0) \arrow[d, "\Delta H_{tr}°"] & & \\
\text{Li}^+(\text{org}, \bar{m} = 0) + \text{Br}^-(\text{org}, \bar{m} = 0) \arrow[uuurr, "-\Delta\bar{H}_{dil}(\bar{m} \to 0)"'] & &
\end{tikzcd} \qquad (1)$$

The general equation for the observed heat effect q_{obs} when Δn moles of salt are transferred includes the heats of dilution of the extracted part and the remaining part in the two phases, in addition to $\Delta H_{tr}°$:

$$q_{obs} = n_i \int_i^f \Delta H_{dil}' dm + \Delta n \int_f^0 \Delta H_{dil}' dm - \Delta n_i \Delta H_{tr}° + \Delta\bar{n} \int_f^0 \Delta\bar{H}_{dil}' d\bar{m} + \bar{n}_i \int_f^i \Delta\bar{H}_{dil}' d\bar{m} \qquad (2)$$

In Equation 2, $\Delta H_{dil}'$ is the differential molal heat of dilution, and the subscripts i and f designate the initial and final states of the system. Transfer of salt in the direction indicated in Equation 1 will be considered as in a positive direction: $\bar{n}_i = 0$, $\bar{n}_f = \Delta\bar{n} = n_i - n_f > 0$, and the last term of Equation 2 is zero. For convenience, the dilution

---

[1] Present address, Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel.

of the concentrated aqueous solution has been divided into two parts: first from m_i to 10m, then from 10m to 0. The standard enthalpy of transfer for direct extraction is therefore given by Equation 3:

$$-\Delta H_{\mathrm{tr}}{}^{\circ} = q_{\mathrm{obs}}/\Delta\bar{n} - (n_i/\Delta\bar{n}) \int_{m_i}^{m_f} \Delta H_{\mathrm{dil}}{}' dm - \int_{m_f}^{10} \Delta H_{\mathrm{dil}}{}' dm - \int_{10}^{0} \Delta H_{\mathrm{dil}}{}' dm + \int_{\bar{m}_f}^{0} \Delta \bar{H}_{\mathrm{dil}}{}' d\bar{m} \quad (3)$$

For reverse extraction from the organic to the aqueous phase, $n_i = 0$, $\Delta\bar{n} = \bar{n}_f - \bar{n}_i = -\Delta n = -n_f < 0$, and incidentally, $m_f < 1$. In this case, the first term in Equation 2 vanishes, and the standard enthalpy of transfer is:

$$-\Delta H_{\mathrm{tr}}{}^{\circ} = q_{\mathrm{obs}}/\Delta\bar{n} - \int_{m_f}^{0} \Delta H_{\mathrm{dil}}{}' dm + \int_{\bar{m}_f}^{0} \Delta \bar{H}_{\mathrm{dil}}{}' d\bar{m} - (\bar{n}_i/\Delta\bar{n}) \int_{\bar{m}_i}^{\bar{m}_f} \Delta \bar{H}_{\mathrm{dil}}{}' d\bar{m} \quad (4)$$

The Gibbs energy of transfer $\Delta G_{\mathrm{tr}}{}^{\circ}$ is obtained as the difference of the standard chemical potentials, from equating the chemical potentials of the equilibrium phases.

$$\mu_{\mathrm{LiBr}} = \mu_{\mathrm{LiBr}}{}^{\circ} + 2\,RT \ln m_{\mathrm{LiBr}}\gamma_{\pm} = \bar{\mu}_{\mathrm{LiBr}}{}^{\circ} + 2\,RT \ln \bar{m}_{\mathrm{LiBr}}\bar{\gamma}_{\pm} = \bar{\mu}_{\mathrm{LiBr}} \quad (5)$$

$$\Delta G_{\mathrm{tr}}{}^{\circ} = \bar{\mu}_{\mathrm{LiBr}}{}^{\circ} - \mu_{\mathrm{LiBr}}{}^{\circ} = -RT \ln K \quad (6)$$

$$\log \bar{m}_{\mathrm{LiBr}} - \log m_{\mathrm{LiBr}} - \log \gamma_{\pm} = \tfrac{1}{2} \log K - \log \bar{\gamma}_{\pm} \quad (7)$$

In practice, since lim log $\bar{\gamma}_{\pm}$ ($\bar{m} \rightarrow 0$) = 0, log K is obtained by extrapolation.

Results

Integral heats of dilution of aqueous solutions of lithium bromide obtained at concentrations above 10m are shown in Figure 1. They are compared with the "best" literature data, compiled by Parker (*12*), which can be expressed as

$$\Delta H_{\mathrm{dil}}/\mathrm{J(mol\ LiBr)^{-1}} = -6740 - 845(m - 10) - 61.0(m - 10)^2 + 2.76(m - 10)^3 \quad (8)$$

The results obtained here at 9.94m are $\Delta H_{\mathrm{dil}} = -6700 \pm 20$ J mol^{-1}, and above that they can be expressed for the differential heat by

$$\Delta H_{\mathrm{dil}}{}' = -q_{\mathrm{dil}}(n_{\mathrm{LiBr}}\Delta m)^{-1}/\mathrm{J\ mol^{-1}(mol/kg)^{-1}} = -(1050 \pm 50)(m - 10) \quad (9)$$

which is seen in Figure 1 to be compatible with the literature data. For the dilute range,

$$\Delta H_{\mathrm{dil}}{}'/\mathrm{J\ mol^{-1}(mol/kg)^{-1}} = -840 - 14250\,m_i \quad (10)$$

expressed the data for $m_i < 1m$ and $m_f = 0$.

Integral heats of dilution of the alcoholic solutions were obtained by diluting an initially 1.447m solution (Table I), yielding the quadratic:

$$-\bar{q}_{\mathrm{dil}}(\bar{n}_{\mathrm{LiBr}})^{-1}/\mathrm{J\ mol^{-1}} = -(1465 \pm 135)(\bar{m}_i + \bar{m}_f)\Delta\bar{m} \quad (11)$$

(Figure 2) which gives the differential heat of dilution $\Delta\bar{H}_{\mathrm{dil}}{}' = -(2930 \pm 270)\bar{m}$ J mol^{-1} (mol/kg)$^{-1}$, and the integral heat of dilution from $\bar{m}_f$ to infinite dilution

$$\int_{\bar{m}_f}^{0} \Delta\bar{H}_{\mathrm{dil}}{}' d\bar{m} = -1465\,\bar{m}_f{}^2\ \mathrm{J\ mol^{-1}} \quad (12)$$

In the dilution of the water-saturated organic phase obtained on extraction to the standard state of infinite dilution of salt, there occurs, however, a corresponding increase in the concentration of water (Figure 3). The heat effect of this is small: the addition of excess water to dry 2-ethylhexan-1-ol evolves 18.2 ± 0.2 J(mol 2-EtHxOH)$^{-1}$ or 113.7 J(mol H_2O)$^{-1}$ for the water that saturates the alcohol at a mole fraction of $\bar{x}_{H_2O} = 0.16$. The maximal amount of heat corresponds to $\Delta\bar{m}_{H_2O} = 1.5m$ and 0.02 kg alcohol, i.e., 3.4 J for a total heat evolved of several hundred J. This was applied as a correction to $\Delta\bar{H}_{\mathrm{dil}}$.

These data were used, with measured heats of extraction, q_{obs}, and analytical data on the amounts extracted, to calculate from Equations 3 and 4 the standard enthalpies of transfer shown in Table II. The table shows that for both direct and reverse extraction, concordant values are obtained, averaging $\Delta H_{\mathrm{tr}}{}^{\circ} = -7.69 \pm 0.21$ kJ mol^{-1}.

To obtain the standard Gibbs energy of transfer (molal scale), $\Delta G_{\mathrm{tr}(m)}{}^{\circ}$, corresponding pairs $\bar{m}(m)$ from distribution data, and $\gamma_{\pm}$ values (*6*) were obtained, and log $(\bar{m}/m\gamma_{\pm})$ was plotted against $\bar{m}$ (Figure 4). Extrapolation to $\bar{m} = 0$ yielded 1/2 log $K = -(2.20 \pm 0.06)$ and

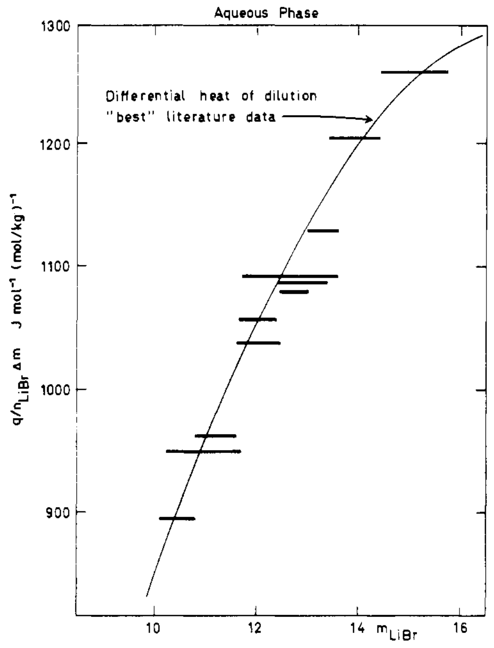

Figure 1. Differential heats of dilution of lithium bromide in concentrated aqueous solutions, $-\Delta H_{\mathrm{dil}}{}' = q/n_{\mathrm{LiBr}}\ \Delta m$ plotted against m

Table I. Heat of Dilution of Lithium Bromide in 2-EtHxOH, $\bar{m}_i = 1.447$

$\bar{m}_f$, m	$\bar{n}_{\mathrm{LiBr}}$, mmol	q, J	$\bar{q}/\bar{n}_{\mathrm{LiBr}}\Delta\bar{m}(\bar{m}_i + \bar{m}_f)$, kJ mol^{-1}(mol kg^{-1})$^{-2}$
1.150	91.2	111.7	1.590
0.968	91.2	142.7	1.351
0.780	113.8	241.0	1.427
0.659	80.6	177.4	1.326
0.468	45.6	125.2	1.464
0.456	44.5	115.9	1.381
0.281	23.2	74.1	1.540
0.277	22.9	73.6	1.594
			Average 1.465 ± 0.135

$\Delta G_{tr(m)}^\circ = +24.95 \pm 0.68$ kJ mol^{-1}. The standard entropy of transfer $\Delta S_{tr(m)}^\circ = (\Delta H_{tr}^\circ - \Delta G_{tr(m)}^\circ)/T = -110.3 \pm 2.4$ J K^{-1} mol^{-1}.

It was attempted to measure the heat of solution of lithium bromide in 2-ethylhexan-1-ol, but the anhydrous salt did not dissolve sufficiently rapidly in either anhydrous or water-saturated alcohol. On the other hand, the dihydrate, obtained by slow crystallization at ~8°C, analyzing 2.07 mol water/mol salt, dissolved easily in the water-saturated alcohol. For the reaction:

$$LiBr\cdot 2H_2O(c) + 90\ 2\text{-}EtHxOH(l) = LiBr\ 0.086m \text{ in } 2\text{-}EtHxOH(l, H_2O\text{-satd.}) \qquad (13)$$

the heat evolved was 14.0 ± 0.1 kJ (mol LiBr)$^{-1}$.

Discussion

The standard enthalpy of transfer found here can be combined with the standard enthalpy of solution of lithium bromide dihydrate in the water-saturated alcohol to give an estimate of ΔH_{soln}°/kJ mol^{-1} = $-14.0 - (-7.69) = -6.3$ for the standard enthalpy of solution in water (Figure 5). The standard enthalpy of solution of the anhydrous salt is known with good confidence (*12*) as -48.83 ± 0.20 kJ mol^{-1} at 25°C. The standard enthalpy of formation of the dihydrate from the anhydrous salt and liquid water has been reported as −42.05 (*2*), −45.77 (*7*), and −40.12 (*13*), all values being recalculated from the original data with consistent values of the enthalpy of vaporization of water. These lead to the values −6.78, −3.06, and −8.71, respectively, for ΔH_{soln}°/kJ mol^{-1} of the dihydrate in water, so that our own estimate -6.3 ± 0.2 is of the correct magnitude and of good accuracy.

The thermodynamic functions of transfer at infinite dilution can be interpreted in terms of the interactions of the ions with the solvents. Conversion of $\Delta G_{tr(m)}^\circ$ to the corresponding unitary values (*11*) by multiplying K by

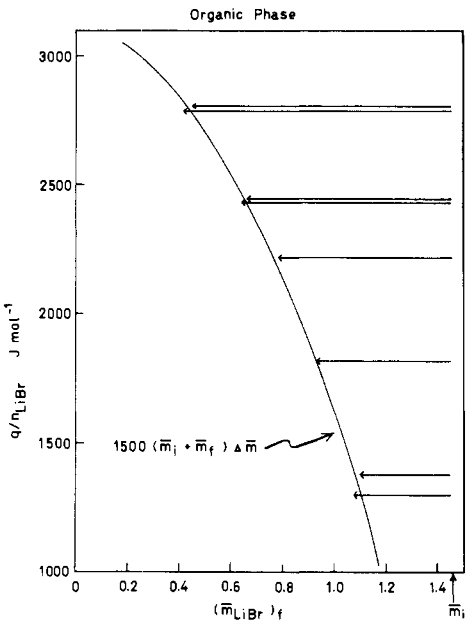

Figure 2. Integral heats of dilution of lithium bromide in 2-ethylhexan-1-ol solutions, $-\Delta H_{dil} = q/n_{LiBr}$ plotted against $\bar{m}$

Table II. Standard Enthalpy Change for Extraction of Lithium Bromide

m_i, m	m_f, m	$\bar{m}_f$, m	n_{LiBr}, mmol	q, J	q/n_{LiBr}, kJ mol^{-1}	$-H_{tr}^\circ$, kJ mol^{-1}
			Direct extraction (aq to org)			
10.10	9.98	0.503	8.20	208.4	25.41	7.69
10.22	10.11	0.413	6.68	165.3	24.75	7.03
11.52	11.31	0.840	13.34	355.6	26.66	7.41
13.60	11.23	0.468	31.04	906.7	29.21	7.59
13.60	13.33	0.990	15.94	499.6	31.34	8.46
15.75	15.41	1.252	20.22	690.8	34.16	7.43
17.41	16.85	1.538	22.06	815.9	36.99	8.01
$\bar{m}_i$, m	$\bar{m}_f$, m	m_f, m	n_{LiBr}, mmol	q, J	q/n_{LiBr}, kJ mol^{-1}	$-H_{tr}^\circ$, kJ mol^{-1}
			Reverse extraction (org to aq)			
0.468	0.018	0.089	−6.85	−50.8	7.42	7.90
0.780	0.125	0.120	−10.45	−74.5	7.13	8.41
0.968	0.008	0.199	−16.35	−95.8	5.86	7.69
1.447	0.037	0.137	−10.50	−36.0	3.43	6.95
1.447	0.072	0.271	−21.90	−66.9	3.06	6.99

Average $H_{tr}^\circ = -7.69 \pm 0.21$ (kJ mol^{-1})

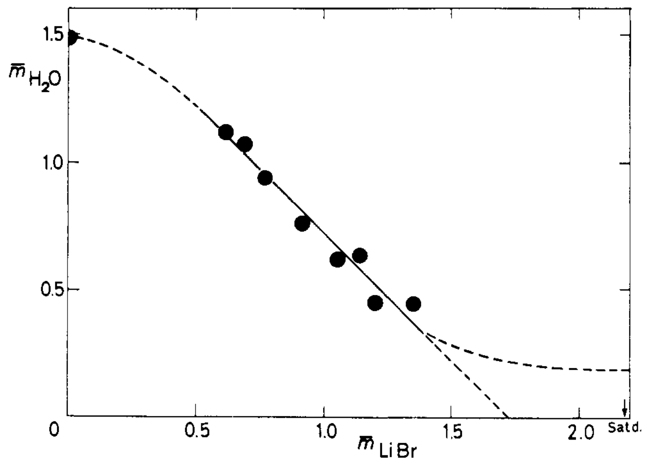

Figure 3. Water contents of extracts of lithium bromide into 2-ethylhexan-1-ol, $\bar{m}_{H_2O}$ plotted against $\bar{m}_{LiBr}$

Straight line portion extrapolates to $\bar{m}_{H_2O} = 0$ at $\bar{m}_{LiBr} = 1.72$, but constant activity coefficient $\bar{\gamma}_{H_2O} = 2.30$ leads to $\bar{m}_{H_2O} = 0.18$ at saturation, $\bar{m}_{LiBr} = 2.18m$, $m_{LiBr} = 21.1m$

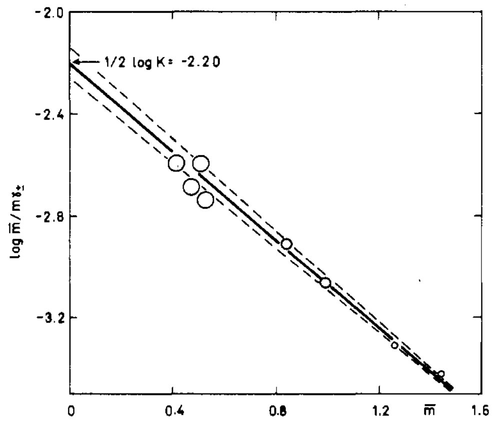

Figure 4. Extrapolation of distribution ratio for calculation of K, log $\bar{m}/m\gamma_\pm$ plotted against $\bar{m}$

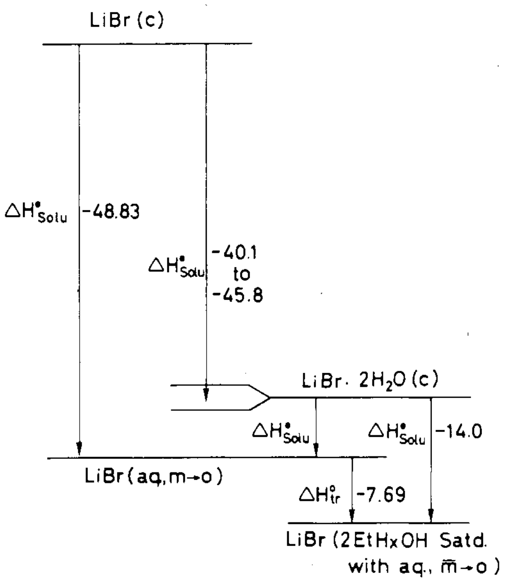

Figure 5. Enthalpy change scheme for calculation of heat of solution of $LiBr{\cdot}2H_2O$ in water

(mol water/kg)^2 (mol 2-EtHxOH/kg)$^{-2}$, leads to $\Delta G_{tr(x)}{}^\circ = +15.21$ kJ mol^{-1} and $\Delta S_{tr(x)}{}^\circ = -77.3$ J K^{-1} mol^{-1}. Comparison with $\Delta H_{tr(x)}{}^\circ = -7.69$ kJ mol^{-1} shows that the transfer at infinite dilution is entropy controlled.

It is reasonable to assume that the strongly hydrated lithium ions will be in similar states in both phases, seeking the alcohol phase the water molecules (present in the ratio of 1:5.3). The bromide ions, however, are strongly structure breaking in water but have no structure left to break in the alcohol phase. Therefore, when they leave the aqueous phase to the organic phase, they permit structure to be reformed in the system, with a large negative entropy change. The standard molar entropy of aqueous lithium bromide (*13*) is 95.0 J K^{-1} mol^{-1}, that for the alcohol solution is only 17.7 J K^{-1} mol^{-1}. If it is assumed that the lithium ions retain their aqueous environment and therefore do not contribute to $\Delta S_{tr}{}^\circ$, the entropy contribution of the bromide ions S° (Br^-, solv)/J K^{-1} mol^{-1} decreases from an estimated 103.0 in water to only 25.7 J K^{-1} mol^{-1} in the alcohol, corresponding to a sharp decrease in their structure-breaking property.

The situation is quite different in the concentrated solutions, from which extraction is actually taking place. In $>10m$ aqueous lithium bromide, there is very little structure left for the bromide ions to break, so that this entropy barrier to transfer must be considerably lowered. On the other hand, in the organic phase the dielectric constant is small, $\epsilon = 9.85$ at 25° and 10.30 at 20° for dry 2-ethylhexan-1-ol (*16*), which may increase to 11.6 in the water-saturated alcohol, assuming weight fraction additivity and decrease in the presence of ions. Considerable ion-pairing is therefore expected in salt solutions of any appreciable concentration in this solvent.

The ion-pairing equilibrium constant may be calculated according to the theory of ion association of Bjerrum (*1*) for a solvent of the given dielectric constant and for the interionic distance of $2.55 \times 10^{-10}m$, obtained from the crystal radii. The association constant is $10^{6.1}M^{-1}$, so that only a small fraction will be dissociated at the concentrations $\bar{m} > 10^{-3}$ (mol kg^{-1}) encountered here. The Gibbs energy of association may be calculated from electrostatics (*4*) as -46.5 kJ(mol LiBr)$^{-1}$, which more than compensates the positive value of $\Delta G_{tr(x)}{}^\circ$. (The association constant corresponding to this is $10^{8.1}$, which as is usual in such calculations, does not agree with the esimate from Bjerrum's theory but leads to the same conclusion concerning extensive association.)

On the other hand, a considerable amount of enthalpy of hydration is lost on extraction from concentrated solutions, since the water remaining in the alcohol does not suffice to hydrate the lithium ions. Water is directly displaced from the organic phase, in such a manner that

$$\bar{m}_{H_2O} = (1.72 \pm 0.02) - \bar{m}_{LiBr} \qquad (14)$$

and also

$$\bar{x}_{H_2O} = (2.30 \pm 0.16)a_{H_2O} \qquad (15)$$

as obtained from water activity data (*6*) and the data in Figure 3. The constant activity coefficient of water $\bar{f}_{H_2O} = \bar{a}_{H_2O}/\bar{x}_{H_2O} = a_{H_2O}/\bar{x}_{H_2O} = 2.30$, as the lithium bromide increases from 0.62 to 1.35m, indicates that the water is not bound to the salt very strongly. In fact, extrapolation to saturation of salt in the system leads to practically zero water content of the organic phase. The ion pairs are probably solvated efficiently enough by the 2-ethylhexan-1-ol without the need for hydration. The difference in solvation enthalpies of the ion pair (*8*) in water and the alcohol is $\Delta H_{solv}{}^\circ$ (LiBr, aq) $-$ $\Delta H_{solv}{}^\circ$ (LiBr, 2-EtHxOH) $= -247.0 - (-210.5) = -36.5$ kJ mol^{-1} reduces somewhat the ion association energy calculated above, so that $\Delta G_{tr(x)}$ at high concentrations is not as negative as expected. A quantitative estimate is however impossible, since the degree of ion-pairing in the aqueous phase and the entropy changes involved are not known, and no data are available near saturation of the phases by the salt, the natural standard state for concentrated solutions, where, of course, $\Delta G_{tr}{}^{sat} = 0$.

Acknowledgment

Thanks are due to the Alexander von Humboldt Stiftung for the stipend and to F. Baumgärtner for his invitation, which made this work in Germany possible. H. A. C. McKay is thanked for fruitful discussions, and N. Ben-Zwi for obtaining the data shown in Figure 3.

Literature Cited

(1) Bjerrum, N., *Kgl. Dan. Vidensk. Selsk., Mat. Fys. Medd.*, **7** (9) (1926).
(2) Bodisko, A., *Zh. Russ. Fiz. Khim. Obshchest.*, **21**, 7 (1898); *Z. Phys. Chem.*, **4**, 482 (1898).
(3) Celanese Chemicals, "2-Ethylhexanol Product Bulletin," New York, N.Y., 1961.
(4) Denison, J. T., Ramsay, J. B., *J. Amer. Chem. Soc.*, **77**, 2615 (1955).
(5) Doolittle, A. K., *Ind. Eng. Chem.*, **27**, 1169 (1935).
(6) Gazith, M., "Israel AEC Report IA-1004," 1964.
(7) Hüttig, G. F., Renscher, F., *Z. Anorg. Chem.*, **137**, 155 (1924).
(8) Humbelin, R., *Electrochim. Acta*, **10**, 705 (1968).
(9) Krasnov, K. S., Kasas, T. S., Proc. 3rd International Conf. Chem. Thermodyn., Vol IV, p 65, Baden near Vienna, Germany, September 1973.
(10) Marcus, Y., Ben-Zwi, N., Blinderman, J. M., Abstracts 42nd Meeting, Israel Chemical Society, p 161, Rehovot, Israel, 1972.
(11) Marcus, Y., Kolarik, Z., *J. Chem. Eng. Data*, **18**, 155 (1973).
(12) Parker, V. B., "Thermal Properties of Aqueous Uni-Univalent Electrolytes," NSRDS-NBS-2, pp 54-55, National Bureau of Standards, Washington, D.C., 1965.
(13) Rossini, F. D., "Selected Values of Chemical Thermodynamic Properties," NBS Circular 500, National Bureau of Standards, Washington, D.C., 1952.
(14) Rozen, A. M., Mikhailichenko, A. I., *Russ. J. Inorg. Chem.*, **12**, 380 (1967).
(15) Union Carbide Corp., "Alcohols," New York, N.Y., 1961.
(16) Wemelle, R., *Compt. Rend.*, **244**, 775 (1957).

Received for review January 28, 1974. Accepted December 14, 1974. Presented at the Third International Conference on Chemical Thermodynamics, Baden near Vienna, September 1973. A preliminary presentation occurred at the 42nd Meeting of the Israel Chemical Society, Rehovot, December 1972.