Nomenclature

$\bar{d}_B$	= average bubble diameter (Sauter)	[m]
I	= electric current flowing between electrodes	[A]
L	= electrode gap distance	[m]
M	= gas flow rate	[m³/s]
P	= hydrostatic pressure	[Pa]
V	= applied dc voltage	[kV]
W	= total energy imposed on system (PM + VI)	[W]
γ	= surface tension of liquid	[Pa·m]
η	= energy efficiency defined by Eq. (1)	[%]
κ	= specific electric conductivity of liquid	[S/m]

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ADSORPTION EQUILIBRIA OF MOISTURE IN ORGANIC SOLVENTS ON MOLECULAR SIEVE AND ION-EXCHANGE RESIN

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The moisture content of some organic solvents such as transformer oils, fuel oils and refrigerants must be reduced as low as possible because the presence of moisture in those solvents causes poor insulation, corrosion of apparatus and freezing, respectively. In some cases of organic synthetic reactions, moisture in liquid reactions may poison the catalysts.

Liquid-phase adsorption may be useful for drying organic solvents. The drying of several organic solvents including benzene, butadiene, isoprene, cyclohexane and *n*-heptane has been investigated at 20°C by using drying agents such as silica gel, molecular sieve and alumina.[1] Dynamic drying of xylene, ethyl ether, ethanol and 2-propanol has been studied at room temperature with zeolite-A synthesized from halloysite.[2] Strong acid cation-exchange resins (Dowex 50W) have been used for drying ethanol and 1,1,1-trichloroethane as examples of relatively polar and nonpolar solvents, respectively.[5]

A new periodic operation in which a thermally regenerable ion-exchange resin in a basket was alternately immersed in cold and hot reservoirs has been proposed for desalting water.[3,4] To apply this operation to the drying of organic solvents, the great temperature dependency and the reversibility of adsorption equilibria may be required.

In the present study, adsorption equilibria of moisture in a polar solvent (ethanol) and a nonpolar solvent (benzene) were determined at 10 and 60°C by using two drying agents (molecular sieve and ion-exchange resin).

1. Experiments

Molecular sieve MS-4A, manufactured by Nishio Kogyo Co., Ltd. (8–12 mesh, average diameter = 1.6 mm), and a sodium form of strong acid cation-exchange resin, Dowex HCR-S manufactured by Dow Chemical Co., Ltd. (20–50 mesh, average diameter = 0.57 mm) were used as the drying agents. Prior to the adsorption measurements, the molecular sieve was heated at 400°C in an electric furnace for 4 hours and the ion-exchange resin at 105°C in a

vacuum dry over for 5 days. These drying agents were cooled to room temperature and kept in glass ampoules.

Ethanol and benzene of special reagent grade were used as the organic solvents. The initial concentration of moisture in the organic solvent was adjusted by adding a given amount of distilled water to the organic solvent.

If a conventional adsorption cell with one chamber was used, data were unreliable. Thus, the adsorption cell with two chambers shown in **Fig. 1** was prepared. About 0.1–3.5 g of weighed drying agent was packed in the samll chamber and $4.0 \times 10^{-5}\,m^3$ of organic solvent was poured into the large chamber. Then portion "A" in Fig. 1 was fused and closed by fire. The adsorption cell was immersed in a water bath at a constant temperature of 10 or 60°C. When the cell attained the desired adsorption temperature, the drying agent in the small chamber was transferred to the large chamber and mixed well with the organic solvent.

All adsorption runs were carried out for four days to ensure complete equilibration. At the end of the runs, a part of the organic solvent in the large chamber was moved to the small chamber while the drying agent remained in the large chamber. This was done with care to prevent an additional adsorption or desorption due to changes from the adsorption temperature to room temperature.

Portion "B" in Fig. 1 was cut and $1.0 \times 10^{-6}\,m^3$ of organic solvent in the small chamber was withdrawn with a syringe to obtain the final concentration of water, C_∞. The initial and final concentrations of moisture in the organic solvents were determined by a Karl-Fisher coulometric titrator.

When the above operations were conducted in the atmosphere, moisture in air moved into the adsorption cell and the titrator, and adsorption equilibria data became unreliable. Therefore, an apparatus for dehumidification was arranged as shown in **Fig. 2**. Nitrogen gas from a cylinder was introduced through a liquid nitrogen trap into the dry box, in which the adsorption cell and the titrator were put. After the humidity in the dry box attained a low level of about 15%, contamination from the gas phase could be avoided and reliable data were obtained.

2. Results and Discussion

The equilibrium capacity of drying agent, q_∞, was determined from the difference between initial and final concentrations in the liquid phase.

For two drying agents (MS-4A and HCR-S), the adsorption equilibria of moisture in ethanol are shown in **Fig. 3** and those in benzene in **Fig. 4**. A Langmuir-type expression, Eq. (1), fairly well correlated experimental data for the molecular sieve MS-
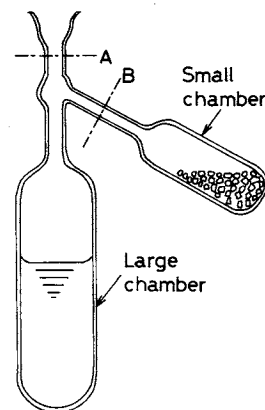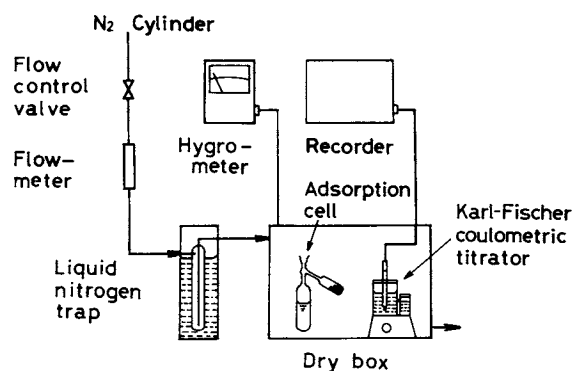

Fig. 1. Adsorption cell.

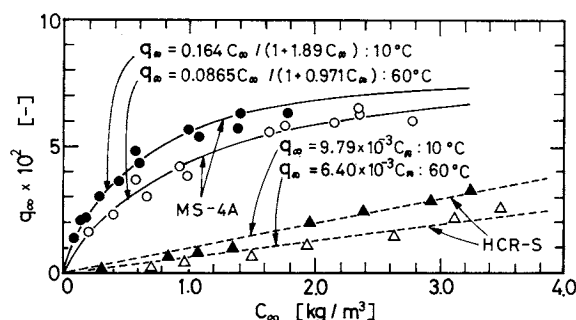**Fig. 2.** Apparatus for dehumidification.

Fig. 3. Adsorption isotherms of moisture in ethanol.

4A and a Henry-type expression, Eq. (2), for the ion-exchange resin HCR-S.

$$q_\infty = K_{L,1} C_\infty / (1 + K_{L,2} C_\infty) \qquad (1)$$

$$q_\infty = K_H C_\infty \qquad (2)$$

The constants, $K_{L,1}$, $K_{L,2}$ and K_H in Eqs. (1) and (2) were determined by the least square method and are shown in Figs. 3 and 4. The solid lines in those figures indicate the results calculated from Eq. (1), the broken lines those from Eq. (2).

It is evident from comparison of Figs. 3 and 4 that the adsorption capacities in ethanol (polar solvent) are much lower than those in benzene (nonpolar solvent). It is considered that both water and ethanol, which are polar materials, may be adsorbed on the
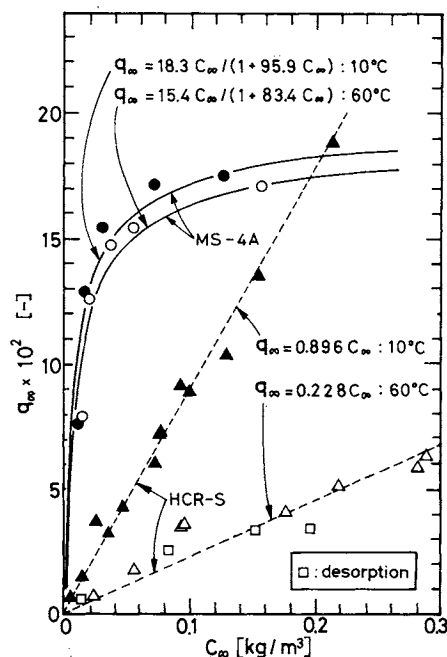
Fig. 4. Adsorption isotherms of moisture in benzene.

adsorbents simultaneously and that the adsorption of water must be hindered by ethanol.

The adsorption capacities at 10°C are higher than those at 60°C for any case, as seen in Figs. 3 and 4. Especially, the effect of temperature on adsorption capacities is most significant for the case of benzene and HCR-S in Fig. 4.

To confirm the reversibility of adsorption, de-

sorption experiments were made as follows. After the adsorption cell with benzene and HCR-S was immersed in the water bath at 10°C for 4 days, it was moved to the water bath at 60°C for 4 days and the final concentration of water C_∞, at 60°C was determined. As shown in Fig. 4, the desorption data are not different from adsorption data, and adsorption is reversible in this case.

Periodic operation may be effective in the case of HCR-S and benzene because of the great temperature dependency and reversibility of adsorption equilibria.

Nomenclature

C_∞	= equilibrium concentration of moisture in organic solvent	[kg-water/m³-solvent]
K_H	= constant in Eq. (2)	[m³/kg]
$K_{L,1}$	= constant in Eq. (1)	[m³/kg]
$K_{L,2}$	= constant in Eq. (1)	[m³/kg]
q_∞	= equilibrium capacity	[kg-water/kg-dry adsorbent]

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