PHYSICAL CHEMISTRY

1962

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

E. S. RUDAKOV

THERMODYNAMIC CALCULATION OF THE SOLVATING ABILITY OF SOLVENTS

(Presented by Academician V. N. Kondrat' ev, 21 VI 1961)

In papers ([1],[2]), to describe the nonspecific solvation of polar particles, the equation

$$\Delta E'_{1c} = 2.3RT \lg \gamma_{1c} = V_1^{-2/3} \left(E_1^{1/2} V_1^{-1/3} - E_c^{1/2} V_c^{-1/3} \right)^2, \qquad (1)$$

was proposed, where $\Delta E'_{1c}$ is the change in solvation energy upon transfer of a mole of particles 1 from pure liquid 1 into medium C; γ_{1c} is the activity coefficient of particles 1 in medium C, referred to pure liquid 1 as the standard state; V_1 and V_c are molar volumes; E_1 and E_c are the energies of nonspecific interaction between identical molecules in pure liquid 1 and in medium C, respectively. From (1) follows the dependence of the rate constant of a monomolecular reaction k_c on the medium ([1])

$$\lg k_c = \lg k_r + E_c^{1/2} V_c^{-1/3} \left[\frac{2}{2.3RT} \left(E_{\neq}^{1/2} V_{\neq}^{1/3} - E_1^{1/2} V_1^{1/3} \right) \right], \qquad (2)$$

where k_r is the reaction rate in the gas phase; $E_{\neq}$ and $V_{\neq}$ are the interaction energy and molar volume for a hypothetical liquid consisting only of activated complexes; the factor in square brackets does not depend on the medium. By eliminating from the two equations the unknown parameter $E_c^{1/2} V_c^{-1/3}$, which depends only on the medium, one can obtain equations that relate already known quantities and verify that they agree well with experimental data.

Since an equation of type (1) is obtained directly from the van der Waals equation ([3]), the applicability of (1) and (2) to the calculation of nonspecific medium effects means that the problem of solvating ability in the first approximation can be considered on the basis of the simplest model of a liquid as a strongly compressed gas.

Let us consider the possibility of directly calculating interaction energies from the properties of pure liquids.

1. **Calculation of E.** Applying the van der Waals equation ([4],[5]) to the equilibrium between a liquid and its vapors, we have

Fig. 1. Dependence of A on temperature: I –water, II –ammonia, III –ethyl alcohol, IV –n-pentane

Figure 1: Fig. 1. Dependence of A on temperature: I –water, II –ammonia, III –ethyl alcohol, IV –n-pentane

$$E = RT \ln \frac{V_r}{V_\ell - B} - p_s(V_r - V_\ell) + E^r, \qquad E^r = \int_{V_r}^{\infty} \left(\frac{RT}{V} - p \right) dV, \qquad (3)$$

where V_r and V_ℓ are the molar volumes of the phases; p_s is the saturated vapor pressure; $E^r = 0$ if the vapor behaves as an ideal gas. According to the equation of state, we replace the "free volume" $V_\ell - B$ by RTV_ℓ/E. For the case $E^r = 0$ we have

$$E = RT(\ln E - \ln V_\ell - \ln p_s - 1). \qquad (4)$$

In (3) and (4), E has the meaning of the van der Waals potential $E = A/V_\ell$. Calculation of E from (4) using data for p_s and V_ℓ for various liquids shows that the "force constant," as might be expected, decreases noticeably with increasing temperature: $A = A_0 + A_1/T$, and formally

the term A_0 can be correlated with the dispersion component, and A_1/T with the orientational component of the intermolecular interaction (Fig. 1).

It is now possible to calculate the values of E_c from the properties of pure liquids, determine for each liquid the parameter $E_c^{1/2}V_c^{-1/3}$, and compare the thermodynamic scale of values of $E_c^{1/2}V_c^{-1/3}$ obtained in this way with data on the influence of the medium on various uncomplicated processes in solutions.

2. Reaction kinetics. Figure 2 presents the dependence of $\lg k_c$ for the solvolysis of $(CH_3)_3CCl$ in liquid media ([8–10,1]) and in the gas phase ([11]) (*I*) and of $(CH_3)_3CBr$ in liquid media ([12–14]) and in the gas phase ([15]) (*II*) on the values of $E_c^{1/2}V_c^{-1/3}$. These reactions are among the most remarkable examples of the exceptionally strong influence of an indifferent solvent on reactivity. We see that in both cases the data for different media, as should follow from (2), lie near the corresponding straight lines, and that extrapolation of the straight line to $E_c = 0$ corresponds to the experimental value of the reaction rate in the gas phase.

Fig. 1. Dependence of A on temperature:
I –water, *II* –ammonia, *III* –ethyl alcohol, *IV* –*n*-pentane

3. Spectral shifts. The problem of the displacement of electronic absorption bands upon variation of the medium is in principle no different from the problem of the influence of the medium on the kinetics of monomolecular reactions: in

both cases the effect of the medium is connected with the difference in solvation of the normal molecule and of the excited (or activated) state. If ν_r denotes the position of the band in the gas phase and ν_c in medium C, then $h(\nu_c - \nu_r)$ must be equal to the difference between the solvation energies of the molecule and of the excited state in medium C. According to (1), the solvation energy of particle 1 relative to vacuum ($E_c = 0$) as the absolute standard is equal to $\Delta E_{1c} - E_c$. Consequently,

$$h\nu_c = h\nu_r + (\Delta E_{\neq c} - \Delta E_{\neq}) - (\Delta E_{1c} - E_1), \tag{5}$$

where the index $\neq$ characterizes the excited state of the molecule. Simplifying (5) with account of (1), under the natural assumption $V_{\neq} = V_1$, we have

$$h\nu_c = h\nu_r + E_c^{1/2} V_c^{-1/3} \{2V_1^{1/3}(E_1^{1/2} - E_{\neq}^{1/2})\}. \tag{6}$$

According to (6), in uncomplicated cases the frequency ν_c must be a linear function of $E_c^{1/2} V_c^{-1/3}$. In Fig. 2 *III* are shown Kosower' s data ([16]) $Z = h\nu_{\max}$ (h is Planck' s constant) for 1-ethyl-4-carbomethoxypyridinium iodide. In the investigated region, ν_c varies from 254 to 282 mμ. We see that dependence (6) is fulfilled.

The number of such examples could be considerably increased, taking into account the data systematized by Bronshtein ([6]).

4. Solubility. Starting from the model of a liquid as a compressed gas, the solubility equation has been obtained

$$\ln \frac{\varphi_c}{\varphi_1 N_{1c}} + \left(\frac{\varphi_1}{\varphi_c} - 1\right) = \frac{V_1^{2/3}}{RT} \left(E_1^{1/2} V_1^{-1/3} - E_c^{1/2} V_c^{-1/3}\right)^2, \tag{7}$$

where N_{1c} is the solubility of liquid 1 in solvent C in mole fractions; $\varphi_i = V_i - B_i = RTV_i/E_i$ is the "free volume" of liquid i. It is applicable to the entire range of media up to the gas phase: at $E_c = 0$ (the medium is vacuum) $\varphi_c = V_r$, $N_{1c} = 1$, and (7) passes into equation (3), which serves

by determining E_1. The left-hand side of (7) may approximately be replaced by $\ln(1/\varphi_1 m_{1c})$, where m_{1c} is the solubility in moles per liter.

In Fig. 2 IV the application of formula (7) to the solubility of glycine in neutral media is shown (in liquid media ([17]) and in the gas phase ([18]); the latter value was obtained by extrapolating to 25° the data on the vapor pressure over crystalline glycine). On the ordinate is plotted $\sqrt{\lg(1/m_{1c}\varphi_1)}$. We see that the data lie on a single straight line and that its continuation to $E_c = 0$ corresponds to the experimental value of the solubility of glycine in vacuum.

In the case of *n*-nitroaniline the value $E_1^{1/2} V_1^{-1/3}$ lies within the range of the scale of the media used, and therefore a maximum is observed on the solubility

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

curve. In Fig. 3 the two half-lines correspond to the plus and minus signs before the root. Continuing the count into the region of negative ordinates, we obtain one straight line encompassing all media: from water to vacuum. The strong deviation in the case of ether must apparently be ascribed to the formation of a molecular compound with *n*-nitroaniline. In these calculations the solubility N_{1c} was referred to the ideal solubility N_{id}. The best value of $\lg N_{\text{id}}$, satisfying the data of Fig. 3, is equal to

Fig. 2.

Fig. 3

Fig. 2. Application of the scale of values $E_c^{1/2}V_c^{-1/3}$ to the calculation of nonspecific polar effects of the medium; 25° (see explanation in the text). Solvents (in Figs. 2 and 3): 1 —water, 2 —formamide, 3 —formic acid, 4 —glycerol, 5 —ethylene glycol, 6 —methyl alcohol, 7 —acetic acid, 8 —nitromethane, 9 —ethyl alcohol, 10 —ammonia, 11 —*n*-butyl alcohol, 12 —isopropyl alcohol, 13 —tert.-butyl alcohol, 14 —acetone, 15 —dichloromethane, 16 —tert.-butyl chloride, 17 —isooctane, 18 —benzene, 19 —chloroform, 20 —ethyl ether, 21 —carbon tetrachloride, 22 —carbon disulfide. The ordinate axis (left) is the vacuum line. (Regarding solvents 2, 3, and 7 see § 5)

Fig. 3. Solubility of *n*-nitroaniline ([19]) as a function of the parameter $E_c^{1/2}V_c^{-1/3}$; 20–25°. The numbering of the solvents is given in the caption to Fig. 2. Point *i* corresponds to ideal solubility; at this point $E_c^{1/2}V_c^{-1/3} = E_1^{1/2}V_1^{-1/3}$, E_1 being calculated from the vapor pressure over *n*-nitroaniline.

−1.52; calculated by the Schröder equation from ΔH_{m} and T_{m}, $\lg N_{\text{id}} = -1.13$.

5. Solvents with variable solvating ability. Liquids capable of dimerization, for example carboxylic acids, can solvate dissolved particles, evidently, either in the form of monomers, or in the form of dimers, or partly in both forms. Since the degree of dissociation of dimers in the vicinity of the dissolved particle depends on its properties (and on temperature), these liquids may be called solvents with variable solvating ability. In the case of carboxylic acids, the energies corresponding to the maximum solvating ability (in the form of monomers), E_{max}, and the minimum (in the form of dimers), E_{min}, can be calculated from the properties of the pure liquids; E_{min} is determined from (4), taking into account the doubled molecular weight at $E^{\text{r}} = 0$, since in vapors

these acids are almost completely dimerized; E_{max} is determined from (3). The work of separation of dimers in vapors was found by direct integration of E^r in (3):

$$E^r = RT\left(\ln\frac{x}{2} + \frac{1}{x} - \frac{1}{2}\right), \qquad x = \sqrt{1 + \frac{8kRT}{V_r}} + 1,$$

where $k = p_2/p_1^2$ is the equilibrium constant; p_1 is the vapor pressure of monomers; p_2, of dimers. Such a calculation from the data of (7) gives, for HCOOH and CH_3COOH, the same value $E^r = 1.3$ kcal/mole. Formamide, apparently, likewise represents a medium with variable solvating ability. In this case E_{max} was determined from (4), and E_{min} from (3), on the assumption that $E^r = -1.3$ kcal/mole and that the molecular weight is doubled. The results are shown in Fig. 2 in the form of horizontal segments. It is seen that HCOOH appears, in the examples considered, as a medium with maximum solvating ability, while CH_3COOH and $HCONH_2$ have intermediate solvating abilities.

Conclusion. The solvating ability of a solvent with respect to polar particles is closely connected with the magnitude of the work of separation of molecules in the pure liquid against cohesive forces and can be determined from the saturated-vapor pressure and the density of the liquid. This makes it possible, on a thermodynamic basis, to construct a unified scale of solvating ability of media, $E_c'^{1/2}V^{-1/3}$, including vacuum as the limiting case of a medium with solvating ability equal to zero, and to approach a semi-quantitative description of nonspecific polar effects of the medium (kinetics, solubility, spectra) over a broad range of media with different chemical properties. The theory also leads to the qualitatively correct conclusion about the state of solvent molecules in the vicinity of the dissolved particle, namely to the conclusion that HCOOH solvates particles in the form of monomers, whereas CH_3COOH does so partly in the form of monomers and partly in the form of dimers.

I express my gratitude to D. G. Knorre for discussion of the manuscript.

Received
25 V 1961

CITED LITERATURE

1. E. S. Rudakov, DAN, **129**, 1100 (1959).

2. E. S. Rudakov, *Influence of the Medium on the Kinetics of Solvolysis of tert-Butyl Chloride*, Dissertation, Novosibirsk, 1960.

3. I. I. van Laar, *Zs. anorg. allgem. Chem.*, **145**, 239 (1925).

4. M. P. Vukalovich, I. I. Novikov, *Equation of State of Real Gases*, Moscow, 1948.

5. L. Boltzmann, *Lectures on Gas Theory*, Moscow, 1953.

6. S. Brownstein, *Canad. J. Chem.*, **38**, 1590 (1960).

7. M. S. Vrevsky, *Works on the Theory of Solutions*, Moscow, 1953.

8. A. H. Fainberg, S. Winstein, *J. Am. Chem. Soc.*, **78**, 2770 (1956).

9. G. S. Markova, A. I. Mateshtein, DAN, **35**, 73 (1942).

10. Y. Pocker, *J. Chem. Soc.*, 1960, 1972.

11. D. H. R. Barton, P. F. Onyon, *Trans. Farad. Soc.*, **45**, 725 (1949).

12. A. H. Fainberg, S. Winstein, *J. Am. Chem. Soc.*, **79**, 1602 (1957).

13. L. J. le Roux, E. R. Swart, *J. Chem. Soc.*, 1955, 1475.

14. K. D. Hughes, C. K. Ingold et al., *J. Chem. Soc.*, 1954, 2918, 2930.

15. G. D. Harden, A. MacColl, *J. Chem. Soc.*, 1955, 2455.

16. E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).

17. T. L. McMeekin, E. J. Cohn, J. H. Weare, *J. Am. Chem. Soc.*, **58**, 2173 (1936).

18. S. Takagi, H. Chihra, S. Seki, *Bull. Chem. Soc. Japan*, **32**, 84 (1959).

19. A. Seidell, *Solubilities*, N. Y., **2**, 1941.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.