# Mechanism of Acetic Acid Transfer from Aqueous Sodium Chloride Solutions to Some Orgranic Solvents

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## ABSTRACT

*Salting out of acetic acid from aqueous solutions containing various concentrations of sodium chloride into some organic solvents has been studied at various temperatures. The solvents include cyclohexane, carbon tetrachloride, 1,2-dichloroethane, isopropyl ether, 2-pentanone and 1-heptanol. The results are consistent with a transfer mechanism involving monomer partitioning, dimerization and dimer return to the aqueous phase. Factors favoring monomer partitioning such as rise in both temperature and salt level retard dimer return, a process which is found to be significant in dimerization-enhancing solvents. The sensitivity of various solvents towards salt effect increases in the order 1-heptanol < isopropylether < 1,2-dichloro-ethane < 2-pentanone < cyclohexane < carbon tetrachloride which generally parallels in the reverse order the extent of stabilization of the acid by various solvent interactions.*

*Key words: Acetic acid monomers and dimers, organic solvents and salting out.*

## 1 INTRODUCTION

Salting out involved in transfer of solutes between aqueous solutions and organic solvents by various salts is a well known phenomenon.[1] This process is of a paramount importance in the extraction technique because of two reasons; (i) it enhances the transfer of a solute into an organic phase thereby lowering the number of stages required for separation, and (ii) it lowers both the water content in the extract phase and the organic solvent content in the raffinate phase. These factors

seem to be economically attractive particularly in the chemical or the thermal treatment of aqueous and organic phases after completion of the extraction stages.[2]

Several papers have been reported for the transfer of carboxylic acids from aqueous solutions containing various inorganic salts into a number of organic solvents.[2-5] Nevertheless, a refined picture of salt effect on various equilibria involved in the transfer has not as yet been emerged.

The purpose of the present work is to elucidate the mechanism by which acetic acid is transferred from aqueous solutions containing various concentrations of sodium chloride into some organic solvents of variable degree of interaction characteristics. The results have allowed the estimation of the salting out parameter, which seems to be solvent-dependent.

## 2 EXPERIMENTAL

### 2.1 Materials

Acetic acid and sodium chloride (Analytical Univar Reagent), cyclohexane, 2-pentanone, 1-heptanol (Merck), 1,2-dichloroethane, carbon tetrachloride (Fluka) and isopropyl ether (Riedel De Haen) were used without further purification. Double distilled water was used throughout the work.

### 2.2 Procedure

All aqueous acetic acid solutions containing various concentrations of NaCl were prepared by weight and the concentration of acetic acid in these solutions was checked by titration. Appropriate amounts of conc. HCl were added to all aqueous solutions so that the final HCl concentration was always $0.01$ mol dm$^{-3}$. Partition experiment was made by shaking equal volumes of aqueous and organic phases ($20.0$ cm$^3$ each) in a stoppered conical flask in a flask shaker (200 rpm) for 2 h. The contents were transferred into a glass-stoppered test tube and incubated in a thermostated water bath at the desired working temperature (accuracy $\pm 0.1^\circ$C) for 30 min. A test tube was removed from the water bath for a few seconds during which it was shaken vigorously on a vortex test tube shaker to reequilibrate at the desired temperature. This was followed by incubation in the water bath overnight for complete phase separation. Acetic acid concentration in the organic layer was determined by titrating an aliquot with standardized NaOH using phenolphthalein as an indicator. Duplicate determinations were made for each organic layer and the acetic acid concentration in the aqueous phase was determined by difference from initial acetic acid concentration in the aqueous phase. A blank partition experiment, in the absence of acetic acid was carried out similarly for each solvent and for each NaCl concentration used and the volumes of NaOH required in the main partition experiment were corrected accordingly. In most cases the volume of NaOH required for the blank did not exceed 5% of the total volume of NaOH equivalent to the lowest acetic acid concentration used.
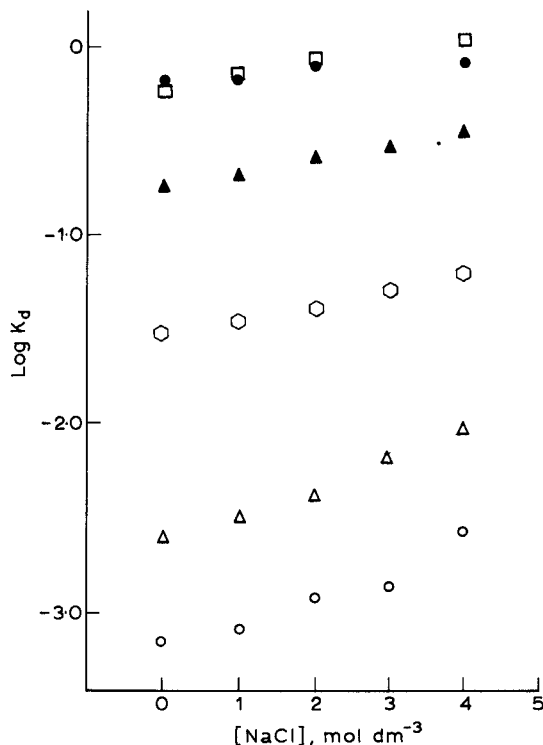
**Fig. 1.** Manomer partition constants of acetic acid between various solvents and aqueous phases containing various concentrations of NaCl at 30°C. The solvents include cyclohexane, ○, carbon tetrachloride, △, 1,2-dichloroethane, ⬡, isopropyl ether, ▲, 3-pentanone, □ and 1-heptanol, ●.

## 3 RESULTS AND DISCUSSION

The partition coefficient, $D$, of a carboxylic acid between an aqueous phase, where $pH \ll pKa$, and an organic phase is related to the monomer partition constant, $K_d$, and the dimerization constant, $K_{dm}$ by eqn (1)

$$D = K_d + 2K_d^2 K_{dm}[HA]_{aq} \tag{1}$$

where $[HA]_{aq}$ denotes the equilibrium acid concentration in an aqueous phase.[5,6] Data for $D$ as a function of $[HA]_{aq}$ for acetic acid transfer between aqueous solutions containing various concentrations of NaCl and various organic solvents are assembled in Table 1. Analysis of these data in terms of eqn (1) generates the $K_d$ and $K_{dm}$ values listed in Table 2. The $K_{dm}$ values are reported only for those data obtained in the absence of NaCl in aqueous phases. If $K_{dm}$ had been calculated from the slopes of eqn (1) for data determined in the presence of NaCl, a gradual decrease in these constants would have been obtained as NaCl concentration progressively increases in the aqueous phase. Such decrease in $K_{dm}$ values (not shown) would seem to be unreasonable in view of the fact that the dimerization

**TABLE 1**

Partition Coefficients of Acetic Acid Between Various Organic Solvents and Aqueous Solutions Containing Various NaCl Concentrations at Different Temperatures. All Data were Experimentally Determined in this Work

| Temperature ($°C$) | Solvent | $[NaCl]$ ($mol\ dm^{-3}$) | $10^3 D$ ($[Acetic\ acid]_{aq}/mol\ dm^{-3}$) |
|---|---|---|---|
| 10 | Cyclohexane | 0·0 | 1·49 (0·407); 1·73 (0·560; 2·45 (0·712); 2·88 (0·864); 3·07 (1·02) |
|  |  | 4·0 | 6·81 (0·547); 8·49 (0·696); 10·4 (0·843); 11·5 (0·991) |
| 20 |  | 0·0 | 1·60 (0·407); 2·03 (0·560); 2·34 (0·712); 2·94 (0·864); 3·36 (1·02) |
|  |  | 4·0 | 5·16 (0·399); 7·39 (0·547); 9·33 (0·695); 9·90 (0·843) |
| 30 |  | 0·0 | 2·14 (0·407); 2·77 (0·559); 3·37 (0·712); 3·92 (0·864); 4·31 (1·02) |
|  |  | 1·0 | 2·95 (0·411); 3·69 (0·564); 4·69 (0·717); 5·42 (0·871); 6·05 (1·02) |
|  |  | 200 | 4·31 (0·410); 5·63 (0·563); 7·30 (0·716); 7·80 (0·869) |
|  |  | 3·0 | 5·79 (0·409); 9·12 (0·714); 10·8 (0·866); 12·4 (1·02) |
|  |  | 4·0 | 7·86 (0·410); 9·94 (0·562); 12·2 (0·714); 13·9 (0·866); 15·7 (1·02) |
| 40 |  | 0·0 | 2·60 (0·407); 3·09 (0·559); 3·78 (0·711); 4·45 (0·864); 5·09 (1·01) |
|  |  | 4·0 | 9·31 (0·397); 11·6 (0·545); 14·4 (0·691); 16·5 (0·838); 18·9 (0·983) |
| 30 | Carbon tetrachloride | 0;· | 6·11 (0·253); 6·85 (0·304); 8·13 (0·405); 9·87 (0·505); 11·1 (0·605); 12·6 (0·705); 16·8 (1·00) |
|  |  | 1·0 | 11·3 (0·407); 14·7 (0·558); 17·4 (0·708); 20·5 (0·858); 23·5 (1·01) |
|  |  | 2·0 | 15·9 (0·406); 20·8 (0·555); 25·3 (0·703); 29·5 (0·850); 33·5 (0·996) |
|  |  | 3·0 | 22·3 (0·403); 29·2 (0·550); 35·3 (0·696); 41·1 (0·840); 46·6 (0·984) |
|  |  | 4·0 | 30·0 (0·401); 37·8 (0·547); 53·2 (0·833); 60·0 (0·974) |
| 30 | 1,2-dichloroethane | 0·0 | 43·2 (0·246); 38·1 (0·347); 48·7 (0·490); 54·5 (0·634); 37·3 (0·729); 61·1 (0·824); 66·1 (0·964) |
|  |  | 1·0 | 56·7 (0·390); 64·9 (0·532); 73·4 (0·672); 80·6 (0·810); 87·5 (0·947) |
|  |  | 2·0 | 74·0 (0·384); 87·1 (0·521); 97·3 (0·657); 108 (0·790); 121 (0·919) |
|  |  | 3·0 | 94·3 (0·376); 111 (0·510); 127 (0·639); 140 (0·767); 155 (0·891) |
|  |  | 4·0 | 117 (0·370); 137 (0·499); 157 (0·625); 173 (0·748); 192 (0·866) |
| 30 | Isopropyl ether | 0·0 | 185 (0·130); 192 (0·259); 193 (0·431); 198 (0·601); 200 (0·729); 204 (0·854) |

**TABLE 1**—*contd*

| Temperature (°C) | Solvent | [NaCl] (mol dm$^{-3}$) | $10^3D$ ([Acetic acid]$_{aq}$/mol dm$^{-3}$) |
|---|---|---|---|
| | | 1·0 | 227 (0·336); 236 (0·458); 237 (0·583); 243 (0·704); 247 (0·826) |
| | | 2·0 | 275 (0·323); 287 (0·440); 293 (0·558); 303 (0·672); 305 (0·789) |
| | | 3·0 | 335 (0·424); 348 (0·535); 356 (0·645); 368 (0·753) |
| | | 4·0 | 368 (0·150); 392 (0·294); 400 (0·440); 411 (0·580); 430 (0·716) |
| 30 | 1-Heptanol | 0·0 | 640 (0·063); 677 (0·123); 672 (0·185); 658 (0·279); 588 (0·388); 681 (0·459); 684 (0·519); 677 (0·613) |
| | | 1·0 | 706 (0·242); 710 (0·331); 706 (0·423); 690 (0·518); 696 (0·607) |
| | | 2·0 | 790 (0·230); 728 (0·328); 823 (0·396); 794 (0·488); 790 (0·575) |
| | | 4·0 | 819 (0·227); 815 (0·313); 831 (0·395); 819 (0·483); 829 (0·564) |
| 30 | 3-Pentanone | 0·0 | 574 (0·065); 579 (0·163); 595 (0·322); 728 (0·060); 733 (0·149); 722 (0·299) |
| | | 2·0 | 918 (0·054); 840 (0·140); 874 (0·275) |
| | | 4·0 | 1004 (0·051); 1072 (0·123); 1097 (0·244) |

process takes place in organic phase and should not be influenced by the presence of salt in aqueous phase. The present results suggest a transfer mechanism including in addition to the above two equilibria, a process by which the formed dimer in the organic phase returns directly to the aqueous phase with spontaneous dissociation into its hydrated monomers, eqn (2)

$$K_{dm-r} = [HA]_{aq}^2/[HA]_{org}^2 \qquad (2)$$

This proposed step must satisfy the linear relationship observed between $D$ and $[HA]_{aq}$ and must also be chemically acceptable. Inclusion of eqn (2) into eqn (1) leads to

$$D = K_d + 2(K_d^2 K_{dm} - 1/K_{dm-r})[HA]_{aq} \qquad (3)$$

The $K_{dm-r}$ values determined for acetic acid dimer in cyclohexane and carbon tetrachloride at various temperatures and in the presence of various NaCl concentrations are listed in the last column of Table 2. Factors which are known to destabilize the acid in aqueous phase such as rise in both temperature and salt level would be expected to enhance monomer partitioning and retard dimer return. This is borne out to be true.

In the absence of salt, the slope of the $D$–$[HA]_{aq}$ plot equals the product $2K_d^2 K_{dm}$, and in such cases $K_{dm-r}$ is assumed to be very large. As the concentration of the salt increases in aqueous phase the $2K_d^2 K_{dm}$ term exceeds the value of the slope

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**TABLE 2**

$K_d$, $K_{dm}$ and $K_{dm-r}$ Data for Acetic Acid Transfer between Aqueous Solutions Containing Various Concentration of NaCl and Various Organic Solvents at Various Temperatures

| Temperature (°C) | Solvent | [NaCl] ($mol\,dm^{-3}$) | $10^4\,K_d$ | $10^4\,Slope,^a\,M^{-1}$ ($mol^{-1}\,dm^3$) | $K_{dm},\,M^{-1}$ ($mol^{-1}\,dm^3$) | $2 \times 10^4\,K_d^2 K_{dm}\,M^{-1}$ ($mol^{-1}\,dm^3$) | $K_{dm-r}\,M$ ($mol\,dm^{-3}$) |
|---|---|---|---|---|---|---|---|
| 10·0 | Cyclohexane | 0·0 | 3·0 ± 1·5 | 28 ± 3 | 15 555 ± 11 620 | 311 ± 240 | 98 |
| | | 4·0 | 20 ± 3 | 108 ± 8 | | | |
| 20·0 | | 0·0 | 3·9 ± 0·1 | 29 ± 2 | 9426 ± 2530 | 271 ± 200 | 123 |
| | | 4·0 | 117 ± 6 | 109 ± 20 | | | |
| 30·0 | | 0·0 | 7 ± 1 | 36 ± 2 | 3674 ± 578 | | 13 182$^b$ |
| | | 1·0 | 8 ± 1 | 52 ± 3 | | 47 ± 10 | 3548$^b$ |
| | | 2·0 | 12 ± 4 | 80 ± 11 | | 106 ± 40 | 775 |
| | | 3·0 | 14 ± 1 | 108 ± 1 | | 144 ± 22 | 555 |
| | | 4·0 | 27 ± 2 | 129 ± 4 | | 536 ± 96 | 49 |
| 40·0 | | 0·0 | 83 ± 1 | 42 ± 1 | 3281 ± 319 | | 57 |
| | | 4·0 | 28 ± 2 | 164 ± 4 | | 515 ± 67 | 3020$^b$ |
| 30·0 | Carbon tetrachloride | 0·0 | 25 ± 1 | 143 ± 2 | 1135 ± 68 | 235 ± 20 | 607 |
| | | 1·0 | 32 ± 1 | 202 ± 3 | | 378 ± 43 | 253 |
| | | 2·0 | 41 ± 3 | 298 ± 6 | | 855 ± 108 | 45 |
| | | 3·0 | 61 ± 5 | 414 ± 11 | | 1900 ± 140 | 15 |
| | | 4·0 | 91 ± 4 | 526 ± 6 | | | |
| 30·0 | 1,2-Dichloroethane | 0·0 | 303 ± 28 | 370 ± 40 | 20 ± 4 | 505 ± 90 | |
| | | 1·0 | 354 ± 6 | 555 ± 13 | | 707 ± 103 | |
| | | 2·0 | 419 ± 11 | 847 ± 26 | | 1042 ± 190 | |
| | | 3·0 | 508 ± 11 | 1143 ± 28 | | 1551 ± 280 | |
| | | 4·0 | 620 ± 12 | 1498 ± 30 | | | |
| 30·0 | Isopropyl ether | 0·0 | 1840 ± 20 | 230 ± 26 | 0·34 ± 0·04 | 320 ± 36 | |
| | | 1·0 | 2161 ± 20 | 378 ± 52 | | 447 ± 51 | |
| | | 2·0 | 2556 ± 30 | 663 ± 85 | | 592 ± 67 | |
| | | 3·0 | 2941 ± 14 | 974 ± 58 | | 863 ± 99 | |
| | | 4·0 | 3553 ± 47 | 1007 ± 109 | | | |

$^a$ The slope of linear least square fit of $D$ versus $[HA]_{aq.}$ plots.

$^b$ These values were calculated by extrapolation from the values obtained at higher NaCl concentrations.

**TABLE 3**

A Comparison between the Experimental and the Calculated Dimer Concentrations[a] ($10^3$ mol $dm^{-3}$) in Cyclohexane and Carbon Tetrachloride Associated with the Transfer of Acetic Acid from 4·0 M NaCl Aqueous Solutions

| Cyclohexane | | Carbon tetrachloride | |
|---|---|---|---|
| $[(HA)_2]_{exp.}$ | $[(HA)_2]_{calcd.}$ | $[(HA)_2]_{exp.}$ | $[(HA)_2]_{calcd.}$ |
| 1·06 | 1·12 | 4·22 | 4·56 |
| 2·04 | 2·10 | 7·85 | 8·50 |
| 3·39 | 3·39 | 18·4 | 19·7 |
| 4·84 | 4·98 | 24·8 | 26·9 |
| 6·59 | 6·86 | | |

[a] These results were calculated according to eqns (4) and (5) using the data in Table 1.

by a factor $1/K_{dm-r}$ which is a salt-dependent parameter. Dimer return in 1,2-dichloroethane and isopropyl ether have been found to be insignificant and slopes of $D-[HA]_{aq}$ plots overlap with the calculated $2K_d^2 K_{dm}$ values within their standard errors. This seems to be a reasonable result in view of the fact that the dimerization in these solvents is negligible.

An additional test for the presence of the dimer return step comes from a comparison of dimer concentration in organic phase calculated from the measured total acid concentration in the organic phase, $C_{org}$ using eqn (4) and that obtained on the basis of dimer return process, eqn (5)

$$[(HA)_2]_{exp.} = (C_{org} - K_d[HA]_{aq})/2 \qquad (4)$$

$$[(HA)_2]_{calcd} = (K_d^2 K_{dm} - 1/K_{dm-r})[HA]_{aq}^2 \qquad (5)$$

The reasonable agreement between the dimer concentrations calculated from both equations (Table 3) substantiates the occurrence of the dimer return step in systems involving cyclohexane and carbon tetrachloride.

The $k_d$ data obtained in the present work in various solvents and at various NaCl concentrations in aqueous phase have allowed a comparison to be made among various solvents concerning their potentialities in the salting out process. Such comparisons have been made by determining the salting out parameter, $k_s$ through eqn (6).

$$\log(k_d^s/k_d^o) = k_s \text{ [salt]} \qquad (6)$$

where $k_d^s$ and $k_d^o$ denote the monomer partition constants in the presence and in the absence of NaCl in aqueous phase, respectively. In the above well-known Sechenov equation, $k_s$ has been considered to be a measure of the sensitivity of a solute to be salted in (salted out) by variation of salt concentration in aqueous phase.[7] Since in the present work only one salt and only one solute are being used and the solvent is the only variable, it is not unreasonable, therefore, to consider $k_s$ as a reflection of the role of a solvent in the salting in (salting out) process. In

**TABLE 4**
Variation of the Salting Out Parameters with Solvents

| Solvent | Salting out parameter |
|---|---|
| Carbon tetrachloride | $0.121 \pm 0.017$ |
| Cyclohexane | $0.098 \pm 0.033$ |
| 2-Pentanone | $0.084 \pm 0.017$ |
| 1,2-Dichloroethane | $0.073 \pm 0.005$ |
| Isopropyl ether | $0.071 \pm 0.002$ |
| 1-Heptanol | $0.029 \pm 0.007$ |

Table 4, the variation of $k_s$ values as a function of the solvent opens the question concerning the dependence on various solvent properties of salting out parameter. Correlation of $k_s$ data in terms of solvent properties such as solvatochromic parameters[8] would require the use of a large number of data in order to obtain a more general as well as a more justified conclusion. Nevertheless, from Table 4 the salt effect appears to be more pronounced, i.e. $k_s$ is relatively large in weakly interacting solvents such as cyclohexane and carbon tetrachloride as compared with the effect observed with strong interacting solvents such as 1-heptanol and isopropyl ether generating relatively smaller $k_s$ values.

In summary, the present work demonstrates that acetic acid transfer from aqueous NaCl solution to the studied organic solvents involves three equilibria; monomer partitioning, dimerization and dimer return to an aqueous phase with spontaneous dissociation into its hydrated monomers. The latter equilibrium is enhanced by lowering both the temperature and the salt level and occurs only in dimerization promoted solvents. The sensitivity of various solvents towards the salting out process increases in the order 1-heptanol < isopropyl ether < 1,2-dichloroethane < 2-pentanone < cyclohexane < carbon tetrachloride which roughly parallels, in the reverse order, the extent of stabilization of the acid by various solvent interactions.

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