cell designs tested, the pipet-type cell[24] with capillary filling and overflow tubes appears the most easily adapted to the kinetic requirements that vapor phase above the solution be absent. Shiny platinum electrodes of such size that cell working resistance was in the range 1–50 KΩ proved satisfactory. No particular precaution was required in filling the cells provided the solution had been degassed previously. With high boiling esters this could be done directly just before filling. With the lower boiling halides, it was necessary to freeze the sample in a side arm prior to degassing the backing electrolyte and then to make up the solution under vacuum. Aside from certain rather obvious precautions with respect to the determination of temperature, the chief refinement of technique since the earlier paper is a growing appreciation of the defects of glass as a cell material and the precautions required to ensure highest accuracy in results. In this connection it is wise to regard glass as a sponge which must be thoroughly saturated prior to use in rate determinations with the anion to be produced; *e.g.*, cells in which alkyl iodides are studied must be repeatedly washed with the backing electrolyte solution, the exact number of washes depending on the previous history of the cell.

Temperature Control and Measurement.—The use of a platinum thermometer would seem to be the most satisfactory method of ensuring reliable temperature measurement, other methods being more subject to human frailty. Frequent determinations of the ice point cannot be safely neglected[25] where the thermometer is subject to normal bath vibrations and normal hazards of handling. Adequate stirring of the bath to ensure the same temperature at all cell positions is an obvious requirement. We have found that a large volume sump pump of brass or bronze similar to Eastern Industries model 17-S which drives water through a fan-shaped jet under a perforated false bottom and end baffle creates the required condition.

The necessity for positioning the contact thermometer (Labora) and intermittent heater to ensure feed-back conditions is well known.

Acknowledgment.—It is a pleasure to acknowledge the careful rate determinations made by Mr. S. Sugamori throughout the course of this investigation.

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[24] G. Jones and G. M. Bollinger, THIS JOURNAL, **53**, 411 (1931).

[25] E. H. McLaren, *Can. J. Phys.*, **35**, 78 (1957).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY, CHICAGO 16, ILL.]

Secondary Deuterium Isotope Effects in the Reactions of Carboxylic Acid Derivatives[1a]

BY MYRON L. BENDER[1b] AND MARY S. FENG

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Ethyl acetate-d_3, acetyl chloride-d_3 and acetic anhydride-d_6 have been synthesized. The effect of β-deuterium substitution on the rates of hydrolysis of these carboxylic acid derivatives has been determined. In the basic hydrolysis of ethyl acetate in aqueous solution at 25.0°, $k_H/k_D = 0.90$, a reverse isotope effect. In the hydrolysis of acetyl chloride in 10% and 20% water–acetone (v./v.) at −22°, $k_H/k_D = 1.51$ and 1.62, respectively. The solvolyses of acetyl chloride in cyclohexane containing 0.2665 *M* ethanol and in 5% water–acetone at 25.0° and the solvolysis of acetic anhydride in water at 20.0° showed essentially no secondary deuterium isotope effect. The secondary deuterium isotope effects that occur in the saponification of ethyl acetate and in the hydrolysis of acetyl chloride in 10% and 20% water–acetone can be explained in terms of differences in hyperconjugation in the ground and transition states of these hydrolysis reactions. It is postulated that the transition state of the hydrolysis of acetyl chloride is similar to an acylium ion and that this increase in positive charge leads to an isotope effect in the same direction as that found in SN1 solvolyses. Its magnitude depends on the amount of positive charge developed in the transition state, which in turn is a function of the solvating power and dielectric constant of the medium. It is predicted that the secondary deuterium isotope effect in the hydrolysis of ethyl acetate should be the reverse of that found in SN1 solvolyses, on the basis of the hyperconjugation hypothesis and the known mechanism of the reaction in which the positive charge on the carbonyl carbon atom of the ester in the ground state decreases in the transition state. This prediction is borne out by experiment.

Introduction

A number of kinetic isotope effects of mechanistic consequence involve the substitution of deuterium for hydrogen at a position in the molecule where these atoms cannot be involved in any covalent bond breaking in the chemical reaction under consideration. These so-called secondary (or indirect) isotope effects were first detected in the kinetics of SN1 solvolysis[2,3] of compounds containing β-deuterium atoms and were attributed to differences in hyperconjugative ability between deuterium and hydrogen. It was postulated that the greater reactivity of β-hydrogen compounds compared to β-deuterium compounds resulted from greater stabilization of the electron-deficient transition state by β-hydrogen than by β-deuterium. For instance, in the solvolysis of *t*-amyl chlorides, in which the transition state is believed to resemble the carbonium ion intermediate, it was found that the substitution of deuterium in the methylene group or the methyl groups alpha to the tertiary carbon atom resulted in a lower rate of reaction.[3]

Like the primary deuterium isotope effect which involves the direct cleavage of a carbon–deuterium bond, the secondary deuterium isotope effect has been generally attributed to a mass effect on the frequency of the carbon–hydrogen bond, making the zero-point energy of the carbon–deuterium bond lower than that of the carbon–hydrogen bond. Since the potential energy curve of isotopic molecules is the same, this difference in zero-point energy results in a difference in dissociation energy. Non-bonded structures, important to the resonance hybrid in hyperconjugation would then contribute less in deuterium substituted compounds; an electron-deficient transition state demanding hyperconjugation stabilization would consequently be less stabilized by deuterium and the reaction would thus be slower. These views on the origin of the isotope effect were supported by

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[2] E. S. Lewis and C. E. Boozer, THIS JOURNAL, **74**, 6306 (1952).

[3] V. J. Shiner, Jr., *ibid.*, **75**, 2925 (1953).

the discovery that it was transmitted at least to some extent through a conjugated system,[4] although it was unaccountably absent in the electrophilic substitution of toluene.[5,6]

In the ground state of carboxylic acid derivatives, the carbon atom of the carbonyl group has some net positive charge, and this may *increase* or *decrease* in the transition state of a reaction depending on the mechanism. When the positive charge increases in the transition state, as for instance when an acylium ion is formed as a reaction intermediate, the direction of the isotope effect should be the same as in SN1 solvolysis, and its magnitude should depend on the amount of positive charge developed. When, however, the positive charge decreases in the transition state, for example in the basic hydrolysis of an ester which involves a nearly-tetrahedral transition state, the direction of the isotope effect, on the above hypothesis, should be the opposite of that observed in SN1 solvolyses. A compound containing deuterium alpha to the carbonyl group should react faster than the corresponding hydrogen-containing compound. Such a phenomenon would be a reverse isotope effect.

Since these mechanistic arguments propose qualitatively different secondary deuterium isotope effects for reactions of carboxylic acid derivatives which proceed by means of acylium ion or tetrahedral addition intermediates, it seems reasonable that the circle may be completed by utilizing secondary deuterium isotope effects as a mechanistic criterion for distinguishing between these two processes. Ordinarily no ambiguity exists between these two mechanisms. However, in the spontaneous hydrolyses of acetyl chloride and acetic anhydride, no unambiguous kinetic evidence exists to indicate which of these processes is operative. Both reactions are susceptible to some extent to catalysis by hydroxide ion, indicating the possibility of a tetrahedral addition intermediate (or an SN2 reaction); but the spontaneous reactions, involving the weak nucleophile water, are mechanistically ambiguous. Since kinetic criteria of covalent water participation in these hydrolytic reactions are obviously confused by the problem of participation of water in solvation, non-kinetic criteria of mechanism are needed. It was hoped that the empirical correlation between the relative electron deficiency in the ground and transition states and the secondary deuterium isotope effect could be used as mechanistic criterion for the spontaneous hydrolyses of acetyl chloride and acetic anhydride. Therefore, the kinetic isotope effects in the hydrolysis of acetyl chloride-d_3, acetic anhydride-d_6 and ethyl acetate-d_3 have been determined.

Experimental

Materials.—Ethyl acetate (Eastman Kodak Co. white label), $n^{19.2}\text{D}$ 1.3723, was used without further purification. Acetyl chloride (Eastman Kodak Co. white label), b.p., 52°, was used without further purification. Acetic anhydride (Eastman Kodak Co. white label), b.p. 140°, was used without further purification. The cyclohexane and acetone used as solvents were Eastman Kodak Co. Spectro grade chemicals. Tetrahydrofuran (Fisher Scientific Co.) was treated with potassium hydroxide pellets overnight, distilled over lithium aluminum hydride and passed through an alumina column to remove residual traces of peroxides immediately before use.

Ethyl acetate-d_3 was prepared from acetic acid-d_3 (99%) (Volk Radiochemical Co.) and absolute ethanol by condensation with concentrated sulfuric acid. After treatment with saturated sodium carbonate, the distillate was dried with sodium sulfate and the ester redistilled; b.p. 78°, $n^{19.2}\text{D}$ 1.3713 (lit.[7] $n^{20}\text{D}$ 1.3712). The infrared spectrum of this compound showed a very weak carbon–deuterium stretching vibration around 2200 cm.$^{-1}$ in agreement with previous work,[8] together with a carbonyl stretching band at 1740 cm.$^{-1}$, carbon–hydrogen deformation frequencies around 1370 and 1460 cm.$^{-1}$ and an absorption at 1080 cm.$^{-1}$ characteristic of the CD_3CO (skeletal) vibration.[8]

Acetyl chloride-d_3 was prepared from acetic acid-d_3 (99%) (Volk Radiochemical Co.) and benzoyl chloride by refluxing for 3 hours followed by distillation of the acetyl chloride. Redistillation from a micro-Vigreux column gave a product, b.p. 52°, whose infrared spectrum showed no carbon–hydrogen stretching vibrations, exceedingly weak carbon–deuterium stretching vibration around 2200 cm.$^{-1}$, a carbonyl stretching band at 1800 cm.$^{-1}$ and the characteristic CD_3CO skeletal vibration at 1080 cm.$^{-1}$.

Acetic anhydride-d_6 was prepared from sodium acetate-d_3 (made by the neutralization of acetic acid-d_3 with sodium hydroxide followed by fusion) and acetyl chloride-d_3 by refluxing for 4 hours. The anhydride was distilled from the reaction mixture and redistilled from a micro-Vigreux still, b.p. 142°. Infrared spectroscopy showed no carbon–hydrogen stretching vibrations, very weak carbon–deuterium stretching vibration, carbonyl bands at 1820 and 1747 cm.$^{-1}$ and the characteristic CD_3CO skeletal vibration at 1080 cm.$^{-1}$.

Kinetic Procedures.—The kinetics of the basic hydrolysis of ethyl acetate were determined by usual acid-base titration procedures employing phenolphthalein as indicator. Infinity values were utilized in order to check the initial concentrations of ester and of base (and as a check on the purity of the ester). The concentrations were equivalent to one another in some cases and differed by a factor of two in others. Both ethyl acetate and sodium hydroxide solutions were prepared from carbon dioxide-free distilled water. The kinetics of the hydrolysis of acetyl chloride was followed by two methods: (1) conductometric measurements utilizing a General Radio Co. type 650-A impedance bridge and type 650-PI oscillator amplifier, for reactions in 10 and 20% water-acetone; (2) spectrophotometric measurements utilizing a thermostated Beckman DK2 recording spectrophotometer, for reactions in 5% water–acetone and in ethanol–cyclohexane mixtures. The reactions were initiated by mixing cyclohexane solutions of acetyl chloride and of ethanol in the latter case or by adding 100 λ of acetyl chloride in acetone to a 5% water–acetone solution in the former case. In the spectrophotometric determinations the disappearance of the acetyl chloride was followed at 240 mμ.[9] The kinetics of the hydrolysis of acetic anhydride were followed by titration at constant *p*H (5.3) using a thermostated *p*H-stat manufactured by the International Instrument Co., Canyon, Calif. The reaction was initiated by the introduction of 25 λ of acetic anhydride into the thermostated solution at *p*H 5.3.

In the hydrolysis of ethyl acetate, the usual second-order rate equations were used for the calculations of the rate constants. In the hydrolysis of acetyl chloride and acetic anhydride both the usual first-order rate equations and Guggenheim plots[10] were used; least squares analysis of the data was used for the determination of the rate constants.

Results and Discussion

The rate constants of the hydrolysis of ethyl acetate-d_3, acetyl chloride-d_3 and acetic anhydride-

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[4] E. S. Lewis, R. R. Johnson and G. M. Coppinger, THIS JOURNAL, **81**, 3140 (1959).

[5] C. G. Swain, T. E. C. Knee and A. J. Kresge, *ibid.*, **79**, 505 (1957).

[6] A. J. Kresge and D. P. N. Satchell, *Tetrahedron Letters*, **13**, 20 (1959).

[7] B. Nolin, *Can. J. Chem.*, **31**, 1257 (1953).

[8] B. Nolin and R. N. Jones, *ibid.*, **34**, 1392 (1956).

[9] Following the procedure of R. F. Hudson and I. Stelzer, *Trans. Faraday Soc.*, **54**, 213 (1958).

[10] E. A. Guggenheim, *Phil. Mag.*, [7] **2**, 538 (1926).

TABLE I

KINETIC ISOTOPE EFFECTS IN THE HYDROLYSIS OF ETHYL ACETATE-d_3, ACETYL CHLORIDE-d_3 AND ACETIC ANHYDRIDE-d_6 AND THEIR CORRESPONDING HYDROGEN COMPOUNDS

Substrate	Substrate, M	T, °C.	Nucleophile, M	Solvent[f]	$k \times 10^4$, sec.$^{-1}$ Hydrogen cmpd.[a]	$k \times 10^4$, sec.$^{-1}$ Deuterium cmpd.	k_H/k_D
Ethyl acetate	0.01067	25.0	0.01067 M NaOH	Water	11.4 ± 0.15[b,c]	12.7 ± 0.16[c]	0.90 ± 0.01
Acetyl chloride	.01678	25.0	0.2665 M ethanol	Cyclohexane	10.3 ± .2[h]	10.5 ± .2	0.98 ± .02
Acetyl chloride	.0500	25.0	Water	5% water–tetrahydrofuran	1.64 ± .03	1.62 ± .05	1.01 ± .02
Acetyl chloride	.0050	−22.0[d]	Water	10% water–acetone	10.3 ± .5	6.8 ± .5	1.51 ± .07
Acetyl chloride	.013	−22.0[d]	Water	20% water–acetone	63 ± 3	39 ± 2	1.62 ± .08
Acetic anhydride		20.0	Water	Water[e]	20.7 ± 1[g]	19.0 ± 1	1.05 ± .04

[a] Each value is the average of at least two and usually more runs. [b] In a very careful study E. M. Terry and J. Stieglitz, THIS JOURNAL, **49**, 2216 (1927) report 11.3 × 10^{-2} l./mole sec.; *cf.* E. Salmi and A. Korte, *Ann. Acad. Sci. Fennicae*, **A54**, No. 12, 13 (1940). [c] l./mole sec. × 10^2. [d] A carbon tetrachloride slush was used as a thermostat. [e] *p*H 5.3. [f] Mixed solvents are on a volume/volume basis. [g] From V. Gold, *Trans. Faraday Soc.*, **44**, 511 (1948), an interpolated value of 20.5 × 10^{-4} sec.$^{-1}$ was obtained. [h] R. F. Hudson and I. Stelzer, *ibid.*, **54**, 213 (1958), give a value of 9.1 × 10^{-4} at 21.6°.

d_6 and of their corresponding hydrogen compounds are given in Table I. The reactions appear to fall into three groups: (1) one reaction, the saponification of ethyl acetate, which shows a k_H/k_D significantly less than one; (2) a number of reactions which within experimental error show no deuterium isotope effect including the ethanolysis of acetyl chloride in cyclohexane, the hydrolysis of acetyl chloride in 5% water-tetrahydrofuran and the hydrolysis of acetic anhydride; and (3) two reactions, the hydrolyses of acetyl chloride in 10 and 20% water–acetone, which show k_H/k_D ratios considerably greater than one.

In the saponification of ethyl acetate-d_3 a so-called reverse kinetic isotope effect occurs; that is, the deuterated substance reacts faster than the hydrogenated substance, in contrast to the majority of known reactions. This result was predictable on the basis of the empirical observations in the Introduction. Reverse deuterium isotope effects have also been observed in two recent studies of the addition of various substances to deuterated olefins including *trans*-stilbene and maleic acid. In addition to *trans*-stilbene it was found that k_H/k_D varied from 0.82 to 0.93 for the addition of a large number of substances to the double bond.[11] The *cis–trans* isomerization of maleic acid catalyzed by potassium thiocyanate gave a value of k_H/k_D of 0.89.[12] The reverse deuterium isotope effects in the olefin addition reactions have been explained in terms of the differences in changes of energy associated with the α-carbon-hydrogen and carbon-deuterium vibrational frequencies in the trigonal ground states and the approximately tetrahedral transition states.[13]

However, in the ethyl acetate hydrolysis we are dealing with the effect of a β-deuterium atom on the rate of reaction.[14] The kinetic isotope effect in the hydrolysis of ethyl acetate-d_3 is the first example of a reverse isotope effect caused by a β-deuterium atom. In this hydrolysis the slow step of the reaction involves the addition of hydroxide ion to the trigonal carbon atom to produce a transition state approximating a tetrahedral carbon atom. The carbon atom containing the deuterium atoms in the ester is adjacent to a carbon atom which becomes less electron-deficient in the transition state than it was in the ground state.

This situation would presumably lead to a difference in hyperconjugative stabilization between the ground state (which is presumably stabilized to a greater degree by hyperconjugation) and the transiton state (which is stabilized to a lesser degree by hyperconjugation) and would, therefore, lead to a reverse indirect β-deuterium isotope effect. These arguments are essentially the inverse of the arguments put forth before to rationalize the observations of the secondary deuterium isotope effects in the SN1 solvolysis of alkyl halides, and thereby add to the empirical correlation between the qualitative direction of the secondary isotope effect and the mechanism of organic reactions. However, it should not be inferred that this empirical correlation is a justification for claiming hyperconjugation as the ultimate source of the causal relationship of the secondary isotope effect. This correlation is simply a convenient and apparently useful empirical mechanistic correlation that is capable of accounting for most experimental data up to this time, with the exception of the electrophilic aromatic substitutions mentioned earlier, and with the exception of the basic hydrolysis of methyl *p*-methyl-*t*-benzoate (k_h/k_t = 1.05).[15,16]

The solvolysis of acetyl chloride in ethanol–cyclohexane solution, the solvolysis of acetyl chloride in 5% water–tetrahydrofuran and the solvolysis of acetic anhydride in water show essentially no deuterium isotope effect. It is difficult to translate these negative results into mechanistic conclusions in an unambiguous fashion. Certainly these reactions do not involve any well-developed acylium ion intermediates since such reactions would be expected to become slower upon substitution of deuterium for hydrogen in a β-position. Furthermore, it appears that these reactions do not seem to involve a tetrahedral addition intermediate in the same sense that the

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(11) D. B. Denney and N. Tunkel, *Chemistry & Industry*, 1383 (1959).

(12) S. Seltzer, *ibid.*, 1313 (1959).

(13) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey and S. Suzuki, THIS JOURNAL, **80**, 2326 (1958).

(14) β-Deuterium effects are also possible in the olefin addition reactions but presumably they would be of lesser importance than the α-deuterium effect.

(15) E. M. Hodnett, R. D. Taylor, J.-V. Tormo and R. E. Lewis, THIS JOURNAL, **81**, 4528 (1959).

(16) The difficulties brought to light by these exceptions are discussed in detail in the accompanying paper, J. M. Jones and M. L. Bender, THIS JOURNAL, **82**, 6322 (1960).

ethyl acetate saponification does. Probably these processes involve a complicated mechanistic pathway involving kinetically important proton transfers as well as possible nucleophilic attack by water.

The hydrolyses of acetyl chloride in 10% and 20% water–acetone at −22° exhibit strong rate depression upon substitution by deuterium. The isotope effects observed in these hydrolyses correspond to a $\Delta\Delta F^{\ddagger}$ per deuterium atom[17] of 69 cal./mole and 81 cal./mole for hydrolyses in 10 and 20% water–acetone, respectively, and are comparable in magnitude to the effects observed by Streitwieser,[13] Lewis,[17] and Shiner[18] in various solvolytic reactions at a saturated carbon atom. The effects noted here should specifically be compared with effects of $CH_3(CD_3)$ groups since primary, secondary and tertiary hydrogen (deuterium) atoms have different effects. For a primary hydrogen (deuterium) atom, a typical value of $\Delta\Delta F^{\ddagger}$ is 56 cal./mole.[18] It is significant that of the four solvolyses of acetyl chloride whose secondary deuterium isotope effect was measured, that solvolysis in the medium of highest dielectric (20% water–acetone) shows the largest kinetic isotope effect. This may be interpreted most easily in terms of the hyperconjugation hypothesis by saying that the acylium ion is most fully developed in that medium whose dielectric constant is the highest and whose solvation through hydrogen bonding is the highest. It is, of course, not proper to compare isotope effects at different temperatures and thus those at room temperature cannot be compared with those at −22°,[19] but qualitatively it appears that the whole family of acetyl chloride solvolyses do conform to the correlation that the kinetic isotope effect and the degree of acylium ion formation parallel one another. A parallel observation has been made in the secondary isotope effects in S_N1 solvolyses.[20]

The hydrolysis of acetyl chloride has been studied in pure water[21] and in acetone–water mixed solvents.[22,23] Swain's proposal of a termolecular concerted mechanism was suggested by Zimmerman and Yuan[20] to explain the apparent dependence of the observed rate constant of acetyl chloride hydrolysis on the second-order concentration of water in 1 to 5% water in acetone solution. Archer and Hudson indicated that this reaction in dioxane also gave third-order results (first order with respect to acetyl chloride and second order with respect to water).[24] Gold and Hilton,[21] on the other hand, have proposed that the acetyl chloride hydrolysis is a bimolecular reaction. Furthermore, the benzoyl chloride hydrolysis is believed to follow a predominantly bimolecular mechanism for its hydrolysis in the presence of acetone, at water concentrations up to 50% by weight.[25] At higher water concentrations, there is presumably an appreciable unimolecular ionization contribution.

More recently the hydrolysis of acetyl chloride in 10 to 25% water–acetone solutions was investigated over a considerable temperature range.[26] By means of a relationship of the effect of temperature and dielectric constant on the rate constant, Cairns and Prausnitz[26] concluded that the reaction is first order with respect to water in addition to being first order with respect to acetyl chloride. The dielectric constant of the medium had a large effect on the rates, consistent with electrostatic theory based on the dipole–dipole type of dielectric constant dependence. The dipole moment of the activated complex was estimated to be 16 debyes, which corresponds to a highly polarized molecule.[27] If one accepts this calculation, it appears that the dipole moment of the transition state could correspond equally well to an ion pair comprised of an acylium ion and a chloride ion (both of which would presumably be hydrated) or to a transition state involving a molecule of water in covalent binding to the carbonyl carbon atom. It thus appears that this very careful study is mechanistically equivocal and that its results will fit equally well with the conclusions of the deuterium isotope study, namely, that in 10% and 20% aqueous acetone an acylium ion intermediate is formed in the acetyl chloride hydrolysis.

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[17] E. S. Lewis and G. M. Coppinger, THIS JOURNAL, **76**, 4495 (1954).

[18] V. J. Shiner, Jr., *ibid.*, **78**, 2653 (1956); V. J. Shiner, Jr., *ibid.*, **76**, 1603 (1954).

[19] The kinetic isotope effect will in general be smaller at a higher temperature; see ref. 18 and R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, Chap. XI.

[20] E. S. Lewis and C. E. Boozer, THIS JOURNAL, **76**, 791 (1954).

[21] V. Gold and J. Hilton, *J. Chem. Soc.*, 838 (1955).

[22] C. G. Swain and C. B. Scott, THIS JOURNAL, **75**, 246 (1953)

[23] G. Zimmerman and C. Yuan, *ibid.*, **77**, 332 (1955).

[24] B. L. Archer and R. F. Hudson, *J. Chem. Soc.*, 3259 (1950).

[25] V. Gold, J. Hilton and E. G. Jefferson, *ibid.*, 2756 (1954).

[26] E. J. Cairns and J. M. Prausnitz, *J. Chem. Phys.*, **32**, 168 (1960).

[27] J. G. Kirkwood, *ibid.*, **2**, 351 (1934).