Thermodynamic Quantities of Hydrochloric Acid in Isopropanol–Water, 1,2-Dimethoxyethane–Water, and Tetrahydrofuran–Water Mixtures

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The thermodynamic quantities ΔG^0, ΔS^0, and ΔH^0 for the process of transfer of HCl from water to isopropanol–water, 1,2-dimethoxyethane–water, and tetrahydrofuran–water mixtures have been evaluated from the E_N^0 values and the variations of E_m^0 with temperature. The cell previously used was of the type Pt, H_2 (gas, 1 atm)|HCl(m), organic solvent (X), water (Y| AgCl, Ag. For isopropanol–water mixtures, the electrostatic part of the total Gibbs energy (free energy), entropy, and enthalpy of transfer were calculated using the Born equation and hence the chemical (nonelectrostatic effect of the thermodynamic functions has been obtained by subtracting the electrostatic contribution from the total transfer quantities). The significance of the data in relation to the acid-base properties for all the mixed solvents and the breakdown of the structure of water on the gradual addition of isopropanol have been discussed.

The effect of mixed solvents in the elucidation of reaction mechanisms, acid-base properties, and in the thermodynamics of chemical equilibria has recently been a subject of interest. The properties of hydrochloric acid in dipolar aprotic solvent media such as tetrahydrofuran (THF)-water mixtures containing 18.21, 73.03, and 89.00 wt % tetrahydrofuran (*16, 17*) and 1,2-dimethoxyethane (monoglyme)-water mixtures containing 8.68, 17.81, 46.52, and 67.03 wt % 1,2-dimethoxyethane (*11*) have been derived from thermodynamic data. The hydroxylic solvent (amphiprotic solvent) media, such as isopropanol-water mixtures containing 20.76, 44.04, 70.28, and 87.71 wt % isopropanol (*15*), have also been used as models for understanding the behavior of HCl with regard to the acid-base properties and the changes in the structural effects of the solvents.

The present paper reports our results (the Gibbs energy, entropy, and enthalpy of transfer) on these aspects, since to the knowledge of the authors no data for the thermodynamic quantities of these solvent mixtures are available in the literature. The choice of the mixed solvents (dipolar aprotic-water and amphiprotic-water) needs justification. Dipolar aprotic solvents have been observed to strongly accelerate the rates of many reactions involving nucleophiles or bases (*13*). The anion is much less solvated in dipolar aprotic media than its highly solvated counterpart in hydroxylic solvents (*21*).

In previous investigations (*11, 15, 16, 17*), the measurements of emf were made using a cell of the type

$$\text{Pt, H}_2\,(\text{gas, 1 atm})\,|\,\text{HCl}(m),\ \text{organic solvent}\ (X),\ \text{water}\ (Y)\,|\ \text{AgCl, Ag}$$

EXPERIMENTAL

The purification of the hydrogen gas, the preparation of the electrodes, and the general experimental details have been described previously (*15, 16*). The dielectric constant, D, for isopropanol-water mixtures used in computing the electrostatic Gibbs energy, was calculated at various temperatures from the following equations

$$\log D\ (X = 20.76) = 1.8150 - 0.00213\ (t - 20) \qquad (1)$$

$$\log D\ (X = 44.04) = 1.6830 - 0.00231\ (t - 20) \qquad (2)$$

$$\log D\ (X = 70.28) = 1.4690 - 0.00262\ (t - 20) \qquad (3)$$

$$\log D\ (X = 87.71) = 1.3390 - 0.00290\ (t - 20) \qquad (4)$$

derived from the data of Akerlof (*1*). The Equations 1–4 are valid over a temperature range of 0–80° C. The stock solution of hydrochloric acid was prepared from a twice distilled sample of the acid. Its chloride content was determined gravimetrically as silver chloride. The molality of the acid in all the solutions is accurate within ±0.05%. All of the cell solutions were prepared volumetrically and the weight percent of the mixed solvent was calculated from the appropriate volume and density data. The organic solvent contents of the solution may be relied upon within ±0.05%.

Measurements were made at 0°, 15°, 25°, and 35° C with a Leeds and Northrup K-3 Universal Type potentiometer. The thermostat maintained a temperature within ±0.01° C. All measurements were taken by two silver–silver chloride electrodes and two hydrogen electrodes. The equilibrium was reached in 3–4 hr after the initiation of hydrogen bubbling. After equilibrium had been attained, the emf remained constant for ½ hr with a variation of 0.05 mV.

CALCULATION AND RESULTS

The standard potentials on the molal scale of the cell for THF-water (*16*), monoglyme-water (*11*), and isopropanol-water (*15*) were evaluated by a polynomial curve-fitting technique (*19*). The values of E_m^0 obtained from the above references as well as for water (*3*) can be represented as a function of temperature by the expressions, obtained by the method of least squares

$$E_m^0 = E_{m,25}^0 - a(t - 25) - b(t - 25)^2 \qquad (5)$$

where t is in degrees Celsius. The constants of Equation 5 with the standard error for the respective media are given in Table I. These have a range of validity between 0–35° C.

The standard potentials, E_N^0, on the mole fraction scale for all the solvent mixtures were computed by the equation

$$E_N^0 = E_m^0 + (4.6052\ RT/F)\ \log_{10}\ (1000/M_{xy}) \qquad (6)$$

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Table I. Coefficients of Empirical Equation

$$E_m^0 = E_{m,25}^0 - a(t-25) - b(t-25)^2$$

Wt %	$E_{m,25}^0(V)$	$a \times 10^4$	$b \times 10^6$	S.d.
	Tetrahydrofuran			
0[a]	0.2224	6.438	2.989	0.0000
18.21	0.2038	6.001	4.332	0.0004
73.03	0.0931	18.895	24.441	0.0007
89.00	−0.0258	27.472	11.928	0.0012
	Monoglyme			
8.68	0.2155	6.000	6.003	0.0000
17.81	0.2090	7.450	6.503	0.0000
46.52	0.1794	11.218	3.606	0.0000
67.03	0.1262	17.289	2.144	0.0006
	Isopropanol			
20.76	0.1952	6.986	7.160	0.0001
44.04	0.1783	8.761	5.740	0.0003
70.28	0.1298	13.226	1.249	0.0003
87.71	0.0725	19.778	8.523	0.0000

[a] Data taken from ref. *3*.

Table II. Standard Potentials (E_N^0) of Cell

Pt, H_2 (gas, 1 atm) HCl(m), Organic Solvent (X), Water (Y) AgCl, Ag X and Y are weight percentages

X	M_{xy}	$t/°C = 0$	15	25	35
		Tetrahydrofuran			
0[a]	18.01	0.0474	0.0291	0.0159	0.0024
18.21	20.87	0.0345	0.0185	0.0049	−0.0072
73.03	39.85	−0.0257	−0.0484	−0.0725	−0.0978
89.00	54.21	−0.1032	−0.1475	−0.1756	−0.2117
		Monoglyme			
8.68	19.36		0.0250	0.0128	−0.0005
17.81	21.01		0.0240	0.0105	−0.0042
46.52	28.70	0.0381	0.0142	−0.0031	−0.0206
67.03	38.85	0.0159	−0.0163	−0.0407	−0.0626
		Isopropanol			
20.76	21.08	0.0266	0.0101	−0.0031	−0.0172
44.04	26.05	0.0245	0.0045	−0.0091	−0.0254
70.28	35.47	0.0046	−0.0237	−0.0417	−0.0615
87.71	46.69	0.0277	−0.0609	−0.0849	−0.1109

[a] Calculated from the data of E_m^0 given in ref. *3*.

where M_{xy}, the mean molecular weight of the solvent, is given by

$$M_{xy} = 100/[(X_1/M_1) + (X_2/M_2)] \tag{7}$$

In this equation M_1 and M_2 are the molecular weights of the solvents and X_1 and X_2 are the weight percentages of each solvent. Values of M_{xy} are also listed in Table II.

THERMODYNAMIC QUANTITIES

The thermodynamic quantities for the transfer of HCl from water to another amphiprotic solvent (isopropanol) involves an acid-base proton transfer of the type

$$H_3O^+ + ROH \rightleftarrows ROH_2^+ + H_2O$$

which depends not only on the strengths of the acid and base, but is also dependent on the dielectric constant of the mixed solvent. The nature of the parameters that can adequately explain the effect of a changing medium is not well known. There is considerable evidence, however, that the transfer process involves two kinds of effects, one electrostatic and the other chemical. Thus, the associated thermodynamic functions can be regarded to comprise two parts: electrostatic (el) and nonelectrostatic or chemical (ch). The chemical part involves the solvating capacity as well as the specific chemical interaction which includes the disruption of one type of solvation shell and the creation of another (*2*). For the Gibbs energy change of the transfer process (t)

$$\Delta G_t^0 = \Delta G_{\text{el}}^0 + \Delta G_{\text{ch}}^0 \tag{8}$$

and similar equations exist for the other thermodynamic quantities ΔS_t^0 and ΔH_t^0.

The total transfer quantity, ΔG_t^0, for isopropanol-water, THF-water, and monoglyme-water mixtures were computed by the equation

$$\Delta G_t^0 = F({}^wE_N^0 - {}^sE_N^0) \tag{9}$$

where the superscripts w and s refer to water and the

Table III. Free Energy[a], Enthalpy[a], and Entropy[b] of Transfer of HCl from Water to Isopropanol–Water Mixtures at Different Temperatures

$t/°C$	ΔG_t^0	ΔG_{el}^0	ΔG_{ch}^0	ΔH_t^0	ΔH_{el}^0	ΔH_{ch}^0	ΔS_t^0	ΔS_{el}^0	ΔS_{ch}^0	D
					$X = 20.76$					
15	437	414	23	812	−366	1178	1.3	−2.7	4.0	66.99
25	440	441	−1	231	−415	646	−0.7	−2.9	2.2	63.78
35	451	471	−20	−350	−469	119	−2.6	−3.1	0.5	60.73
					$X = 44.04$					
0	530	1099	−569	339	−867	1206	−0.7	−7.2	6.5	53.64
15	569	1212	−643	−180	−1062	882	−2.6	−7.9	5.3	49.53
25	579	1293	−714	−584	−1208	624	−3.9	−8.4	4.5	46.96
35	640	1380	−740	−932	−1370	438	−5.1	−8.9	3.8	44.53
					$X = 70.28$					
0	989	2835	−1846	−3108	−2543	−565	−15.0	−19.7	4.7	33.24
15	1219	3146	−1927	−2757	−3120	363	−13.8	−21.7	7.9	30.36
25	1330	3370	−2040	−2546	−3556	1010	−13.0	−23.2	10.2	28.59
35	1472	3610	−2139	−2287	−4036	1749	−12.2	−24.8	12.6	26.91
					$X = 87.71$					
0	1733	4350	−2617	−3894	−4596	702	−20.6	−32.7	12.1	24.96
15	2076	4868	−2792	−4955	−5641	686	−24.4	−36.5	12.1	22.58
25	2326	5246	−2920	−5724	−6435	711	−27.0	−39.2	12.2	21.12
35	2613	5652	−3039	−6477	−7316	839	−29.5	−42.1	12.6	19.76

[a] ΔG^0 and ΔH^0 are expressed in cal/mol. [b] ΔS^0 values are in cal/mol-deg.

mixed solvent media, respectively. The values of these quantities are listed in Table III for isopropanol-water mixtures, Table IV for THF-water mixtures and in Table V for monoglyme-water mixtures.

According to Born's equation, the electrical contribution to the Gibbs energy change is given by

$$\Delta G^0_{el} = \{Ne^2/2\}\{1/D_s - 1/D_w\}\{1/r_+ + 1/r_-\} \tag{10}$$

where D_s and D_w are the dielectric constants of the mixed solvent and water, r_+ and r_- are the effective radii of the cation and the anion, respectively. The radius of the solvated hydrogen ion (the diameter of a water molecule) is taken as 2.76 Å (*22*) and is arbitrarily assumed to be constant for all isopropanol-water mixtures. The radius of the chloride ion is taken as 1.81 Å (the crystallographic radius). The electrostatic contribution is due to the relative amounts of work required to charge the ions in the two media of different dielectric constant. The computed values of ΔG^0_{el}, with the dielectric constant data, are given in Table III. The values of ΔG^0_{ch} can easily be obtained from Equation 8.

The total entropy change for the transfer process

$$HCl \text{ (in } H_2O) \rightarrow HCl \text{ (in isopropanol-water mixtures)}$$

can be calculated from the standard potential (E^0) of the cell in the two solvents (water and the mixed solvent) and from the variation of E^0 with temperature listed in Table I. The pertinent thermodynamic relation used for this purpose is

$$\Delta S^0_t = -[\partial(\Delta G^0_t)/\partial T]_p \tag{11}$$

The values of ΔS^0_t for isopropanol-water, THF-water, and monoglyme-water mixtures are presented in Tables III, IV, and V, respectively. The related thermodynamic functions have been computed on the mole fraction scale because it will eliminate energy changes due to concentration changes.

The change in the electrostatic part of the entropy of transfer can be estimated by differentiating Equation 10 and the substitution of the following equation

$$d \ln D/dT = -1/\theta \tag{12}$$

into the resulting equation yields

$$\Delta S^0_{el} = [-Ne^2/2][1/D_s\theta_s - 1/D_w\theta_w][1/r_+ + 1/r_-] \tag{13}$$

In Equation 12, D is the dielectric constant at temperature T and θ is a constant characteristic of the medium (*9*). The values for θ_s for the respective isopropanol-water mixtures were obtained from slopes of Equations 1-4. The value for θ_w was evaluated from the slope of the linear plot of ln D vs. T. These data are shown below

Wt % isopropanol (X) =	0	20.76	44.04	70.28	87.71
Constant (θ) =	220	204	188	166	150

From a knowledge of ΔG^0_{el} and ΔS^0_{el}, the electrostatic part of the enthalpy change can be computed by the relation

$$\Delta H^0_{el} = \Delta G^0_{el} + T\Delta S^0_{el} \tag{14}$$

and hence the chemical part of the quantity can be evaluated by the difference between ΔH^0_t and ΔH^0_{el}. These data for isopropanol-water mixtures are presented in Table III and those of ΔH^0_t for THF-water and monoglyme-water mixtures are given in Tables IV and V, respectively.

Table IV. Free energy,[a] Enthalpy,[a] and Entropy[b] of Transfer from Water to Tetrahydrofuran-Water Mixtures at Different Temperatures

t/° C	ΔG^0_t	ΔH^0_t	ΔS^0_t
	X = wt % Tetrahydrofuran		
	X = 18.21		
15	246	887	2.2
25	255	734	1.6
35	221	525	1.0
	X = 73.03		
0	1688	1460	−0.8
15	1787	−2722	−15.7
25	2040	−5572	−25.5
35	2310	−8601	−35.4
	X = 89.00		
0	3476	−5756	−33.8
15	4074	−7447	−40.0
25	4418	−8733	−44.1
35	4936	−9926	−48.2

[a] ΔG^0 and ΔH^0 values are in cal/mol. [b] ΔS^0 values are expressed in cal/mol-deg.

DISCUSSION

Tables III, IV, and V show that the total free energy of transfer, ΔG^0_t, in a variety of isopropanol-water, THF-water, and monoglyme-water mixtures is positive and that the magnitude increases with increasing concentration of the organic solvent at a particular temperature. Hydrochloric acid thus appears to be in a lower Gibbs energy state in water than in the respective solvent composition. In other words, water is more basic than the mixed solvents. The error in ΔG^0_t for all the solvent compositions may be estimated to be within ±10 cal.

Quantitative significance of the data cannot be given to the Born electrostatic treatment, because of the uncertainty in the appropriate values of the radii and the dielectric constant of the medium in Equation 10. The Born equation predicts that the plots of E^0_m and E^0_N against $1/D$ should be linear. It is evident from Figure 1 that both plots are almost linear up to X = 87.71 (the maximum region of the present study) and convex downward in X = 95 (*18*). It is indeed remarkable that the predictions of the Born equation are so often qualitatively correct. To calculate the electrostatic free energy changes on the transfer of electrolytes from H_2O to D_2O, Hepler (*10*) used

Table V. Thermodynamic Quantities[a] Accompanying the Transfer of HCl from Water to Monoglyme-Water Media at Various Temperatures

t/° C	ΔG^0_t	ΔH^0_t	ΔS^0_t
	X = wt % monoglyme		
	X = 8.68		
15	94	872	2.7
25	72	462	1.3
35	67	143	−0.1
	X = 17.81		
15	118	86	−0.1
25	126	−391	−1.7
35	152	−881	−3.3
	X = 46.52		
0	215	−2109	−8.5
15	345	−2231	−8.9
25	439	−2312	−9.2
35	529	−2401	−9.5
	X = 67.03		
0	728	−5555	−23.0
15	1049	−5410	−22.4
25	1306	−5260	−22.0
35	1498	−5169	−21.6

[a] ΔG^0 and ΔH^0 are in cal/mol and ΔS^0 is in cal/mol-deg.

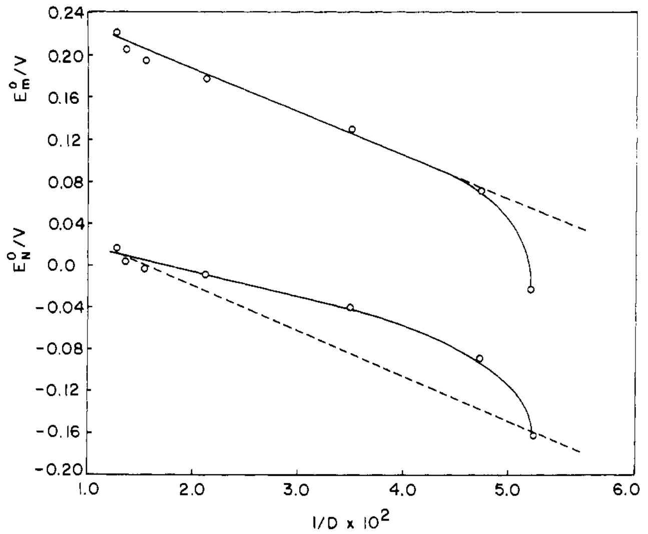

Figure 1. Plots of E_m^0 and E_N^0 vs. $1/D$ at 25° C

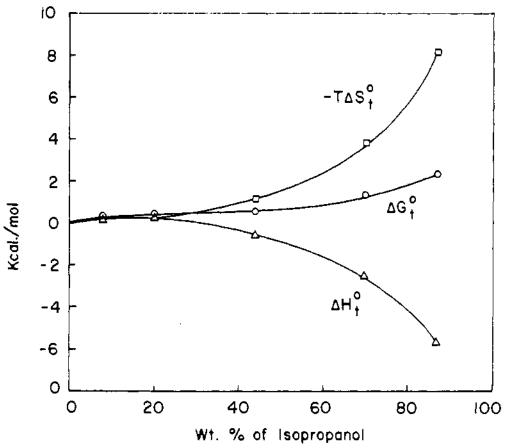

Figure 2. Plots of the thermodynamic functions of HCl in isopropanol–water mixtures at 25° C

a modified model suggested by the work of Ritson and Hasted (*14*). Hepler's equation takes into account the dielectric saturation, assuming that the orientation of the negative ends of the solvent molecules are pointing toward the ions. Thus, probably better values of ΔG_{el}^0 might be evaluated.

The negative values of ΔG_{ch}^0 over the mixed solvent range up to $X = 87.71$ indicate the gradual increment in the basicity which may be due to a breakdown of water structure by the introduction of isopropanol. It was suggested by Braude and Stern (*5, 6*) that the addition of alcohol may destroy the water structure, making available a larger number of basic centers located on the free water molecules. A similar situation might happen in isopropanol as well. Transfer of HCl from water to ethylene glycol–water mixtures (*20*) and dissociation constants of some cation acids in methanol–water mixtures (*4, 12*) indicate that as the respective organic solvent is added to water, the basicity increases going through a maximum. No such maximum was observed for isopropanol-water mixtures up to $X = 87.71$.

Some insight with regard to the changes in the structural aspects of the solvent accompanying the transfer process might be obtained from the values of ΔH_t^0 and ΔS_t^0, since these contain important structural contributions and allow limited interpretations of the structural changes in the solutions (*8*). Figure 2 shows the experimental points of ΔG_t^0, ΔH_t^0, and $-T\Delta S_t^0$ for isopropanol-water mixtures at 25° C. All structure-breaking processes, including desolvation of the ions, are endothermic and ΔH_t^0 shows the endothermic peak in the water-rich region with maxima at $X = 20$. Furthermore, in the alcohol-rich region, the values of $-T\Delta S_t^0$ and ΔG_t^0 are predominant.

In Table III, the total entropy change, ΔS_t^0, for $X = 20.76$ at 15° C is positive which suggests that the amount of order (*7*) created by HCl in the mixed solvent is less. Since addition of small amounts of alcohol to water enhances the three-dimensional hydrogen bonded polymeric form of water (*7*), there will be relatively more structure to break than to promote. Upon further addition of alcohol, the probability of existence of alcohol molecules around the ion increases considerably and the ions now create more order in the mixed solvent than in water.

In other words, there begins a gradual breakdown of the structure of water upon the addition of isopropanol. This is characterized by the negative values of ΔH_t^0 and ΔS_t^0. Similar reasonings may apply equally well to the data listed in Tables IV and V for THF-water and monoglyme–water media, respectively. As anions are much less solvated in dipolar aprotic solvents (*13*) than in protic solvents, the hydrogen ion will be solvated more in THF-water and monoglyme-water media than in the pure aqueous medium.

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NOMENCLATURE

E_m^0 = standard electrode potential (molal scale), volts
$^wE_N^0$, $^sE_N^0$ = standard electrode potential (mole fraction scale) in water and in a mixed solvent, respectively, volts
$a, b \ldots$ = empirical constants of Equation 5
D_s, D_w = dielectric constant of the mixed solvent and water, respectively
r_-, r_- = effective radii of the cation (H^-) and anion (Cl^-), respectively, angstroms
θ_s, θ_w = constants of Equation 12 for the mixed solvent and water, respectively
X = weight % organic solvent in a mixture with water
M_{xy} = average molecular weight of the solvent
ΔG_t^0 = standard transfer Gibbs free energy, cal/mol
ΔG_{el}^0 = electrostatic Gibbs free energy, cal/mol
ΔS_t^0 = standard transfer entropy, cal/mol-deg
ΔH_t^0 = standard transfer enthalpy, cal/mol

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Vapor-Liquid Equilibria for Fourteen Systems Consisting of Chlorinated Hydrocarbons and Alcohols

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Vapor-liquid equilibrium of 14 binary systems was determined with the help of a dynamic ebulliometer "Cathala," at the pressure of 760 mm Hg. Nine systems were constituted only with chlorinated solvents and the other five systems with chlorinated solvents and ethyl, methyl, or *n*-propyl alcohol. The tests of a thermodynamic consistency were carried out, and all the systems yielded smooth curves of $(y - x)$ plotted against x.

An ebulliometric study of nine binary systems composed of chlorinated solvents and five binary systems of chlorinated solvents with methyl, ethyl, and *n*-propyl alcohol was undertaken for the purpose of developing a method of predicting the distillation curves of the binary and ternary systems of these compounds. These data are of interest in the vinylic polymer industry. With regard to these 14 systems, only the following ones have already been studied (*1, 2, 9, 14*), at a pressure of 760 mm Hg: carbon tetrachloride and ethylene chloride, carbon tetrachloride and trichloroethene, and trichloroethene and tetrachloroethene. These 14 systems are quoted in Table I.

Table I. Binary Systems

Carbon tetrachloride-ethylene chloride[a]
Carbon tetrachloride-trichloroethene
Ethylene chloride-trichloroethene
Ethylene chloride-trichloroethene
Ethylene chloride[a]-ethyl alcohol
Ethylene chloride-*n*-propyl alcohol
Ethylene chloride-1,1,1-trichloroethane
Trichloroethene-tetrachloroethene
Trichloroethene-*n*-propyl alcohol
Tetrachloroethene-methyl alcohol
Tetrachloroethene-*n*-propyl alcohol
1,2-*trans*-Dichloroethene-1,2-*cis*-dichloroethene
1,1,1-Trichloroethane-1,2-*trans*-dichloroethene
1,2-*cis*-Dichloroethene-1,1,1-trichloroethane

[a] Ethylene chloride of Matheson, Coleman and Bell.

CHEMICALS

The boiling points, the refractive indices at 20° C, and the grades of each pure compound are given in Table II. Alcohols were distilled with sodium through a reflux column. The ethylene chloride of Matheson, Coleman and Bell used in various systems is not pure enough even after distillation. Therefore, the experiments were carried out using the reagent grade ethylene chloride of Merck, whose physical properties draw nearer to those which are in the tables.

The dichloroethenes 1,2-cis and -trans, and trichloroethane-1,1,1 were distilled before their use to obtain a grade material of 99.8%. The gas chromatographic analysis did not reveal impurities in the other compounds; therefore, they were used without further purifications.

Table II. Physical Properties of Chemicals

Materials	Grade	Boiling point, ° C		Refractive index, n_D^{20}	
		Exptl	Lit. (*7*)	Exptl	Lit. (*7*)
Carbon tetrachloride	Prolabo, Reagent Grade	76.7	76.7	1.4607	1.4604
Tetrachloroethene	Merck, Reagent Grade	120.9	121.0	1.5058	1.5044
Ethylene chloride	Matheson, Coleman and Bell	82.7	82.7	1.4450	1.4448 1.44476 (*5*)
Ethylene chloride	Merck, Reagent Grade	83.4	84.0 83.47 (*5*)	1.4450	1.4448 1.44476 (*5*)
Trichloroethene	Merck, Reagent Grade	86.7	87.0	1.4777	1.4784
1,2-*cis*-Dichloroethene	Pechiney Saint Gobain, 99.8%	60.0	60.3	1.4491	1.4490
1,2-*trans*-Dichloroethene	Pechiney Saint Gobain, 99.8%	47.4	47.5	1.4458	1.4454
1,1,1-Trichloroethane	Pechiney Saint Gobain, 99.8%	73.9	74.0 74.05 (*8*)	1.4381	1.43838 (*11*)
Methyl alcohol	Pure Grade	64.7	64.96	1.3290	1.3288
Ethyl alcohol	Pure Grade	78.3	78.5	1.3621	1.3611
n-Propyl alcohol	Prolabo, Pure Grade	97.1	97.1	1.3851	1.3850

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