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Miscibility of Trihexyl(tetradecyl)phosphonium Chloride with Alkanes

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Liquid−liquid miscibility temperatures as a function of composition have been determined experimentally for the binary systems formed by trihexyl(tetradecyl)phosphonium chloride with hexane, octane, decane, undecane, and dodecane. All the measured systems present solubility curves characterized by asymmetry with respect to equimolar composition and represent the phase diagrams with the upper critical solution temperatures (UCST). For a given set of binary mixtures with trihexyl(tetradecyl)phosphonium chloride, the solubility decreases with increasing alkane chain length. The experimental liquid−liquid equilibrium data were satisfactorily correlated by the NRTL equation.

Introduction

Soon after the discovery that certain nitrogen-based room temperature liquid salts could be useful as battery electrolytes,[1,2] interest in these and similar salts as novel fluids and solvents developed. Almost the entire volume of ionic liquid literature deals with imidazolium-based systems. Other nitrogen-based salts such as pyridinium salts are not as common, and investigation of other ionic liquids, i.e., those based on the phosphonium cation, are even less so. The phosphonium cation contains four substituents and different combinations along with the multitude of various available anions which represent an enormous number of possible salts. Even when one restricts the cation to the generic formula $-[PR_3R']^+$, the number is still very large. There are several reasons why one might consider a phosphonium ionic liquid. The most important is that phosphonium ionic liquids are much more stable than the corresponding ammonium salts and even have an edge on imidazolium salts. This is very important for processes that operate at temperatures greater than 373 K. In addition to being slightly less thermally stable, the imidazolium cation contains protons, which are not entirely inert. They are somewhat acidic which can result in carbine formation. Phosphonium salts, on the other hand, have no such acidic protons. The fact that alkylphosphonium salts are in general less dense than water can be beneficial in product workup steps while decanting aqueous streams which contain inorganic salt byproducts. They are also attractive because the steric bulk of the large side chains around the phosphonium cation interferes with electrostatic interactions between the anions and cation—which is generally localized on the phosphorus—allowing for greater impact of the properties of the anion itself, as compared to salts with more strongly interacting smaller cations. Naturally, there are also disadvantages such as very high viscosities. Relatively poorly understood solubility properties demand further studies as well. There are only a few papers dealing with the phase equilibria of phosphonium-based ionic liquids. Saracsan et al.[3] reported miscibility data on trihexyl(tetradecyl) phosphonium chloride ([P666 14]Cl) and bromide ([P666 14] Br) with hydrocarbons, while Domanska et al.[4,5] presented extensive data on the phase behavior of tetrabutylphosphonium methanesulfonate and tetrabutylphosphonium *p*-toluenesulfonate + alcohols and aromatic hydrocarbon systems. More recently, Anderson et al.[6] reported on the phase behavior of trihexyl(tetradecyl)phosphonium chloride with nonane and water. In this paper, we present the miscibility study of ([P666 14]Cl) with aliphatic hydrocarbons ranging from hexane up to dodecane.

Experimental Section

Trihexyl(tetradecyl)phosphonium chloride was purchased from Merck (stated mass fraction purity > 98 %). To reduce the water content and volatile compounds, the sample was kept under vacuum (0.1 Pa) at 333 K in the presence of P_2O_5 for 72 h always immediately prior to their use.

The list of alkanes used in the study is as follows: hexane, octane, decane, undecane, and dodecane (all from Aldrich, stated mass fraction purity > 99 %, anhydrous). They were additionally distilled and dried over molecular sieves 5 Å. All the samples were analyzed by Karl Fischer titration (Metrohm, 716 DMS Titrino), and the water contents were as follows: 100 ppm for alkane and 1400 ppm for trihexyl(tetradecyl)phosphonium chloride. The samples for the miscibility measurements were prepared gravimetrically. The relative uncertainty of the mass fraction was estimated to be less than $2 \cdot 10^{-3}$. The technique and apparatus used for the determination of the phase transitions were described earlier.[7] The special advantage of the apparatus is the small amount of sample (about 1 cm^3) needed to determine cloud point temperatures. The samples were placed in a thermostatted cell equipped with a fiber optic cable. Pressure was kept constant at 0.1 MPa as measured by a Heisse 710A digital indicator. Temperature was measured by using an RTD probe (100 Ω of Omega Engineering calibrated against ITS-90) coupled to a Keithley 199 DMM with a precision of ± 5 mK. The phase transition (cloud point) was detected by the loss of the transmitted light intensity from a 5 mW Polytec HeNe laser shining through the set of the fiber optic cables and the cell and detected by a photodiode. The temperature

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Table 1. Miscibility Data of Trihexyl(tetradecyl)phosphonium Chloride (1) with Alkanes

IL + Hexane		IL + Octane		IL + Decane	
x_1	T/K	x_1	T/K	x_1	T/K
0.004	291.66	0.007	300.76	0.007	309.19
0.005	293.29	0.008	303.40	0.009	312.49
0.008	295.71	0.009	306.80	0.010	314.96
0.010	296.64	0.012	309.17	0.011	317.84
0.014	297.13	0.016	310.72	0.013	319.87
0.020	297.08	0.018	311.22	0.015	321.66
0.026	296.21	0.023	311.69	0.017	322.85
0.029	295.94	0.029	311.60	0.021	323.50
0.033	294.99	0.034	311.20	0.024	323.80
0.038	293.85	0.038	310.81	0.029	323.82
0.046	291.26	0.045	309.69	0.034	323.60
0.053	289.11	0.052	308.22	0.039	322.90
		0.069	304.08	0.046	321.85
		0.085	300.01	0.051	321.17
		0.120	290.02	0.056	319.96
				0.062	319.05
				0.070	317.63
				0.083	314.79
				0.099	310.39
				0.126	303.14
				0.150	295.08

IL + Undecane		IL + Dodecane	
x_1	T/K	x_1	T/K
0.009	291.10	0.008	324.61
0.011	322.13	0.012	330.31
0.016	326.99	0.019	333.75
0.024	329.31	0.032	335.62
0.032	329.95	0.043	336.02
0.038	330.46	0.055	335.40
0.050	329.73	0.074	333.62
0.060	328.40	0.100	329.01
0.070	327.15	0.123	324.01
0.090	323.66	0.148	318.40
0.115	318.60	0.180	311.11
0.170	305.37	0.220	300.00
0.236	286.65		

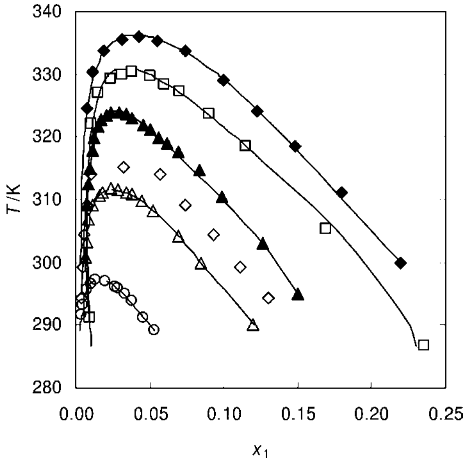

Figure 1. Phase diagrams for trihexyl(tetradecyl)phosphonium chloride with different hydrocarbons: ○, hexane; Δ, octane; ▲, decane; □, undecane; ◆, dodecane. Lines calculated with the NRTL parameters fitted to experimental data. Comparison is made with data for nonane (◇) from Anderson et al.[6]

Table 2. Fitting Parameters of Equation 2 and Values of Variation, $\sigma^2(x_1)$, for Calculated Solubilities of the Trihexyl(tetradecyl)phosphonium Chloride in the Hydrocarbons

alkane	T_c/K	x_c	A_1	A_2	β	$\sigma^2(x_1)\cdot 10^4$
hexane	297.02 ± 0.02	0.017 ± 0.001	0.13 ± 0.01	35 ± 2	0.51 ± 0.01	0.070
octane	311.69 ± 0.03	0.023 ± 0.002	0.9 ± 0.1	24 ± 1	0.50 ± 0.01	0.325
decane	323.01 ± 0.05	0.029 ± 0.001	1.0 ± 0.1	22 ± 2	0.50 ± 0.02	1.163
undecane	330.45 ± 0.03	0.037 ± 0.003	1.2 ± 0.2	11 ± 1	0.49 ± 0.04	0.532
dodecane	336.02 ± 0.03	0.043 ± 0.002	1.4 ± 0.5	12 ± 1	0.50 ± 0.03	1.102

was changed very slowly with a rate of $< 0.1\ \mathrm{K\cdot min^{-1}}$ (typically $0.05\ \mathrm{K\cdot min^{-1}}$), and cloud point temperatures have been determined with uncertainty of 0.02 K. The details of the procedure for the determination of the transition temperatures are given elsewhere.[8]

Results and Discussion

The experimental values of the liquid–liquid miscibility temperature, T, as a function of composition, x, for the binary systems of trihexyl(tetradecyl)phosphonium chloride with different alkanes are listed in Table 1 and shown graphically in Figure 1.

The critical solution temperature and critical composition of each binary system were evaluated after fitting each set of experimental $T-x$ data to the scaling equation[9−11] including the first Wegner correction ($t^{\beta+0.5}$)

$$|x - x_c| = A_1\theta^{\beta}(1 + A_2 t^{0.5}) \qquad (1)$$

In the above equation $t = 1 - T/T_c$; x and T are mole fraction of ionic liquid and temperature; x_c and T_c are the corresponding critical values; and A_1, A_2, and β are the critical amplitudes and critical exponent, respectively. The results of the analysis are listed in Table 2.

The data presented in Figure 1 show that the miscibility curves represent the phase diagrams with the upper critical solution temperature, UCST. It can also be seen that the (T, x) projection of these binary phase diagrams is visibly skewed toward low molar fractions of the ionic liquid. All the measured systems present solubility curves characterized by asymmetry with respect to equimolar composition. It is a consequence of much higher molar volumes of ionic liquid ($583.49\ \mathrm{cm^3\cdot mol^{-1}}$ for [P_{66614}]Cl) in comparison to that of hydrocarbons (from $130.8\ \mathrm{cm^3\cdot mol^{-1}}$ for hexane to $227.3\ \mathrm{cm^3\cdot mol^{-1}}$ for dodecane). All reported values are at T/K = 293.15. This is similar to polymer solutions where the asymmetry in phase diagrams is due to the mixing entropy effect caused by the large difference between volumes occupied by the mixture's components. As can be seen in Figure 2, the critical concentrations shift visibly to the higher values with the increasing alkyl chain length of the solvent.

Comparison of the present results with the previous ones reported by Saracsan et al.[3] and Anderson et al.[6] reveals the same general picture. However, these qualitative similarities do not translate into a quantitative agreement. The critical tem-

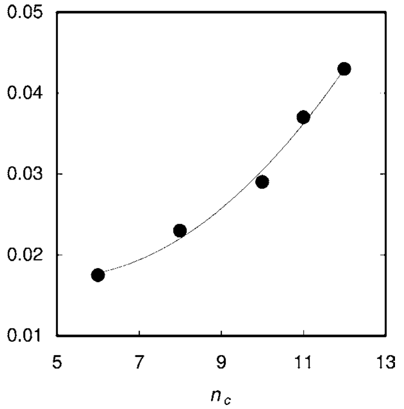

Figure 2. Dependence of the critical concentration on number of carbon atoms in alkane. Trihexyl(tetradecyl)phosphonium chloride + hydrocarbons systems.

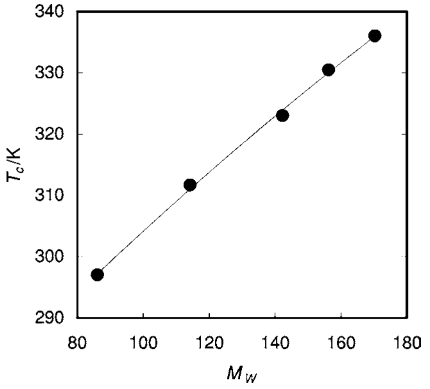

Figure 3. Dependence of the critical solution temperature on molar mass of hydrocarbon. Trihexyl(tetradecyl)phosphonium chloride + hydrocarbons systems.

peratures obtained presently are visibly higher than the values observed by Saracsan et al. The differences in phase transition temperatures may be due to different water content (they did not state it) or other impurities in ionic liquids and/or alkanes. As pointed out above, we put special attention on purification and drying both ionic liquid and hydrocarbons used in experiments. In particular, alkanes used in the present experiments, although of the highest quality available, were additionally distilled and carefully dried. On the other hand, the data presented by Anderson et al. for [$P_{666\ 14}$] Cl + nonane system fit very well to our results. We suspect that the source of [$P_{666\ 14}$] Cl may play an essential role. (Using samples of IL coming from Merck, we obtained for the [$P_{666\ 14}$] Cl + heptane system the critical parameters comparable with those obtained by Saracsan et al.) The data presented in Figure 1 clearly show the miscibility behavior with changing alkane. For a given set of binary mixtures with a trihexyl(tetradecyl)phosphonium chloride, the solubility decreases with increasing alkane chain length (Figure 3). One would anticipate that the shorter alkyl chain of alkanes would favor their better accommodation in the hydrophobic region of the alkyl side chains of the phosphonium cation of the ionic liquid. In general, it seems to be a typical behavior observed earlier for nitrogen-based ionic liquids—the longer chain length in the solvent like hydrocarbon or alcohol the worse miscibility is observed.

As can be taken from Table 2, the exponent β for all the systems studied is close to 0.5. It seems appropriate to interject a comment on β values at this point. While fits to nonclassical scaling yields $\beta = 0.33$ for many binary mixtures, for others they do not. Most theories that correlate thermodynamic properties with molecular structure and molecular parameters are mean-field theories. Thus, it seems to be important to accurately determine the extent of the different regions where nonclassical scaling and mean-field theories apply. For nonelectrolyte solutions, this boundary, the Ginzburg limit, is expressed by the approximate reduced temperature t_g below which the nonclassical theory is expected to be correct.[12] A reasonable estimate for the asymptotic application of nonclassical scaling theory is $t_g = 10^{-3}$. Then, for $t = (T_c - T)/T_c > t_g$, the mean-field theory is appropriate to describe data outside that limit (also including the present data). As was shown by Pitzer,[13] certain electrolyte solutions which phase separate are well described with $\beta = 0.5$, even close to (T_c, x_c). He has suggested that differences in the patterns of coexistence curve are related to the range of interparticle forces in both the near-critical and wide-ranging region. Let us recall that IL solutions are in some aspects closer to electrolyte solutions than to nonelectrolyte ones.

Table 3. NRTL Parameters and Standard Deviation, $\sigma(x_1)$, for Calculated Solubilities of the Trihexyl(tetradecyl)phosphonium Chloride in the Hydrocarbons

alkane	a_{ij}/K	c_{ij}	d_{ij}/K	e_{ij}/K^2	$\sigma(x_1)$/rmsd
hexane	a_{12}	4069.32	−17.61166		0.0012
	a_{21}	240.042	7.9581		0.0010
octane	a_{12}	11870.94	−68.16354	0.0860151	0.0025
	a_{21}	−77653.77	510.281	−0.813409	0.0019
decane	a_{12}	−18350.33	126.9896	−0.2269922	0.0029
	a_{21}	25226.68	−161.047	0.2798649	0.0024
undecane	a_{12}	−11553.7	82.93445	−0.1537397	0.0055
	a_{21}	−2782.599	15.32842		0.0043
dodecane	a_{12}	2623.279	−10.39546		0.0024
	a_{21}	−22005.65	146.8809	−0.2229299	0.0018

Experimental data can be reduced using one of the local composition models for excess Gibbs energy. To this end, the NRTL model has been used.[14] For a binary system, this equation is given as

$$\frac{G^E}{RT} = x_1x_2\left(\frac{\tau_{21}G_{21}}{x_1 + x_2G_{21}} + \frac{\tau_{12}G_{12}}{x_2 + x_1G_{12}}\right) \tag{2}$$

where

$$\tau_{12} = \Delta g_{12}/RT = g_{12} - g_{22}/RT = a_{12}/T,$$
$$\tau_{21} = \Delta g_{21}/RT = g_{21} - g_{11}/RT = a_{21}/T,$$
$$G_{12} = \exp(-\alpha_{12}\tau_{12}),\ G_{21} = \exp(-\alpha_{21}\tau_{21}),\ \text{and}\ \alpha_{12} = \alpha_{21}$$

In the above equations, g_{ij} represents the Gibbs energy of interaction between molecules, where subscript j refers to the central molecule, and α_{12} is a constant that is assumed to be characteristic of the nonrandomness of the mixture. The activity coefficients for a binary mixture are given by

$$\begin{aligned} \ln\gamma_1 &= x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + G_{21}x_2}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2 + G_{12}x_1)^2}\right] \\ \ln\gamma_2 &= x_1^2\left[\tau_{21}\left(\frac{G_{12}}{x_2 + G_{12}x_1}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1 + G_{21}x_2)^2}\right] \end{aligned} \tag{3}$$

Such complex phase equilibria as measured cannot be represented by simple, temperature-independent parameters a_{12} and a_{21}. For proper representation of data, we have used temperature-dependent parameters in the form of quadratic polynomials

$$a_{ij} = c_{ij} + d_{ij}T + e_{ij}T^2 \tag{4}$$

Parameters c_{ij}, d_{ij}, and e_{ij} were adjusted to experimental data using the sum of squares of relative differences between experimental and calculated phase (boundary) compositions as an objective function. During calculations, the constant value of α_{12} (equal to 0.3) was taken into account. The calculated parameters are reported in Table 3. Comparison between experimental and calculated data is presented in Figure 1.

Conclusions

New experimental results for the miscibility of quaternary phosphonium salt—trihexyl(tetradecyl)phosphonium chloride with C_6, C_8, C_{10}, and C_{12} aliphatic hydrocarbons—are presented. All systems investigated show a liquid−liquid phase split with an upper critical solution temperature (UCST). Generally, the trend observed in the miscibility behavior of the phosphonium salt is the same as was observed for imidazolium-based salts—an increase in the alkyl chain length of the hydrocarbon decreases the solubility of IL. The well-known NRTL equation was used to satisfactorily correlate the experimental liquid−liquid equilibrium data.

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