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Complex Formation in Mixed Solvents[1]

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Received July 12, 1963

The degrees of complexing between solutes and cosolvents have been investigated by a method described in an earlier publication. Results indicate that $(C_2H_5)_2Mg$, $(n\text{-}C_3H_7)_2Mg$, and $(i\text{-}C_3H_7)_2Mg$ form a one-to-one complex with tetrahydrofuran in ethyl ether containing tetrahydrofuran. The degrees of complexing between some derivatives of lithium aluminum hydride (*e.g.*, alkoxoaluminates) and cosolvents were studied. Interaction between solute and cosolvent was in some cases indicated by an increase in solubility in the presence of the cosolvent. Chemical exchange between lithium aluminum alcoholates and alcohols as cosolvents was found to take place, and the equilibrium of the methanol and ethanol exchange has been studied.

Introduction

In an earlier publication[2] results were reported concerning the degree of complexing between some solutes and cosolvents in mixed solvent systems. The purpose of the present paper is to report similar results for several more systems.

The method by which the results were obtained uses the lowering of the vapor pressure of the cosolvent in the presence of the solute to determine the extent of complexing between solute and cosolvent. The procedure is to plot the vapor pressure of the cosolvent (or some quantity that is proportional to the vapor pressure) as a function of the concentration of the cosolvent when a known amount of solute is present. When the curve has the form of a displaced Henry's law, it is possible to estimate the amount of cosolvent that is bound to the solute from the magnitude of the displacement as given by linear extrapolation. That is, the intercept of the extrapolated linear portion with the abscissa (axis corresponding to the concentration of cosolvent in the liquid) gives directly an estimate of the value of m in the formula $M \cdot mP$, where M represents the uncomplexed solute and P represents the cosolvent.

Although the idea behind this treatment is basically simple, and one is confident that the result is in some sense an estimate of the value of m, questions do arise concerning the nature of the assumptions and approximations involved. Some of these questions are answered by the mathematical treatment given in the Appendix of this paper.

Experimental

Apparatus and Procedure.—The apparatus and general procedure have been described in an earlier publication.[2] Briefly, the method used involves the determination of the relative concentrations of cosolvent in the vapor which was in equilibrium with the refluxing mixtures of solvent and cosolvent, with and without solute. These relative cosolvent concentrations in the vapor were determined by gas chromatography in terms of peak areas (or peak heights, since they were found to be proportional to the areas). In all cases the temperature was 38°.

Reagents.—The ethyl ether solutions of the **dialkylmagnesiums** which were used in these studies were also used for kinetic studies and have been described elsewhere.[3]

The **lithium aluminum hydride derivatives** were prepared *in situ* by the addition of the appropriate reagent to an ethyl ether solution of lithium aluminum hydride. In all cases the only products were the desired derivative and hydrogen. In many cases the derivatives were insoluble in ethyl ether but dissolved when small amounts of the appropriate cosolvent (*i.e.*, not more than two or three moles of cosolvent per liter of solution) were added. For these systems the peak height *vs.* cosolvent molality in the liquid were similar to those in which no precipitation occurred, and values of m could be determined. However, in some cases the precipitate was not readily dissolved by the cosolvent and low values of m were obtained.

Alcohols in ethyl ether do not obey Henry's law (see Fig. 4), and for these cosolvents it was necessary to extrapolate a nonlinear curve.

Results and Discussion

Complexes of Some Dialkylmagnesiums with Tetrahydrofuran in Ethyl Ether.—The relative concentrations (peak areas) of tetrahydrofuran in the vapor as a function of the concentration of tetrahydrofuran in solutions of some dialkylmagnesiums in ethyl ether are shown in Fig. 1. The values of m obtained from these curves are as follows: $(n\text{-}C_3H_7)_2Mg$, 0.91; $(C_2H_5)_2Mg$, 0.95; $(i\text{-}C_3H_7)_2Mg$, 1.0.

These results suggest that the complexing equilibria are

$$R_2Mg\cdot\text{ether} + \text{THF} \rightleftharpoons R_2Mg\cdot\text{THF} + \text{ether}$$

However, it is possible that the equilibria are really more complex, as shown below

$$R_2Mg\cdot 2\text{ether} + \text{THF} \rightleftharpoons R_2Mg\cdot\text{ether}\cdot\text{THF}$$
$$R_2Mg\cdot\text{ether}\cdot\text{THF} + \text{THF} \rightleftharpoons R_2Mg\cdot 2\text{THF}$$

where the equilibrium constant, K_2, for the second step is small. Values of K_1 and K_2 calculated from the data (see Appendix, eq. 16) are not accurate, since the values of K_1 and K_2 can be varied concertedly over a large range without observable changes, in agreement between the experimental points and the calculated

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[1] This work was supported by the U. S. Army Research Office (Durham) and the National Science Foundation.

[2] L. V. Guild, C. A. Hollingsworth, D. H. McDaniel, and S. K. Podder, *Inorg. Chem.*, **1**, 921 (1962). This paper gives references to earlier work by other authors.

[3] S. K. Podder, E. W. Smalley, and C. A. Hollingsworth, *J. Org. Chem.*, **28**, 1435 (1963).

TABLE I

LITHIUM ALUMINUM HYDRIDE DERIVATIVES IN ETHYL ETHER COSOLVENT SYSTEMS

Solute, M	Cosolvent, P	Mole ratio P/M	Value of *m* in complex M·*m*P
$LiAlH_4$	THF	0	2.0
$LiAlH_3(C\equiv CC_4H_9)$	THF	0	1.1
$LiAlH_2(C\equiv CC_4H_9)_2$	THF	0	1.0
$LiAlH(C\equiv CC_4H_9)_3$	THF	0	0.9
$LiAl(C\equiv CC_4H_9)_4$	THF	>0.9, <1.4	0.2
$LiAlH_2[N(C_6H_5)_2]_2$	THF	>0.2, <1.3	2.1
$LiAl(OCH_3)_4$	CH_3OH	>13, <14	(0.0)[a]
$LiAl(OCH_3)_4$	C_2H_5OH	>2.5, <3	(1.9) 1.1
$LiAlH_3(OC_2H_5)$	THF	>3, <4	0.9
$LiAlH_2(OC_2H_5)_2$	THF	>3, <4	0.3
$LiAl(OC_2H_5)_4$	CH_3OH	>0.9, <1.8	(2.0) 1.1
$LiAl(OC_2H_5)_4$	C_2H_5OH	>4, <4.7	(0.0)
$LiAlH_3(n\text{-}OC_3H_7)$	THF	0	1.0
$LiAlH_2(n\text{-}OC_3H_7)_2$	THF	>0.2, <1	0.9
$LiAlH_3(n\text{-}OC_4H_9)$	THF	0	1.0
$LiAlH_2(n\text{-}OC_4H_9)_2$	THF	>1, <2.4	1.0
$LiAlH(n\text{-}OC_4H_9)_3$	THF	>1, <2.4	0.4
$LiAl(n\text{-}OC_4H_9)_4$	CH_3OH	>1, <1.8	(1.5)
$LiAl(n\text{-}OC_4H_9)_4$	C_2H_5OH	>1, <2	(1.2)
$LiAlH_3(t\text{-}OC_4H_9)$	THF	0	1.0
$LiAlH_2(t\text{-}OC_4H_9)_2$	THF	0	1.2
$LiAlH(t\text{-}OC_4H_9)_3$	THF	>3, <4	1.3
$LiAlH_3(s\text{-}OC_4H_9)$	THF	>2, <3	1.0
$LiAlH_3(i\text{-}OC_4H_9)$	THF	>3, <4	1.0
$LiAl(OC_2H_5)_3(OCH_3)$	C_2H_5OH	>2.5, <3.0	(1.1) 1.0
$LiAl(OC_2H_5)_2(OCH_3)_2$	C_2H_5OH	>1.8, <2.5	(1.50) 1.1
$LiAl(OC_2H_5)(OCH_3)_3$	C_2H_5OH	>1.8, <2.5	(1.8) 1.1
$LiAl(OC_2H_5)_3(OCH_3)$	CH_3OH	>0.9, <1.8	(2.0) 1.2
$LiAl(OC_2H_5)_2(OCH_3)_2$	CH_3OH	>1.8, <2.7	(1.0) 1.0

[a] The parentheses indicate that these values of *m* include chemical exchange effects (see text).

curves. Rough estimates of these ranges are as follows: $(n\text{-}C_3H_7)_2Mg$, $90 < K_1 < 130$, $0 \leq K_2 < 5$; $(C_2H_5)_2Mg$, $50 < K_1 < 130$, $0 \leq K_2 < 20$; $(i\text{-}C_3H_7)_2Mg$, $60 < K_1 < 170$, $0 \leq K_2 < 15$.

It is clear, however, that an average of only one tetrahydrofuran molecule is complexed per magnesium. Analysis of the data published previously[2] for some Grignard reagents, C_2H_5MgBr, C_6H_5MgBr, and $C_6H_5CH_2MgBr$, gives comparable results: Only one tetrahydrofuran molecule is complexed per magnesium in these ethyl ether–tetrahydrofuran solutions. This, of course, does not rule out the possibility that two ether molecules are complexed per magnesium in pure ether, and an average of only one of these is replaced by tetrahydrofuran. Stucky and Rundle report[4] that C_6H_5MgBr crystallizes from ethyl ether as the dietherate.

Complexes of Lithium Alkoxoaluminates and Some Other Derivatives of Lithium Aluminum Hydride in Ethyl Ether–Cosolvent Mixtures.—The relative concentrations of tetrahydrofuran in the vapor as a function of the concentration of tetrahydrofuran in the ethyl ether solutions are shown for the solutes $LiAlH_{4-n}(C\equiv CC_4H_9)_n$, for $n = 0, 1, 2, 3$, and 4, in Fig. 2 and for some other $LiAlH_4$ derivatives in Fig. 3. All of these solutes were soluble in ether or in ether with only a small amount of cosolvent. Some other solutes required more cosolvent for solution to take place, and the curves for most of these solutes are not included in Fig. 2 and 3. The results are summarized in Table I. The major component of the mixed solvent was in all cases ethyl ether. The third column of the table indicates the amount of cosolvent (per mole of solute M) required to dissolve all of the solute (0.84 to 0.91 mole of M per liter of ether).

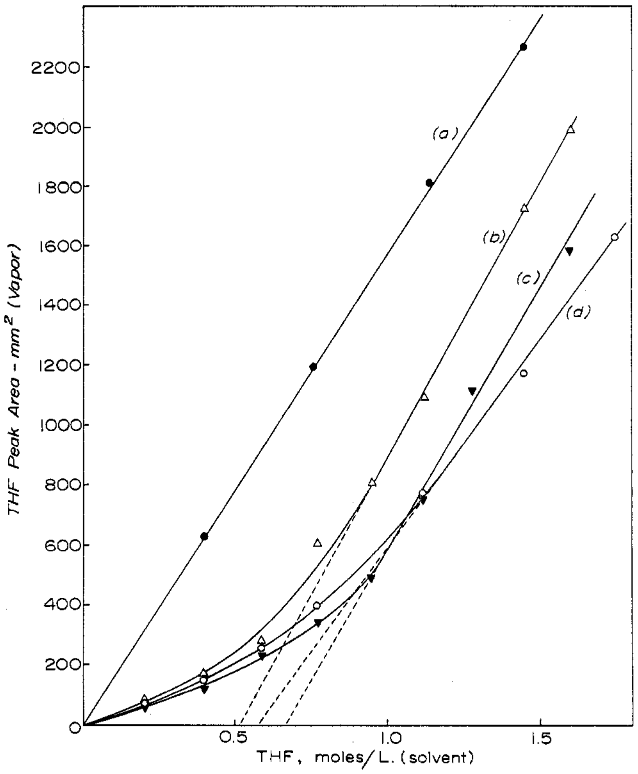

Fig. 1.—Relative concentration of tetrahydrofuran in the vapor (peak area) *vs.* the molar concentration of tetrahydrofuran in the solution of some dialkylmagnesiums: curve a, no solute; b, $(n\text{-}C_3H_7)_2Mg$, 0.52 *M*; c, $(C_2H_5)_2Mg$, 0.72 *M*; d, $(i\text{-}C_3H_7)_2Mg$, 0.62 *M*.

Solutes which are not included in Table I because their values of *m* were not determined, but which were found to be made soluble by the presence of small amounts of cosolvent, are the following: $LiAl(OCH_3)_4$, $LiAl(OC_2H_5)_4$, $LiAl(n\text{-}OC_3H_7)_4$, and $LiAl(n\text{-}OC_4H_9)_4$ with $n\text{-}C_4H_9OH$ as cosolvent; $LiAl(n\text{-}OC_3H_7)_4$ with CH_3OH; $LiAl(n\text{-}OC_3H_7)_4$ with C_2H_5OH or $n\text{-}C_3H_7OH$; $LiAl(n\text{-}OC_4H_9)_4$ with THF.

The following compounds did not dissolve to an observable extent in the presence of small amounts of THF as cosolvent: $LiAlH_3(OCH_3)$, $LiAlH(OC_2H_5)_3$, $LiAlH(n\text{-}OC_3H_7)_3$, $LiAlH_3(i\text{-}OC_3H_7)$, $LiAlH_2(s\text{-}OC_4H_9)_2$, $LiAlH_2(i\text{-}OC_4H_9)_2$, $LiAl(OCH_3)_2(n\text{-}OC_4H_9)_2$, and $Li(OCH_3)_2(OC_2H_5)_2$.

The compound $LiAl(OC_2H_5)(OCH_3)_3$ did not dissolve with CH_3OH as cosolvent. The compound $LiAl(i\text{-}OC_3H_7)_4$ did not dissolve to an observable extent in the presence of C_2H_5OH, $n\text{-}C_3H_7OH$, or $i\text{-}C_3H_7OH$ as cosolvents, although it did dissolve with CH_3OH as cosolvent in somewhat larger amounts (about 6 moles of CH_3OH per mole of solute).

Some generalizations which can be drawn from these results and those shown in Table I are the following:

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[4] G. D. Stucky and R. E. Rundle, *J. Am. Chem. Soc.*, **86**, 1002 (1963).

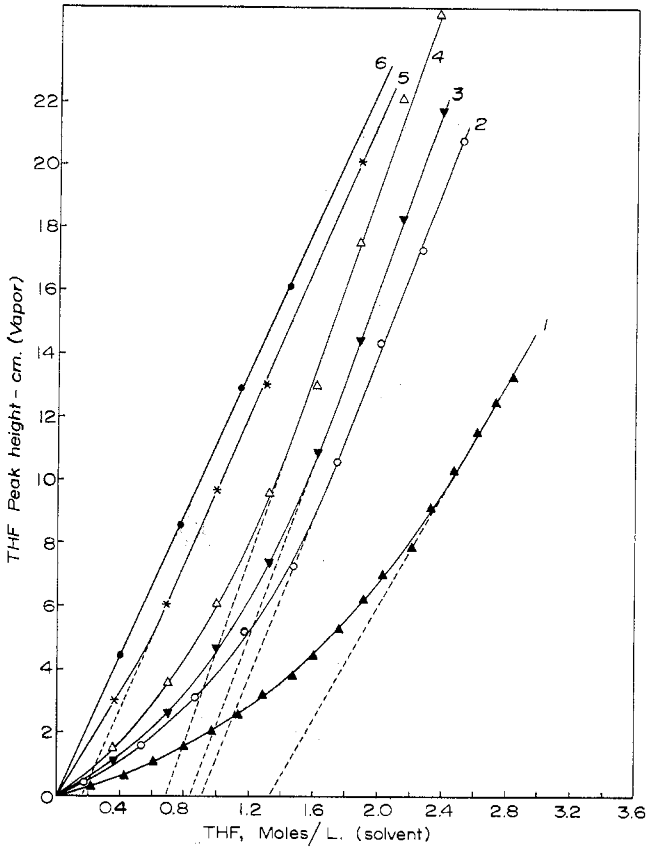

Fig. 2.—Relative concentration of tetrahydrofuran in the vapor (peak height) *vs.* the molar concentration of tetrahydrofuran in the solutions of some lithium aluminum hydride derivatives: curve 1, $LiAlH_4$; 2, $LiAlH_3(C{\equiv}CC_4H_9)$; 3, $LiAlH_2(C{\equiv}CC_4H_9)_2$; 4, $LiAlH(C{\equiv}CC_4H_9)_3$; 5, $LiAl(C{\equiv}CC_4H_9)_4$; 6, no solute.

The two solutes which are most highly complexed with tetrahydrofuran are lithium aluminum hydride and diphenylamide. That the latter forms a ditetrahydrofuranate is perhaps surprising in view of the fact that the compound $LiAlH_2[N(C_6H_5)_2]_2$ does not react further with diphenylamine,[5] presumably because of steric factors.

Solubility generally decreases as the hydrogens in $LiAlH_4$ are replaced by other groups. Some increase in solubility is usually produced by the presence of tetrahydrofuran.

The solubilities of the derivatives of the smaller alcohols, *e.g.*, $LiAlH_3(OCH_3)$, are less than those of the derivatives of the larger alcohols, *e.g.*, $LiAlH_3(n\text{-}OC_3H_7)$.

Although $LiAl(OCH_3)_4$ is insoluble in ether–tetrahydrofuran or ether–methanol mixtures, it is soluble in ether–ethanol mixtures; and, although $LiAl(OC_2H_5)_4$ is insoluble in ether–tetrahydrofuran and ether–ethanol mixtures, it is soluble in ether plus methanol. The mixed compounds $LiAl(OC_2H_5)_n(OCH_3)_{4-n}$ are soluble in mixtures of ether and either methanol or ethanol. The mixed compound $LiAl(OC_2H_5)(OCH_3)_3$ in ether–methanol is an exception.

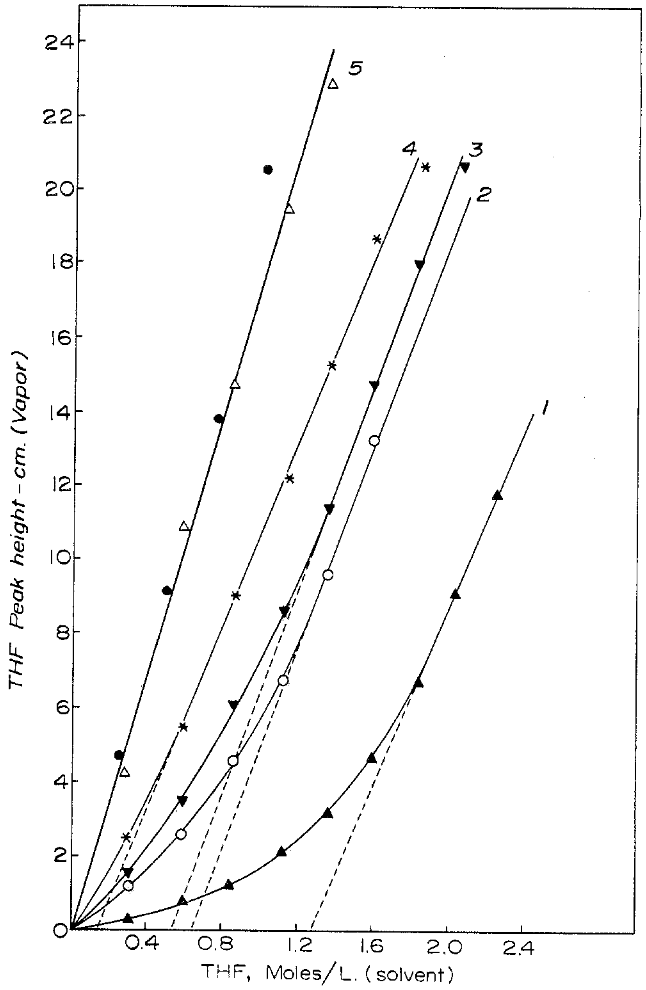

Fig. 3.—Relative concentration of tetrahydrofuran in the vapor (peak height) *vs.* the molar concentration of tetrahydrofuran in solution of some lithium aluminum hydride derivatives: curve 1, $LiAlH_2[N(C_6H_5)_2]_2$; 2, $LiAlH_3(n\text{-}OC_4H_9)$; 3, $LiAlH_2(n\text{-}OC_4H_9)_2$; 4, $LiAlH(n\text{-}OC_4H_9)_3$; 5 (Δ), $LiAl(n\text{-}OC_4H_9)_4$; 5 (●), $LiAl(OCH_3)_4$.

It was observed that in the case of the alcoholates exchange takes place between solute and cosolvent. For example, when ethanol is added to the heterogeneous refluxing system of $LiAl(OC_2H_5)_n(OCH_3)_{4-n}$ in ether, dissolution of the precipitate takes place, and some methanol appears in the vapor. This exchange of the ethoxo and methoxo groups was studied by comparing the ethanol and methanol content in the vapor in equilibrium with solutions of $LiAl(OC_2H_5)_n(OCH_3)_{4-n}$ in ether–methanol and ether–ethanol mixtures. All species of the type $LiAl(OC_2H_5)_n(OCH_3)_{4-n}$-*i.e.*, from $n = 1$ to 4, were used as starting solutes with ethanol as cosolvent and, also, with methanol as cosolvent. In this way the exchange equilibrium was approached from both directions. For some of these systems two values of m are given in Table I. The value in parentheses was obtained by extrapolation of the curve for the cosolvent peak height as illustrated in Fig. 4 for the starting solute $LiAl(OCH_3)_3(OC_2H_5)$ and ethyl alcohol as cosolvent. This value of (m) must include the cosolvent which is bound by chemical exchange as well as that bound by complexing. How-

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(5) G. B. Smith, D. H. McDaniel, E. Biehl, and C. A. Hollingsworth, *J. Am. Chem. Soc.*, **82**, 3560 (1960).

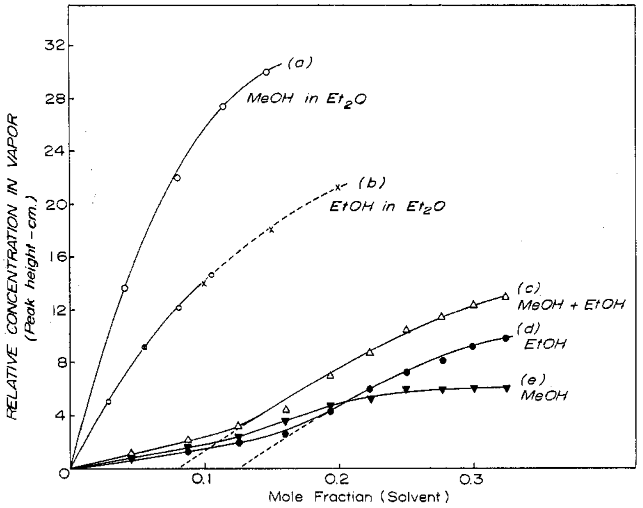

Fig. 4.—Relative concentration of ethanol or methanol in the vapor *vs.* the mole fraction in the solution: curve a, methanol in ether; b, ethanol in ether; c, solute—$LiAl(OCH_3)_3OC_2H_5$, methanol plus methanol equivalent of ethanol peak height; solvent was ethanol in ether; d, solute—$LiAl(OCH_3)_3OC_2H_5$), ethanol peak height; solvent was ethanol in ether; e, solute—$LiAl(OCH_3)_3OC_2H_5$, methanol peak height; solvent was ethanol in ether. Points designated ×, curve b, were calculated from literature data.

ever, since the ethanol–ether system and the methanol–ether system do not obey Henry's law (see Fig. 4), and the mixture ethanol–methanol–ether can be expected to deviate similarily from Henry's law, an additional uncertainty is thereby introduced into the meaning of the values of (m). The values of m, without the parentheses, were obtained from plots of "total alcohol" peak heights. The "total alcohol" peak height was obtained by adding to the methanol peak height an appropriately scaled ethanol peak height, where the scaling factor was obtained from the alcohol–ether (no solute) curves (Fig. 4). Thus, those values of m not in parentheses should give the number of alcohol molecules per molecule of solute bound by complexing.

By assuming that the value of m is 1 and by use of the ratio of the methanol to ethanol peak heights, it was possible to calculate the ratio of total methoxo to ethoxo groups bound as a function of the ratio of methanol to ethanol free. These results are shown in Fig. 5. They are scattered about the linear plot $[(M)/(E)]_b = K[(M)/(E)]_f$ with $K = 1.4$, where $[(M)/(E)]_b$ and $[(M)/(E)]_f$ represent methoxo to ethoxo bound and methanol to ethanol free, respectively. No distinction can be made here between alcohol bound as alkoxo groups and that complexed as alcohol. The linear relationship is consistent with a pseudo-one-step type of mechanism, represented by one equilibrium constant K, and suggests (but is not proof of) independence of reactivity of groups (see Appendix).

Exchange reactions of other alcohols such as methyl with n-butyl and ethyl with n-butyl were observed to take place, but their equilibria have not been investigated.

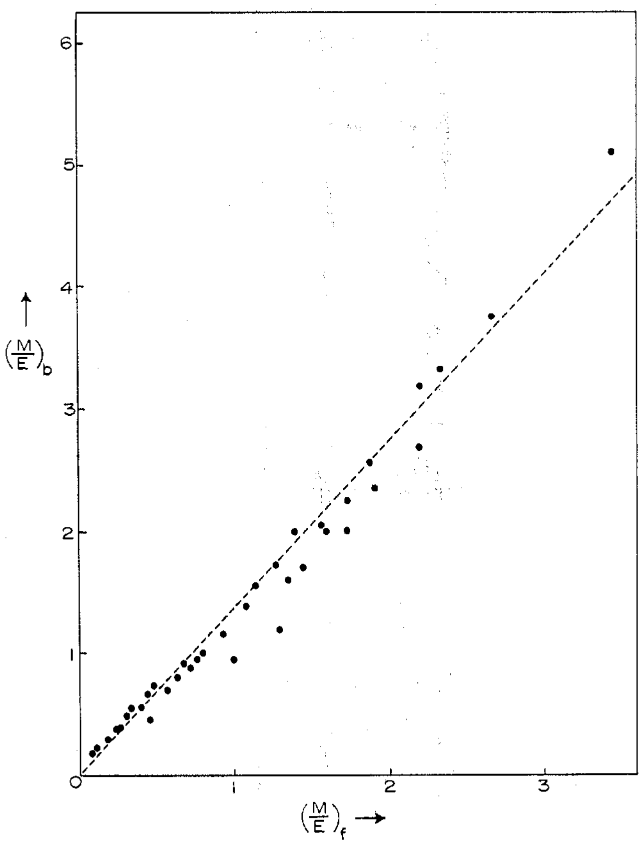

Fig. 5.—Ratio of methoxo to ethoxo groups bound *vs.* ratio of methanol to ethanol free in ethyl ether–methanol–ethanol systems containing solutes $LiAl(OC_2H_5)_n(OCH_3)_{4-n}$.

Appendix

It is clear that the values of m have a degree of uncertainty in their meaning when the solute–cosolvent complex is not sufficiently stable or when there may be more than one solute–cosolvent species present. Although the mathematical analysis presented in this section cannot really solve this problem, it does help to clarify the situation and to permit a better estimate of the significance of the experimental results.

Consider an exchange reaction which can be represented by m steps as follows

$$\left.\begin{array}{r} MQ_m + P \rightleftharpoons MQ_{m-1}P + Q \\ MQ_{m-1}P + P \rightleftharpoons MQ_{m-2}P_2 + Q \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ MQP_{m-1} + P \rightleftharpoons MP_m + Q \end{array}\right\} \qquad (I)$$

where the equilibrium expression for the ith step is

$$\frac{[MQ_{m-i}P_i][Q]}{[MQ_{m-i+1}P_{i-1}][P]} = K_i \qquad (1)$$

We neglect variations in activity coefficients and assume that the brackets [ ] indicate molar concentrations.

If β and φ are defined as the mole ratios

$$\beta = \left[\frac{P}{Q}\right]_{\text{bound}} \text{ and } \varphi = \left[\frac{P}{Q}\right]_{\text{free}} \qquad (2)$$

then it follows that

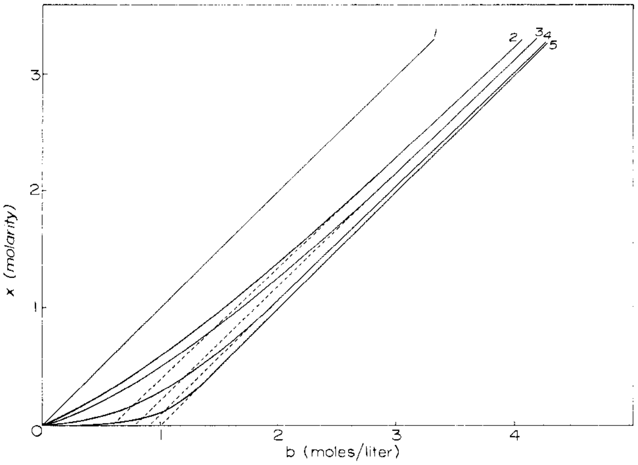

Fig. 6.—Curves illustrating the behavior of eq. 14. Curve 1, no solute; curves 2, 3, 4, and 5 are for K/s = 1, 2, 10, and 100, respectively.

$$\beta = \frac{K_1\varphi + 2K_1K_2\varphi^2 + \ldots + mK_1K_2\ldots K_m\varphi^m}{m + (m-1)K_1\varphi + (m-2)K_1K_2\varphi^2 + \ldots + K_1K_2\ldots K_{m-1}\varphi^{m-1}} \quad (3)$$

We are interested here in cases for which the experimental data are equivalent to values of β as a function of φ. Even when experimental accuracy is not a problem, it is not likely that one can have sufficient confidence in the assumption of constant activity coefficients to consider very meaningful the use of eq. 3 to obtain the values of several equilibrium constants. Thus, when m is larger than one or two, further assumptions to reduce the number of parameters in eq. 3 will ordinarily be necessary. One assumption, which may correspond to a realistic physical model and leads to a one-parameter result, is the assumption of independent reactivity as described by the equations

$$k_1 = mk,\ k_2 = (m-1)k,\ \ldots,\ k_m = k$$

$$k_1^* = k^*,\ k_2^* = 2k^*,\ \ldots,\ k_m^* = mk^* \quad (4)$$

where k_i and k_i^* are the forward and reverse rate constants of the ith step, *i.e.*

$$\mathrm{MQ}_{m-i+1}\mathrm{P}_{i-1} + \mathrm{P} \underset{k_i^*}{\overset{k_i}{\rightleftharpoons}} \mathrm{MQ}_{m-i}\mathrm{P}_i + \mathrm{Q}$$

In this case the equilibrium constants are related by

$$K_i = \frac{k_i}{k_i^*} = \frac{(m-i+1)}{i}K \quad (5)$$

where

$$K = k/k^* \quad (6)$$

Substitution into eq. 3 leads to

$$\beta = K\varphi \quad (7)$$

Thus, as one would expect from physical considerations, independent reactivity as described by eq. 4 leads to a pseudo-one-step process.

Another assumption that one may wish to try in some cases is to suppose that all of the equilibrium constants are equal

$$K_i = K\ (i = 1, 2, \ldots, m) \quad (8)$$

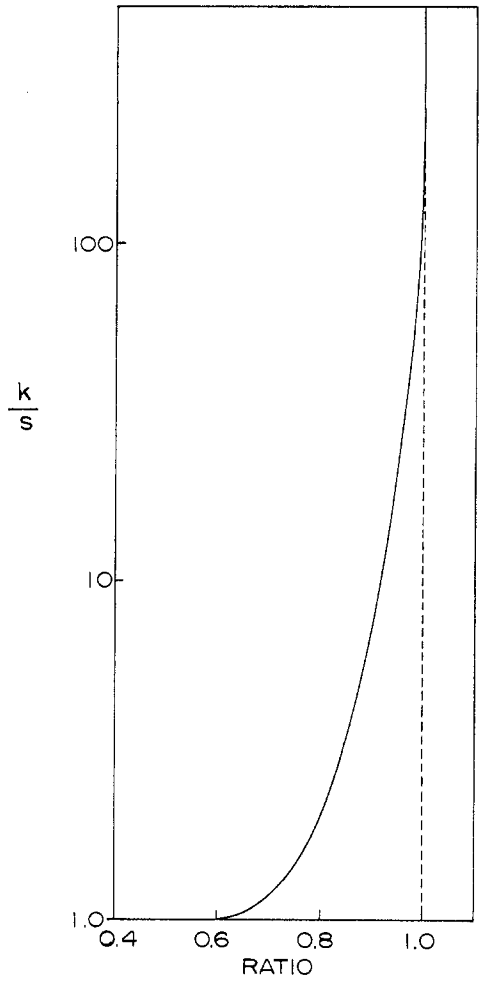

Fig. 7.—Ratio of the value obtained by linear extrapolation to the true value of m as a function of K/s.

This leads to

$$\beta = K\varphi\left(\frac{1 - (m+1)(K\varphi)^m + m(K\varphi)^{m+1}}{m - (m+1)K\varphi + (K\varphi)^{m+1}}\right) \quad (9)$$

Comparison of conditions (8) with (5) shows that the latter corresponds to a case in which replacement of P by Q becomes progressively more favorable as the extent of replacement increases. The analogous case in which there is a progressive decrease in the tendency for P to replace Q as more Q is replaced could be treated by using the reverse of reactions I and the reciprocal of β, φ, and K in eq. 9.

To obtain a third approximation involving only one apparent equilibrium constant one might neglect all species $\mathrm{MQ}_{m-i}\mathrm{P}_i$ except MQ_m and MP_m. In this case eq. 3 reduces to

$$\beta = K\varphi^m \quad (10)$$

where

$$K = K_1K_2\ldots K_m \quad (11)$$

This corresponds to the assumption that

$$K_m \gg K_i\ (i = 1, 2, \ldots, m-1) \quad (12)$$

All of the applications in the previous sections were for systems in which m = 1 or 2, or for which conditions (4) were, apparently, a reasonable approximation. Therefore, much of the subsequent discussion is restricted to eq. 7 and modifications of it. Our applications were also restricted to the case in which Q is the solvent, always present in large excess, and P is a cosolvent, present in limited amounts. If we treat [Q] as a constant, Q, eq. 7 can be written

$$\frac{p - [\mathrm{P}]}{(mM - p + [\mathrm{P}])[\mathrm{P}]} = \frac{K}{Q} \tag{13}$$

where p represents the total cosolvent (bound plus free) per liter, and M represents the total moles of solute per liter, *i.e.*, $M = \sum_i [\mathrm{MQ}_{m-i}\mathrm{P}_i]$.

To obtain a picture of the general behavior of eq. 13, it is convenient to use the form

$$\frac{b - x}{(1 - b + x)x} = \frac{K}{s} \tag{14}$$

where $x = [\mathrm{P}]/mM$, $b = p/mM$, and $s = Q/mM$. That is, x, b, and s are, respectively, the ratios of the moles of the free cosolvent, the total cosolvent, and the solvent to the total moles of solvent plus cosolvent bound. In the notation of eq. 14, the case in which the cosolvent does not complex (*i.e.*, $K = 0$) corresponds to the line $x = b$, and complexing is indicated by displacement from that line. Perhaps the easiest way to picture the behavior, according to eq. 14, is from plots such as those shown in Fig. 6. These curves approach their linear asymptote

$$x = b - 1 \tag{15}$$

closely when K/s is 10 or larger. When K/s is 2 or smaller, a fairly large error would be obtained by extrapolation of that portion of the curve that appears to be linear. The ratio of the value of m obtained by such extrapolation to the true value of m is shown as a function of log (K/s) in Fig. 7.

It will be noted that the linear portions of the curves in Fig. 6 have almost reached their limiting slope even when they are not yet close to the asymptote. This means that one should not use the slope (for example, by comparing it with the slope of the Henry's law line for the solvent–cosolvent system without solute) as a criterion to decide if extrapolation is justified. On the other hand, failure of the curve to become parallel to the Henry's law line for the solvent–cosolvent system does not necessarily mean that extrapolation would be bad, since there is no guarantee that the presence of the solute does not change the Henry's law constant for the cosolvent.

It, perhaps, should be mentioned that because [Q] was assumed constant to obtain eq. 13 and 14, these results also apply to equilibria of the type

$$\mathrm{M} + \mathrm{P} \rightleftharpoons \mathrm{MP}$$
$$\mathrm{MP} + \mathrm{P} \rightleftharpoons \mathrm{MP}_2$$

etc., in which the solvent is not involved, provided the independent reactivity corresponding to conditions (4) can be used as an approximation for cases in which $m > 1$.

With the same notation as that used in eq. 14, eq. 3 for $m = 2$ can be expressed

$$\frac{b - x}{(1 - b + x)x} = \frac{K_1}{s}\left(\frac{1 + 2(K_2/s)x}{2 + (K_1/s)x}\right) \tag{16}$$

where, again we have used $s \cong$ constant.

The relationship in form between eq. 16 and 14 emphasizes the difficulty which might be encountered in attempts to separate the effects of experimental errors or variations in activity coefficients from deviations from conditions (4). The values of m obtained by extrapolation should not be very sensitive to small experimental errors or variations in the activity coefficients. Also, it was found that the experimental values of m were not changed significantly by the use of mole fraction or volume fraction in place of the molarity of cosolvent. However, values of K calculated from eq. 13, 14, or 16 can be very greatly affected by small errors, particularly along the linear part of the curve where the quantity $mM - p + [\mathrm{P}]$, or $1 - b - x$, is approaching zero, and the effect of an error, say in [P], can be greatly magnified in K.