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NOTES

A Viscometric Study of Poly*iso*butene–Solvent Interaction at Different Temperatures

M.M. HUSAIN*, M.I. ISLAM and RAJ KUMAR
Department of Chemistry
University of Lucknow, Lucknow-226 007, India

The interaction of poly*iso*butene fraction of known molecular weight (1.46×10^6) with a number of organic solvents has been investigated in terms of its intrinsic viscosity at different temperatures. Moreover, on the basis of this study an attempt has been made to classify the concerned solvents either good or poor.

The intrinsic viscosity, $[\eta]$, being directly dependent on the effective size[1] of the molecule in dilute solution just like viscosity B-coefficient[2] and parameter, K, of Mark-Houwink relation is a useful index to study polymer-solvent interaction, in general. Based on this concept, several workers[3–8] have investigated the macromolecular solutions containing different high polymers. For and Flory[4] have even arranged the solvents for poly*iso*butene in order of their decreasing power of solvation, employing the concept of intrinsic viscosity, $[\eta]$ and the exponent 'a' of Mark-Houwink equation at varying temperatures showing that the solvent behaving as good (*e.g.*, toluene) at higher temperature, say 90°C, can be a poor solvent at a much lower temperature, say 0°C. The studies by above workers have suggested that perhaps the idea of intrinsic viscosity and its variation with temperature can be substantially used in giving a qualitative and to some extent a quantitative description of the extent of interaction between a polymer and the solvents.

The present paper reports a comparative account of the interaction of poly*iso*butene with a number of aliphatic and aromatic solvents based on the available viscosity data[5] in the temperature range of 20°–80°C. Further, an attempt has been made to arrange these solvents as good or poor for polyisobutene.

The numerical value of the intrinsic viscosity of a polymer in different solvents appears to give an insight into a comparative account regarding the nature of the solvent (*i.e.*, good or poor) and hence of their solvating efficiency. The better the solvent, the lower the secondary valence links which form within a polymer coil, and, therefore, the intrinsic viscosity is higher. On the other hand, the poorer the solvent, the more undissolved associated segments are usually found within a polymer coil, giving thereby, a lower value of intrinsic viscosity[9], $[\eta]$. Moreover, at the same temperature the intrinsic viscosity decreases from best to the poorest solvent[4]. Alfrey *et al.*[10], working on several polymers, have suggested that the viscosity-temperature coefficient, $\frac{d[\eta]}{dt}$, should have a large positive value for a poor solvent and a large negative value for a very good solvent. Furthermore, in a good solvent, the temperature dependence of the intrinsic viscosity is only small[9]. In the light of the above facts, the intrinsic viscosities $[\eta]$ of poly*iso*butene at various temperatures in some organic solvents[5] are recorded in Table 1.

TABLE 1

THE VALUES OF INTRINSIC VISCOSITY OF POLY*ISO*BUTENE IN SOME ORGANIC SOLVENTS AT DIFFERENT TEMPERATURES

Solvent	Intrinsic viscosity, [η], (°C)						
	20°	30°	40°	50°	60°	70°	80°
cyclohexane	5.15	5.15	5.15	5.15	5.15	5.15	5.15
trimethylbutane	3.55	3.51	3.47	3.40	3.33	3.26	3.18
di*iso*butene	3.26	3.25	3.25	3.18	3.05	2.86	2.61
n-hepatane	3.20	3.18	3.15	3.11	3.05	2.98	2.88
n-hexadecane	2.53	2.52	2.53	2.54	2.53	2.53	2.53
toluene	2.56	2.80	3.00	3.13	3.25	3.35	3.43
benzene	0.95	1.70	2.13	2.50	2.78	2.90	3.05

*Intrinsic viscosity values are either experimental[5] or those obtained graphically from the experimental[η]-t plots at convenient temperatures.

It may be seen from Table 1 that in the first five aliphatic solvents, the value of $[\eta]$ decreases from cyclohexane to n-hexadecans at any temperature between 20°–50°C. Thus the goodness of the above solvents appears to decrease for poly*iso*butene in the same sequence as shown in Table 1. However, at 60°C di*iso*butene and *n*-heptane tend to be equally good towards poly*iso*butene and at still higher temperatures *i.e.*, 70° and 80°C, a reversal in trend of solvents' goodness predeminates.

This observation is not surprising as the nature of a solvent (in terms of goodness or poorness) does change[9] with a variation in temperature. Again, the goodness of all the aliphatic solvents towards poly*iso*butene is also supported by a similarity in their environment.

The dissimilar environment presented by the aromatic solvents toluene and benzene, perhaps, restricts their favourable interaction with poly*iso*butene facilitating intramolecular association within the polymer coil giving in them lower values of $[\eta]$ for poly*iso*butene which increases with increasing temperature. Comparing toluene and benzene at any single temperature the solvating efficiency seems to be improving with temperature particularly in the former. It may further be observed from Table 1 that upto 40°C, toluene replaces *n*-hexadecane; at 50°C replaces *n*-heptane; at 60°C replaces di*iso*butene and finally at 70° and 80°C, it even replaces trimethyl-butane in terms of its degree of interaction with poly*iso*butene. It may perhaps be safely concluded from this trend that with a rise in temperature, the nature of the solvent also improves and probably at higher temperatures due to the breaking of intramolecular association of the polymer coil, toluene experiences significantly greater interaction with poly*iso*butene as compared to other aliphatic solvents excepting cyclohexane. This argument appears to be amply supported by a noticeable increase in the value of Mark-Houwink exponent[4] 'a' from 0.60 to 0.72 in case of toluene between 0°–90°C.

However, in benzene the intramolecular association of poly*iso*butene appears to be predominant over poly*iso*butene-benzene interaction so that there is every likelihood for an insignificant solvation of the polymer as is clearly characterized by low values which are strongly dependent on temperature in comparison to this behaviour in other solvents. Interestingly, it may be pointed out that at 80°C, benzene appears to experience a comparatively larger interaction with poly*iso*butene than the solvents di*iso*butene, *n*-heptane and *n*-heptane and *n*-hexadecane. This dual nature of toluene and benzene is in agreement with the arguments advanced by Fox and Flory[4].

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