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Thermodynamic Study on Heat of Mixing of Polyisobutylene with Ethylbenzene

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Summary

The heat of mixing of polyisobutylene with ethylbenzene was measured from 18.2 to 69.2 °C with a Tian-Calvet twin micro-calorimeter, and the exchange enthalpy parameter X_{12} in Flory's theory was estimated. The X_{12} obtained was discussed also in comparison with the one based on Manzini model. Further combining with osmotic pressure data, temperature dependence of the entropy parameter Q_{12} was referred.

Introduction

Thermodynamic properties of polyisobutylene(PIB) solution are of particular interest in respect that PIB exists in an amorphous liquid state near room temperature and pertains to an important class of liquid characterized by low coefficients of thermal expansion $\alpha[=V^{-1}(\partial V/\partial T)_p]$, and of isothermal compressibility $\beta[=V^{-1}(\partial V/\partial p)_T]$, where V, T, and p denote volume, temperature, and pressure, respectively. The mixing properties of PIB in n-alkane(aliphatic) and in benzene(aromatic) have been investigated in detail by FLORY et al.(1968a, 1968b). However, only few has been reported (MARON and DANIELS 1968) on PIB-ethylbenzene(EB) system, in which EB is of both aliphatic and aromatic characters. The well-known Flory's theory(1964) is believed to give a better representation for thermodynamic properties of non-polar binary mixtures.

In applying Flory's theory to binary mixtures, three measurable quantities, i.e., the density ρ, the thermal expansion coefficient α, and the thermal pressure coefficient $\gamma[=(\partial p/\partial T)_V]$ for pure components, and a properly chosen parameter X_{12} characterizing mixture are needed. Among these, the parameter X_{12}, reflecting an average characteristic energy change associated with the formation of relatively weak contacts beteen unlike species 1-2 in exchange for the contacts between like species, 1-1 and 2-2, may in principle be evaluated from any one of the experimental thermodynamic excess function of mixing.

In view of its character, the X_{12} chosen to get

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the best fit with reliable experimental data on the integral heat of mixing may lead to a better agreement between theory and experiment for other excess functions. The present investigation was undertaken to compare the value of χ, calculated according to Flory theory using X_{12} estimated from the integral heat of mixing $\Delta H_M(\infty)$ at infinite dilution obtained from direct calorimetric measurements, with that of χ obtained through the osmotic pressure measurements at different temperatures for EB-PIB system.

Materials

Polyisobutylene used for the experiment is a fraction having a viscosity-average molecular weight of 48,000 obtained by fractional precipitation of Vistanex-LMMS. Ethylbenzene was treated with concentrated sulphuric acid, washed with water, with 10% aqueous sodium carbonate, again with water, and was dried over calcium chloride. The ethylbenzene thus treated was finally distilled just before the use. The mercury used in calorimetric measurements was purified by usual procedure. Benzene and n-hexane used for the performance and model tests were of spectroquality and used without purification.

Calorimetric Measurements

Integral heat of mixing for EB-PIB system was determined by using a Tian-Calvet twin micro-calorimeter over a temperature range of 18.2 to 69.2°C. The details of its working principle are described elsewhere(CALVET and PRAT 1963). For the measurement about 0.09 g of PIB was mixed with about 7 g of EB. The integral heat of mixing was obtained from the recorded thermogram.

To make the performance test of our calorimeter and cell assembly, $\Delta H_M(\infty)$ for PIB-benzene system at 30.2°C was measured. As is obvious in TABLE 1, our result well agrees with literature values.

TABLE 1

Integral heat of mixing for PIB-benzene

$T^{o}K$	Mole weight of PIB	$\Delta H_M(\infty)$ J/mole	Reference
303.2	4.5×10^{4}	900	CUNIBERTI 1966
297.7	3.0×10^{4}	1088	DELMAS 1962
298	6.3×10^{4}	1097	WATTERS 1960
300	7.2×10^{4}	1076	LIDDEL 1970
303.4	4.8×10^{4}	1082	This work

The values of $\Delta H_M(\infty)$ for PIB-EB system were obtained by taking an average of three measurements with an accuracy of ±0.5% near 18° and ±6% near 70°C.

Results and Discussion

Characteristic Properties of Pure Components

The equation-of-state data comprising the density ρ, α, and γ for EB and PIB were cited from the works of FLORY et al.(1968a,1971). The reduced volume $\tilde{v}$, and the characteristic parameters were calculated through the use of ρ, α, and γ from eqs.(1)-(4).

$$\tilde{v}^{1/3} - 1 = (\alpha T/3)(1 + \alpha T)^{-1} \tag{1}$$

$$v^* = (\rho v)^{-1} \tag{2}$$

$$\tilde{T} = T/T^* = (\tilde{v}^{1/3} - 1)\,\tilde{v}^{-4/3} \tag{3}$$

$$p^* = \gamma T \tilde{v}^2 \tag{4}$$

These quantities are assembled in TABLE 2.

TABLE 2
Equation-of-state data and characteristic parameters

(A) Ethylbenzene

Temp. °C	v_1 cm^{3}g^{-1}	$\alpha_1\times10^3$ deg^{-1}	γ_1 J/cm^{3}deg	$\tilde{v}_1$	$v^*_{1,sp}$ cm^{3}g^{-1}	p^*_1 J/cm^3	T^*_1 °K
18.2	1.1512	1.008	1.227	1.2447	0.9249	554	5154
30.3	1.1655	1.028	1.147	1.2571	0.9272	550	5195
50.5	1.1904	1.064	1.027	1.2787	0.9310	544	5260
59.6	1.2021	1.082	0.979	1.2889	0.9327	541	5288
69.2	1.2148	1.103	0.933	1.3000	0.9345	540	5315

(B) Polyisobutylene

Temp.	v_2	$\alpha_2\times10^3$	γ_2	$\tilde{v}_2$	$v^*_{2,sp}$	p^*_2	T^*_2
18.2	1.0865	0.554	1.170	1.1455	0.9484	447	7537
30.3	1.0938	0.556	1.110	1.1515	0.9499	447	7609
50.5	1.1062	0.560	1.017	1.1613	0.9525	444	7729
59.6	1.1119	0.561	0.977	1.1658	0.9538	442	7783
69.2	1.1179	0.563	0.938	1.1677	0.9573	438	7936

α_2 is very small compared to α_1, which will be fundamentally attributable to that the number of intermolecular degrees of freedom per unit volume of PIB is much fewer than that of EB, this difference being reflected in the values of T*. As a result, the difference between the reduced volumes of PIB and EB will become marked. According to the theory, the greater the disparity between the characteristics of the component liquids is, the greater the equation-of-state contributions to the excess properties of mixing are.

Enthalpy of Mixing

According to Flory's theory, the characteristic pressure p* of a mixture is given by a function of p^*_1, p^*_2, and X_{12} as

$$p^* = \varphi_1 p_1^* + \varphi_2 p_2^* - \varphi_1 \theta_2 X_{12} \qquad (5)$$

φ_1 ($= 1 - \varphi_2$) is the volume fraction component 1 as defined by $\varphi_1 = N_1V_1^*/(N_1V_1^*+N_2V_2^*)$, where N_i and V_i^* are the number of moles and characteristic molar volume of i-component, respectively, and θ_2 is denoted by

$$\theta_2 = 1 - \theta_1 = \frac{(s_2/s_1)\varphi_2}{\varphi_1+(s_2/s_1)\varphi_2} \qquad (6)$$

in which s_2/s_1 is the ratio of surface areas per segment of components, being estimated from molecular dimensions of the components. With some premises to simplify the matter, Flory's theory gives for the enthalpy ΔH_M of mixing of N_1 moles of solvent with N_2 moles of polymer.

$$\Delta H_M = N_1p_1^*V_1^*[(1/\tilde{v}_1)-(1/\tilde{v})]+N_2p_2^*V_2^*[(1/\tilde{v}_2)-(1/\tilde{v})] +(N_1V_1^*\theta_2/\tilde{v})X_{12} \qquad (7)$$

$\tilde{v}$ is the reduced volume of the mixture. From eq(7), there follows the integral heat of mixing $\Delta H_M(\infty)$ of a base mole of amorphous polymer with an abundance of solvent as

$$\Delta H_M(\infty) = p_2^*V_u^*[(s_2/s_1)\frac{X_{12}(1+\alpha_1T)}{p_2^*\ \tilde{v}_1} + \left\{(\frac{1}{\tilde{v}_2} - \frac{1}{\tilde{v}_1}) - \frac{\alpha_1T}{\tilde{v}_1}(1- \frac{T_1^*}{T_2^*})\right\}] \qquad (8)$$

where V_u^* is the hard core volume per mole of polymer repeating unit. The ratio s_2/s_1 for evaluation of X_{12} from $\Delta H_M(\infty)$ was estimated from molecular dimensions of PIB and EB. PIB was approximated by a cylinder with a length of 2.325Å and a volume of V_u^* per repeating unit, and EB is treated as a sphere of mole volume of V_1^*. The ratio of surface areas of the repeating unit of PIB and EB after division by V_u^*/V_1^* on the basis of segments of equal volume yields s_2/s_1 =0.65 for this system.

In Fig.1, the integral heat of mixing at infinite dilution $\Delta H_M(\infty)$ (in Joules per mole of repeating unit of PIB) for EB-PIB system, experimentally determined with micro-calorimeter, is plotted against temperature.

The values of X_{12} calculated according to eq.(8) through the use of these observed values of $\Delta H_M(\infty)$ and the choice of s_2/s_1=0.65 are shown in TABLE 3.

TABLE 3

X_{12} for ethylbenzene-polyisobutylene system.

Temp.($^\circ$C)	18.2	30.3	50.5	59.6	69.2
X_{12}(Jcm^{-3})	18.0	16.7	13.5	12.2	10.7

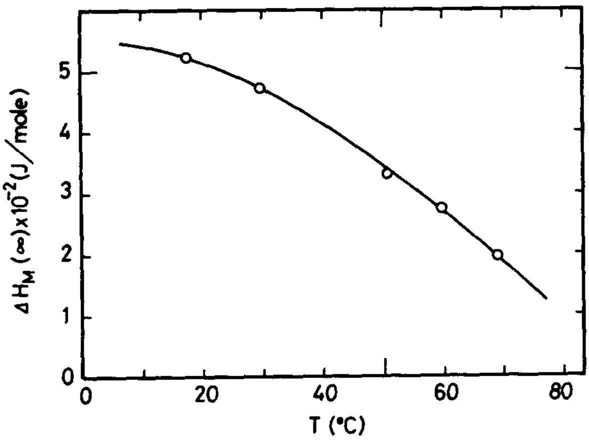

Fig. 1. Integral heat of mixing at infinite dilution for polyisobutylene in ethylbenzene.

The values of X_{12} are positive over the temperature range studies, as should be expected on systems of non-polar molecules. Further, it can be understood that X_{12} decreases with temperature, which violates substantially the low of the corresponding states, in analogy to the case of p*, V*, and T*. From Fig.1, we can realize that $\Delta H_M(\infty)$ is of positive sign over the temperature range of 18.2 to 69.2°C and its first and second derivatives with respect to temperature are both of negative sign. These observations may be quantitatively explained from scrutiny of eq.(8). In essence, the $\Delta H_M(\infty)$ consists of the sum of contributions arising from contact interactions including the X_{12} term, and those arising from the equation-of-state terms traceable to the disparity between the properties of the component liquids. As the temperature increases, the first term of positive sign decreases, while the latter contribution with negative sign increases in magnitude, thus causing $\Delta H_M(\infty)$ to decrease for the present system. For instance, calculated values of contributions of the contact interactions and equation-of-state terms to $\Delta H_M(\infty)$ are found to be 647.0 J/mole and -118.9 J/mole at 18.2°C, 395.9 J/mole and -204.68 J/mole at 69.2°C, respectively. In general, the enthalpy of mixing for non-polar binary mixture depends strongly on X_{12} near room temperature in contrast to the case for excess volume.

According to the Berthelot geometric mean rule for the intermolecular interaction, X_{12} becomes

$$X_{12}/p_1^* = [1 - (s_1/s_2)^{1/2}(p_2^*/p_1^*)^{1/2}]^2 \qquad (9)$$

The value of X_{12} calculated from eq.(9) is 7.7 J/cm^3 at 30.3°C, which differs from the observed value of 16.7 J/cm^3 given in TABLE 3. Such result suggests that the Berthelot rule is not applicable to this system.

Residual Chemical Potential

The chemical potential of the solvent in polymer solution, μ_1, is expressed as a sum of its combinatory part and residual part(FLORY et al. 1964):

$$(\mu_1 - \mu_1^0) = (\mu_1 - \mu_1^0)_{comb} + (\mu_1 - \mu_1^0)_R \qquad (10)$$

where, $(\mu_1 - \mu_1^0)_{comb} = RT[\ln(1-\varphi_2)+(1-\frac{1}{r})\varphi_2] \qquad (11)$

The residual part in eq.(10) is expressed in terms of the conventional interaction parameter χ identified as the reduced residual chemical potential as

$$\begin{aligned}\chi &= (\mu_1 - \mu_1^0)_R/RT\varphi_2^2 \\ &= (p_1^* V_1^*/RT\varphi_2^2)[3\tilde{T}_1 \ln\{(\tilde{v}_1 - 1)/(\tilde{v}-1)\} + (\tilde{v}_1^{-1} + \tilde{v}^{-1})] \\ &\quad + V_1^* \overline{X}_{12}\, \theta_2^2/(\tilde{v}\, RT\, \varphi_2^2) \qquad (12)\end{aligned}$$

where, $\overline{X}_{12}$, including entropic as well as energetic contributions to χ and associated with the exchange of neighboring species, is given by

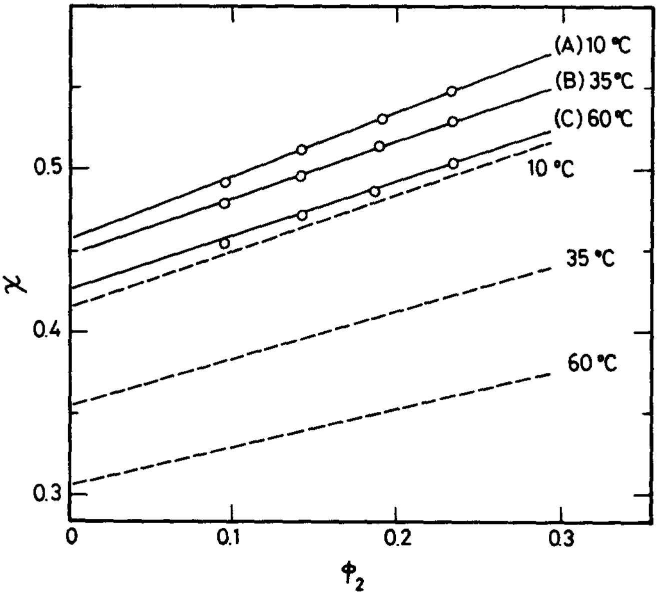

Fig.2. Reduced residual chemical potential χ for EB-PIB mixtures plotted against core volume fraction φ_2.
Solid curves: calculated by eq.(12) with X_{12} given in TABLE 3, and with Q_{12}(J cm^{-3}deg^{-1}) of -0.0090 (A), -0.0182(B), and -0.0238(C).
Dashed curves: calculated by eq.(12) with X_{12} used above, and with Q_{12}=0.

$$\overline{X}_{12} = X_{12} - \tilde{v}TQ_{12} \qquad (13)$$

where Q_{12} is an additional exchange entropy parameter introduced subsequently to achieve the agreement between theory and experiment.

Experimentally, the values of χ were estimated from osmotic pressure (π) measurements on dilute polymer solution of PIB in EB at 10, 35, and 60°C from the relation: $(\mu_1 - \mu_1^0) = -\pi V_1^0$, where V_1^0 is the molar volume of solvent.

In Fig.2, the experimentally obtained results were compared with theoretical curves (solid and dashed curves) calculated by means of eq.(12) using the values of X_{12} in TABLE 3, and Q_{12} chosen to reproduce the experimental values of χ. As is obvious from Fig.2, disagreements were found between calculation and observation without invoking to an additional parameter Q_{12}. Although the source of the Q_{12} may in part occurs in consequence of the over-estimation of the combinatory entropy and in part in consequence of the incorrect assignment of the s_2/s_1 value, the origin of this source still remains unexplained yet. On inspection of eq.(12), χ is separable into an equation-of-state contribution(first term in eq.12) coming from the difference between the properties of components, and a contact exchange contribution(including $\overline{X}_{12}$ in eq.12) reflecting the difference of chemical structure or the force fields. It was found that the former increases slightly, whereas the latter decreases considerably, and consequently the total decreases with increasing temperature for the present system.

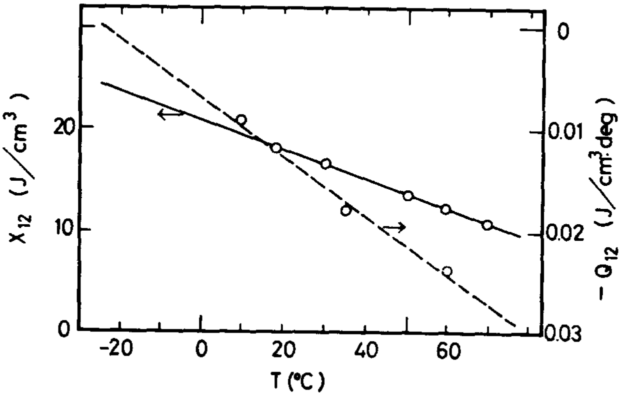

Fig.3. Temperature dependences of exchange enthalpy parameter X_{12} and entropy parameter Q_{12}.

Fig.3 summarizes the temperature dependences of X_{12} and Q_{12}. The comparatively large value of Q_{12} for this system particularly at high temperatures may be ascribed to an over-estimation of the lattice combinatory entropy,and to arbitrariness in the values of s_2/s_1. It is worth to note that the extrapolated value of Q_{12} at -24°C, the upper critical solution temperature observed by FOXand FLORY(1951),is nearly equal zero.

Further Comments on X_{12}

Heat of mixing was measured with EB-n-hexane system as a model of EB-PIB. The X_{12} value obtained therefrom was 19.1 J/cm^3,which is close to the value 16.5 for EB-PIB. But differently from the case of EB-PIB, X_{12} estimated from Berthelot rule(=19.6) is in excellent agreement with the observed value.Further X_{12} was examined after the model proposed by MANZINI(1975):

$$X_{12} = -\sum_{i>j}(\alpha_{i,1} - \alpha_{i,2})(\alpha_{j,1} - \alpha_{j,2})X_{ij} \qquad (14)$$

where, X_{ij} is the characteristic exchange energy contribution to X_{12} associated with formation of contacts between dissimilar chemical groupings i and j, and with breaking of an equivalent number of i-i and j-j ones. $\alpha_{i,1(2)}$ and $\alpha_{j,1(2)}$ are the site fractions of contacts accessible for neighbor interactions of the i and j type(aliphatic, aromatic,etc.) per mole of component 1(or 2). To estimate the site fractions, van der Waals group surfaces given by BONDI(1964),i.e., 2.12,1.35,and 5.33(x10^9 cm^2/mole) for CH_3,CH_2 and C_6H_5, respectively, were used. Further, with respect to X_{ij}, it was assumed that $X_{al,al}$=$X_{ar,ar}$=0, and $X_{al,ar}$=42 J/cm^3. With these presises, finally we have X_{12}=15.6 J/cm^3 for systems as EB-PIB and EB-n-hexane. Agreement with observed values seems to be considerably good.

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