Electronic Supplementary Information

Unusual liquid-liquid phase transition in aqueous mixtures of a wellknown dendrimer.

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S1 Composition of ternary dendrimer-salt-water systems

Ternary mixtures were prepared by weight, and the dendrimer and salt weight fractions, w_D and w_S , were calculated. These weight fractions were then converted into dendrimer volume fraction, ϕ_D , and salt molar concentration, C_S , after estimating the sample density using the known¹ volumetric properties of binary sodium sulfate-water solutions and used the dendrimer specific volume specific volume² of 0.817 g cm⁻³ assumed to be constant.

Sample density was estimated in the following way. Salt molality, m_s , was calculated from

$$m_{\rm S} = 1000 (w_{\rm S} / M_{\rm S}) / (1 - w_{\rm S} - w_{\rm D})$$

where $M_s = 142.037 \text{ g mol}^{-1}$. The density d_s of the corresponding binary salt-water solution was calculated from the literature expression $d_s(m_s)$:¹

$$d_{\rm s} / \text{g cm}^{-3} = 0.997045 + 0.129483 (m_{\rm s} / m^0) - 0.0086616 (m_{\rm s} / m^0)^{1.5} - 0.0061207 (m_{\rm s} / m^0)^2 + 0.0007909 (m_{\rm s} / m^0)^{2.5}$$

where $m^0 \equiv 1 \mod \text{kg}^{-1}$. The specific volume, v_{soln} , of the ternary dendrimer-salt-water solution was the calculated using the following expression:

$$v_{\rm soln} = w_{\rm D} v_{\rm D} + (1 - w_{\rm D}) / d_{\rm S}(m_{\rm S})$$

where v_D is the dendrimer specific volume reported above.² Dendrimer volume fraction and salt molar concentrations were then calculated using

$$\phi_{\rm D} = w_{\rm D} v_{\rm D} / v_{\rm soln}$$

$$C_{\rm S} = 1000 (w_{\rm S} / M_{\rm S}) / v_{\rm soln}$$

S2. LLPS experimental data

Tables S1. LLPS temperature (T_{ph}) as a function of salt molar concentration (C_S) at several dendrimer volume fractions (ϕ_D) obtained from turbidity experiments.

Table S1a. $T_{\rm ph}$ at $\phi_{\rm D}$ =0.38		
$\phi_{\rm D}$	C _S /M	$T_{\rm ph}/^{\circ}{\rm C}$
0.384	0.289	4.0
0.383	0.305	13.2
0.384	0.309	16.5
0.384	0.313	19.6
0.383	0.320	24.8
0.383	0.336	34.2

Table S1b. $T_{\rm ph}$ at $\phi_{\rm D}=0.29$		
$\phi_{\rm D}$	$C_{\rm S}/{\rm M}$	$T_{\rm ph}/^{\circ}{\rm C}$
0.292	0.372	9.4
0.291	0.374	12.5
0.291	0.377	15.0
0.291	0.378	17.8
0.291	0.380	21.8
0.291	0.385	29.8

Table S1c. $T_{\rm ph}$ at $\phi_{\rm D}$ =0.27		
$\phi_{ m D}$	$C_{\rm S}/{\rm M}$	$T_{\rm ph}/^{\circ}{\rm C}$
0.265	0.412	4.8
0.266	0.413	10.0
0.266	0.415	21.0
0.267	0.417	42.0

Table S1g. $T_{\rm ph}$ at $\phi_{\rm D}$ =0.14

	O P ¹¹	15
$\phi_{\rm D}$	$C_{\rm S}/{\rm M}$	$T_{\rm ph}/^{\circ}{\rm C}$
0.140	0.691	36
0.142	0.690	32
0.143	0.690	28

Table S1h. $T_{\rm ph}$ at $\phi_{\rm D}$ =0.084		
$\phi_{\rm D}$	$C_{\rm S}/{\rm M}$	$T_{\rm ph}/^{\circ}{\rm C}$
0.0834	0.806	33.2
0.0835	0.814	27.6
0.0836	0.822	22.9
0.0835	0.830	17.8
0.0835	0.837	13.8

Table S1i. $T_{\rm ph}$ at $\phi_{\rm D}$ =0.049			
$\phi_{\rm D}$	$C_{\rm S}/{\rm M}$	$T_{\rm ph}/^{\circ}{\rm C}$	
0.0492	0.958	35.4	
0.0495	0.964	31.4	
0.0492	0.970	28.2	
0.0493	0.974	26.6	
0.0493	0.978	24.4	

Table S1j. $T_{\rm ph}$ at $\phi_{\rm D}$ =0.00126

4	C/M	
$\varphi_{\rm D}$	C _S /IVI	$I_{\rm ph}/C$
0.237	0.475	0.2
0.235	0.477	3.2
0.235	0.484	12.4
0.234	0.486	12.8

$\phi_{\rm D}$	$C_{\rm S}/{\rm M}$	$T_{\rm ph}/^{\circ}{\rm C}$
0.0125	0.994	36.8
0.0127	1.002	33.4
0.0125	1.010	30.4
0.0126	1.022	25.3
0.0127	1.026	23.0

Table S1k. $T_{\rm ph}$ at $\phi_{\rm D}$ =0.0096

Table S1e. $T_{\rm ph}$ at $\phi_{\rm D}=0.22$		
$\phi_{\rm D}$	$C_{\rm S}/{\rm M}$	$T_{\rm ph}/^{\circ}{\rm C}$
0.224	0.500	-4.4
0.224	0.501	-2.0
0.223	0.504	0.8
0.223	0.507	5.0
0.223	0.508	9.2

$\phi_{ m D}$	$C_{\rm S}/{\rm M}$	$T_{\rm ph}/^{\circ}{\rm C}$
0.0096	1.267	35.0
0.0096	1.269	34.0
0.0096	1.271	32.0
0.0097	1.271	32.0
0.0096	1.274	30.0

Table S1f. $T_{\rm ph}$ at $\phi_{\rm D}$ =0.21		
$\phi_{ m D}$	$C_{\rm S}/{\rm M}$	$T_{\rm ph}/^{\circ}{\rm C}$
0.208	0.526	-8.0
0.208	0.527	-5.8
0.208	0.529	-2.5
0.208	0.531	-0.4

Table S11. $T_{\rm ph}$ at $\phi_{\rm D}$ =0.0091		
$\phi_{ m D}$	$C_{\rm S}/{\rm M}$	$T_{\rm ph}/^{\circ}{\rm C}$
0.0092	1.384	32.0
0.0091	1.387	27.0
0.0091	1.392	26.0
0.0091	1.396	20.0
0.0091	1.401	19.0

Estimation of dendrimer critical volume fraction from salt-dendrimer partitioning data.



Figure S1. Plots of $(\phi_D^{(I)} + \phi_D^{(II)})/2$ as a function of $|\phi_D^{(II)} - \phi_D^{(I)}|^{1/\beta}$, where $\beta = 0.325$ and $\beta = 0.5$ are the Ising (A) and mean-field (B) exponents, respectively. Linear extrapolation to $|\phi_D^{(II)} - \phi_D^{(I)}|^{1/\beta} = 0$ yield estimates of the critical volume fraction, $\phi_D^{(c)}$.

Estimation of the partitioning coefficient, $(\partial C_{\rm s} / \partial \phi_{\rm D})_T$, from salt-dendrimer partitioning data.



Figure S2. Plots of $\Delta C_{\rm s} / \Delta \phi_{\rm D}$ as a function of $|\phi_{\rm D}^{(\rm II)} - \phi_{\rm D}^{(\rm I)}|^{1/\beta}$, where $\beta = 0.325$ and $\beta = 0.5$ are the Ising (A) and mean-field (B) exponents, respectively. Linear extrapolation to $|\phi_{\rm D}^{(\rm II)} - \phi_{\rm D}^{(\rm I)}|^{1/\beta} = 0$ yield estimates of the critical partitioning coefficient, $(\partial C_{\rm s} / \partial \phi_{\rm D})_T$.

Estimation of the partitioning coefficient, $(\partial C_{\rm S} / \partial \phi_{\rm D})_T$, from the experimental binodal curve.



Figure S3. Plot of $C_{\rm S}$ as a function of $\phi_{\rm D}$ from binodal data at 25 °C.

S3. Thermodynamic model

We consider a ternary dendrimer-salt-water system of volume, V, in equilibrium with an infinitely large reservoir consisting of a binary salt-water system through a membrane not permeable to dendrimer particles. The thermodynamic properties of the reservoir are fixed at constant temperature. We denote as Π the pressure difference between the two compartments. This is the osmotic-pressure contributions due to the dendrimer particles. To determine Π , we treat the dendrimer solution as a suspension of N dendrimer gas particles. The corresponding canonical partition function, Q, is given by³

$$Q = \frac{1}{N!} \left(\frac{q_{\text{int}}}{\Lambda^3}\right)^N \int_V d\mathbf{r} \, e^{-w(\mathbf{r})/k_{\text{B}}T}$$
(S1)

where $k_{\rm B}$ is the Boltzmann constant, V is the volume of the system, A is the particle thermal wavelength, $q_{\rm int}$ it the particle internal partition function, **r** collectively represents the 3N spatial coordinates of the N particles and $w(\mathbf{r})$ is the potential of mean force, which is given by:

$$w(\mathbf{r}) = w_{\rm DD}(\mathbf{r}) + w_{\rm DS}(\mathbf{r}) \tag{S2}$$

where $w_{DD}(\mathbf{r})$ is the potential contribution associated with dendrimer-dendrimer interaction in the absence of bulk domain, with $w_{DD}(\infty) = 0$, where " ∞ " denotes that all particle-particle distances are infinitely large. The remaining contribution in Eq. S2, $w_{DS}(\mathbf{r})$, describes the effect of salt on dendrimer-dendrimer interactions. Using Eq. S2, Eq. S1 can be rewritten in the following way:

$$Q = Q_{\rm D} \left\langle e^{-w_{\rm DS}(\mathbf{r})/k_{\rm B}T} \right\rangle \tag{S3}$$

with

$$Q_{\rm D} = \frac{1}{N!} \left(\frac{q_{\rm int}}{\Lambda^3}\right)^N \int_V d\mathbf{r} \, e^{-w_{\rm DD}(\mathbf{r})/k_{\rm B}T} \tag{S4}$$

$$\left\langle e^{-w_{\rm DS}(\mathbf{r})/k_{\rm B}T} \right\rangle = \frac{\int\limits_{V} d\mathbf{r} \, e^{-w_{\rm DD}(\mathbf{r})/k_{\rm B}T} e^{-w_{\rm DS}(\mathbf{r})/k_{\rm B}T}}{\int\limits_{V} d\mathbf{r} \, e^{-w_{\rm DD}(\mathbf{r})/k_{\rm B}T}}$$
(S5)

The osmotic pressure of the dendrimer particles is given by

$$\Pi = k_{\rm B} T \left(\frac{\partial \ln Q}{\partial V} \right)_{T,N} = \Pi_{\rm D} + k_{\rm B} T \left(\frac{\partial \ln \left\langle e^{-w_{\rm DS}(\mathbf{r})/k_{\rm B}T} \right\rangle}{\partial V} \right)_{T,N}$$
(S6)

where $\Pi_{\rm D} = k_{\rm B}T(\partial \ln Q_{\rm D} / \partial V)_{T,N}$. We start by considering the osmotic pressure of the dendrimer particles in the absence bulk domain ($w_{\rm DS} = 0$). Here, we propose the following type of equation of state:

$$\frac{\Pi_{\rm D} v_{\rm D}}{k_{\rm B} T} = \left(1 + b \,\phi_{\rm D} + \frac{e}{k_{\rm B} T} \,\phi_{\rm D}\right) \phi_{\rm D} \tag{S7}$$

where we have introduced the dendrimer volume fraction, $\phi_D = v_D N / V$ with v_D being the particle volume, and $b(\phi_D)$ and $e(\phi_D)$ are temperature-independent entropic and energetic terms, respectively. For $b(\phi_D)$, we use the Carnahan-Starling result.³ Specifically, we write:

$$b(\phi_{\rm D}) = \frac{4 - 2\phi_{\rm D}}{\left(1 - \phi_{\rm D}\right)^3} \tag{S8}$$

Expressions for related functions are reported below:

$$b'(\phi_{\rm D}) = \frac{db}{d\phi_{\rm D}} = \frac{10 - 4\phi_{\rm D}}{(1 - \phi_{\rm D})^4}$$
(S9)

$$b''(\phi_{\rm D}) \equiv \frac{d^2 b}{d\phi_{\rm D}^2} = \frac{36 - 12\phi_{\rm D}}{(1 - \phi_{\rm D})^5}$$
(S10)

$$\hat{b}(\phi_{\rm D}) \equiv \int_{0}^{\phi_{\rm D}} b(x) \, dx = \frac{4 - 3\phi_{\rm D}}{\left(1 - \phi_{\rm D}\right)^2} \phi_{\rm D} \tag{S11}$$

To obtain an expression for $e(\phi_D)$, the excess internal energy of the system is introduced:

$$U_{\rm D} = \langle w_{\rm DD}(\mathbf{r}) \rangle = \frac{\int_{V} d\mathbf{r} \, w_{\rm DD}(\mathbf{r}) e^{-w_{\rm DD}(\mathbf{r})/k_{\rm B}T}}{\int_{V} d\mathbf{r} \, e^{-w_{\rm DD}(\mathbf{r})/k_{\rm B}T}}$$
(S12)

To obtain an expression for U_D , we apply thermodynamic relations starting from the expression of Π_D in Eq. S7 and derive an expression for the Helmoholtz free energy, F_D :

$$\frac{F_{\rm D} - F_{\rm D}^{0}}{N k_{\rm B} T} - \ln \frac{\phi_{\rm D}}{\phi_{\rm D}^{0}} = \int_{0}^{\phi_{\rm D}} \frac{Z - 1}{\phi_{\rm D}} d\phi_{\rm D} = b^{0} + \frac{\partial}{k_{\rm B} T}$$
(S13)

where $Z \equiv v_{\rm D} \prod_{\rm D} / (\phi_{\rm D} k_{\rm B} T)$ is the compressibility factor, $\partial f \equiv \int_0^{\phi_{\rm D}} e(x) dx$, and $F_{\rm D}^0$ and $\phi_{\rm D}^0$ are the standard-state Helmoholtz free energy and dendrimer volume fraction, respectively. The excess internal energy is then obtained from:

$$U_{\rm D} = \left[\frac{\partial (F_{\rm D} - F_{\rm D}^0) / T}{\partial (1/T)}\right]_{N,V} = N \mathscr{Y}$$
(S14)

The excess internal energy can be linked to microscopic properties by using³

$$U_{\rm D} = \frac{N^2}{2V} \int_0^\infty (4\pi r^2) u(r) g(r) \, dr \tag{S15}$$

where u(r) is the pairwise particle-particle potential energy, r is the particle-particle distance and g(r) is the corresponding radial distribution function. If the interaction range is infinitely short, we can set $u(r) = \varepsilon v_D \delta(r - \sigma)$ with $r \ge \sigma$, where σ is the particle diameter, ε is the energy parameter and $\delta(r - \sigma)$ is the radial Dirac function with $4\pi \int_0^\infty r^2 \delta(r - \sigma) dr = 1$. For g(r), we use the Carnahan-Starling contact value, $g(\sigma) = (1 - \phi_D / 2) / (1 - \phi_D)^3 = b/4$. Thus Eq. S15 becomes:

$$U_{\rm D} = N \frac{\varepsilon}{8} b \phi_{\rm D} \tag{S16}$$

From Eqs. S14,S16, we also derive:

$$\mathscr{Y} = \int_0^{\phi_{\rm D}} e(x) \, dx = \frac{1}{8} \varepsilon \, b \, \phi_{\rm D} \tag{S17}$$

$$e = \frac{1}{8}\varepsilon \left(b + b' \phi_{\rm D}\right) \tag{S18}$$

$$e' \equiv \frac{de}{d\phi_{\rm D}} = \frac{1}{8} \varepsilon \left(2b' + b'' \phi_{\rm D}\right) \tag{S19}$$

To obtain an expression for the second factor in Eq. S3, an expression for $w_{DS}(\mathbf{r})$ is needed. This is obtained by assuming a two-domain model.⁴ Each particle is surrounded by a salt-depleted local domain, v_L . When particles are far from each other, the total volume of the local domain has its maximum value of $V_L(\infty) = N v_L$. In general, we have $V_L(\mathbf{r}) < N v_L$ due to presence of particle-particle contacts. The remaining space occupied by the system is represented by the bulk domain with volume: $V_B = V - V_L(\mathbf{r})$. This second domain is assumed to be a homogeneous binary salt-water solution with the same internal composition of that of the reservoir. Due to the presence of the salt component, the change from a generic \mathbf{r} to ∞ results in an increase in $V_L(\mathbf{r})$ and corresponding compression of the bulk-domain volume. This decrease in volume is given by $[V_L(\mathbf{r}) - V_L(\infty)]$. The corresponding positive work performed by the dendrimer particles on the bulk domain is $\Pi_S \cdot [V_L(\infty) - V_L(\mathbf{r})]$, where Π_S is the salt osmotic pressure associated with the bulk domain (and the reservoir). If this is the only mechanism of action of salt, we can write:

$$w_{\rm DS}(\mathbf{r}) = -\Pi_{\rm S} \cdot [N v_{\rm L} - V_{\rm L}(\mathbf{r})] \tag{S20}$$

We now introduce the ensemble-average local-domain volume:

$$\langle V_{\rm L} \rangle = \frac{\int d\mathbf{r} V_{\rm L}(\mathbf{r}) e^{-w_{\rm DD}(\mathbf{r})/k_{\rm B}T}}{\int V_{\rm L} d\mathbf{r} e^{-w_{\rm DD}(\mathbf{r})/k_{\rm B}T}} = (1-\alpha)V$$
(S21)

where α is the corresponding bulk-domain volume fraction. The ensemble-average of $w_{DS}(\mathbf{r})$ is then given by

$$\langle w_{\rm DS}(\mathbf{r}) \rangle = -\Pi_{\rm S} \cdot [N v_{\rm L} - (1 - \alpha)V]$$
(S22)

To link Eq. S22 to Eq. S5, we now make the first-order (mean-field) approximation:

$$\ln\left\langle e^{-w_{\rm DS}(\mathbf{r})/k_{\rm B}T}\right\rangle = -\frac{\langle w_{\rm DS}(\mathbf{r})\rangle}{k_{\rm B}T}$$
(S23)

which is based on the Taylor's series expansion: $\ln \langle e^{-x} \rangle = \ln \langle 1 - x + x^2 / 2 + ... \rangle = -\langle x \rangle + (\langle x^2 \rangle - \langle x \rangle^2) / 2 + ...$ This gives:

$$\ln\left\langle e^{-w_{\rm DS}(\mathbf{r})/k_{\rm B}T}\right\rangle = \frac{\Pi_{\rm S}}{k_{\rm B}T} \cdot [N v_{\rm L} - (1 - \alpha)V]$$
(S24)

We are now in position to write the following expression for Π starting from Eq. S6:

$$\Pi = \Pi_{\rm D} - \left[\frac{\partial (1-\alpha)V}{\partial V}\right]_{T,N} \Pi_{\rm S} = \Pi_{\rm D} - \left[1-\alpha + \left(\frac{\partial \alpha}{\partial \phi_{\rm D}}\right)_T \phi_{\rm D}\right] \Pi_{\rm S}$$
(S25)

For α in Eq. S25, we use the temperature-independent expression obtained from the Mansoori-Carnahan-Starling-Leland equation of state for a binary hard-sphere mixture:⁵

$$\alpha = (1 - \phi_{\rm D}) \exp\left[-A\eta_{\rm D} - B\eta_{\rm D}^{2} - C\eta_{\rm D}^{3} + D\ln(1 + \eta_{\rm D})\right]$$
(S26)

where $\eta_{\rm D} \equiv \phi_{\rm D} / (1 - \phi_{\rm D})$, $A \equiv 3q + 6q^2 - q^3$, $B \equiv 3q^2 + 4q^3$, $C \equiv 2q^3$, $D \equiv 3q^2 - 2q^3$ and q is the ratio between the thickness of the local-domain layer surrounding the dendrimer particle and the particle radius. The expressions of its derivatives, $\alpha'(\phi_{\rm D}) \equiv d\alpha / d\phi_{\rm D}$ and $\alpha''(\phi_{\rm D}) \equiv d^2\alpha / d\phi_{\rm D}^2$ are included below:

$$\alpha' = \frac{d\alpha}{d\phi_{\rm D}} = -\frac{\alpha}{1 - \phi_{\rm D}} \left[1 + \frac{A + 2B\eta_{\rm D} + 3C\eta_{\rm D}^2 - D/(1 + \eta_{\rm D})}{1 - \phi_{\rm D}} \right]$$
(S27)

$$\alpha'' = \frac{d^{2}\alpha}{d\phi_{\rm{D}}^{2}} = -\frac{\alpha}{(1-\phi_{\rm{D}})^{2}} \left[1 + 2\frac{A + 2B\eta_{\rm{D}} + 3C\eta_{\rm{D}}^{2} - D/(1+\eta_{\rm{D}})}{1-\phi_{\rm{D}}} + \frac{2B + 6C\eta_{\rm{D}} + D/(1+\eta_{\rm{D}})^{2}}{(1-\phi_{\rm{D}})^{2}} \right] + \frac{\alpha'^{2}}{\alpha}$$
(S28)

The dendrimer chemical potential can be introduced through the Gibbs-Duhem equation at constant T and Π_s :

$$\phi_{\rm D} \left(\frac{\partial \mu_{\rm D}}{\partial \phi_{\rm D}} \right)_{T,\Pi_{\rm S}} = \left(\frac{\partial \Pi}{\partial \phi_{\rm D}} \right)_{T,\Pi_{\rm S}}$$
(S29)

After inserting Eqs. S7,S25 in Eq. S29, we obtain:

$$\frac{\Pi v_{\rm D}}{k_{\rm B}T} = \left(1 + b\,\phi_{\rm D} + \frac{e}{k_{\rm B}T}\phi_{\rm D}\right)\phi_{\rm D} - (1 - \alpha + \alpha'\,\phi_{\rm D})\frac{\Pi_{\rm S}v_{\rm D}}{k_{\rm B}T}$$
(S30)

$$\frac{v_{\rm D}}{k_{\rm B}T} \left(\frac{\partial\Pi}{\partial\phi_{\rm D}}\right)_{T,\Pi_{\rm S}} = 1 + (2b + b'\phi_{\rm D})\phi_{\rm D} + \frac{2e + e'\phi_{\rm D}}{k_{\rm B}T}\phi_{\rm D} - \alpha''\phi_{\rm D}\frac{\Pi_{\rm S}v_{\rm D}}{k_{\rm B}T}$$
(S31)

$$\frac{v_{\rm D}}{k_{\rm B}T} \left(\frac{\partial\mu_{\rm D}}{\partial\phi_{\rm D}}\right)_{T,\Pi_{\rm S}} = \frac{1}{\phi_{\rm D}} + (2b + b'\phi_{\rm D}) + \frac{2e + e'\phi_{\rm D}}{k_{\rm B}T} - \alpha''\frac{\Pi_{\rm S}v_{\rm D}}{k_{\rm B}T}$$
(S32)

$$\frac{\mu_{\rm D} - \mu_{\rm D}^0}{k_{\rm B}T} = \ln \phi_{\rm D} + b' \Phi b \phi_{\rm D} + \frac{\partial' \Phi e \phi_{\rm D}}{k_{\rm B}T} - \alpha' \frac{\Pi_{\rm S} v_{\rm D}}{k_{\rm B}T}$$
(S33)

where we have used the mathematical relation: $\int_0^{\phi_D} x f'(x) dx = \phi_D f(\phi_D) - f'(\phi_D)$ with $f' = \int_0^{\phi_D} f(x) dx$. After inserting Eqs. S17,S18 in Eqs. S30,S33, we finally obtain the two thermodynamic functions used to construct the boundary of the liquid-liquid phase transition:

$$\frac{\Pi v_{\rm D}}{k_{\rm B}T} = \left[1 + b\,\phi_{\rm D} + \frac{1}{8}\frac{\varepsilon}{k_{\rm B}T}(b + b'\,\phi_{\rm D})\,\phi_{\rm D}\right]\phi_{\rm D} - (1 - \alpha + \alpha'\,\phi_{\rm D})\frac{\Pi_{\rm S}v_{\rm D}}{k_{\rm B}T}$$
(S34)

$$\frac{\mu_{\rm D} - \mu_{\rm D}^0}{k_{\rm B}T} = \ln \phi_{\rm D} + b' \phi_{\rm D} + \frac{1}{8} \frac{\varepsilon}{k_{\rm B}T} (2b + b' \phi_{\rm D}) \phi_{\rm D} - \alpha' \frac{\Pi_{\rm S} v_{\rm D}}{k_{\rm B}T}$$
(S35)

S4. Isothermal Calorimetry Data

In this section, we report our experimental ITC data and the extracted energy parameters.

Table S2. Differential molar heat, $q^{(k)}$, associated with consecutive injections, k, of the titrant solution containing PAMAM-OH with volume fraction, ϕ_D^0 , into the titrand solution with increasing dendrimer volume fraction, ϕ_D . These heat-of-dilution experiments were performed in aqueous salt buffer (ACES, pH7.0, 0.10M; sodium sulfate, 0.03 M; ionic strength, 0.14M) and 25.0 °C.

k	$\phi_{ m D}$	$q^{(k)}$ / (kJ mol ⁻¹)	
1	0.0019	_	
2	0.0037	-3.159	
3	0.0055	-3.201	
4	0.0073	-3.142	
5	0.0091	-3.098	
6	0.0109	-3.100	
7	0.0127	-3.035	
8	0.0144	-3.067	
9	0.0161	-3.001	
10	0.0178	-3.017	

Table S2a. $q^{(k)}$ values at $\phi_D^0 = 0.191$.

k	$\phi_{ m D}$	$q^{(k)}$ / (kJ mol ⁻¹)
11	0.0195	-2.992
12	0.0212	-2.967
13	0.0228	-2.915
14	0.0244	-2.881
15	0.0260	-2.885
16	0.0276	-2.865
17	0.0292	-2.827
18	0.0307	-2.815
19	0.0323	-2.764

Table S2b. $q^{(k)}$ values at $\phi_{D}^{0} = 0.173$.

k	ϕ_{D}	$q^{(k)}$ / (kJ mol ⁻¹)
1	0.0017	_
2	0.0034	-2.830

k	$\phi_{ m D}$	$q^{(k)}$ / (kJ mol ⁻¹)
11	0.0177	-2.560
12	0.0193	-2.624

3	0.0050	-2.817	
4	0.0067	-2.774	
5	0.0083	-2.740	
6	0.0099	-2.710	
7	0.0115	-2.692	
8	0.0131	-2.670	
9	0.0147	-2.613	
10	0.0162	-2.575	

13	0.0207	-2.576
14	0.0222	-2.507
15	0.0237	-2.438
16	0.0251	-2.402
17	0.0266	-2.433
18	0.0280	-2.421
19	0.0294	-2.259

k	ϕ_{D}	$q^{(k)}$ / (kJ mol ⁻¹)	
1	0.0013	_	
2	0.0025	25 -1.690	
3	0.0038	-1.681	
4	0.0050	-1.711	
5	0.0063	-1.683	
6	0.0075	-1.628	
7	0.0087	-1.626	
8	0.0099	-1.648	
9	0.0110	-1.619	
10	0.0122	-1.556	

Table S2c. $q^{(k)}$ values at $\phi_{\rm D}^0 = 0.130$.

k	$\phi_{ m D}$	$q^{(k)}$ / (kJ mol ⁻¹)
11	0.0133	-1.538
12	0.0145	-1.546
13	0.0156	-1.567
14	0.0167	-1.577
15	0.0178	-1.489
16	0.0189	-1.505
17	0.0200	-1.486
18	0.0210	-1.422
19	0.0221	_

Table S2d. $q^{(k)}$ values at $\phi_{\rm D}^0 = 0.103$.

k	$\phi_{ m D}$	$q^{(k)}$ / (kJ mol ⁻¹)	
1	0.0010	_	
2	0.0020	-1.181	
3	0.0030	-1.219	
4	0.0040	-1.207	
5	0.0050	-1.141	
6	0.0059	-1.113	
7	0.0069	-1.135	
8	0.0078	-1.167	
9	0.0087	-1.097	

k	$\phi_{ m D}$	$q^{(k)}$ / (kJ mol ⁻¹)
11	0.0106	-1.087
12	0.0115	-1.072
13	0.0124	-1.021
14	0.0132	-1.049
15	0.0141	-0.990
16	0.0150	-1.012
17	0.0158	-1.020
18	0.0167	-0.995
19	0.0175	-0.944

10	0.0097	-1.104		

$\phi_{\rm D}$	ε / kJ·mol ⁻¹	$\omega_{\rm D}$ / kJ·mol ⁻¹	$k_{\rm ITC}$ / kJ·mol ⁻¹
0.103	18.1	0.127	-3.3
0.130	18.8	0.227	-5.7
0.173	20.6	0.500	-3.5
0.191	19.8	0.612	-7.9

Table S3. Summary of ITC results.

S5. Salt osmotic coefficient

According to Ref. S6, the salt osmotic coefficient at 25 °C is given by

$$\varphi_{\rm S}(25\,^{\circ}{\rm C}) = 1 - 2\frac{0.391475\,I^{1/2}}{1 + 1.2\,I^{1/2}} + \frac{4}{3}\frac{m_{\rm S}}{m^0} \Big[0.011976 + 0.951276 \times \exp(-2I^{1/2}) \Big] + \frac{16}{3} \Big(\frac{m_{\rm S}}{m^0}\Big)^2 \Big[0.0024359 + 0.236044 \times \exp(-2.5\,I^{1/2}) \Big]$$

where $m_{\rm S} = \frac{C_{\rm S}^*}{M_{\rm W}C_{\rm W}^*}$ and $I = 3 \frac{m_{\rm S}}{m^0}$.

For other temperatures, we fit the experimental data to the following empirical expression:

$$\varphi_{\rm S}(T) = \varphi_{\rm S}(25\,^{\circ}{\rm C}) + 1000 \frac{m_{\rm S}}{m^0} \left[21.377 - 9.1906 \,\frac{m_{\rm S}}{m^0} + 0.95293 \left(\frac{m_{\rm S}}{m^0}\right)^2 \right] \left[(T / \,^{\circ}{\rm C})^{1/2} - (25 / \,^{\circ}{\rm C})^{1/2} \right]$$

where *T* is in Celsius. In Fig. S4, the plots of φ_s as a function of C_s^* at 5, 15, 25 and 37 °C show that φ_s increases with temperature at a given C_s^* .



Figure S4. Osmotic coefficient for the Na₂SO₄-water system.

S6. Diffusion Coefficient

In this section, we report the measured DLS diffusion coefficients and their theoretical examination.

Table S4. DLS dendrimer diffusion coefficient, D_{DLS} , as a function of dendrimer volume fraction, ϕ_{D} , at two salt concentrations (C_{s} / mol dm⁻³ = 0.044 and 0.949) and two temperatures (25.0 and 37.0 °C).

$\phi_{\rm D}$	25.0 °C	37.0 °C		
0.0067	0.0924	0.1248		
0.0100	0.0947	0.1268		
0.0149	0.0944	0.1268		
0.0183	0.0945	0.1265		
0.0205	0.0955	0.1293		

Table S4a. Values of $D_{\text{DLS}}/10^{-9} \text{ m}^2\text{s}^{-1}$ at 25.0 and 37.0 °C for C_{s} / mol dm⁻³ = 0.044.

$\phi_{ m D}$	25.0 °C	37.0 °C			
0.0076	0.0562	0.0774			
0.0102	0.0537	0.0733			
0.0133	0.0526	0.0715			
0.0169	0.0493	0.0671			
0.0212	0.0463	0.0622			

Table S4b. Values of $D_{\rm DLS}/10^{-9} \, {\rm m^2 s^{-1}}$ at 25.0 and 37.0 °C for $C_{\rm S}$ / mol dm⁻³ = 0.949.

The DLS diffusion coefficient can be written as⁷

$$D_{\text{DLS}} = D_0 H(\phi_{\text{D}}, T) S(\phi_{\text{D}}, T)$$
(S36)

where $H(\phi_D, T)$ and $S(\phi_D, T)$ are the hydrodynamic and thermodynamic factors, respectively. Note that $S(\phi_D, T) = (v_D / k_B T) (\partial \Pi / \phi_D)_T$. At low ϕ_D , we can write:

$$H(\phi_{\rm D},T) = 1 + k_H \phi_{\rm D} + \dots$$
(S37)

$$S(\phi_{\rm D}, T) = 1 + k_S \phi_{\rm D} + \dots$$
 (S38)

where the slopes, k_H and k_s , characterize hydrodynamic and thermodynamic interactions, respectively. The hydrodynamic slope, k_H , is expected to be negative, while the thermodynamic slope, k_s , is positive (negative) for repulsive (attractive) particle-particle thermodynamic interactions. From Eqs. S36-S38, we can write:

$$D_{\rm DLS} = D_0 \left[1 + (k_H + k_S)\phi_{\rm D} + \dots \right]$$
(S39)

If the observed slope, $k_D = k_H + k_s$, is positive then particle-particle thermodynamic interactions are repulsive. The following expression for k_s can be extracted from Eq. S31 in the limit of $\phi_D = 0$.

$$k_{\rm s} = 2b(0) + \frac{2e(0)}{k_{\rm B}T} - \alpha''(0)\frac{\Pi_{\rm s}v_{\rm D}}{k_{\rm B}T} = 8 + \frac{\varepsilon}{k_{\rm B}T} - (12 + 15q + 6q^2 + q^3)q^3p_{\rm s}$$
(S40)

where $p_{\rm S} \equiv \Pi_{\rm S} v_{\rm D} / k_{\rm B} T$. If we set the value of k_D at $C_{\rm S}$ / mol dm⁻³ = 0.044 and 25.0 °C as the reference $k_D^{(R)} = 1.8$ and assume that k_H is independent of salt concentration and temperature, Eqs. S39,S40 yield:

$$k_{D} = k_{D}^{(R)} + \frac{\varepsilon}{k_{B}} \left(\frac{1}{T} - \frac{1}{T_{R}} \right) - (12 + 15q + 6q^{2} + q^{3})q^{3} \left(p_{S} - p_{S}^{(R)} \right)$$
(S41)

where $p_{\rm S}^{(R)}$ is the value of $p_{\rm S}$ at $C_{\rm S}$ / mol dm⁻³ = 0.044 and 25.0 °C. In Table S5 (last four columns), we report the values of k_D calculated from Eq. S41 and q = 0.30 ($k_{\rm DLS}^{(q=0.30)}$), q = 0.33 ($k_{\rm DLS}^{(q=0.33)}$), 0.35 ($k_{\rm DLS}^{(q=0.35)}$) and 0.40 ($k_{\rm DLS}^{(q=0.40)}$).

$C_{\rm S}$ / mol dm ⁻³	T∕°C	$\varepsilon / k_{\rm B} T$	p _s	k _D	$k_D^{(q=0.30)}$	$k_D^{(q=0.33)}$	$k_D^{(q=0.35)}$	$k_D^{(q=0.40)}$
0.044	25.0	8.0	1.28	1.8±0.4	(1.8)	(1.8)	(1.8)	(1.8)
0.949	25.0	8.0	21.95	-11.6±0.4	-7.7	-11.6	-14.2	-23.4
0.044	37.0	7.7	1.28	1.8±0.4	1.5	1.5	1.5	1.5
0.949	37.0	7.7	22.43	-12.7±0.4	-8.2	-12.2	-14.8	-24.3

Table S5. DLS parameters.

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