Thermodynamics of the Acid Dissociation of Tertiary Aliphatic Ammonium Ions in 60% w/w Methanol–Water Solution and of the Quinuclidinium Ion in Water

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Values of $\Delta G^\ominus$, $\Delta H^\ominus$, $\Delta S^\ominus$, and $\Delta C_p^\ominus$ are reported for the acid dissociation of the quinuclidinum ion in water and of the following ions in 60% w/w methanol–water solution: trimethyl-, triethyl-, tri-n-propyl-, and tri-n-butylammonium and quinuclidinium. An e.m.f. method was used. The results indicate that hydrophobic solvation is important and that in the mixed solvent there is evidence for selective solvation of the ammonium ions by water.

THE low solubility of tertiary aliphatic amines in water has been a considerable deterrent to the collection of precise data on the thermodynamics of the dissociation of their ammonium ions. The only reported results are those for trimethyl- and triethyl-ammonium ions.[1] The tertiary amines are particularly important for any coherent appraisal of the structural factors governing the thermodynamics of proton transfer because the absence of non-transferable protons reduces the opportunity for hydrogen-bonded solvation effects.

For these purposes it was decided that the four straight-chain tertiary amines up to tri-n-butylamine plus quinuclidine would be required and that the solvent would consequently have to be a methanol–water mixture sufficiently rich in methanol to enable a maximum concentration of 0.01M to be made up but not so high that the precision of the hydrogen electrode was reduced to $<\pm 10$ μV. Quinuclidine is sufficiently soluble in water and results for this system have been obtained. It was found that the solubility of tri-n-butylamine in 60% w/w methanol–water mixtures was 0.035M at 20 °C. Previous workers have shown that the hydrogen electrode behaves satisfactorily in this solvent.[2]

The hydrogen electrode has been used in this solvent [3] for the determination of precise proton transfer data for ammonia, methylamine, and dimethylamine. It has also been used for ammonia in a series of methanol–water mixtures extending to 70% w/w.[4]

EXPERIMENTAL

Measurements.—The comparator cell of Everett and Wynne-Jones [5] was used. This cell is as nearly electrochemically symmetrical as possible and consists of two electrode compartments joined by a salt bridge (Scheme 1) where

H_2, Pt	BHCl(c) B (c) KCl ($I - c$)	KCl Saturated in 60% w/w MeOH– H_2O	HCl($c/2$) KCl ($I - c/2$)	Pt, H_2

SCHEME 1

c indicates stoicheiometric concentrations (in M) and I is the ionic strength. Each compartment carries a hydrogen electrode. One is charged with an accurately known

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[1] M. C. Cox, D. H. Everett, D. A. Landsman, and R. J. Munn, *J. Chem. Soc.* (*B*), 1968, 1373.

[2] H. S. Harned and N. D. Embree, *J. Amer. Chem. Soc.*, 1935, **57**, 1669.

[3] D. H. Everett and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, 1952, **48**, 531.

[4] M. Paabo, R. G. Bates, and R. A. Robinson, *J. Phys. Chem.*, 1966, **70**, 247.

buffer solution of the amine, B, under test and the other with a solution of hydrogen chloride of accurately known concentration. The ionic strengths of both compartments are equalized by adding potassium chloride. The technique of using this cell has been fully described [5,6] elsewhere and in the present work care has been taken to observe the precautions previously reported to be necessary.

The temperature range covered was from 5 to 50° with a precision of $\pm 0.002°$ and an accuracy of $\pm 0.01°$. The reproducibility of the measured values of the cell e.m.f. was found to be $\pm 10\ \mu V$ under favourable conditions falling to $\pm 20\ \mu V$ at the extremes of temperature.

For each amine eight independent temperature runs were made using different values of c and ionic strength. Ionic strengths I were 0.05, 0.075, 0.10, and 0.15 and for each ionic strength two values of c in the range 0.015—0.030M were used. Thus there were eight independently prepared solutions for each amine.

The solutions were made up and diluted volumetrically using Metrohm piston burettes in a thermostatted room ($20 \pm 0.5°$) and the precision of this technique was found to be satisfactory by comparison with a fully gravimetric procedure.

Materials.—A sample containing 25—30% w/v of trimethylamine (B.D.H.) in water was analysed and used for the experiments. The purity was established by g.l.c. Triethyl-, tri-n-propyl-, and tri-n-butyl-amine (B.D.H.) were initially distilled and the middle fraction collected and dried over potassium hydroxide pellets for several days. They were then re-distilled and the middle fractions boiling at 89.4, 156, and 215°, respectively were collected and stored in flasks with ground glass stoppers. The purity of these samples was checked by g.l.c.

Quinuclidine hydrochloride. A research sample was obtained from Ralph N. Emanuel Ltd. The hydrochloride was dried in a vacuum oven at a pressure of 6 650 Pa (50 mmHg) and heated to 100° for 3 h. A sample was used to prepare the picrate. The latter, recrystallized several times from absolute alcohol, had m.p. 274.5—276.5° (lit.,[7,8] 275—276°).

Hydrochloric acid (B.D.H. AristaR grade) was used and all solutions were checked by gravimetric chloride determination using AnalaR grade silver nitrate. The standard deviation derived from four determinations was 0.01%.

Potassium chloride (B.D.H. AnalaR) was first dried in a vacuum oven at a pressure of 6 650 Pa and heated to 100° for *ca.* 2.5 h. Concentrations of solutions were checked gravimetrically by the silver nitrate method.

Potassium hydroxide. Carbonate-free solutions were prepared by the method described by Everett and his coworkers [9,10] using B.D.H. AnalaR material. Solutions were standardized by electrometric titration against standard potassium hydrogen phthalate solutions using an automatic piston burette (Metrohm Multi-Dosimat). The mean deviation for three titrations was 0.1%.

Water was first de-ionised using two Bateman portable de-ionisers in series and conductance water was obtained by distillation with the addition of potassium hydroxide and potassium permanganate in a silica still. The specific conductance was $< 1.6 \times 10^{-6}$ ohm^{-1}. It was found that this value could be maintained after storage overnight in a polypropylene container, an integral part of the closed system. The container was equipped with a carbon dioxide trap and facilities for flushing out with nitrogen.

Methanol (spectrograde) was used without further purification.

The mixed solvent containing 60% methanol and 40% water was prepared by weight. This gave 45.77 mol % methanol.

RESULTS

Calculation.—The cell reaction is $H^+{}_{RHS} \longrightarrow H^+{}_{LHS}$, hence the cell e.m.f. is given by equation (1) where $E_{L.J.}$ is

$$FE = \Delta G_T{}^{\ominus} + RT\ln\frac{a_B - a_{OH^-} - a_{OMe^-}}{a_{BH^+} + a_{OH^-} + a_{OMe^-}} + RT\ln \alpha_{H^+,RHS} + FE_{L.J.} \qquad (1)$$

the liquid junction potential and the other symbols have their usual meanings. This equation incorporates the so-called hydrolysis correction but numerical investigation showed that this correction affected the derived values of the thermodynamic functions by $< 10\%$ of their standard deviations. To arrive at this result one may obtain the values of a_{OH^-} and a_{OMe^-} from $a_{H_3O^+}$ and $a_{MeOH_2^+}$ using the Debye–Hückel limiting law for $\log \gamma_{\pm}$, and the paper of Parsons and Rochester [11] for the free energy and enthalpy of autoprotolysis in the mixed solvent. Without the hydrolysis correction, equation (1) becomes (2).

$$FE = \Delta G_T{}^{\ominus} + RT\left[\ln\frac{[B]}{[BH^+]} + \ln\,[H^+]_{RHS} + \ln\gamma_{H^+,RHS} - \ln\gamma_{BH^+}\right] + FE_{L.J.} \qquad (2)$$

The expression used for activity coefficients is an extended Debye–Hückel expression (3) in which $A = 1.826 \times 10^6/(DT)^{3/2}$, $B' = 5.029 \times 10^9/(DT)^{\frac{1}{2}}$. D is the dielectric

$$-\log\gamma_i = AI^{\frac{1}{2}}/(1 + \mathring{a}_iB'I^{\frac{1}{2}}) - C_iI \qquad (3)$$

constant, $\mathring{a}_i$ is the ion size parameter, and C_i is a temperature-dependent correction factor. To express the temperature dependence of C_i we have assumed equation (4) in the absence of experimental evidence. Two expressions (5) and (6) have been used in the literature for the description of the variation of dielectric constant with

$$C_i = c_i + d_iT \qquad (4)$$

$$D = D_0e^{LT} \qquad (5)$$

$$D = D_0 + 10^3\,M/T \qquad (6)$$

temperature. Reliable values for the dielectric constant of 60% w/w methanol–water and of pure water are given by Parsons.[12] Equations (5) and (6) were fitted by least

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[5] D. H. Everett and W. F. K. Wynne-Jones, *Proc. Roy. Soc.*, 1941, *A*, **177**, 499.

[6] D. H. Everett and W. F. K. Wynne-Jones, *Proc. Roy. Soc.*, 1938, *A*, **169**, 190.

[7] 'Beilsteins Handbuch der Organische Chemie,' Julius Springer, Berlin, 1935.

[8] J. Timmermans, 'Physico-chemical Constants,' Elsevier, Amsterdam, vol. II, 1965.

[9] D. H. Everett, D. A. Landsman, and B. R. W. Pinsent, *Proc. Roy. Soc.*, 1952, *A*, **215**, 403.

[10] D. H. Everett and D. A. Landsman, *Trans. Faraday Soc.*, 1954, **50**, 1221.

[11] G. H. Parsons and C. H. Rochester, *J.C.S. Faraday I*, 1972, 523.

[12] R. Parsons, 'Handbook of Electrochemical Constants,' Butterworths, London, 1959.

squares to these data and chi-square calculated. The test showed that (5) gives the better fit and the parameters are:

	D_0	10^3L
60% Methanol–water	288.2	−5.767 4
Water	177.0	−4.535 5

The quantity $FE_{\mathrm{L.J.}}$ in (2) should be small since the cell is operated with the same total ionic strength on both sides of the liquid junction. It will however, be temperature dependent and a linear relation is assumed in the absence of any experimental evidence. At zero ionic strength I and buffer concentration $\bar{B}$, the value of $E_{\mathrm{L.J.}}$ would be zero since the cell is operated with $2[\mathrm{H}^+]_{\mathrm{RHS}} = [\mathrm{B}] = [\mathrm{BH}^+]$. Hence $\bar{B}$ and I are both factors in the expressions for $E_{\mathrm{L.J.}}$. The complete expression assumed is therefore (7) where e and f are constants.

TABLE 1

Values of thermodynamic functions at 298.15 K and other constants in equation (10) based on concentration in M for proton transfer equilibria of tertiary ammonium ions in 60% w/w methanol–water solution and of the quinuclidinium ion in water

	60% w/w Methanol–water					Water
	$\mathrm{Me_3NH^+}$	$\mathrm{Et_3NH^+}$	$\mathrm{Pr^n{}_3NH^+}$	$\mathrm{Bu^n{}_3NH^+}$	$\mathrm{QH^+}$	$\mathrm{QH^+}$
c			0.935 ± 0.099		1.157 ± 0.058	
d	0.005 1 ± 0.000 3	0.003 1 ± 0.000 2		−0.001 1 ± 0.000 7		−0.003 3 ± 0.000 3
e	2.2 ± 1.3	3.1 ± 1.4		2.21 ± 0.41	0.234 ± 0.077	
f	−0.0089 ± 0.0045	−0.0098 ± 0.0046	−0.003 5 ± 0.001 2			0.005 3 ± 0.000 2
$\Delta H^\ominus$/J mol^{-1}	46 454 ± 45	52 173 ± 32	52 474 ± 65	52 206 ± 96	52 423 ± 38	55 497 ± 36
$\Delta G^\ominus$/J mol^{-1}	49 620 ± 120	54 650 ± 100	53 300 ± 110	53 030 ± 160	56 238 ± 60	62 995 ± 58
$\Delta S^\ominus$/J K^{-1} mol^{-1}	−10.60 ± 0.39	−8.31 ± 0.33	−2.78 ± 0.29	−2.78 ± 0.44	−12.79 ± 0.15	−25.15 ± 0.15
$\Delta C_p{}^\ominus$/J K^{-1} mol^{-1}		−18 ± 12	−99 ± 26	−57 ± 37	−41 ± 14	146 ± 13
pK_a	8.692 ± 0.022	9.575 ± 0.018	9.338 ± 0.019	9.291 ± 0.028	9.853 ± 0.011	11.036 ± 0.010

$$FE_{\mathrm{L.J.}} = F(e + fT)\bar{B}I \qquad (7)$$

Using the above expressions for activity coefficients and liquid junction potential we have equation (8) where

$$FE = \Delta G_T{}^\ominus + RT\{\ln[\mathrm{H}^+]_{\mathrm{RHS}} - g(a_{\mathrm{H}^+}) + g(a_{\mathrm{BH}^+})\} + RT(c + dT)I + (e + fT)F\bar{B}I \qquad (8)$$

$g(a_i) = 2.303\ AI^{\frac{1}{2}}/(1 + \mathring{a}_iB'I^{\frac{1}{2}})$, $c = c_{\mathrm{H}^+} - c_{\mathrm{BH}^+}$, and $d = d_{\mathrm{H}^+} - d_{\mathrm{BH}^+}$. Expansion of $\Delta G_T{}^\ominus$ about $\Delta G_\theta{}^\ominus$ using a Taylor series[13] gives equation (9).

$$\Delta G_T{}^\ominus = -T\left[-\frac{\Delta G_\theta{}^\ominus}{\theta} + \Delta H_\theta{}^\ominus\left(\frac{1}{\theta} - \frac{1}{T}\right) + \Delta C_{p\theta}{}^\ominus\left(\frac{\theta}{T} - 1 + \ln\frac{T}{\theta}\right) + \frac{\theta}{2}\left(\frac{\mathrm{d}\Delta C_{p\theta}{}^\ominus}{\mathrm{d}T}\right)\left(\frac{T}{\theta} - \frac{\theta}{T} - 2\ln\frac{T}{\theta}\right) + \ldots\right] \qquad (9)$$

For computational purposes we rearrange equation (8), collecting the terms involving parameters for determination by regression on the right-hand side [equation (10)].

$$FE - RT\ln[\mathrm{H}^+] + RT[g(a_{\mathrm{H}^+}) - g(a_{\mathrm{BH}^+})] = \Delta H_\theta{}^\ominus + cRIT + dRIT^2 + Fe\bar{B}I + Ff\bar{B}IT - \left(\frac{\Delta S_\theta{}^\ominus T^2}{\theta}\right) + \Delta C_{p\theta}{}^\ominus\left[T\left(1 - \ln\frac{T}{\theta}\right) - \theta\right] - \frac{\mathrm{d}\Delta C_{p\theta}{}^\ominus}{\mathrm{d}T}\left[\tfrac{1}{2}(T + \theta)(T - \theta) - T\theta\ln\frac{T}{\theta}\right] \qquad (10)$$

To avoid computational errors when $T - \theta$ is small compared with T we change the temperature variable to x in the logarithmic expressions where $x = (T - \theta)/\theta$ and expand these functions of T as power series in x. The function on the left-hand side of equation (10) is known for every experimental observation provided values are assigned to $\mathring{a}_{\mathrm{H}^+}$ and $\mathring{a}_{\mathrm{BH}^+}$. It was found that the choice of values did not affect the derived thermodynamic functions and the following values were used: $\mathring{a}_{\mathrm{H}^+} = 4.3 \times 10^{-8}$ and $\mathring{a}_{\mathrm{BH}^+} = 2.8 \times 10^{-8}$ cm.

The whole computation was therefore regarded as a multilinear regression on a fundamental formula of the form (11) requiring the following constants and variables

$$\xi = \alpha + \sum_{i=1}^{7} \beta_i \upsilon \qquad (11)$$

to be evaluated:

i	b_i (estimator of β_i)	U_i (estimator of ν_i)
1	c	RIT
2	d	RIT^2
3	e	$F\bar{B}I$
4	f	$F\bar{B}IT$
5	$\Delta S_\theta{}^\ominus$	$-T^2/\theta$
6	$\Delta C_{p\theta}{}^\ominus$	$-\theta(1 + x)x^2 \sum_{n=1}^{\infty}\left(\frac{n}{n+1}\right)(-x)^{n-1}$
7	$\frac{\mathrm{d}\Delta C_{p\theta}{}^\ominus}{\mathrm{d}T}$	$-\frac{1}{2}\theta^2(1 + x)x^3 \sum_{n=1}^{\infty}\left(\frac{n}{n+2}\right)(-x)^{n-1}$

Computation and Selection of Data.—The computer program was arranged: (i) to evaluate the b_i values (i = 1—7) and their standard deviations; (ii) to select and eliminate iteratively the b_i values with the largest fractional standard deviation; (iii) to evaluate σ^2 for each iteration; (iv) to evaluate $\Delta H^\ominus$ and its standard deviation; (v) to calculate $\Delta G^\ominus$ and its standard deviation.

To decide which iteration carries the maximum number of meaningful parameters the value of σ^2 was graphed against the dimension of the matrix of the regression analysis. A large change in σ^2 as the dimension was reduced by unity was taken as an indication that there were too few parameters for the number of data points and the preceding set was therefore chosen.

The results are summarized in Table 1.

DISCUSSION

In discussions of structural effects on proton transfer equilibria it is helpful to regard one chosen system as a reference system and to look at the differences between the thermodynamic functions for this system and all others. For cation acids, in water, the ammonium ion–ammonia system has been used as the reference.[5]

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[13] E. C. W. Clarke and D. N. Glew, *Trans. Faraday Soc.*, 1966, **62**, 539.

We use the δ_R notation of Leffler and Grunwald[14] for changes in thermodynamic functions which occur when the structure of the carbon skeleton attached to the basic centre is changed. As all thermodynamic quantities, ΔX, refer to infinitely dilute solutions at 298.15 K and as concentrations are expressed in molarities throughout, the symbols for temperature and standard state are omitted. Instead, the process to which Δ refers is indicated by a subscript on X (i for proton transfer, w for hydration, and s for solvation in the aqueous methanol) and, where necessary, the phase is indicated by a superscript (g for gas, w for water, s for aqueous methanol). Changes in thermodynamic functions accompanying proton transfer in solution are known to be affected greatly by the varying extents to which uncharged molecules and ions are solvated. Therefore a discussion of these effects is assisted by the use of the cycle of processes in Scheme 2. Hence

$$\begin{tikzcd}
BH^+ \arrow[d, "\Delta X_s(BH^+)"] & + & NH_3 \arrow[r, shift left, "\delta_R\Delta X_i^g"] \arrow[d, "\Delta X_s(NH_3)"] & B \arrow[l, shift left] \arrow[d, "\Delta X_s(B)"] & + & NH_4^+ \arrow[d, "\Delta X_s(NH_4^+)"] \\
BH^+ & + & NH_3 \arrow[r, shift left, "\delta_R\Delta X_i^s"] & B \arrow[l, shift left] & + & NH_4^+
\end{tikzcd}$$

SCHEME 2

equation (12) applies, leading to (13). Thus a full discussion of structural effects on proton transfer reactions requires a knowledge of the values of three of the δ_R quantities in equation (13) for X = enthalpy,

$$\Delta X_s(BH^+) + \Delta X_s(NH_3) + \delta_R\Delta X_i^s - \Delta X_s(B) - \Delta X_s(NH_4^+) - \delta_R\Delta X_i^g = 0 \quad (12)$$

$$\delta_R\Delta X_i^s - \delta_R\Delta X_i^g = \delta_R\Delta X_s(B) - \delta_R\Delta X_s(BH^+) \quad (13)$$

entropy, and partial molar heat capacity. For those systems for which the free energies of proton transfer in the gas phase have been measured by mass spectrometric techniques, discussions along these lines have already been given[15] assuming that $\delta_R\Delta S_i^g$ takes the statistical value of $-R\ln n/4$ where n is the number of protons in the ammonium ion. We use the same assumption together with the following: (*a*) that $\delta_R\Delta C_{pi}^g$ is zero since in the reaction to which reference is implied there is conservation of translational, rotational, and (approximately) vibrational degrees of freedom; (*b*) that, in the absence of mass spectrometric data for quinuclidine, the value of ΔH_i^g for this compound is equal to that for triethylamine. Table 2 gives the values of $\delta_R\Delta X_s(B) - \delta_R\Delta X_s(BH^+)$ under these assumptions.

TABLE 2

Values of $\delta_R\Delta X_s(B) - \delta_R\Delta X_s(BH^+)$ using the ammonium ion as the reference acid[10]

	Solvent methanol–water			Solvent water X_w		
Amine	H/kJ mol^{-1}	S/J mol^{-1} K^{-1}	C_p/J mol^{-1} K^{-1}	H/kJ mol^{-1}	S/J mol^{-1} K^{-1}	C_p/J mol^{-1} K^{-1}
MeNH$_2$ *	−38.8	−15.9	−50.4	−36.8	−14.1	33.5
Me$_3$N *	−88.1	−10.2	*a*	−96.9	−48.9	183
Et$_3$N *	−110.4	−7.88	−18 ± 12	−122	−45.8	187
Pr$^n{}_3$N	*b*	−2.35	−99 ± 26	*b,c*	*b,c*	*b,c*
Bu$^n{}_3$N	*b*	−2.35	−57 ± 37	*b,c*	*b,c*	*b,c*
Q	−110.1	−12.4	−41 ± 14	−106 †	−10.5	146 ± 13

* See refs. 1, 3, and 5. † Assumes that $\Delta H_i^g(Q) = \Delta H_i^g(Et_3N)$.

[a] No estimate is possible from the experimental data. [b] ΔG_i^g is not available, thus ΔH_i cannot be calculated. [c] Low solubility of amine in water prevents precise measurements.

According to the concept of hydration described by Frank and Wen,[16] any solute may be considered to be solvated in solution and the solvent to have some degree of structure itself. Between these two there would be a layer of relatively non-associated solvent. The introduction of a radical substituent on to a solute can be considered as initiating movement of solute in one or other direction across this system (Scheme 3).

[Solute : Solvent] Non-associated solvent [Associated solvent]

SCHEME 3

Enthalpies.—It has been found[1,17] that replacement of hydrogen in ammonia by alkyl groups gives rise in water to hydrophobic hydration in amines. This causes $\delta_R\Delta H_w(B)$ to be negative. Corresponding values of $\delta_R\Delta H_w(BH^+)$ are less negative because of the hydrophilic shielding of the charge centre and hence the difference between these has a net negative value. This is seen in Table 2 for methylamine, trimethylamine, triethylamine, and quinuclidine in water and the same effect is apparent for this quantity in the methanol–water mixed solvent.

Entropies.—Because the $\delta_R\Delta S_i^g$ values are assumed to be $-R\ln n/4$, we have available $\delta_R\Delta S_s(B) - \delta_R\Delta S_s(BH^+)$ for all those amines whose ionization equilibria have been determined in solution. In both water and the mixed solvent the effect of introducing trialkyl substitution of ammonia is to cause a decrease in $\delta_R\Delta S_s(B) - \delta_R\Delta S_s(BH^+)$ through the uncharged base molecule becoming solvated for the reasons given in the previous paragraph. The magnitude of this negative entropy of solvation is greater in water than in aqueous methanol and we consider this to be an indication that the solute (amine) breaks the associative bonds between methanol and water in order to form its own solvation shell.

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[14] J. E. Leffler and E. Grunwald, 'Rates and Equilibria of Organic Reactions,' Wiley, New York, 1963.

[15] E. M. Arnett, F. M. Jones, III, M. Taagepera, W. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Amer. Chem. Soc.*, 1972, **94**, 4724.

[16] H. S. Frank and W. Y. Wen, *Discuss. Faraday Soc.*, 1957, **24**, 133.

[17] T. S. Sarma and J. C. Ahluwalia, *Chem. Soc. Rev.*, 1973, **2**, 203.

Heat Capacities.—Structural effects on $\delta_R\Delta C_{ps}(B) - \delta_R\Delta C_{ps}(BH^+)$ are again assumed to derive mainly from $\delta_R\Delta C_{ps}(B)$. The values are large and positive in water but smaller and negative in methanol–water mixtures. The results in water are consistent with an increase in hydrophobic hydration with the size of the alkyl group leading to an extension of the non-associated solvent region in the Frank and Wen model. The results in methanol–water can be understood if preferential solvation of the amine by one solvent species releases molecules of the other species which then join the associated solvent region leading to a decrease in the size of the non-associated region.

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