Partition of Carboxylic Acids between Benzene and Aqueous Solution as Considered from the Regular Solution Theory

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The partition of carboxylic acids between benzene and 0.1 mol dm^{-3}(H,Na)ClO_4 aqueous solution has been studied at 25 °C. Carboxylic acids used include acetic, propanoic, butanoic, pentanoic, hexanoic, and decanoic acids. The hydration of monomeric acids in benzene being taken into account, the hydration-corrected partition constant has been calculated. The effect of the chain length on the partition is accounted for with the aid of the newly estimated solubility parameters and empirical binary coefficients. Applicability of the empirical solubility parameter of water (35.89 $J^{1/2}$ $cm^{-3/2}$) has also been discussed.

The distribution behaviors of various organic compounds between two immiscible solvents have been extensively reviewed.[1-3] Milicevic[4] and Koshimura[5] have tried a systematic consideration on the solubility leading to a quantitative prediction of the partition of some organic compounds and metal chelates, respectively.

Of many attempts to introduce basic concepts into a general treatment of partition equilibria, the most successful one is the approach based on the theory of regular solution,[6] although its application to liquid-liquid partition is limited in some cases.[7]

The regular solution theory has been used to interpret the solvent effects on the extraction of organic compounds,[8,9] metal chelates,[10-12] halide complexes,[13,14] and ion pairs.[12,15] The same theory has been found useful in discussing the substituent effects on the partition of pyridine bases.[16]

In the previous papers,[17,18] we have presented the results of the partition of carboxylic acids between benzene and the aqueous solution. In this paper we attempt to interpret the effect of the chain length on the partition of carboxylic acids.

Theoretical

According to Hildebrand and Scatchard's theory of regular solution,[6] the activity of a solute HA, a_{HA}, is given by:

$$RT \ln a_{HA} = RT \ln x_{HA} + V_{HA}\phi_S^2(\delta_S - \delta_{HA})^2, \quad (1)$$

where x_{HA}, V_{HA}, and δ_{HA} denote the mole fraction, molar volume and solibility parameter, respectively, of the solute HA, and ϕ_S and δ_S the volume fraction and solubility parameter of the solvent S, respectively. The pure liquid was chosen as a standard state. The entropy of mixing molecules of the different size being taken into account, the following equation is relevant:

$$RT \ln a_{HA} = RT[\ln \phi_{HA} + \phi_S(1 - V_{HA}V_S^{-1})] + V_{HA}\phi_S^2(\delta_S - \delta_{HA})^2, \quad (2)$$

where the volume fraction of HA, ϕ_{HA}, is related with the molar concentration of HA, $[HA]_S$, as:

$$[HA]_S = 1000\,\phi_{HA}/V_{HA}. \quad (3)$$

Instead of using *the rigid geometric mean assumption* involved in the usual regular solution theory, we include an empirical binary coefficient,[19] $l_{HA,S}$, in Eq. 2. Then, we obtain:

$$RT \ln a_{HA} = RT(\ln [HA]_S - \ln 1000V_{HA}^{-1} + \phi_S(1 - V_{HA}V_S^{-1})) + V_{HA}\phi_S^2[(\delta_S - \delta_{HA})^2 + 2l_{HA,S}\delta_{HA}\delta_S]. \quad (4)$$

When the solute is partitioned between the aqueous and organic phases, *i.e.*, $a_{HA,w} = a_{HA,o}$, and that the concentration of HA is sufficiently low in both phases, *i.e.*, $\phi_w = 1$ and $\phi_o = 1$, we obtain from Eq. 4 the following expression for the partition constant of HA, $K_{D,HA}$:

$$\log K_{D,HA} = V_{HA}[(\delta_w - \delta_{HA})^2 - (\delta_o - \delta_{HA})^2 + 2l_{HA,w}\delta_{HA}\delta_w - 2l_{HA,o}\delta_{HA}\delta_o + RT(V_o^{-1} - V_w^{-1})]/2.303RT, \quad (5)$$

where subscripts w and o denote the aqueous and organic phases, respectively. In Eq. 5 the aqueous solution is considered as a hypothetical regular solution.

Results and Discussion

Hydration and Partition Constants. At low pH, where anionic species may be neglected in the aqueous phase, the conditional partition constant of a monomeric carboxylic acid between the aqueous and organic phases, $K'_{D,HA}$, is written as:

$$HA_w \overset{\beta_{11}}{\rightleftharpoons} HA'_o, \quad K'_{D,HA} = [HA']_o/[HA]_w. \quad (6)$$

Measurement of water solubility[17,18] revealed that the monomeric acids are more or less hydrated in benzene contacted with water:

$$HA_o + H_2O_o \overset{\beta_{11}}{\rightleftharpoons} HA \cdot H_2O_o$$
$$\beta_{11} = [HA \cdot H_2O]_o/[HA]_o[H_2O]_o, \quad (7)$$

where β_{11} denotes the hydration constant. The conditional partition constant, $K'_{D,HA}$, determined from partition data is related with $K'_{D,HA}$, which is corrected for the hydration, as follows:

$$K_{D,HA} = K'_{D,HA}(1 + \beta_{11}[H_2O]_o)^{-1}, \quad (8)$$

where the monomer concentration of water in benzene at 25 °C is taken to be 0.0345 mol dm^{-3}.[18] The values for some aliphatic carboxylic acids are summarized in Table 1.

Evaluation of Solubility Parameters. If the heat of vaporization, ΔH^v/J mol^{-1}, is determined at a certain temperature, say 25 °C, the solubility parameter is given by:

$$\delta_{HA} = (\Delta H^v_{298} - RT)^{1/2}V_{HA}^{-1/2} \quad (9)$$

Table 1. Partition constant and hydration constant of carboxylic acids at 25 °C

Acid	$\log K'_{D,HA}$	$\log \beta_{11}$	$\log K_{D,HA}$ (obsd)	$\log K_{D,HA}$ (calcd)[g]
Acetic acid	−2.08	1.13	−2.25[a]	(−2.25)[f]
Propanoic acid	−1.34	0.99	−1.43[b]	−1.50
Butanoic acid	−0.97	0.98	−1.04[c]	−1.08
Pentanoic acid	−0.27	0.95	−0.39[c]	−0.43
Hexanoic acid	0.28	0.90	0.17[c]	0.16
Heptanoic acid	—	—	—	0.78
Octanoic acid	1.67[d]	—	—	1.35
Nonanoic acid	—	—	—	1.99
Decanoic acid	2.70[e]	—	2.62[a]	2.60

a) Y. Fujii, Y. Kawachi, and M. Tanaka, *J. Chem. Soc., Faraday Trans. 1*, **77**, 63 (1981). b) This work. c) Y. Fujii and M. Tanaka, *J. Chem. Soc., Faraday Trans. 1*, **73**, 788 (1977). d) G. K. Schweitzer and D. K. Morris, *Anal. Chim. Acta*, **45**, 65 (1969). e) M. Tanaka, N. Nakasuka, and S. Sasane, *J. Inorg. Nucl. Chem.*, **31**, 2591 (1969). f) Observed value used for calculation. g) Eq. 5.

where V_{HA}/cm^3 mol^{-1} is the molar volume of the pure liquid acid.

The lower monocarboxylic acids are known to dimerize in gas phase[20] even at pressure as low as 1 mmHg, and hence the heat of vaporization calculated from vapor pressure data only leads to erroneous results. The heat of vaporization from the vapor pressure data should be corrected for the heat of dimerization in the gas phase.[21] The heat of fusion should also be taken into account for the solid acids.[22] The corrected values of vaporization enthalpy in kJ mol^{-1} unit for fatty acids are given in Table 2. It has been shown by a number of workers[22-24] that there is a linear relationship between ΔH^v_{298} of the pure acids of a homologous series and its chain length. For a fatty acids, $CH_3(CH_2)_nCOOH$, we obtain the following best-fitting relation for the heat of vaporization ΔH^v_{298}/kJ mol^{-1} in Table 2:

Table 2. Heat of vaporization, molar volume, and solubility parameter of carboxylic acids at 25 °C

Acid	ΔH^v_{298} / kJ mol^{-1}	V_{HA}[d] / cm^3 mol^{-1}	δ_{HA}[e] / J$^{1/2}$ cm$^{-3/2}$
Acetic acid	51.5±1.7[a]	61.0	28.0
Propanoic acid	55.2±2.1[a]	77.5	26.1
Butanoic acid	58.6±4.2[a]	92.5	24.7
Pentanoic acid	62.3±2.9[b]	110.5	23.8
Hexanoic acid	73.2±2.1[b]	127.0	23.0
Heptanoic acid	72.0±1.7[b]	143.5	22.4
Octanoic acid	82.8±0.8[b]	160.0	21.9
Nonanoic acid	82.4±0.4[c]	176.5	21.5
Decanoic acid	89.5±2.1[c]	193.0	21.2

a) T. Konicek and I. Wadsö, *Acta Chem. Scand.*, **24**, 2612 (1970). b) C. G. Kruif and H. A. J. Oonk, *J. Chem. Thermodyn.*, **11**, 287 (1979). c) D. P. Baccanari, J. A. Novinski, Y. Pan, M. M. Yevitz, and H. A. Swain, *Trans. Faraday Soc.*, **64**, 1201 (1968). d) Calculated according to Eq. 11. e) Calculated according to Eq. 9 by employing calcul ated values of ΔH^v_{298} (Eq. 10) and V_{HA} (Eq. 11).

$$\Delta H^v_{298} = 50.3 + 4.9\,n, \tag{10}$$

where n denotes the number of CH_2 group. The increment in the heat of vaporization per CH_2, 4.9 kJ mol^{-1}, is in good agreement with that of (4.9±0.1) kJ mol^{-1} for normal alkanes, 1-alkenes, 1-alkanols, 1-alkanethiols, 1-chloro-, and 1-bromoalkanes and alkanoates.[23]

For the fatty acids, the molar volumes are proportional to chain length.[24-26] According to Rheineck and Lin,[26] the group contribution to the molar volume in cm^3 mol^{-1} unit is 34.0, 16.5 and 27.0 for methyl, methylene and carboxyl groups, respectively. Then the molar volume V_{HA}/cm^3 mol^{-1} for the fatty acids at 25°C is given by:

$$V_H = 61.0 + 16.5\,n, \tag{11}$$

where 61.0 cm^3 mol^{-1} for acetic acid was used as a standard for convenience.

With values of ΔH^v_{298} and V_{HA} in hand we calculate δ_{HA} of fatty acid by Eq. 9. Calculated δ_{HA} values are tabulated in Table 2.

As solubility parameter of the aqueous solution we used 47.9 J$^{1/2}$ cm$^{-3/2}$ calculated from the heat of vaporization of pure water.[27]

Determination of Binary Coefficients. We assume the additive property of excess enthalpy of mixing, ΔH^E, for functional groups in an organic compound X-$(CH_2)_n$-Y (abbreviated as X-n-Y), X, Y, and CH_2:

$$\Delta H^E_{X\text{-}n\text{-}Y} = \Delta H^E_X + n\Delta H^E_{CH_2} + \Delta H^E_Y. \tag{12}$$

The excess enthalpies of mixing of this compound and X, Y, and CH_2 are given by:

$$\Delta H^E_{X\text{-}n\text{-}Y} = V_{X\text{-}n\text{-}Y}\,[(\delta_s - \delta_{X\text{-}n\text{-}Y})^2 + 2l_{X\text{-}n\text{-}Y,s}\delta_{X\text{-}n\text{-}Y}\delta_s], \tag{13}$$

$$\Delta H^E_X = V_X[(\delta_s - \delta_X)^2 + 2l_{X,s}\delta_X\delta_s], \tag{14}$$

$$\Delta H^E_Y = V_Y[(\delta_s - \delta_Y)^2 + 2l_{Y,s}\delta_Y\delta_s], \tag{15}$$

$$\Delta H^E_{CH_2} = V_{CH_2}[(\delta_s - \delta_{CH_2})^2 + 2l_{CH_2,s}\ \delta_{CH_2}\delta_s], \tag{16}$$

where the subscript s denotes a solvent with which X-n-Y is mixed.

Substituting Eqs. 13—16 into Eq. 12 and assuming the additivity for the molar volume and the cohesive energy,[26] we obtain

$$(l_{X\text{-}n\text{-}Y,s} - 1)\delta_{X\text{-}n\text{-}Y}V_{X\text{-}n\text{-}Y} = (l_{X,s} - 1)\delta_X V_X + n(l_{CH_2,s} - 1)\delta_{CH_2}V_{CH_2} + (l_{Y,s} - 1)\delta_Y V_Y \tag{17}$$

$$= (l_{X\text{-}Y,s} - 1)\delta_{X\text{-}Y}V_{X\text{-}Y} + n(l_{CH_2,s} - 1)\delta_{CH_2}V_{CH_2}. \tag{18}$$

For an aliphatic carboxylic acid HA, X=CH_3 and Y=COOH. Then we may rewrite Eq. 18 as follows:

$$(l_{HA,s} - 1)\delta_{HA}V_{HA} = (l_{HA°,s} - 1)\delta_{HA°}V_{HA°} + n(l_{CH_2,s} - 1)\delta_{CH_2}V_{CH_2}, \tag{19}$$

where HA° denotes acetic acid. Then the plot of the left hand side of Eq. 19 against n should give rise to a straight line with the intercept of $(l_{HA°,s}-1)\delta_{HA°}V_{HA°}$ and the slope of $(l_{CH_2,s}-1)\delta_{CH_2}V_{CH_2}$.

The binary coefficient $l_{HA,W}$ of hexanoic to nonanoic acids was determined according to the following equation derived from Eq. 4:

$$\log[HA]_w = 3 - \log V_{HA} - 0.434\phi_w(1 - V_{HA}V_w^{-1}) - 0.434V_{HA}\phi_w^2[(\delta_w - \delta_{HA})^2 + 2l_{HA,w}\delta_{HA}\delta_w]/RT, \tag{20}$$

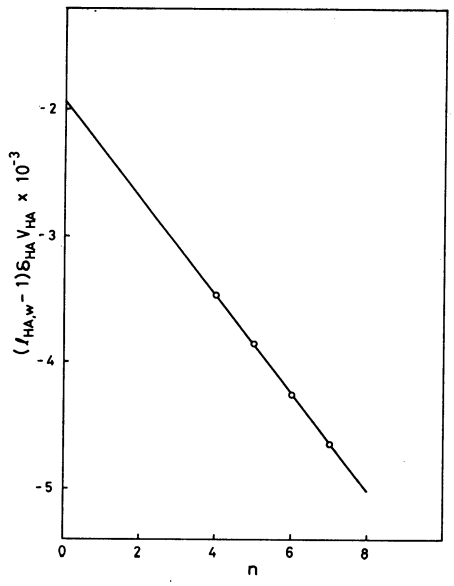

Fig. 1. Correlation between $(l_{HA,w}-1)\delta_{HA}V_{HA}$ and chain length. The line was drawn using the values $l_{CH_2,w}=-0.350$ and $l_{HA\circ,w}=-0.136$.

where $[HA]_w$ is the solubility of monomeric acid in water, corrected for the ionic dissociation. We utilized the solubility of carboxylic acids given by Ralston and Hoerr[28] interpolated to 25 °C.

As predicted from Eq. 19, $(l_{HA,w}-1)\delta_{HA}V_{HA}$ is linearly related with the number of methylene groups in carboxylic acids, n (see Fig. 1). By means of the method of least squares according to Eq. 19, we obtain

$$(l_{HA,w}-1)\delta_{HA}V_{HA}=-1940-386\,n. \quad (21)$$

That is $(l_{HA\circ w}-1)\,\delta_{HA\circ}V_{HA\circ}=-1940$ and $(l_{CH_2,w}-1)\times\delta_{CH_2}V_{CH_2}=-386$ in $J^{1/2}\,cm^{3/2}$ unit. From these equations together with values of $\delta_{HA\circ}V_{HA\circ}$ (Table 2) and $\delta_{CH_2}V_{CH_2}=286$ given by Rheineck and Lin,[26] the following binary coefficients are determined: $l_{HA\circ,w}=-0.136$ and $l_{CH_2,w}=-0.350$.

For hydrocarbons (abbreviated as HC), X=Y=CH_3 in Eq. 17. Then we obtain Eq. 22 for the subscript s=o

$$(l_{HC,o}-1)\delta_{HC}V_{HC}=2(l_{CH_3,o}-1)\delta_{CH_3}V_{CH_3}+n(l_{CH_2,o}-1)\delta_{CH_2}V_{CH_2}. \quad (22)$$

Table 3. Excess enthalpy of equimolar mixture at 298.15 K and derived binary coefficient

System	ΔH^E_{HC}/J mol^{-1}	$l_{HC,o}$
Pentane+Benzene	857[a]	0.028
Hexane+Benzene	898[b]	0.034
Heptane+Benzene	933[c]	0.037
Octane+Benzene	969[a]	0.039
Undecane+Benzene	1060[a]	0.045
Dodecane+Benzene	1101[a]	0.046
Tetradecane+Benzene	1183[a]	0.048
Pentadecane+Benzene	1207[a]	0.049
Hexadecane+Benzene	1256[a]	0.050
Heptadecane+Benzene	1289[a]	0.052

a) C. Menduina and M. Diaz-Pena, *Int. DATA Ser., Selec. Data Mixture, Ser. A*, p. 53, 55, 57—62 (1976). b) M. I. Paz-Andrade, *ibid.*, p. 100 (1973). c) J. P. E. Grolier, *ibid.*, p. 223 (1974).

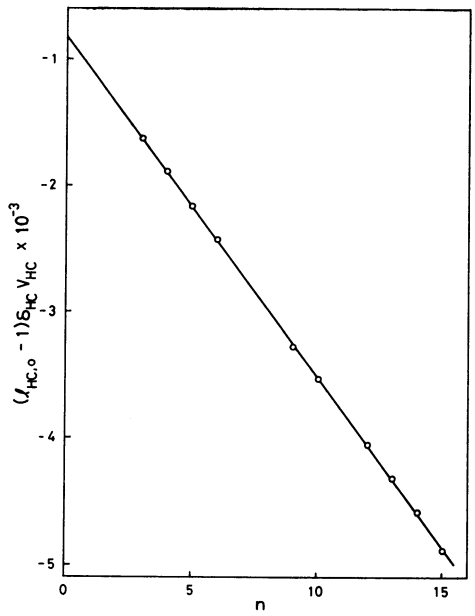

Fig. 2. Correlation between $(l_{HC,o}-1)\delta_{HC}V_{HA}$ and chain length. The line was drawn using the values $l_{CH_2,o}=0.055$ and $(l_{CH_3,o}-1)\delta_{CH_3}V_{CH_3}=-409$.

Values of $l_{HC,o}$ for benzene was evaluated from the excess enthalpy of the system $C_6H_6+CH_3(CH_2)_nCH_3$ by means of Eq. 13. The results are tabulated in Table 3. Then the plot of the left hand side of Eq. 22 against n (Fig. 2) gives us the value $(l_{CH_3,o}-1)\,\delta_{CH_3}V_{CH_3}$ from the slope. By means of the method of least squares we obtain $(-270.3\pm1.0)J^{1/2}\,cm^{3/2}$ as $(l_{CH_3,o}-1)\,\delta_{CH_3}V_{CH_3}$ for benzene. $\delta_{CH_3}V_{CH_3}=286\ (J^{1/2}\,cm^{3/2})$,[26] then we obtain $l_{CH_3,o}=0.055$.

Now according to Eq. 5 together with the known value of the partition constant of acetic acid (Table 1), we can determine the value of $l_{HA\circ,o}=0.034$ for benzene.

With these values of binary coefficients for benzene, we can rewrite Eq. 19 as follows:

$$(l_{HA,o}-1)\delta_{HA}V_{HA}=-1650-270\,n. \quad (23)$$

Values of $l_{HA,w}$ and $l_{HA,o}$ calculated by Eqs. 21 and 23, respectively, are summarized in Table 4.

Partition Constant of Aliphatic Carboxylic Acids. With thus determined values of $l_{HA,w}$ and $l_{HA,o}$ in hand, Eq. 5 enable us to predict the partition constant of aliphatic carboxylic acids. We utilized $\delta_w=47.9\,J^{1/2}$

Table 4. Binary coefficients of carboxylic acids

Acid	$l_{HA,w}\times10$		$l_{HA,o}\times10^2$
	Eq. 21	Solubility[a]	Eq. 23
Acetic acid	−1.36	—	3.4
Propanoic acid	−1.50	—	4.7
Butanoic acid	−1.68	—	5.4
Pentanoic acid	−1.78	—	6.2
Hexanoic acid	−1.93	−1.90	6.3
Heptanoic acid	−2.04	−2.05	6.5
Octanoic acid	−2.15	−2.14	6.5
Nonanoic acid	−2.23	−2.24	6.6
Decanoic acid	−2.29	—	6.7

a) Calculated from the data in Ref. 28.

$cm^{-3/2}$ and $\delta_o = 18.7\ J^{1/2}\,cm^{-3/2}$. Calculated values of the partition constant are listed in Table 1. It is evident that the values calculated by Eq. 5 compare very favorably with the experimental.

It is known that, in a homologous series, the partition constant $\log K_D$ is a linear function of the number of carbon atoms involved. According to Eq. 5, the increment of $\log K_D$ for an added methylene group may be written as:

$$\Delta \log K_D/CH_2 = V_{CH_2}[(\delta_w - \delta_{CH_2})^2 - (\delta_o - \delta_{CH_2})^2 + 2l_{CH_2,w}\delta_{CH_2}\delta_w - 2l_{CH_2,o}\delta_{CH_2}\delta_o + RT(V_o^{-1} - V_w^{-1})]/2.303RT. \quad (24)$$

Here we assume the additivity of molar volume and cohesive energy of functional groups. Now with $V_{CH_2} = 16.5$, $\delta_{CH_2} = 17.44$(Ref. 26), $l_{CH_2,w} = -0.350$ and $l_{CH_2,o} = 0.055$ for benzene, we obtain $\Delta \log K_D/CH_2 = 0.59$ for this solvent from Eq. 24. This value is consistent with the previous findings, *i.e.*, $\Delta \log K_D/CH_2 = 0.56$—$0.64$ for partition of alkanoic acids[3,29] and 1-alkanols[3] between benzene and water. It is worth noting from Eq. 24 that $\Delta \log K_D/CH_2$ depends on the organic solvent used, while it is independent of a polar group of alkyl compounds attached to the terminal. In Table 5 are listed values of $\Delta \log K_D/CH_2$ for several water-organic solvent systems together with $l_{CH_2,o}$, δ_o, and V_o. Interestingly values of $l_{CH_2,o}$ are very near to zero for all solvents as compared to $l_{CH_2,w} = -0.350$.

Table 5. $\Delta \log K_D/CH_2$ values for several organic solvent–water systems

Organic solvent	δ_o [e]	V_o [e]	$l_{CH_2,o} \times 10^2$ [f]	$\Delta \log K_D/CH_2$
Hexane	14.91	131.6	2.1	0.59
Cyclohexane	16.73	108.7	4.5	0.60
Carbon tetrachloride	17.48	97.1	3.9	0.59, 0.60[a]
Benzene	18.73	89.4	5.5	0.57, 0.60[b]
Nitrobenzene	20.45	102.7	4.0	0.56, 0.60[b]
1,2-Dichloroethane	20.16	79.6	2.2	0.60, 0.58[b]
Diisopropyl ether	14.48	142.3	2.3	0.57, 0.56[b]
1-Octanol	21.06	158.5	1.5	0.56, 0.54[c] 0.50[d]

a) S. S. Davis, T. Higuchi, and J. H. Rytting, *J. Pharm. Pharmacol.*, **24**, 30P (1972). b) I. Kojima, M. Yoshida, and M. Tanaka, *J. Inorg. Nucl. Chem.*, **32**, 987 (1970). c) A. Leo, C. Hansch, and D. Elkins, *Chem. Rev.*, **71**, 525 (1971). d) R. Collander, *Acta Chem. Scand.*, **5**, 774 (1951). e) Solubility parameter ($J^{1/2}\,cm^{-3/2}$) and molar volume ($cm^3\,mol^{-1}$) obtained from Refs. 24 or 27. f) Calculated according to Eq. 19.

Wakahayashi *et al.*[9] have used the following relationship for the partition constant $K_{B,o}$ of β-diketones and β-diketonates

$$\log K_{D,B} = V_B[(\delta'_w - \delta_B)^2 - (\delta_o - \delta_B)^2 + RT(V_o^{-1} - V_w^{-1})]/2.303RT, \quad (25)$$

where the subscript B denotes a solute partitioned between the aqueous and organic phases. Eq. 25 was successfully used for these systems with the empirical solubility parameter of water $\delta_w' = 35.89\ J^{1/2}\,cm^{-3/2}$.

Table 6. Empirical solubility parameter of water for different solute and solvent

System(solute–solvent)	$\delta'_w/J^{1/2}\,cm^{-3/2}$
Hexanoic acid–Benzene	34.6[a]
Decanoic acid–Benzene	35.1[a]
Aniline–Hexane	33.5[b]
Aniline–Carbon tetrachloride	33.8[c]
Aniline–Benzene	33.5[c]
Aniline–1-Octanol	34.5[d]
Nitropropane–Cyclohexane	34.4[e]
Nitropropane–Carbon tetrachloride	34.5[f]
Nitropropane–Toluene	36.0[e]
Nitropropane–Chloroform	36.4[e]
1-Pentanol–Hexane	35.4[g]
1-Pentanol–Benzene	35.3[g]
1-Pentanol–1-Octanol	37.1[h]
Phenol–Hexane	34.9[i]
Phenol–Benzene	35.5[i]
Phenol–1,2-Dichloroethane	35.1[j]
Phenol–1-Octanol	38.1[k]

Data source: a) This work. b) T. Sekine, Y. Suzuki, and N. Ihara, *Bull. Chem. Soc. Jpn.*, **46**, 995 (1973). c) W. Kemula, H. Buchowski, and W. Pawlowski, *Rocz. Chem.*, **43**, 1555 (1969). d) T. Fujita, J. Iwasa, and C. Hansch, *J. Am. Chem. Soc.*, **86**, 5175 (1964). e) W. Kemula, H. Buchowski, and J. Teperek, *Bull. Acad. Pol. Sci., Ser. Sci. Chem.*, **12**, 343 (1964). f) E. Kuznetsova, *Zh. Fiz. Khim.*, **48**, 2865 (1974). g) I. M. Korenman and Z. G. Chernorukova, *Zh. Prikl. Khim.*, **47**, 2523 (1974). h) A. Leo, C. Hansch, and D. Elkins, *Chem. Rev.*, **71**, 525 (1971). i) D. S. Abrams and J. M. Prausnitz, *J. Chem. Thermodyn.*, **7**, 61 (1975). j) W. Herz and W. Rathmann, *Z. Electrochem.*, **19**, 552 (1913). k) Ya. I. Korenman and V. Yu. Udalova, *Zh. Fiz. Chem.*, **48**, 1223 (1923).

δ_w' is considerably lower than the value obtained from the heat of vaporization $\delta_w = 47.9\ J^{1/2}\,cm^{-3/2}$. Comparison of Eq. 5 with Eq. 25 leads to the following:

$$(\delta'_w - \delta_B)^2 = (\delta_w - \delta_B)^2 + 2l_{B,w}\delta_B\delta_w - 2l_{B,o}\delta_B\delta_o, \quad (26)$$

in which δ'_w is correlated with the binary coefficients $l_{B,w}$ and $l_{B,o}$. From Eq. 26 it is obvious that δ'_w differs from solvent to solvent and from solute to solute. In Table 6 are listed values of δ'_w calculated for different solvents and solutes. If the values of δ'_w are compared for the same solute, they are close to each other for organic solvents of low polarity and limited tendency of hydrogen bonding. From this table may be seen the limit of the use of the empirical δ'_w values in the study of solvent effect on the extraction.

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