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Ion Exchange Studies of Zinc Chloride and/or Perchlorate in Ethylene Glycol

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The formation constants of zinc chloride and/or perchlorate in ethylene glycol were measured by a cation exchange method using the resin for forced-flow liquid chromatography in three systems: zinc chloride, zinc perchlorate, and zinc chloride and perchlorate together. The values obtained for the formation constants were: $\log\beta_1^{\mathrm{Cl}}=3.03$, $\log\beta_2^{\mathrm{Cl}}=4.80$, $\log\beta_1^{\mathrm{ClO_4}}=2.34$, and $\log\beta_2^{\mathrm{ClO_4}}=2.50$. The formation constant for the mixed complex of zinc, $\log k_{\mathrm{m}}^{\mathrm{ClO_4}}$, was 0.7 at the ionic strength of 0.1. The formation constants of zinc chloride in ethylene glycol containing 5 v/v% of water were 2.73 for $\log\beta_1^{\mathrm{Cl}}$ and 4.18 for $\log\beta_2^{\mathrm{Cl}}$, and those containing 10% of water were 2.32 for $\log\beta_1^{\mathrm{Cl}}$ and 3.46 for $\log\beta_2^{\mathrm{Cl}}$.

There are many methods to investigate the chemical equilibria of metal-ion complexes in aqueous solution, such as photometry, polarography, conductivity measurement, ion exchange method,[1-8] solvent extraction,[9-11] and potentiometric measurement.[12] However, the detailed studies in nonaqueous solution have been so far performed mainly by electrochemical methods. The cation exchange method using a radioactive tracer is expected to be available for studies of the chemical equilibria in nonaqueous systems. The method may be applicable to sparingly soluble compounds in nonaqueous solvents by the rise in specific activities of radio isotopes. The resins for the forced-flow liquid chromatography may withstand most of the organic solvents and attain equilibrium fairly rapidly with the ions in the solvents, compared with the ordinary ion exchangers. In the previous paper,[14] we investigated the distribution of zinc chloride and bromide complexes between the aqueous methanol solution and the cation exchange resin. The present work has extended the research to the distribution of zinc chloride and perchlorate between the cation exchange resin and ethylene glycol and has estimated the consecutive formation constants of zinc chloride and perchlorate by using a computer.

Data Treatment

The equilibria in the ethylene glycol solutions are expressed as follows:

$$\mathrm{Zn^{2+} + 2Cl^- = ZnCl_2} \qquad \beta_1^{\mathrm{X}},\ \beta_2^{\mathrm{X}}, \tag{1}$$

$$\mathrm{Zn^{2+} + 2ClO_4^- = Zn(ClO_4)_2} \qquad \beta_1^{\mathrm{Y}},\ \beta_2^{\mathrm{Y}}, \tag{2}$$

$$\mathrm{ZnCl^+ + ClO_4^- = ZnClClO_4} \qquad K_{\mathrm{m}}^{\mathrm{Y}}, \tag{3}$$

$$\mathrm{ZnClO_4^+ + Cl^- = ZnClClO_4} \qquad K_{\mathrm{m}}^{\mathrm{X}}, \tag{4}$$

$$\mathrm{Zn^{2+} + Na_2R = ZnR + 2Na^+} \qquad \beta_1^{\mathrm{R}},\ \beta_2^{\mathrm{R}}, \tag{5}$$

$$\mathrm{ZnCl^+ + Na_2R = ZnClNaR + Na^+} \qquad K_{\mathrm{m}}^{\mathrm{RX}}, \tag{6}$$

$$\mathrm{ZnClO_4^+ + Na_2R = ZnClO_4NaR + Na^+} \qquad K_{\mathrm{m}}^{\mathrm{RY}}. \tag{7}$$

Here the superscripts are $\mathrm{X{=}Cl^-}$ and $\mathrm{Y{=}ClO_4{}^-}$. Concentrations of zinc in two phases are described as

$$\begin{aligned}(C_{\mathrm{Zn}})_{\mathrm{R}} &= C_{\mathrm{ZnR}} + C_{\mathrm{ZnXNaR}} + C_{\mathrm{ZnYNaR}}\\ &= m_{\mathrm{ZnR}} + m_{\mathrm{ZnXNaR}} + m_{\mathrm{ZnYNaR}},\end{aligned} \tag{8}$$

$$\begin{aligned}(C_{\mathrm{Zn}})_{\mathrm{E}} &= C_{\mathrm{Zn}} + C_{\mathrm{ZnX}} + C_{\mathrm{ZnX_2}} + C_{\mathrm{ZnY}}\\ &\quad + C_{\mathrm{ZnY2}} + C_{\mathrm{ZnXY}}\\ &= (m_{\mathrm{Zn}} + m_{\mathrm{ZnX}} + m_{\mathrm{ZnX_2}} + m_{\mathrm{ZnY}} + m_{\mathrm{ZnY_2}} + m_{\mathrm{ZnXY}})/\rho,\end{aligned} \tag{9}$$

$$D = (C_{\mathrm{Zn}})_{\mathrm{R}}/(C_{\mathrm{Zn}})_{\mathrm{E}}. \tag{10}$$

Here $(C_{\mathrm{Zn}})_{\mathrm{R}}$ is total zinc in the resin at equilibrium, $(C_{\mathrm{Zn}})_{\mathrm{E}}$ is total zinc in the solution at equilibrium, m_{X} is weight molarity and ρ is density. The distribution ratio, D, of zinc can be expressed as the ratio of $(C_{\mathrm{Zn}})_{\mathrm{R}}$ and $(C_{\mathrm{Zn}})_{\mathrm{E}}$. Equations 8—10 can be rewritten using equations 1—7 as follows:

$$\begin{aligned}(C_{\mathrm{Zn}})_{\mathrm{R}} &= \left(\frac{\gamma_{\mathrm{Zn}}m_{\mathrm{Zn}}}{\gamma_{\mathrm{ZnR}}\gamma_{\mathrm{Na}}^2 m_{\mathrm{Na}}^2}\cdot\beta_2^{\mathrm{R}} + \frac{\gamma_{\mathrm{Zn}}\gamma_{\mathrm{X}}m_{\mathrm{Zn}}m_{\mathrm{X}}}{\gamma_{\mathrm{Na}}\gamma_{\mathrm{ZnXNaR}}m_{\mathrm{Na}}}\cdot K_{\mathrm{m}}^{\mathrm{RX}}\beta_1^{\mathrm{X}}\right.\\ &\quad\left. + \frac{\gamma_{\mathrm{Zn}}\gamma_{\mathrm{Y}}m_{\mathrm{Zn}}m_{\mathrm{Y}}}{\gamma_{\mathrm{Na}}\gamma_{\mathrm{ZnYNaR}}m_{\mathrm{Na}}}\cdot K_{\mathrm{m}}^{\mathrm{RY}}\beta_1^{\mathrm{Y}}\right)\cdot\gamma_{\mathrm{Na_2R}}m_{\mathrm{Na_2R}},\end{aligned} \tag{8'}$$

$$\begin{aligned}(C_{\mathrm{Zn}})_{\mathrm{E}} &= \left(m_{\mathrm{Zn}} + \frac{\gamma_{\mathrm{Zn}}\gamma_{\mathrm{X}}m_{\mathrm{Zn}}m_{\mathrm{X}}}{\gamma_{\mathrm{ZnX}}}\cdot\beta_1^{\mathrm{X}} + \frac{\gamma_{\mathrm{Zn}}\gamma_{\mathrm{X}}^2 m_{\mathrm{Zn}}m_{\mathrm{X}}^2}{\gamma_{\mathrm{ZnX_2}}}\cdot\beta_2^{\mathrm{X}}\right.\\ &\quad + \frac{\gamma_{\mathrm{Zn}}\gamma_{\mathrm{Y}}m_{\mathrm{Zn}}m_{\mathrm{Y}}}{\gamma_{\mathrm{ZnY}}}\cdot\beta_1^{\mathrm{Y}} + \frac{\gamma_{\mathrm{Zn}}\gamma_{\mathrm{Y}}^2 m_{\mathrm{Zn}}m_{\mathrm{Y}}^2}{\gamma_{\mathrm{ZnY_2}}}\cdot\beta_2^{\mathrm{Y}}\\ &\quad\left. + \frac{\gamma_{\mathrm{Zn}}\gamma_{\mathrm{X}}\gamma_{\mathrm{Y}}m_{\mathrm{Zn}}m_{\mathrm{X}}m_{\mathrm{Y}}}{\gamma_{\mathrm{ZnXY}}}\cdot\beta_1^{\mathrm{X}}K_{\mathrm{m}}^{\mathrm{Y}}\right)\Big/\rho,\end{aligned} \tag{9'}$$

$$\begin{aligned}D &= \gamma_{\mathrm{Zn}}m_{\mathrm{Na_2R}}\rho\cdot\left\{\frac{\beta_2^{\mathrm{R}}}{\gamma_{\mathrm{Na}}^2 m_{\mathrm{Na}}^2} + \frac{\gamma_{\mathrm{X}}m_{\mathrm{X}}}{\gamma_{\mathrm{Na}}m_{\mathrm{Na}}}\cdot K_{\mathrm{m}}^{\mathrm{RX}}\beta_1^{\mathrm{X}}\right.\\ &\quad\left. + \frac{\gamma_{\mathrm{Y}}m_{\mathrm{Y}}}{\gamma_{\mathrm{Na}}m_{\mathrm{Na}}}\cdot K_{\mathrm{m}}^{\mathrm{RY}}\beta_1^{\mathrm{Y}}\right\}\Big/\\ &\quad\{1 + \Sigma\gamma_{\mathrm{X}}^{\mathrm{n}}m_{\mathrm{X}}^{\mathrm{n}}\beta_{\mathrm{n}}^{\mathrm{X}} + \Sigma\gamma_{\mathrm{Y}}^{\mathrm{n}}m_{\mathrm{Y}}^{\mathrm{n}}\beta_{\mathrm{n}}^{\mathrm{Y}} + \gamma_{\mathrm{X}}\gamma_{\mathrm{Y}}m_{\mathrm{X}}m_{\mathrm{Y}}\beta_1^{\mathrm{X}}K_{\mathrm{m}}^{\mathrm{Y}}\}.\end{aligned} \tag{10'}$$

Here γ stands for the activity coefficient of each ion, $\gamma_{\mathrm{Na_2R}}$, γ_{ZnR}, γ_{ZnXR}, and γ_{ZnYR} can be regarded as 1 and $\gamma_{\mathrm{ZnX}}=\gamma_{\mathrm{ZnY}}$, $\gamma_{\mathrm{ZnX_2}}=\gamma_{\mathrm{ZnY_2}}=\gamma_{\mathrm{ZnXY}}\cdot\gamma_{\mathrm{X}}$, γ_{Y}, γ_{Zn}, and γ_{Na} are calculated from Debye-Hückel's theory as

$$\gamma_{\mathrm{X}} = \gamma_{\pm}{}^{1/2} = \left\{\frac{-A|\mathrm{Z^+Z^-}|I^{1/2}}{1+BdI^{1/2}}\right\}^{1/2}, \tag{11}$$

$$A = 8.1622\times\frac{\rho^{1/2}}{\varepsilon^{3/2}}\times10^2 \quad B = 2.9127\times\left\{\frac{\rho}{\varepsilon}\right\}^{1/2}\times10^8 \quad \text{at } 25\ {}^\circ\mathrm{C}. \tag{12}$$

Here d denotes parameter of ionic radius, I represents ionic strength, $m_{\mathrm{Na_2R}}$ is expressed as g resin (Na-form)/dm^3 ethylene glycol, and ε is the dielectric constant of ethylene glycol. The constant of 5% aqueous ethylene glycol was obtained graphically by interpolation of the constants of 100, 90, and 80% ethylene glycol.[13]

In the Zn^{2+}-Cl^--ClO_4^- system, the distribution coefficient can be transformed as a function of chloride ion concentration, m_X, because m_X+m_Y=const. Sodium ions are originated from sodium chloride and sodium perchlorate, and these compounds are assumed to be completely dissociated in pure or aqueous ethylene glycol. Hence the relation that $m_{Na}=m_X+m_Y$ holds good. β_1^R is negligible, because it is expected that $\beta_2^R \gg \beta_1^R$. Equation 10 is arranged into fractional functions as follows:

1. ($X=Cl$ or ClO_4)

$$D^* = \frac{P_{(1)}+P_{(2)}L^2}{1+P_{(3)}L+P_{(4)}L^2} \tag{13}$$

$L=\gamma_X m_X$, $D^*=D\gamma_{Na}^2 m_{Na}^2/\gamma_{Zn}$, $P_{(1)}=\beta_2^R m_{Na_2R}$, $P_{(2)}=\beta_1^X K_m^{RX} m_{Na_2R}$, $P_{(3)}=\beta_1^X$, and $P_{(4)}=\beta_2^R$.

2. ($X=Cl$ and $Y=ClO_4$)

$$D^* = \frac{P_{(1)}+P_{(2)}m_X+P_{(3)}m_Y}{1+P_{(4)}m_X+P_{(5)}m_X^2+P_{(6)}m_Y+P_{(7)}m_Y^2+P_{(8)}m_Xm_Y} \tag{14}$$

$D^*=D\gamma_{Na}^2 m_{Na}^2/\gamma_{Zn}$, $P_{(1)}=m_{Na_2R}\beta_2^R$,
$P_{(2)}=m_{Na_2R}\beta_1^X K_m^{RX}\gamma_X\gamma_{Na}m_{Na}m_X$,
$P_{(3)}=m_{Na_2R}\beta_1^Y K_m^{RY}\gamma_{Na}\gamma_Y m_{Na}m_Y$, $P_{(4)}=\gamma_X\beta_1^X$,
$P_{(5)}=\gamma_X{}^2\beta_2^X$, $P_{(6)}=\gamma_Y\beta_1^Y$, $P_{(7)}=\gamma_Y{}^2\beta_2^Y$,
$P_{(8)}=\gamma_X\gamma_Y m_X m_Y\beta_1^X K_m^Y$.

γ_X, γ_Y, γ_{Na}, and γ_{Zn} were calculated from Eqs. 11 and 12 as a function of the ionic strength. These coefficients have constant values at constant ionic strenth. Parameters P_i were calculated by the nonliner least-squares method, a modified Gauss-Newton method, using a computer and were determined by enlisting the aid of a curve fitting method using computer graphics.

Experimental

Ethylene glycol was purified by distilling it under reduced pressure after drying over zeolite and was stored in closed bottles. Zinc-65 tracer was supplied as chloride by New England Nuclear, Boston, Mass., U.S.A. It was heated on a hot plate, adding perchloric acid to convert it into a zinc perchlorate form, and was dissolved in ethylene glycol. Sodium chloride and sodium perchlorate were dried at 110 °C and stored over phosphrous pentaoxide in a desiccator. Perchloric acid, sodium chloride, sodium perchlorate, and zinc perchlorate were guaranteed reagent grade. The cation exchange resin (mean radius, 15.5 μm), Hitachi custom ion exchange resin 2611 for the liquid chromatograph, was washed with hydrochloric acid and was transformed into the Na-form by sodium chloride solution. After washed with water to remove chloride ion, the resin was dried in vacuum and stored in a desiccator.

From 25 to 100 mg of the resin was taken in an Erlenmyer flask with a glass-stopper, and 20 ml of ethylene glycol solution containing sodium chloride and/or sodium perchlorate, zinc perchlorate, perchloric acid, and a radio-zinc tracer was added. Perchloric acid was added to minimize the loss of zinc that was caused by the adsorption on the vessel wall. The flask was set in the water bath with a thermostat at 25 °C and stirred by a teflon-coated bar. After the equilibrium was attained, both the solution and the resin were transferred to a centrifugal tube, and the two phases were separated centrifugally. Distribution coefficients were calculated from the ratio of radioactivity between the two phases. Two milliliters of solution phase were pipetted into a test tube and radioactivities were counted by a well-type scintillation counter (Metro Electronics Model PbW-6).

Results and Discussion

The attainment of the distribution equilibrium was checked by measuring the variation of the distribution coefficient of zinc *vs.* the stirring time. As shown in Fig. 1, little influence of the stirring time was observed upon the distribution of zinc between the glycol phase and the resin; the distribution attained equilibrium within 1 h at the latest and varied little within at least 48 h.

Stirring for 24 h was adopted in the experiment, because ethylene glycol has a somewhat higher viscosity than water, and then the resin was more difficult to disperse in the glycolic solution than in the aqueous one. The correct distribution coefficients can not be observed in high concentration range of zinc because of the comparatively low exchange capacity of the resin and in very low zinc concentration because of the adsorption on the resin. Figure 2 shows the influence of zinc perchlorate concentration on the distribution coefficients. The coefficients have a constant value for solutions ranging in concentration from 5×10^{-7} to 10^{-4} mol dm^{-3}. Therefore the initial zinc concentration was kept at 1×10^{-6} mol dm^{-3} throughout the experiment. It is expected from Eq. 10 that there exist a proportional relation between the distribution coeffi-

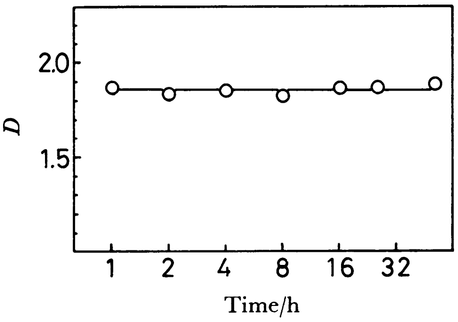

Fig. 1. Influence of stirring time.
NaCl: 0.05 mol dm^{-3}, resin: 2.5 g dm^{-3}, $Zn(ClO_4)_2$: 1×10^{-6} mol dm^{-3}.

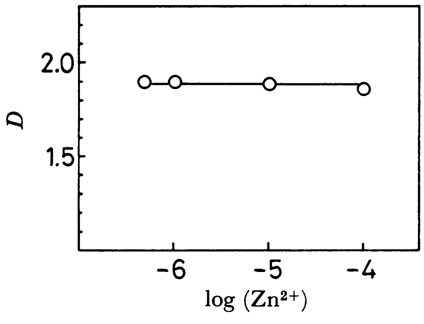

Fig. 2. Influence of initial zinc concentration.
NaCl: 0.05 mol dm^{-3}, resin: 2.5 g dm^{-3}.

cient and the resin amount. The relation is shown in Fig. 3; plots of log D^* *vs.* the resin amount give straigth lines with the slope of about 1 in the various concentrations of sodium perchlorate and chloride.

Figures 4—7 show the plot of log D^* *vs.* a_{Cl} or $a_{\mathrm{ClO_4}}$ on the distribution of zinc chloride and perchlorate between the glycol phase and the ion exchanger; the concentrations of chloride and perchlorate ions in the figures are converted into the activities by using Debye-Hückel's theory. The curves in these figures are depicted by means of regression analysis on Eqs. 13—

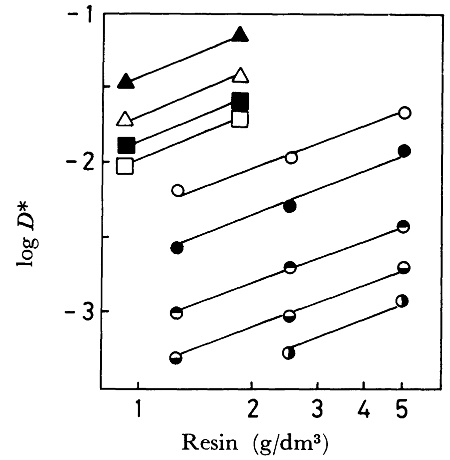

Fig. 3. Effect of resin amount in sodium chloride and sodium perchlorate system.
▲: $NaClO_4$ 0.02 mol dm^{-3}, △: $NaClO_4$ 0.04 mol dm^{-3}, ■: $NaClO_4$ 0.1 mol dm^{-3}, □: $NaClO_4$ 0.2 mol dm^{-3}, ○: NaCl 0.02 mol dm^{-3}, ●: NaCl 0.04 mol dm^{-3}, ◓: NaCl 0.07 mol dm^{-3}, ◒: NaCl 0.1 mol dm^{-3}, ◑: NaCl 0.2 mol dm^{-3}.

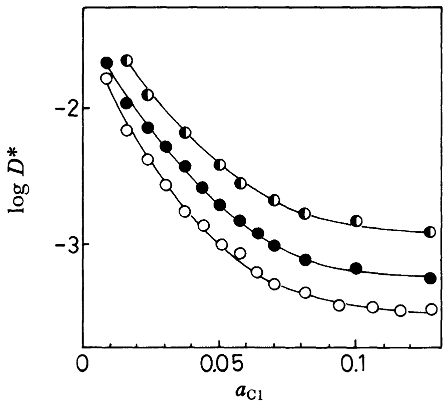

Fig. 4. Distribution coefficients of zinc chloride system.
○: Resin 1.27 g dm^{-3}, ●: resin 2.52 g dm^{-3}, ◐: resin 5.0 g dm^{-3}.

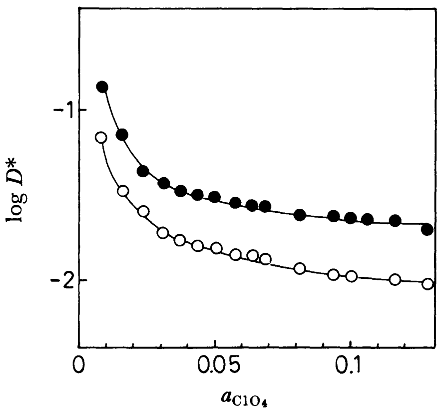

Fig. 5. Distribution coefficients of zinc perchlorate system.
○: Resin 0.909 g dm^{-3}, ●: resin 1.82 g dm^{-3}.

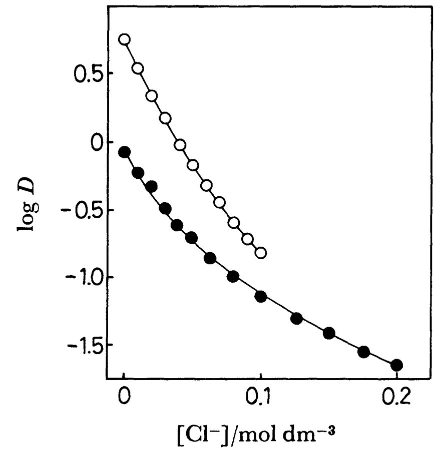

Fig. 6. Distribution coefficients of zinc at constant ionic strength (zinc–sodium chloride–sodium perchlorate system).
○: Ionic strength 0.1, ●: ionic strength 0.2, resin 2.5 g dm^{-3}

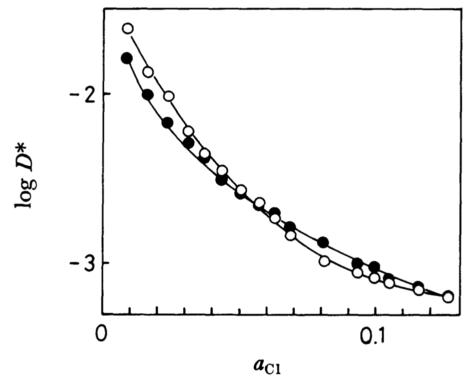

Fig. 7. Distribution coefficients of zinc chloride in the ethylene glycol solutions containing water.
○: 5% water ethylene glycol, resin 1.82 g dm^{-3}.
●: 10% water ethylene glycol, resin 1.36 g dm^{-3}.

TABLE 1. FORMATION CONSTANTS OF ZINC CHLORIDE AND ZINC PERCHLORATE

log β	β_1^{X}	β_2^{X}	$K_{\mathrm{m}}^{\mathrm{X}}$
X=Cl, pure E.G.	3.03±0.05	4.80±0.05	—
X=Cl, 5% water-E.G.	2.73±0.05	4.18±0.05	—
X=Cl, 10% water-E.G.	2.32±0.06	3.46±0.06	—
X=ClO_4	2.34±0.07	2.50±0.07	—
Ionic strength 0.1	—	—	0.7±0.1

E.G.=Ethylene glycol.

14, and these show good accordance with the experimental data. The formation constants of zinc chloride and perchlorate are listed in Table 1.

In the zinc chloride and perchlorate system, the number of parameters in Eq. 14 are too many to get exact values. Consequently, the values of β_n^X and β_n^Y in Eq. 14 were calculated by substituting β_n^X and β_n^Y obtained in the zinc chloride and zinc perchlorate system in Eq. 13. The values of the formation constant obtained by the present ion exchange method are close to those determined by the nonaqueous liquid-liquid extraction method.[10]

The ion exchange method has a bright prospect for developing research on the chemical equilibria of metals in the nonaqueous system, especially in terms of the application to the sparing by soluble salts in nonaqueous solvent.

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