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Prediction of gas solubility in binary polymer + solvent mixtures

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Abstract

This paper is devoted to a theory of gas solubility in highly asymmetrical mixed solvents composed of a low molecular weight (such as water, alcohol, etc.) and a high molecular weight (such as polymer, protein, etc.) cosolvents. The experimental solubilities of Ar, CH_4, C_2H_6 and C_3H_8 in aqueous solutions of polypropylene glycol and polyethylene glycol were selected for comparison with the theory. The approach for predicting these solubilities is based on the Kirkwood–Buff formalism for ternary mixtures, which allowed one to derive a rigorous expression for the Henry constant in mixed solvents. Starting from this expression, the solubilities could be predicted in terms of those in each of the two constituents and the properties of the mixed solvent. This expression combined with the Flory–Huggins equation for the activity coefficient in a binary mixed solvent provided very accurate results, when the Flory–Huggins interaction parameter was used as an adjustable quantity. A simple expression in which the solubility could be predicted in terms of those in each of the two constituents and the molar volumes of the latter was also derived. While less accurate that the previous expression, it provided more than satisfactory results.

Keywords: Gas solubility; Mixed solvents; Polymer solutions

1. Introduction

The prediction of the solubilities of gases in mixed solvents composed of water and a high molecular weight cosolvent such as a polymer, protein, detergent, biomolecule, drug, etc. is important from a practical point of view [1]. One modern example relevant to this topic is the gas antisolvent recrystallization process [2], which is widely used for refining explosives, pharmaceuticals, proteins, etc. The present paper is devoted to the development of equations able to predict the gas solubility in a mixed solvent composed of water (or any other low molecular weight solvent) and a high molecular weight constituent (cosolvent) such as polymers, proteins, etc.

The solubilities of nonpolar nonacidic gases in water are usually small compared to those in nonaqueous solvents; this behavior is usually attributed to the hydrophobic effect [3]. However, the solubility of the same gases in nonpolar solvents is much higher. The solubilities of gases in high molecular weight solvents, such as liquid (or molten) polymers differ in major ways from those in low molecular weight solvents. Indeed, Table 1 which provides a comparison (in terms of the Henry constant and Ostwald coefficient) between the solubilities of gases in different kinds of solvents, reveals that the solubilities [4,5] of nonpolar, nonacidic gases in liquid polymers, such as polypropylene glycol (PPG) and polyethylene glycol (PEG), are much higher than those in water. They are even comparable with the solubilities [6,7] of the same gases in *n*-decane. This means that the well-known principle 'like dissolves like' cannot be applied to high molecular weight solvents. Indeed, the high molecular weight compounds that possess polar groups are often very good solvents for nonpolar, nonacidic gases, and one can generally state that small size gases are fairly soluble in high molecular weight solvents. This probably can be explained by the larger free space between the polymer molecules than between the low molecular weight solvents.

In a previous paper [9] we developed an equation which could predict the gas solubility in a mixed solvent from the solubilities in the individual constituents and the properties of their mixture. This equation was applied to mixed solvents composed of small molecules. In the present paper, we will apply it to the solubility of a gas in a polymer + water mixture.

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Table 1
The solubility of several nonpolar gases in water, decane and liquid polymers at $T = 298.15$ K and gas partial pressure 1 atm

Gas	Solubility[a], Henry constant (H, MPa)[b] (Ostwald coefficient, 10^2 L)[c]			
	Water	*n*-decane	PPG-400[d]	PEG-200[e]
Argon	4025 (3.4)	40.9 (31.0)	41.8 (14.9)	202.5 (6.9)
Methane	4039 (3.4)	39.3 (32.3)	21.0 (29.7)	114.9 (12.1)
Ethane	3027 (4.5)	2.8 (464)	4.1 (154)	24.0 (58.1)
Propane	3745 (3.7)	0.7 (2060)	1.3 (510)	10.6 (132)

[a] The data for the solubilities in water and polymers were taken from Refs. [4,5], and those in *n*-decane from Refs. [6,7].

[b] The Henry constant is defined as the limiting value of the ratio of the gas partial pressure to its mole fraction in solution as the latter tends to zero [8].

[c] The Ostwald coefficient is the ratio of the volume of gas absorbed to the volume of the absorbing liquid, both measured at the same temperature [8].

[d] Polypropylene glycol with average molecular weight of 400.

[e] Polyethylene glycol with average molecular weight of 200.

The aqueous mixtures of polymers (PEG and PPG) were selected for comparison with the theory, because accurate data [4,5] regarding the solubility of argon (Ar), methane (CH_4), ethane (C_2H_6) and propane (C_3H_8) in the individual constituents and the polymer + water mixtures are available. In addition, the above polymers and water are miscible in all proportions and solubility data [4,5] are available for the entire composition range. The theoretical approach regarding the solubility of gases in polymer + water mixed solvents can be extended to the correlation of their solubility in mixed solvents formed of water and pharmaceuticals, proteins, biomolecules, etc.

2. Theory

The gas solubility will be expressed in terms of the Henry constant. There are a number of expressions for the Henry constant in binary mixed solvents. The oldest and simplest relationship between the Henry constant in binary solvents and those in the individual constituents is that proposed by Krichevsky [10]:

$$\ln H_{2,t} = x_1^{b,1-3} \ln H_{2,1} + x_3^{b,1-3} \ln H_{2,3} \qquad (1)$$

where $H_{2,t}$, $H_{2,1}$ and $H_{2,3}$ are the Henry constants in the binary mixed solvent 1–3 and the individual solvents 1 and 3, respectively, and $x_1^{b,1-3}$ and $x_3^{b,1-3}$ are the mole fractions of components 1 and 3 in the binary solvent 1–3 (throughout this paper the following subscripts for the components will be used: 1, high molecular weight cosolvent, 2, solute (gas), 3, low molecular weight cosolvent). Krichevsky's relationship (1) is valid when the ternary and binary mixtures (1–2 and 2–3) are ideal [9]. However, the ternary 1–2–3 and binary mixtures (1–2 and 2–3) do not always satisfy the ideality conditions. Indeed, the activity coefficients at infinite dilution for the binary mixtures gas/solvent (particularly for high molecular weight solvents) have values much larger [11,12] than unity. On the basis of the Kirkwood–Buff theory of solutions [13] for ternary mixtures [14] the authors derived [9] the following relation for the Henry constant in a binary solvent mixture

$$\ln H_{2,t} = \frac{(\ln H_{2,1})(\ln V^{ID} - \ln V_3^0) + (\ln H_{2,3})(\ln V_1^0 - \ln V^{ID})}{\ln V_1^0 - \ln V_3^0} \qquad (2)$$

where V_1^0 and V_3^0 are the molar volumes of the individual solvents 1 and 3, and V^{ID} is the molar volume of the ideal binary mixture 1–3 ($V^{ID} = x_1^{b,1-3} V_1^0 + x_3^{b,1-3} V_3^0$). Eq. (2) is less restrictive than the Krichevsky Eq. (1), because it requires that only the binary mixed solvent 1–3 be an ideal mixture. Such an approximation is reasonable because the activity coefficient of water in the binary mixture PEG + water [15,16] is small and at infinite dilution [11] is about 0.5, while those between the gas and each of the constituents of the solvent are very large.

Eq. (2) does not contain any adjustable parameter and can be used to predict the gas solubility in mixed solvents in terms of the solubilities in the individual solvents (1 and 3) and their molar volumes. Eq. (2) provided a very good agreement [9] with the experimental gas solubilities in binary aqueous solutions of nonelectrolytes; a somewhat modified form correlated well the gas solubilities in aqueous salt solutions [17]. The authors also derived the following rigorous expression for the Henry constant in a binary solvent mixture [9] (Appendix A for the details of the derivation):

$$\ln H_{2,t} = -\int \frac{B}{V}\left[1 + x_3^{b,1-3}\left(\frac{\partial \ln \gamma_3^{b,1-3}}{\partial x_3^{b,1-3}}\right)_{P,T}\right] dx_3^{b,1-3} + \frac{1}{2}\int \frac{(x_1^{b,1-3} - x_3^{b,1-3})}{x_1^{b,1-3}}\left(\frac{\partial \ln \gamma_3^{b,1-3}}{\partial x_3^{b,1-3}}\right)_{P,T} dx_3^{b,1-3} + A \qquad (3)$$

where V is the molar volume of the binary mixed solvent 1–3, $B = (\Delta_{12} - \Delta_{23})_{x_2^t = 0}/2$, x_2^t is the mole fraction of the solute (component 2) in the ternary mixture 1–2–3, $A(P,T)$ is a composition-independent constant of integration, $\gamma_3^{b,1-3}$ is the activity coefficient of component 3, the superscript b, 1–3 indicates that the activity coefficient is for the binary 1–3 mixture, and Δ_{12} and Δ_{23} are functions of the Kirkwood–Buff integrals (Appendix A). If B is considered independent of the composition of the binary mixed solvent 1–3, Eq. (3) can be rewritten in the form

$$\ln H_{2,t} = -BI_1 + \frac{I_2}{2} + A \qquad (4)$$

where the integrals

$$I_1 = -\int \frac{\left[1 + x_3^{b,1-3}\left(\frac{\partial \ln \gamma_3^{b,1-3}}{\partial x_3^{b,1-3}}\right)_{P,T}\right]}{V} dx_3^{b,1-3}$$

and

$$I_2 = \int \frac{(x_1^{b,1-3} - x_3^{b,1-3})}{x_1^{b,1-3}} \left(\frac{\partial \ln \gamma_3^{b,1-3}}{\partial x_3^{b,1-3}} \right)_{P,T} dx_3^{b,1-3}$$

can be calculated if the composition dependencies of the activity coefficient and molar volume of the binary mixed solvent 1–3 are known. The combination of Eq. (4) with the following limiting expressions

$$(\ln H_{2,t})_{x_1^{b,1-3}=0} = \ln H_{2,3} \tag{5}$$

and

$$(\ln H_{2,t})_{x_3^{b,1-3}=0} = \ln H_{2,1} \tag{6}$$

allows one to obtain the constants $A(P,T)$ and $B(P,T)$. Expressions (1), (2) and (4) will be used to calculate the gas solubility in a mixed solvent composed of water and polymer.

3. The solubility of gases in binary polymer + solvent mixtures

3.1. The systems considered

The experimental solubilities [4,5] of Ar, CH_4, C_2H_6 and C_3H_8 in the aqueous solutions of PPG with the average molecular weight of 400 (PPG-400), PEG with the average molecular weight of 200 (PEG-200) and PEG with the average molecular weight of 400 (PEG-400) were selected for comparison with the theory.

3.2. The calculation procedure

The experimental Ostwald coefficients [4,5] were converted into the Henry constants. The molar volumes of the aqueous solutions of PPG-400, PEG-200 and PEG-400 were calculated from experimental densities [4,5] to conclude that they are well approximated by the expression

$$V = x_1^{b,1-3} V_1^0 + x_3^{b,1-3} V_3^0 \tag{7}$$

The Flory–Huggins equation [18,19] for the activity coefficient of water in the binary mixed solvent polymer (1) + water (3) will be employed. It has the form

$$\ln \gamma_3^{b,1-3} = \ln\left[1 - \left(1 - \frac{1}{r}\right)\varphi_1\right] + \left(1 - \frac{1}{r}\right)\varphi_1 + \chi\varphi_1^2 \tag{8}$$

where χ is the Flory–Huggins interaction parameter considered here as composition-independent, $\varphi_1 = rx_1^{b,1-3}/(rx_1^{b,1-3} + x_3^{b,1-3})$ is the volume fraction of polymer in the mixed solvent polymer + water and r is the number of segments in the polymer molecule (taken as the ratio of the molar volumes of the polymer and water, $r = V_1^0/V_3^0$). For the derivative of the activity coefficient $(\partial \ln \gamma_3^{b,1-3}/\partial x_3^{b,1-3})_{P,T}$, the Flory–Huggins equation provides the following expression

$$\left(\frac{\partial \ln \gamma_3^{b,1-3}}{\partial x_3^{b,1-3}} \right)_{P,T} = -\frac{x_1^{b,1-3}(-r^3 x_1^{b,1-3} - 3r^2 x_3^{b,1-3} + 3r x_3^{b,1-3} + 2r^2 - x_3^{b,1-3} - r + 2r^2\chi)}{(r x_1^{b,1-3} + x_3^{b,1-3})^3} \tag{9}$$

The insertion of Eqs. (7) and (9) into Eq. (4) provides an expression which can be integrated analytically (Appendix B). The Flory–Huggins interaction parameter χ can be used either as an adjustable parameter, or can be obtained from phase equilibrium data for the binary mixture polymer + water.

3.3. Results

The comparison of the experimental solubilities [4,5] of Ar, CH_4, C_2H_6 and C_3H_8 in the binary aqueous mixtures of PPG-400, PEG-200 and PEG-400 with the calculated ones is presented in Figs. 1–3 and Table 2. They show that Eq. (4) coupled with the Flory–Huggins equation, in which the interaction parameter χ is used as an adjustable parameter, is very accurate. The Krichevsky equation (1) does not provide accurate predictions. While less accurate than Eq. (4), the simple Eq. (2) provides very satisfactory results without involving any adjustable parameters. It should be noted that Eq. (4) coupled with the Flory–Huggins equation with $\chi = 0$ (athermal solutions) does not involve any adjustable parameters and provides results comparable to those of Eq. (2).

4. Discussion

A simple and reliable method for the correlation of the gas solubility in a mixed solvent composed of two cosolvents, one of high molecular weight and the other of low molecular weight, was proposed. It was shown that the well-known Krichevsky equation could not provide accurate predictions of the gas solubilities in such mixed solvents. The failure of Krichevsky's equation is not surprising since it requires the ternary 1–2–3 and the binary 1–2 and 2–3 mixtures to be ideal. Such conditions cannot be satisfied by the highly asymmetrical mixtures of a high molecular weight cosolvent (1)–gas (2)–low molecular weight cosolvent (3). Eq. (2) obtained on the basis of the Kirkwood–Buff formalism is less restrictive, because it involves the more realistic assumption [9] that the nonidealities of the gas/cosolvent mixtures are much higher

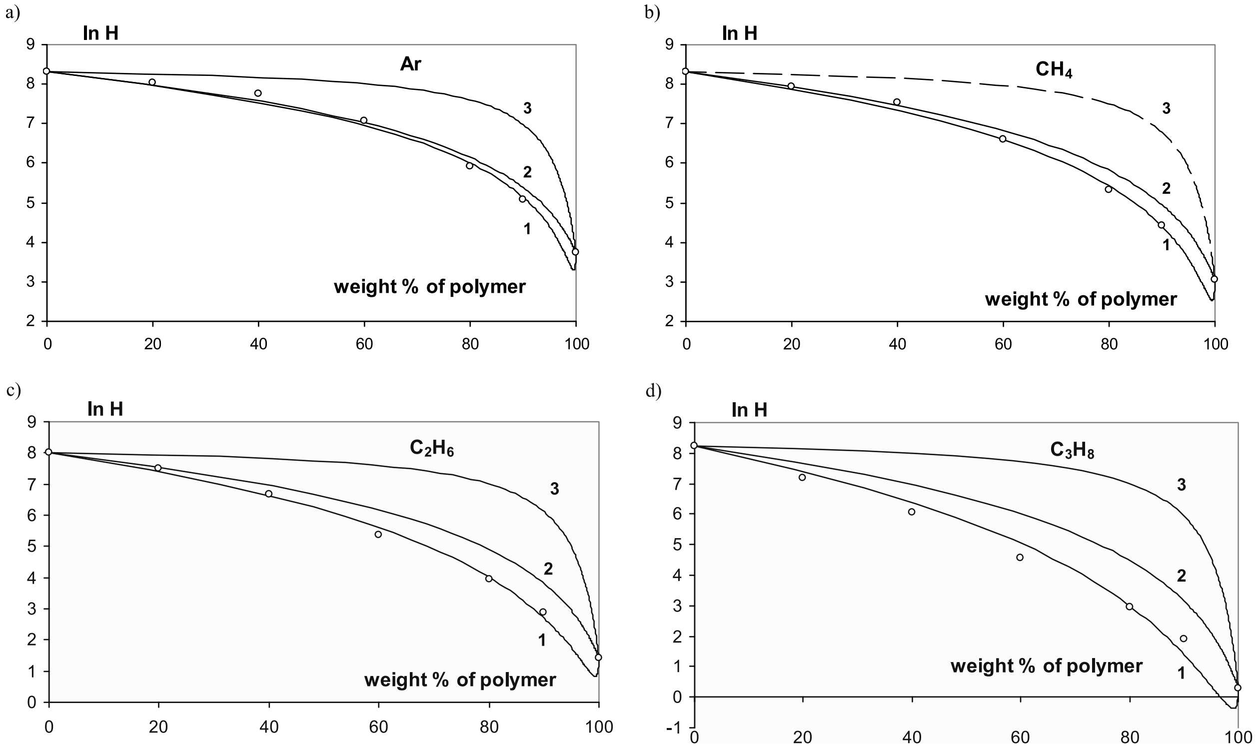

Fig. 1. The solubilities of Ar (a), CH_4 (b), C_2H_6 (c), and C_3H_8 (d) in PPG-400 at 25 °C. ○, experimental data [4], curve 1, the solubility calculated with Eq. (4) combined with the Flory–Huggins Eq. (8) with χ as adjustable parameter, curve 2, the solubility calculated with Eq. (2), curve 3, the solubility calculated with Krichevsky's Eq. (1).

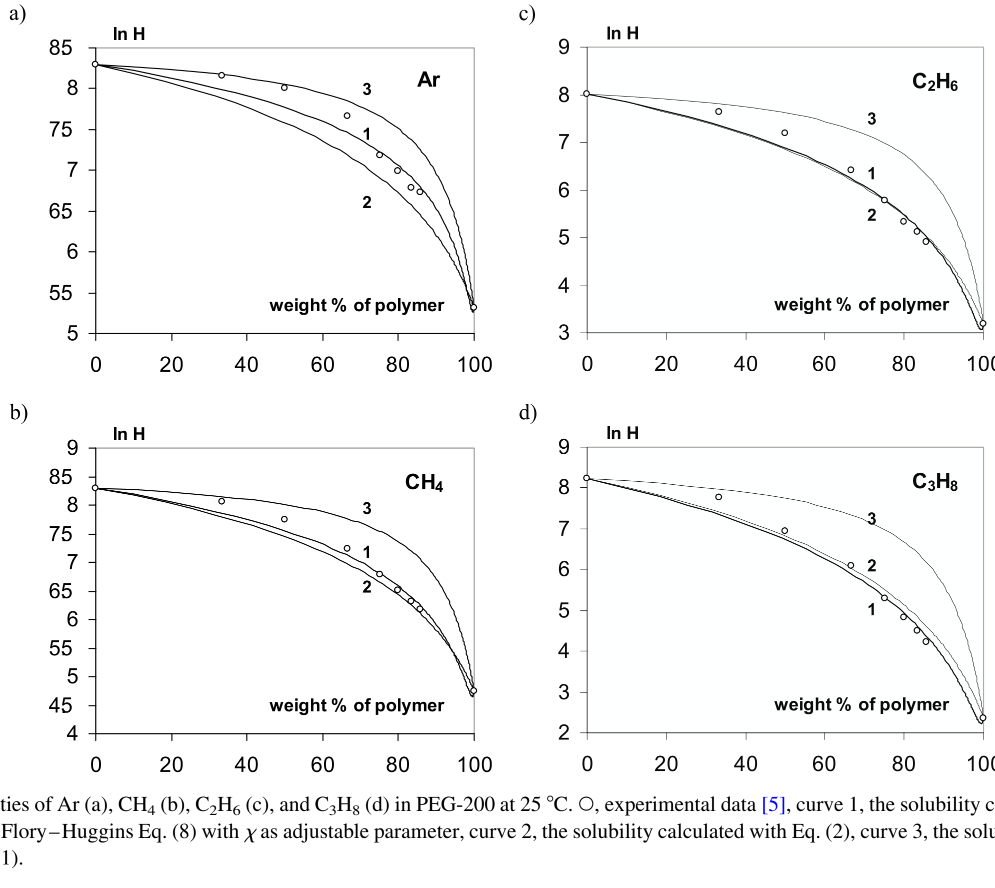

Fig. 2. The solubilities of Ar (a), CH_4 (b), C_2H_6 (c), and C_3H_8 (d) in PEG-200 at 25 °C. ○, experimental data [5], curve 1, the solubility calculated with Eq. (4) combined with the Flory–Huggins Eq. (8) with χ as adjustable parameter, curve 2, the solubility calculated with Eq. (2), curve 3, the solubility calculated with Krichevsky's Eq. (1).

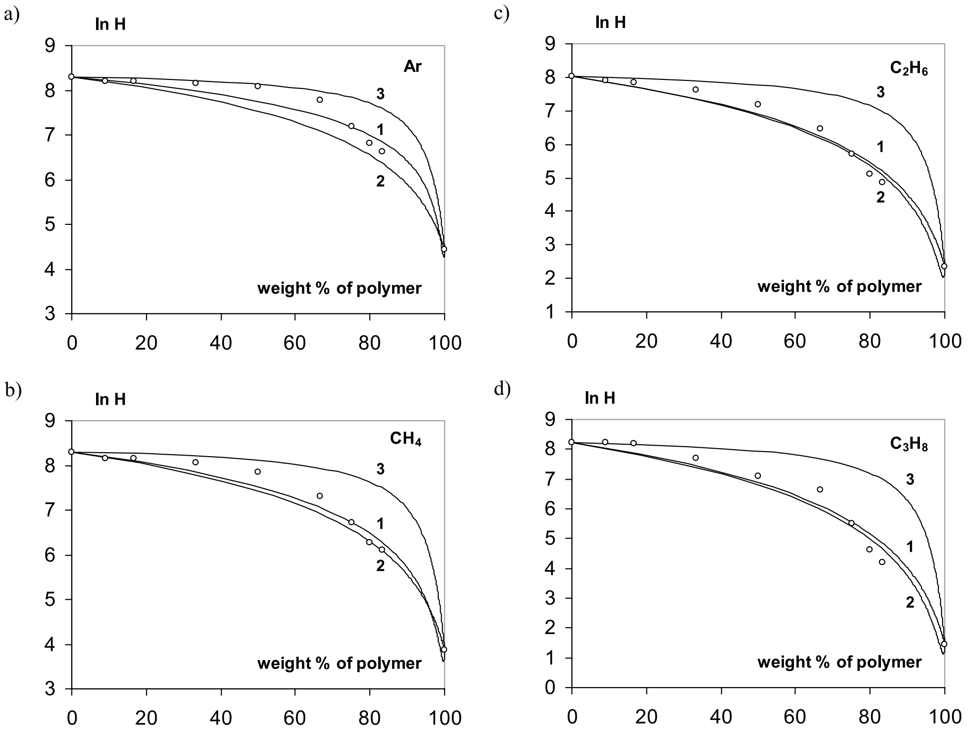

Fig. 3. The solubilities of Ar (a), CH_4 (b), C_2H_6 (c), and C_3H_8 (d) in PEG-400 at 25 °C. ○, experimental data [5], curve 1, the solubility calculated with Eq. (4) combined with the Flory–Huggins Eq. (8) with χ as adjustable parameter, curve 2, the solubility calculated with Eq. (2), curve 3, the solubility calculated with Krichevsky's Eq. (1).

Table 2

Comparison between experimental and calculated Henry constants in a binary mixed solvent polymer + water at 298.15 K

Systems		Deviations (%) of experimental data [4,5] from calculations[a]			
Gas	Mixed solvent	Krichevsky's equation	Eq. (2)	Eq. (4)[b]	Eq. (4)[c]
Argone	PPG-400 + water	12.5	1.9	1.1 (−0.17)	1.2
	PEG-200 + water	3.7	3.3	1.3 (−1.77)	4.8
	PEG-400 + water	4.8	3.8	2.0 (−2.52)	5.2
Methane	PPG-400 + water	18.1	3.9	0.9 (0.55)	2.3
	PEG-200 + Water	7.1	1.8	1.2 (−0.94)	3.2
	PEG-400 + water	8.5	2.0	2.0 (−1.17)	3.3
Ethane	PPG-400 + water	36.4	11.5	1.8 (1.49)	9.3
	PEG-200 + water	13.9	2.1	2.0 (−0.29)	2.1
	PEG-400 + water	15.9	3.7	2.1 (−0.10)	2.6
Propane	PPG-400 + water	66.4	25.3	6.5 (2.20)	23.1
	PEG-200 + water	21.5	3.8	2.3 (0.30)	3.2
	PEG-400 + water	21.2	5.5	5.0 (0.18)	5.1
Average (%)		19.2	5.7	1.9	5.5

[a] Defined as

$$\frac{100\sum_i \left|\dfrac{\ln(H^{(i)}_{2,t(\mathrm{exp})}) - \ln(H^{(i)}_{2,t(\mathrm{calc})})}{\ln(H^{(i)}_{2,t(\mathrm{exp})})}\right|}{m}$$

where m is the number of experimental points.

[b] Eq. (4) combined with the Flory–Huggins equation with adjustable parameter χ (the value of the parameter χ is given in parenthesis).

[c] Eq. (4) combined with the Flory–Huggins equation with parameter $\chi = 0$ (athermal solution).

than those of the mixed solvents. For this reason, Eq. (2) provides more accurate predictions. This equation does not require information about the ternary mixture 1–2–3 nor about its binary constituents, requiring only the gas solubilities in the individual solvents and the molar volumes of the latter.

The most accurate correlation was obtained with the rigorous Eq. (4) coupled with the Flory–Huggins equation for the activity coefficient of water in the polymer + water binary mixture, when the Flory–Huggins interaction parameter χ was considered as an adjustable parameter independent of composition. The values of the Flory–Huggins parameter χ for the systems investigated are listed in Table 2. While, according to the theory, the interaction parameter χ should be independent of the polymer concentration and weight, in reality, in most cases χ changes considerably with both [20]. In particular, for the binary mixtures PPG + water and PEG + water, χ depends on both composition and average molecular weight of the polymer [15,16]. Therefore, the values of χ used in our calculations constitute adjustable parameters. The calculations (Table 2) show that χ depends not only on the average molecular weight of the polymer, but has different values for each of the gases considered.

The figures show that Eq. (4) coupled with the Flory–Huggins equation for the activity coefficient of water in polymer + water mixed solvents provides a minimum for the Henry constant at high (>95 wt%) polymer compositions. Because gas solubility data are not available for such high polymer compositions, one cannot determine whether this minimum is due to the empirical nature of the adjustable parameter χ or reflects an experimental feature of the gas solubility in such mixed solvents at high polymer concentrations.

5. Conclusion

The Kirkwood–Buff theory of solutions for ternary mixtures was used to analyze the gas solubility in a mixed binary solvent composed of a high molecular weight and a low molecular weight cosolvent, such as the aqueous solutions of water soluble polymers. A rigorous expression for the composition derivatives of the gas activity coefficient in ternary solution was used to derive the composition dependence of the Henry constant under isobaric and isothermal conditions. The obtained expressions as well as the well-known Krichevsky equation were tested for the solubilities of Ar, CH_4, C_2H_6 and C_3H_8 in the aqueous solutions of PPG-400, PEG-200 and PEG-400. It was shown that the coupling of our Eq. (4) with the Flory–Huggins equation for the activity coefficient of the water in the binary mixed solvent provides an accurate correlation for the gas solubility with a single adjustable parameter. However, the more simple Eq. (2) has a satisfactory accuracy and is recommended because it requires only the gas solubilities in the individual solvents and the molar volumes of the latter.

Acknowledgements

We are indebted to Prof. A.D. King, Jr (Department of Chemistry, University of Georgia) for providing information regarding the densities of aqueous mixtures of polyethylene glycol and polypropylene glycol.

Appendix A

The following expression can be written for the Henry constant in a binary solvent [21]

$$\ln H_{2,t} = \lim_{x_2^t \to 0} \ln \gamma_{2,t} + \ln f_2^0(P,T) \tag{A1}$$

where $\gamma_{2,t}$ is the activity coefficient of the solute in the ternary mixture 1–2–3 and $f_i^0(P,T)$ is the fugacity of component i [20]. The Kirkwood–Buff theory of solutions [13] for ternary mixtures [14] provides the following expression for the composition derivatives of $\gamma_{2,t}$ at infinite dilution

$$\lim_{x_2^t \to 0} \left(\frac{\partial \ln \gamma_{2,t}}{\partial x_3^t} \right)_{T,P,x_2^t} = - \frac{(c_1^0 + c_3^0)((c_1^0 + c_3^0)(\Delta_{12} - \Delta_{23})_{x_2^t=0} + (c_1^0 - c_3^0)(\Delta_{13})_{x_2^t=0})}{2(c_1^0 + c_3^0 + c_1^0 c_3^0 (\Delta_{13})_{x_2^t=0})} \tag{A2}$$

where x_3^t is the mole fraction of component 3 in the ternary mixture, c_k^0 ($k = 1, 3$) is the bulk molecular concentration of component k in the binary mixture 1–3 and $G_{\alpha\beta}$ is the Kirkwood–Buff integral given by

$$G_{\alpha\beta} = \int_0^\infty (g_{\alpha\beta} - 1) 4\pi r^2 \, \mathrm{d}r \tag{A3}$$

In the above expressions, $g_{\alpha\beta}$ is the radial distribution function between species α and β, r is the distance between the centers of molecules α and β, and $\Delta_{\alpha\beta}$ are defined as follows

$$\Delta_{\alpha\beta} = G_{\alpha\alpha} + G_{\beta\beta} - 2G_{\alpha\beta}, \quad \alpha \neq \beta \tag{A4}$$

It should be noted that Δ_{ij} is a measure of the nonideality [22] of the binary mixture α–β, because for an ideal mixture $\Delta_{\alpha\beta} = 0$.

The combination of Eqs. (A1) and (A2) leads to

$$\left(\frac{\partial \ln H_{2,t}}{\partial x_3^t}\right)_{P,T,x_2^t=0} = -\frac{(c_1^0+c_3^0)((c_1^0+c_3^0)(\Delta_{12}-\Delta_{23})_{x_2^t=0}+(c_1^0-c_3^0)(\Delta_{13})_{x_2^t=0})}{2(c_1^0+c_3^0+c_1^0c_3^0(\Delta_{13})_{x_2^t=0})} \tag{A5}$$

In addition, for the binary 1–3 mixture one can write the following relation [13]

$$\left(\frac{\partial \ln \gamma_1^{\mathrm{b},1-3}}{\partial x_3^{\mathrm{b},1-3}}\right)_{P,T} = \frac{c_3^0\Delta_{13}}{1+c_1^0x_3^{\mathrm{b},1-3}\Delta_{13}} \tag{A6}$$

Combination of Eqs. (A5) and (A6) leads to

$$\ln H_{2,t} = -\int (c_1^0+c_3^0)\frac{(\Delta_{12}-\Delta_{23})_{x_2^t=0}}{2} \times\left[1+x_3^{\mathrm{b},1-3}\left(\frac{\partial \ln \gamma_3^{\mathrm{b},1-3}}{\partial x_3^{\mathrm{b},1-3}}\right)_{P,T}\right]\mathrm{d}x_3^{\mathrm{b},1-3} + \frac{1}{2}\int \frac{(x_1^{\mathrm{b},1-3}-x_3^{\mathrm{b},1-3})}{x_1^{\mathrm{b},1-3}}\left(\frac{\partial \ln \gamma_3^{\mathrm{b},1-3}}{\partial x_3^{\mathrm{b},1-3}}\right)_{P,T}\mathrm{d}x_3^{\mathrm{b},1-3} + A \tag{A7}$$

which is just Eq. (3) in the text.

Appendix B

The aim of this appendix is to provide analytical expressions for the integrals I_1 and I_2 of Eq. (4)

$$I_1 = -\int \frac{\left[1+x_3^{\mathrm{b},1-3}\left(\frac{\partial \ln \gamma_3^{\mathrm{b},1-3}}{\partial x_3^{\mathrm{b},1-3}}\right)_{P,T}\right]}{V}\mathrm{d}x_3^{\mathrm{b},1-3} \tag{B1}$$

and

$$I_2 = \int \frac{(x_1^{\mathrm{b},1-3}-x_3^{\mathrm{b},1-3})}{x_1^{\mathrm{b},1-3}}\left(\frac{\partial \ln \gamma_3^{\mathrm{b},1-3}}{\partial x_3^{\mathrm{b},1-3}}\right)_{P,T}\mathrm{d}x_3^{\mathrm{b},1-3} \tag{B2}$$

The Flory–Huggins Eq. (8) was employed for the activity coefficient of water $\gamma_3^{\mathrm{b},1-3}$ in a mixed solvent polymer (1) + water (3). Because the integrated expressions require a too large space, we provide only the results obtained for $\chi = 0$ (athermal mixtures).[1] Using Eqs. (7) and (9), the integration of Eqs. (B1) and (B2) leads to the following expressions

$$I_1 = \frac{\alpha_1+\alpha_2\ln(ax_3^{\mathrm{b},1-3}+b)+\alpha_3\ln(rx_1^{\mathrm{b},1-3}+x_3^{\mathrm{b},1-3})}{(rx_1^{\mathrm{b},1-3}+x_3^{\mathrm{b},1-3})(ra+rb-b)^2} \tag{B3}$$

and

$$I_2 = \frac{2(rx_1^{\mathrm{b},1-3}+x_3^{\mathrm{b},1-3})\ln(rx_1^{\mathrm{b},1-3}+x_3^{\mathrm{b},1-3})+(1+r)}{(rx_1^{\mathrm{b},1-3}+x_3^{\mathrm{b},1-3})} \tag{B4}$$

where $a = V_3^0 - V_1^0$ and $b = -V_1^0$. The coefficients α_1, α_2 and α_3 have the following forms

$$\alpha_1 = -r^2b - r^2a + rb \tag{B5}$$

$$\alpha_2 = r^3ax_1^{\mathrm{b},1-3} + r^3bx_1^{\mathrm{b},1-3} + r^2ax_3^{\mathrm{b},1-3} + r^2bx_3^{\mathrm{b},1-3} - rbx_1^{\mathrm{b},1-3} - bx_3^{\mathrm{b},1-3} \tag{B6}$$

and

$$\alpha_3 = -r^3ax_1^{\mathrm{b},1-3} - r^3bx_1^{\mathrm{b},1-3} - r^2ax_3^{\mathrm{b},1-3} - r^2bx_3^{\mathrm{b},1-3} + rbx_1^{\mathrm{b},1-3} + bx_3^{\mathrm{b},1-3} \tag{B7}$$

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[1] The results of integration for $\chi \neq 0$ can be obtained from the authors by request.